Optimization of UV light source conditions for photocatalytic activity of methyl orange using TiO₂

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Abstract. Methyl orange is one of the azo compounds which carcinogenic and damages the water system if untreatted properly. This compound is used in the textile industry as a coloring agent. Dyestuff waste produced from the textile industry is generally a non-biodegradable organic compound, which cause environmental pollution, especially at the aquatic environment. As organic waste, it is necessary to treat this compound to be harmless and safe for the environment. One of the method to remove dye waste is by using photocatalytic reaction using TiO₂ as semiconductor. In this study, optimization of UV light source conditions of the photocatalytic reaction was carried out inside a photoreactor system using TiO₂ synthesized by hydrothermal method. Optimization of the distance of UV lamps from the surface of methyl orange solution and UV lamps power has been done under the artificial UV light sources with 254 nm wavelength. The percentage of degradation was determined by measuring the absorbance of methyl orange solution before and after degradation using UV-Vis spectrophotometer. It shows that the optimum photocatalytic activity for the distance of UV lamps and UV lamps power is 20 cm and 20 Watt respectively. Physically, there was color changing during the reaction from orange to colorless.

1. Introduction
The textile industry has recently been growing rapidly because clothing is a primary need for humans. The development of this industry has a negative impact on pollution water, because the dyeing process waste containing dye from the industry is discharged into rivers thus changing the quality of the water. The textile industry that does not have good waste treatment can have an impact on environmental pollution [1,2], specially the process of dyeing and staining when the dyed waste is just thrown away without any more processing. One of the methods of treating waste from the dyeing process in the textile industry is to use a photocatalyst [3,4,5]. The semiconductor material that can be used as a photocatalyst is TiO₂, whose structure and characteristics can be changed. Photocatalyst is defined as a compound whose function is to accelerate a chemical reaction which is activated by photon absorption. The compounds that are used as photocatalysts are semiconductors with various types. Photocatalyst semiconductors have come to the fore over the past three decades as solutions to environmental and energy problems. The semiconductor materials that are usually used as photocatalyst compounds are ZnO [6], Fe₂O₃ [7], CdS [8], ZnS [9], SnO₂ [10], WO₃[11], Al₂O₃[12], Ag₃PO₄[13] and BiOCl[14]. The ideal photocatalyst is one that is stable to light, does not react chemically, and can be provided at an inexpensive price [15]. The photocatalytic process has great potential as an inexpensive technology that
is good for the environment and is compatible with the concept of zero waste. This means that this technology is environmentally friendly and produces reaction products that are not dangerous. One of the semiconductor materials that is most often used as research material as a photocatalyst recently is TiO$_2$ because of its stable nature to treat pollutants and organic waste. In addition, TiO$_2$ has advantages to be photocatalyst because it has high photocatalytic activity, excellent stability on physical and chemical, low cost, non-corrosive, nontoxicity and reusability [16,17]. Reactions involving photocatalytic compounds are called photocatalytic reactions. The basis of photocatalysis is photoexitation as a result of absorption of radiation. Photocatalyst technique is a photochemical process combined with an integrated catalyst to carry out a chemical reaction. This chemical reaction takes place on the surface of the photocatalyst material involving light source which comes from photons with certain energy. In other words the process photocatalysts can decompose compounds with the help of light. Basic mechanism from this process is formation of electron-hole pairs on the surface semiconductor catalyst when induced by the appropriate photon energy [18].

2. Research method
This research was conducted at laboratory of Organic Chemistry, Department of Chemistry, Institut Teknologi Bandung. Material TiO$_2$ that used in this research was synthesized by hydrothermal method. TiO$_2$ was synthesized using titanium (IV) etoxide (pro analysis grade, Sigma-Aldrich, USA) as precursor and isopropyl alcohol (pro analysis grade, Sigma Aldrich, USA) as solvent. In addition, methyl orange (Merck, Germany) was used as analyte. All chemicals were purchased and used without further purification.

Optimization of photocatalytic activities in this research was done by the procedure below. For the distance of UV lamps to the surface of analyte optimization, a total of 50 mL methyl orange solution 10 ppm was put into five 250 mL beaker glasses with pH 5. Into each beaker glass containing methyl orange solution were added 0.03 g of TiO$_2$. Each beaker glass was put inside a photoreactor system (Figure 1) where the photodegradation process took place. The mixture was stirred for 20 minutes under dark condition. Then, it was irradiated under 10-40 Watt UV light sources for 3 hours with 20 cm lamp distance from the surface of solution. The results of photodegradation process were centrifuged to separate the precipitate particles. For UV lamps power optimization, a total of 50 mL methyl orange solution 10 ppm and pH 5 was put into four 250 mL beaker glasses. The parameters were the same as the distance of UV lamps optimization method. To optimize the UV lamps power, it was adjusted to 20-40 cm. Finally, the remaining methyl orange concentration was determined by using UV-Vis spectrophotometer at 467 nm wavelength by calculating the percentage of degradation using this following equation,

$$%D = \frac{C_0 - C}{C_0} \times 100\%$$  

(1)

Where $C_0$ is the initial concentration of methyl orange in ppm and $C$ is the concentration of methyl orange after photo degradation process in ppm.

The sample were characterized by scanning electron microscope (SEM JEOL JSM-6360LA), X-ray diffraction (XRD Shimadzu XRD-7000 Maxima), diffuse reflectance spectroscopy (DR-UV Thermo Scientific Evolution 220) and brunauer emmett teller (BET Quantachrome Quadrasorb SI)
3. Results and discussion

3.1 Characterization of Synthesized Material.
SEM characterization was done to find out the morphology of synthesized TiO$_2$. Figure 2 shows the SEM images of synthesized TiO$_2$ in 5000x and 25,000x zoom.

The crystallinity degree of synthesized TiO$_2$ is 45.1% by using the X-ray diffractogram characterization. Figure 3 shows the diffractogram of synthesized TiO$_2$. It can be seen that this synthesized TiO$_2$ still has rutile on its structure.
The band gap value of synthesized TiO$_2$ was calculated by Kubelka-Munk formula and DR-UV characterization.

\[ F(R) = \frac{(1-R)^2}{2R} \]  \hspace{1cm} (2)

with \( F(R) \) is Kubelka-Munk factor and \( R \) is reflectance.

From the DR-UV data result, the band gap of synthesized TiO$_2$ is 2.98 eV. It means that the range of light source to initiate the photocatalytic process is in the UV light source area. If the band gap value is smaller, the larger the wavelength range of the rays means that photocatalytic reactions can be carried out in visible light [19].

BET characterization was done to find out the surface area, total pore volume, and average pore size. Table 1 shows the result data of BET characterization. Surface area and pore size affect the photocatalytic activity of TiO$_2$. The larger the surface area and the pore size of the photocatalyst, the higher the photocatalytic activity because the larger the active side is used during the photocatalytic process [20].

**Table 1. BET Characterization.**

| TiO$_2$              | Surface Area (m$^2$/gram) | Total Pore Volume (cc/gram) | Average Pore Size (nm) |
|----------------------|---------------------------|----------------------------|------------------------|
| Synthesized TiO$_2$  | 204, 431                  | 0.3184                     | 5.96                   |

### 3.2. Optimization of Photocatalytic Activity

Optimization of lamp power is carried out by varying the power of lamps starting from 10 to 40 Watt. From the research result, the optimum lamp power to degrade the methyl orange solution was 20 Watt as shown at Figure 4. The greater the lamp power, the greater percent of degradation of methyl orange solution. UV rays caused electrons in the valence band excited to the conduction band which results in positive holes and free radicals. The greater power of the light that initiates photochemical reaction, the higher photocatalytic activity because the electron pairs are formed quickly.
Optimization of lamp power on photocatalytic activity of TiO$_2$.

Optimization of the distance of the lamp was done by varying the distance of lamps from the surface analytic starting from 20 to 50 cm. From the research results, the optimum lamp distance to degrade the methyl orange solution was 20 cm as shown at Figure 5. The closer the lamp distance, the greater the degradation percent of the methyl orange solution. UV rays will cause electrons in the valence band to be excited to the conduction band which results in positive holes and free radicals. The closer the distance between the lamps that initiate the photochemical reactions, the higher the photocatalytic activity because the electron pairs are formed quickly.

Figure 4. Optimization of lamp power on photocatalytic activity of TiO$_2$.

![Graph showing the optimization of lamp power on photocatalytic activity of TiO$_2$.](image)

4. Conclusion
Photocatalytic activity of synthesized TiO$_2$ for the photodegradation of methyl orange solution had been carried out. From the results of the study, it was found that the optimum condition of the UV lamps distance to the surface of analyte was 20 cm and the UV lamps power was 20 Watt.

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