Indonesian Journal of Material Research
e-ISSN: 2987-1654
Vol. 1, No. 1, March 2023

Indonesian Journal of MATERIAL RESEARCH

Research Paper

Synthesis of Graphene Oxide using Hummers Method as Adsorbent of Malachite Green Dye

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Abstract
Graphene oxide materials were successfully synthesized using the Hummer method with XRD, FTIR, and BET characterization results. Graphene oxide material was used as malachite green dye adsorbent. The surface area of graphene oxide material and the maximum adsorption capacity were 157.360 m^2/g and 106.383 mg/g. The selectivity process of graphene oxide material to the three dyes showed the most effective malachite green dye. The optimum pH of adsorption was obtained at pH 4. The optimum time of adsorption occurred at 120 minutes and the kinetics model followed PSO. The isotherm data followed Langmuir isotherm and the adsorption process was endoetrmic and spontaneous. The regeneration results showed the ability up to five cycles with a decrease of 40.019% from 96.698% to 56.679%.

Keywords
Graphene Oxide, Malachite Green, Adsorption

Received: 2 January 2023, Accepted: 25 March 2023
https://doi.org/10.26554/ijmr.2023113

1. INTRODUCTION

Water is a very important resource whose existence is central to human survival (Buvaneswari and Singanan, 2022). It is known that in the last decade, water pollution is an issue that has been discussed throughout the world (Raval et al., 2022). Water pollution is one of the environmental pollution that is included in the ten problems that the world prioritizes in dealing with the issue (Jabeen et al., 2023).

Synthetic dyes are wastewater pollutants generated from the textile, paper, food, paper powder, and cosmetic industries (Gouasmia et al., 2022; Chamoli et al., 2023). Synthesis dyes are very dangerous for health because they can cause heart disease, carcinogenic, mutagenic, skin irritation, and allergies (Brahma et al., 2022; Van Tran et al., 2022). One example of a synthetic dye is malachite green (MG) which is a water-soluble cationic dye commonly used in the textile industry (Dahlan et al., 2023).

There are many ways to remove MG pollutants including coagulation, ion exchange, filtration, photocatalyst, and adsorption methods (Liu et al., 2022; Modwi et al., 2023; Palapa et al., 2021; Sabit and Ebrahim, 2023). Among the above methods, adsorption is the most widely used method due to its high removal rate, low cost, and easy work (Mohadi et al., 2023; You et al., 2022). Many adsorbents have been used in the MG adsorption process including using graphite carbon-based materials. Research conducted by Yin et al. (2021) conducted MG adsorption using expanded graphite which obtained a maximum adsorption capacity of 41.49 mg/g and a surface area of 124 m^2/g. It is known that there are many types of graphite-based materials that can be made or modified other than using expanded graphite, including using graphene oxide material.

Graphene oxide (GO) is a very interesting carbon structure with oxygen groups (carboxyl, epoxy, hydroxyl, phenol) attached to it and sp^2 and sp^3 hybridized carbon atoms (Bulin, 2023; Heshami et al., 2023). GO is produced from the oxidation process on graphite material using the Hummer method and peeling the coating into thin sheets by reducing the coating (Banda et al., 2023). The presence of oxygen groups and large surface area makes GO good for use as an adsorbent in various water pollution (Bulin, 2023).

In this study, MG adsorption was carried out using GO as an adsorbent by treating variations in pH, time (kinetics), temperature and concentration (isotherms and thermodynamics), and regeneration.) Characterization of GO material was done by XRD, FT-IR and BET.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Characterizations

The chemicals used in this study are graphite, sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2), potassium

permanganate ($KMnO_4$), hydrochloric acid (HCl), distilled water (H_2O), rhodamin B ($C_{28}H_{31}N_2O_3Cl$), methylene blue ($C_{16}H_{18}ClN_3S$), and malachite green ($C_{23}H_{25}ClN_2$). The material was characterized using a Rigaku Miniflex-600 X-ray Diffractometer, Shimadzu Prestige-21 FTIR spectrophotometer, and Quantachrome Instruments for surface area analysis. Absorbance measurements of the malachite greens solution were conducted using a UV-Visible Biobase spectrophotometer UV BK-1800PC.

2.2 Synthesis of Graphene Oxide (Yang and Cao, 2022)

The synthesis of graphene oxide was carried out by the Hummers method. A total of 3 grams of graphite and 1.5 grams of $NaNO_3$ were put in a glass beaker, then 69 mL of H_2SO_4 was added and stirred until homogeneous. 9 grams of $KMnO_4$ was added slowly at a temperature below 20°C. The mixture was stirred for 7 hours at a temperature of 35°C. Another 9 grams of $KMnO_4$ was added to the mixture and stirred for 14 hours. The mixture obtained was allowed to stand at room temperature and slowly added 400 mL of distilled water and 3 mL of H_2O_2. In the next process, the mixture was filtered and washed with distilled water, and dried in an oven at 65°C for 72 hours.

2.3 Determination of pH pzc (Point Zero Charge)

The pH pzc was determined by adding 0.02 g of each adsorbent to 20 mL of 0.1 M NaCl solution, which had been adjusted to pH with variations of 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. The pH of the NaCl solution was changed by adding 0.1 M NaOH and HCl solutions. The mixture was agitated for 24 hours, then filtered, and the filtrate's final pH was recorded with a pH meter, and a graph was created to show the link between beginning pH and final pH.

2.4 Selectivity of Graphene Oxide for the Adsorption of Rhodamine B, Methylene Blue, and Malachite Green

Selectivity tests were carried out by mixing rhodamine B, methylene blue, and malachite green dyes. A total of 20 mL of rhodamine B, methylene blue, and malachite green dyes with the same concentration were homogenized. The dye mixture was added 0.02 gram of each adsorbent, then the wavelength in the range of 500-700 nm was measured using time variations of 0, 2, 4, 6, 8, and 10 minutes. Separate the adsorbate from the adsorbent and calculate the residual concentration and adsorbed concentration of each dye. Furthermore, the most adsorbed dye is used for the next process.

2.5 Adsorption Study

2.5.1 Effect of pH

20 mL of dye at a concentration of 50 mg/L was put into a 100 mL beaker and adjusted the pH using NaOH and HCl solutions with variations in pH 2; 3; 4; 5; 6; 7; 8; 9; and 10, then measured the initial absorbance of each pH using a UV-Vis spectrophotometer to determine the initial concentration of various pH. A total of 0.02 grams of adsorbent was added to the dye solution and stirred for 2 hours. The separation process was carried out using centrifugation, and the filtrate obtained was measured using a UV-Vis spectrophotometer.

2.5.2 Effect of Contact Time

0.02 g of adsorbent was added to the dye with a concentration of 100 mg/L as much as 20 mL, then stirred with a variation of adsorption contact time of 0, 10, 15, 30, 45, 60, 75, 90, 120, 150, 180, 210, and 240 minutes. After the stirring, the adsorbent is separated from the dye solution. Furthermore, a UV-Vis spectrophotometer measured each solution for its absorbance value.

2.5.3 Effect of Initial Concentration and Temperature

0.02 g of adsorbent was added to 20 mL of dye solution with varying concentrations of 70 mg/L, 80 mg/L, 90 mg/L, 100 mg/L, and 110 mg/L with varying temperatures of 30, 40, 50, 60, and 70°C. The solution was stirred for 2 hours. After the stirring, the adsorbent was separated from each dye solution using centrifugation. The separated solution was measured for absorbance value using UV-Vis spectrophotometer.

2.5.4 Desorption and Regeneration Study

The dye desorption process is carried out using an ultrasonic device. The desorption process was carried out first by using 30 mL of cationic dye selective solution with a concentration of 100mg/L then added 0.3 g of adsorbent and stirred for 2 hours. The adsorbent that has been used is then dried, after drying the residue is taken and added to 10 mL of water solvent and desorbed for 2 hours using an ultrasonic device. The filtrate was measured for absorbance using a UV-Vis spectrophotometer.

The regeneration process is carried out by adding adsorbents that have gone through the desorption process with 100 mg/L of dye solution as much as 30 mL. The mixture was stirred for 2 hours, and the residual concentration was measured using a UV-Vis spectrophotometer. The adsorbent was dried and continued with the desorption process using an ultrasonic device by adding 10 mL of water solvent and stirring for 2 hours. Then the filtrate obtained was measured using a UV-Vis spectrophotometer. The remaining residue was then dried and reused in the next regeneration process.

3. RESULTS AND DISCUSSION

3.1 Characterization of Graphene Oxide Material

Based on the XRD analysis shown in Figure 1, a sharp diffraction peak is obtained at an angle of 9.45°, which is a typical graphene oxide peak. The (001) plane at this angle indicates that the Graphene Oxide material has a hexagonal structure (Gogoi and Chowdhury, 2019). Figure 2 is the result of FT-IR analysis of the graphene oxide material. The absorption peaks at wavenumbers 3387 cm^{-1}, 1720 cm^{-1}, and 1620 cm^{-1} indicate the presence of O-H vibrations, C=O in COOH and C=C in the ring (Rahman and Raheem, 2022). The wavelength of 1080 cm^{-1} and 1400 cm^{-1} indicates the presence of epoxy groups (C-O-C) and C-OH (carboxyl) (Haydari et al., 2023; Rahman and Raheem, 2022).

Figure 3 shows the adsorption and desorption of nitrogen on GO. This describes the adsorption isotherm of GO materials that follows the type IV isotherm. This type of isotherm indicates that the GO material has a mesoporous structure (2-50 nm) (Ni'mah

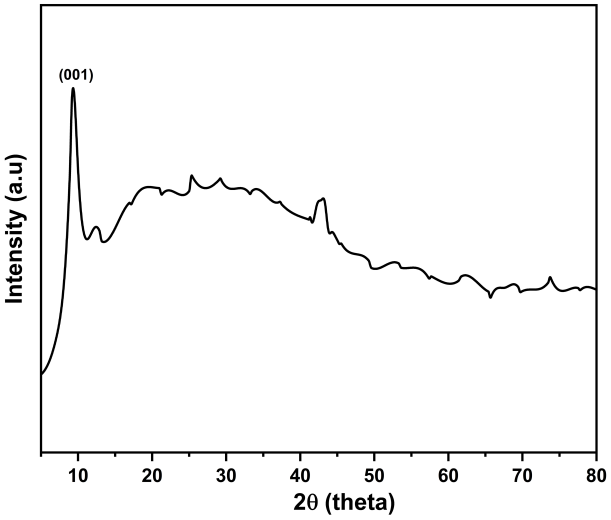

Figure 1. XRD Pattern of Graphene Oxide

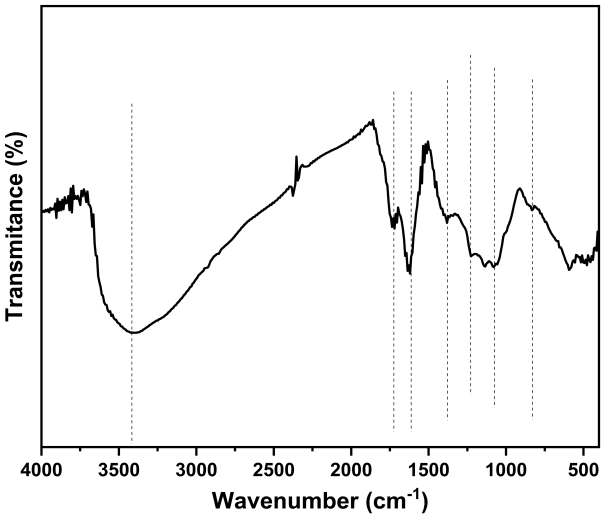

Figure 2. FT-IR Spectra of Grafena Oxide

et al., 2022). It is also shown in Table 1, where the pore size of GO material is 5.13 nm, which includes the mesoporous structure region. The pore size, diameter, and surface area of GO material are shown in Table 1.

3.2 Selectivity of Cationic Dyes

The dye selectivity was carried out to see the ability of GO material to absorb the three cationic dyes (rhodamine B (RhB), malachite green (MG), and methylene blue (MB)). The results obtained in the form of a decrease in the intensity of the wavelength of the three dyes due to absorption by GO material measured within 10 minutes. Based on Figure 4, it can be seen that GO material absorbs more MG dye which is then followed by MB dye. The insignificant decrease in RhB dye indicates that GO material is not very selective for rhodamine B dye.

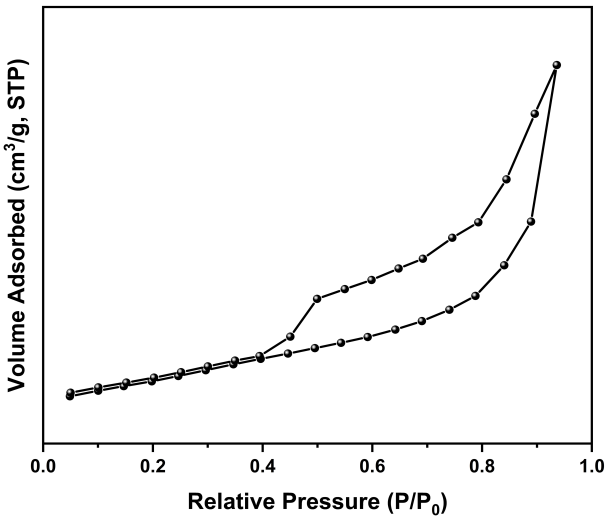

Figure 3. Nitrogen Adsorption-Desorption of Grafena Oxide

Table 1. BET Result of Grafena Oxide

Parameter	Result
Surface area	157.360 m^2/g
Pore size	5.126 nm
Pore volume	0.403 cm^3/g

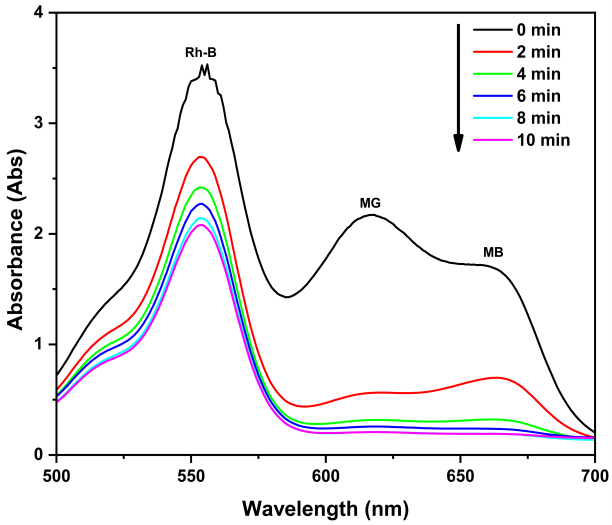

Figure 4. Selectivity of Graphene Oxide Towards Various Dyes

3.3 Effect of optimum pH and pHpzc

The optimum pH and pHpzc obtained on GO material are pH 4 and pH 3.6, respectively (Figure 5). pHpzc is used to see the state of the material when it is uncharged. When pH<pHpzc indicates a lot of positive charges that cover the surface, while pH>pHpzc indicates a lot of negative charges due to the addition of OH^- (Ahmad et al., 2023). Based on the results obtained, the

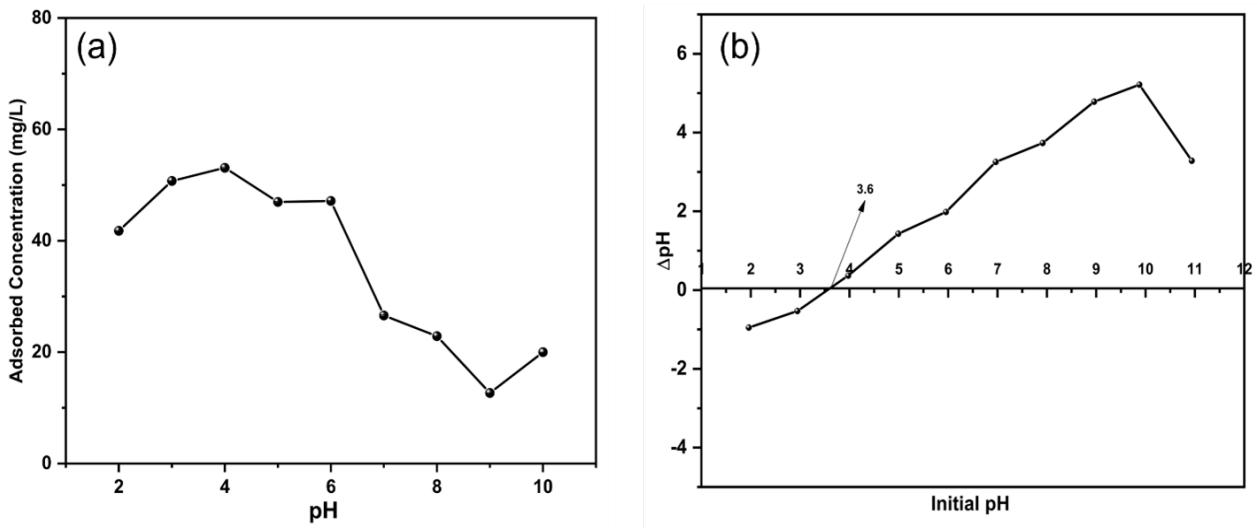

Figure 5. Optimum pH (a) Value and pHpzc (b) on Graphene Oxide

optimum pH>pHpzc on GO material indicates that there are many negative charges on the GO surface. Therefore, there is an electostatic interaction between GO material and positively charged MG dye due to the difference in charge between GO and MG dye.

3.4 Effect of Time and Kinetics study

The effect of contact time was used to see the optimal time of GO material in absorbing MG dye and determine the adsorption kinetics model (Figure 6). The results obtained showed that the optimal time for GO to adsorb MG dye was 120 minutes. The adsorption kinetics model followed is a pseudo second order (PSO) kinetics model, where the R^2 value in the pseudo second order (PSO) kinetics model is closer to 1 than the R^2 value in the pseudo first order (PFO) kinetics model. The Qe_{calc} value in the PSO kinetics model is more similar to the Qe_{exp} value (see Table 2).

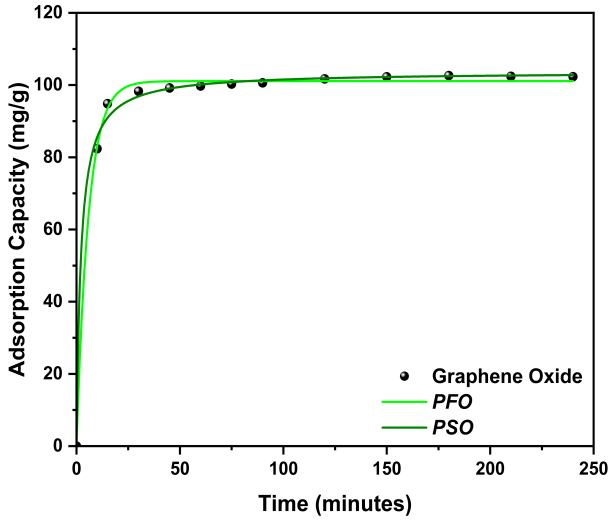

Figure 6. Effect of Time Between Graphene Oxide and Malachite Green

Table 2. Parameters of Adsorption Process Kinetics

kinetic model	Parameter	Grafena oxide
pseudo first order	Qe_{exp} (mg/g)	102.320
	Qe_{calc} (mg/g)	29.465
	k_1 (min^{-1})	0.039
	R^2	0.875
pseudo second order	Qe_{exp} (mg/g)	102.320
	Qe_{calc} (mg/g)	103.093
	k_2 (g/mg.min)	0.005
	R^2	1.000

3.5 Effect of isotherms and thermodynamic studies

Adsorption isotherms are used to see the interaction between GO material and MG dye until equilibrium occurs. In addition, adsorption isotherms are used to determine the type of isotherm model that is suitable for the adsorption process. The isotherm models observed are Langmuir and Freundlich isotherms by looking at the R^2 value in each isotherm model. Based on the results obtained, the R^2 value in the Langmuir isotherm is closer to 1 than the Freundlich isotherm model, so it can be assumed that the adsorption process that occurs follows the Langmuir isotherm model (Table 3). The Langmuir isotherm model describes a homogeneous adsorbent surface and the adsorbed molecules do not disturb the absorption site nearby (Zhang et al., 2021). In addition, the maximum capacity value of MG dye adsorption can be seen in Table 3.

Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are shown in Table 4. The results

Table 3. Isoterm Parameters the Adsorption Process

Adsorbent	T (°C)	Langmuir			Freundlich		
		Q_{max}	kL	R^2	n	kF	R^2
Graphene Oxide	30	97.087	0.691	0.987	6.165	57.597	0.456
	40	102.041	0.560	0.986	4.697	52.529	0.570
	50	106.383	0.701	0.983	4.902	58.345	0.527
	60	104.167	1.280	0.992	6.394	68.659	0.427
	70	104.167	1.455	0.981	14.368	79.195	0.091

Table 4. Thermodynamic Data of MG Dye Adsorption

Concentration (mg/L)	T (K)	Qe (mg/g)	ΔH (kJ/mol)	ΔS (J/K mol)	ΔG = ΔH-TΔS (kJ/mol)
111.711	303	90.155	15.020	0.061	-3.588
	313	92.284			-4.202
	323	96.579			-4.816
	333	98.249			-5.430
	343	99.333			-6.044

obtained show negative values in the Gibbs free energy which indicates the adsorption process takes place spontaneously. The positive value of enthalpy indicates the adsorption process is endothermic. The entropy value indicates the degree of disorder where the value obtained is so small.

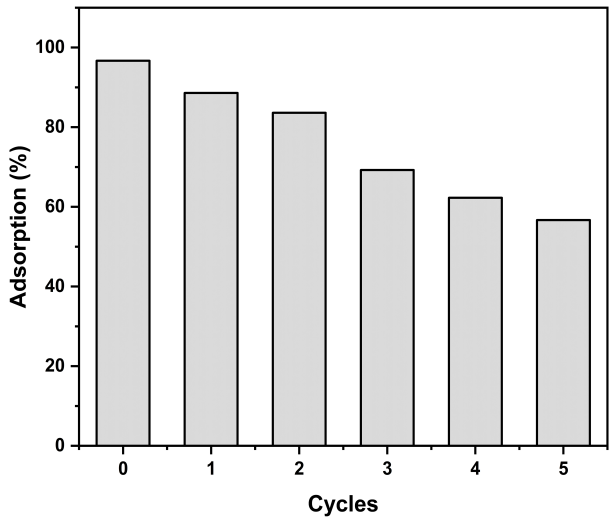

Figure 7. Regeneration of Graphene Oxide Material in Malachite Green Adsorption

3.6 Regeneration Process

The regeneration process demonstrated the ability of repeated use of graphene oxide material as an adsorbent in MG adsorption for up to five cycles. The results obtained can be seen in Figure 7. Based on the % adsorption value, it shows that the graphene oxide material from the first cycle to the fifth cycle has decreased by 40.019% from 96.698% to 56.679%.

4. CONCLUSIONS

In brief, graphene oxide material as malachite green dye adsorbent was successfully prepared using the Hummer method. The success of the synthesis was seen from XRD, FTIR, and BET analysis. The optimum pH of malachite green dye was obtained at pH 4. The kinetics and isotherm data followed PSO and Langmuir. Thermodynamic data showed that adsorption was spontaneous and endothermic. Regeneration results showed a decrease of 40.019% from 96.698% to 56.679% in the fifth cycle.

5. ACKNOWLEDGEMENT

Thanks to the Research Center of Inorganic Materials and Coordination Complexes at FMIPA Sriwijaya University for their help and support so that this research runs smoothly.

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