Influence of Fe₃O₄ Addition in TiO₂ Catalyst on The Degradation Process of Methylene Blue

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Abstract. Synthesis of composite titanium dioxide with iron oxide magnetic material (Fe₃O₄/TiO₂ composite) has been successfully carried out by precipitation method. Photocatalytic performance test of this composite Fe₃O₄/TiO₂ was performed for degradation process of the methylene blue solution with the experiment parameters consist of the solution pH, lighting time, type of light, amount of catalyst, and the concentration of methylene blue. The experimental results showed that the Fe₃O₄ addition in TiO₂ catalyst can simplify recovery process of the catalyst, and able to broaden the absorption area up to visible light, so that the degradation process can be carried out with UV and visible light. Degradation of methylene blue by Fe₃O₄/TiO₂ composite in under sunlight more effectively compared UV light.

1. Introduction
Titatium dioxide nanoparticles (TiO₂) of anatase phase are a catalyst material that has proven to be very efficient in the degradation of organic compounds because it has a relatively large energy gap of about 3.2 eV [1]. However, there are obstacles in its use in the recovery process of the catalyst material after the degradation process. It is given that the catalyst material was dispersed into the solution so that the separation process needs to use centrifuges. The separation process using the centrifuges needed a lengthy period of time to finish. Therefore, we need further development namely combines these TiO₂ catalyst materials with magnetic material to form a composite material to facilitate the recovery process of TiO₂ catalyst after degradation process. This composite development is expected to shorten the separation process so that it becomes more effective and economical. Magnetic materials which are suitable for use as magnetic composite photocatalyst, are of the superparamagnetic type. Because this magnetic material has no spontaneous magnetic moment, it can be well dispersed in the water, and also easier to be collected back because it can produce a maximum magnetic response when given an external magnetic field. The best iron oxide-based superparamagnetic materials to be used as a carrier magnetis Fe₃O₄ and γ-Fe₂O₃ because it has a fairly high magnetization. In addition, synthesis of this magnetic material is much simpler and non-toxic so that is safe for the environment.

Photocatalysts magnetic composite of Fe₃O₄/TiO₂ can be prepared by various methods, such as sol-gell[2], plasma spray [3], precipitation [4-5], solvothermal [5], sonochemical [7-8], and micro-emulsion [9]. In addition, various forms morphology of Fe₃O₄/TiO₂ catalyst have been successfully made also include core/shell [6], the nanotube core/shell [7,8] and hollow [6,10].

In the previous study, TiO₂-based catalyst material with good performance has been successfully synthesized and it is able to degrade almost 100% methylene blue with a degradation time of 150
minutes using ultraviolet light [12]. However, the process of recovery of the catalyst material is still using the centrifuge equipment with a relatively limited capacity. Based on these results, in the present research a composite of Fe₃O₄/TiO₂ catalyst will be developed, it is to be synthesized by precipitation method using the precursors FeCl₂.4H₂O, FeCl₃.6H₂O, and titanium ortho titanate. The photocatalyst performance of the Fe₃O₄/TiO₂ composite catalyst was done through the degradation process of organic compounds (methylene blue), and then will be compared with the performance capabilities of the result of previous studies (TiO₂ photocatalyst). Therefore, the objective of this study was to observe the effect of Fe₃O₄ addition in TiO₂ catalyst in the recovery processes of methylene blue degradation with research parameters include pH, lighting time, type of light, the amount of catalyst, and the concentration of methylene blue.

2. Materials and Methods

Materials
TiO₂ and Fe₃O₄ synthesis results of previous experiment with specification of anatase (TiO₂) and particle size of ±10 nm, methylene blue, NaOH, H₂SO₄, NH₄OH, tetra bythyl ortho titanate (TBOT), and demineralization water.

Method
The photocatalytic performance test was carried out in a solution of methylene blue in a catalytic reactor with magnetic stirrer and UV-pen light (wavelength 356 nm). While the experimental procedure was performed as follows; the Fe₃O₄/TiO₂ powder was incorporated into the catalytic reactor containing methylene blue solution whose pH level has been set. The suspension was stirred in accordance with the desired time, and then after the photocatalytic process the catalyst material was retrieved by using a magnet. After that the solution was analyzed using a UV-Vis spectrophotometer to determine the remaining concentration of methylene blue. The photocatalytic test result of catalyst composite Fe₃O₄/TiO₂ was compared with the TiO₂ catalyst (the result of previous study). The study parameters consist of the solution pH (2, 4, 6, 8, 10, and 12); lighting time (30, 45, 60.75, 90, 120, and 150 minutes); concentration of methylene blue (10, 20, 30, 40, and 50 mg/L) and the amount of TiO₂ catalyst (10, 25, 50, 100, 150, and 200 mg).

3. Result and Discussion

Effect of pH solution on the efficiency of methylene blue degradation
In the photocatalytic process, the pH scale of the solution has a profound influence on the efficiency of methylene blue degradation, because the presence of forming free radicals that contribute to the oxidization of organic compounds into simpler compounds that are not harmful to the environment depends on the pH value of the surrounding solution.
The reaction of free radical formation in the process of photocatalytic TiO2 by UV light has been discussed in the previous study [12]. Effect of pH values on the efficiency of methylene blue degradation photocatalytic composite Fe3O4/TiO2 is shown in Figure 1. Figure 1 shows that the effect of photocatalytic Fe3O4/TiO2 on the methylene blue degradation is very effective and it occurs at bases pH of about 10-12. In these case the degradation process nearly perfect (100%). While the methylene blue degradation has not occurred at acidic pH (pH ≤ 4.0). This is due to Fe3O4 magnetic composites with TiO2 will change the properties of the catalyst material. Fe3O4 at acidic pH will not be stable, because Fe3O4 under acidic conditions will react with the acid around it as shown in the following reaction:

\[
Fe_3O_4 + HNO_3 \rightarrow 3 Fe(NO_3)_3 + NO_2 + 5 H_2O
\]

With the reduction of Fe3O4 in the catalyst material, it becomes very influential on the degradation efficiency, because Fe3O4 was absorbing the methylene blue. The absorption properties appeared from the experimental results of methylene blue degradation in the dark atmosphere (without light) as shown in Figure 2. Experimental methylene blue degradation in the dark atmosphere was conducted to show that the degradation process occurs not because of the photocatalytic process but because of the absorption process. In Figure 2 it is clearly shown that the occurrence of the decrease in the concentration of methylene blue in the dark atmosphere is relatively high with an efficiency of 76%, whereas when using TiO2 catalyst in the same condition it only reaches an efficiency of about 19%.
Effect of the addition of Fe$_3$O$_4$ on the performance of TiO$_2$ catalyst

Degradation process of the photocatalytic method is strongly influenced by the strength of light, light distance and lighting time. The longer it takes for the lighting degradation process to finish, the more effective it will be. In the photocatalyst method, degradation will occur when the photon energy of UV-Vis absorbed by the catalyst material is greater than the threshold energy between electrons on the valence band and the conduction band. In addition, the presence of other compounds in this material will also affect the performance of the catalyst material.

Investigation of the effect of the addition of Fe$_3$O$_4$ on the performance of TiO$_2$ catalyst materials was carried out with a variety of lighting experiments using UV light and sunlight in the duration of 15-150 min as shown in Figure 3.
As shown in Figure 3, the performance of TiO$_2$ catalyst is very low when using sunlight, because TiO$_2$ only absorb the UV light, while the UV light content in the sun ray spectrum was only around 4-5% \cite{13}. However, when using UV light from a UV lamp of pen models with a wavelength of 356 nm, there is an indication that the photocatalytic performance is very good. The degradation process of methylene blue by Fe$_3$O$_4$/TiO$_2$ using sunlight is more effective compared with using UV light, this is due to the Fe$_3$O$_4$ addition in the TiO$_2$ catalysts will cause a widening of the absorption region from the UV light into the visible light region. This is evident from the measurement results of absorbance TiO$_2$ Fe$_3$O$_4$/TiO$_2$ using reflectance of UV-Vis Spectrophotometer as shown in Figure 4.

In Figure 4 it appears that the addition of Fe$_3$O$_4$ in the TiO$_2$ catalyst can broaden the light absorption from UV light (wavelength ≤ 400 nm) up to the visible light region with wavelength > 400 nm. In another work, the authors have successfully synthesized a photocatalyst Fe$_3$O$_4$/TiO$_2$ by sol-gel method and come up with the same result that the efficiency degradation occurs up to the visible light region, but the concentration of methylene blue in this study can be three times higher \cite{14}. When compared with the Fe$_3$O$_4$/TiO$_2$ research results reported by Chen-Yu Hsieh and Yung-Hsu, 2014, the authors have used precursor tetra orthotitanate isopropanol and have shown that the optimum photocatalytic performance only occurs in the UV light region whereas in this study it occurs up to the visible light region.

![Figure 4](image)

**Figure 4.** Measurement of light absorption TiO$_2$ and Fe$_3$O$_4$/TiO$_2$ catalyst material by UV-Visible Diffuse Reflectance spectroscopic

**Effect of the amount of catalyst on the effectiveness of photocatalytic**

Based on the photocatalytic method, the amount of catalyst does affect the effectiveness of the organic compounds degradation. The higher the amount of catalyst, the more amount of free radicals will be formed in a manner that the decomposition of organic compounds will be more effective, but it is limited by the maximum amount of catalyst because these catalyst can hinder the incoming light \cite{12, 14-15}. Therefore the amount of catalyst has influence on the effectiveness of methylene blue degradation as shown in Figure 5.
Figure 5 shows that the degradation efficiency of Fe$_3$O$_4$/TiO$_2$ initially increases by increasing the amount of catalyst, but after reaching the optimal value up to 50 mg, the reaction rate does not change and even decreased. This is due to the active surface area of the catalyst has increased so that the reaction becomes faster. However, after the amount of catalyst becomes greater than 50 mg, it is suspected that agglomeration has occurred among the particles, and causes the incoming light to be blocked. With obstruction of light on the catalyst material will reduce the formation of free radicals so that the process of degradation decreases. This also occurs in the use of TiO$_2$ catalyst as shown in Figure 5. At the same amount of Fe$_3$O$_4$/TiO$_2$ and TiO$_2$ catalyst, the efficiency degradation with Fe$_3$O$_4$/TiO$_2$ is much higher than with TiO$_2$, because Fe$_3$O$_4$/TiO$_2$ have adsorption properties and wider absorbency regions.

Effect of the methylene blue concentration on the efficiency of degradation by Fe$_3$O$_4$/TiO$_2$ catalyst material

The concentration of methylene blue will affect the degradation efficiency. The higher concentration of methylene blue would affect a decrease in the degradation efficiency. This is due to the higher concentration of methylene blue, the available load of Fe$_3$O$_4$/TiO$_2$ catalyst to degrade the organic compounds is also higher. The influence of the methylene blue concentration on the residual methylene blue was shown in Figure 6.
Figure 6. Effect of the methylene blue concentration on the efficiency degradation by Fe$_3$O$_4$/TiO$_2$ catalyst material (Fe$_3$O$_4$/TiO$_2$ of 50 mg, methylene blue solution of 100 mL, pH of 10, and irradiation time of 45 min).

Figure 6 show that with the increase in the concentration of methylene blue, the efficiency degradation decreased. It is consistent with the results of research Salmin S. Al-Shamali et al [13] who said that with the increase of methylene blue will increase the number of molecules methylene blue to be adsorbed on the surface of TiO$_2$, so would inhibit light which will penetrate TiO$_2$ and resulted in the formation of free radicals is reduced so that the efficiency of degradation of methylene blue decreasing. The success rate of the photocatalytic properties can be measured by the repetition of use of catalyst to degrade of dyes. From the experimental results showed that repetition Fe$_3$O$_4$/TiO$_2$ synthesized have very good photocatalytic properties. In this researche of repetition of degradation of methylene blue by Fe$_3$O$_4$/TiO$_2$ done untill 6 times still give high relative degradation efficiency of about 88 %.

The experimental results presented by the authors have demonstrated that the composite catalyst Fe$_3$O$_4$/TiO$_2$ can shorten the process of degradation, because for the recovery of the catalyst material it was sufficient to just use permanent magnets as shown in Figure 7. Beside that addition of Fe$_3$O$_4$ on TiO2 catalyst can widen the absorption of the UV light up to visible light region, so that the degradation process could be achieved by the sunlight.

Figure 7. The recovery of catalyst after methylene blue degradation processing.
Figure 7 (a) shows the TiO$_2$ catalyst prior to the addition of Fe$_3$O$_4$-shaped suspension in the water and is not attracted by a magnet, therefore in this case it is necessary for the recovery process to use a centrifuge. After the addition of Fe$_3$O$_4$ in the TiO$_2$ catalyst (Figure 7 (b)), these catalyst material is easily attracted by a magnet, so it no longer needs centrifugation (separation process becomes much simpler).

4. Conclusion
In this study the composite Fe$_3$O$_4$/TiO$_2$ catalyst has been successfully synthesized by using precipitation method for application in photocatalytic materials. The experimental results showed that the Fe$_3$O$_4$ addition in TiO$_2$ catalyst can simplify recovery process of the catalyst, and able to broaden the absorption area up to visible light, so that the degradation process can be more effectively carried out by using sunlight compared with only using the ultra violet light. The composite Fe$_3$O$_4$/TiO$_2$ catalyst is very appropriately used for waste treatment industry, especially the textile industry.

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