Adsorption of methylene blue using Fe$_3$O$_4$/CuO/ZnO/ nanographene platelets (NGP) composites with various NGP concentration

H. Tju$^{1,2}$, 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. This study will examine the use of Fe$_3$O$_4$/CuO/ZnO nanocomposites that have been modified by Nanographene Platelets (NGP) as an adsorbent to degrade organic dye waste Methylene Blue (MB). The nanocomposites were synthesized using the sol-gel method then combined with three variations of NGP weight percents by simple hydrothermal method. The Fe$_3$O$_4$/CuO/ZnO/NGP composites were characterized using the X-Ray Diffraction (XRD) spectroscopy, Fourier Transform Infrared (FTIR), Energy Dispersive X-Ray (EDX), Thermogravimetric Analysis (TGA) and Vibrating Sample Magnetometer (VSM). The composites exhibit ferromagnetic behaviour. The presence of hexagonal wurtzite of ZnO, monoclinic of CuO and cubic spinel of Fe$_3$O$_4$ were found in the composites. The graphitic-like structure represents the presence of the NGP in the composites. However, the addition of NGP weight percent reduces the thermal stability of the composites. The adsorption capability of the composites are analyzed by observing the degradation of organic dye Methylene Blue (MB) under dark condition. The NGP addition of 15 wt% show the best result of the composites to degrade Methylene Blue in alkaline condition. Adsorption mechanism of the composites with NGP addition tend to follow the model Langmuir adsorption kinetic models.

1. Introduction

Each year, the total amount of dye wastes disposed into the environment from the food and textile industry kept increasing which will cause more water pollution [1-2]. To cope with the problem, an effective waste water treatment is required to reduce the content of environmental pollution. There are various methods for dye wastes treatment such as adsorption, coagulation, flocculation, reverse osmosis, biological treatment, and catalytic activity [1-5]. Adsorption is one of reliable methods in overcoming water pollution because of its several advantages such as low cost, simple design, and easy operations [2,6]. However there are constraints applying it since its adsorption capacity is not too high.

In recent years, semiconductor material draws an attention because of its capability in degrading wastes [7-8]. ZnO is a semiconductor that is widely used because of its low cost, high photochemical, biological stability, and low toxicity. However, the use of single material such as ZnO still has shortage in term of efficiency in waste degradation. Combination of two or more semiconductors has been proven to improve the process of waste degradation because of the synergistic effect of each
semiconductor [8-10]. CuO is one of semiconductors with relatively small band gap hence it is expected that by combining it with ZnO we could modify the band gap of the combination these two semiconductor to improve the ability of waste degradation. Another problem in using ZnO semiconductor in the degradation process of wastes is the difficulty in separating the ZnO material from the solution after the reaction process. Therefore further modification is required to facilitate the separation process of the adsorbent material from the waste solution. Using magnetic materials such as Fe₃O₄ has been proven to facilitate the separation process of adsorbent materials from the solution [11].

Some researchers have also reported that carbon materials such as graphene could be an ideal supporting material for nanoparticles or composites because of its unique properties such as high surface area, high carrier mobility, and high electrical conductivity [6,12]. High surface area of graphene is considered able to increase the adsorption capacity of nanomaterials. Therefore, in this paper, NGP will be combined with Fe₃O₄/CuO/ZnO nanocomposites with several variation of NGP weight percent (wt%). Here the influence of NGP addition into nanocomposites in degrading Methylene Blue (MB) as the model pollutant was examined under the adsorption method, and the influence of initial pH and MB concentration were also investigated.

2. Experiment

Materials: Iron (II) sulfate heptahydrate (FeSO₄·7H₂O, 99%), copper sulfate pentahydrate (CuSO₄·5H₂O, 99%), zinc sulfate heptahydrate (ZnSO₄·7H₂O, 99%), sodium hydroxide (NaOH), ethanol, ethylene glycol (EG), methylene blue, were purchased from Merck. All chemical reagents (Merck) were of analytical grade and used without further purification. Nano graphene platelets (NGP-N006-P) were purchased from Angstron Materials. All solutions were used without further purification.

Nanocomposites Synthesis: Fe₃O₄/CuO/ZnO is synthesized using the method that was applied in the previous study by Taufik, et al. [13-14] without modification. Fe₃O₄/CuO/ZnO/NGP composites were made using simple hydrothermal method [15]. In brief, a certain amount of NGP was first added into aquades solution and ethanol before being sonicated for 2 hours. After sonication process, Fe₃O₄/CuO/ZnO was poured and stirred for 2 hours to get homogeneous suspension. The resulting solution was further heated at the temperature of 120 °C for 3 hours, and then centrifuged and vacuumed at the temperature of 70 °C for 12 hours. The amount of NGP addition into Fe₃O₄/CuO/ZnO nanocomposites was varied from 5wt%, 10wt%, and 15wt%.

Characterizations: The samples were characterized by X-Ray Diffraction (XRD) using Raigaku Miniflex 600 monochromatic Cu-Kα (λ = 1.5 Å) radiation operated at 30 kV and 15 mA at the span angle of 10° to 80° and the absorption spectrum were characterized using Shimadzu FTIR spectrophotometer in the range of 400-4000 cm⁻¹. Thermogravimetric Analysis (TGA) was measured at the heating rate of 10 °C/min in N₂ atmosphere, and magnetic measurement was performed using Oxford type 1.2 T vibrating sample magnetometer (VSM).

Adsorption measurement: A certain amount of samples that have been synthesized were dissolved into Methylene Blue (MB) solution with the concentration of 20 mg/L at pH 13. The solution was stirred using magnetic stirrer. At a determined time, 5 mL of solution was collected and centrifuged to separate it from Fe₃O₄/CuO/ZnO nanocomposites and then the concentration was measured using UV-VIS spectroscopy. The efficiency of the adsorption process can be calculated using the equation of C/C₀, where C is the MB concentration at a certain interval and C₀ is the initial concentration of MB. Subsequently, several parameter measurements are carried out in the form of initial dye concentration: (20-150 mg/L) and initial pH of the solution: (3-13).
3. Results and discussion

Figure 1 indicates the XRD spectrum of Fe$_3$O$_4$/CuO/ZnO/NGP with different variations of NGP wt%. The XRD diffraction pattern of Fe$_3$O$_4$/CuO/ZnO/NGP indicates the existence of cubic spinel phase of Fe$_3$O$_4$ detected at the angles of 2θ = 30.14°, 35.49°, 43.28°, 53.76°, 57.20°, and 62.83°. The diffraction pattern at the angle of 2θ = 38.81° and 48.7° indicates the existence of monoclinic CuO phase. Several peaks at the angle of 2θ = 34.47°, 36.26°, 47.50°, 56.70°, 68.06°, and 69.21° conform to the crystal structure of hexagonal wurtzite of ZnO, and at the angle of 2θ = 26.40° there is a peak conforming to the graphitic like structure of nanographene platelets. The result of XRD spectra indicates that Fe$_3$O$_4$/CuO/ZnO/NGP has been successfully synthesized without any impurity detected. An increased intensity is observed at NGP peak by increasing the wt% of NGP given in composites. The average particle size (D) is calculated using Scherer formulation D = 0.9λ/(β cosθ) where λ is the wavelength of incident X-Ray, β is the full width at half maximum and θ as the Bragg angle. The result of average particle size analysis is tabulated in Table 1.

The FTIR absorption spectrum of Fe$_3$O$_4$/CuO/ZnO/NGP is shown in Fig. 2. In the range of wavenumber 1722 cm$^{-1}$ and 1626 cm$^{-1}$, there are absorptions that correspond with the vibration mode of C=O and C=C stretching while at wavenumber of 3411 cm$^{-1}$, there is an absorption that corresponds with the vibration mode of O-H stretching. The absorption spectra of Fe$_3$O$_4$/CuO/ZnO is presented in Fig. 2b. It can be observed that the absorption spectrum of Fe$_3$O$_4$/CuO/ZnO is detected at wavenumber of ~400 cm$^{-1}$, ~420 cm$^{-1}$ and ~590 cm$^{-1}$ which correspond with the Zn-O [17], Cu-O [18] and Fe-O stretching [19]. The infrared spectra of Fe$_3$O$_4$/CuO/ZnO/NGP also consists of the vibration mode of NGP material and the vibration mode from the material of Fe$_3$O$_4$/CuO/ZnO nanocomposites. From the FTIR result we could confirm the existence of Fe$_3$O$_4$, CuO, ZnO, and NGP that have been mixed in Fe$_3$O$_4$/CuO/ZnO/NGP composites. The thermal stability of Fe$_3$O$_4$/CuO/ZnO/NGP composites is identified using Thermalgravimetry Analysis. Based on the measurement result (Fig. 3(A)), the Fe$_3$O$_4$/CuO/ZnO have quite good thermal stability up to the temperature of 1000°C. When NGP is added by 5, 10 and 15 wt% into Fe$_3$O$_4$/CuO/ZnO nanocomposites, there is mass loss by 7.26%, 12.67%, and 18.53%. Such significant

![Figure 1. XRD pattern of Fe$_3$O$_4$/CuO/ZnO/NGP with variation NGP wt%](image)

![Figure 2. FTIR spectra of NGP, Fe$_3$O$_4$/CuO/ZnO, and Fe$_3$O$_4$/CuO/ZnO/10wt%-NGP](image)

| Samples | ZnO | CuO | Fe$_3$O$_4$ | M-S |
|---------|-----|-----|------------|-----|
| Fe$_3$O$_4$ | –   | –   | 45         | 82  |
| CuO      | –   | 15  | –          | –   |
| ZnO      | 19  | –   | –          | –   |
Fe$_3$O$_4$/CuO/ZnO  
26 15 42 46
Fe$_3$O$_4$/CuO/ZnO-0.5wt% NGP  
25 15 41 52
Fe$_3$O$_4$/CuO/ZnO-10wt% NGP  
22 15 41 57
Fe$_3$O$_4$/CuO/ZnO-15wt% NGP  
16 15 39 55

Figure 3. TGA curve (A) and VSM spectra (B) of Fe$_3$O$_4$/CuO/ZnO dan Fe$_3$O$_4$/CuO/ZnO/NGP with variation NGP wt%.

Figure 4. Adsorption (A) and adsorption capacity (B) of methylene blue using Fe$_3$O$_4$/CuO/ZnO and Fe$_3$O$_4$/CuO/ZnO/NGP with variation NGP wt%.

Table 2. Adsorption of Fe$_3$O$_4$/CuO/ZnO/NGP nanocomposite

| Samples                  | Degradation (%) | Adsorption Capacity (mg/g) |
|--------------------------|-----------------|-----------------------------|
| Fe$_3$O$_4$/CuO/ZnO      | 28              | 18                          |
| Fe$_3$O$_4$/CuO/ZnO-0.5wt% NGP  | 36              | 24                          |
| Fe$_3$O$_4$/CuO/ZnO-10wt% NGP | 40              | 27                          |
| Fe$_3$O$_4$/CuO/ZnO-15wt% NGP | 43              | 29                          |

decreased was caused by combustion from carbon materials in the samples originating from NGP material [20]. The mass lost well correspond to the wt% of NGP in the composites. The magnetic saturation of Fe$_3$O$_4$/CuO/ZnO nanocomposites and Fe$_3$O$_4$/CuO/ZnO/NGP composites at room temperature is shown in Fig. 3(B). As comparison, the magnetic saturation curve of Fe$_3$O$_4$ nanoparticles is also presented in Fig. 3(B). The result obtained indicates that all the samples have ferromagnetic behaviour. The magnetic saturation value of all samples is tabulated in the last column of Table 1. The magnetic saturation value of Fe$_3$O$_4$/CuO/ZnO nanocomposites is lower than that of Fe$_3$O$_4$ nanoparticles, this may be caused by less amount of Fe$_3$O$_4$ when it was formed into Fe$_3$O$_4$/CuO/ZnO nanocomposites. However, addition of nanographene platelets by 5wt% and 10wt%
causes an increase of the magnetic saturation value compared to \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO} \) nanocomposites and addition of 15wt% NGP lowers the magnetic saturation value but still higher than \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO} \).

Increase of magnetic saturation value when NGP material is added can be caused by \( \text{Fe}_3\text{O}_4 \) material sticking on the NGP surface which causes defect and stabilize NGP-based magnetic material [21].

The adsorption capacity measurement of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}/\text{NGP} \) nanocomposites is analyzed by observing the methylene blue degradation represented by \( C_t/C_0 \) (\( C_t \)=MB concentration at certain interval, \( C_0 \)=initial concentration) as seen in Fig 4(A).

It can be seen in the figure an increase in the adsorption capacity simultaneously with NGP material addition.

The adsorption process is also influenced by the acidity of the waste solution being used; therefore in this study we also analyze the influence of methylene blue solution acidity on the adsorption capacity of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO} \) using NaOH and CH\(_3\)COOH. The result obtained can be seen in Fig. 5(A).

The adsorption capacity of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}/\text{NGP} \) can reach optimum condition in alkaline condition while in acid condition the adsorption capacity of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}/\text{NGP} \) decreases. This may be caused by the fact that the maximum interaction occurs between negative surface of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}/\text{NGP} \) composites and positive charge MB in the alkaline condition [22].

Fig. 5(B) shows the influence of difference in the concentration of methylene blue solution on the adsorption capacity of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}/\text{NGP} \). In this study the concentration of methylene blue solution is varied from 20 mg/L – 150 mg/L. The result indicates that the adsorption capacity of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}/\text{NGP} \) decreases simultaneously with an increase in methylene blue solution.

![Figure 5](image_url)

**Figure 5.** Effect of pH (A) and initial concentration (B) of MB on adsorption capacity
Subsequently, to know the mechanism of adsorption process, Freudlich and Langmuir adsorption kinetic model are applied. The result obtained is indicated in Fig. 6 (A) for Freudlich model and Fig. 6 (B) for Langmuir model. In Fig. 6, we could see the adsorption process of $\text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP}$ follows the Freudlich and Langmuir adsorption kinetic model with the correlation coefficient ($R^2$) obtained for Freudlich and Langmuir of 0.9638 and 0.9805 respectively. Based on the study carried out using several parameters, the optimum condition obtained to degrade MB from aqueous solution (MB concentration of 20 mg/L) using the adsorption method is obtained for $\text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}$ nanocomposites with 15wt% NGP addition, for the dosage of 0.3 mg/L and pH 13. In this study, maximum condition of the degradation and adsorption capacity is reached 43% and 29 mg/g.

### 4. Conclusion

In this study, $\text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP}$ composites with different added amount of NGP has been successfully synthesized using two step method, sol-gel and simple hydrothermal method. The XRD and FTIR characterization result indicate the existence of structure and vibration of $\text{Fe}_3\text{O}_4$, CuO, ZnO and NGP in the composites. The result also indicates the amount of NGP addition in accordance with the result of TGA measurement. Addition of NGP may improve efficiency in the adsorption process of methylene blue in aqueous solution, with the addition of 15wt% the degradation efficiency and adsorption capacity increased by 15% and 11 mg/g. The experimental result follows properly the adsorption of Freundlich dan Langmuir kinetic model, where the conformity value of Langmuir is higher than the Freundlich.

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