Research Article
A Novel Fe$_3$O$_4$/Graphene Oxide Composite Prepared by Click Chemistry for High-Efficiency Removal of Congo Red from Water

Hongliu Jiang$^{1,}$, Yao Cao$^{1}$, Fengtao Zeng$^{2}$, Zewu Xie$^{2}$, and Fuan He$^{2}$

$^1$School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330069, China
$^2$School of Materials Science and Engineering, Guangdong University of Petrochemical Technology, Maoming 525000, China

Correspondence should be addressed to Fuan He; he-fu-an@163.com

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In this paper, a magnetic graphene oxide (MGO) composite was prepared by the click reaction between the alkyne-modified Fe$_3$O$_4$ nanoparticles and the azide-modified graphene oxide for the purpose of removing the Congo red (CR) dye from water. The deposition of the Fe$_3$O$_4$ nanoparticles on the graphene oxide to successfully prepare the MGO composite was evidenced by the Fourier-transform infrared spectrometer, wide-angle X-ray diffraction equipment, scanning electron microscope, thermal gravimetric analyzer, and Raman spectrometer. The value of saturation magnetization for the MGO composite was 34.9 emu/g. The CR absorption capacities of the MGO composite increased first and then decreased as the pH value increased. It was found that the maximum adsorption capacity of the MGO composite for the CR was as high as 769.2 mg/g. In the absorption-desorption experiment, the CR absorption capacities of the MGO composite from the second cycle to the fifth cycle remained stable to be about 130 mg/g. Moreover, both the Langmuir model for the adsorption isotherm and the pseudo-second-order kinetic model could be used to describe the CR absorption behaviors of the MGO composite.

1. Introduction

Recently, the problem of wastewater caused by organic dyes has aroused great concern and became an urgent event to be solved. So far, the commonly used technologies for the dye treatment of wastewater include biological treatment, coagulation/flocculation treatment, ozone treatment, chemical oxidation, membrane separation, and photocatalytic degradation [1–6]. Although the above methods have some advantages such as good decontamination ability, high efficiency, and convenient operation, they will consume enormous energy or have poor repeatability. For example, the degradation process needs not only exciting energy (e.g., gamma radiation or ultraviolet light) but also some additional chemicals (e.g., S$_2$O$_4^{2-}$ or/and H$_2$O$_2$) [7–9]. On the other hand, the adsorption method exhibited great potential for the treatment of wastewater containing various dyes [10–12]. Ahmed et al. have deposited magnesium/magnesium-layered double hydroxide nanoparticles on waste foundry sand. The adsorption capacity of the resultant composite for the Congo red (CR) dye reached as high as 9127.08 mg/g [10]. Zubair et al. have prepared the starch-NiFe-layered double hydroxide composite by the coprecipitation method, which possessed a high adsorption capacity of 387.59 mg/g for the methyl orange dye [11].

Graphene is a new material with many excellent properties such as its huge surface area and the possession of a number of free π electrons, which can be used as a good adsorbent for some dyes [13–15]. As a graphene derivative, graphene oxide (GO) has a two-dimensional planar structure similar to that of the graphene. GO contains a number of functional groups including carboxyl, hydroxyl, and epoxy on its surface, making it has a wide application prospect in the field of adsorbents with good absorption ability [16]. Magnetic nanometal oxides have been extensively studied and applied in magnetic fluid, data storage, catalysis, biomedicine, and pollutant treatment [17]. Graphene combined with magnetic nanomaterial can be used as an adsorbent to treat wastewater contaminants and then easily separated from an aqueous solution under external magnetic field conditions. It has been reported that the above magnetic GO composites simultaneously have the characteristics of GO and the magnetic...
property, which are new materials widely used in environmental treatment in recent years [18–24].

There are many methods for the preparation of magnetic graphene-based composites [25–36]. The chemical precipitation method has been reported on the preparation of the Fe₃O₄/GO composites [25, 26]. In addition, by using the hydrazine hydrate or the gas/liquid interface reaction, the Fe₃O₄/GO composites were also prepared [28, 29]. Moreover, the superparamagnetic Fe₃O₄ nanoparticles could be synthesized by the solvothermal method. Hence, the solvent thermal reduction is one of the most common methods to obtain the magnetic Fe₃O₄/GO composites [30–36]. In particular, in order to enhance the binding force of the Fe₃O₄ particles and the GO, the Fe₃O₄/GO composites could be formed by the covalent bonding [26].

“Click chemistry” is an advanced synthesis method discovered by Sharpless et al., which can complete the chemical synthesis of the molecules quickly and reliably by the conjugation of small units [37]. This synthesis method has mild experimental conditions and usually can be operated at room temperature. In recent years, the synthetic method is widely used in the functionalized biological drug, the modification of nanoparticle surface, the application of complex drugs, the magnetic nanocomposites, and so on [38–44].

In recent years, the adsorption behaviors of the graphene and its derivatives were extensively studied. Graphene and its derivatives have a remarkable adsorption capacity on methylene blue (MB), fluoride, and other substances [41–50]. Chen et al. prepared the GO by the solvothermal method for the adsorption of the MB in the aqueous solution [44]. Leng et al. prepared the GO by the modified Hummers method and then used it to absorb the toxic metal ion antimony with a high adsorption rate of 99.5% [49]. The adsorption of GO and reduced GO (RGO) absorb the toxic metal ion antimony with a high adsorption rate of nanoparticle surface, the application of complex drugs, the magnetic nanocomposites, and so on [38–44].

In recent years, the adsorption behaviors of the graphene and its derivatives were extensively studied. Graphene and its derivatives have a remarkable adsorption capacity on methylene blue (MB), fluoride, and other substances [41–50]. Chen et al. prepared the GO by the solvothermal method for the adsorption of the MB in the aqueous solution [44]. Leng et al. prepared the GO by the modified Hummers method and then used it to absorb the toxic metal ion antimony with a high adsorption rate of 99.5% [49]. The adsorption of GO and reduced GO (RGO) for the acridine orange dye was also investigated [49]. Furthermore, the research studies on the adsorption of the organic dyes by the low-dimensional magnetic carbon nanomaterials have been increased. The magnetic Fe₃O₄/GO composites were used to absorb the MB and CR dyes with the adsorption capacities of 190.14 mg/g and 140.79 mg/g, respectively [42]. The magnetic iron nanoparticles/graphene (Fe/G) composites were also prepared for the absorption of MB [43].

In the current work, we had prepared the alkynylated Fe₃O₄ nanoparticles and then used the click chemistry to effectively attach them onto the azide-modified GO surface for the fabrication of a novel magnetic graphene oxide (MGO) composite, as shown in Figure 1. The resultant MGO composite was characterized by the Fourier-transform infrared (FTIR) spectrometer, the wide-angle X-ray diffraction (WAXD) equipment, the Raman spectrometer, the vibrating sample magnetometer (VSM), the X-ray photoelectron spectrometer (XPS), the thermogravimetric analyzer (TGA), and the scanning electron microscope (SEM). Furthermore, the adsorption behavior of the MGO composite for the CR dye was studied in detail.

2. Materials and Methods

2.1. Materials. Graphite (average particle size 48 μm), Fe₃O₄ nanoparticles, aminopropyltriethoxysilane (APTES) as a silane coupling agent, propionic acid, dicyclohexylcarbodi-
spectrophotometer. The magnetic property was characterized using a VSM magnetic measuring instrument (Quantum Design, model MPMS, SQUID, US). XPS spectra were obtained from an X-ray photoelectron spectrometer in the Axis Ultra DLD model.

2.4. Adsorption Experiments. After the absorption by the MGO composite and the following separation of the MGO composite by a magnet, the equilibrium concentration \( C_e \) of the CR in the aqueous solution was measured with a UV-Vis spectrophotometer at the wavelength of 497 nm. The absorption capacity and the removal rate of the MGO composite for the CR were calculated by

\[
q_t = \frac{(C_0 - C_e) \times V}{m},
\]

where \( C_0 \) was the initial concentration of the CR in the aqueous solution before the absorption, \( V \) was the CR aqueous solution volume, and \( m \) was the MGO composite mass.

3. Results and Discussion

3.1. Characterization of the MGO Composite. It could be clearly observed from the SEM images of the MGO composite (see Figure 2) that a lot of \( \text{Fe}_3\text{O}_4 \) nanoparticles had been homogeneously attached on the surface of GO, which intuitively confirmed the formation of the magnetic \( \text{Fe}_3\text{O}_4/\text{GO} \) composite after the click reaction.

The FTIR spectra of the GO and the GO-N\(_3\) are shown in Figure 3. The FTIR spectrum of the GO displayed the C=O stretching vibration of the carboxyl groups, the O-H stretching vibration of the hydroxyl groups in both the graphene skeleton and the carboxyl groups, the C=C stretching vibration of the graphene skeleton, and the C-O stretching
vibration of the epoxy groups on the graphene skeleton at 1722 cm\(^{-1}\), 3436 cm\(^{-1}\), 1624 cm\(^{-1}\), and 1062 cm\(^{-1}\), respectively. After the modification of the GO, the resultant GO-N\(_3\) exhibited a series of FTIR peaks at 1547 cm\(^{-1}\) for the N-H stretching vibration of the amide groups (band II), 1463 cm\(^{-1}\) for the C-N stretching vibration of the amide groups, 2912 cm\(^{-1}\) as well as 2843 cm\(^{-1}\) for the C-H stretching vibration of the methylene groups, and 2092 cm\(^{-1}\) for the N=\(_3\) stretching vibration of the azide groups, respectively. Moreover, compared with the FTIR spectrum of GO, both the higher peak intensity of the C-O stretching vibration for epoxy groups at 1052 cm\(^{-1}\) and the significantly decreased peak intensity of the O-H stretching vibration for carboxyl groups at 3436 cm\(^{-1}\) could be found in the FTIR spectrum of GO-N\(_3\). These FTIR results confirmed the successful amidation reaction between the GO and the N\(_3\)-PEG-NH\(_2\), indicating that the N\(_3\)-PEG-NH\(_2\) macromolecules were linked to the GO by the covalent amide bonding.

The FTIR spectra of the Fe\(_3\)O\(_4\) nanoparticles, the Fe\(_3\)O\(_4\)-NH\(_2\) nanoparticles, the alkyne-Fe\(_3\)O\(_4\) nanoparticles, and the MGO composite are shown in Figure 4. In the FTIR spectrum of the Fe\(_3\)O\(_4\) nanoparticles, the peak at 582 cm\(^{-1}\) was related to the Fe-O stretching vibration and the other two peaks at 3443 cm\(^{-1}\) and 1631 cm\(^{-1}\) could be attributed to the hydroxyl groups on the surface of the Fe\(_3\)O\(_4\) nanoparticles. In the FTIR spectrum of Fe\(_3\)O\(_4\)-NH\(_2\) nanoparticles, the existence of a series of peaks at 1031 cm\(^{-1}\) for the Si-O stretching vibration, 1561 cm\(^{-1}\) for the N-H stretching vibration, and 2927 cm\(^{-1}\) along with 2867 cm\(^{-1}\) for the C-H stretching vibration indicated that the APTES had been successfully coated on the surface of Fe\(_3\)O\(_4\) nanoparticles. After the further treatment of the Fe\(_3\)O\(_4\)-NH\(_2\) nanoparticles with the propiolic acid, the resultant alkyne-Fe\(_3\)O\(_4\) nanoparticles showed the characteristic FTIR peaks of the C=O stretching vibration of the amide groups, the N-H stretching vibration of the amide groups (band I as well as band II), the C-N stretching vibration of the amide groups, and the C≡C stretching vibration of alkyne groups at 1712 cm\(^{-1}\), 1638 cm\(^{-1}\), 1585 cm\(^{-1}\), 1448 cm\(^{-1}\), and 2092 cm\(^{-1}\), respectively. This indicated that the alkyne functionalization of the Fe\(_3\)O\(_4\) nanoparticles has been realized. After the click reaction between the GO-N\(_3\) and the alkyne-Fe\(_3\)O\(_4\), there were two characteristic peaks at
580 cm⁻¹ for the Fe-O stretching vibration and 880 cm⁻¹ for the C-H stretching vibration of the benzene ring in the FTIR spectrum of the MGO composite, which proved the existence of both the Fe₃O₄ nanoparticles and the GO. Besides, it could also be found in the FTIR spectrum of the MGO composite that the characteristic peaks of the alkynyl groups at 2092 cm⁻¹ and the azide groups at 2092 cm⁻¹ disappeared and a new peak appeared at 1660 cm⁻¹ for the triazole ring formed from the click reaction. This showed that the Fe₃O₄ nanoparticles have been covalently attached to the graphene by the click chemistry.

The Raman spectra of the graphite, the GO, and the GO-N₃ are shown in Figure 5. The Raman shifts of the D peak and the G peak for the graphite were at 1324 cm⁻¹ and 1572 cm⁻¹, respectively, and the intensity ratio of the D peak to the G peak (I_D/I_G) for the graphite was 0.25. For the GO obtained from the oxidation of the graphite, its Raman shifts of the D peak and the G peak were at 1324 cm⁻¹ and 1601 cm⁻¹, respectively, along with a I_D/I_G value of 1.36. These results indicated that there were many defects on the GO surface due to the breaking of carbon-carbon double bonds and the attachment of a lot of the oxygenating groups during the oxidation process. For the GO-N₃, its Raman shifts of the D peak and the G peak were at 1336 cm⁻¹ and 1593 cm⁻¹, respectively, along with a I_D/I_G value of 1.48. This indicated that, after the grafting of the N₃-PEG-NH₂ on the graphene surface by the amidation reaction, the surface structure of the resultant GO-N₃ had been changed in comparison with that of the GO.

The WAXD patterns of the GO and the MGO composite are shown in Figure 6. In the WAXD pattern of the GO, the diffraction peak appearing at 2θ = 10.6° corresponded to the (001) crystal plane. In the WAXD pattern of the MGO composite, the (111), (220), (311), (400), (422), and (511) crystal planes of the Fe₃O₄ nanoparticles could be found at 2θ = 18.27°, 30.1°, 35.4°, 43.05°, 56.94°, and 62.51°, respectively, indicating that the Fe₃O₄ nanoparticles were successfully loaded on the GO [51]. Moreover, the diffraction peaks of

[Figure 5: The Raman spectra of (a) the graphite, (b) the GO, and (c) the GO-N₃.]

[Figure 6: The WAXD patterns of the GO and the MGO composite.]

[Figure 7: The TGA curves of (a) the GO, (b) the GO-N₃, (c) the Fe₃O₄ nanoparticles, (d) the Fe₃O₄-C≡C nanoparticles, and (e) the MGO composite.]

the GO at 2θ = 10.6° disappeared in the MGO composite. It means that, by the incorporation of the Fe₃O₄ nanoparticles, the nanosheets of the GO in the MGO composite were in the exfoliated state without agglomeration.

The TGA curves of the GO, the GO-N₃, the Fe₃O₄ nanoparticles, the Fe₃O₄-C≡C nanoparticles, and the MGO composite under the argon atmosphere from room temperature to 800°C are shown in Figure 7. There were two significant weight loss stages in the TGA curve of the GO with a weight loss of 63.1 wt.% at 800°C. The first thermal decomposition stage of the GO below 100°C with a weight loss of 15.2 wt.% was mainly due to the evaporation of the adsorbed water while the second one between 150°C and 230°C with a weight loss of 29.6 wt.% could be ascribed to the decomposition of oxygen-containing functional groups. Similarly, the GO-N₃ also had two main thermal decomposition stages with a weight loss of 41.2 wt.% at 800°C and exhibited much more stability than the GO because the molecular weight of the
attached PEG chains was higher in comparison with the oxygen-containing functional groups. On the other hand, the pristine Fe3O4 nanoparticles only had a trace amount of weight loss at 800°C. After surface modification, the thermal stability of the resultant Fe3O4-C≡C nanoparticles was much lower than that of the pristine Fe3O4 nanoparticles with a weight loss of 59.2 wt.% at 800°C since there was a lot of organic component in it. In particular, the weight loss of the Fe3O4-C≡C nanoparticles occurred between 730°C and 780°C, which was probably caused by the breakage of the Si-O covalent bond between the silane coupling agent and the Fe3O4 nanoparticles. It was interesting that the thermal stability of the MGO composite obtained from click reaction was higher than that of the reactants including Fe3O4-C≡C nanoparticles and GO-N3 with a weight loss of 46.0 wt.% at 800°C. Such a weight loss of the MGO composite could be attributed to the different components originating from the N3-PEG-NH2, the propiolic acid, the GO, and the silane coupling agent.

The XPS result of the MGO composite is shown in Figure 8, exhibiting several characteristic peaks for various elements including Si2p (102.8 eV) as well as Si2s (154.0 eV), O1s (531.7 eV), C1s (284.9 eV), N1s (400.6 eV), and Fe2p (711.0 eV and 717.1 eV). The existence of these elements in the MGO composite could be attributed to the different components originating from the Fe3O4 nanoparticles, the GO, the N3-PEG-NH2, the APTES, and the propiolic acid.

The magnetic properties of the pristine Fe3O4 nanoparticles and the MGO composite were measured by VSM at room temperature. As shown in Figure 9, the coercivities of the pristine Fe3O4 nanoparticles and MGO composite were 114 Oe and 106 Oe, respectively, while the remanences of the pristine Fe3O4 nanoparticles and MGO composite were 6.4 emu/g and 3.4 emu/g, respectively. On the other hand, the values of saturation magnetization (Ms) for the pristine Fe3O4 nanoparticles and the MGO composite were 81.1 emu/g and 34.9 emu/g, respectively, proving the existence of the magnetic Fe3O4 nanoparticles in the MGO composite. It was reasonable that the Ms values of the MGO composite were significantly lower than those of the pristine Fe3O4 nanoparticles because the components of the GO and the modifiers in the MGO composite were nonmagnetic.

3.2 Adsorption Studies of the MGO Composite. According to the relationship between the contact time (t) and the absorption capacity within t minute (qt) of the MGO composite (see Figure 10) at the t moment, the MGO composite quickly absorbed the CR dye in the aqueous solution in 10 minutes and the absorption equilibrium was reached within 30 minutes. The CR absorption capacity of the MGO composite at equilibrium (qe) was about 490 mg/g with a removal rate of about 98%. We believed that the good CR absorption ability of the MGO composite could be explained by two reasons: (1) both the high-surface area MGO composite and the CR had the benzene ring structure, leading to the mutual attraction by the π-π interaction, and (2) the MGO composite containing the hydroxyl group and the imide group could
effectively absorb the CR containing the amine group by the hydrogen bonding and the dipole-dipole mutual interaction [52–55]. Moreover, the MGO composite after the CR absorption could be recollected by a magnet, as shown in the inset of Figure 9. Furthermore, the mechanism of the CR absorption kinetic model for the MGO composite was studied by the quasi-first-order model and the quasi-second-order model by the fitting of the $t$ and the $q_t$ as follows.

**Figure 11:** The experimental fitting results of the quasi-first-order kinetic model and the quasi-second-order kinetic model.

| Pseudo-first-order kinetics | Pseudo-second-order kinetics |
|-----------------------------|-------------------------------|
| $k_1 \times 10^{-3}$ g×mg⁻¹×min⁻¹ | $k_2 \times 10^{-3}$ g×mg⁻¹×min⁻¹ |
| $R^2$ | $R^2$ |
| 0.3689 | 0.14 |
| 0.02565 | 0.0125 |
| 0.9998 | 0.9998 |

**Figure 12:** The experimental fitting results of the Langmuir isotherm model and the Freundlich isotherm model.

| Langmuir isotherm | Freundlich isotherm |
|-------------------|---------------------|
| $b$ (L/mg) | $q_{ind}$ (mg/g) |
| $R^2$ | $K_f$ |
| $n$ | $R^2$ |
| 0.164 | 769.2 | 0.949 | 418.857 | 0.121 | 0.459 |
Quasi-first-order kinetic model:

\[ \ln (q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303}. \]  

(2)

Quasi-second-order kinetic model:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}. \]  

(3)

where \( k_1 \) and \( k_2 \) were the constant. The experimental fitting results (see Figure 11 and Table 1) showed that the CR adsorption process of the MGO composite could be well fitted by the quasi-second-order kinetic model with \( R^2 = 0.9998 \), indicating that the CR adsorption kinetic model of the MGO composite was accurately simulated by the quasi-second-order kinetic model.

Both the Langmuir isotherm model (see Equation (4)) and the Freundlich isotherm model (see Equation (5)) were used to study the absorption isotherm of the MGO composite for the CR.

Langmuir isotherm model:

\[ \frac{C_e}{q_e} = \frac{1}{b q_{\text{ml}}} + \frac{C_e}{q_{\text{ml}}}. \]  

(4)

Freundlich isotherm model:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e, \]  

(5)

where both \( b \) and \( K_f \) were the constant, and \( q_{\text{max}} \) was the maximum CR absorption capacity of the MGO composite basing on the Langmuir isotherm model. As shown in Figure 12 and listed in Table 2, the adsorption process of the MGO composite was more consistent with the uniform monolayer CR adsorption described by the Langmuir model with the \( R^2 = 0.9494 \). The \( q_{\text{ml}} \) value was calculated to be 769.2 mg/g, which was much higher than many other reported absorbents (see Table 3) [54–60].

Figure 13 shows the effect of the pH value on the CR absorption capacities of the MGO composite, which increased first and then decreased as the pH value increased. It is well known that the concentration of the H\(^+\) decreases as the pH value increases. When the pH value was low, there was a competition between the protonated positive CR molecules and there was a lot of H\(^+\) on the active adsorption site of the negative MGO composite. On the other hand, when the pH value was high, the CR became negatively charged, which resulted in the reduction of the mutual interaction with the negative MGO composite. Therefore, the maximum CR absorption capacity by the MGO composite could be obtained at \( \text{pH} = 7 \) with the maximum CR absorption capacity of 442.8 mg/g and the removal rate of 88.6%.

The MGO composite was subjected to the absorption-desorption experiment for the CR in five cycles (see Figure 14), and the resultant CR absorption capacities of the MGO composite were 442.8 mg/g with the removal rate of 88.6%, 133.3 mg/g with the removal rate of 26.7%,

| Adsorbents                        | \( q_{\text{max}} \) (mg/g) | Ref. |
|-----------------------------------|------------------------------|-----|
| Fe\(_2\)O\(_3\)/GO composite      | 113.2                        | [54]|
| Fe\(_2\)O\(_3\)/GO composite      | 33.66                        | [55]|
| GO/Fe\(_2\)O\(_3\)/PEI composite  | 575                          | [56]|
| MgO-GO composite                  | 237                          | [57]|
| Fe\(_2\)O\(_3\)/TSPED-tryptophan  | 183.15                       | [59]|
| Fe\(_2\)O\(_3\)/sepiolite composites | 126.4                       | [60]|
| MGO composite                     | 769.2                        | This work |
by the strong mutual interaction between some absorption sites of the MGO composite and the absorbed CR molecules, which were difficult to desorb. Although the regenerated ability of the MGO composite for the CR absorption was not ideal, the CR absorption capacities of the MGO composite from the second cycle to the fifth cycle remained stable to be about 130 mg/g. These values were still obviously higher than those (113.2 mg/g and 33.66 mg/g) of the other reported magnetic graphene-based absorbents [54–57].

4. Conclusion

Both the alkyne-modified Fe3O4 nanoparticles and the azide-modified GO were prepared and then attached together by the click chemistry to obtain the MGO composite. The successful attachment of the Fe3O4 nanoparticles onto the GO surface was testified by FTIR, WAXD, SEM, and Raman spectrum, and VSM. The optimized condition of the CR containing the CR dye could be a potential adsorbent to purify the wastewater containing the CR dye. Moreover, the CR absorption behaviors of the MGO composite possessed a high CR absorption capacity of 769.2 mg/g and could be magnetically recollected after absorption. Moreover, the CR absorption behaviors of the MGO composite could be explained by the pseudo-second-order kinetic model and the Langmuir model. All of the experimental results indicated that the MGO composite could be a potential adsorbent to purify the wastewater containing the CR dye.

Data Availability

Any data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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