Photocatalyst based on TiO$_2$ and its application in organic wastewater treatment using simple spray method

F D Utami$^1$, D Y Rahman$^1$, Sutisna$^1$, Kamirul$^1$, D O Margareta$^1$ and M Abdullah$^1$

$^1$Department of Physics, Faculty of Mathematical and Natural Sciences, Bandung Institute of Technology, Jalan Ganeca 10 Bandung 40132, Indonesia

$^*$Email: din@fi.itb.ac.id

Abstract. In present research, we reported a successfully coating of TiO$_2$ particle on the transparent plastic applied for photocatalyst process by spray method. This method was employed to degrade organic wastewater (Methylene Blue) under solar exposure. A total of 300 ml of blue methylene was used in the photocatalyst test. From the absorbance spectrum and the degradation rate of methylene blue, it is confirmed that the methylene blue successfully degraded about 98% in 16 hours of irradiation. The result suggests a faster rate of degradation than previously reported studies. This method was selected due to its simplicity, environmentally friendly, reasonably priced, and has the potential to continue to be developed further.

1. Introduction

Water is life. Clean water becomes the most crucial issue rising to be apprehensive particularly in developing countries including Indonesia. Based on WHO data, one of the major factors contributing to the deaths of millions of children and affecting the health of billions of people is polluted water. From the reported data, some of the issues associated with the provision of clean water include 2.3 billion people who have difficulty getting drinking water, 2.5 billion people have no major sanitation, 3900 children die due to illness resulting from unsafe water usage [1].

The dominant factor causing water contamination is the disposal of waste directly into the river without standardized process of wastewater treatment. Organic textile dye wastewater becomes the focus of concern due to its physical properties (it will be apparent even in low concentrations, below 1 ppm) [2] and its optical properties; dye reduce light penetration that can influence the life of microorganisms in water [3,4], ruin ecosystems, and produce harmful byproducts from oxidation and hydrolysis [5]. And in large quantities, it can be toxic and carcinogenic in the body [2].

Many methods of organic textile wastewater treatment have been reported, including the method of biodegradation that is using "activated sludge" [6,7] can eliminate textile dyes around 90% but have shortcomings such as the degradation rate is still low, unstable success and high cost. In addition, some dyes have a fairly complex molecular structure that might make this method has a distance to be applied [8]. Coagulation-flocculation system can also be applied in degradation insoluble organic contaminants, however, less effective for soluble organic contaminants [9]. Coagulation using aluminum inorganic sulfate salts, iron chloride and iron sulfate also produces sludge that is difficult to dehydrate; its efficiency depends on pH and has a high toxicity probability [10,11].

Recently, the Advanced Oxidation Process has appeared into a highly promising dye destructive technology. AOPs use hydroxyl radicals. There are several methods that employ hydroxyl radicals such as Fenton based, UV-based, ozone-based and photocatalyst processes [2].
Photocatalyst system is selected as an attractive choice in organic effluent treatment due to its properties. This process has been widely investigated as a promising technology for the efficient wastewater treatment since the photocatalyst is an environmentally friendly process and has considerable advantages such as the ability to destroy pollutants without the exertion of potentially hazardous oxidants (e.g. ozone, chlorine) [12]. This process can be conducted under room conditions and organic pollutants can be completely decomposed into CO₂ and H₂O [2].

Photocatalysis is a photo-induced process on the semiconductor surface by photons. This process begins with photo-excitation that can transfer electrons from the valence band to the empty conduction band. The electron-hole pairs will react to form hydroxyl radicals that hold the main role in destructive of organic dye [13].

TiO₂ technical anatase structure is chosen as an alternative semiconductor material the application of photocatalyst due to its photo-stability after repetitive catalytic cycles, high oxidation, decomposition of organic wastewater clearly, preventing the formation of undesirable byproducts, and reasonable price [14]. In addition, TiO₂ catalysts possess other properties such as thermal stability and strong mechanical properties that are immensely potential for applications in polluted water treatment using photocatalytic principles [15].

The use of TiO₂ which is dispersed directly into wastewater is efficient due to the large catalyst surface area. It increases the potential of photocatalytic reactions [16]. Meanwhile, it has limitation such as catalyst shifting process after the treatment. This post-treatment makes capital costs rise. Immobilization of TiO₂ particles on the surface of transparent material is an interesting option to eliminate post-treatment requirements. In previous works, some simple methods have been reported. Isnaeni coated TiO₂ on the surface of plastic fiber using vibration method which was then applied to organic pollutant processing [17]. Further work was reported, Aliyah et al and Sutisna et al immobilized TiO₂ on the plastic granules surface using thermal milling which was then developed with a combination of electrostatic methods [18,19]. In present work, we suggest a simple method of further improving degradation rate and photo-efficiency using spray method. The pollutant degradation has been investigated to see the catalyst performance.

2. Material and Methods

2.1. Materials
In this study, TiO₂ technical powder (density: 4.32 g cm⁻³, particle size: 166 nm, BET surface area: 7.005 m² g⁻¹, total pore volume: 9.68 x 10⁻² cc/g, crystalline structure: anatase) was used as a semiconductor catalyst obtained from Bratachem (Indonesia) [20]. This material was selected because of its affordable price. DI Water, methylene blue powder and Alcohol 95% were purchased from Sakura (Indonesia), transparent plastic (with the commercial brand: Yashica, from the local suppliers) used as a buffer material and adhesive polymer (Araldite, Alteco, G, from the local supplier).

2.2. TiO₂ Coating Process
The coating of anatase TiO₂ on the substrate surface (transparent plastic) was using spray method. This method is selected since it is simple, inexpensive, and enables fabrication in large quantities. The coating process begins by mixing the anatase TiO₂ powder and DI Water with the ratio of 5 gr : 50 mL respectively using magnetic stirrer for 30 minutes. The next step is washing the transparent mica plastic using 95% alcohol. The solution is placed in the spray equipment. In this step, parameters are optimized to obtain samples with more TiO₂ surfaces that can be in direct contact with the pollutant. The optimized parameters are the use of additional adhesive polymers (Araldite, Alteco, G glue) and spray frequency (5-20 times). Additional adhesive polymers superimposed on plastic substrates by doctor blade method.
2.3. Photocatalytic Testing

The photocatalyst test begins with design a photocatalyst reactor. The TiO$_2$/plastic sheet is formed to be a cylinder and placed into the reactor. The diameter and height of the cylinder are 2 cm and 13 cm respectively. A tubular container is used as a reactor with a diameter of 8 cm. The base side of the cylinder base is attached to the base of the reactor. The pollutant is placed outside the cylinders that there is an empty space inside of the cylinder. In this reactor, the depth of the solution is about 4 cm and 12 cm when each solution is placed up to 100 ml and 300 ml. This reactor design aims to make the incoming light more optimal to the bottom of the reactor. The empty space is intended to make the incoming light reach the bottom of the reactor. The experiments were conducted under solar exposure. Methylene blue was used as the organic pollutant. Photocatalysis effect test on methylene blue has been done with the concentration of 15 mg L$^{-1}$. To investigate the performance of the catalyst, the number of catalyst cylinder was varied from 1 to 4 cylinders in 100 ml of MB with an initial concentration of 15 mg L$^{-1}$. Furthermore, to determine the effect of the photocatalytic activity for each of the varied samples, a quantity of 300 ml MB was used with an initial concentration of 15 mg L$^{-1}$. The experiments were conducted in Bandung, Indonesia with latitude and longitude coordinates are -6.89 and 107.61 respectively. The experiments were operated from 8 A.M until 4 P.M during December 2016. To measure the photocatalytic degradation, 2 ml of solution were taken periodically. This experiment was illustrated in Fig 1.

![Figure 1. TiO$_2$/Plastic cylinder catalysts (left) and Photocatalyst test (right)](image)

2.4. Characterization of Sample and Methylene Blue Solution

UV-vis spectrometer was employed to measure the value of sample transmittance and degradation of methylene blue. The photocatalytic activity effect was investigated from degradation level of methylene blue. The degradation level was determined from the absorbance spectrum of methylene blue using a UV-vis spectrometer.

3. Result and Discussion

TiO$_2$ coating on a transparent plastic substrate using the spray method has been successfully performed. Firstly, we analyzed the transmittance spectrum of TiO$_2$-coated plastic with variation of spraying numbers as shown in Figure 2a. It proved that the transmittance of the TiO$_2$-coated plastic decreased with the increase of spraying numbers. The number of spraying affects the amount of TiO$_2$ attached to the plastic surface. The more TiO$_2$ attached to the surface, the less the transmittance value will be. The number of spraying is varied from 5 to 20 times of spraying since the spraying of more than 20 times will form a larger droplet and affect coating strength which is going to decrease due to the release of some TiO$_2$ particles under the washing process. The release of TiO$_2$ particle was revealed from the fact that the cohesion force among TiO$_2$ particle was greater than the adhesion force between TiO$_2$ and plastic substrate.
Figure 2. (a) Transmittance spectra of sample with variation of spraying numbers and (b) variation of used polymer.

Furthermore, we investigated the transmittance property of TiO$_2$-coated plastic with the addition of polymer on the surface of plastic as shown in figure 2b. Figure 2b revealed that TiO$_2$-coated plastic without polymer has higher transparency compared to polymer-coated TiO$_2$/plastic. It exhibits that less amount of TiO$_2$ particle was immobilized on the plastic surface. The addition of polymer on the surface of plastic improved the number of TiO$_2$ particles attached on the plastic surface. The presence of glue between the plastic and the TiO$_2$ has provided an adhesive force between the glue and the TiO$_2$ which is of greater value than the cohesion forces between the TiO$_2$ particles, as well as the adhesive forces between the TiO$_2$ and the plastic. This improvement of the adhesive forces, in addition to causing more bound TiO$_2$, has also increased the bond strength between the TiO$_2$ and the polymer glue (which indirectly increases the bond between the TiO$_2$ particles and the plastic surfaces). It was also confirmed after the washing process (the less TiO$_2$ released during the washing process). Figure 2b also informed us that the use of Araldite polymer has the lowest transparency since more TiO$_2$ particle attached on the surface of the plastic. From this result, we can conclude that, of the three polymeric types of glue used, the Araldite glue provides the highest bond strength with TiO$_2$.

Based on transmittance and the number of catalysts (TiO$_2$ particles) attached on the substrate, we used the sample of 10 times spraying number for the application of methylene blue degradation process. It needs a sufficient transparent sample, however, the amount of TiO$_2$ coated on the surface of mica plastic must be concerned. It is because the light intensity of the photon and the amount of catalyst coated to the substrate are the main keys that hold an important role in the photocatalytic process that can be applied to the processing of organic effluent [21]. The higher the light intensity of the photon source (in this study, the source of photons is sunlight) and the more surface TiO$_2$ that can be in direct contact with the pollutant then the organic pollutant degradation process will be faster.
Figure 3. The degradation rate of catalyst number variation using sample TiO$_2$ and adhesive polymer (Alteco) with spray frequency is 10 times in 100 ml of MB with concentration 15 mg L$^{-1}$.

Photocatalysts were tested to see the effect of the amount of catalyst in the photocatalyst process with 100 mL of MB solution 15 mg L$^{-1}$ (Fig. 3). The number of sample cylinders containing the coating TiO$_2$ is varied from 1 to 4 cylinders. Figure 3 exhibits the difference in the value of the decreasing of MB concentration is impacted by the variation in the number of catalyst cylinders (1 to 4 catalyst cylinders). The improvement of the degradation ability of MB solution occurs with increasing the amount of catalyst used. It is caused due to an increase in the amount of catalyst used will extend the catalyst in contact directly with contaminants. After 5 hours exposure, the MB compound was decomposed completely.
Figure 4. (a) Degradation levels & Absorbance Spectra of Methylene blue 15 mg L\(^{-1}\); volume 300 mL; (b) control; (c) TiO\(_2\) without polymer and spray 10 times; (d) TiO\(_2\) spray 10 times + Araldite; (e) TiO\(_2\) spray 10 times + Alteco; (f) TiO\(_2\) spray 10 times + G glue.

To see the effect of the adhesive polymer (Araldite, Alteco, G glue) on the performance of the photocatalyst activity, the test was performed using MB solution under the sun exposure. Unlike the amount of solution that was previously tested only 100 ml, in this test more volume of 300 ml of MB were used to see if the performance of the catalyst is still optimal enough to be able to compare it with the previous work (Figure 4). The cylindrical sample used was 10 spray samples. The degradation of MB solution due to the photocatalytic process can also be seen from the absorbance spectrum of methylene blue using the UV-vis instrument shown in Figure 4. It can be observed that the extent of irradiation time affects the process of degradation of MB. The increasing the irradiation time the greater the degradation of MB solution. It is marked by the change in the solution color from blue to clear which indicates the concentration of MB in the solution was reduced. The concentration of methylene blue in the solution is also marked from the absorbance value of the solution. The longer the irradiation time, the methylene blue absorbance spectrum decreases and the methylene blue absorption peak is shifting towards the lower wavelength. The methylene blue absorption spectrum is about 663-664 nm. This phenomenon can be explained by the hypsochromic effect caused by demethylation process on the N-methyl group of MB resulting in changes in the structure of MB [20, 22, 23].

From the absorbance spectrum and the level of blue methylene degradation during 4 days of irradiation, it appears that methylene blue successfully degraded close to 100% in 16 hours or 2 days of irradiation. When compared with previous studies by Nirmala and Subiyanto, each degraded 15 mg L\(^{-1}\) of 200 mL of methylene blue and 150 mL in 8 days and 7 days of irradiation under solar exposure [24,
25]. Aliyah conducted a photocatalyst test at 2.6. $10^5$ M or about 8,3161 mg L$^{-1}$ methylene blue as much as 250 mL and successfully degraded close to 100% in 4 days of irradiation [18]. Sutisna succeeded in degrading the organic methylene blue waste model with the concentration of 40. $10^4$ M or about 12,794 mg L$^{-1}$ in 4 days of irradiation [19]. It can be shown that the results of this experiment have increased the photocatalytic effect seen from the increased degradation rate.

4. Conclusion

Successful coating of anatase TiO$_2$ powder has been applied on a transparent plastic substrate using a simple spray method. Based on transmittance and the number of catalysts (TiO$_2$ particles) attached to the substrate, the optimal degradation result is a TiO$_2$-coated plastic with Alteco polymer. The more TiO$_2$ particles found on the surface allows more TiO$_2$ in direct contact with the pollutant then the organic pollutant degradation process will be faster.

References

[1] WHO/UNICEF 2014 UN-Water Global Analysis and Assessment of Sanitation and Drinking-Water (GLAAS) 2014 : Investing in Water and Sanitation : Increasing Access, Reducing Inequalities Geneva

[2] Zangeneh H, Zinatizadeh A A L, Habibi M, Akia M and Isa M H 2015 J. Ind. Eng. Chem. 26 1-36

[3] Borker P and Salker A V 2006 Mater. Sci. Eng. B 133 55-60

[4] Zheng Z, Levin R E, Pinkham J L and Shetty K 1999 Process Biochem. 34 31-37

[5] Farouk H U, Raman A B A and Daud W M A W 2016 J. Ind. Eng. Chem. 33 11-21

[6] Kapdan I K and Kargi F 2002 Process Biochem. 37 973-981

[7] Pala A and Tokat E 2002 Water Res. 36 2920-2925

[8] Sanghi R and Bhattacharya B 2002 Color. Technol. 118 256-269

[9] Allegre C, Moulin P, Maissier M and Charbit F 2006 J. Membr. Sci. 269 15-34

[10] Renault F, Sancey B, Badot P M and Crini G 2009 Eur. Polym. J. 45 1337-1348

[11] Teh C Y, Budiman P M, Shak K P Y and Wu T Y 2016 Ind. Eng. Chem. 55 4363-4389

[12] McCullagh C, Robertson P K J, Adams M, Pollard P M and Mohhamed A 2010 J. Photochem. Photobiol. A 211 42-46

[13] Fujishima A, Rao T N and Tryk D A 2000 J. Photochem. Photobiol. C: Photochem. Rev. 1 1-21

[14] Xikong L, Kongreong B, Kantachote D and Suithisripok W 2010 Energy Res. J. 1 120-125

[15] Chong M N, Jin B, Chow C W K and Saint C 2010 Water Res. 44 2997-3027

[16] Mehos M S and Turchi C S 1993 Environ. Prog. 12 194-199

[17] Isnaeni V A, Arutanti O, Sustini E, Aliyah H, Khairurrijal and Abdullah M 2013 Environ. Prog. Sustainable Energy 32 42-51

[18] Aliyah H, Aji M P, Masturi, Sustini E, Budiman M and Abdullah M 2012 Am. J. Environ. Sci. 8 280-290

[19] Sutisna, Rokhmat M, Wibowo E, Murniati R, Khairurrijal and Abdullah M 2015 Adv. Mater. Res. 1112 149-153

[20] Sutisna, Rokhmat M, Wibowo E, Murniati R, Khairurrijal and Abdullah M 2017 Environ. Nanotech. Monitoring and Management 8 1-10

[21] Rajeswari R and Kanmani S 2009 Iran J. Environ. Health. Sci. Eng. 6 61-66

[22] Castillo N C, Heel A, Graule T and Pulgarin C 2010 Appl. Catal. B 95 335-347

[23] Slimen H, Houas A and Nogier J P 2011 J. Photochem. Photobiol. A Chem 221 13-21

[24] Nirmala S S 2013 Fabrication of Nylon Fiber as Photocatalyst Material Coated with Titanium Dioxide and Its Application for Wastewater Purification, Final Project Undergraduate, Institut Teknologi Bandung

[25] Subiyanto H 2010 Water Purification of Liquid Textile Wastewater Model Using TiO2 Photocatalyst Coated on Transparent Fiber Material, Final Project Undergraduate, Institut Teknologi Bandung