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Degradation of Methylene Blue in TiO₂-Fe(VI) System With UV Radiation

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Abstract. Photocatalytic degradation is a combination of photochemical and catalytic processes in which light and a catalyst are needed to carry out chemical transformations. In this research, a photocatalytic degradation method has been developed using the TiO₂-Fe(VI) system with UV light activation. This method is one of the appropriate alternative methods for the treatment of azo dye waste because it is safe, economical, and environmentally friendly. The purpose of this study was to determine the effect of pH and contact time on the TiO₂-Fe(VI)-UV system on the photocatalytic degradation of methylene blue. The results showed that in the TiO₂-Fe(VI)-UV system, the percentage of methylene blue degradation reached 99.97% at pH 2.

Keywords: Photocatalytic, degradation, methylene blue, ferrate, UV radiation

INTRODUCTION

Methylene blue is the most commonly used dye for textile dyes. Although Methylene blue has a side effect that can irritate the digestive tract with symptoms of nausea, vomiting, and diarrhea. In addition, it can also cause methemoglobinemia, cyanosis, and convulsions when inhaled [1]. Currently, many azo dye removal methods have been used, including using coagulants, activated carbon, and biological processing, the coagulant method will cause new problems with the presence of large amounts of sludge so that further processing is needed to handle it [2]. The dye removal method using activated carbon will also produce sludge. The resulting sludge is then burned and produces harmful chlorine oxide compounds [3]. Another method is to use various types of bacteria, but the decomposition products are toxic and require further processing [4].

In this study, an efficient and effective photocatalytic degradation method was developed to overcome the problem of dye pollution. Photocatalytic degradation is a combination of photochemical and catalytic processes, therefore light and a catalyst are needed to carry out chemical transformations [5]. Generally, the catalyst used is a good semiconductor such as a TiO₂ catalyst. Photocatalytic degradation methods usually use a catalyst (TiO₂/UV-A) and ozonation, H₂O₂/UV-B. Heterogeneous photocatalytic oxidation using sunlight (TiO₂/H₂O₂, Fe³⁺/H₂O₂) is also effectively used for the treatment of wastewater from various industries and contaminated water or air [6]. In this research, a ferrate oxidizing agent was used. Ferrate, Fe(VI) has received much attention for its uses in green organic synthesis, 'super-iron' batteries, and wastewater treatment [7, 8, 9]. Previous studies have shown that ferrate is very effective in degrading methyl orange dye with a 100% reduction percentage [10]. Photodegradation of methylene blue with UV light and Al₂O₃ catalyst is less effective because the percentage of degradation is only 30.22% [11]. The combination of ferrate with TiO₂ is a very promising photocatalytic degradation method, especially for the treatment

of methylene blue dye waste. This method is one of the alternative methods of waste treatment that is safe, economical, and environmentally friendly.

MATERIAL AND METHOD

Material

TiO₂ (Merck), methylene blue (Sigma), KOH (Merck), NaOH (Merck), H₂SO₄ (Merck), (NH₄)₂SO₄ (Merck), Fe(NO₃)₃ (Merck), NaOCl (technical), KCl (Merck), KCl-HCl buffer (technical), acetate buffer (technical), phosphate buffer (technical), borax-HCl buffer (technical), Na₂HPO₄-NaOH buffer (technical), brucine (technical), phenol (Merck), 95% ethanol (Merck), KNO₃ (Merck), NH₄Cl (Merck), sodium nitroprusside (Merck), trisodium citrate (Merck), and distilled water.

Instrumentation

pH-meter, magnetic stirrer, hot plate stirrer, glass wool, UV reactor, centrifuge (Quantum), vacuum desiccator, UV lamp, incandescent lamp, UV-Vis spectrophotometer Shimadzu 1800, and XRD (X-ray Diffraction) XD 700 Shimadzu.

Synthesis of Potassium Ferrate (K₂FeO₄) [10]

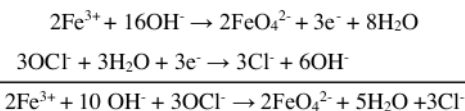
As much as 40 mL of 5.25% NaOCl solution was reacted with 12 g of KOH. The solution was stirred until all of the KOH dissolved completely, then added 1 mL of Fe(NO₃)₃ dropwise and stirred again until the solution turned purple. The solution was then stored in a dark room for ± 24 hours, thus forming a dark purple ferrate solution.

Characterization of Potassium Ferrate (K₂FeO₄)

The synthesized ferrate solution was filtered using glass wool over an Erlenmeyer containing 30 mL of KCl solution. Next, Erlenmeyer was covered with aluminum foil and left for ± 24 hours. The mixture was then centrifuged for 10 minutes at a speed of 2000 rpm. The precipitate is separated from the solution and then dried under an incandescent lamp and stored in a vacuum desiccator. The dried solids were characterized by XRD.

RESULT AND DISCUSSION

The potassium ferrate synthesis process begins by reacting KOH with a 5.25% NaOCl solution. NaOCl was used as an oxidizing agent. NaOCl can oxidize Fe(III) to Fe(VI) [12]. In this process, KOH is also used to make the solution alkaline. Ferrate in alkaline conditions has high stability compared to acidic conditions [13]. In this process, KOH is used to make a solution under alkaline conditions. Ferrate under alkaline conditions has high stability compared to acidic conditions [13]. This is because in alkaline conditions ferrate is formed, while in acidic conditions the more dominant species is HFeO₄⁻. After the KOH dissolved, then a solution of Fe(NO₃)₃.9H₂O was added dropwise. The addition of Fe(NO₃)₃.9H₂O solution causes the solution to change from yellow to purple. This indicates that Fe³⁺ derived from Fe(NO₃)₃.9H₂O has been oxidized by NaOCl to FeO₄²⁻. The reaction for the formation of ferrate is as follows [14] :



Potassium ferrate was synthesized using the oxidation method, and the product was characterized using XRD. The diffractogram of synthesized potassium ferrate (K_2FeO_4) solid is shown in Figure 1.

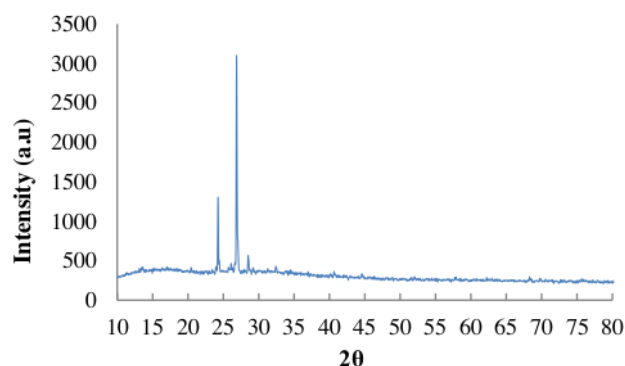


FIGURE 1. XRD pattern of synthesized potassium ferrate

Based on the diffractogram in Figure 1, three main peaks appear at 2θ 24.2377°, 26.8599°, and 27.0326°. The resulting diffractogram has the highest peak at $2\theta = 27.0326^\circ$ with lattice parameters (340). According to Li (2005) [13], potassium ferrate has 2θ at 30.1° with the main peak intensities of 75%, 90%, and 99% purity, respectively, namely 767, 912, and 1001. The diffractogram obtained in this study differs slightly. The wet method in the synthesis of K_2FeO_4 produces solids that have high purity (99%) [13]. Based on the results of the study, it can be concluded that the resulting precipitate has high crystallinity. FeO_4^{2-} has a tetrahedral structure in its crystalline form [15].

Photocatalytic Degradation of Methylene Blue

1. Effect of contact time

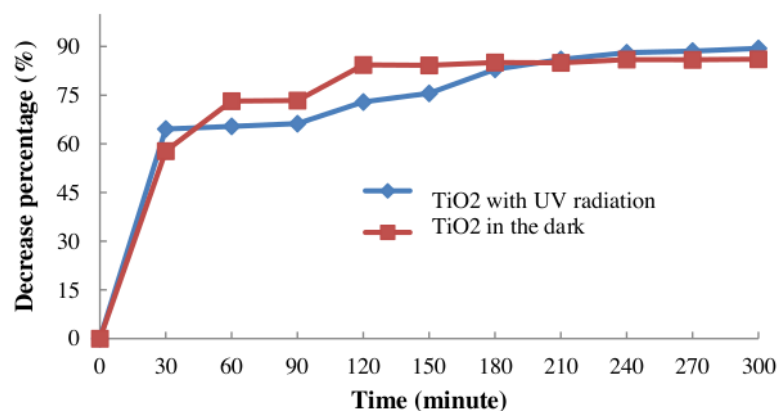


FIGURE 2. Effect of contact time

The maximum contact time is the time required for the photocatalyst to degrade methylene blue dye to obtain the largest percent reduction in methylene blue dye. Figure 2 shows the effect of contact time on the reduction of methylene blue dye levels using TiO_2 in two conditions (dark and UV radiation). The percentage decrease in

methylene blue levels with UV radiation in the time range of 30 to 330 is 62.68%, 64.57%, 65.38%, 66.23%, 72.92%, 75.57%, 82.97%, 86.02%, 88.1%, 88.59%, and 89.41%. Meanwhile, the percentage decrease in the concentration of methylene blue solution in the darkroom was 56.83%, 57.78%, 73.18%, 73.35%, 84.32%, 84.18%, 85.07%, 84.97%, 85.96%, 85.91%, and 86.08%. Based on these results, the largest decrease in methylene blue levels using Fe(VI) was obtained at a contact time of 330 minutes, namely 89.41% with UV lamp radiation and 86.08% in the darkroom. The presence of TiO₂ and a photon source from UV light will accelerate the reduction of ferrate.

2. Effect of pH

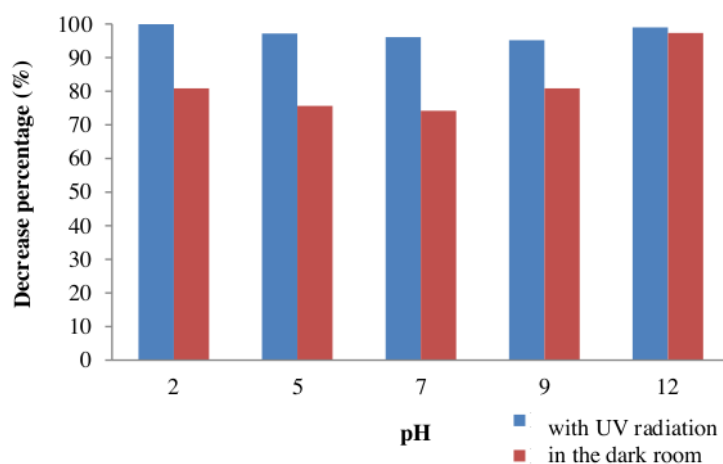


FIGURE 3. Effect of pH

Figure 3 shows the effect of pH variations on decreasing levels of methylene blue dye using the TiO₂-Fe(VI) system. The decrease in methylene blue levels under UV radiation at pH 2 was 99.97%, pH 5 was 97.17%, pH 7 was 96.09%, pH 9 was 95.19%, and pH 12 was 98.99%. The largest percentage decrease occurred in an acidic environment with pH 2. Meanwhile for the treatment carried out in a dark room the decrease in methylene blue levels at pH 2 was 80.85%, pH 5 was 75.63%, pH 7 was 74.18%, pH 9 is 80.87%, and pH 12 is 97.35%. The largest percentage decrease occurred in an alkaline environment with a pH of 12. The presence of TiO₂ and photons from UV light will accelerate the ferrate reduction process so that the combination of TiO₂-Fe(VI) produces a significant decrease in methylene blue levels.

The largest percentage decrease in the concentration of methylene blue solution under the influence of UV light at pH 2 was 99.97%. Methylene blue at a low pH (acidic) should be more difficult to adsorb on the surface of TiO₂ because TiO₂ and methylene blue are both positively charged so that they repel. But based on the results of the study, due to the influence of photons from UV light, a large decrease at pH 2 can occur. Fe(VI) changes to Fe(III) because in an acidic environment the H₃FeO₄⁺ species are more dominant. This large percentage decrease was due to a large number of •OH radicals. The formation of •OH radicals is influenced by the abundance of H⁺ ions in methylene blue which has been conditioned in acidic pH reacting with oxygen radicals (•O₂) which are formed from the interaction of TiO₂ electrons with oxygen in water (Peral, 1990). When degradation occurs in an alkaline environment, the positively charged methylene blue will be more easily adsorbed on the negative TiO₂ surface so that electrostatic interactions occur. That's why in the darkroom the largest percentage decrease occurred at pH 12. TiO₂ can be active at a certain pH, namely acid, while ferrate is more dominant at alkaline pH.

CONCLUSION

The degradation of methylene blue in the TiO₂-Fe(VI) system under UV lamp radiation reached a maximum at pH 2 and a contact time of 330 with a percentage decrease of 99.97%. Degradation of dyes using the TiO₂-Fe(VI)-UV system can be used as an alternative method for wastewater treatment.

REFERENCES

1. T.O. Zhang, A. Aoshima, H. Hidaka, J. Zhao, and N. Serpone, *Journal of Photochemistry and Photobiology A: Chemistry*, **140**, 163 – 172 (2002).
2. A. Tuty, "Pengembangan TiO₂ pada abu dasar batubara (bottom ash) dan uji aktivitasnya sebagai fotokatalis dalam degradasi zat warna metilen biru," Thesis, Universitas Gadjah Mada, 2012.
3. M. Christina, dan S.R. Marjanto, *Jurnal Forum Nuklir*, **1**, 31-44 (2007).
4. J. S. Chang, C. Chou, Y. C. Lin, J.Y. Ho, dan T.L. Hu, *Wat. Res.*, **35**, 2841-2850 (2001).
5. E. Palupi, "Degradasi methylene blue dengan metode fotokatalis dan fotoelektrokatalis menggunakan film TiO₂", Skripsi, FMIPA IPB, 2006.
6. M. Muruganandham, and M. Swaminathan, *Dyes Pigments*, **72**, 137–143 (2007).
7. L. Delaude, P. Laszlo, *J. Org. Chem.*, **61**, 6360–6370 (1996).
8. V.K. Sharma, *Environ. Res.*, **6**, 143–156 (2002).
9. S. Licht, V. Naschitz, and S. Ghosh, *J. Phys. Chem. B.*, **106**, 5947–5955 (2002).
10. D.W. Dwiasi, "Studi Degradasi Zat Warna Azo Menggunakan Ferrat (FeO₄²⁻)", Tesis, Universitas Gadjah Mada, 2008.
11. I. Ayu, Ida, N.P. Diantariani, dan Y.F. Nikmah, "Fotodegradasi Metilen Biru dengan Sinar UV dan Katalis Al₂O₃", (Jurusan Kimia FMIPA Universitas Udayana, Bukit Jimbaran, 2011).
12. H.J. Lee, I. H. Oh, and D. C. Kim, , *Theories and Applications of Chem. Eng.*, **12**, 2-10 (2004)
13. C. Li, X. Z. Li, and N. Graham, *Chemosphere*, **61**, 537-543 (2005).
14. D. W., Dwiasi, dan K. Mardiyah, *J.Ilm. Kim. Mol.*, **3**, 1-52 (2010).
15. J.Q. Jiang, and B. Lloyd, *Water Res.*, **36**, 1397–1408 (2002).

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