



REMOVAL OF METHYLENE BLUE DYES USING GRAPHENE OXIDE-INTERCALATED BENTONITE COMPOSITES

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ABSTRACT

Reduction of methylene blue levels has been carried out using the adsorption method with Bentonite-GO adsorbent. Adsorption is used because it has advantages at a low cost and is easy to modify. Bentonite is modified using GO because it has properties that are suitable for reducing dye waste. Bentonite-GO was characterized using XRD, SEM-EDS, and BET. Based on the XRD characterization results, GO is obtained with peaks at an angle of 10.57° and in bentonite there are several peaks, namely 22.10° ; 28.1° ; and 35.63° . For bentonite/GO composites, it is best found at a 1:3 ratio with a peak of 25.61° . SEM-EDS is used to determine morphological changes of bentonite and after composite with GO. In the Bentonite-GO composite, it can be seen where in the pores of bentonite there is GO that fills the gap in bentonite which has a porous structure. Based on the EDS results on the Bentonite-GO composite, there was also a very large increase in carbon atoms. In BET, the surface area of the Bentonite-GO composite was $91.5059 \text{ m}^2/\text{g}$ and the pore volume was $0.1997 \text{ cm}^3/\text{g}$. Methylene reduction obtained the best adsorption capacity at 60 minutes contact time with a percentage of 89.83% and a Q_e value of 9.5 mg/g and a maximum composite concentration at a concentration of 35 mg/L with a percentage of 97.83 and a Q_e value of 10.272 mg/g.

Keywords: composite, graphene, graphene oxide, adsorption, methylene blue, intercalated, bentonite, bentonite-GO.

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INTRODUCTION

Methylene blue is one of the cheap cationic dyes widely used for dyeing cotton, wool, silk, and paper. Methylene blue has a negative impact on the environment (Peng *et al.*, 2016) so a technique is needed to remove methylene blue content from industrial waste. One method that can be used to reduce the dyestuff content in textile waste is adsorption (Modirshahla *et al.*, 2011)

Bentonite is clay that is often used as an adsorbent material in adsorption methods. Bentonite has a main structure in the form of Montmorillonite which has a characteristic material structure that has layers and enlarges when dispersed in water. The properties of this material can make it an excellent adsorbent (Purwaningrum *et al.*, 2021). Bentonite also has a layered structure that on its surface has negative ions that can be used as cation exchangers. Because it has a layered structure, bentonite can be modified by forming a composite with GO (Said *et al.*, 2023).

GO is one of the sheet-shaped allotropes of carbon. Graphene oxide is the oxidized form of graphene (Li *et al.*, 2006), functionalized by a range of active oxygenous groups, including epoxide and hydroxyl in the planes and carbonyl and carboxyl groups at the edges. The oxygenous functional groups (such as -OH, -COOH) on

the GO surface are extremely beneficial to the hydrophilicity and high negative charge density, which were directly related to the removal of contaminants (Bian *et al.*, 2015; Ramesha *et al.*, 2011). The excellent dispersibility of GO and strong tendency of GO can remove dyes from aqueous solutions (Sitko *et al.*, 2013). Based on research by Hakan, the percentage of methylene blue removal is 100% at the best variations in concentration, pH, and contact time (Çiftçi, 2022). Therefore, research on adsorption using bentonite with the addition of GO will be expected to increase the adsorption capacity. Therefore, this study aims to synthesize and characterize Bentonite/GO composites to determine the ability of Bentonite/GO composites to reduce Methylene Blue dyes. This is done with several variables including variations in the initial concentration of dyes and adsorption time. In addition, bentonite/GO composites were characterized using XRD and SEM EDX.

MATERIALS AND METHODS

Synthesis of Bentonite/GO with Variation of Mass

Graphene oxide (GO) is made by oxidizing natural graphite powder based on the modified Hummers method. Briefly, the process begins by dispersing (5 g)



pure graphite powder with some chemical compounds such as 250 mL of sulfuric acid for 24 hours, 30 g of potassium permanganate, 5 g of sodium nitrate, 25 mL of hydrogen peroxide, 50 mL of hydrochloric acid and deionized water. In addition, controlling factors such as temperature, pH, and some stirring using a magnetic stirrer are carried out every step of the way. To extract graphite oxide, ultrasonication was carried out for 4 hours so that GO was obtained. (Zankana *et al.*, 2023)

Bentonite is activated using HCl for 12 hours to produce activated bentonite. As much as 1 gram of bentonite has been activated and then mixed with 1 gram of GO. Then both mixtures are put into a hydrothermal reactor which is heated for 12 hours at a temperature of 175°C. So, a Bentonite/GO composite was obtained. The procedure is carried out with mass variations between Bentonite and GO in the ratio of 1: 1, 1: 3, 1: 5.

Effect of INITIAL Concentration of Methylene Blue Dye and Adsorption Time

A total of 10 mg of the composite was added to 15 mL of methylene blue solution with concentration variations of 15, 20, 25, 30, and 35 ppm. Then mix in the stirrer at 25 ° C at a speed of 150 rpm for 30 minutes. Then it is centrifuged at a speed of 2000 rpm to separate the dye solution from the composite. The supernatant solution is measured for absorbance with a UV-Vis Spectrophotometer.

A total of 10 mg of composite in 15 mL of methylene blue solution with the best concentration. The mixture is stirrer at 25°C at a speed of 150 rpm with time variations of 15, 30, 45, 60, 75, and 90 minutes. Then centrifuged at a speed of 2000 rpm to separate the dye solution from the composite. Then the absorbance is measured with a UV-Vis Spectrophotometer.

RESULTS AND DISCUSSIONS

Materials Characterizations

The characterization results with various XRD, SEM, and pHpzc instruments are shown in Figure-1,-2, and-3, respectively. Figure-1a compares the XRD data for composites bentonite/GO results were obtained in the form of a diffractogram showing the peak of GO at $2\theta = 10.57^\circ$ with d-spacing of 0.836 nm. A similar study included GO with a value of 2θ which is very similar to showing a peak at $2\theta = 10.5$ with a d-spacing of 0.84 nm (Amir Faiz *et al.*, 2020).

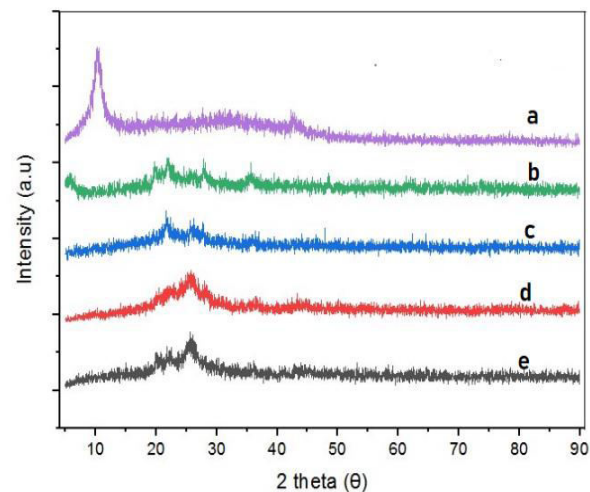


Figure-1. Diffractograms of (a) GO (b) Bentonite (c) Bentonite/GO (1:1) (d) Bentonite/GO (1:3) and (e) Bentonite/GO (1:5).

Based on the diffraction pattern bentonite produces three peaks, namely at position $2\theta = 22.10^\circ$; 28.1° ; 35.63° . These peaks may indicate the presence of montmorillonite where montmorillonite is one of the most abundant bentonite constituent minerals (Ayodele *et al.*, 2012). This diffraction pattern corresponds to JCPDS (01-088-0891). Figure-1c shows the Bentonite-GO composite diffractogram with a variation in the ratio (1:1), where this ratio yields peaks of $2\theta = 21.71^\circ$; 26.3° ; 63.9° ; 77.2° . Figure-1d shows the diffractogram of the Bentonite-GO composite with a variation in the ratio (1:3) yielding a peak of $2\theta = 22.39^\circ$; 25.61° ; 28.14° ; 29.7° ; 43.8° and 78.1° , while Figure-1e shows the diffractogram of the Bentonite-GO composite with a variation in the ratio (1:5), where for this ratio yields a peak of $2\theta = 20.00^\circ$; 25.6° ; and 26.20° . Two strong diffraction peaks for Bentonite appeared at 19.787 which indicates the presence of montmorillonite, a main component of bentonite. The peak at 26.682 corresponds to SiO_2 (Elsayed *et al.*, 2020). The layer d-spacing of bentonite/GO increased to 2.35 nm from 1.706 nm of bentonite. This change indicated that GO has intercalated into bentonite, thus enlarging the layer spacing of bentonite (H. Liu *et al.*, 2018). The best composite can be seen by looking at its crystal size. In Table-1 it can be seen that the composite with a ratio of 1:5 has the largest crystal size, but there are some distinctive peaks of bentonite missing. So in the application of methylene blue dye removal, a bentonite/GO 1:3 composite is used to analyze the surface morphology of the bentonite/GO composite, and SEM is performed. The morphology of the GO, Bentonite, and Bentonite/GO samples is shown in Figure-2.

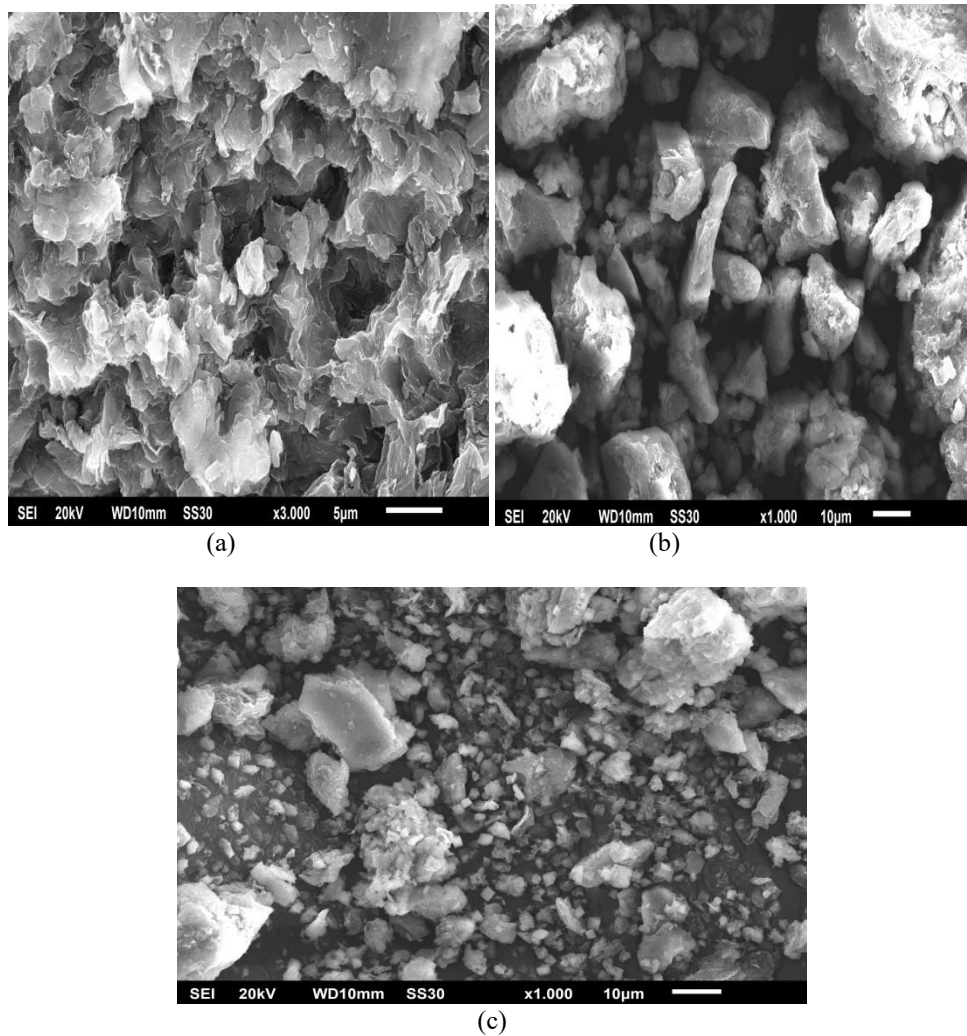


Figure-2. Morphological surface of (a) GO and (b) Bentonite and (c) Bentonite/GO 1:3

In Figure-2a, the morphology of GO is in the form of pieces, this is a special characteristic of GO. This is the result of the exfoliation of graphite after oxidation and ultrasonication, while in Figure-2b there is bentonite morphology which is characterized by chunks that have many pores. In Figure-2c it is seen that the morphology is clear of bentonite but the pore is covered by GO. This is because GO has a nano-size while bentonite is a macromolecule. In samples of the Bentonite-GO composite, it can be observed that it looks like a gravel

chunk with many wrinkles on a much rougher surface. This has the potential to help increase the adsorption of dyes (L. Liu *et al.*, 2015).

The filling of the gap in bentonite by GO causes the formation of an intercalation of bentonite by GO. In the EDS data contained in Table-2, it can be seen that there is an increase in carbon elements in bentonite/GO composites, this indicates that this composite was successfully synthesized because GO is a carbon compound.

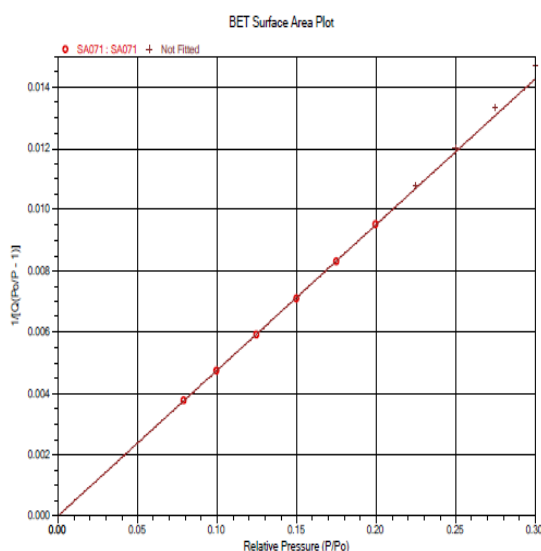
**Table-1.** XRD peak and distance were calculated using Bragg's Law equation.

Materials	2 θ (degree)	d-spacing (nm)	Crystal size (nm)
GO	10.57°	0.836	4.432
Bentonite	22.10°; 28.1°; 35.63°	0.317	1.706
Bentonite/GO 1:1	21.71°; 26.3°; 63.9°; 77.2	0.338	1.962
Bentonite/GO 1:3	22.39°; 25.61°; 28.14°; 29.7°; 43.8° and 78.1	0.348	2.354
Bentonite/GO 1:5	20.00°; 25.6°; and 26.20°.	0.339	2,874

Table-2. EDS result of bentonite and bentonite/GO.

Material	C (%)	O (%)	Al (%)	Si (%)	Fe (%)
Bentonit	27.14	35.17	5.78	24.12	4.13
Bentonit- GO	85.7	13.6	0.1	0.4	-

BET characterization on Bentonite-GO composites aims to determine the specific surface of the composite and can determine the pore volume and pore size of Bentonite-GO composites. In the Bentonite-GO composite study, the surface area obtained was 91.5059 m²/g and the pore volume was 0.1997 cm³/g. High surface area will increase the ability to adsorb dyes and the increase in surface area is caused by increased pores. According to Liu *et al.*, (2015) on BET characterization the specific surface area of Bentonite-GO composites is 9.13 m²/g and the surface area in Bentonite-GO composites is high because GO is coated by bentonite. The BET analysis curve for the Bentonite-GO composite can be seen in Figure-3.

**Figure-3.** BET analysis.

The pH_{pzc} value was determined at the beginning to identify the most suitable pH for optimal dye adsorption. The pH_{pzc} curve data is presented in Figure-4.

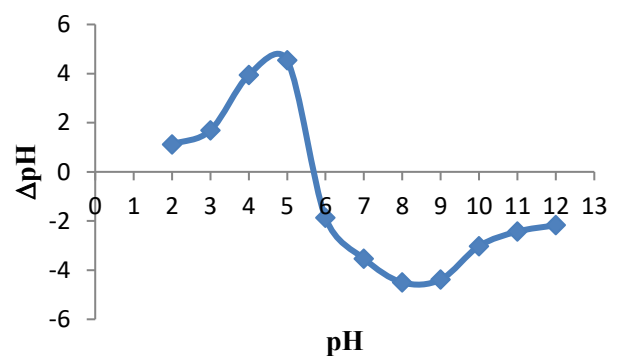
**Figure-4.** pH_{pzc} curve of Bentonite/GO 1:3.

Figure-4 shows that the pH value of pzc was pH 6. This means that at a low or acidic pH, more H⁺ ions are produced in the solution, hence, the composite charge becomes positive, in contrast, a high pH or alkaline solution tends to be more negatively charged, and the composite's charge becomes negative (Azeez *et al.*, 2018). Furthermore, the methylene blue used in this study was a cationic dye or positively charged, consequently, to maximize the photodegradation process, the pH of the composite was set above pH_{pzc}. The previously measured pH of methylene blue showed a pH range of 5-6. This indicates that there is a match between the pH of the Bentonite/GO composite and the dye used.

Effect of Adsorption Time Variations

The methylene blue dye curve of effectiveness in concentration reduction based on the effect of time variations is shown in Figure-5.

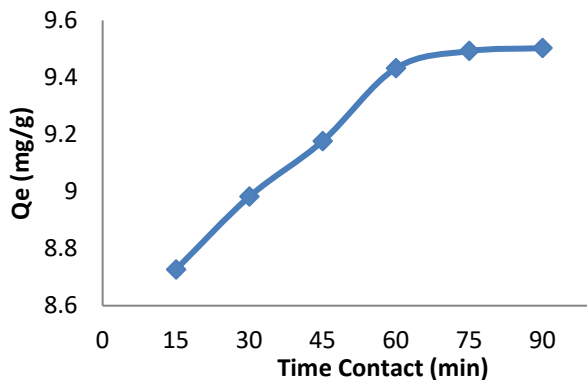


Figure-5. Effect of adsorption time over dye concentration reduction effectiveness.

Figure-5 shows an increase in the percentage of adsorption efficiency due to adsorbents in the solution and indicates that the adsorption process has not reached the optimum point. A contact time of 15-45 minutes increases slowly, this is because the amount of adsorbed substance has not reached the maximum capacity of compounds that can be adsorbed by adsorbents. At 60-90 minutes there is no significant increase or decrease. This indicates that the adsorption process has reached maximum capacity at minute 60 with an adsorption value of 9.5 mg/g with a percentage of 89.83%.

Effect of Variation in Initial Concentration of Methylene Blue Dye

The Adsorption results of methylene blue dye based on the effect of concentration are shown in Figure-6. The percentage increase in the concentrations of 15 to 35 ppm.

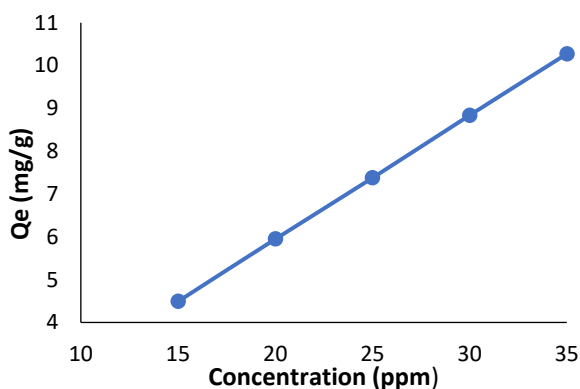


Figure-6. Effect of initial concentration of Methylene Blue over dye concentration reduction effectiveness

Figure-6 shows that the effectiveness of dye reduction increases as the initial concentration of the dye increases. On the graph, it can be seen that there is a constant increase from a concentration of 15 to 35 ppm. This indicates that bentonite/GO composites can still adsorb at greater concentrations seen from graphs that

have not reached the equivalent point. However, based on this study, the maximum capacity was obtained at a concentration of 35 mg/L with a Q_e value of 10.272 mg/g with a percentage of 97.83 %.

CONCLUSIONS

Bentonite/GO composites with mass ratios of 1:1, 1:3, and 1:5 have been successfully synthesized and XRD test results show that composites with a mole ratio of 1:3 have the largest particle size. In the results of SEM, GO enters the gap of bentonite resulting in intercalation. The maximum condition of the adsorption process is achieved at a contact time of 60 minutes and an initial dye concentration of 35 ppm.

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