Photocatalytic degradation of methylene blue by TiO$_2$/WO$_3$-deoiled spent bleaching earth

N Hindrayawati*,1,2, A S Panggabean3, RR D J N Subagyono1 and J Y Sitinjak1,2

1Department of Chemistry, Faculty of Mathematics and Natural Sciences, Mulawarman University, Jl. Barong Tongkoko No.4 Gunung Kelua, Samarinda, East Kalimantan, Indonesia
2Physical- Inorganic Laboratory, Faculty of Mathematics and Natural Sciences, Mulawarman University, Jl. Barong Tongkoko No.4 Gunung Kelua, Samarinda, East Kalimantan, Indonesia

*Corresponding Author: ienwati@yahoo.com

Abstract. Degradation of methylene blue using pillared TiO$_2$-WO$_3$ onto deoiled spent bleaching earth (DSBE) has been conducted. Pillarization with TiO$_2$-WO$_3$ on DSBES using rarasaponin as surfactant. The structural and morphological of material has been carried out by X-ray fluorescence (XRF), and scanning electron microscopy coupled to the energy dispersive spectroscopy (SEM-EDX). Characterizations results show the increase composition of SiO$_2$. The calcination result at 500°C show the TiO$_2$-WO$_3$ was deposited on the DSBES surface and suspected there is existence of Ti and W metals on the DSBES layer. The catalytic performance of TiO$_2$-WO$_3$/DSBE for photodegradation of methylene blue under visible light was 99.85% within 30 minutes.

1. Introduction

Dye waste has become a serious problem for the environment along with the rapid growth of the textile industry sector in Indonesia. Industrial liquid waste that contains dyes is immediately discharged into the environment causing water pollution. Dye waste is an organic compound that is non-biodegradable and toxic. Waste produced by the textile industry process contains dyes with levels of 20-30 mg/L so that it is difficult to decompose naturally [1]. Dye that are commonly used in the textile industry are methylene blue which is a cationic aromatic compound [2].

Photodegradation is an smart solution to solve these problems. TiO$_2$ is the most effective photocatalyst because it has high photocatalyst activity. However, TiO$_2$ photocatalysts are only active under ultraviolet (UV) radiation because of the large bandgap (3.2 eV) [3]. WO$_3$ coupling can be done to increase the photocatalyst activity of TiO$_2$ under visible light radiation [4]. WO$_3$ has a small bandgap (2.7-2.8 eV) so it is very sensitive to visible light [5].

In this paper, TiO$_2$/WO$_3$ was pillared on Deoiled Spent Bleaching Earth (DSBE) as a template with the addition of rarasaponin as surfactant. SBE itself is a porous material that has been widely used as an adsorbent. With montmorillonite as the main composition of DSBE, this material has the potential as a template for making photocatalysts [6]. It is expected that TiO$_2$/WO$_3$ material pillared in DSBE can degrade methylene blue.
This photocatalyst material was characterized using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX).

2. Experimental

The materials used were TiO\(_2\), WO\(_3\), deoiled spent bleaching earth, lerak fruit, HCl, pH indicator, filter paper, aluminum foil, 96% ethanol and distilled water. The equipment used was standard glass laboratory chemistry, analytical balance sheet, 100 mesh sieve, oven, set of reflux equipment, microwave, Shimadzu FT-IR 501, SEM-EDX JEOL JED-2300, XRF Shimadzu 900 HS, XRD Shimadzu 700.

2.1 Rarasaponin extraction in lerak fruit

Lerak fruit was dried for 4 days, then reduced in size. Then extraction was performed using a soxhlet extractor at 70°C for 180 minutes with an aqueous solvent. Aquadest volume ratio (mL): klerak (g) was 2:1. The results obtained were separated by evaporation at 100°C.

2.2 Synthesis of pillared TiO\(_2\)/WO\(_3\) on DSBE and characterization

DSBE was activated first using 2M HCl then refluxed for 4 hours at 70°C. The activated DSBE was washed with distilled water to pH 7 then dried for 1 hour at 105°C. The resulting material is denoted as DSBE-SA. Five grams of DSBE-SA was mixed with 0.5 g of rarasaponin extract. The mixture was then heated in a microwave for 90 seconds at 700 watts then dried for 24 hours at 60°C. The resulting material was denoted as DSBE-RS. The process of pillarization TiO\(_2\)/WO\(_3\) on DSBE-RS was done by mixing 0.4 g of TiO\(_2\) into a 100 mL beaker glass that has been filled with 1 g deoiled spent bleaching earth (DSBE-RS). Then 6 mL of 95% ethanol is added while stirring using a magnetic stirrer for 5 hours. The mixture was then separated by centrifugation followed by drying at 120°C for 5 hours. Then the same thing was done on WO\(_3\). Then proceed to the calcination step at a temperature of 500°C for 2 hours.

2.3 Photodegradation test of methylene blue using DSBE-TiO\(_2\)/WO\(_3\)

A grow Light LED lamp was used as light source. Different amounts of DSBE-TiO\(_2\)/WO\(_3\) (0.025; 0.05; 0.125 g) were added to the dye methylene blue with a concentration of 150 ppm. The reaction time was set for 10, 20, 30 and 40 minutes. The mixture was separated using a centrifuge. Then the filtrate was analyzed using a UV-Vis Spectrophotometer at a wavelength of 665 nm. The optimum condition was used for performance test between DSBE and DSBE-TiO\(_2\)/WO\(_3\).

3. Results and discussion

3.1 Characterization with XRF

Table 1 showed that there was a decreasing of composition of metal oxide such as CaO, Fe\(_2\)O\(_3\), ZnO, Cr\(_2\)O\(_3\) and MnO after activation process. This is because the metals dissolve during the activation process using HCl solution. The use of HCl it self aims to open the pores on the DSBE material by dissolving small ions on the surface [7], and causes the material pores to become more open.

| Sample name | Parameter (%) |
|-------------|--------------|
|             | Fe\(_2\)O\(_3\) | CaO | K\(_2\)O | SiO\(_2\) | MnO | SO\(_3\) | ZnO | P\(_2\)O\(_5\) | Cr\(_2\)O\(_3\) | CuO |
| DSBE        | 30.914       | 2.770 | 0.877   | 63.207   | 0.489 | 1.502   | 0.053 | -          | 0.189     | -   |
| DSBE SA     | 29.641       | -    | 0.913   | 69.078   | 0.223 | -       | 0.051 | -          | 0.095     | -   |
3.2 Characterization with SEM-EDX

Characterization using SEM was conducted to see the morphology of the material. The results of this characterization are cross-sectional photos of the material layer.

![Figure 1. SEM DSBE-SA micrograph Magnification 20,000 times.](image1)

![Figure 2. SEM DSBE-TiO\textsubscript{2} micrograph Magnification 20,000 times.](image2)

![Figure 3. SEM DSBE-TiO\textsubscript{2}/WO\textsubscript{3} micrograph Magnification 20,000 times.](image3)

From figure 1, it can be seen that the layer of DSBE-SA has large cavities heterogenous. Through this, it is suspected that the layer has the possibility to be inserted with Ti and W metals. Figure 2 shows the morphology of DSBE-TiO\textsubscript{2}, from the picture it can be seen that there are particles attached to the DSBE layer. It is assumed that there is a white Ti metal on the layer. Figure 3 shows the morphology of DSBE-TiO\textsubscript{2}/WO\textsubscript{3}. From the picture it can be seen that there is a change in particle size. the morphology of DSBE is different after being pilarized with TiO\textsubscript{2}/WO\textsubscript{3}. Before being pilarized with WO\textsubscript{3}, cavities can still be seen in the DSBE layer as shown in figure 2. After the presence of WO\textsubscript{3}, the cavities decrease. This is suspected due to the presence of W metal attached to the cavity in the layer as well as Ti metal.
Figure 4. EDX results of DSBE-Ti/W.

The characterization of EDX (figure 4) was conducted on DSBE-Ti/W material to find out the components contained in the material and also to determine the composition (%) of TiO₂ and WO₃ in the DSBE-Ti/W photocatalyst material. Through the EDX analysis the composition of TiO₂ is 3% and WO₃ is 11%, and there are other compound such as C, MgO, Al₂O₃, SiO₂, FeO and CuO.

3.3 Methylene blue photodegradation test

3.3.1 Contact time variations. In determining the contact time variation (figure 5), 4 variations of contact time were used (10; 20; 30 and 40 minutes) and the test was conducted on 150 ppm methylene blue (MB) dye under the visible light source. The results of % degradation obtained at 10 minutes contact time were 58%; 20 minutes were 77%; 30 minutes were 99% and 40 minutes were 86%. The contact time of 30 minutes is the optimum time for DSBE-TiO₂/WO₃ material to degrade 150 ppm of methylene blue. The longer reaction duration will increase the contact opportunity between catalyst and reactant and increase the production of electron-hole pairs on the surface of TiO₂/WO₃ and the high reactive of •OH was improved [8], but at 40 minutes the degradation MB almost constant.

Figure 5. Contact time variations against methylene blue.
3.3.2 *Catalyst weight variations.* In determining the variation of catalyst weight, 3 variations of weight were used (0.025; 0.05 and 0.125 g) and the test was conducted on 150 ppm methylene blue dye under the visible light source (figure 6). Percent degradation with a catalyst weight of 0.025 g was 30%; with a weight of 0.05 g was 62.5% and with a catalyst weight of 0.125 g was 99%. The weight of 0.125 g was the optimum weight of DSBE-TiO$_2$/WO$_3$ material to degrade methylene blue. The photocatalytic performance was substantially improved with increasing the amount of DSBE-TiO$_2$/WO$_3$ and reached optimum stage at a dosage of 0.125 g due to the enhancement of production of hydroxyl radicals.

![Figure 6. Catalyst weight variations against methylene blue.](image)

3.3.3 *Performance between DSBE and DSBE- TiO$_2$/WO$_3*.* This study was to investigate the effect of the differences material used in the decreasing concentration MB. The concentration MB was 150 ppm, the dosage of material was 0.125 g and the contact time was 30 minutes.

![Figure 7. Performance between DSBE and DSBE- TiO$_2$/WO$_3$.](image)

Figure 7 presents a comparison for MB removal using DSBE and DSBE-TiO$_2$/WO$_3$. The DSBE-TiO$_2$/WO$_3$ has better performance (99.5%) compare DSBE (59%). The photocatalytic method has the higher capability to decrease the dye. It seems DSBE has no photocatalytic activity. Hence, the process in DSBE was adsorption of dye on its surface.
4. Conclusion
The results of SEM analysis showed morphological changes in DSBE after being pilarized with TiO₂/WO₃ and suspected the existence of Ti and W metals on the DSBE layer. The optimum condition of DSBE-TiO₂/WO₃ photocatalyst material to degrade 10 mL of 150 ppm methylene blue dye is 0.125 grams of catalyst weight and 30 minutes of contact time.

Acknowledgement
The authors are thankful to KEMENRISTEK DIKTI for funding the research project under research grants PDUPT No: 075/UN17.41/Kl/2018.

References
[1] Widjajanti E, Tutik R, and Utomo M P 2011 Pola adsorpsi zeolit terhadap pewarna azometil merah dan metil jingga Pendidikan dan Penerapan MIPA, Yogyakarta
[2] Wijaya K, Yeslia U, Triyono, and Eko S 2006 Preparation and characterization of TiO₂-zeolite and its application to degrade textile wastewater by photocatalytic method Indo. J. Chem 6(3) pp 231–37
[3] Puddu V, Robert M, and Gianluca L P 2007 Novel one step hydrothermal synthesis of TiO₂/WO₃ nanocomposites with enhanced photocatalytic activity Chem. Commun. 4749–51
[4] Ke D, Liu H, Peng T, Liu X and Dai K 2008 Preparation and photocatalytic activity of WO₃/TiO₂ nanocomposite particles Materials Letters 62 pp 447–50
[5] Georgieva J, Armanyov S, Valova E, Poulios I, Sotiropoulos S 2007 Enhanced photocatalytic activity of electrosynthesised tungsten trioxide – titanium dioxide bi-layer coatings under ultraviolet and visible light illumination Electrochemistry Comm. 9 365–70
[6] Loh S K, James S, Ngatiman M, Cheong K Y, Choo Y M, Lim W S 2013 Enhancement of palm oil refinery waste – Spent Bleaching Earth (SBE) into bio organic fertilizer and their effects on crop biomass growth Industrial Crops & Products 49 775–81
[7] Tsai W T, Chen H P, Hsieh M F, Sun H F, and Lai C W 2003 Regeneration of bleaching clay waste by chemical activation with chloride salts. Journal Environment Science 38(4) 685–9
[8] Gar M, Taw A, and Ookawara S 2016 Enhancement of photocatalytic activity of TiO₂ by immobilization on activated carbon for degradation of pharmaceuticals J Environ Chem Eng 4 1929–37