

Photocatalytic activity of MgFe₂O₄:TiO₂ composite for degrading methylene blue

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Abstract

We reported the methylene blue (MB) degradation by the photocatalysis method. This work aimed to know the effectiveness of degradation using a MgFe₂O₄:TiO₂ composite. Synthesis of the composite used the sol-gel method. We synthesized three samples with ratios between MgFe₂O₄ and TiO₂. Those were 100:0, 50:50, and 75:25, respectively. Sample (75:25) degraded MB of 47.23% with a reaction rate of $5.326 \times 10^{-3} \text{ minute}^{-1}$ under solar irradiation. Whereas, without solar irradiation, a sample showed a lower reaction rate. It happened because the sunlight produced photon energy to produce OH* radical so that it could activate the sample to absorb the dye. Reusable test resulted 19.73% degradation of MB for 100:0, 17.03% for 50:50, and 20.59% for 75:25 for 120 minutes. The XRD result for 75:25 has three phases, which are MgFe₂O₄ with cubic structure, TiO₂ with tetragonal structure, and Fe₂O₃ with hexagonal structure. This work indicated that the sol-gel method could synthesize composite structures, and the sample may be used to remove methylene blue.

Keywords: Degradation; photon energy; composite; cubic; solar irradiation.

How to Cite: Aliah, H., Hidayah, E.S., Iman, R.N., Sawitri, A., & Setiawan, A. (2022). Photocatalytic activity of MgFe₂O₄:TiO₂ composite for degrading methylene blue. *Jurnal Pendidikan Fisika dan Keilmuan (JPFK)*, 8(1), 191-201. doi: <http://doi.org/10.25273/jpfk.v8i1.13510>

INTRODUCTION

Throwing waste into the environment causes a toxic effect and reduces light penetration in waterways (Prado et al., 2008). Besides the heavy metal waste, there are colored organic compounds that are difficult to separate. Methylene blue (MB) is usually used as a dye in the textile industry. The waste from MB that is thrown into a river is a danger because the high organic content and the long separation process can destroy the molecule structure of the water. So, a living thing cannot live in the environment (Widjajanti et al., 2011). Therefore, it is necessary for wastewater treatment technology to separate the dye waste rapidly.

There are many methods of wastewater treatment, such as chlorination (Joseph et al., 2022), ozonation (Ben'ko et al., 2021), membrane separation (Xu et al., 2022), biodegradation (Demissie et al., 2021), oxidation (Wu et al., 2021), adsorbent (Tan et al., 2015), and photocatalysis (Aliah & Karlina, 2015). In this

work, we used the photocatalysis method with semiconductor materials. We argue that photocatalysis is the most effective method for handling pollution from organic waste. It is because the method can separate a dye waste becomes a simple component, easy to use, and not make a sludge (Safni et al., 2007).

Some researchers synthesized a catalyst powder from many types of the semiconductor materials like TiO_2 (Aliah & Karlina, 2015), (Aliah et al., 2012), (Aliah et al., 2013), ZnO (Chen et al., 2017), Fe_2O_3 (Hitam & Jalil, 2020), and MgO (Zheng et al., 2019). Fe_2O_3 and MgO have band gap energy of 2.2 eV and 4.2 eV, respectively. Mixing MgO and Fe_2O_3 can create MgFe_2O_4 , which has a spinel cubic structure with a type of inverse spinel. Besides that, they are soft magnetic, have a low coercivity (Heidari & Masoudpanah, 2020), and can absorb the whole of the visible light well (McDonald & Bartlett, 2021). Some studies of MgFe_2O_4 catalyst were reported, like antibiotic photocatalytic (Becker et al., 2020), degrading 2-propanol photocatalytic (Kim et al., 2009), and degrading methylene blue photocatalytic (McDonald & Bartlett, 2021). So, they indicate that MgFe_2O_4 can be used as a photocatalyst.

On the other hand, MgFe_2O_4 is easy to oxidize with free oxygen and easy to make aggregation, and the size and the shape of crystallite are not controlled as well (Rathinavel et al., 2021). Hence, it needs to modify a surface to enhance the stability of chemistry and create a homogeneous crystallite shape and size. To modify a surface, we can use TiO_2 because it has good chemical stability in all reaction conditions and high photocatalytic activity (Y. Li et al., 2005). The other previous study reported the composite of TiO_2 with other semiconductor materials and resulting the high efficiency with the spinel structure (Natarajan et al., 2016), (Ziarati Saravani et al., 2019). So, we hypothesize that adding TiO_2 into MgFe_2O_4 can increase photocatalytic activity.

In the previous study, as far as we know, the researcher synthesized MgFe_2O_4 using a microwave (McDonald & Bartlett, 2021). To improve the characteristics of MgFe_2O_4 , we synthesized MgFe_2O_4 and dope with TiO_2 using the sol-gel method. The sol-gel method has an advantage as an efficient method in synthesis and can improve the photocatalytic efficiency to visible light (Natarajan et al., 2016). Therefore, this method is chosen to enhance the performance of $\text{MgFe}_2\text{O}_4\text{-TiO}_2$ on photocatalytic activity.

METHODS

This work consists of synthesizing MgFe_2O_4 with different TiO_2 concentrations, testing the degradation performance on MB, crystal structure characterization using XRD, and optical properties with UV-Vis spectrophotometer.

2.1 Synthesis of composite powder

MgO powder was solved by water and mixed using a magnetic stirrer. Every sample was added by PEG 1000 with a ratio of 3:1. The sample was mixed and stirred for 30 minutes. After that, the solution was mixed into Fe_2O_3 until homogeneous. Then, a mixed solution was added with different TiO_2 concentrations, 0, 25%, and 50%, then mixed again. The solution was heated at 150 °C until it formed gel. The gel was dried at 400 °C for one hour to obtain a dried sample. Then it was calcined for two hours at 500 °C to omit the water content.

2.2 Characterizations of composite

Before doing testing of degrading a dye, it is necessary to calibrate a standard solution. Five solutions were made with different concentrations of 0.5×10^{-5}

5 M , $1.0 \times 10^{-5} \text{ M}$, $2.0 \times 10^{-5} \text{ M}$, $3.0 \times 10^{-5} \text{ M}$, and $4.0 \times 10^{-5} \text{ M}$. Then, every solution was measured its peaks by a UV-Vis spectrophotometer in the range of 400-800 nm.

The dye degradation testing was done under two conditions: under solar irradiation and without solar irradiation. As much as 50 mg of each composite powder was put into three vial bottles and added 50 mL of MB solution with a concentration of 20 mg/L. The bottles were put under solar irradiation and without that. Every 40 minutes, the concentration of MB solution was measured by UV-Vis spectrophotometer at 664 nm wavelength.

Mathematically, degradation of MB solution can be stated as the rate of kinetical reaction [17]:

$$\ln \frac{C}{C_0} = -k \quad (1)$$

where C_0 is the initial concentration of MB (M), C is the concentration of MB after a specific time t , and k is the degradation rate constant (minutes^{-1}).

The repeatability of $\text{MgFe}_2\text{O}_4\text{-TiO}_2$ composite powder was known by repeatedly testing MB degradation as much as three times. This technic was done as the following procedure. The previously used powder of composite or catalyst was separated from MB solution and then washed with water and ethanol as many as three times. Afterward, the powder was dried in an oven for 5 hours at $70 \text{ }^\circ\text{C}$. The dried powder was reused and tested in the same concentration of MB. Then, the absorbance of MB solution was measured by UV-Vis after having been degraded by a composite powder and analyzed to know the final concentration. On the other hand, the crystal structure of composite powder was measured by X-Ray Diffractometer and analyzed by Match3! Software

RESULTS AND DISCUSSION

Characterization of crystal structure used XRD in 2 thetas of $5\text{-}100^\circ$. Figure 1 showed an X-ray diffraction pattern for MgFe_2O_4 doped by 25% mol of TiO_2 . The composite matched the database from JCDPS number 96-900-1470 for MgFe_2O_4 with the phase of cubic spinel and a lattice parameter $a = 8.3806 \text{ \AA}$. Number 96-720-6076 for TiO_2 with a phase of anatase tetragonal and lattice parameter $a = 3.7850 \text{ \AA}$ and $c = 9.5196 \text{ \AA}$. And number 96-901-5965 for Fe_2O_3 with a phase of hematite and lattice parameter $a = 5.0346 \text{ \AA}$ and $c = 13.7473 \text{ \AA}$. In this composite powder of formed MgFe_2O_4 are four peaks at (30.20°) , (35.59°) , (43.18°) , and (53.44°) . TiO_2 is four peaks (25.32°) , (38.59°) , (48.05°) , and (55.07°) and Fe_2O_3 is eight peaks at (24.15°) , (33.16°) , (40.87°) , (49.47°) , (57.53°) , (62.64°) , (71.96°) , and (77.96°) degree.

The peak of MgFe_2O_4 is sharp and intense, indicating the sample's crystallinity characteristics. The higher and sharper the peak indicated the better crystallinity of the sample. Whereas the peak of the TiO_2 is width and low, it indicates that the size of crystallinity is small and low. Another phase is Fe_2O_3 , which indicates that not all molecules of Fe_2O_3 reacted with MgO to form MgFe_2O_4 . On the other hand, adding TiO_2 into MgFe_2O_4 created the composite structure, or TiO_2 only covering the surface of MgFe_2O_4 . Therefore, we argue that this crystallite phase affected performance in photocatalytic activity. Besides the crystal phase, the size of the crystal also affected photocatalytic activity (D. Li et al., 2020). To get the crystal size, we can use the Debye-Scherrer equation (Equation 2):

$$d \cong k \frac{\lambda}{B \sin \theta} \quad (2)$$

where d is crystallite size, k is the constant of the material, λ is the wavelength of x-ray, and B is the Bragg angle. Using Equation 2, MgFe_2O_4 has a crystallite size of 47.66 nm at 2θ of 35.59° , TiO_2 has a crystallite size of 38.1 nm at 2θ of 25.32° , and Fe_2O_3 has a crystallite size that is 60.89 at 2θ of 33.16° . So, the $\text{MgFe}_2\text{O}_4\text{-TiO}_2$ composite will have a high surface area to enhance photocatalytic activity (Zhang et al., 2011).

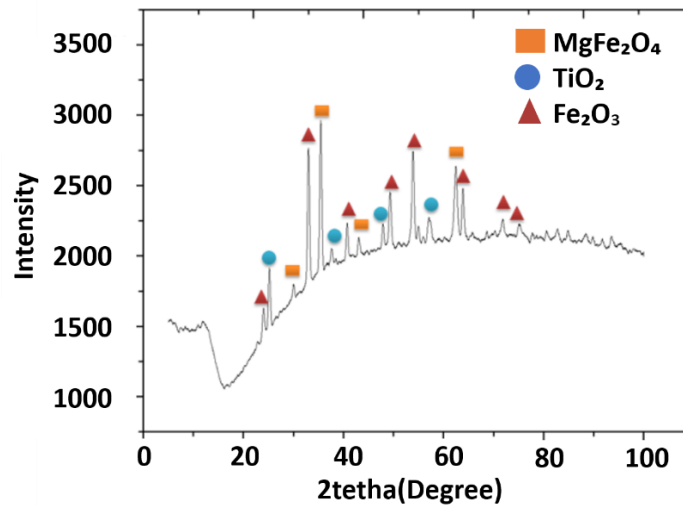


Figure 1 XRD pattern of $\text{MgFe}_2\text{O}_4\text{-TiO}_2$ composite powder

The MB was used in the technical phase. The results of measuring for the standard solution used UV-Vis spectrophotometer indicated a characteristic graph of MB absorbance with a maximum peak at the wavelength of 664 nm. The formed graph is based on the absorbance value of some MB solutions with different concentrations. Figure 2 shows the maximum wavelength of the solution at 664 nm. This wavelength was used as a reference for measuring the absorbance value. The graph of the standard solution is necessary for testing the performance of the photocatalytic of the sample.

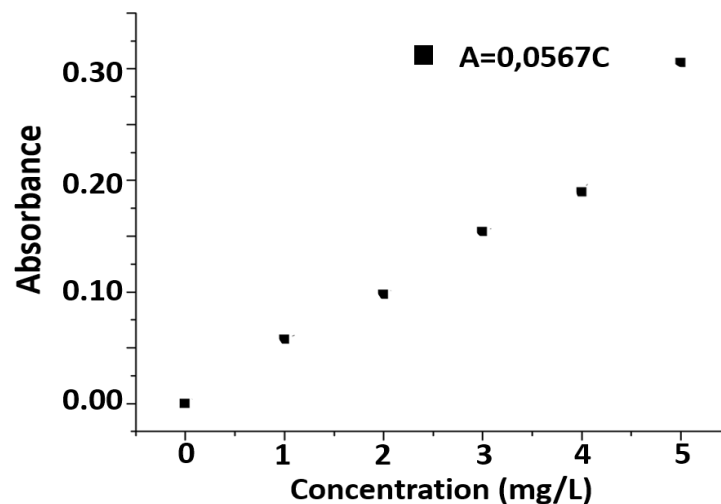


Figure 2 Graph of standard solution calibration of MB

Lambert-Beer stated that the absorbance and concentration of the solution have a linear relation. Based on Figure 2, by using the feature of analysis on the OriginPro software, it can be obtained that the regression equation is $A = 0.0567C$, where C is a variable as a concentration of the MB solution with a constant of calibration is 0.0567. This equation was used for measuring the degraded concentration of MB solution.

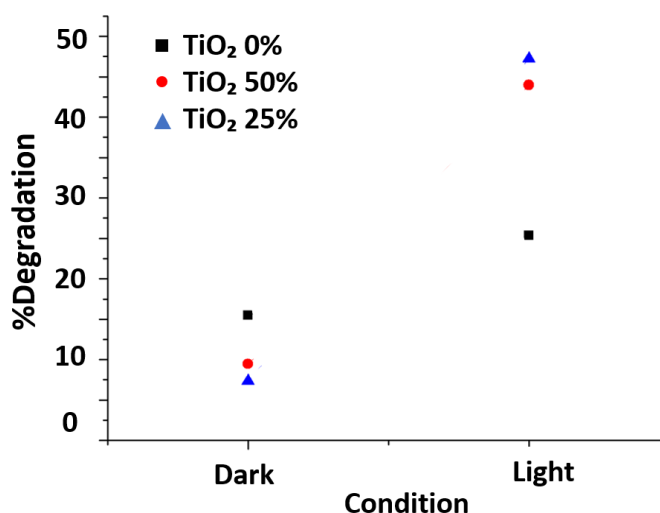


Figure 3 relationship between %degradation and under [without] solar irradiation

The following is the procedure of the photodegradation mechanism. When the composite receives the energy from the solar, an electron from the valence band will excite the conduction band, resulting in a hole in the valence band. The hole that contains a positive charge (h^+) takes an electron from H_2O in order to be able to come back to the initial condition. H_2O that loses one electron will have a positive charge and become hydroxyl radical (OH^*). At the same time, an electron in the conduction band will have a negative charge (e^-) which can reduce the oxygen around it and result in a superoxide anion (O_2^-). Superoxide anion (O_2^-) and hydroxyl radical (OH^*) that result from the process of electron transfer become strong oxidation that can degrade organic molecules, that is methylene blue which will become CO_2 and H_2O (Jarariya, 2022).

The photocatalytic activity on MB by $MgFe_2O_4$ - TiO_2 composite was tested under and without solar irradiation. This test is to know the effectivity of photocatalyst in the resulting radical of OH^* . Figure 3 showed that the value of Mb degradation increased under two conditions for three samples. In the dark condition, it obtained low degradation because there is no light, so photon energy to create OH^* radical is low. Therefore, MB solution was only adsorbed on the surface of the composite, and its degradation was not optimum. Whereas when sample under solar irradiation resulted in a higher degradation value than under dark conditions. It was because more hydroxyl radical (OH^*) formed.

Sunlight has a wavelength of 300-2000 nm (Cheng et al., 2021), which consists of UV light and visible light. Hence, the sunlight has high energy and can give more photon energy to the catalyst. The sample without adding TiO_2 on $MgFe_2O_4$ only enhanced photocatalytic activity until $\pm 10\%$ from the dark to the light condition. Whereas samples with the addition of TiO_2 could enhance photocatalytic activity until $\pm 40\%$, so that resulted in they can degrade MB solution more optimum.

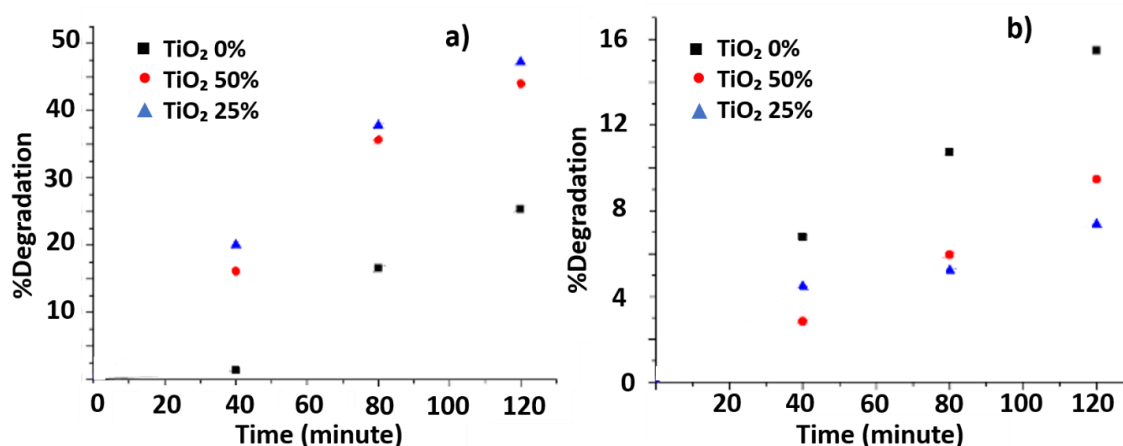


Figure 4 relation between irradiation time and: a) light condition; b) dark condition

From Figure 4, it can be known that the role of light as a source of energy for the photocatalytic reaction is significant in helping the process of dye degradation. When the sunlight irradiates MB solution that contains a composite material with higher energy than band gap energy, it will create a hole with a substantial oxidation property to generate OH^* radical. The radical will degrade MB to become a simpler compound.

A contact time in the photodegradation process describes how long the interaction between catalyst and the light ($h\nu$) in resulting OH^* radical and contact between OH^* radical with MB substrate in the degradation process. When the photodegradation process happens, a contact time affects the percentage of degradation of MB. The longer of contact time, the more MB compound is degraded. Similarly, on adsorption process was conducted without irradiation. In this work, a contact time was used 0, 40, 80, and 120 minutes as described by the previous statement.

Figure 4 indicated that degradation of MB enhanced while a contact time was longer either with irradiation or without irradiation of the sunlight. When under irradiation, at the time of irradiation for 120 minutes happened, enhancing the high degradation. It was because the more prolonged irradiation, the more solution of MB degraded. The color of the solution indicated it was dull (see Figure 5).

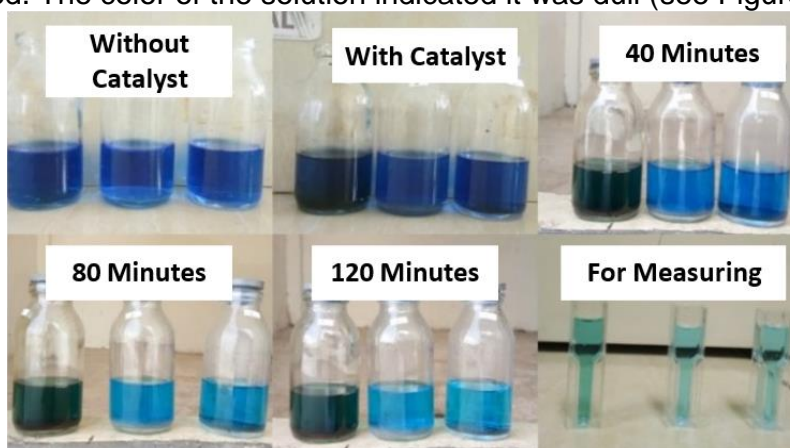


Figure 5 Results of photodegradation under the sunlight irradiation

We also tested the sample with different concentrations of MB 20, 30, and 40 mg/L. In this testing, we just used the sample with the best sample in

performance of degradation ($\text{MgFe}_2\text{O}_4\text{-25\% TiO}_2$). With a similar procedure, a bottle was filled with 50 mL of each MB concentration and added 50 mg of composite powder, and it was put under solar irradiation for 120 minutes. After that, some of the solutions were measured by UV-Vis spectrophotometer.

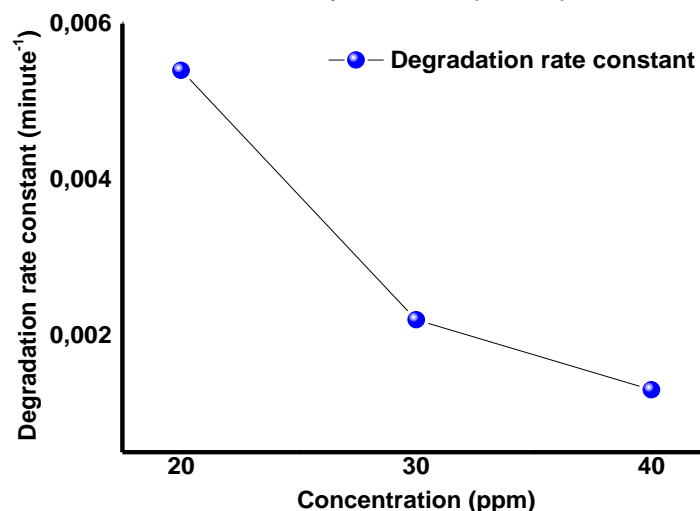


Figure 6 Profile of MB degradation rate on different concentrations under sunlight irradiation

Figure 6 showed a relation between constant of degradation rate and concentration of MB solution. The rate constant for 20, 30, and 40 mg/L of MB were 0.0054, 0.0022, and 0.0013 minutes⁻¹, respectively. It reduced from 20 mg/L to 40 mg/L. It was because they needed more catalyst materials to degrade the MB concentration faster. It was similar to the work of (Sakthivel et al., 2003), which showed that more high concentration of MB lowers the degradation rate. The degradation rate relates to the structuring of OH* radical, where this radical is important in the degradation process (Laouedj, 2011). Enhancement of the initial concentration of MB caused a long photon path that irradiated the solution, reducing the degradation rate (Sakthivel et al., 2003).

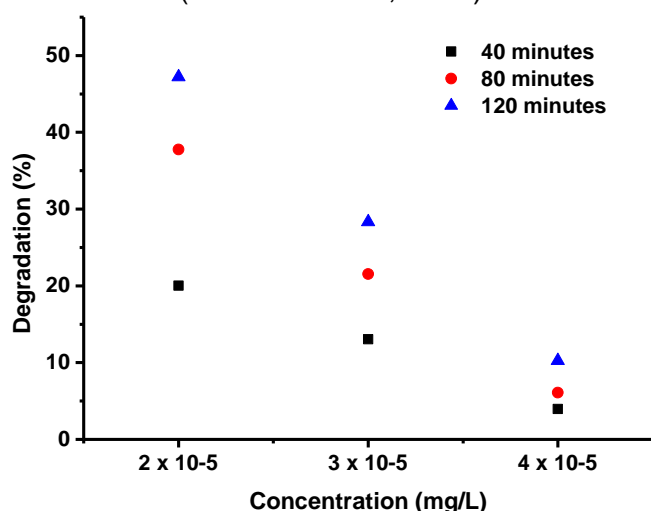


Figure 7 Effect of irradiation time on the degradation efficiency of various concentration

The degradation efficiency of the $\text{MgFe}_2\text{O}_4\text{-TiO}_2$ composite catalyst is shown in Figure 7. It showed that increasing MB concentration reduces the degradation efficiency. Drastically reduction of the performance can be seen in a 40 mg/L solution. The high concentration of the solution reduced the excitation of an electron in the catalyst (Tichapondwa et al., 2020), so the energy that comes from photons to activate the catalyst is low. In contrast, the catalyst was faster in degrading the MB solution with 20 mg/L simultaneously. In the solution with a high concentration, the amount of MB molecule contained in the solution will be higher. With the MB molecule being higher, it is necessary for more hydroxyl radicals in the degradation process, which means that it needs more catalysts to degrade the higher concentration of MB.

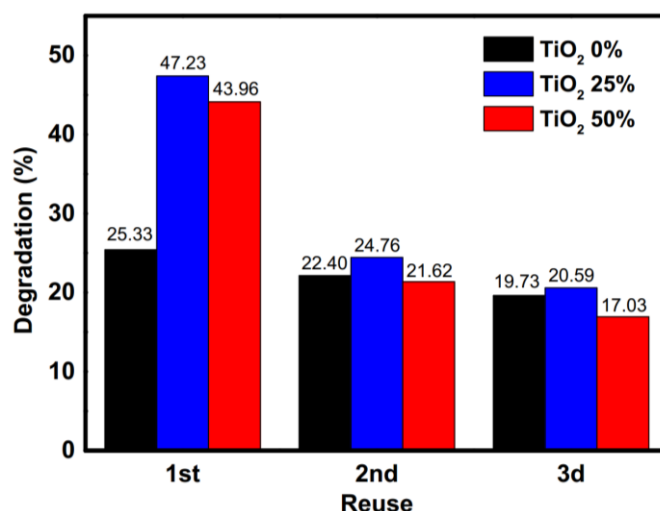


Figure 8 relation between reuse of catalyst on MB degradation

Figure 8 shows the relation between the percentage of degradation on the reuse amount of catalyst powder. The figure showed that the second and third use reduced degradation performance. It happened because MB molecules still adsorbed or aggregated around catalyst particles. Hence, they covered the active part of the catalyst surface. It would reduce the effectivity of OH^* radical production and photocatalytic efficiency.

Theoretically, reusing $\text{MgFe}_2\text{O}_4\text{-TiO}_2$ is reusable. However, it is not practical to result in high degradation like initial use. It was reducing degradation value until roughly 50% of initial use. It was because of reducing catalyst mass in the second and third use. Moreover, the catalyst mass was reduced because of the catalyst's filtering, washing, and drying process for the second and third use. Therefore, the photocatalytic activity to degrade MB solution reduces. The amount of measured mass of catalyst for first, second, and third use can be seen in Table 1.

Table 1 mass of catalyst powder in every use

No.	Sample	Mass of sample (gram)		
		First use	Second use	Third use
1.	MgFe_2O_4	0.05	0.0086	0.0042
2.	$\text{MgFe}_2\text{O}_4\text{:TiO}_2$ 50%	0.05	0.0305	0.0244
3.	$\text{MgFe}_2\text{O}_4\text{:TiO}_2$ 25%	0.05	0.0303	0.0229

CONCLUSION

The nanocomposite of $\text{MgFe}_2\text{O}_4:\text{TiO}_2$ has been synthesized by the sol-gel method. They created three structure phases: spinel cubic for MgFe_2O_4 , tetragonal for TiO_2 , and hexagonal for Fe_2O_3 . The crystallite size was also measured with a nanometer scale. The degradation of methylene blue showed that the sample under solar irradiation was better than without solar irradiation. It showed that the role of the light was necessary. The more prolonged irradiation was, the more much the MB degraded. The optimum catalyst for the sample was $\text{MgFe}_2\text{O}_4:\text{TiO}_2$ 25% resulting in a degradation of 47.23%. Increasing the MB concentration reduced the degradation rate constant and efficiency. Re-testing showed that the catalyst performance reduced because of the lack of catalyst mass, so the photocatalytic activity decreased. Therefore, the synthesis of the $\text{MgFe}_2\text{O}_4:\text{TiO}_2$ composite can be used to remove MB in solution media. For further research, we recommend investigating the effect of catalyst mass in specific concentrations and the pH of MB solution.

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