Study on Photocatalytic Properties of TiO₂ Nanoparticle in various pH condition

Nasikhudin¹², M Diantoro¹, A Kusumaatmaja¹, K Triyana¹
¹ Departement of Physics, Faculty of Mathematics and Natural Sciences Universitas Gadjah Mada
² Departement of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang

Email: triyana@ugm.ac.id

Abstract: Titanium dioxide has been widely studied for its ability to photocatalytic and applications have high performance for photovoltaic applications. In this paper TiO₂ nanoparticle was investigated for the degradation of methylene blue under UV light in various pH condition. The TiO₂ nanoparticle was characterized by SEM and XRD. The results showed that TiO₂ nanoparticle has the structure of anatase and have a particle size of 27 nm. The photocatalytic activity of TiO₂ nanoparticle show that the degradation of methylene blue under UV light have dye removal of 97% dye was degraded in 3 h, but the degradation of methylene blue without UV light have dye removal of 15% dye was degraded in 3 h. It indicated that The photocatalytic activity of TiO₂ nanoparticle could occur if there the UV light. If not UV light the photocatalytic activity cannot occurs, the degradation of Methylene Blue 15% is not a photocatalytic activity but it is adsorption of Methylene Blue by TiO₂ nanoparticle. The photocatalytic activity of TiO₂ nanoparticle has pH-sensitive. The photocatalytic activity of TiO₂ nanoparticle in acid condition (pH 4.1) is 40%, in neutral condition (pH 7.0) is 90%, and in base condition (pH 9.7) is 97%. The highest photocatalytic activity occurs in base condition, it causes in base condition OH- can be direct reaction with a hole to produce hydroxyl radical (OH*).

Keywords: TiO₂, pH, Methylene Blue, photocatalytic.

1 Introduction
Titanium dioxide has been widely studied for its ability to photocatalytic and applications have high performance for photovoltaic applications [1]. Recently, environmental purification using TiO₂ as a photocatalytic has attracted a great interest due to its high Activity [2]. It also shows chemical stability, low toxicity, low pollutant load, and availability at low-cost [3] [4]. TiO₂ size has been reduced to increase the reactive surface area to improve efficiency [5]. Wastewater treatment for environmental preservation-based TiO₂ photocatalytic has been proven to degrade many organic pollutants effectively [6]. TiO₂ has been widely used as photocatalytic due to its chemical stability and availability in the commercial. Many forms of TiO₂ nanomaterial have been prepared including nanoparticle, nanotube, nanofiber, and nanosheet [7]. Many efforts are focused on the application of TiO₂ in the wastewater treatment system [8]. An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms [9] Water and oxygen molecules dissociation is a phenomenon commonly observed as a result of the achieved extremely conditions. [10] The pH might play an important role for the elimination mechanism of the pharmaceuticals in the environment. About photolysis, the different species might have various photolytic degradation pathways, transformation products, and kinetics of mechanism-based degradation [11]. The better degradation rate in acidic or basic pH may also be attributed by the fact that the structural orientation of the molecule is favoured for the attack of the reactive species under that condition. The degradation rate for the decomposition and
mineralization of acid red was found to increase with the increase pH solution, while the degradation rate
for the decomposition and mineralization of the pesticide was found to decrease with the increase pH
solution [9]. The interpretation of pH effects on the photocatalytic process is a very difficult task because of
its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules,
substrate and charged radicals formed during the reaction process. Many efforts have been done, but no
clear explanation. In this study we will discuss the effect of pH of Methylene Blue solution as a pollutant
on photocatalytic activity of TiO2 nanoparticle.

2 Experiment Methods
The material used in the research were: Titanium (IV) oxide, anatase, nanopowder < 25 nm particle size,
99.7% trace metal basis and methylene blue powder, all of them purchased from Sigma-Aldrich.
Characterizations of TiO2 nanoparticle using XRD and SEM. The nanofibers surface morphology was
studied using SEM (FEI, Type: Inspect-S50). Image processing software was used to measuring the grain
size of the nanofibers captured in the SEM micrograph. XRD (PanAnalytical, Type: Expert Pro) were
used to determine the structure of TiO2 nanoparticle. Retica program was used to analysis XRD pattern.
Photocatalytic activities of TiO2  nanoparticle were investigated by observing degradation of methylene
blue (MB) under UV light. The experiment was set up with conditions 4 x 10 W lamp as the UV light
source (365 nm). The reaction was prepared by using 0.1 g of TiO2 nanoparticle into the beaker
containing 10 ppm of Methylene blue solution (10mL). Degradation of methylene blue was observed by
UV-vis spectroscopy each 1 hours during 5 hours which suggested TiO2 nanoparticle could degrade the
methylene blue solution. Photocatalytic activities of TiO2 nanoparticle were also investigated in various
condition (without UV and with UV light) and various pH (acid, neutral, and base).

3 Results and Discussion
The SEM image of TiO2 nanoparticle is shown in Figure 1. The morphology of TiO2 nanoparticle shows
that TiO2 nanoparticles have agglomeration [12]. The nature of the agglomeration of TiO2 nanoparticles
in aqueous suspension [13]. The agglomeration occurs because the TiO2 is unstable in the nanoparticles
form so that they will tend to join each other until they are relatively stable. The result of SEM analysis in
Figure 1.(a) with image j program shows the agglomeration size of TiO2 is about 975 nm. To know the
size of these tio2 particles, SEM performed with 50,000 times magnification. SEM results with 50000
magnification this time can be seen the arrangement of TiO2 nanoparticles that form agglomeration. SEM
analysis results with image j program in Figure 1.(c) shows the particles size of TiO2 is about 25 nm.

Figure 1. SEM image of TiO2 nanoparticle with magnification of (a) 5000x, (b) 10.000x, and (c) 50.000x.
The XRD used to investigate the crystal structure of TiO$_2$ nanoparticle. The XRD patterns of TiO$_2$ nanoparticle have some diffraction peaks shown in Fig. 2. The peaks occur at 20 of 25.3° for crystal plane 101; 37.9° for crystal plane (004); 48.2 for crystal plane (200), and other peaks show in figure 2. The XRD result was analysis with Retica program to identify cited the structure and parameter of the crystal. The result show that the crystal structure of the TiO$_2$ is anatase (tetragonal) with parameter $a = b = 3.789603$ Å, and $c = 9.516015$ Å, cell volume = 136.660339 Å$^3$, molecular weight = 319.600, density = 3.882, particle size of 25.25 nm.

![Figure 2. XRD pattern of TiO$_2$ nanoparticle](image)

The UV-Vis spectroscopy used to observe the concentration of Methylene Blue solution after photocatalytic treatment. The UV-Vis spectroscopy observes every 1 hours during 5 hours. Figure 3 shows that the Methylene Blue (MB) solution is degraded by TiO$_2$ nanopowder. Degradation of Methylene Blue solution by TiO$_2$ without UV light very less than TiO$_2$ with UV light. Comparison of photocatalytic activity to degrade Methylene Blue solution between TiO$_2$ without UV light and TiO$_2$ with UV light is shown in Figure 3.

![Figure 3. UV-Vis spectroscopy](image)
Figure 3. Photocatalytic activity of TiO$_2$ nanoparticle in dark (No UV) and bright (with UV) condition.

Figure 3 shows that in the absence of UV rays there will be no photocatalytic process, MB degradation of about 15% occurring is not a photocatalytic process, but this is due to the adsorption of MB by the TiO$_2$ particles. On the other hand, the process using UV mc degradation rays that occurred showed significant results. TiO$_2$ can degrade MB to 95% for 3 hours. This suggests that the photocatalytic process occurs only when there is light (UV light), this can be explained by the photocatalytic mechanism.

Figure 4. Photocatalytic mechanism of TiO$_2$.

The photocatalytic mechanism of TiO$_2$ can be explained as follows.

\[
\begin{align*}
    TiO_2 + h\nu & \rightarrow e_{cb}^- + h_{vb}^+ \\
    h_{vb}^+ + H_2O & \rightarrow H^+ + HO^+ \\
    e_{cb}^- + O_2 & \rightarrow O_2^{-} \\
    O_2^+ + H^+ & \rightarrow HO_2^- \\
    HO_2^- + HO_2^- & \rightarrow H_2O_2 + O_2 \\
    H_2O_2 + e_{cb}^- & \rightarrow HO^+ + HO^- \\
    H_2O_2 + h\nu & \rightarrow 2HO^+ \\
    R + HO^+ & \rightarrow CO_2 + H_2O
\end{align*}
\]

The photocatalytic mechanism of TiO$_2$ can be explained as follows in figure 4. When TiO$_2$ semiconductor is illuminated with greater energy than a band gap, an electron will move from the valence band to the conduction band to produce holes ($h_{vb}^+$) in the valence band and the electrons ($e_{cb}^-$) in the conduction band. The electrons will interact with the surrounding oxygen and produce superoxide radicals ($O_2^-$), while the holes will interact with the surrounding water to produce hydroxyl radicals ($HO^+$). Both of these free radicals will interact with water-soluble compounds in the vicinity, especially organic compounds or polymers. This hydroxyl radical will decompose the organic compound or polymer into
water ($H_2O$) and carbon dioxide ($CO_2$). The superoxide radicals ($O_2^-$) will interact with water ($H_2O$) to produce hydrogen peroxide ($H_2O_2$), then this hydrogen peroxide will react with electrons that will produce hydroxyl radicals. Peroxide ($H_2O_2$) reacts with the light energy ($h\nu$) which will also produce a hydroxyl radical ($HO^+$). This hydroxyl radical ($HO^+$) will decompose the organic polymer (R) into water ($H_2O$) and carbon dioxide ($CO_2$).

Photocatalytic activities of TiO$_2$ nanoparticle were also investigated in various condition (without UV and with UV light) and various pH; acidic pH conditions (pH = 4.1), neutral (pH = 7), and base (pH = 9,7). The results of the photocatalytic investigation are shown in Figure 5.

![Figure 5](image)

**Figure 5.** Photocatalytic activity of TiO$_2$ nanoparticle in acid, neutral, and alkaline condition.

Figure 5 shows that a photocatalytic process that takes place under alkaline conditions will be faster than in neutral conditions. Otherwise the photocatalytic process that takes place in acidic conditions will be slower than in neutral conditions, this can be explained as follows.

In the neutral condition the hydroxyl radical ($HO^+$) is produced from the reaction

$$h_{vb}^+ + H_2O \rightarrow H^+ + HO^+$$

Under alkaline conditions, the hydroxyl radical may also be produced directly from the ($OH^-$) ion which interacts with the hole according to the following reaction

$$h_{vb}^+ + OH^- \rightarrow HO^+$$

Therefore under alkaline conditions, the resulting hydroxyl radical ($HO^+$) will be more numerous so that its photocatalytic ability will be better.

In acidic conditions there exists an excess of $H^+$, so that this excess $H^+$ will interact with the free electrons ($e^-$) to form radicals ($H^*$). The formation of this radical ($H^*$) will cause a backlash with $HO^+$ and $H^*$ return to $H_2O$.

$$H^+ + e^- \rightarrow H^*$$
\[ H^* + HO^* \rightarrow H_2O \]

This reduces the amount of the resulting hydroxyl radical resulting in a photocatalytic activity under acidic conditions the ability of the photocatalytic activity to decrease. It indicate that in the alkaline pH conditions the ability of photocatalytic activity is better than in neutral conditions, otherwise the acid pH conditions of the photocatalytic activity are slower than in neutral conditions.

4 Conclusions

The photocatalytic activity of TiO\(_2\) nanoparticle for degradation of methylene blue under UV light have dye removal of 97% dye was degraded in 3 h, but the degradation of methylene blue without UV light have dye removal of 15% dye was degraded in 3 h. It indicated that The photocatalytic activity of TiO\(_2\) nanoparticle could occur if there the UV light. The photocatalytic activity of TiO\(_2\) will increase if the photocatalytic activity is performed under alkaline conditions, otherwise it will decrease if done under acidic conditions.

5 Acknowledgement

This research was supported by the Directorate General of Higher Education (DIKTI), the ministry of research and higher education, the Republic of Indonesia Contract No PUPT Lanjutan Fiscal Year 2017: 2383/UN1.PII/DIT-LIT/LT/2017. The authors would also thank Mr. Kunto Wandono for maintaining the electrospinning machine.

6 References

[1] Gupta S M and Tripathi M 2011 A review of TiO2 nanoparticles Chinese Sci. Bull. 56 1639–57
[2] Nasikhudin, Diantoro M, Kusumaatmaja A, Triyana K, Diantoro M, Kusumaatmaja A and Triyana K 2016 Preparation of PVA / Chitosan / TiO2 nanofibers using electrospinning method Preparation of PVA / Chitosan / TiO 2 Nanofibers using Electrospinning Method 150002 2–8
[3] Mau D, Risti A, Dra G and Pintar A 2017 Titania versus zinc oxide nanoparticles on mesoporous silica supports as photocatalysts for removal of dyes from wastewater at neutral pH
[4] Wu Y, Zhao J, Li Y and Lu K 2016 Preparation and freezing behavior of TiO 2 nanoparticle suspensions Ceram. Int. 42 15597–602
[5] Yun J, Jin D, Lee Y and Kim H 2010 Photocatalytic treatment of acidic waste water by electrospun composite nano fi bers of pH-sensitive hydrogel and TiO 2 Mater. Lett. 64 2431–4
[6] Im J S, Kim M Il and Lee Y-S 2008 Preparation of PAN-based electrospun nanofiber webs containing TiO2 for photocatalytic degradation Mater. Lett. 62 3652–5
[7] Bo Y I N, Ji-tong W, Wei X U, Dong-hui L and Wen-ming Q 2013 Preparation of TiO 2 / mesoporous carbon composites and their photocatalytic performance for methyl orange degradation New Carbon Mater. 28 47–54
[8] Qu X, Alvarez P J J and Li Q 2013 Applications of nanotechnology in water and wastewater treatment Water Res. 47 3931–46
[9] Haque M M, Bahnemann D and Muneer M 2012 Photocatalytic Degradation of Organic Pollutants : Mechanisms and Kinetics Photocatalytic Degrad. Org. Pollut. Mech. Kinet. 3 294–326
[10] Hassani A, Khataee A, Karaca S, Karaca C and Gholami P 2016 Ultrasoundsonochemistry Sonocatalytic degradation of ciprofloxacin using synthesized TiO 2 nanoparticles on montmorillonite Ultrason. - Sonochemistry 1–12
[11] Salma A, Thorie-boveleth S, Schmidt T C and Tuerk J 2016 Dependence of transformation product formation on pH during photolytic and photocatalytic degradation of ciprofloxacin J.
Hazard. Mater. 313 49–59

[12] Nasikhudin, E P Ismaya, M Diantoro, A Kusumaatmaja and K T Preparation of PVA / TiO 2 Composites Nanofibers by using Electrospinning Method for Photocatalytic Degradation 012011

[13] Li G, Lv L, Fan H, Ma J, Li Y, Wan Y and Zhao X S 2010 Journal of Colloid and Interface Science Effect of the agglomeration of TiO 2 nanoparticles on their photocatalytic performance in the aqueous phase J. Colloid Interface Sci. 348 342–7