Highly adsorption-photocatalytic tablet-shaped graphite oxide-TiO_2 composites for handling organic dye pollutants

ABSTRACT

Designing effective adsorption-photocatalysts on graphite oxide-TiO_2 (G/TiO_2) nanocomposites tablet with easy synthesis and low cost is a challenge in treating organic dye pollutants. Here, we invented an advanced adsorption-photocatalyst based on a TiO_2 framework coupled with graphite oxide to form tablets using a physical mixing method. Furthermore, these tablets were molded using metal chips for extremely high adsorption photocatalysts towards organic dyes. The mass composition has been evaluated to compare the high degradation performance of the composite mass variation in degrading organic dyes, namely methyl orange (MO) and methylene blue (MB). We discovered the 1:2 mass variation of G/TiO_2 resulted in an improvement in the adsorption-photocatalytic degradation of organic dyes. The degradation rate of MO dye was 93.99% after treatment with UV light irradiation for 60 min, and the reaction rate constant was $k = 0.01726\ min^{-1}$. Meanwhile, MB dye also showed good performance with a degradation percentage of 80.22% and a reaction rate constant of $k = 0.00947\ min^{-1}$. This constant was much higher than the two mass variations (1:1 and 2:1) of G/TiO_2 due to the increased availability of good sites for graphite oxide adsorption and TiO_2 electron-hole pair separation. In addition, the G/TiO_2 tablets showed excellent reuse and reasonable degradation for wastewater treatment.

Keywords: TiO_2; graphite; adsorption; photocatalyst; organic dyes

Introduction

Organic dyes are widely used in many industrial processes such as pulp and paper, food processing, pharmaceutical, and other fields due to their excellent color stability to materials and low cost [1–3]. However, excessive use of organic dyes causes damage to the aquatic environment. So, it is necessary to take serious measures to protect the dye industry waste to create a green environment [4]. Dye effluent treatment still uses conventional methods such as adsorption, coagulation, electro-flotation, etc. [5,6]. However, these treatment methods have not solved the problem of environmental pollution thoroughly and even cause secondary pollution. This condition can impact river flow and affect the life of biota in the aquatic environment [7].

Thus, organic dye degradation is one of the efforts to reduce organic dye pollutants and not cause negative effects from the treatment results (safety environment). It is known that organic dyes have a negative impact on environmental health from dyes based on their toxic properties [8,9]. The impact of dyes affects environmental health, which can affect direct impacts such as allergies, nausea, and vomiting [10,11]. While indirect impacts can result in cancer, organ damage, and developmental disorders. If the water used contains synthetic organic dyes, it is very dangerous for humans [12,13]. In addition, dye effluents can cause eutrophication, which is an increase in nutrient levels in waters that can cause excessive algae growth. The dead algae will decompose and produce toxins that can kill fish and other aquatic organisms. Dyestuff waste can also cause soil and air pollution [14]. Synthetic dyes can break down into harmful compounds that can harm human and animal health.

Recently, photodegradation has been successfully explored to treat organic dyes using TiO_2 photocatalysts [15,16]. This method is unique and produces environmentally safe degradation effects such as CO_2 and H_2O, which is an environmentally friendly way to deal with organic dye waste [16–18]. TiO_2 photocatalysts are activated under sufficient UV light irradiation, and the photogenerated carriers (electrons and holes) initiate reduction-oxidation (redox) reactions that command hydroxyl and superoxide radicals to degrade organic dye compounds [19,20]. TiO_2 photocatalysts have been considered one of the most effective and promising technologies for degrading organic pollutants from water [21]. TiO_2 material has high photocatalytic activity, non-toxicity, chemical stability, low cost, and wide application [22–24]. Nurdin et al. [13] and Azis et al. [25] reported that TiO_2 is a valid photodegradation for various organic and inorganic pollutant treatment and sensor applications. However, it is difficult to prepare and apply when using TiO_2-P25 material because it has fine particles and dissolves easily in the liquid phase. For this reason, it is necessary to make a better material with high stability and hardness to be durable and tested in the test solution.

Aiming to overcome the above-mentioned problems, some researchers proposed to combine TiO_2 with carbon materials, hoping that carbon materials with high adsorption ability would rapidly adsorb and enrich organic compounds, followed by mass transfer to TiO_2 and hence increase the possibility of organic dyes and intermediates to contact with TiO_2 [26,27]. In addition, reducing the agglomeration process of over-tested TiO_2 in water is important. To date, there have not been many studies on tablet construction (pressed pellet) construction to facilitate the formation of G/TiO_2 composites for handling organic dyes. Studies conducted by Wang et al. [28] and Chen et al. [29] explained that preparing tablet-like C/TiO_2 composites provides good effectiveness in degrading tetracycline organic compounds because the two materials are highly synergized in accelerating the photocatalysis process. It would be very interesting to develop G/TiO_2 composite-based adsorption-photocatalysis materials that are easy to manufacture, inexpensive, and have excellent photocatalysis activity to remove organic contaminants in aquatic environments. The G/TiO_2 tablets are a new and promising technology to handle wastewater organic pollutants. The urgency of achieving these results is driven by the need for easy preparation, smaller, and lighter in wastewater pollutants treatment.

Materials and Methods

Chemical and instrument

All chemicals used in this experiment were analytical grade and purchased from Sigma-Aldrich, USA. The materials used included TiO_2-P25, graphite oxide, and paraffin oil (ρ = 0.890 g.mL^{-1}). The equipment used was a press pellet with metal rings, an ultraviolet (UV) reactor (13 Watts, Graxindo, Indonesia), and a UV-Vis spectrophotometer (Single Beam DV-8200, Drawell, China).

Synthesis of graphite oxide-TiO_2 tablet

The graphite oxide powder and TiO_2-P25 were sifted separately using a 200-mesh sieve. Then, they were each weighed to vary different masses. For a 1:1 ratio, graphite oxide was weighed as 1.5 g and mixed with 1.5 g TiO_2-P25 (+3.0 mL paraffin oil). The G/TiO_2 composite was mixed evenly in porcelain and heated in an oven at 70°C. This treatment was also applied for mass variations of 1:2 (w/w) and 2:1 (w/w). For G/TiO_2 tablet construction, the composite was pressed using the pellet press method (3Mpa for 30 sec.) with a diameter of 2.0 cm and a thickness of 0.5 cm. We simulated the preparation of G/TiO_2 tablets, as shown in Fig. 1 and Fig. 3.

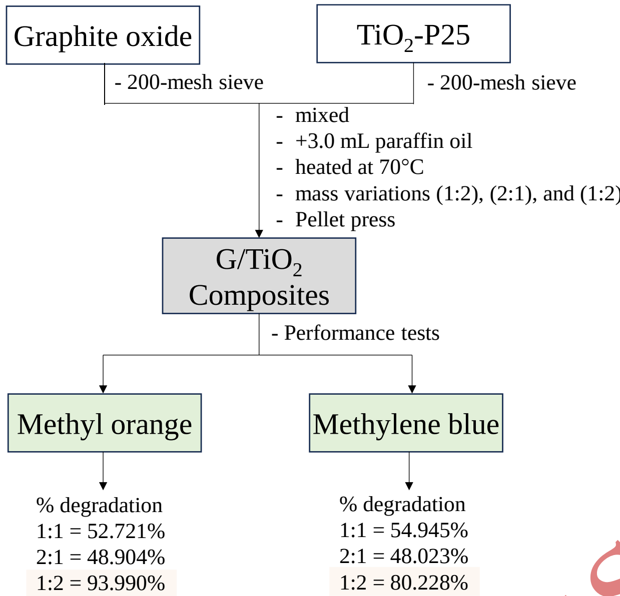

Fig. 1. The flow chart of G/TiO_2 tablet-shaped fabrication

Adsorption-photocatalysis test

Adsorption-photocatalysis test of organic dyes (methyl orange and methylene blue) was carried out using a UV lamp as a light source in a 25.0 mL cylindrical Pyrex reactor (Fig. 2). Firstly, the concentration of organic dyes was made with variations, namely 1.0 $mg.L^{-1}$; 3.0 $mg.L^{-1}$; 5.0 $mg.L^{-1}$; 7.0 $mg.L^{-1}$; and 10.0 $mg.L^{-1}$. These concentrations were directly identified to obtain the real concentration using a UV-Vis spectrophotometer (Single Beam DV-8200, Drawell, China) and linearity equation. In each experiment, the G/TiO_2 composites was inserted into a cylindrical Pyrex reactor under aerator stirring followed by the addition of 10.0 mL (5.0 $mg.L^{-1}$) of organic dye solution. Then, the sample was tested for 60 min, every 10 min it was checked to obtain absorbance values. In the final step, the absorbance values were determined by referring to the linearity equation to observe the final concentration, the percentage of degradation, and the rate constant.

Fig. 2. Adsorption-photocatalysis test over G/TiO_2 tablet in cylindrical Pyrex reactor

Results and Discussion

Graphite oxide-TiO_2 tablet composites

The total mass variation used for the tablet construction was 3.0 g, in which for each variation of mass composition under graphite oxide and TiO_2 materials. In addition, it was the maximum composition of the total tablet mold volume. The tablet construction of G/TiO_2 composites was fabricated with a diameter of 2.0 cm and a thickness of 0.5 cm in order to insert into a cylindrical Pyrex reactor (Fig. 1). Several mass variations of composites were made, namely of 1:1 (w/w), 2:1 (w/w), and 1:2 (w/w). The tablet construction of G/TiO_2 composites can be seen in Fig. 3.

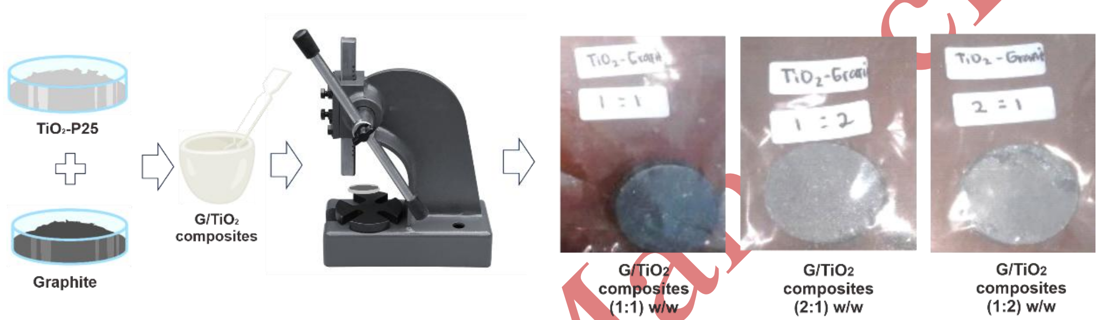

Fig. 3. The mass variations of G/TiO_2 tablet

The fundamental concept in this study is an effective combination in dealing with organic dye effluents accumulated in wastewater. We simulate in Fig. 4, it starts from the first step the role of graphite oxide material in adsorbing organic compounds. This accelerates the adsorption process and is passed on to the surface of the TiO_2 material which plays an important role in the photocatalyst process. This is a unique process because the efficiency is very good under the influence of UV light and adding aeration effect to homogenize and minimize saturation on the surface of the material. In general, the photocatalyst of TiO_2 will form positive hole species and electrons that start the reduction-oxidation (redox) reaction process. Mineralization of organic compounds starts when the positive hole species oxidize and on the other hand reduction also plays a role in securing inorganic ions accumulated in organic dye effluents. The same product also as reported by Wang & Yu [28] and Chen et al. [29] with carbon-doped TiO_2 tablets provides a powerful way to reduce the concentration of tetracycline compounds. Variations in composition, light, and test compounds used produced different results as this relates to the molecular size of the target compound to be treated whether colored or clear compounds.

Based on Figs 3a and 3b show the photodegradation process against MO and MB organic compounds adopted from Fu et al. [30] and Wang et al. [31], respectively. If we compare both photodegradation processes, different approaches impact the degradation rate of organic dyes (MO and MB). Evaluation of the photodegradation process exhibited that the degradation of chemical bonds of MO is easily breaking compared with MB compound. This is due to the ability of the organic compounds to self-stabilize. Aromatic rings have an important role in stabilizing chemical bonds because of the delocalization of electrons to stabilize the broken chemical bonds. The more aromatic ring in the sample affects the photodegradation ability [32]. Finally, TiO_2 photocatalysis takes a long time to degrade the organic compound. Meanwhile, the residual adsorbent can be powder can be safely stored in accordance with the hazardous waste application.

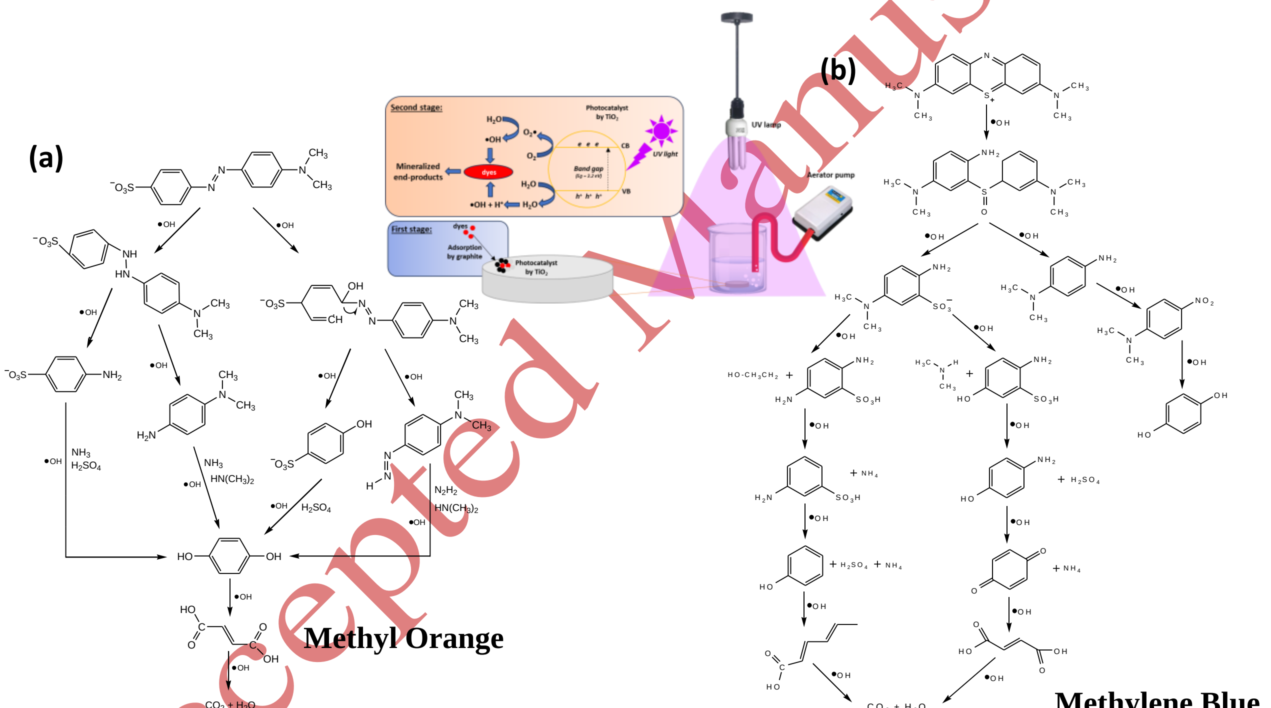

Fig. 4. Mechanism of adsorption-photocatalytic degradation toward organic dyes over G/TiO_2 tablet, (a) Degradation of methyl orange (MO) modified from Fu et al. [30] , and (b) Degradation of methylene blue (MB) modified from Wang et al. [31]

Adsorption-photocatalysis capability of graphite oxide-TiO_2 tablet

In this work, the organic dyes used namely methyl orange (MO) and methylene blue (MB) were applied for adsorption-photocatalysis degradation capability over G/TiO_2 tablet. Concentrations of organic dyes in a water environment are extremely low so the sample concentrations were made by varying such as 1.0 mg.L^{-1}; 3.0 mg.L^{-1}; 5.0 mg.L^{-1}; 7.0 mg.L^{-1}; and 10.0 mg.L^{-1}. These concentrations are used as a standard solution to obtain the linearity curve henceforth adsorption-photocatalysis performance test. In the first step, the determination of absorbance values was conducted over organic dyes such as MO dye under a wavelength of 465 nm and MB at 664 nm. Fig. 5 represents the linearity curve of MO and MB dyes. It could be clearly seen that the difference in concentration over two samples made has a significant difference to the value made. The linearity curves of the MO and MB dyes are $y = 0.01277 + 0.06717*x$ (Fig. 5a) and $y = -0.00354 + 0.02866*x$ (Fig. 5b). From both linearity lines, we can conclude that the higher absorbance value (Fig. 4a) means that the adsorbent surface can adsorb a larger number of molecules from the solution when compared to the absorbance value of the MB compound (Fig. 5b). This could indicate that the adsorbent has a good adsorption capacity or high efficiency in removing certain molecules from the solution.

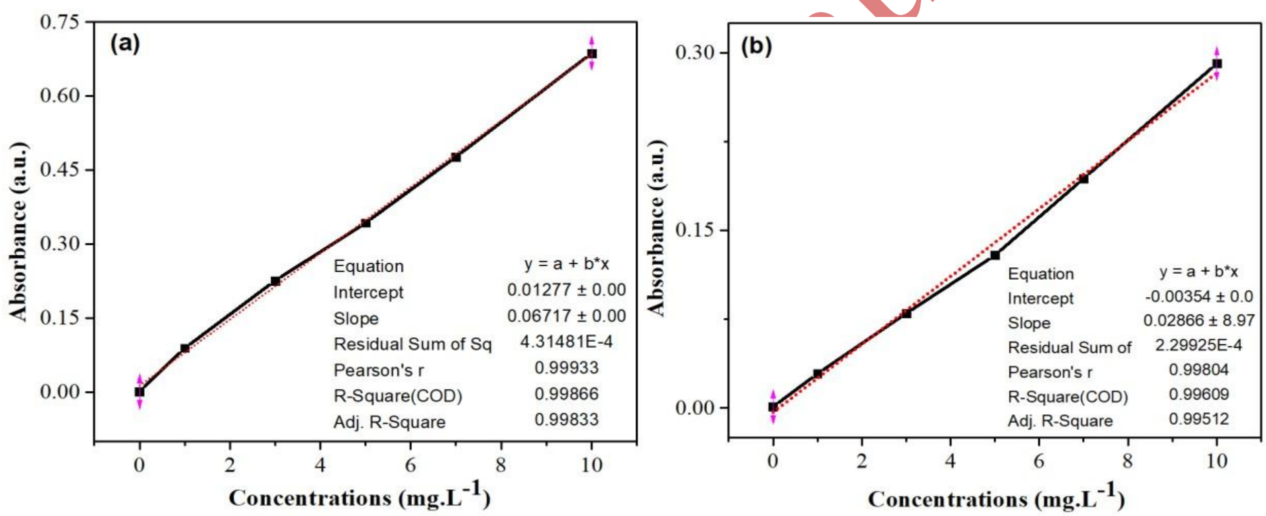

Fig. 5. Linearity curve of organic dyes, (a) MO dye, and (b) MB dye

When the absorption values were plotted against the linearity equation, the actual concentration changed. Table 1 shows that the concentration deviation of MB was greater than MO because MB compound is more soluble in organic solution than in distilled water. In this case, the dissolution process for MB compound uses distilled water because the color waste treatment process in industry tends to only use distilled water. On the other hand, there is also the possibility of measurement errors in the preparation of the test solution.

Table 1. Determination of the actual concentration refers to the linearity equation

Organic dyes	Concentrations (mg.L^{-1})	Absorbance (a.u)	b	a	Actual concentrations (mg.L^{-1})
MO	0.0	0.001	0.06717	0.01277	-0.175
	1.0	0.089	0.06717	0.01277	1.134
	3.0	0.226	0.06717	0.01277	3.174
	5.0	0.343	0.06717	0.01277	4.916
	7.0	0.477	0.06717	0.01277	6.911
	10.0	0.687	0.06717	0.01277	10.037
MB	0.0	0	0.02866	-0.00354	0.1235
	1.0	0.029	0.02866	-0.00354	1.1353
	3.0	0.080	0.02866	-0.00354	2.9148
	5.0	0.129	0.02866	-0.00354	4.6245
	7.0	0.194	0.02866	-0.00354	6.8925
	10.0	0.291	0.02866	-0.00354	10.2770

To elucidate the degradation mechanism of organic dyes, we determined the rate constant using the first-order reaction that has been calculated via equation (1), while the removal efficiency was calculated using equation (2) below [28,33]:

$$Ln\frac{C_t}{C_0} = k.t \quad (1)$$

$$\%\ Degradation = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

Where *Ct* is the concentration after degradation using composites and C_0 is the concentration before degradation. While the *t* is the degradation times effort of 10 min. and *k* is the rate constant. Based on Fig. 6 can be seen that the adsorption-photocatalytic performance of G/TiO_2 composites tablet over MO (Fig. 6a) and MB dyes (Fig. 6b). During the test process, the mixture solution of organic dyes and composites was aerator stirred for 10 min in the UV light irradiation to reach an adsorption-photocatalysis reaction. After 10 min the UV light and aerator stir were turned off and composites for the cylindrical Pyrex reactor halted reaction. Subsequently, the organic dye was slowly taken for 3 mL to identify the absorbance using a UV-Vis spectrophotometer. This process was continuously repeated for 60 min and recorded a decrease in organic dye degradation.

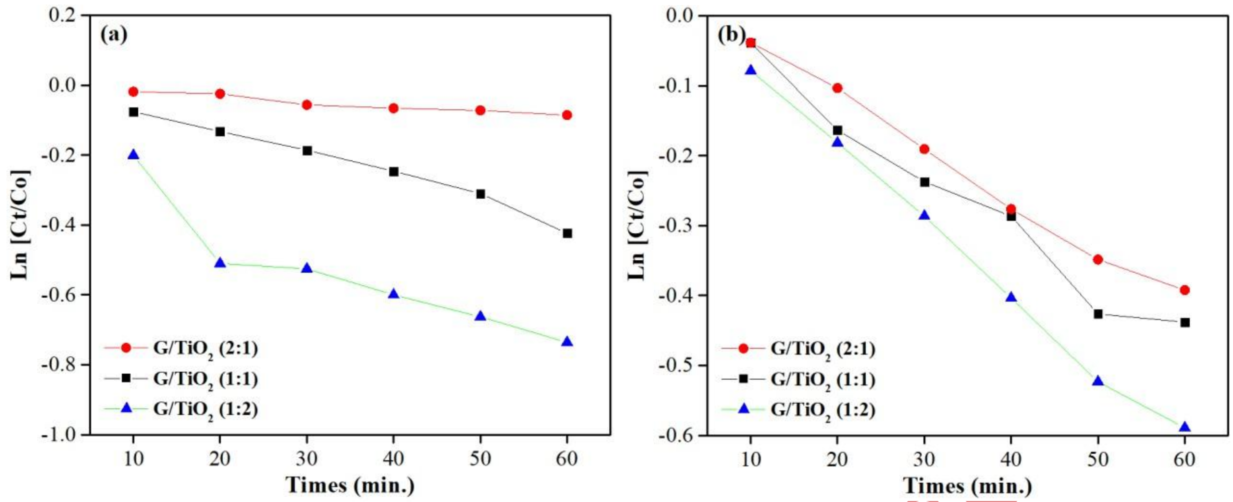

Fig. 6. Plots of ln (*Ct/C₀*) versus reaction time for the adsorption-photocatalysis of G/TiO_2 tablet (a) MO dye, and (b) MB dye

The G/TiO_2 tablet with 1:2 mass variation demonstrated the highest adsorption-photocatalysis activity among the two mass variations with 93.99% MO and 80.22% MB degraded after irradiation for 60 min. The order of the adsorption-photocatalysis degradation efficiency for MO and MB dyes by the two mass variations of composites is as follows: 1:2>1:1>2:1. Obviously, the 1:2 mass variation of G/TiO_2 shows the highest adsorption-photocatalysis degradation of organic dyes among the two mass variations. It is due to the high TiO_2 composition in composites resulting in the high photocatalytic performance to decrease organic dyes [34]. Meanwhile, the graphite oxide has a good performance for the first 10 min. Based on Zheng et al. [26] reported that the carbon graphite adsorption was initiated in the first minute of the test process. This is due to the increased pore area of the dry carbon making it easier to reach an adsorption-desorption equilibrium. The kinetics of adsorption-photocatalysis of organic dyes degradation were investigated by calculating the chemical reaction rate constant (*k*) from the pseudo-first-order kinetic model under the Langmuir-Hinshelwood model (Eq. 1). Table 2 exhibits that the 1:1 G/TiO_2 composites has a larger k value with 0.01726 min^{-1} for MO and 0.00947 min^{-1} for MB. The larger *k* value indicates a fast degradation process in short time duration.

Table 2. Plot the rate constant (*k*) against the difference in organic dyes

Concentrations	Organic dyes	Mass Variations of G/TiO_2 tablet	% Degradation	Average of rate constant (*k*)	Deviation Standard
5 ppm	MO	1:1	52.721	0.00662	0.00057
		2:1	48.904	0.00157	0.00025
		1:2	93.990	0.01726	0.00494
	MB	1:1	54.945	0.00715	0.00170
		2:1	48.023	0.00596	0.00122
		1:2	80.228	0.00947	0.00092

One of the problems that needs to be considered in testing G/TiO_2 tablets is that it is made from a combination of powders, so researchers need to be careful in paying attention to the durability of the tablets made. This is also related to the compressive strength and the wax (paraffin) added as a binding medium between powder particles. When these conditions are not considered, the tablet shows high adsorption performance, but the durability will be reduced because the material is easier to absorb water molecules which results in the ease of the G/TiO_2 tablet material being brittle and settling like particles under the test media. Then the adverse impact is the release of graphite oxide and TiO_2 nanoparticles into the environment even though it is safe to have an impact on deposits in the test reactor. For researchers who want to develop this model can pay attention to the use of compressive strength and wax used for binding between powder particles.

Table 3. literature studies toward TiO_2-based tablet composites

Composites	Methods	Photocatalytic performance	Time degradation	Ref.
Tetra butyl titanate – Cellulose	Pyrolysis	• 100% degradation of tetracycline	(60 min.)	[28]
Tetra butyl titanate – terephthalic acid	Pyrolysis	• 91% degradation of tetracycline	(120 min.)	[29]
Fe – TiO_2	Electrothermal	• 98% degradation of Rhodamine B	(180 min.)	[35]
TiO-P25 – Graphite oxide	Solid-Solid	• 93.99% degradation of Methyl Orange • 80.22% degradation of Methylene Blue	(60 min.) (60 min.)	This Study

Some literature study was examined by referring to the WoS search engine, we found three papers relevant to this research study (Table 3). TiO_2-based tablet composites have been tried by several researchers with different applications to tackle organic compounds. Based on their studies' results, TiO_2 tablet-based photocatalysis has good activity above 50% with selected degradation time capability. However, the methods developed also have differences and the chemicals used. This shows that the design of TiO_2 tablets provides great potential in overcoming the problem of organic liquid waste in the environment. This greatly affects the economic aspect of the removal method, where the applied method is very easy to work with and has a significant effect on the removal of organic dyes.

This research highlights the development of a novel adsorption-photocatalyst for treating organic dye pollutants in wastewater. By integrating TiO_2 with graphite oxide through a simple physical mixing method, nanocomposite tablets were synthesized with enhanced efficiency and cost-effectiveness. The study revealed that a specific mass ratio of the composite (1:2 G/TiO_2) significantly improved the degradation of organic dyes, indicating a pathway for optimizing adsorption-photocatalytic materials. Furthermore, the demonstrated reusability of the tablets underscores their sustainability and potential for widespread adoption in wastewater treatment applications. Overall, this research offers promising implications for environmental remediation efforts, cost-effective technology development, and sustainable water pollution mitigation strategies.

Conclusions

In summary, we reported an adsorption-photocatalyst for the catalytic degradation of organic dyes (MO and MB) based on graphite oxide incorporated with TiO_2 to form a tablet construction, in which graphite oxide plays a role in adsorption and TiO_2 for photocatalyst performance. Based on the experimental results, we found that the G/TiO_2 tablet with a mass variation of 1:2 shows the highest adsorption-photocatalysis activity among the two mass variations, namely 1:1 and 2:1. The chemical reaction rate constant showed that the composite was easier to degrade MO dyes than MB. This work describes a new strategy for using highly photoactive adsorption tablets in the form of G/TiO_2 as a material for the effective degradation of organic dyes.

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