Effect of nanographene platelets (NGP) surface area on organic dye adsorption using Fe$_3$O$_4$-NGP composites

A. Taufik$^{1,2}$, and R. Saleh$^{1,2,*}$

$^1$Departemen Fisika, Fakultas MIPA-Universitas Indonesia, 16424 Depok, Indonesia

$^2$Integrated Laboratory of Energy and Environment, Fakultas MIPA-Universitas Indonesia, 16424 Depok, Indonesia

E-mail: rosari.saleh@ui.ac.id

Abstract. Fe$_3$O$_4$-NanoGraphene Platelets (NGP) composites with different surface area were successfully synthesized using sol gel method. The inverse cubic spinel structures as well as graphitic like structure from NGP were detected using X-Ray Diffraction (XRD) Measurement, while the ferromagnetic behavior for all samples were detected using Vibrating Sample Magnetometry (VSM) measurement. The vibrational mode for all samples were characterized using Fourier Transform Infrared Spectroscopy (FT-IR), and thermal stability for all samples were characterized using Thermogravimetric Analysis (TGA). The adsorption process were tested using methylene blue (MB) as a model of organic pollutant445

1. Introduction

Organic dye is the main organic pollutant compound in wastewater that released from various industries such as leather, textile, paper, and plastic [1-3]. This dye could be toxic and probably mutagenic and carcinogenic. Even at low concentration organic dye is very harmful to human being and microorganism [4]. Therefore it is necessary and important to find an effective method to treat organic dye effluent from industrial process before discharge into water resources. Adsorption process has received special attention in wastewater treatment due to its high efficiency, cost effectiveness, and simple operation [5-6].

Nowadays, there are a lot of adsorbents that have been used in organic dye adsorption such as zeolite, activate carbon, and clay [4,7]. However the low adsorption capacities and low separation efficiencies of these adsorptions limit their application. Recently, magnetic nanomaterials have attracted huge interest due to its high adsorption capacity, high separation efficiency and reusability [8]. Fe$_3$O$_4$ has been found as a good adsorption due to high adsorption capacity and unique magnetic properties [9-13]. However Fe$_3$O$_4$ nanoparticles are restricted due to its small specific surface area.

Graphene as a new carbon material, has attracted huge attention in adsorption process due to its high surface area [14]. Combination of Fe$_3$O$_4$ with graphene materials are expected could enhance the adsorption efficiency. Not only having high adsorption capacity due to its high surface area but also high separation efficiency and reusability of catalyst due to magnetic properties of Fe$_3$O$_4$.
nanoparticles. So in this research will be reported the adsorption process of Fe₃O₄ with the addition of nanographene platelets with different surface area on the degradation of methylene blue as a model of organic pollutant. The kinetic models of adsorption process are also studied.

2. Experimental

2.1. Chemicals
All chemical reagents are analytical grade and used without further purification. Iron (II) sulfate heptahydrate (FeSO₄·7H₂O, 99%), sodium hydroxide (NaOH), ethanol and ethylene glycol (EG) were purchased from Merck. Three types of Nanographene Platelets with different surface area were purchased from Angstron Materials, N006-P10 (Surface area 15 m²/g), N008-100N Surface area (30 m²/g), and N006-P10 (Surface area 40 m²/g).

2.2. Preparation Fe₃O₄-NGP composites
Fe₃O₄-NGP were synthesized using the same method in our previous study [15]. Briefly 200 mg of NGP was dissolved in 80 mL water solution and 40 mL ethanol through ultrasonic treatment for 2 h, followed by the addition of 2 g of Fe₃O₄ to the NGP solution and an additional 2 h of stirring to achieve a homogeneous suspension. The suspension was then heated at 120°C for 3 h to affect the deposition on the graphene sheets. The resulting composite was isolated by centrifugation and dried at 70 °C for 12 h. The all samples were denoted as S1, S2, and S3 for Fe₃O₄-NGP composites with surface area 15 m²/g, 30 m²/g, and 40 m²/g respectively.

2.3. Characterizations
The samples were characterized by X-ray diffraction (XRD) measurements using a Rigaku Miniflex 600. The infrared absorption spectra of the samples were recorded using a Shimadzu FT-IR spectrophotometer in the range of 400-4000 cm⁻¹. Thermal stability of the samples were analyze using thermal gravimetric analyzer (Rigaku Thermo Plus EVO2) while the magnetic measurements were performed on Oxford Type 1.2T vibrating sample magnetometer (VSM).

2.4. Adsorption processes
Adsorption experiments were carried out at room temperature for the different time. 0.04 g Fe₃O₄-NGP composites were put into the glass vessel containing 100 mL methylene blue (MB) solution as model of pollutant at concentration of 20 mg/L. The pH solution was adjusted using NaOH or CH₃COOH. After adsorption Fe₃O₄-NGP composites were separated using a permanent magnetic bar from the solution and the dye concentration was analyzed using UV-vis spectrophotometer. The amount of dye adsorbed at different time intervals was calculated using the following equation:
\[
q_t = \frac{(C_0 - C_t)V}{m}
\]  
(1)
where \(q_t\) is the amount of dye adsorbed per unit mass of adsorbent (mg/g) at time t and \(C_t\) is concentration of dye (mg/L) at time t, \(m\) is amount of adsorbent (g), and \(V\) is amount of dy solution (L).

The data of adsorption kinetics of MB on adsorbent are fitted by the pseudo-first-order and pseudo-second-order model. The equations of pseudo-first-order and pseudo-second-order model can be described by Eq. (2) and (3) respectively [16].
\[
\ln q_e - q_t = \ln q_e - k_1 t
\]  
(2)
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]  
(3)
where $q_e$ and $q_t$ represent the amount of equilibrium adsorption capacity and adsorption capacity at particular times. $k_1$ is pseudo first order rate constant while $k_2$ is pseudo second order rate constant.

3. Results and discussion

Figure 1(a) shows the XRD spectra from Fe$_3$O$_4$-NGP with different NGP surface areas, for comparison the XRD spectra of Fe$_3$O$_4$ nanoparticles were also plotted. On Figure 1a all of the composites samples consisted of cubic spinel structure that detected at $2\theta = 30.14^\circ$, $35.49^\circ$, $43.28^\circ$, $53.76^\circ$, $57.20^\circ$, and $62.83^\circ$. Thus peak were attributed to (220), (311), (400), (442), (511), and (440) planes respectively. In $2\theta = 26.16^\circ$ the graphitic like structure from NGP were detected for all samples which attributed to (220) plane. The grain size of Fe$_3$O$_4$ were estimated using Scheerer equation with analyze peak at (311) plane of Fe$_3$O$_4$ and the results were tabulated in Table 1. As can be seen that the grain size value were slightly decrease with the incorporation of NGP materials. The decrease of grain size probably will help in the adsorption process. The lattice parameter of the samples were calculated using Retvield refinement method and the result were also tabulated in Table 1. The lattice parameter of all samples did not change significantly, indicated there were no change in structural properties of Fe$_3$O$_4$ nanoparticles and NGP materials.

The molecular vibration of all samples were investigated using FT-IR measurement. The results were plotted in Figure 1(b). In the region of 500 cm$^{-1}$ attributed to binding vibration between Fe and O, while in the region of 1752 cm$^{-1}$ attributed to C=O binding vibration which attributed to NGP materials [17-18].

![Figure 1](image.png)

**Figure 1.** (a) XRD spectra and (b) FT-IR analysis of Fe$_3$O$_4$-NGP with different NGP surface area.

**Table 1.** Lattice parameter, and grain size Fe$_3$O$_4$ and Fe$_3$O$_4$-NGP composites.

| Sample | Lattice Parameter (Å) | $<D>$ (nm) |
|--------|-----------------------|------------|
|        | Fe$_3$O$_4$ | NGP | a=b=c | a |
| Fe$_3$O$_4$ | 8.364 | - | 45 |
| S-1 | 8.372 | 3.632 | 39 |
| S-2 | 8.373 | 3.633 | 40 |
| S-3 | 8.375 | 3.635 | 38 |
The TGA result were performed in Figure 2(a). It can be seen from Figure 2a that the samples Fe₃O₄ nanoparticles has good stability until 1000°C. However the incorporation of carbon materials like NGP reduce the stability of the samples under 700°C due to the combustion of carbon materials. Almost 10 wt% were lost after heating treatment 1000°C which attributed to amount of carbon content of the samples.

Magnetic hysteresis curves of Fe₃O₄-NGP composites with the highest surface area (S3) was plotted in Figure 2(b). The magnetic hysteresis from Fe₃O₄ nanoparticle was also plotted as comparison. The both samples exhibited ferromagnetic behavior under room temperature. The saturation magnetization were slightly increase with the incorporation of NGP materials in Fe₃O₄ nanoparticles. These magnetic properties of the samples is important in separation process and also reusability of adsorbent. The inset of Figure 2b is the example of separation process using Fe₃O₄-NGP composites. It is clearly seen that the adsorbent could be easily attracted by external magnetic bar indicated that Fe₃O₄-NGP composites is potential as adsorbent with high efficiency, reusability and stability.

The adsorption ability of the samples were plotted in Figure 3(a) and (b). Figure 3(a) demonstrated the decolorization of MB at particular time. It can be seen from this figure that the incorporation of NGP

---

**Figure 2.** (a) TGA measurement of Fe₃O₄ and Fe₃O₄-NGP composites with different NGP surface area, (b) VSM spectra of Fe₃O₄ nanoparticles and Fe₃O₄-NGP composites.

**Figure 3.** (a) Decolorization and (b) adsorption capacity of Fe₃O₄ nanoparticles, S1, S2, and S3 composites.
materials enhance the decolorization of MB in aqueous solution. The highest decolorization ability occurred using S-3 followed by S-2, S-1 and Fe₃O₄ nanoparticles. Figure 3(b) shows the adsorption capacity for all samples at particular times. As can be seen in Figure 3(b) the highest adsorption capacity was performed using S-3 materials with adsorption capacity approximately 23 mg/g, while the lowest adsorption capacity was performed using Fe₃O₄ nanoparticles with adsorption capacity value 6 mg/g. Based on this result it assumed that specific surface area from NGP is crucial factor in adsorption process. NGP N008–P10 with highest NGP specific surface area provided more active sites for adsorption process compared to NGP N008–100 N, N006–P10 and Fe₃O₄ nanoparticles.

The fitted data from first and second order were plotted in Figure 4 (a) and (b). As can be seen from Figure 4 (a) and (b) the adsorption process of the samples followed pseudo second order kinetic model. The result of fitted data were tabulated in Table 2. As can be seen in the tables that the equilibrium adsorption capacity value from pseudo second order kinetic reaction almost the same with the experimental value.

The stability of the samples were tested using S-3 materials. Figure 5 demonstrated the percentage degradation of methylene blue using S-3 composites for four repetitive experiment. It can be seen from Figure 5 that the samples has good stability after four repetitive usage. The degradation of methylene blue were decreased only 10% from the initial usage. It means that the magnetic separation process is a powerfull method for separate adsorbent from the solution and produce high stability of catalyst due to it is ability to minimize weight lost of adsorbent.

### Table 2. Kinetic adsorption process of Fe₃O₄ nanoparticles and Fe₃O₄-NGP composites.

| Sample      | qₑₑ (mg/g) | qₑₑ cal (mg/g) | k₁     | R²   | qₑₑ cal (mg/g) | k₂     | R²   |
|-------------|------------|----------------|--------|------|----------------|--------|------|
| Fe₃O₄       | 6.75       | 6.05           | 0.0172 | 0.95 | 7.26           | 0.005909 | 0.98 |
| S-1         | 15.68      | 14.29          | 0.0141 | 0.94 | 16.36          | 0.002609 | 0.97 |
| S-2         | 23.21      | 11.03          | 0.0114 | 0.81 | 22.99          | 0.004576 | 0.99 |
| S-3         | 21.40      | 13.90          | 0.0108 | 0.92 | 21.50          | 0.002691 | 0.98 |

**Figure 4.** Linear plot of (a) Pseudo First Order Kinetic Models (b) Pseudo Second Order Kinetic Models.
4. Conclusion
Magnetic $\text{Fe}_3\text{O}_4$-NGP composites with different NGP surface area were successfully synthesized using co-precipitation method. The all prepared samples consist of inverse cubic spinel structures and graphitic like structures from $\text{Fe}_3\text{O}_4$ and NGP respectively. The adsorption experiment showed that the higher surface area enhance the adsorption efficiency. The adsorption process followed pseudo second order kinetic model and the samples exhibit good stability after four times cycling process.

5. References
[1] Cao C, Xiao L, Chen C, Shi X, Cao Q, Gao L 2014 Powder Technology 260 90–97
[2] Golka K, Kopps S, Myslak ZW 2004 Toxicology Letters 151 203–210
[3] Bao N, Li Y, Wei ZT, Yin GB, Niu JJ 2011 The Journal of Physical Chemistry C 115 5708–5719
[4] Chang J, Ma J, Ma Q, Zhang D, Qiao N, Hu M, Ma H 2016 Applied Clay Science 119 132–140
[5] Zhang WJ, Zhou CJ, Zhou WC, Lei AH, Zhang QL, Wan Q, Zou BS 2011 Bulletin of Environmental Contamination and Toxicology 87 86–90
[6] Kumar KY, Muralidhara HB, Nayaka YA, Balasubramanyam J, Hanumanthappa H 2013 Powder Technology 246 125–136.
[7] Cheng WP, Gao W, Cui X, Ma JH, Li RF, Journal of the Taiwan Institute of Chemical Engineers 62 192–198
[8] Hoa NV, Khong TT, Quyen TTH, Trung TS 2016 Journal of Water Process Engineering 9 170–178
[9] Lin CC, Lin YS, Ho JM 2016 Journal of Alloys and Compounds 666 153-158
[10] Giri SK, Das NN, Pradhan GC 2011 Colloids and Surfaces A: Physicochemical and Engineering Aspects 389 43-49
[11] Shi HT, Tan LF, Du QJ, Chen X, Li LL, Liu TL, Fu CH, Liu HY, XW Meng 2014 Dalton Transactions 43 12474-12479
[12] Ghaedi M, Hajjati S, Mahmudi Z, Tyagi I, Agarwal S, Maity A, Gupta VK 2015 Chemical Engineering Journal 268 28–37
[13] Saha B, Das S, Saikia J, Das G 2011 The Journal of Physical Chemistry C 115 (2011) 8024-8033
[14] Boruah PK, Borah DJ, Handique J, Sharma P, Sengupta P, Das MR 2015 Journal of Environmental Chemical Engineering 3 1974-1985
[15] Taufik A, Saleh R 2016 Materials Science Forum 864 106-111
[16] Anirudhan TS, Deep JR, Binusreejayan 2015 Chemical Engineering Journal 273 (2015) 390-400.
[17] Shang Y, Li T, Li H, Dang A, Zhang L, Yin Y, Xiong C, Zhao T 2016 Composites Part B 99 (2016) 106-111
[18] Lin CC, Ho JM 2014 Ceramics International 40 10275-10282

Figure 5. Reusability of Adsorbent.