Photocatalytic Decolorization of Acid Red 4 Azo Dye by Using Immobilized TiO2 Microparticle and Nanoparticle Catalysts

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Abstract

This research studied the synthesis of immobilized TiO2 microparticle and nanoparticle catalyst materials and evaluated its photocatalytic activity on the decolorization of Acid Red 4 (AR4) azo dye solution. TiO2 microparticles were immobilized on an acrylic plate, while TiO2 nanoparticles were immobilised on a glass plate. TiO2 nanoparticles were embedded in a nanofiber support layer to enhance photocatalytic performance, forming a nanofiber-nanoparticle composite on the glass plate. In the catalyst load 2.0 g/l, the performance of the photocatalytic layer of immobilized catalyst ($k'$ = 0.013/min) was better than that of the suspended catalyst ($k'$ = 0.008/min). Photocatalytic decolorization efficiency of TiO2 immobilized catalysts of nanoparticle sized reached 82.3% in irradiation time of 2 hours, which was higher than microparticle sized catalysts (77.8%). The technique of TiO2 nanofiber–nanoparticle composite showed improved photocatalytic kinetics ($k'$ = 0.018/min) compared to a single layer of nanoparticle catalyst ($k'$ = 0.015/min). Immobilized TiO2 catalysts remain effective with repeated use despite a slight decrease in processing efficiency.

Keywords: azo dye, decolorization, photocatalytic, TiO2, wastewater

1. Introduction

The textile industry is one of the largest contributors of waste water in Indonesia. Specific characteristics of textile wastewater are high quantity and color content, especially from dyeing and finishing processes. Approximately 1-20% of dyes that do not fixed to the material will be carried away in textile wastewater [1]. Nowadays the class of azo dyestuffs is very commonly used in textile processing due to its several advantages, but the product also has the potential for contamination if its waste becomes an aromatic compound that is hazardous in water bodies [2-3]. Besides the existence of color in wastewater being aesthetically unacceptable, it blocks penetration of sunlight on water bodies and is relatively non-biodegradable in nature and in wastewater treatment plants (WWTP). Decolorization processing using methods of coagulation, adsorption and filtration has proven to be effectively capable of removing color substance in wastewater [4-6]. However,
those methods above simply separate contaminants without breaking down the dye compound, leaving the problem of sludge.

Photocatalytic degradation is an advanced oxidation process on color in wastewater using a photocatalytic reaction from a catalyst material, activated by UV irradiation. Generally the material is a metal oxide semiconductor, of which TiO$_2$ is one of the most widely studied. Oxidative species produced can break down dye molecules rapidly and effectively, so it is very suitable to apply in the treatment of colored textile wastewater. The photocatalytic treatment method has a number of advantages such as: rapid reaction, no sludge production, reusable and relatively economical cost [7-8]. The TiO$_2$ suspended particles method has been proven effective in photocatalytic wastewater treatment, but the application has difficulty in separating the catalyst particles. As a solution, TiO$_2$ catalysts were immobilized on media such as glass [9], polymer [10], activated carbon [11] and zeolite [12]. Increasing the active surface area of the catalyst to anticipate the effect of immobilization can be achieved through the use of transition metal doping [13], or through applying nanosized catalysts like nanoparticles and nanofibers. This paper contains the results of photocatalytic research on the use of immobilized TiO$_2$ microparticle and nanoparticle in the decolorization of colored textile wastewater.

2. Methods

Research materials. Materials used in the synthesis of TiO$_2$ immobilized catalysts were: anatase TiO$_2$ microparticles (Brataco), chloroform, titanium tetraisopropoxide, zinc acetate, polyvinyl acetate, acetic acid, ethanol and nitric acid (Merck), and silicone rubber sealant (Klebermann). The dye used was Acid Red 4 (Sigma Aldrich). All experiments performed used demineralized water (Brataco). The immobilization media used was acrylic plates (4 mm thickness) and glass plates (2 mm thickness).

Preparation for synthesis of catalyst. TiO$_2$ microparticle layers were immobilized on acrylic fiber plates with a size of 80 mm x 40 mm x 4 mm.

Immobilization of the catalyst was performed using the method of coating TiO$_2$ microparticles on the acrylic surface. TiO$_2$ microparticles were mixed with 70% ethanol (4-5 drops) on the surface of the fiber plate then spread out evenly. A total of 4-5 drops of chloroform was dropped onto a layer of microparticles to stabilize the TiO$_2$ adhesion layer on the fiber plate.

TiO$_2$ nanoparticle catalyst layer on the surface of a glass plate measuring 25 mm x 65 mm x 2.5 mm was used as the immobilization medium using the method of dip coating a glass plate in a solution of sol-gel TiO$_2$ nanoparticles. 3.5% of TiO$_2$ sol-gel solution was made with the composition: 58.6 g titanium tetraisopropoxide, 200 mL of ethanol and 100 ml of 50% nitric acid, and stirred rapidly for 18 h. The glass plate attached to the TiO$_2$ nanoparticles was heated at a temperature of 80°C for 1 h, followed by calcination at a temperature of 500°C for 60 min, to convert the catalyst layer into the crystalline phase.

TiO$_2$ nanofiber was made using electrospinning (Eltekindo, Indonesia) and then attached onto the surface of glass plates measuring 25 mm x 65 mm x 2.5 mm as the immobilization media. Nanofiber was made applying optimum electrospinning operational conditions as follows: voltage 20 kV, flow rate 4 ml/h, nozzle size 16 and distance of spinneret-collector at 15 cm. The electrospinning solution was made with the composition: titanium tetraisopropoxide precursor (20%), polyvinylacetate (20%), acetic acid (10%) and ethanol (50%). The TiO$_2$ nanofiber layer on the glass plate was coated with silicone rubber and calcined at a temperature of 500°C for 60 min. The TiO$_2$ nanofiber-nanoparticle composite was made by dipping (dip coating) the glass plate with nanofiber attached into TiO$_2$ nanoparticle sol-gel solution. TiO$_2$ composite on the glass plate medium was heated at a temperature of 80°C for 1 h, followed by calcination at a temperature of 500°C for 60 minutes.

Photocatalytic experiments. Photocatalytic decolorization experiments were performed on a laboratory scale horizontal batch photoreactor, volume 1000 cm$^3$, using three UV-C 15 watt lamps (Vilber Lourmat) with a wavelength of 245 nm (Figure 2).

Catalyst-coated glass plates were arranged horizontally at the bottom of the wastewater tank (400 mm x 100 mm x 25 mm). It was stirred with a magnetic stirrer and circulated by a peristaltic pump used for the homogenizing.

Figure 1. The Chemical Structure of Acid Red 4 Azo Dye

Figure 2. Photoreactor Scheme

and aeration of wastewater during the experiment. Simulated wastewater was made by heating a dye solution at a temperature of 90 °C stirring for 30 min (fixation), and then allowing it to stand for 12 hours at room temperature (hydrolysis). In each photocatalytic degradation experiment, the wastewater and catalyst-coated glass plate was first left in the dark for 1 hour to obtain adsorption-desorption equilibrium. Optimal photocatalytic experiments have previously been done by the author [14], optimum conditions include the application of pH 11, concentration of catalyst 2 g/l and \( \lambda_{\text{max}} \) at 510 nm.

**Reaction kinetic.** Pseudo first-order equation of the Langmuir-Hinshelwood (Equation 1) is used to calculate color degradation rate [9].

\[
\ln \left( \frac{C_0}{C} \right) = k'Kt = k't
\]

Where, \( C_0 \) is the initial color concentration (mg/l), \( C \) is the color concentration at time of \( t \) (mg/l), \( t \) is the irradiation time, \( k' \) is the decolorization rate constant (/min), \( k \) is the rate of reaction constant (/min) and \( K \) is the adsorption coefficient (l/mg).

**Characterization and analysis.** Characterization of the structure and morphology of immobilized TiO\(_2\) microparticles and nanoparticles were taken by image acquisition using SEM/scanning electron microscope (JEOL, JSM 6360 LA). Absorbance measurements for dye concentration analysis were performed using spectrophotometer UV-Vis (Perkin Elmer Lambda 35). pH measurements were taken with a pH meter (SchootGeräte Handylab 1).

### 3. Results and Discussion

**Photocatalyst characteristics.** SEM images of the TiO\(_2\) microparticles and nanoparticles immobilized on the media are shown in Figures 3a-3b. SEM images show the fiber diameter ranges of TiO\(_2\) microparticles between 1-10 μm and TiO\(_2\) nanoparticles between 50-100 nm. The TiO\(_2\) nanofiber-nanoparticle composite (Fig. 3c) shows fiber diameter between 200 nm and 500 nm and a solid attachment to the TiO\(_2\) nanoparticles. Catalyst distribution per unit area of the microparticle layer of the immobilization media was determined in the synthesis process of the immobilization media was determined in the synthesis process of the immobilization layer on top of the fiberplate at 6.25 mg TiO\(_2\)/cm\(^2\). The TiO\(_2\) nanoparticle layer was formed quite densely after dip coating process repeated by 5 times. Based on the gravimetric calculation, the TiO\(_2\) mass that attaches to the media in each repetition of nanoparticle coating was as much as 0.43 mg TiO\(_2\)/cm\(^2\). Merging the TiO\(_2\) mass with nanofiber and nanoparticle can determine the mass distribution of TiO\(_2\) in the composite catalyst to be as much as 4.26 mg TiO\(_2\)/cm\(^2\).

**Effect of catalyst immobilization.** Catalyst concentrations on photocatalytic processes using suspended and immobilized catalysts can influence photocatalytic activity differently. In the use of suspended catalysts (Figure 4), photocatalytic decolorization efficiency reaches optimum catalyst concentration of 0.5 g/l with \( k' \) of 0.018/min and achieved 87% decolorization within 2 hours of irradiation.

The addition of catalyst concentration up to 2 g/l actually lowered the decolorization efficiency \( (k' \) of 0.008/min). Using immobilised catalysts (Figure 5), the addition of catalyst concentration can improve decolorization efficiency. In a catalyst concentration of 2 g/l, 78% decolorization was achieved with \( k' \) at 0.013/min.
This data confirms that an increase of catalyst concentration in the suspension catalyst is not proportional to an increase in photocatalytic performance. Table 1 shows that the decolorization kinetic constant (k') from the suspended catalyst shows optimal decolorization efficiency at low catalyst concentrations (0.5 g/l). The results of other studies [2,15,16], suggest similar results, and can be explained by the fact that in high catalyst concentrations, the microparticles in the color solution tend to cause turbidity. This turbidity causes inhibition of UV photons from the light source toward the catalyst particles, thereby reducing the effectiveness of the photocatalytic reaction.

Increase of catalyst concentration for immobilized catalysts correlates with increased photocatalytic performance (Table 1). This can occur in immobilized catalysts because the additional catalyst mass does not hinder photons on the catalyst particles as it does in the suspension catalyst. However, the effect of increased catalyst concentration on photocatalytic performance is not linear because at higher concentrations part of the catalyst particles can be covered by other surface particles.

**Application of nanoparticle and nanofiber composite.**

One effort to improve the efficiency of photocatalytic reaction is to reduce the catalyst particle size of microparticles into nanoparticles. The composite method aims to increase the performance of photocatalytic nanoparticles by providing a nanofiber base to attach onto. Effect of changes in particle size and the use of the catalyst composite method on AR4 decolorization through adsorption and photocatalytic reactions are shown in the UV-Vis spectra graph in Figure 6. The UV-Vis absorbance spectra graph of AR4 at wavelength range 200-700 nm shows a maximum absorbance peak at wavelength 510 nm (λ_{max}).

Based on the difference in absorbance peaks at λ_{max}, the variations of catalyst particle size has a relatively small effect on the efficiency of decolorization by adsorption, with percentages of decolorization on microparticle, nanoparticle and composite catalysts respectively at

<table>
<thead>
<tr>
<th>Concentration of catalyst (g/l)</th>
<th>Suspended k' (/min)</th>
<th>Immobilized k' (/min)</th>
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<tr>
<td>0</td>
<td>0.005</td>
<td>0.005</td>
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<tr>
<td>0.5</td>
<td>0.018</td>
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<td>1</td>
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<td>2</td>
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**Figure 6.** UV-Vis Spectra Graph on the Adsorption Effects (1 Hour) and the Photocatalytic Reaction (2 Hours) on Decolorization of AR4 by Using Immobilized Microparticle, Nanoparticle and Nanofiber–Nanoparticles Composite Catalysts (AR4 Conc.: 10 mg/l, Catalyst Conc.: 2.0 g/l, pH 11, MP: Microparticle, NP: Nanoparticle, C: Composite)
1.3%, 1.9% and 3.2%. After going through a photocatalytic irradiation process for 2 hours, the variations of catalyst particle size showed a significant difference in decolorization efficiency by a considerable margin. Percentage of decolorization achieved in the photocatalytic process using microparticle catalysts, nanoparticle catalysts and composites amounted to 77.8%, 82.3% and 88.6% respectively.

Percentage of decolorization based on intervals in the photocatalytic process using three types of catalysts is shown in Figure 7. In addition to the photocatalytic reaction, decolorization also occurs as a result of UV photolysis (without catalyst) at a decolorization rate of \( k' \) at 0.005/min, until it reached approximately 48% color removal within 2 h of irradiation. In a 2 h photocatalytic process, the composite catalyst also shows better kinetics \( (k' = 0.018/min) \) compared to microparticle \( (k' = 0.013/min) \) and nanoparticle \( (k' = 0.015/min) \).

Decolorization performance of the catalyst in the photocatalytic processes related to effective surface area and the difference in pore structure of the catalyst layer on the surface of the glass [17-18]. Based on SEM images it appears that the pore structure of the TiO\(_2\) microparticle coating has micropores and the structure of the nanofiber layer has nanopores. Micropore structure allows the adsorption of dye molecules faster than nanopore structures that require a longer time to diffuse. But nanopore structure is able to provide greater surface area allowing for a more effective photocatalytic reaction to take place. A greater semi-conductor surface area causes the process of photoexcitation electrons to be more intensive, resulting in more oxidative species that play a major role in the degradation of organic dyes [7-8].

The TiO\(_2\) nanofiber-nanoparticle catalyst composite has micropore and nanopore structures so it can produce a combination of both the phenomena described above.

The photocatalytic process that takes place in the catalyst composite is more effective due to the greater contact surface area supported by the rapid adsorption of organic molecules on the layer structure of the catalyst composite.

**Decrease in catalyst performance after repeated use.**

A decrease in immobilised catalyst performance (TiO\(_2\) microparticle, TiO\(_2\) nanoparticle and TiO\(_2\) composite) after repeated use in the photocatalytic process after 3 times repetition (duration 2 h) is shown in Figure 8.

A decreased performance of photocatalytic decolorization is shown by the change in kinetic reaction and decolorization efficiency. The experiment results showed that after 3 times reuse of microparticle catalyst there was a decrease in \( k' \) from 0.013/min to 0.010/min with an average decrease in decolorization percentage of 4.5% in each iteration process. Nanoparticle catalysts \( k' \) changed from 0.015/min to 0.012/min with an average decrease in decolorization efficiency of 4.2%. Using the composite catalyst, \( k' \) went from 0.018/min to 0.017/min with an average decrease in decolorization efficiency of 0.7%.

The composite catalyst was able to maintain photocatalytic decolorization performance better than the microparticle and nanoparticle catalysts. This is made possible by a stronger composite structure which is supported by a nanofiber layer so as to better maintain the attachment of particles to the immobilizing media. In other photocatalytic studies [19-21], some kinds of composite polymer materials are also reported to increase decolorization performance significantly. Loss in performance is caused by the adsorption of organic material in the micropore and nanopore surface of the catalyst layer, causing a small part of the catalyst’s active surface become covered. Covered parts of the photocatalyst surface area leads to less production of hydroxyl radicals from the photocatalytic reaction rate causing photon inhibition that gradually reduces performance. Calcination at 500 °C for 60 min heat would theoretically eliminate the residual organic which

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Figure 7. Photocatalytic Decolorization of AR4 Dye Wastewater by Using TiO\(_2\) Immobilized Catalyst (AR4 Conc.: 10 mg/L, Catalyst Conc.: 2.0 g/L, pH 11)

Figure 8. Decrease in Photocatalytic Decolorization Efficiency after Repeated Use of the Catalyst (AR4 Conc.: 30 mg/L, Catalyst Conc.: 2.0 g/L, pH 11)
covered nanoparticles and composite layers on glass plates, while the remaining organic layer on acrylic plate microparticles can be rinsed with low concentrations of ethanol.

4. Conclusions

TiO₂ microparticle, TiO₂ nanoparticles and TiO₂ nanoparticle-nanofiber composite catalyst layers have been successfully immobilized on acrylic plates and glass plates media. The suspended particle catalyst in the amount of 0.5 g/l proved to be effective, but the immobilized particles catalyst showed improved performance at higher amount of catalyst. The reduced size of immobilized TiO₂ became nanoparticle catalyst able to increase TiO₂ photocatalytic decolorization activity compared to the immobilized microparticle sized catalyst. Efforts to improve the photocatalytic decolorization performance of nanoparticle catalyst via development of TiO₂ nanoparticle-nanofiber composite were quite successful when compared to a single layer of nanoparticle catalyst. However, photocatalytic degradation of organic compounds still needs to be further studied to determine final product degradation. Immobilized TiO₂ catalysts remain effective in repeated use despite a slight decrease in processing efficiency.

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