Synergistic Effect of Bentonite-TiO_2-GO Hybrid Composite for High-Performance Adsorption and Photodegradation of Methylene Blue

Said M.[1,2*], Buand N.[1,2], Alfarado D.[1,2], Fatma F.[1,2] and Nurnawati E.[3]
1. Department of Chemistry, Faculty of Mathematics and Natural Sciences Faculty, Sriwijaya University, Palembang, INDONESIA
2. Research Centre of Advanced Material and Nanocomposite, Faculty of Mathematics and Natural Sciences, Sriwijaya University, Palembang, INDONESIA
3. Department of Biology, Faculty of Mathematics and Natural Science, Sriwijaya University, Palembang, INDONESIA
*msaidusman@unsri.ac.id

Abstract

This study focuses on synthesizing and characterizing Bentonite-TiO_2-GO composite as an advanced material for removing methylene blue dye from aqueous solution. Methylene blue, a commonly used dye in the textile industry, contributes significantly to water pollution when discharged as wastewater, posing serious threats to human health and aquatic ecosystems. To mitigate this problem, adsorption and photocatalytic degradation methods are used as effective strategies for dye removal. This study modified bentonite with TiO_2 and graphene oxide (GO) to increase its surface area, introduce active sites and enhance its photocatalytic adsorption efficiency. The synthesized (Bentonite-TiO_2)-GO composite was characterized using X-ray diffraction (XRD) and Scanning electron microscopy (SEM), which confirmed the successful formation of the composite.

The optimal conditions for removing methylene blue were achieved at an initial dye concentration of 1 mg/L, with a contact time of 30 min and an adsorbent dosage of 25 mg. The highest adsorption efficiency was recorded at 87.98% in dark conditions and 89.70% under UV irradiation. Furthermore, the adsorption isotherm analysis showed that the composite followed the Langmuir and Freundlich models, indicating a combination of monolayer and multilayer adsorption mechanisms. These findings highlight the potential of Bentonite-TiO_2-GO composite as an efficient and sustainable solution for dye wastewater treatment.

Keywords: Methylene Blue, Bentonite-TiO_2-GO Composite, Adsorption and Photocatalytic.

Introduction

Dyes are extensively used in the textile industry to impart color to fabrics and other materials. Methylene blue is a widely utilized basic dye characterized by its heterocyclic aromatic chemical structure, which contributes to its strong affinity for textile fibers[15,22]. Every year, more than 100,000 types of commercial dyes are produced globally, with an annual production exceeding 700,000 tons. Approximately 10–15% of these dyes are discharged as waste into industrial waterways, posing significant threats to human health and aquatic ecosystems[14,29]. Several methods can be employed to reduce the concentration of dye waste, among which adsorption and photocatalysis are widely utilized due to their cost-effectiveness, simplicity, efficiency and suitability for treating toxic substances[7]. However, adsorption and photocatalysis have limitations depending on the type of adsorbent used. High-quality adsorbents, for instance, are often expensive and many commonly used adsorbents exhibit limited capacity and reusability[11]. Bentonite is a frequently used adsorbent due to its small colloidal particle size and high ion exchange capacity[12].

Despite its advantages, bentonite has drawbacks such as a narrow interlayer space and susceptibility to disintegration[18]. To address these limitations, modifications of bentonite with metal oxides, such as titanium dioxide (TiO_2), have been explored to enhance its adsorption capacity and stability[25]. However, bentonite-TiO_2 composites still have weaknesses, such as agglomeration of TiO_2 particles, which reduces the effectiveness of active sites for adsorption. To overcome this weakness, graphene oxide (GO) was added. GO has conductive properties and a large surface area and can increase the distribution of TiO_2 particles and can create more active sites for adsorption; if combined, it can produce an effective adsorbent in removing methylene blue from wastewater[17,24].

This study presents a novel approach for the synthesis of a Bentonite-TiO_2-GO composite, integrating the high adsorption capacity of bentonite, the photocatalytic activity of TiO_2 and the enhanced surface area and conductivity of graphene oxide (GO). Unlike conventional adsorbents, these composites addresses key limitations such as TiO_2 agglomeration and restricted adsorption sites by leveraging GO as a dispersing and stabilizing agent, thereby improving dye removal efficiency. Furthermore, this research comprehensively evaluates adsorption performance under varying conditions including dye concentration, contact time and adsorbent dosage, contributing valuable insights into the practical application of advanced composite materials for wastewater treatment.

Material and Methods

Materials and Instrumentation: The study used various laboratory instruments such as hydrothermal reactor tubes,

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***** Author for Correspondence***

https://doi.org/10.25303/2911rjce0108

Hettich EBA 20 centrifuges, ultrasonication devices, UV-Vis spectrophotometers (Orion Aquamate 8000) and characterization instruments such as SEM-EDX (Thermo Fisher Scientific Phenom P-Series) and XRD (X'Pert PRO). Chemical reagents used in this study include distilled water, demineralized water, graphite, bentonite, ice cubes, sulfuric acid p.a H_2SO_4 (Merck), titanium dioxide TiO_2 (Merck), sodium nitrate $NaNO_3$ (Merck), potassium permanganate $KMnO_4$ (Merck), hydrogen peroxide H_2O_2 (Merck) and methylene blue dye synthetic (Merck)

Synthesis of Graphene Oxide: Graphite powder 10 g was mixed with 500 mL of concentrated H_2SO_4 in an ice bath and stirred at 500 rpm at 80°C for 24 hours. Afterward, 10 g of $NaNO_3$ was added and stirred for 1 hour, followed by the gradual addition of 60 g of $KMnO_4$ with continuous stirring for 4 hours. The mixture was then heated to 35°C for 1 hour before diluting with 1000 mL of demineralized water, ensuring that the temperature remained below 60°C. After 15 minutes, 50 mL of 30% H_2O_2 (diluted in 250 mL of demineralized water) was added to terminate the reaction. The solution was washed with demineralized water, centrifuged at 8000 rpm for 30 minutes and purified through multiple washings. The resulting GO suspension underwent ultrasonication for 4 hours, followed by vacuum filtration and drying at 90°C[2]. The final GO product was characterized using XRD and SEM-EDX.

Synthesis of Bentonite-TiO_2 Composite: Bentonite and TiO_2, 5 grams were dispersed in 200 mL of demineralized water and stirred using a magnetic stirrer at 60°C for 2 hours. After that, it was precipitated while heated using a hot plate at 70°C for 12 hours. Then, the precipitate was centrifuged to obtain the residue, it was dried using an oven at 80°C for 12 hours[16]. XRD and SEM-EDX characterized the resulting bentonite-TiO_2 composite.

Synthesis of (Bentonite-TiO_2)-GO Composite: A total of 1 gram of bentonite-TiO_2 was mixed with GO, then demineralized water was added to the mixture. After that, the bentonite-TiO_2 and GO that had been mixed, were put into a 100 mL hydrothermal autoclave and heated in an oven at a temperature of 175°C for 10 hours. The (bentonite-TiO_2)-GO mixture was dried using an oven. Then, the dried (bentonite-TiO_2)-GO solid was ground to form a bentonite-TiO_2-GO composite[16]. The resulting bentonite-TiO_2-GO was characterized using XRD and SEM.

Optimalization of Photodegradation Effect for Methylene Blue using (Bentonite-TiO_2)-GO Composite: Optimization of the effect of methylene blue degradation by the composite was carried out by considering several parameters such as the effect of concentration, contact time and adsorbent dose. To evaluate the effect of concentration, 10 mg of (bentonite-TiO_2)-GO composite was added to 15 mL of methylene blue solution (1–5 mg/L) and stirred at 200 rpm for 30 minutes. Samples were collected at specific intervals, centrifuged at 2000 rpm and analyzed using a UV-Vis spectrophotometer at the maximum absorption wavelength of methylene blue. Contact time variations were carried out using the same procedure as the time variations of 15-75 minutes, while the adsorbent dose variations were carried out with composite variations of 5-25 mg composite[5].

Data Analysis and Adsorption Evaluation: The synthesized composite was analyzed through characterization techniques and its application in adsorption. XRD was utilized to determine the crystal structure and size[21]. SEM-EDX was used to examine surface morphology and elemental composition and UV-Vis spectrophotometry to measure concentration and absorbance. Adsorption experiments were conducted to evaluate the composite's dye removal efficiency. The adsorption capacity and efficiency were calculated using equations (1) and (2).

$$Q_e = \frac{V \text{ x } (C_0 - C_e)}{W} \tag{1}$$

$$\text{Adsorption Efficiency } (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\ \% \tag{2}$$

The adsorption isotherm is determined using the Langmuir and Freundlich equations, which determine the isotherm model carried out by the composite. The Freundlich and Langmuir equations can be seen in equations (3) and (4) respectively.

$$\log Q_m = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{4}$$

XRD results can determine the crystal size based on the Debye Scherrer equation which can be obtained through equation (5):

$$d = \frac{K\lambda}{\beta \cos\theta} \tag{5}$$

To change the unit β from deg to rad can be obtained through the following equation (6):

$$\beta = \text{FWHM} \times \frac{\pi}{180} \tag{6}$$

where d is the crystallite size (nm), K is a constant (0.9), β is the FWHM (deg), π is the Archimedes constant (3.14), Qe is the adsorption capacity at equilibrium (mg/g), V is the volume of the dye solution (L), Co is the dye concentration (ppm or mg/L), Ce is the dye concentration at equilibrium (ppm or mg/L), W is the mass of the adsorbent (g), Qm is the maximum adsorption capacity (mg/g), KL is the Langmuir isotherm constant, KF is the Freundlich isotherm constant and n is the adsorption intensity.

Results and Discussion

Composite Synthesis Results (Bentonite-TiO_2)-GO: The synthesis of bentonite-TiO_2-GO composites resulted in notable physical changes. Initially, the activated bentonite appeared light gray with fine particles, TiO_2 was white with fine powder particles and GO was blackish-brown with coarse particles. After synthesis, the mixture of bentonite and TiO_2 produced greyish-white particles with a coarser texture, indicating interaction between the two components. The incorporation of GO into the bentonite-TiO_2 matrix resulted in a darker color and a rougher texture, confirming the successful integration of GO into the composite.

XRD characterization was conducted to determine the samples' crystallite size and interlayer spacing (d-spacing). GO, bentonite-TiO_2 and bentonite-TiO_2-GO composites were analyzed at a diffraction angle of $2\theta = 0–60°$. Figure 1 shows a diffraction peak for GO at $2\theta = 10.57°$, consistent with JCPDS no. 01-0646, with a crystallite size of 4.3194 nm. Bentonite-TiO_2 exhibited characteristic peaks at 2θ = 25.38°, 37.90°, 48.12°, 53.95° and 55.11°, indicating that the crystallinity of TiO_2 remained unchanged. Figure 1 shows that bentonite-TiO_2-GO composites with 1:1, 1:2 and 1:4 ratios produced peaks at approximately 25.46°, 25.74° and 25.44° respectively.

The peak intensity resembled that of bentonite-TiO_2, suggesting that GO primarily adhered to the bentonite surface rather than penetrating the bentonite-TiO_2 interlayer. The absence of distinct diffraction peaks for GO and bentonite was attributed to the low diffraction intensity of GO and the strong peak of TiO_2. The XRD results indicated that the 1:1 bentonite-TiO_2-GO composite exhibited the most favorable properties, including smaller crystallite size, improved component distribution and interaction and a more homogeneous structure (Figure 2). This suggests higher adsorption efficiency due to the increased availability of active sites.

The XRD analysis confirmed the successful synthesis of the composites, as evidenced by the presence of characteristic peaks for both TiO_2 and GO. The crystallite size of the composites was calculated using the Scherrer equation, a widely accepted method for determining crystallite dimensions from XRD data[19]. The interlayer spacing (d-spacing) of GO was calculated to be 0.836 nm, which aligns with recent studies reporting d-spacing values for graphene oxide in the range of 0.8–1.2 nm[26].

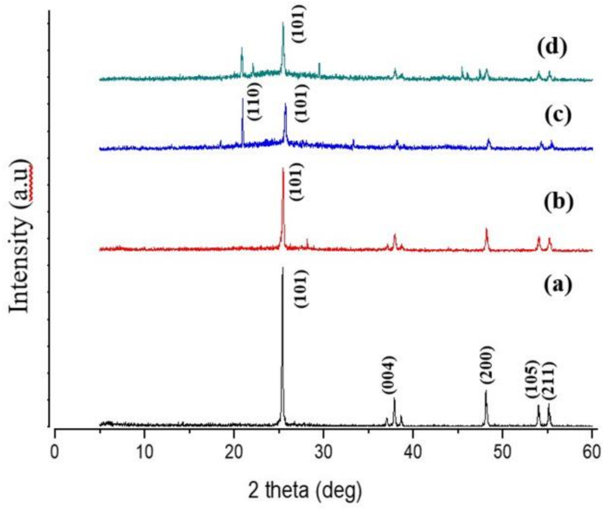


Figure 1: XRD Result: (a) Bentonit-TiO_2, (b) (Bentonit-TiO_2)-GO 1:1, (c) (Bentonit-TiO_2)-GO 1:2, (d) (Bentonit-TiO_2)-GO 1:4

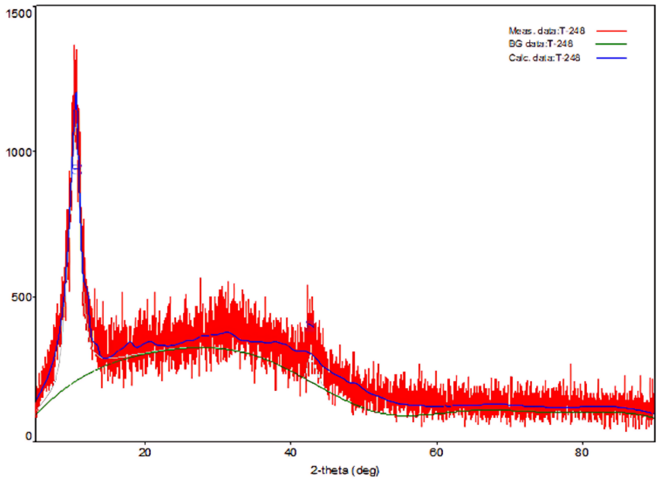


Figure 2: XRD Result on best result (Bentonit-TiO_2)-GO 1:1

The absence of significant shifts in the TiO_2 peaks after the addition of GO suggests that the structural integrity of TiO_2 was preserved which is crucial for maintaining its photocatalytic and adsorptive properties. Furthermore, the homogeneous distribution of GO on the bentonite-TiO_2 surface, as inferred from the XRD results, is expected to enhance the composite's surface area and adsorption capacity, as demonstrated in recent studies on hybrid nanocomposites[25].

SEM characterization was performed to observe the surface structure of bentonite-TiO_2 and bentonite-TiO_2-GO, which is important to determine the success of the synthesis and adsorption potential. SEM showed that adding GO to bentonite-TiO_2 resulted in a more complex structure and larger surface area, increasing the effectiveness of methylene blue adsorption. Figure 3 shows the results of SEM-EDX characterization.

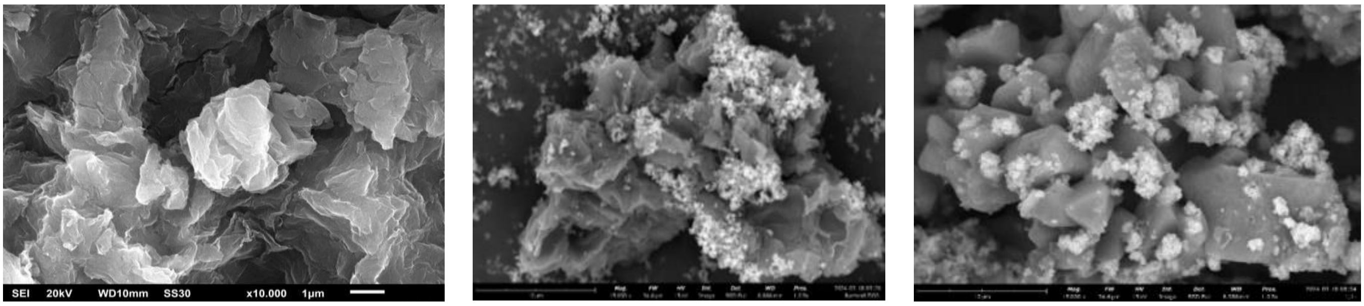
SEM analysis revealed that the incorporation of GO into bentonite-TiO_2 resulted in a more complex and porous structure, significantly increasing the surface area and enhancing the adsorption efficiency for methylene blue[25]. Figure 3(a) depicts the morphology of GO, which exhibits a rock-like structure with a rough and layered surface, typical of graphene oxide[26]. Figure 3(b) shows the morphology of bentonite-TiO_2, where small TiO_2 particles are uniformly dispersed on the bentonite surface, indicating successful composite formation[18]. In contrast, figure 3(c) displays a complex and interconnected structure with GO effectively filling the pores of bentonite, which is expected to enhance the material's adsorption capacity[6].

Table 1 shows that EDX analysis further confirmed the differences in elemental composition between GO and bentonite-TiO_2. GO exhibited a high carbon content (58.74%) and significant oxygen content (39.93%), consistent with its chemical structure as a carbon-based material with oxygen-containing functional groups[9]. In contrast, bentonite-TiO_2 contained a variety of elements, including C (6.92%), O (52.13%), Mg (0.30%), Al (1.33%), Si (8.41%) and Ti (7.03%), reflecting the presence of clay minerals and TiO_2.

The presence of Ti in the composite confirms the successful integration of TiO_2 which is essential for photocatalytic activity[20]. These compositional differences highlight the unique properties of each component and their synergistic effects in the composite, making bentonite-TiO_2-GO a promising material for dye adsorption applications.

Adsorption Ability of Methylene Blue Dyes

Effect of Concentration: The effect of concentration on the adsorption capacity of bentonite-TiO_2-GO was investigated to determine the optimum concentration of methylene blue (MB) that can be effectively adsorbed.



(a) (b) (c)

Figure 3: Characterization results using SEM (a) GO, (b) Bentonite-TiO_2 and (c) bentonite-TiO_2-GO with a magnification of 15,000x.

Table 1
SEM Analysis Compounds on Graphene Oxide and Bentonite-TiO_2

Element	Graphene Oxide	Bentonit-TiO_2
	Mass%	Mass%
C	58.74	6.92
O	39.93	52.13
Mg	-	0.30
Al	-	1.33
Si	-	8.41
S	0.42	0.73
K	0.15	-
Ca	-	-
Ti	-	7.03
Fe	0.25	1.74
Cu	0.5	1.25

The study used varying MB concentrations of 1, 2, 3, 4 and 5 mg/L, with a fixed volume of 15 mL and an adsorbent dosage of 0.01 gram of bentonite-TiO_2-GO for a contact time of 30 minutes. Figure 4 (a) illustrates the relationship between MB concentration and adsorption effectiveness. The results indicate that the highest adsorption efficiency (87.98%) was achieved at the lowest MB concentration of 1 mg/L, using the bentonite-TiO_2-GO composite with a 1:1 ratio. This suggests that at lower concentrations, the active sites on the adsorbent surface are more accessible, allowing for higher adsorption efficiency[25].

As the MB concentration increased, adsorption efficiency decreased, with 84.94% and 81.11% efficiencies for the 1:2 and 1:4 composite ratios respectively. This decline is due to the saturation of active sites at higher dye concentrations, reducing adsorption capacity[18]. The 1:1 ratio showed the best performance, attributed to its optimal surface area and active site availability[6]. The lower efficiency at higher concentrations suggests incomplete pore utilization indicating a need for further optimization of adsorbent structure or process conditions, such as longer contact time or higher adsorbent dosage[15]. These results align with studies showing that adsorption efficiency depends on initial dye concentration and active site availability[22].

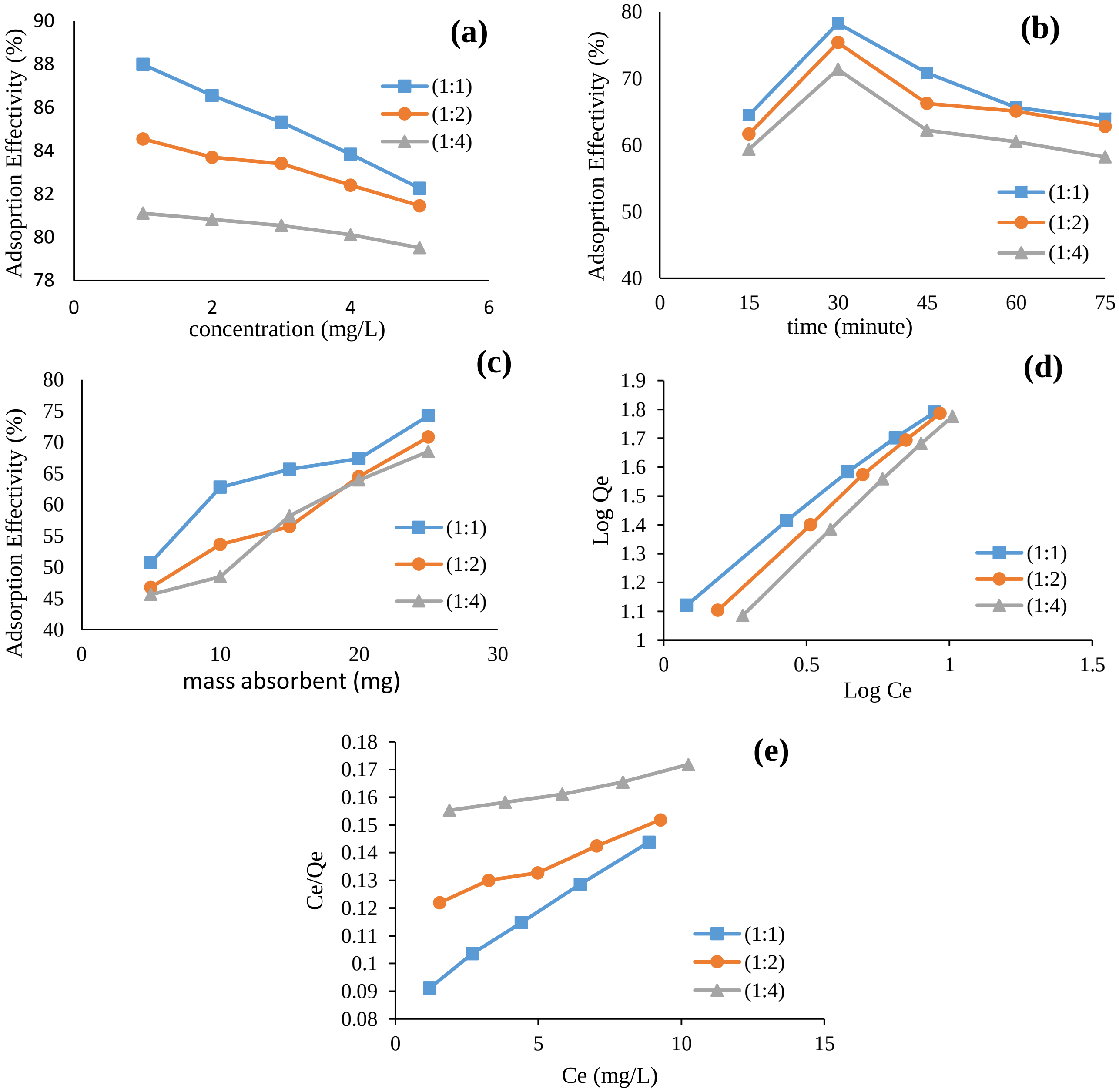


Figure 4: Graphical of Methylene Blue Adsorption ability from GO- effect of contact time on percent (Bentonite-TiO_2)-GO adsorbed (a) effect of concentration; (b) effect of time; (c) effect of adsorbent mass; (d) isotherm models Langmuir and (e) isotherm models Freundlich.

Effect of Contact Time: The effect of contact time on the adsorption of methylene blue by bentonite-TiO_2-GO with varying times of 15, 30, 45, 60 and 75 minutes with the best concentration of methylene blue is 1 mg/L. Figure 4 (b) shows the increase in adsorption effectiveness at 30 minutes, indicating the optimum contact time. The (bentonite-TiO_2)-GO 1:1 composite has the best adsorption, outperforming other ratios due to its superior surface area and active site availability. Adsorption effectiveness increased at contact times of 15 and 30 minutes but then decreased at 45, 60 and 75 minutes because it reached the saturation point.

The adsorption percentage is directly proportional to the contact time until it reaches the optimum point, after which desorption occurs. Adsorption effectiveness increases with contact time until it reaches a certain point, then decreases thereafter[3]. The results from table 2 show that (bentonite-TiO_2)-GO 1:1 has the highest percentage of adsorption effectiveness, namely 64.51%.

Adsorption efficiency initially increased with contact time due to the availability of active sites on the adsorbent surface, enabling greater interaction with dye molecules[28]. However, beyond the optimum contact time (30 minutes), efficiency declined, likely due to active site saturation and desorption. This trend aligns with studies showing that adsorption efficiency is time-dependent, peaking before declining as equilibrium is reached. The decrease in efficiency at longer contact times (45, 60 and 75 minutes) underscores the need to optimize contact time for maximum adsorption capacity.

Prolonged contact may weaken adsorbent-dye interactions, leading to desorption[27]. These findings highlight the importance of controlling process parameters such as contact time, to improve the performance of bentonite-TiO_2-GO composites in dye removal.

Effect of Adsorbent Mass: Variations in the adsorbent mass of 5, 10, 15, 20 and 25 mg with the best concentration of methylene blue of 1 mg/L and the best contact time of 30 minutes showed increased adsorption effectiveness and adsorbent mass. Figure 4 (c) shows a graph of adsorption effectiveness continuing to increase, reaching a maximum of 25 mg. The increase in adsorption effectiveness occurs due to the increase in adsorbent porosity which provides more space for adsorption. The results from table 2 show that (bentonite-TiO_2)-GO 1:1 has the highest percentage of adsorption effectiveness, 74.24%, with an adsorbent mass of 25 mg. An increase in the surface area of the adsorbent causes this.

The (bentonite-TiO_2)-GO 1:1 composite achieved the highest adsorption efficiency (74.24%) at 25 mg, attributed to its optimal surface area and porosity, enhancing interaction with MB molecules[28]. Adsorption effectiveness increased with adsorbent mass, as higher dosages provide more active sites and porous structures[18]. However, further mass increases may not improve efficiency beyond a specific limit due to particle aggregation or overlapping active sites[1]. These results emphasize optimizing adsorbent mass for maximum efficiency and cost-effectiveness in wastewater treatment.

Adsorption Isotherm: The adsorption isotherm study was conducted to investigate the adsorption mechanism of methylene blue (MB) onto (bentonite-TiO_2)-GO composites.

Table 2
Percentage of effectiveness of methylene blue adsorption with all parameters at the composite ratio bentonite-TiO_2-GO

Parameters	**Variation**	**Adsorption Effectiveness (%)**		
		(bentonite-TiO_2):GO (1:1)	**(bentonite-TiO_2):GO (1:2)**	**(bentonite-TiO_2):GO (1:3)**
Concentration (mg/L)	1	87.98	84.54	81.11
	2	86.55	83.69	80.82
	3	85.31	83.4	80.54
	4	83.83	82.4	80.11
	5	82.26	81.45	79.51
Contact time (Minutes)	15	64.51	61.65	59.36
	30	78.25	75.39	71.38
	45	70.81	66.23	62.22
	60	65.66	65.08	60.5
	75	63.94	62.79	58.21
Adsorbent weight (mg)	5	50.77	46.77	45.62
	10	62.79	53.63	48.48
	15	65.66	56.50	58.21
	20	67.37	64.51	63.94
	25	74.24	70.81	68.52

Table 3
Data from adsorption isotherm calculations on (bentonite-TiO_2)-GO

Ratio (Bentonite-TiO_2)-GO	Langmuir			Freundlich		
	K_L (L/mg)	Qm (mg/g)	R^2	KF (L/mg)	N	R^2
1:1	0.0870	147.059	0.9977	11.1757	0.2890	0.9975
1:2	0.3527	263.157	0.9853	8.7680	1.1307	0.9985
1:3	0.0126	263.157	0.9788	6.7499	1.0592	0.9995

The Q_m value (maximum adsorption capacity) presented in table 3 indicates that (bentonite-TiO_2)-GO exhibits excellent adsorption performance, highlighting its potential as an effective adsorbent for MB removal. The Langmuir adsorption constant (K_a) reflects the strength of interaction between MB and the adsorbent, with higher values indicating stronger affinity[10]. Figures 4 (d) and (e) show that the adsorbed MB increased with rising dye concentration, suggesting that the adsorbent surface was not yet saturated at lower concentrations. This behaviour is consistent with the Langmuir and Freundlich isotherm models, which fit the experimental data well, as evidenced by correlation coefficients (R^2) close to 1[23].

For the 1:1 composite ratio, the Langmuir and Freundlich correlation coefficients were 0.9977 and 0.9975 respectively, indicating a strong and homogeneous interaction between MB and the adsorbent surface[13]. For the 1:4 ratio, the Freundlich model showed an even better fit ($R^2 = 0.9995$), suggesting a multilayer adsorption process and heterogeneous surface interactions[4]. The high correlation coefficients for both models demonstrate that the adsorption process is governed by both monolayer and multilayer mechanisms, depending on the composite ratio. These findings align with previous studies, showing that the Langmuir model is suitable for describing adsorption on homogeneous surfaces, while the Freundlich model is more applicable to heterogeneous surfaces[8].

The superior adsorption capacity of the 1:1 composite can be attributed to its optimal surface area and pore structure, which facilitate greater interaction with MB molecules. The results underscore the importance of selecting appropriate isotherm models to understand the adsorption mechanism and to optimize the adsorbent's performance in wastewater treatment applications.

Conclusion

The research successfully synthesized the bentonite-TiO_2-GO composite, producing a dark gray powder with coarser particles. XRD analysis showed that smaller crystal sizes improve the distribution and interaction between composite components while SEM images demonstrated that GO penetrates the bentonite-TiO_2 pores, reducing the surface area. The methylene blue adsorption test revealed that the 1:1 ratio of bentonite-TiO_2 exhibited the highest adsorption capacity at 25 mg adsorbent weight, 1 mg/L concentration and 30 minutes contact time, achieving an adsorption effectiveness of 87.98%. The adsorption process follows the Langmuir and Freundlich isotherm models, with a correlation coefficient close to 1.

Acknowledgement

The research was funded by DIPA of Public Service Agency of Universitas Sriwijaya 2024. Nomor SP DIPA 023.17.2.677515/2024, on November 24, 2023, in accordance with the Rector's Decree Number; 0013/UN9/LP2M.PT/2024, On May 20, 2024"

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(Received 14th March 2025, accepted 16th May 2025)