The Role of graphene in Fe₃O₄/graphene Composites on the Adsorption of Methylene Blue and Their Kinetic Study

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Abstract. In this study Fe₃O₄ with addition of graphene materials were investigated as an adsorbent for removing organic dye from the aqueous solution. Fe₃O₄-graphene were synthesized using hydrothermal method. The contents of graphene were varied from 5, 10, and 15 weight percent (wt%). Their physical properties were investigated using X-ray diffraction (XRD), thermogravimetric analysis (TGA), and surface area analysis. The cubic spinel of the samples was detected which attributed to the existence of Fe₃O₄ materials. The removal of organic dye was investigated using adsorption process. Methylene blue was selected as a model of organic pollutant. Their kinetic reaction indicates that the samples follow the pseudo second order kinetic reaction with maximum adsorption capacity was 48 mg/g. The samples performed good stability for removing methylene blue using adsorption process with 95 % efficiencies.

1. Introduction

During the last few decades, the organic dye removal from waste water is extensively investigated using various method. However, most of these dyes exhibit high resistance to photodegradation and biodegradation which may transfer the primary pollutant to secondary one that may be more toxic. Adsorption was found as a simple and low cost process for removing various hazardous pollutants from wastewater [1].

There are many materials that have been used as catalyst in the adsorption process such as zeolite [2], clay [3], silica [4], and activated carbon [5]. However, the difficulty of separation between catalyst and the organic dye solution is another challenge for improving the adsorption efficiencies [6]. Many strategies have been developed to improve the separation efficiency of the samples such as centrifugation [7]. However this process is expensive and complex system. Using magnetic catalyst as adsorbent is very promising for enhancing the separation efficiency due to its ability to attract by external magnetic that provide magnetic separation process [8]. Among others magnetic materials, magnetite (Fe₃O₄) has been considered as a promising candidate as catalyst due to its unique magnetic properties and also high adsorption capacity.

In practical experiment, Fe₃O₄ adsorption process is still has limitation due to the small specific surface area. Many method has been tried to improve the specific surface area of Fe₃O₄. Recently the incorporation of graphene materials with theoretical surface area about 2600m²/g on semiconductors have been proved could improve the specific surface area of the samples [9].

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Based on that reason in this reasearch we try to evaluate the influence of Fe\textsubscript{3}O\textsubscript{4} modified by graphene materials for enhance the adsorption ability of the samples. The kinetic calculation was so observed to understand the adsorption behaviour of the samples and the reusability was also observed for investigated the stability of the samples.

2. Experimental Detail

2.1. Materials
Fe(SO)\textsubscript{4}.7H\textsubscript{2}O (Iron Sulfate Heptahydrate), NaOH (Sodium Hydroxide), CH\textsubscript{3}COOH (Acetic Acid) were purchased from merk and used without further purifications, while graphene were purchased from Angstrom Materials.

2.2. Synthesis and Characterization
The Fe\textsubscript{3}O\textsubscript{4} nanoparticles were prepared based on our previous study [10]. The Fe\textsubscript{3}O\textsubscript{4}-graphene were synthesized using hydrothermal method. Typically, graphene powder was dispersed in mixture water and ethanol solution. After that, the graphene dispersion was sonicated using ultrasonic bath operated at 40 kHz frequency for 2h. The Fe\textsubscript{3}O\textsubscript{4} nanoparticles were added into the graphene dispersion and stirred for 30 min. The mixture then heated at 120°C for 30 min to deposit Fe\textsubscript{3}O\textsubscript{4} on graphene sheet. After that the samples were collected using centrifugation method and dried under vacuum condition. The all prepared samples were characterized using X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) surface area analysis.

2.3. Adsorption Experiment
The adsorption process was carried out for removal methylene blue from the aqueous solution. Typically, 60 mg/L methylene blue solution was prepared followed by the incorporation of 0.03 g adsorbent. The methylene blue concentration was monitored by UV-Vis spectroscopy. The decolorization of methylene blue and the adsorption capacity of the samples was calculated using the following equation:

\[ \text{Degradation: } \frac{C_t}{C_0} \]  
\[ q_e = \frac{(C_0 - C_e)V}{m} \]

where \( C_0 \) is the initial methylene blue concentration (mg/L), \( C_t \) is the methylene blue concentration after time \( t \) (mg/L), \( q_e \) represents the equilibrium adsorption capacity of the Fe\textsubscript{3}O\textsubscript{4} nanocomposite (mg/g); and \( C_e \) are the initial and equilibrium concentrations of methylene blue (mg/L) in aqueous solutions, respectively; \( V \) is the volume of the aqueous MB (mL); and \( m \) is the amount of Fe\textsubscript{3}O\textsubscript{4}/graphene used (g).

To understand the underlying adsorption mechanisms in this study, two models, including pseudo-first order and pseudo-second order models expressed in Eq. (2) and (3),

\[ \ln(q_e - q_t) = \ln q_e - K_1 t \]  
\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]

were applied to extract the useful information from the experimental kinetic data. In these equations, \( q_e \) and \( q_t \) are the adsorption capacities at equilibrium and time \( t \), respectively. \( K_1 \) is the pseudo-first order kinetic constant (min\(^{-1}\)), and \( K_2 \) is pseudo-second order constant (g/(mg min)).

3. Result and Discussion
Figure 1a shows the XRD spectra of Fe\textsubscript{3}O\textsubscript{4} modified by graphene materials. As comparison, the XRD spectra of Fe\textsubscript{3}O\textsubscript{4} nanoparticles, as well as graphene materials, were also plotted. The XRD result for all samples were detected peak at \( 20 = 30.14^\circ, 35.49^\circ, 43.28^\circ, 53.76^\circ, 57.20^\circ, \) and \( 62.83^\circ \). These peak were
attributed to (220), (311), (400), (442), (511), and (440) plane of cubic spinel structures from Fe3O4 nanoparticles. No undesired peaks were detected that indicated the successfully formation of Fe3O4/graphene composites. The lattice parameter and grain size of the samples were tabulated in Table 1. It can be seen that the grain size value of Fe3O4/graphene was slightly decrease with the increasing of graphene weight percent. It can be due to the existence of graphene inhibits the crystallization of Fe3O4. No diffraction peak was detected from graphene in Fe3O4/graphene composites that probably due to the small amount and broad peak of graphene.

The specific surface area of the samples was tabulated in Table 1. The specific surface area of the samples was gradually increase with the incorporation of graphene from 2.3 m²/g to 106.9 m²/g. The higher specific surface area is beneficial for the enhancement of adsorption process due to its ability to increase the space contact between adsorbent and adsorbate.

The thermal stability of the samples was investigated in the range of room temperature until 800 °C. Results were plotted in Figure 1b. as can be seen from the figure that Fe3O4 nanoparticles exhibit good stability until 800 °C however the incorporation of graphene reduces its stability starting from 400 °C due to the combustion of carbon. The higher graphene weight percent resulting the lower stability of the samples due to the combustion of carbon [11].

The adsorption ability of the samples was recorded on the degradation of methylene blue from the aqueous solution. Figure 2a shows the relative adsorption concentration of methylene blue after and before adsorption process. The removal of methylene blue using Fe3O4 nanoparticles was only 14 %. The incorporation of graphene from 5, 10, and 15 wt% the removal ability of the samples was increase from 53 %, 64 %, and 73 %. It probably due to the increasing of specific surface area of the samples.

Table 1. Lattice parameter, grain size and specific surface area of Fe3O4 nanoparticles and Fe3O4/graphene composites with different weight percent.

| Sample                  | Lattice parameter (Å) | Grain size (nm) | Surface area (m²/g) |
|-------------------------|-----------------------|-----------------|---------------------|
| Fe3O4                   | a=b=c 8.363           | 45              | 2.3                 |
| Fe3O4/5 wt% graphene    | 8.357                 | 42              | 65.0                |
| Fe3O4/10 wt% graphene   | 8.354                 | 39              | 95.0                |
| Fe3O4/15 wt% graphene   | 8.332                 | 39              | 106.9               |

Figure 1. (a) XRD spectra and (b) TGA measurement of Fe3O4 nanoparticles and Fe3O4/graphene nanocomposites with different weight percent.
Figure 2b shows the adsorption capacity for all samples. As can be seen from the figures that the

Figure 2. (a) Decolorization ability and (b) adsorption capacity of Fe$_3$O$_4$ nanoparticles and Fe$_3$O$_4$/graphene composites with different graphene weight percent.

Figure 3. (a) Pseudo first order and (b) second order kinetic reactions

Figure 4. Reusability of adsorbent.

Figure 2b shows the adsorption capacity for all samples. As can be seen from the figures that the
samples with the higher graphene content exhibits the higher adsorption ability. With maximum adsorption capacity about 48 mg/g. It is probably due to the higher surface area of adsorbent that promoted the better contact between adsorbent and adsorbate.

The kinetic model of adsorption was calculated using pseudo first and second order kinetic reaction. The fitted data were plotted in Figure 3. As can be seen in the figure that the linear plot of the experimental data well fitted with the pseudo second order kinetic reaction with R² are about 98 however using pseudo first order kinetic reaction the R² are only about 88. It indicates that pseudo first order kinetic model failed to described the adsorption kinetic of the samples while pseudo second order kinetic reaction successfully described the adsorption kinetic of the samples.

Stability of adsorbent is an important parameter for practical applications. Figure 4 shows the reusability of the Fe₃O₄/graphene with 15 wt% graphene. As can be seen from the figure that the sample performed good stability. After 4 time cycling process the removal ability of the samples was decrease about 95% from the initial experiment. It indicates that Fe₃O₄/graphene is potential as adsorbent for removing waste water.

4. Conclusion
The Fe₃O₄/graphene composites were successfully synthesized using hydrothermal method for removing methylene blue using adsorption process. The incorporation of graphene in Fe₃O₄ significantly enhance the adsorption ability, with the highest graphene content resulting the highest removal efficiencies. The kinetic calculation indicates that the samples followed pseudo second order kinetic reactions.

References
[1] Salem A N M, Ahmed M A, Shahat M F E 2016 J. Mol. Liq. 219 780
[2] Alver E, Metin AÜ 2012 Chem. Engin. J. 200–202 59
[3] Pan Y, Cai P, Farahani M F, Li Y, Hou X, Xiao H 2016 Appl. Surf. Sci. 385 333
[4] Perullini M, Jobbágy M, Japas M L, Bilmes S A 2014 J. Colloid Interf. Sci. 425 91
[5] Demirbas A 2009 J. Hazard. Mater. 160 1–9.
[6] Zhao J, Liu J, Li N, Wang W, Nan J, Zhao Z, Cui F 2016 Chem. Eng. J. 304 737
[7] Jia X, Dai R, Lian D, Han S, Wu X, Song H 2017 Appl. Surf. Sci. 392 268
[8] Kalantari K, Ahmad M B, Masoumi H R F, Shameli K, Basri M, Khandanlou R 2015 Journal of the Taiwan Institute of Chemical Engineers 49 192
[9] Gadipelli S, Guo Z X 2015 Progress in Materials Science 69 1
[10] Taufik A, Saleh R 2016 Mater. Sci. Forum 864 106
[11] Lin C C, Ho J M 2014 Ceram. Int. 40 10275