



Performance Test of Methylene Blue Degradation Using TiO₂–Graphene Oxide Composite Synthesised from Coconut Shells

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Abstract

Industry produces textile liquid waste which contains dangerous compounds such as methylene blue which can damage the environment. One effective method to overcome this problem is to use a TiO₂ nanocomposite-based photocatalyst modified with Graphene Oxide (GO). GO is obtained from the synthesis of coconut shells, which is a biomass waste. This research aims to synthesize and display the performance of a TiO₂/Graphene Oxide composite photocatalyst from coconut shells in degrading methylene blue. The TiO₂/Graphene oxide nanocomposite synthesis method begins by carbonizing coconut shells to form graphite. Carbonization removes volatile compounds and produces a rich carbon structure, which is the initial requirement for the formation of GO. Synthesis of GO from graphite using the Hummer method. Synthesis of TiO₂/Graphene oxide composite using a solvothermal process with various GO mass ratios. The performance of the photocatalyst was tested for degradation using methylene blue. Analysis of the TiO₂/Graphene Oxide Composite using XRD, FTIR, SEM, BET characterisation and UV-Vis Spectrophotometer. The results show that at GO of 15%, the composite showed the highest surface area and optimal anatase crystallinity, resulting in the best degradation efficiency (70%). Graphene Oxide is synthesized from coconut shell biomass waste. This research shows that the TiO₂–Graphene Oxide composite has high efficiency in degrading dangerous synthetic dyes from textile industry wastewater through an efficient photocatalytic mechanism. This composite application is an application of technology that contributes directly to achieving the Sustainable Development Goals (SDGs), especially SDG 6 (Clean Water and Adequate Sanitation), through the development of sustainable, efficient and environmentally friendly waste processing technology.

Keywords: dangerous compounds, environment, photodegradation, processing technology, textile liquid

INTRODUCTION

The textile industry is one of the sectors

that utilises substantial amounts of water in its production processes, leading to the generation

of wastewater. Textile wastewater contains organic compounds, heavy metals, suspended solids, as well as fats and oils. According to the UN Environment Programme (UNEP), Bappenas reported that textile waste accumulation in Indonesia is estimated to reach around 2.3 million tons per year, and this number is projected to increase by 70% if no intervention is made. The Global Fashion organization stated that the total amount of textile waste generated worldwide reaches 92 million tons annually. This number is projected to rise to 134 million tons per year by 2030 if the current trend continues. Textile industrial waste discharged directly into rivers without prior treatment can cause coloration, odor, and changes in water taste, inhibit and eliminate biological activity in water, pollute soil and groundwater, cause physical alterations in animals and humans, and lead to environmental contamination.

One of the components found in textile industry wastewater is methylene blue (MB). Methylene blue is a heterocyclic azo organic dye that is toxic, carcinogenic, and mutagenic (Khan et al., 2022). Even at "therapeutic" levels, the use of MB can suppress the immune system (immunosuppressive effect), for instance by reducing lymphocyte counts, serum total protein, phagocytic activity, and responses to bacterial challenges. One of the impacts of MB on aquatic organisms, including fish, is toxicity symptoms such as erratic swimming, increased respiratory rate, excessive mucus production, behavioral changes (lethargy), and even death at high concentrations (Daulay et al., 2022). Despite its harmful nature, this dye is still widely used in the textile industry due to its relatively low cost and easy availability.

Various methods have been developed to reduce methylene blue concentration in wastewater, including biological, physical, and chemical methods. The commonly used

biological method involves degrading methylene blue with the help of microorganisms, known as the bioremediation system (Abatenh et al., 2017). However, this method requires a large area and has limitations in degrading complex organic compounds. Basically, dye wastewater can be naturally decomposed by sunlight; however, due to the limited intensity of UV light reaching the water, the photodegradation process becomes slower than the accumulation rate of dyes in sediments or soils (Saeed et al., 2022).

The photocatalytic efficiency of TiO_2 can be enhanced by doping with noble metals or non-metal ions (Nasirian et al., 2018). However, its low surface area requires the addition of an adsorbent to improve performance (Irfan et al., 2022). Modifying TiO_2 with carbon-based materials is a common, cost-effective approach due to their abundance (Kuvarega & Mamba, 2017).

The use of coconut shell biomass waste is generally limited to low-value products such as road fillers and cooking fuel. Sohni et al. (2023) reported that peanut shell biomass waste can be utilized as a precursor for graphene synthesis, forming nanocomposites that enhance photocatalytic performance. Peanut shells contain about 52.96% carbon. Exploring coconut shells due to their similar biomass characteristics, particularly cellulose rich in carbon. Coconut shell combustion produces bound carbon of approximately 76.72% (Tumbel & Makalag, 2019), and their high carbon content makes them a promising source of activated carbon (Keppetipola et al., 2021).

Coconut shells are a type of lignocellulosic biomass with great potential as a carbon source (precursor) for the synthesis of Graphene Oxide (GO). The main constituents of coconut shells include high fixed carbon content ($\geq 70\%$), microporous structures, and high thermal stability, making them ideal raw

materials for synthesizing carbon-based materials such as graphene and its derivatives. The type of carbon precursor is one of the crucial parameters in graphite production (Othman et al., 2021), and graphite itself is the base material for graphene synthesis.

In this study, a TiO_2 /Graphene composite will be synthesized from coconut shell biomass to determine the optimal conditions for enhancing photocatalytic efficiency in wastewater treatment. This research supports the reduction of agricultural biomass waste from the coconut sector while producing high-value materials for improving water quality in surrounding areas. The study aligns with SDG 6 (Clean Water and Sanitation) and SDG 12 (Responsible Consumption and Production) by promoting sustainable waste utilization and clean water initiatives.

METHOD

The materials used in this study were coconut shells, H_2SO_4 (98%), H_3PO_4 , KMnO_4 , H_2O_2 (30%), deionised water, distilled water (aquadest), TiO_2 P25 (anatase), and methylene blue. Coconut shells of a certain size were thoroughly washed with water to remove impurities and then dried in an oven for 10 minutes. The dried shells were subsequently carbonised in a furnace at 600°C for 2 hours to produce graphite. The resulting graphite was then ground into fine powder and sieved using a 100-mesh sieve before further use.

Synthesis of Graphene Oxide

Graphene oxide was synthesized using the Hummers method. A total of 3 g of graphite was mixed with 63 mL of 98% H_2SO_4 and 7 mL of H_3PO_4 (with a ratio of 9:1) in a beaker placed in an ice bath maintained at 20°C. The mixture was stirred using a magnetic stirrer at 500 rpm for 30 minutes. Then, 9 g of KMnO_4 was gradually added while stirring for 3 hours at

20°C, followed by an additional 30 minutes of stirring without the ice bath. Next, 150 mL of distilled water was added, and the solution was stirred for 1 hour. After oxidation, 500 mL of distilled water and 15 mL of 30% H_2O_2 were slowly added until the solution color turned dark brown. The mixture was then centrifuged, filtered, and dried at 110°C for 30 minutes.

Synthesis of TiO_2 /Graphene Oxide Composite

The TiO_2 /Graphene Oxide composite was synthesized using the solvothermal method. A graphene oxide solution (4 mg/mL) was mixed with 3 mL of glacial acetic acid and 60 mL of ethanol. Then, 1 g of anatase TiO_2 was added. The reaction mixture was sonicated for 30 minutes, after which the suspension was transferred into an autoclave and heated at 130°C for 4 hours, followed by cooling to room temperature. The final product was filtered, washed several times with ethanol and deionised water, and dried in an oven at 70°C. The resulting samples were then characterised using FTIR, SEM, XRD, and BET analyses.

Photocatalytic Performance Test on Methylene Blue Degradation

The photocatalytic performance of the synthesized TiO_2 /Graphene Oxide composite was evaluated for the degradation of methylene blue in aqueous solution. A total of 0.3 g of the composite was added into 300 mL of 10 ppm methylene blue solution. The mixture was stirred at a speed of 300 rpm. The photocatalytic test was conducted for 4 h, with the first 30 min performed under light-off conditions and the remaining 3.5 h under light-on conditions (Heltina et al., 2023). Photodegradation was conducted using a UV lamp (Figure 1), and the samples were analyzed with a UV-Vis spectrophotometer to determine degradation efficiency.

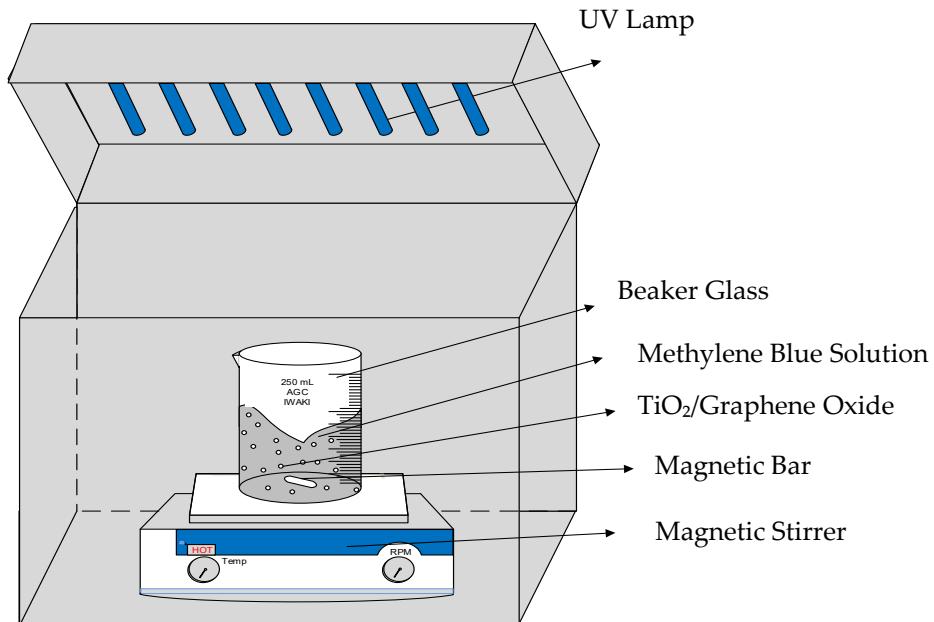


Figure 1. Photodegradation Apparatus Setup for Methylene Blue

The photodegradation process was carried out using a UV lamp shown in Figure 1. The resulting samples were analyzed using a UV–Vis spectrophotometer to determine the degradation efficiency.

RESULT AND DISCUSSION

Surface Morphology Characterisation (SEM)

The formed TiO_2 /Graphene Oxide composite was characterized using Scanning Electron Microscopy (SEM) to observe its surface morphology. SEM analysis was performed to determine whether the Graphene Oxide was uniformly dispersed within the TiO_2 matrix or if aggregation occurred. A good dispersion of Graphene Oxide is essential for enhancing the electrical conductivity and photocatalytic efficiency of the TiO_2 /Graphene Oxide composite. The SEM characterization results are shown in Figure 2.

SEM analysis was carried out at a magnification of $10,000\times$. The SEM images of the TiO_2 /Graphene Oxide composite surface provide information about the surface structure of the composite particles. As shown in the figure, graphene sheets and TiO_2

particles can be observed, where TiO_2 particles are embedded and distributed on the graphene sheets.

A study from Song and Kim, (2019) supported this finding, reporting that SEM analysis of TiO_2 /Graphene Oxide composites revealed nanometer-sized TiO_2 particles uniformly dispersed over the graphene sheets, forming a homogeneous composite structure. Similarly, Wang et al. (2018) confirmed that the integration of TiO_2 with GO resulted in a well-organized morphology, in which TiO_2 nanoparticles were uniformly distributed on the graphene surface, thereby enhancing the photocatalytic activity of the composite.

According to Ramesh et al. (2022), graphene exhibits a sheet-like morphology, while Pallegri et al. (2017) reported that TiO_2 particles have a spherical shape and tend to agglomerate into larger clusters. Minella et al. (2017) stated that graphene acts as a bridge connecting TiO_2 nanoparticles, which significantly improves the separation of photogenerated electron–hole pairs and enhances the photocatalytic performance of the composite.

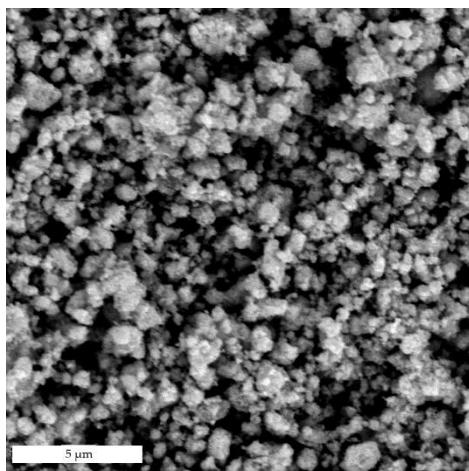


Figure 2. SEM Morphology of TiO_2 /Graphene Oxide Composite

Fourier Transform Infrared (FTIR) Characterisation of TiO_2 /Graphene

In addition to morphological observations, the formation of the TiO_2 /Graphene Oxide composite was confirmed through FTIR analysis. The absorption peaks appearing in the $3600\text{--}2800\text{ cm}^{-1}$ range indicate the presence of $-\text{OH}$ groups as shown in Figure 3, suggesting that water molecules were adsorbed on the photocatalyst surface. These $-\text{OH}$ groups can act as electron donors to photogenerated holes, forming hydroxyl radicals that are crucial in photocatalytic reactions (Bahnemann et al., 2018; Ding et al., 2020).

The absorption bands within $2100\text{--}2000\text{ cm}^{-1}$ correspond to C-H stretching vibrations, while those in the $1670\text{--}1350\text{ cm}^{-1}$ region are attributed to C=O and C-OH functional groups, in agreement with previous findings by Minella et al. (2017). At lower wavenumbers ($600\text{--}400\text{ cm}^{-1}$), characteristic peaks associated with Ti-O-Ti and Ti-O-C bonds are observed, confirming the successful interaction between TiO_2 and graphene oxide. These results are consistent with earlier studies reporting metal-oxygen stretching vibrations typical of TiO_2 -based composites (Nizar et al., 2018; Djellabi et al., 2019).

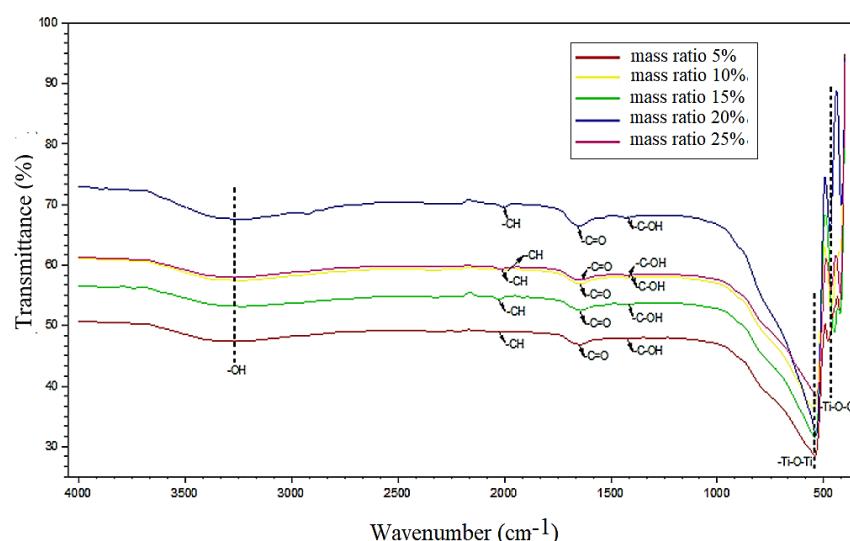


Figure 3. FTIR Spectrum of TiO_2 /Graphene Oxide Composite

When graphene oxide is incorporated into TiO_2 , interactions between carbon atoms in graphene oxide and titanium atoms in TiO_2 can lead to the formation of $\text{Ti}-\text{O}-\text{C}$ bonds. The stretching vibration of $\text{Ti}-\text{O}-\text{Ti}$ bonds typically appears within $400\text{--}700\text{ cm}^{-1}$ due to the relatively large atomic mass of titanium, which results in lower vibrational frequencies compared to those of $\text{C}-\text{H}$ or $\text{O}-\text{H}$ bonds.

X-Ray Diffraction (XRD) Characterization

The crystalline phase of the composite also plays a crucial role in the photocatalytic degradation of methylene blue. The presence of multiple peaks indicates that the $\text{TiO}_2/\text{Graphene Oxide}$ composite has successfully formed a crystalline structure. When a material exhibits crystallinity as shown in Figure 4, several diffraction peaks typically appear in the XRD pattern; conversely, the absence of peaks indicates that the material is amorphous.

From the figure, it can be observed that the diffraction peaks of the $\text{TiO}_2/\text{Graphene Oxide}$ composite with a 15% mass ratio are slightly higher compared to other variations. This is likely due to the fact that, at higher graphene oxide ratios ($>15\%$), the increased dispersion of graphene oxide can interfere with the crystal growth of TiO_2 , leading to smaller crystallite sizes and reduced XRD peak intensity. Sharper and more intense peaks at the 15% mass ratio indicate a higher degree of crystallinity and larger TiO_2 crystallite size (Zhang et al., 2017).

No distinct peaks of graphene oxide are visible in the $\text{TiO}_2/\text{Graphene Oxide}$ composite. This suggests that graphene oxide interacts with TiO_2 through $\text{Ti}-\text{O}-\text{C}$ bonding as shown in Figure 5, which promotes the dispersion of graphene oxide within the TiO_2 matrix. Such

interactions can lead to the disappearance of the characteristic diffraction peak of graphene oxide, as the graphene layers lose sufficient order to produce a detectable XRD signal. This intercalation process often causes graphene to become irregularly distributed, further diminishing its crystalline peaks (Zhang et al., 2018). Similarly, Huang et al. (2016) explained that the main diffraction peak of graphene tends to overlap at approximately 25° , coinciding with the anatase TiO_2 peak.

The crystallite size also affects photocatalytic activity, as smaller crystallites result in a larger surface area and higher adsorption capacity (Chen et al., 2019). The crystallinity fraction and crystallite size of the $\text{TiO}_2/\text{Graphene Oxide}$ composites are presented in Table 1.

It can be observed that all variations of the $\text{TiO}_2/\text{Graphene Oxide}$ composites consist of 100% anatase phase. This is attributed to the calcination temperature and duration used during synthesis. The calcination was carried out at a relatively low temperature of 100°C , which maintains the stability of the anatase phase and prevents transformation into the rutile phase. The anatase-to-rutile transformation in TiO_2 generally occurs at temperatures above $300\text{--}600^\circ\text{C}$ (Byrne et al., 2016). At 100°C , the thermal energy is insufficient to induce structural transformation from anatase to rutile.

Moreover, the presence of Graphene Oxide, when combined with TiO_2 , can inhibit the growth of rutile crystals by stabilizing the anatase phase. This finding is consistent with Timoumi et al., (2018), who reported that the addition of up to 15 wt% graphene in TiO_2 -graphene composites produced the best efficiency and fill factor in Dye-Sensitized Solar Cells (DSSC) performance.

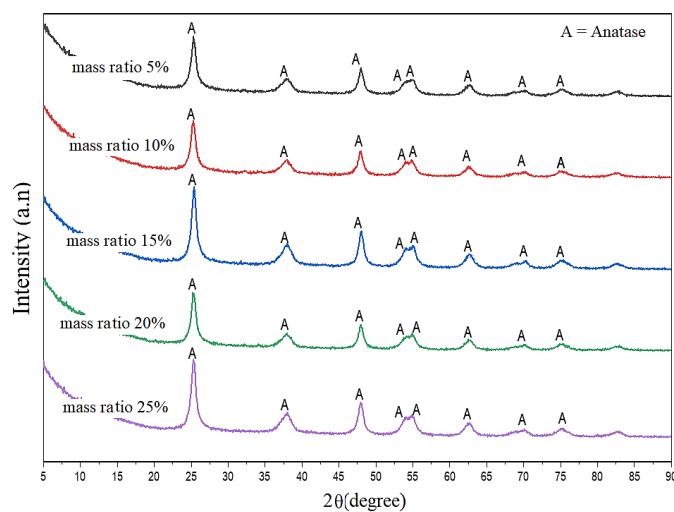


Figure 4. XRD Characterization of TiO_2 /Graphene Oxide Composite

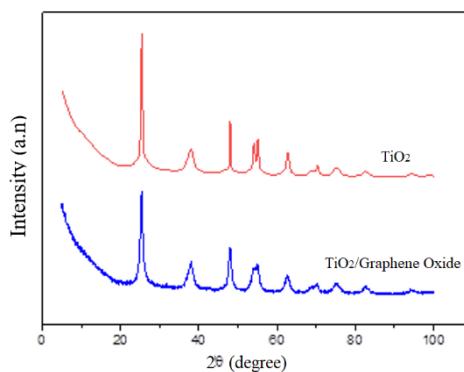


Figure 5. XRD Comparison of TiO_2 /Graphene Oxide Composites at 15% Mass Ratio

Table 1. Crystal Size and Anatase Phase Fraction of TiO_2 /Graphene Oxide Composites

| Composite Sample | Size of Anatase Crystal (nm) | Fraction of Anatase Crystal |
|------------------|------------------------------|-----------------------------|
| Mass Ratio 5% | 20,51 | 100% |
| Mass Ratio 10% | 14,63 | 100% |
| Mass Ratio 15% | 30,31 | 100% |
| Mass Ratio 20% | 15,52 | 100% |
| Mass Ratio 25% | 13,59 | 100% |

BET, Surface area of the Composite Characterization

The surface area of the composite also influences the photocatalytic process in degrading methylene blue. A higher surface area indicates more active sites, which enhances the efficiency of photocatalytic and energy storage applications. The specific surface area values of the TiO_2 /Graphene Oxide composites obtained from BET characterization

are shown in Table 2.

The highest surface area was obtained at a 15% mass ratio, with a value of $168.137 \text{ m}^2/\text{g}$. Graphene Oxide has a lamellar (layered) structure with a high surface area. At a 15% ratio, Graphene Oxide is optimally dispersed within the TiO_2 matrix, preventing TiO_2 nanoparticle agglomeration and increasing the total surface area of the composite.

The addition of Graphene Oxide into

TiO₂ composites can enhance the specific surface area of the material. However, excessive addition of Graphene Oxide may lead to agglomeration, which reduces the effective surface area. Therefore, an optimal GO mass ratio—such as 15%—can provide a balance between increased surface area and agglomeration prevention, resulting in improved photocatalytic performance.

Table 2. Specific Surface Area of TiO₂/Graphene Oxide Composites

| Composite Sample | Surface Area (m ² /g) |
|------------------|----------------------------------|
| Mass Ratio 5% | 148.279 |
| Mass Ratio 10% | 166.114 |
| Mass Ratio 15% | 168.137 |
| Mass Ratio 20% | 130.467 |
| Mass Ratio 25% | 113.939 |

Effect of Photocatalytic Performance on Methylene Blue Degradation

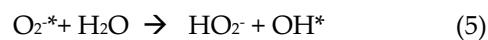
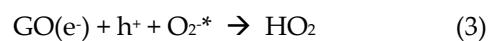
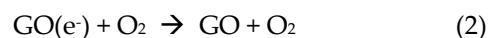
Photocatalytic performance testing was carried out to evaluate the ability of the TiO₂/Graphene Oxide nanocomposite to degrade methylene blue. The results were analyzed using a UV-Vis spectrophotometer. The tests were conducted with varying mass ratios of Graphene Oxide at 5%, 10%, 15%, 20%, and 25%. The relationship between the Graphene Oxide mass ratio and photocatalytic efficiency is shown in Figure 6.

The degradation of methylene blue increased with the addition of Graphene Oxide, from 37.50% at a 5% mass ratio, 52.50% at 10%, and reaching 70% at 15%. The highest degradation efficiency was achieved at a 15% Graphene Oxide ratio. The results indicate that the degradation efficiency of methylene blue increased significantly with the addition of TiO₂-Graphene Oxide (GO) composite up to an optimum point. However, beyond this point, the efficiency began to decrease. This decline suggests that excessive GO in the composite

may reduce photocatalytic activity, possibly due to the blocking of TiO₂ active sites or reduced light transmission caused by the optical properties of excess GO.

This observation is supported by the XRD and BET analyses. The XRD analysis at 15% showed the largest crystal size of 30.31 nm, which aligns with the findings of Bellardita et al. (2017), who stated that the optimum crystal size range for photocatalytic activity in TiO₂ is between 21–40 nm. Meanwhile, BET analysis indicated the highest surface area at the 15% GO ratio, with a value of 168.137 m²/g. This result confirms that a larger composite surface area leads to a higher methylene blue degradation percentage. This finding is consistent with Kurniawan (2020), who reported that the addition of Graphene Oxide to TiO₂ increased the specific surface area by 68%, contributing to an improvement in methylene blue degradation efficiency up to 92% within 25 minutes. An illustration of the photocatalytic process using the TiO₂/Graphene Oxide composite is presented in Figure 7.

The Equation (1)-(6) represent the photodegradation mechanism of methylene blue under UV light using TiO₂/Graphene Oxide:



When photon energy (hv) irradiates the photocatalyst, the material becomes excited, generating electrons (e⁻) and holes (h⁺). The reaction between electrons and holes produces hydroxyl radicals (OH), which play a crucial role in degrading pollutants. The greater the

number of hydroxyl radicals formed, the higher the degradation efficiency of pollutants.

The enhanced efficiency observed at the optimum Graphene Oxide concentration is attributed to its ability to accelerate electron transfer, thereby reducing electron–hole recombination and promoting the formation of hydroxyl radicals. Therefore, the optimal

condition at 15% Graphene Oxide provides a balance between surface area, electrical conductivity, and light absorption capacity—factors that are essential for efficient photocatalytic reactions.

A schematic representation of the methylene blue photodegradation mechanism is shown in Figure 8.

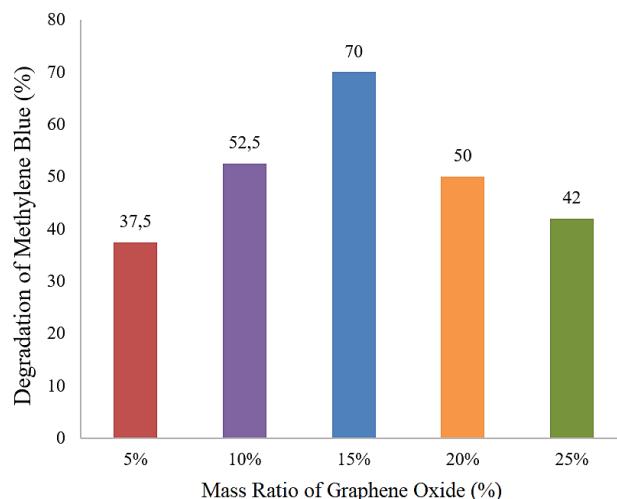


Figure 6. Methylene blue degradation as a function of Graphene Oxide mass ratio

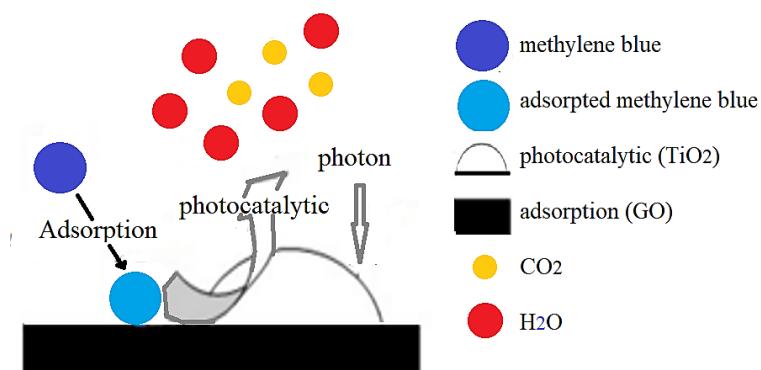


Figure 7. Photocatalytic Mechanism of TiO_2 /Graphene Oxide Composite



Figure 8. Schematic Diagram off Methylene Blue Photodegradation Mechanism

Kinetic Study

Adsorption kinetics describe the rate at which adsorbate molecules are transferred from the liquid phase to the solid surface of the adsorbent until equilibrium is reached. The kinetic study of the adsorption and degradation process of methylene blue on TiO₂/Graphene Oxide (GO) composites is conducted to determine and control the underlying mechanism. Two commonly used kinetic models are the pseudo-first-order and pseudo-second-order models.

Pseudo-First-Order (PFO) Model

The Lagergren equation, which represents the pseudo-first-order model, can be expressed by Equation (7):

$$\log (q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

This equation is used to determine the pseudo-first-order rate constant (k_1) from the linear plot of $\log (q_e - q)$ versus t . Kinetic analysis was carried out to understand the adsorption mechanism of methylene blue on the TiO₂/Graphene Oxide (GO) composite at a GO mass ratio of 15%. The results are shown in Figure 9.

Pseudo-Second-Order (PSO) Model

The pseudo-second-order model can be calculated using Equation (8):

$$\frac{1}{(q_e - q)} = \frac{1}{q_e} + k_2 t \quad (8)$$

Kinetic analysis was conducted to understand the adsorption mechanism of methylene blue on the TiO₂/Graphene Oxide (GO) composite at a GO mass ratio of 15%. The results are shown in Figure 10.

To determine the most suitable kinetic model that accurately describes the adsorption mechanism in this system, a quantitative analysis was performed on the rate constants (k_1 and k_2), equilibrium adsorption capacity (Q_e), and the determination coefficient (R^2) of each model. The calculated parameters are presented in Table 3, which lists k_1 and Q_e for the PFO model, as well as k_2 and Q_e for the PSO model, along with R^2 values as indicators of model fitting quality. This analysis aims to identify the most statistically and physically representative kinetic model for the adsorption of methylene blue by TiO₂/Graphene Oxide composites.

Table 3. Kinetic Constants of Methylene Blue Adsorption Using TiO₂/Graphene Oxide

| Composite | |
|------------------|---------|
| orde satu | |
| k1 | 0.023 |
| Qe PFO | 19.121 |
| R ² | 0.8089 |
| orde dua | |
| k2 | -3.35 |
| Qe PSO | 0.00082 |
| R ² | 0.6190 |

Based on the kinetic adsorption analysis at a Graphene Oxide mass ratio of 5%, the PFO model exhibited the best fit, with a correlation coefficient (r) of 0.8089, a positive rate constant, and a reasonable Q_e value. In contrast, the PSO model was invalid due to a negative k_2 value and an unrealistically low Q_e . Therefore, the adsorption mechanism is most likely governed by a pseudo-first-order kinetic model, indicating that the adsorption rate depends on the solute concentration and proceeds predominantly through a physisorption process.

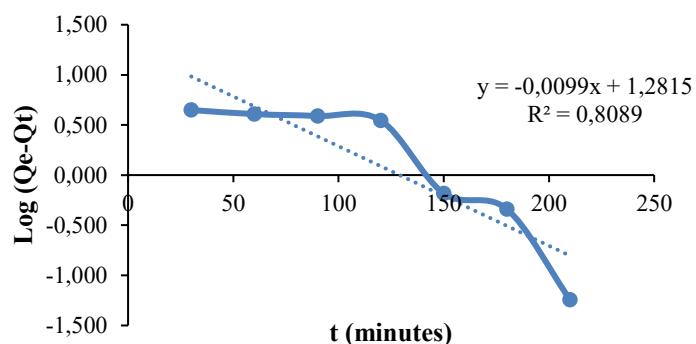


Figure 9. Pseudo-First-Order Adsorption Kinetic Curve (mass ratio GO 5%)

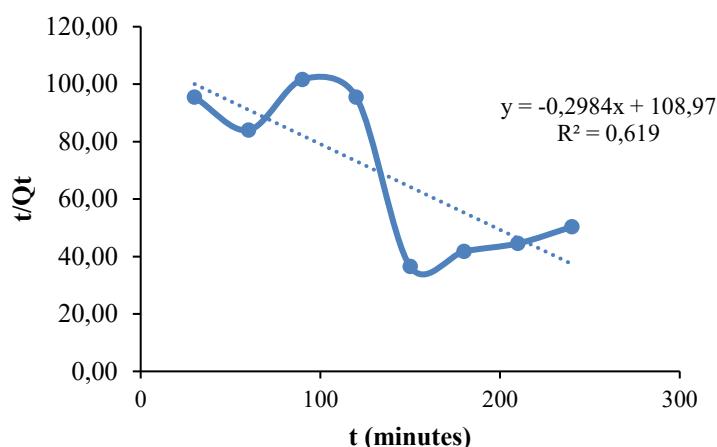


Figure 10. Pseudo-Second-Order Adsorption Kinetic Curve (mass ratio GO 5%)

CONCLUSION

The TiO_2 /Graphene Oxide nanocomposite was successfully synthesized using the solvothermal method, with coconut shell biomass serving as the carbon source. The increase in Graphene Oxide content within the composite resulted in a higher total mass of the nanocomposite, indicating that the synthesis process proceeded effectively and successfully integrated Graphene Oxide into the composite structure. The optimal performance was achieved at a Graphene Oxide concentration of 15%, yielding a methylene blue degradation efficiency of 70%. When the Graphene Oxide concentration exceeded 15%, the efficiency decreased to 50% (at 20% GO) and 42% (at 25% GO). The TiO_2 /Graphene Oxide composite derived from coconut shell biomass demonstrates significant potential for application as an environmentally friendly

wastewater treatment technology, particularly in the textile industry. Moreover, utilizing biomass waste as a precursor for composite materials provides a sustainable approach that supports circular economy-based waste management.

REFERENCES

Abatenh, E., Gizaw, B., Tsegaye, Z., & Wassie, M. (2017). The role of microorganisms in bioremediation-A review. *Open Journal of Environmental Biology*, 2(1), 038-046.

Bahnemann, D., Cunningham, J., Fox, M. A., Pelizzetti, E., Pichat, P., & Serpone, N. (2018). Photocatalytic treatment of waters. In *Aquatic and surface photochemistry* (pp. 261-316). CRC Press.

Bellardita, M., Di Paola, A., Megna, B., & Palmisano, L. (2017). Absolute crystallinity and photocatalytic activity

of brookite TiO_2 samples. *Applied Catalysis B: Environmental*, 201, 150-158.

Byrne, C., Fagan, R., Hinder, S., McCormack, D. E., & Pillai, S. C. (2016). New approach of modifying the anatase to rutile transition temperature in TiO_2 photocatalysts. *RSC advances*, 6(97), 95232-95238.

Chen, K., Fan, Q., Chen, C., Chen, Z., Alsaedi, A., & Hayat, T. (2019). Insights into the crystal size and morphology of photocatalysts. *Journal of Colloid and Interface Science*, 538, 638-647.

Daulay, A. M., Erniati, E., Nurul, C. M., Erlangga, E., & Imamshadiqin, I. (2022). Toxicity test of LC-50 (Lethal Concentration) surfactant LAS (Linear Alkylbenzene Sulfonate) against white snapper (*Lates calcarifer*) fingerlings on a laboratory scale. *Acta Aquatica: Aquatic Sciences Journal*, 133-138.

Ding, L., Li, M., Zhao, Y., Zhang, H., Shang, J., Zhong, J., Sheng, H., Chen, C. & Zhao, J. (2020). The vital role of surface Brönsted acid/base sites for the photocatalytic formation of free- OH radicals. *Applied Catalysis B: Environmental*, 266, 118634.

Djellabi, R., Yang, B., Wang, Y., Cui, X., & Zhao, X. (2019). Carbonaceous biomass-titania composites with TiOC bonding bridge for efficient photocatalytic reduction of Cr (VI) under narrow visible light. *Chemical Engineering Journal*, 366, 172-180.

Heltina, D., Mastura, D. I., Amri, A., & Sembiring, M. P. (2023). Comparison of synthesis methods on TiO_2 -graphene composites for photodegradation of compound waste. *Materials Today: Proceedings*, 87, 293-298.

Huang, M., Yu, J., Hu, Q., Su, W., Fan, M., Li, B., & Dong, L. (2016). Preparation and enhanced photocatalytic activity of carbon nitride/titania (001 vs 101 facets)/reduced graphene oxide ($\text{g-C}_3\text{N}_4/\text{TiO}_2/\text{rGO}$) hybrids under visible light. *Applied Surface Science*, 389, 1084-1093.

Irfan, F., Tanveer, M. U., Moiz, M. A., Husain, S. W., & Ramzan, M. (2022). TiO_2 as an effective photocatalyst mechanisms, applications, and dopants: a review. *The European Physical Journal B*, 95(11), 184.

Keppetipola, N. M., Dissanayake, M., Dissanayake, P., Karunarathne, B., Dourges, M. A., Talaga, D., Servant, L., Oliver, C., Toupance, T., Uchida, S., Tennakone, K., Kumara G.R.A. & Cojocaru, L. (2021). Graphite-type activated carbon from coconut shell: a natural source for eco-friendly non-volatile storage devices. *RSC advances*, 11(5), 2854-2865.

Khan, I., Saeed, K., Zekker, I., Zhang, B., Hendi, A. H., Ahmad, A., Ahmad, F., Zada, N., Shah L.A., Shah, T & Khan, I. (2022). Review on methylene blue: its properties, uses, toxicity and photodegradation. *Water*, 14(2), 242.

Kurniawan, T. A., Mengting, Z., Fu, D., Yeap, S. K., Othman, M. H. D., Avtar, R., & Ouyang, T. (2020). Functionalizing TiO_2 with graphene oxide for enhancing photocatalytic degradation of methylene blue (MB) in contaminated wastewater. *Journal of environmental management*, 270, 110871.

Kuvarega, A. T., & Mamba, B. B. (2017). TiO_2 -based photocatalysis: toward visible light-responsive photocatalysts through doping and fabrication of carbon-based nanocomposites. *Critical Reviews in Solid State and Materials Sciences*, 42(4), 295-346.

Minella, M., Sordello, F., & Minero, C. (2017). Photocatalytic process in TiO_2 /graphene hybrid materials. Evidence of charge separation by electron transfer from

reduced graphene oxide to TiO₂. *Catalysis Today*, 281, 29-37.

Nasirian, M., Lin, Y. P., Bustillo-Lecompte, C. F., & Mehrvar, M. (2018). Enhancement of photocatalytic activity of titanium dioxide using non-metal doping methods under visible light: a review. *International Journal of Environmental Science and Technology*, 15(9), 2009-2032.

Nizar, U. K., Hidayatul, J., Sundari, R., Bahrizal, B., Amran, A., Putra, A., DJ-Latisma, L & Dewata, I. (2018). The Effect of Titanium Tetrahedral Coordination of Silica-Titania Catalyst on the Physical Properties of Biodiesel. In *IOP Conference Series: Materials Science and Engineering* (Vol. 335, No. 1, p. 012036). IOP Publishing.

Othman, R., Kamal, A. S., & Jabarullah, N. H. (2021). The effect of changing graphitization temperature toward bio-graphite from palm kernel shell. *Production Engineering Archives*, 27.

Pellegrino, F., Pellutiè, L., Sordello, F., Minero, C., Ortel, E., Hodoroaba, V. D., & Maurino, V. (2017). Influence of agglomeration and aggregation on the photocatalytic activity of TiO₂ nanoparticles. *Applied Catalysis B: Environmental*, 216, 80-87.

Ramesh, S., Karuppasamy, K., Vikraman, D., Santhoshkumar, P., Bathula, C., Palem, R. R., Kathalingam, A., Kim, H.S., Kim J.H & Kim, H. S. (2022). Sheet-like morphology CuCo₂O₄ bimetallic nanoparticles adorned on graphene oxide composites for symmetrical energy storage applications. *Journal of Alloys and Compounds*, 892, 162182

Saeed, M., Muneer, M., Haq, A. U., & Akram, N. (2022). Photocatalysis: an effective tool for photodegradation of dyes—a review. *Environmental Science and Pollution Research*, 29(1), 293-311.

Sohni, S., Gul, K., Shah, J. A., Iqbal, A., Sayed, M., & Khan, S. B. (2023). Immobilization performance of graphene oxide-based engineered biochar derived from peanut shell towards cationic and anionic dyes. *Industrial Crops and Products*, 206, 117656.

Song, H. J., & Kim, D. W. (2019). Graphene and Graphene-Based Hybrid Composites for Advanced Rechargeable Battery Electrodes. *Handbook of Graphene, Volume 5: Energy, Healthcare, and Environmental Applications*, 147.

Timoumi, A., Alamri, S. N., & Alamri, H. (2018). The development of TiO₂-graphene oxide nano composite thin films for solar cells. *Results in physics*, 11, 46-51.

Tumbel, N., & Makalalag, A. K. (2019). Proses pengolahan arang tempurung kelapa menggunakan tungku pembakaran termodifikasi. *Indonesian Journal of Industrial Research*, 11(2), 83-92.

Wang, Y., Yan, H., & Zhang, Q. (2018). Core shell-structured NiFe₂O₄@ TiO₂ nanoparticle-anchored reduced graphene oxide for rapid degradation of rhodamine B. *Journal of the Chinese Chemical Society*, 65(7), 868-874.

Zhang, S., Xu, J., Hu, J., Cui, C., & Liu, H. (2017). Interfacial growth of TiO₂-rGO composite by pickering emulsion for photocatalytic degradation. *Langmuir*, 33(20), 5015-5024.