Immobilization of TiO$_2$ on transparent plastic and its application in photocatalytic wastewater treatment

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Abstract. A simple spray-coating method of immobilized TiO$_2$ particles on the transparent plastic has been successfully applied in a photocatalytic wastewater treatment process. This method was initiated with a coating of adhesive polymer on plastic using doctor blade technique followed then by a spray-coating process of titania. The photocatalytic activity of the TiO$_2$-coated plastic sheets were tested with the decomposition of Methylene Blue (MB) under solar exposure. Eight layers of the coated sheets have the most powerful degradation effect of about 99% after 6 hours of irradiation. The reusability of the titania coating has also been investigated and still has a powerful photodecomposition ability of removing 98% of the MB compound.

1. Introduction

Lately, organic wastewater has served one of the critical problems due to its increasing concentration and impact on the environment [1]. It led many researchers to develop methods of managing the organic waste. Various methods of organic wastewater treatment have been declared, including biodegradation [2], adsorption [3], activated-carbon [4,5], filtration [6], and coagulation [7]. Those conventional methods still have some drawbacks, such as high cost, the use of hazardous chemicals, incomplete destroying of the contaminant, the formation of toxic secondary product that can endanger health and the impact on the environment. Therefore, a better approach is needed to select the appropriate method of organic waste destruction technology. The developed method focuses on environmentally friendly, easy methods with less energy consumption, safe and low cost [8].

Ultimately, many researchers consider Advanced Oxidation Processes system as a very promising method to deal with organic wastewater. The AOPs method relies on greatly reactive radical species, especially hydroxyl radicals that are activated by solar energy or other energy sources. There are various methods including AOPs such as photolysis, fenton based, ozone-based and photocatalysis [9]. An attractive part of using AOPs is its highly potent and greatly oxidizing radical that would enable us to destroy various organic pollutants with no selectivity.

The photocatalysis process of semiconductor has been received to be a powerful technology in organic effluent destroying. The process is more effective among these AOPs due to an environmentally friendly action, low-cost, and entirely mineralize the organic contaminants [9]. Photocatalysis is an acceleration of the photoreaction process on the surface of semiconductor forming the electron-hole pairs. The reactive radical species can be generated from the electron-hole pairs and react with the contaminants [10].
TiO₂ photocatalysis is selected to be a powerful semiconductor material. Several attractive features of TiO₂ are its photostability after reusable photocatalytic process, preventing the formation of secondary pollution, high oxidation, and reasonable cost [11]. The use of directly dispersed TiO₂ in the suspension is quite efficient since the catalyst surface area reacts widely with the pollutant [12]. However, until now these mechanisms are still experiencing some technical challenges and still being developed. Separation of TiO₂ catalyst from the solution after treatment remains a major obstacle because of the high-cost requirements. Immobilization TiO₂ onto transparent supports can be utilized as an attractive solution to solve the problem.

Previously, several convenient methods have been declared. TiO₂-immobilized plastic fibers using the vibration technique have been successfully applied in organic pollutant processing [13]. Beforehand, the transparent plastic substrate has been effectively used in the graphite powder coating process mechanically [14]. Immobilization TiO₂ onto transparent supports using thermal milling technique has also been reported [15,16]. Here, we propose a facile method to increase the photocatalytic rate using spray method. The catalyst performance was investigated from photocatalytic activity in pollutant destroying process.

2. Material and Methods

2.1. Materials

In this study, the solid buffer material used was transparent plastic (local suppliers; Indonesia). TiO₂ technical powder (density: 4.32 g cm⁻³; crystalline structure: anatase; Bratachem) was used as a semiconductor catalyst. This material was chosen because of its affordable price. DI Water, Alcohol 95%, Methylene blue powder were obtained from Sakura (Indonesia), and adhesive polymer (Alteco) was purchased from the local supplier.

2.2. Spray Coating of Substrates

Anatase TiO₂ powder (5 gr) was added to 50 mL of DI Water and mixed using magnetic stirrer in 30 minutes. The substrate was washed by alcohol 95%. The substrate is limited to using an insulating adhesive plaster to leave an open area to be coated (20 cm²). Before spraying TiO₂, the substrate is coated with an adhesive polymer by doctor blade technique. The uncovered area was then coated by spraying the solution onto the plastic substrate. The TiO₂-coated plastics were dried in room atmosphere. This procedure is repeated until the TiO₂ layer appears uniform on the substrate. Based on the previous work, the optimum sample is TiO₂-coated plastic with spray number of 10 times and the plastic was initially coated with adhesive polymer (alteco).

2.3. Photocatalytic Testing

The photocatalyst tests were conducted under solar irradiation. Previously, we built a photocatalyst reactor. The diameter of reactor was 6 cm. The TiO₂-coated plastic sheet is placed in the reactor vertically. Methylene blue was used as organic pollutant model. Based on ISO 10678 of 2010, MB was used in this photocatalytic test due to its high molar absorption, high color purity (> 90%), drastic color change (From blue to dark caused by broken coloring conjugation due to photooxidative process), non toxic, and high rate decomposition in the water [17]. Photocatalysis effect test on methylene blue has been done with the concentration of 15 mg L⁻¹. The photocatalytic effect was investigated by determining the MB concentration. MB concentration is highly related with absorbance spectrum of the solution. From comparing the absorbance peak before and after irradiation, we can measure the degradation rate of MB by calculating the concentration fraction. To find out the catalyst performance, the number of catalyst sheet was varied from 2 to 16 sheets. Here, a total of 100 mL of MB with an initial concentration of 15 mg L⁻¹ were used. Furthermore, to determine the impact of MB initial concentration toward the degradation rate, we performed photocatalyst test with different MB concentration i.e 15 mg L⁻¹, 30 mg L⁻¹, dan 45 mg L⁻¹. The experiments were undertaken from 8 A.M until 4 P.M during May-July 2018 in Bandung, Indonesia with latitude and longitude coordinates are -6.89 and 107.61
respectively. The sample was examined every one hour to measure the absorbance of MB. The photocatalyst test was illustrated in Fig 1.

![Figure 1. Photocatalyst reactor design](image)

2.4. Characterization of Sample and Methylene Blue Solution
The transmittance and absorbance spectrum of MB solution were determined by UV-vis spectrometer. The photocatalytic activity effect was characterized by degradation level of MB solution. The type of UV-Vis spectrometer is an ocean optic USB2000 spectrometer.

3. Result and Discussion
After the coating process, the TiO$_2$-coated film was then characterized to see its optical transmittance using UV-Vis spectrometer. Figure 2 shows the transmittance spectrum of uncoated plastic and TiO$_2$-coated plastic. The transmittance spectrum of plastic decreased with the presence of TiO$_2$ coated on the surface of the plastic. It is due to the interference and the scatter of light. The transmittance decrease since the light was scattered by the rough surface of TiO$_2$ layer deposited on the substrate [18]. It simultaneously confirmed that TiO$_2$ has been well deposited on the surface of the plastic.

![Figure 2. Transmittance spectra of plastic (blue curve), and TiO$_2$-coated plastic (red curve).](image)
Furthermore, we examined its photocatalytic activity to obtain the film performance after being coated with TiO$_2$. The film was TiO$_2$-coated plastic with spray number of 10 times and the plastic was initially coated with adhesive polymer. Six sheets of catalyst were located vertically in the reactor containing 100 ml MB 15 mg/L.

Figure 3 exhibits the decrease of MB absorbance with catalyst and without catalyst. The decrease of absorbance is strongly related to the decrease of MB concentration in the solution. It appears from the graph that the degradation of MB occurs faster due to the presence catalyst which is activated by the photon. The amount of degraded pollutants increase with the duration of irradiation under the solar exposure. After 6 hours irradiation, 99% of pollutants were successfully degraded. The catalysts have a powerful degradation impact when they can absorb more photon which can transfer the electrons into conduction band generating electron-hole pairs without recombination. The pairs of e$^-$/h$^+$ react directly with water and oxygen, generating superoxide anion radicals and hydroxyl radicals then available for the oxidation-reduction processes. they act as powerful reductant and oxidant element, respectively, therefrom further aid in degradation processing [19]. Previous reports by Nirmala and Subiyanto, methylene blue has been successfully degraded 15 mg L$^{-1}$ of 200 mL after 8 days and 150 mL after 7 days of irradiation, respectively [20, 21]. It states that the photocatalytic effect increases compared previously.

![Figure 3](image)

**Figure 3.** Absorbance Spectra of Methylene blue 15 mg L$^{-1}$ 100 mL (a) without catalyst and (b) with catalyst.

Once we see that the catalyst can work well, the influence of number of coated plastic on the photoactivity performance was also investigated. The photocatalyst activity increased with the increase of catalyst sheet used which was varied from 0-16 sheets. The photocatalyst activity reached optimum condition using 8 sheets of catalyst. The use of catalyst sheets more than 8 returned the photodegraded performance down (Figure 4). The increase was caused by the increase of catalyst surface contacted directly with the pollutant. The catalyst was activated by the photons generating more electron-hole pairs. The two main factors playing the role here, the essential parts in the photocatalytic mechanism, namely: the light intensity of the photon and the amount of catalyst coated to the substrate [22]. The greater the intensity of the light from the photon source, the greater the TiO$_2$ surface that can be in direct contact with the contaminant, so that the photocatalytic process of organic pollutants will be faster. These explained why the photo-activation reached the optimum condition with the increase of catalyst sheets and returned down when catalyst sheet more than eight. The coming light can’t penetrate the catalyst sheets of more than eight which make the electron-hole recombined.
The initial concentration influence of MB on the kinetic rate of photocatalyst reaction has been investigated (figure 5). The elevated initial concentration will cause the degradation process of MB longer. It is stated by the kinetic rate which obtains lower with the rise of effluent concentration. It can be explained that the higher concentration MB in the solution, the more bonds of MB structure should be broken. Besides, high MB concentration doesn’t let the light penetrate to the bottom of the reactor and decrease photocatalytic activation efficiency. From Figure 2-5, it can be interpreted that the correlation of the irradiation time was directly proportional to the major effect of MB degradation. The longer the irradiation time the higher the eliminating of methylene blue. The higher the number of photons absorbed, the greater the quantity of OH· produced, so that the probability of interaction between the catalysts and the contaminants elevates, leading the degradation efficiency raise [22].
In addition, the performance test of the catalyst in various pollutant concentrations was enriched with further test. The reuse of the catalyst has also been investigated through repeated use. Each repetition cycle is carried out during 6 hours of irradiation. In this work, we try to test it repeatedly for 7 times. Figure 6 shows that the catalyst still has a powerful photo-decomposition of skills by eliminating 98% of the MB compound. It decreased only 1.6% from the first using.

4. Conclusion
We have successfully coated TiO$_2$ on transparent plastic substrate using simple spray method. The more TiO$_2$ particles deposited on the surface allows more TiO$_2$ in direct contact with the pollutant and the great light intensity of photon to activated the catalyst then the organic pollutant degradation process will be faster. Since the method was quite easy and inexpensive, it deserved to be proposed as future photocatalyst technology. Although this method produced faster photoactivation compared to the previous method, it still has a space to be improved easier and faster in the future.

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