Removal of Anionic Azo Dye from Aqueous Solution Using the Magnetic NiFe$_2$O$_4$ Decorated-Exfoliated Graphite

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Abstract: Environmental issues have recently become more prevalent with the rapid development of global industrialization. Organic dyes, a common pollutant, are compounds which are constituted by benzene rings, making them stable and presenting a pollution source that is harmful to human health. In this study, a new nanocomposite adsorbent was fabricated using exfoliated graphite (EG) and NiFe$_2$O$_4$ and evaluated for adsorption capacity against Congo Red (CR) dye. A number of reaction parameters (pH, CR concentration, dosage and contact time) that affect CR adsorption were considered. The successful synthesis of EG@NiFe$_2$O$_4$ was confirmed by FT-IR analysis. Herein, EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ adsorbent with dosage of 0.5 g/L were used to removal 100 mL of CR dye at the concentration of 50 ppm. The results showed that adsorption equilibrium was achieved after 120 min for both adsorbents (EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$). The optimal working pH for adsorption using EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ was 6 and 4 respectively. EG@NiFe$_2$O$_4$ could be reused for up to three times without significant loss of adsorption capacity.

1. Introduction

The rapid industrialization has led to increasing pollution in water ecosystems [1–3]. Industries such as textiles, paper, petroleum, pharmaceuticals generate a great deal of hazardous contaminants [4]. Of which, nitroaromatic compounds are abundantly found in effluents from both industrial and agricultural activities, especially Congo Red dye (CR) [5]. The existence of CR dyes, even at low concentrations, can pose serious threat to the ecosystem and public health [6–7].

The spinel ferrites (MFe$_2$O$_4$, M = Ni, Co, Cu, Zn, etc.) have been recognized as highly applicable magnetic materials due to physical and chemical advantages including low conductivity, thermal and chemical stability [8-9] and, most importantly, ferromagnetic property [10–11]. The inverse spinel structure of NiFe$_2$O$_4$ is made up of ferric ions that equally occupies the tetrahedral sites (A-sites) and the octahedral sites (B sites), enabling the material in applications such as high density magnetic recording media, magnetic refrigeration, magnetic liquids and microwave absorber [12-13].

Exfoliated graphite (EG) has recently emerged as a promising material with good applicability in the wastewater treatment field. This is in part due to the low number of functional groups, improved conductivity and mechanical features of EG [14]. However, the difficulty in recovering the EG from
aqueous media has limited its applications and called for measures to improve recoverability of EG. One approach that has been proposed recently is to dope a magnetic component (e.g. iron-based particles) to EG structure, conferring EG the ability to be recovered via a magnetic field [15-17]. This research pathway has been extensively experimented with a wide array of magnetic nanoparticles, producing nanocomposites with enhanced adsorption capacity and novel features.

Herein, a nanocomposite was fabricated using aforementioned precursors and evaluated for adsorption capacity towards Congo Red dye. We assessed the effect of pH, CR concentration, dosage and contact time on CR adsorption capacity. The as-synthesized adsorbent was also characterized using Fourier-Transform Infrared spectroscopy (FT-IR) and reused for recyclability testing.

2. Materials and method

2.1. Chemicals and instruments:
Natural graphite flake (GF) was collected from Yen Bai province, Vietnam. The material was selected to have the particle size of 60 mesh. Chemicals including Congo red, H₂SO₄ (98%), and H₂O₂ (30%) were purchased from Merck. NiCl₂·6H₂O and FeCl₃·6H₂O were from Fisher. Infrared FT-IR spectra produced by the Nicolet 6700 spectrophotometer were used to explore the characteristics of chemical bonds and functional groups of the samples. CR concentration was determined with UV-vis spectrophotometer at wavelength of 500 nm.

2.2. Synthesis of EG@NiFe₂O₄

EG@NiFe₂O₄ was synthesized by sol-gel method. Typically, 1 mmol of NiCl₂·6H₂O, 2 mmol of FeCl₃·6H₂O were dissolved in 60 mL of water. The mixture was then heated under stirring to 90 °C. Then, citric acid solution was added (molecular ratio of acid/molar Fe³⁺ of 4:1) and the mixture was allowed to react at 90°C for 1 hour. Afterwards, EG was added (EG/NiFe₂O₄ ratio of 3:1) slowly and the mixture was slightly stirred. The pH of solution was about 7–8. Afterwards, pH was adjusted a second time until the exfoliant appears on the surface of the reaction vessel, forming a gel solution. The afforded gel was dried at 80°C for 20 hours and then heated in a Muffle Kiln to peel off the graphite layers again.

2.3. Synthesis of NiFe₂O₄

Herein, NiFe₂O₄ was synthesized via our previous report [12]. Briefly, 93 g citric acid, 40 mL of ethylene glycol and 100 mL distilled water were mixed and heated up 80°C under air atmosphere. Then, an amount of 0.36 g of NiCl₂·6H₂O solid was infused into the above mixture and heated up at 130 °C. After 2 hours, the heat-resistant furnace was used to accumulate the mixture and heated up at 1000°C for 2 hours, then allowed to cool down at room temperature.

2.4. Adsorption experiments

Congo red (CR), a type of azo dye, was selected as the adsorbate in this study. The adsorption reaction system consists of 100 mL of CR and 0.05 g of as-synthesized EG@NiFe₂O₄ in a 250 mL beaker. The mixture was shaken at 200 rpm under room temperature. Herein, the effective factors, such as pH solution (2–12), concentration dye (20–60 ppm) and adsorbent dosage (0.03–0.07 g), were carefully tested. The equilibrium adsorption capacity, qₑ (mg/g) and removal efficiency were respectively calculated as follows:

\[ q_e = \frac{C_0 - C_e}{m} \cdot V \] (1) and \% Removal = \frac{C_0 - C_e}{C_0} \cdot 100\% \] (2)

where C is the concentration of CR (mg/L). The subscript 0 and e denotes the initial and equilibrium concentration state of the system, respectively. V is the CR volume and m is the weight of the adsorbent.

2.5. Recyclability test

To explore the stability of EG@NiFe₂O₄ adsorbent, the recyclability test was carried out. In this experiment, 0.05 g EG@NiFe₂O₄ was mixed with 100 mL CR 50 ppm at pH6 in 250 mL beaker, then was stirred for 240 min at 200 rpm. Herein, the adsorption experiments were repeated 5 times using the
same adsorbent of EG@NiFe2O4. Ethanol was used to wash the adsorbent after each adsorption cycle. The CR concentration was determined by UV-Vis spectra at a wavelength of 500 nm.

3. Results and discussion

3.1. Effect of contact time
To determine the required equilibrium time to attain saturation for the two adsorbents, experiments using two adsorbents were conducted and the liquid media was taken at a specific time intervals for measurement of CR concentration (Fig.1a, c). Successful determination of equilibrium time required to reach the saturation state could prevent excessive or insufficient dosing of adsorbent and minimize time loss in wastewater treatment processes [18-21]. Besides, dye concentration was also taken into account in this investigation (Fig.1b, d). The adsorption capacity of EG@NiFe2O4 and NiFe2O4 was quickly increased at the beginning of the experiment and then reached the equilibrium at 120 min. At this equilibrium, EG@NiFe2O4 and NiFe2O4 achieved the adsorption capacity of 89.58 mg/g and 39.72 mg/g, respectively. Overall, the adsorption capacity of EG@NiFe2O4 was higher than NiFe2O4. These results demonstrated that EG decorated over NiFe2O4 may lead to formation of a large amount of functional group onto the surface, resulting in higher uptake in comparison to its precursor NiFe2O4. Moreover, adsorption capacities for both samples showed rapid increases during the first 60 min but then decelerated afterwards to reach the equilibrium. This could be due to the concentration gradient situating between liquid phase and solid phase that hosts a large number of valid adsorption sites [22-25]. As the adsorption time is prolonged, both the number of vacant adsorption sites and CR concentration are decreased. Hence, the rate of adsorption was slowed down afterwards, eventually reaching the equilibrium state.

![Figure 1](image-url). Effect of contact time and concentration on the adsorption of CR onto EG@NiFe2O4 and NiFe2O4.
3.2. The effect of adsorbent dosage
Figure 2 shows variations of CR adsorption with respect to adsorbent dosage. Generally, higher adsorbent dosage seems to associate with improved dye removal efficiency. However, this relationship only holds in the dosage range from 0.03 to 0.05 g, at which point the capacity began to decline sharply afterwards. The sudden drop could be due to the rapid saturation of adsorbent sites when being in contact with the adsorbate and the ineffectiveness of adsorption sites that remained unsaturated when excessive dosage was used. Increasing the dosage of EG@NiFe$_2$O$_4$ from 0.03 g to 0.05 g greatly improved the removal efficiency from 80.43 mg/g to 92.97 mg/g. However, increasing the dosage of EG@NiFe$_2$O$_4$ from 0.06 g to 0.07 g inclined reduction in removal efficiency. This could be explained by the inability of the concentration gradient to overcome the transfer resistance and combine with spare sites [26-27]. Another explanation is that excessive dosage may cause particle aggregation which could be adverse to removal efficiency. The peak removal efficiency for both adsorbents is achieved with the dosage of 0.05 g for 100 mL of CR solution. Therefore, this dosage was used in subsequent studies.

![Figure 2](image)

**Figure 2.** Effect of dosage on the adsorption of CR onto EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$.

3.3. Effect of pH solution
In the adsorption process, pH plays an important role since it alters surface characteristics of the adsorbent [28-30]. Fig.3 illustrates the CR removal efficiency at different pH. It is shown that the CR adsorption efficiency onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ peaked at 6 and 4 respectively. The unfavorable efficiency at low pH could be explained by the abundance of proton in the media, which caused the number of positive charges formed on the surface of EG@NiFe$_2$O$_4$ to be exponentially increased, intensifying the electrostatic repulsion exerted on CR molecules. At high pH, the surface protonation is weakened and thus negative charges are more prevalent on the surface, impairing the CR adsorption process.

![Figure 3](image)

**Figure 3.** Effect of solution pH on the adsorption of CR onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$. 


Moreover, the FTIR spectra in Fig. 4 also provide more information about the functional groups of EG@NiFe$_2$O$_4$ and CR-loaded EG@NiFe$_2$O$_4$. An absorbance band was observed at 3400 cm$^{-1}$ which can be assigned for hydroxyl (−OH) and amine (−NH) group. The peak detected at 1636 cm$^{-1}$ could be attributable to free carboxylic groups. The presence of −SO$_3$ groups could be indicated by three peaks at 1383 cm$^{-1}$ (narrow), 1110 cm$^{-1}$ (strong) and 1107 cm$^{-1}$ (narrow). The metal at the tetrahedral site showed intrinsic stretching vibrations at the wavelength range of 620-550 cm$^{-1}$. At 587 cm$^{-1}$, a similar stretching vibration was observed for the spinel structure. Current results indicated the successful synthesis of EG@NiFe$_2$O$_4$ and suitability for adsorption of the as-synthesized adsorbent (Table 1).

Table 1. Comparison with the previous literatures

| No. | Material                                      | Adsorption capacity | Reference |
|-----|----------------------------------------------|---------------------|-----------|
| 1   | Roots of Eichhornia crassipes                | 96 %                | [19]      |
| 2   | Tunics of the corm of the saffron            | 68 %                | [20]      |
| 3   | Fe$_3$O$_4$ Nanoparticles                    | 97 %                | [21]      |
| 4   | Acid Pretreated Sugarcane Bagasse            | 78 %                | [22]      |
| 5   | EG@NiFe$_2$O$_4$                            | 88.56 %             | This study|

Figure 4. FTIR spectrum of EG@NiFe$_2$O$_4$ and CR-loaded EG@NiFe$_2$O$_4$

3.4. Recyclability of EG@NiFe$_2$O$_4$
Reusability is an important consideration for the feasibility of a material. After 3 cycles, the percentage of removal remained relatively high albeit being suffered from moderate reductions. However, after the fourth and fifth run, major declines (20.2 % and 16.2 %, respectively) in removal capacity were
observed (fig.5). This could be due to the loss of the material during the washing process. Therefore, 3 cycles are considered to be the most suitable for EG@NiFe$_2$O$_4$ in CR adsorption.

**Figure 5.** Removal capacity of of EG@NiFe$_2$O$_4$ after reuses

### 4. Conclusions
In this article, the EG@NiFe$_2$O$_4$ was successfully synthesized by sol-gel method and had its adsorption capacity evaluated against Congo Red dye. Our findings indicated that the adsorption process using the EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ adsorbent reaches the equilibrium at 120 min. The optimal pH for adsorption is 6 for EG@NiFe$_2$O$_4$ and 4 for NiFe$_2$O$_4$. Reusability test revealed that the EG@NiFe$_2$O$_4$ could be reused three times without major compromise in removal capacity.

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