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## Modification of Spent Bleaching Earth with $WO_3$ and the Application for Photocatalytic Degradation of Waste Dyestuff under Solar Light

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### Abstract

Degradation of blue dye waste in Sarong Samarinda production using  $WO_3$ -bleaching earth (BE) has been conducted. Structural and morphological characterization has conducted using X-ray diffraction (XRD), and Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX). The X-ray diffraction results show the mineral on bleaching earth is rectorite dioctahedral mica layer and dioctahedral smectite with a ratio 2:1. The  $WO_3$  pattern is appeared after the calcination. After calcination at  $500^\circ C$ , the  $WO_3$  is deposited homogeneously on the BE surface. The catalytic performance of  $WO_3$ -BE for photodegradation of the blue dye waste under the solar light is 99.85 % within 1 h.

### INTRODUCTION

Environmental pollution is a serious problem in Indonesia. The pollution increases along with the industry growth. The Indonesia's textile industry grows 0.85% per year. This makes the water pollution caused by the dye waste. Dye waste is soluble and visible organic component. It is 15-20% of the dye organic components are difficult to decompose in water. It can cause health problems, such as eye irritation, skin irritation, infection and disrupt the fisheries ecosystem (Agustianingsih et al., 2013).

There are many things have been done in handling dye waste pollution in the environment. There are some chemistry and physics common method to overcome this problem. They are filtering, decantation, adsorption, nanofiltration, electrocoagulation, coagulation ascension,

chemical oxidation, electrochemical oxidation, photo oxidation, ozonation, liquid supported membrane, and liquid-liquid extraction (Mahmoud et al., 2007). Because of its simplicity, adsorption method is the most common method to solve dye contamination problem. However, a weakness of the adsorption method is the saturated adsorbent will become a new solid waste (Ismadji et al., 2010). Another way that is being developed is to use the photocatalyst reaction. Photocatalyst is a reaction that involves light (photoreaction) and increases the speed of reaction due to the catalyst absorbing the ultraviolet (UV) light energy then producing a reducing and oxidizing composition on the catalyst surface.

Although the photocatalytic reaction process gives a high degradation result, the limitation of the process is the time consumption in separating the catalyst from the reaction

medium. The development of existing methods is very necessary. One of them is by doping or coupling TiO<sub>2</sub> metal in a membrane or other solid material. Since the catalyst is not included in the reaction medium, coupling TiO<sub>2</sub> metal in a material will make the photocatalytic reaction more stable, sustainable and efficient. Photocatalytic semiconductors play a large role in the wastewater treatment process. Because of its large catalytic activity, the common semiconductor materials are ZnO and TiO<sub>2</sub>. Based on research conducted by Sadi et al. (2015), combination of ZnO and TiO<sub>2</sub> nanoparticles in the form of films through the layer by layer method shows that the BOD, COD and TSS in wastewater are decrease.

Spent bleaching earth (SBE) is a palm oil refining waste which is used as a blanch oil of the crude palm oil (CPO). There is more than 60 million tons of SBE used worldwide. The content of SBE itself is montmorillonite (Al<sub>2</sub>O<sub>3</sub>.4SiO<sub>2</sub>.nH<sub>2</sub>O) and the oil content is 20-40%. The oil content makes SBE becoming a waste that will be disposed in landfills and causing soil pollution. In Japan, SBE can be used as a cement aggregate, even though its large oil content will make the process becomes more difficult (Loh et al., 2013). The montmorillonite mineral content makes SBE has the potential as a supporting material in the photocatalysis reaction of dyes.

This research explores the waste refining process of crude palm oil, which is spent bleaching earth as a carrier material will be polarized with WO<sub>3</sub> as a photocatalyst material under solar light. The photocatalytic process in this research focuses to degrade blue dye waste from production of sarong Samarinda. The advantages of this method are simple, inexpensive, effective and efficient.

## MATERIALS AND METHODS

### Materials

The spent bleaching earth was collected from Local oil palm industry (Paser) and purified by water dispersion, decantation and ultrasonic extraction of the oil and sieved using 100 sized mesh. WO<sub>3</sub> pro analyst was obtained from sigma Aldrich, sulphuric acid (H<sub>2</sub>SO<sub>4</sub> (98 %)), methanol 95 %, n-hexane is supplied by Sigma-Aldrich.

### WO<sub>3</sub>-Spent Bleaching Earth Preparation

Deoiled-SBE was activated first using 2M HCl then refluxed for 4 hours at 70°C and washed using distilled water to pH 7. As many as 50 grams of SBE were mixed with 20 grams of diluted WO<sub>3</sub> in NH<sub>4</sub>OH 7M. The mixture was then heated at 60-70°C for 5 h. The mixture was dried for 24 hours at 60 °C and given the name WO<sub>3</sub>-DSBE. The mixture then continuously proceeded to the calcination at 500 °C for 2 hours. The material was characterized using XRD, FTIR and SEM-EDX.

### Dye Waste Photodegradation

Photocatalyst material used was WO<sub>3</sub>-DSBE and the light sources used were the solar light and visible lights (Grow Light LED 10 watts). The photocatalysis test was conducted by varying the contact time and weight of the DSBE-WO<sub>3</sub> catalyst. As many as 0.75g of DSBE-WO<sub>3</sub> photocatalyst were put into 10 mL of dye waste. Contact time was set for 30; 60; 90 and 120 minutes. The mixture of DSBE-WO<sub>3</sub> and dye was separated by centrifugation for 5 minutes. The concentration of the dye was then measured using a UV-Vis spectrophotometer. This was also conducted for the weight variations where WO<sub>3</sub>-DSBE was set as many as 0.5; 0.75; 1 and 1.5 g.

### WO<sub>3</sub>-DSBE Photocatalyst Reusability

WO<sub>3</sub>-DSBE as a photocatalyst was tested for optimum reusability by separating WO<sub>3</sub>-DSBE from the dye and then regenerating WO<sub>3</sub>-DSBE photocatalyst by washing using distilled water and then dried in an oven at 110°C for 1 hour. It was then calcined at 500°C for 2 hours. Washed and dried photocatalysts were reused for photocatalysis of the dye waste using the same procedure in the photocatalysis test, but the volume of methylene blue dye waste would be adjusted according to the weight of the photocatalyst material.

## RESULTS AND DISCUSSION

### Material Preparation and Characterization

The activation process in DSBE was conducted using H<sub>2</sub>SO<sub>4</sub> as an activator that can open the active side of DSBE in order to dissolve some metal oxides contained in the DSBE interlayer, so that DSBE can have a larger surface

area. Based on XRF data on previous research (Hindryawati, 2017), it shows a decrease in the amount of impurities after activation process. Data analysis of functional groups using FTIR can be seen in Figure 1.

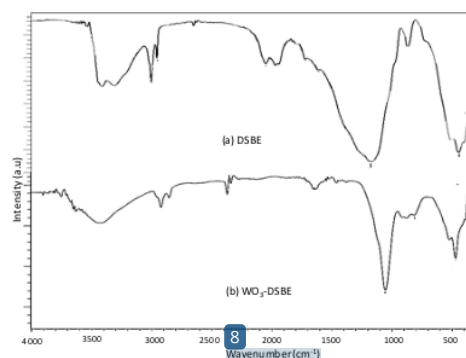


Figure 1. Spectra FTIR of (a) DSBE and (b)  $WO_3$ -DSBE.

From the FTIR analysis results on DSBE, it can be seen that the wave number  $3670.24\text{ cm}^{-1}$  shows the Al-O-H stretching group, then the wave number  $3408.22$  indicates the H-O-H stretching group. In addition, to see the DSBE structural constituent groups, it can be seen in the wave number  $462.92\text{ cm}^{-1}$  shows Si-O-Si bending group and at  $796.60\text{ cm}^{-1}$  shows Si-O stretching group. From those groups, it is concluded that the structure of the DSBE compiler does not change after the addition of rarasaponin (Ismadji, 2010).

Comparing to the FTIR analysis on DSBE- $WO_3$ , the DSBE structural constituents are still found in the spectra shown in the wave number  $470.63\text{ cm}^{-1}$  indicates the Si-O-Si bending group and in  $810.1\text{ cm}^{-1}$  shows Si-O group stretching, but there is a slight shift in wave numbers compared to the results of the first spectra. It indicates the structure of DSBE is stronger because of the effect of high temperatures during calcination (Yusefah, 2014). In the spectra, a new peak is appeared at wave number  $879.54\text{ cm}^{-1}$  stating the W-O stretching group showing that  $WO_3$  was successfully inserted in the DSBE interlayer (Gotic, 2000).

The characterization of DSBE- $WO_3$  material can be conducted using XRD to find out information on the peak of  $WO_3$  diffraction on DSBE- $WO_3$ . The results of XRD analysis for

DSBE activation and DSBE- $WO_3$  can be seen in Figure 2.

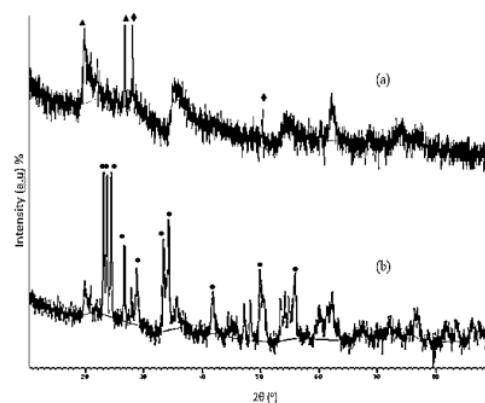


Figure 2. Diffractogram of (a) DSBE after activation and (b) DSBE- $WO_3$  ( $WO_3$  diffraction peak = ●;  $SiO_2$  diffraction peak = ▲;  $Al_2O_3$  diffraction peak = ◆).

From the XRD results in Figure 2(a), the diffraction pattern peaks are obtained at  $2\theta = 19.8714^\circ$  ( $4.46810\text{ \AA}$ );  $26.6552^\circ$  ( $3.34436\text{ \AA}$ );  $28.0675^\circ$  ( $3.17963\text{ \AA}$ ) and  $50.1340^\circ$  ( $1.81963\text{ \AA}$ ). Based on Fadillah et al (2017), there are some similarities in diffraction patterns indicating the mineral is montmorillonite. Peaks indicating the presence of  $SiO_2$  are found at  $2\theta = 21.8714^\circ$  and  $26.6552^\circ$ . While peaks indicating the presence of  $Al_2O_3$  are found at  $2\theta = 26.6552^\circ$  and  $50.1340^\circ$ . The same result conducted by Aziz and Shareef (2013), the peak at  $2\theta = 26^\circ$  and  $50^\circ$  indicated the  $Al_2O_3$ .

After pillarization with  $WO_3$ , the XRD results data are shown in Figure 2(b), where the data obtained diffraction patterns peak at  $2\theta = 23.1571^\circ$  ( $3.84102\text{ \AA}$ );  $24.4047^\circ$  ( $3.64742\text{ \AA}$ ) and  $34.2186^\circ$  ( $2.62049\text{ \AA}$ ) which are typical diffraction peaks of  $WO_3$  metal oxides. This is adjusted to the  $WO_3$  diffraction pattern standard in JCPDS data No. 43-1035, where the  $WO_3$  has a monoclinic structure.

The results of SEM analysis that provides information on the morphological appearance of the activation DSBE and DSBE- $WO_3$  can be seen in Figure 3.

In Figure 3(a), the SEM result shows that the morphology surfaces of the activation DSBE are not similar. Figure 3 (b) showing the condition

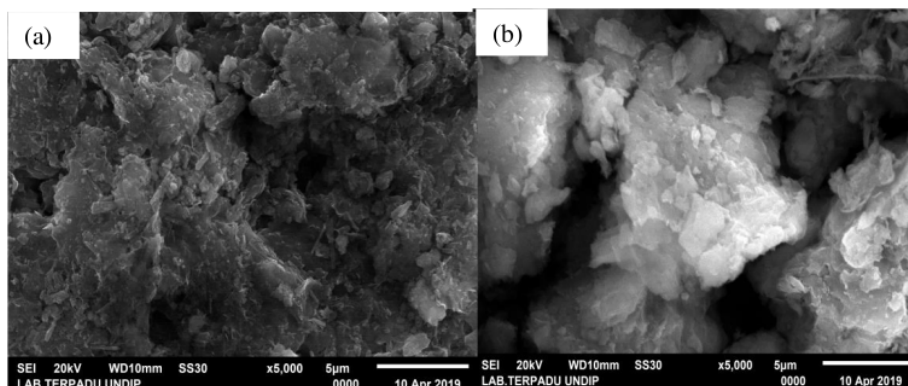


Figure 3. SEM result of (a) DSBE after activation, (b) DSBE-WO<sub>3</sub> (5.000 times magnification).

DSBE after pillarization with WO<sub>3</sub>, it shows that the morphology surfaces of DSBE are not in the same particle shape. It is because of the calcination process that greatly affects the structural order of the DSBE. In addition there are also white dots in the DSBE surface indicating that WO<sub>3</sub> has successfully doped on the DSBE.

**Photocatalytic Test on Dye Waste under Solar light**

Contact time optimization was conducted to determine the optimum contact time used in the photocatalysis reaction when the methylene blue dye is contacted with DSBE-WO<sub>3</sub> material. Data showing the relationship between percent degradation to time can be seen in Figure 4.

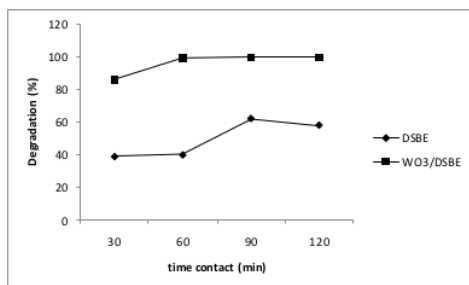


Figure 4. Contact time variations on degradation percentage.

The graph shows that in 30 minutes the percentage of degradation is 84.56%, then in the 60th minute there is an increase as many as 99%. The increase in percent degradation up to the 60th minute due to the photocatalysis reaction is still ongoing. At 90-120 min% the degradation is the same as the 60th minute. It can be concluded that the optimum contact time in the photocatalysis

reaction is 15 minutes. Meanwhile, DSBE without WO<sub>3</sub> shows the waste absorption is not as much as DSBE-WO<sub>3</sub>

DSBE-WO<sub>3</sub> weight optimization is conducted to determine the optimum weight of DSBE-WO<sub>3</sub> used in the photocatalysis reaction when the waste is contacted with DSBE-WO<sub>3</sub> material. The relationship between percent degradation to DSBE-WO<sub>3</sub> weight is shown in Figure 5.

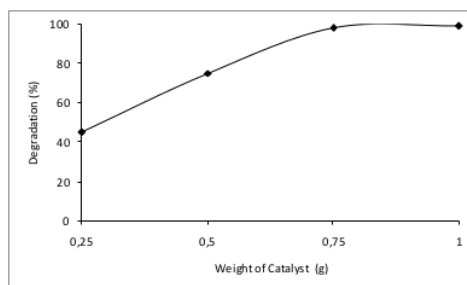


Figure 5. Weight variations on degradation percentage.

The graph shows that there is a significant increase in percent degradation from 48% using 0.25 grams DSBE-WO<sub>3</sub> to 99.8% by using 0.75 gram DSBE-WO<sub>3</sub>. That is because the more DSBE-WO<sub>3</sub> contacted with dyes, the more dye is absorbed in the DSBE-WO<sub>3</sub> cavity (Wismayanti, 2015). The increase of percent degradation from a mass of 0.25 gram to 0.75 grams is quite big indicating the optimum photocatalytic reaction process is by using 0.75 gram. Using 1 gram mass is tend to show a constant graph. It can be concluded that the optimum weight of DSBE-WO<sub>3</sub> used in the photocatalysis reaction is 0.75 gram.

In order to know the effectiveness of the DSBE-WO<sub>3</sub> photocatalyst, light condition variations was conducted. The results of the photodegradation test using various lighting conditions can be seen in Figure 6.

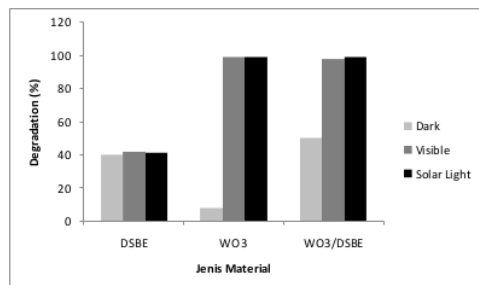


Figure 6. Light source variations on degradation percentage (*methylene blue* dye waste, at 60minutes of contact time and using DSBE-WO<sub>3</sub> 1.5 gram).

In Figure 6, it can be seen that the photodegradation test does not occur optimally in dark condition. Since the photocatalysis reaction requires a source of light in the process, only the dye waste is absorbed on the material surface. In situations using visible lamps and solar light, the photocatalytic reaction occur more optimally because the intensity of the visible light and solar light is greater and the energy is more in accordance with the band gap of WO<sub>3</sub>.

#### Catalyst Reusability

Reusing DSBE-WO<sub>3</sub> aimed to find out how many times the photocatalyst DSBE-WO<sub>3</sub> can be used in the photocatalysis reaction to degrade dye waste. This process was conducted by washing DSBE-WO<sub>3</sub> which had been used for the previous photodegradation test by using distilled water until the waste that is still present in the material dissolves with the distilled water. After that the same procedure was conducted during the photodegradation test. The results of the reusing DSBE-WO<sub>3</sub> can be seen in Figure 7.

Figure 7 shows that DSBE-WO<sub>3</sub> can be used to degrade as many 3 cycles. During the reuse of the catalyst, the degradation percent decreased from 98% to 91%. This is due to the WO<sub>3</sub> being leached after repeatedly usage so that it reduces the effectiveness of radical production •OH and also decreases its photocatalytic ability (Lestari, 2015).

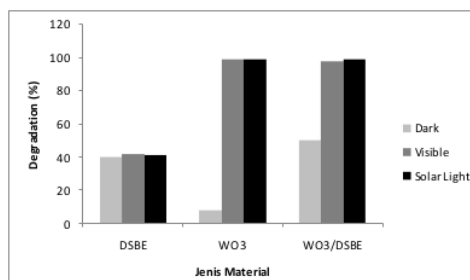


Figure 7. DSBE-WO<sub>3</sub> Reused (*methylene blue*, 1.5 g catalyst, 60 minutes contact time).

#### CONCLUSION

In this research, WO<sub>3</sub> has been successfully loaded to DSBE as a catalyst in photocatalytic reaction to degrade dye waste in producing Sarong Samarinda. Optimum conditions are found at 60 minutes of reaction time, 0.75 g of catalyst under solar light. Furthermore, the material can be reused up to 3 cycles with degradation in 90%.

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