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Modification of Spent Bleaching Earth with WO3 and the Application for Photocatalytic Degradation of Waste Dyestuff under Solar Light

Noor Hindryawati, Aman Sentosa Panggabean, Dirgarini Julia Nurlianti Subagyono, Rinda Anisyah Putri, Prilanda Kuamaty, Gaanty Pragas Maniam

Abstract

Degradation of blue dye waste in Sarong Samarinda production using WO3-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 WO3 pattern is appeared after the calcination. After calcination at 500Â°C, the WO3 is deposited homogeneously on the BE surface. The catalytic performance of WO3-BE for photodegradation of the blue dye waste under the solar light is 99.85 % within 1 h.

Keywords

photocatalytic; bleaching earth; WO3; waste dye stuff; solar light

Full Text

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To: ienwati@yahoo.com

Date: Wednesday, November 20, 2019 at 10:59 AM GMT+7

Dear Dr Noor,

We have reached a decision regarding your submission to Jurnal Bahan Alam Terbarukan entitled "Modification of Spent Bleaching Earth with WO3 and the Application for Photocatalytic Degradation of Waste Dyestuff under Solar Light". Based on the reviewers' recommendations, the manuscript requires MINOR REVISIONS before it can be reconsidered for publication in the JBAT. The comments from the reviewer(s) can be found in your JBAT account.

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--
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Reviewer #1:
1. Unclear in certain section of the discussion please revised
2. Fig. 1: The symbols used for designation of peaks needs correcting.
3. Fig. 2: (a) and (b) needs to be around to match discussion
4. Sentence needs to be revised for English.

Reviewer 2:
1. Please add the visible lights that the authors used in method
2. The authors does not state how the effective of the material was used, please add data reusability
3. Please check again grammatical error and the sentence

Title: Modification of Spent Bleaching Earth with WO3 and the Application for Photocatalytic Degradation of Waste Dyestuff under Solar Light

Response to Reviewer

No.	Comment Reviewer	Response to Reviewer
	Reviewer #1:	
1.	Unclear in certain section of the discussion please revised	The term has been standardized throughout the manuscript
2.	Fig. 1: The symbols used for designation of peaks needs correcting.	The symbol has been corrected
	Fig. 2: (a) and (b) needs to be around to match discussion	The figure has been discussed
3.	Sentence needs to be revised for English.	The sentence in revised manuscript has been improved for its clarity
	Reviewer 2:	
1.	Please add the visible lights that the authors used in method	The light has been added
2.	The authors does not state how the effective of the material was used, please add data reusability	The sentences have been rephrased for clear argument
3.	Please check again grammatical error and the sentence	The grammatical error was corrected

Modification Spent Bleaching Earth with WO_3 and The Application For Photocatalytic Degradation of Waste Dyestuff Under Solar Light

Noor Hindryawati[1,2*], Aman Sentosa Panggabean[1], Dirgarini Julia Nurlianti Subagyono[1,2], Rinda Anisyah Putri[1], Prilianda Kusmiaty[1,2], GaantyPragas Maniam[3]

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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°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.

Keywords: photocatalytic, bleaching earth, WO_3, waste dye stuff, solar light

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_2 metal in a membrane or other solid material. Since the catalyst is not included in the reaction medium, coupling TiO_2 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_2. Based on research conducted by Sadi et al. (2015), combination of ZnO and TiO_2 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 montmorrilonite ($Al_2O_3.4SiO_2.nH_2O$) 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 montmorrilonite 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_3 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.

MATERIAL AND METHODS

Material

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_3

pro analyst was obtained from sigma Aldrich, sulphuric acid (H_2SO_4 (98 %)), methanol 95 %, n-hexane is supplied by Sigma-Aldrich.

WO_3-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_3 in NH_4OH 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_3-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_3-DSBE and the light sources used were the solar light and visible lights (Grow Light LED 10 watts). The photocatalysis test wass conducted by varying the contact time and weight of the DSBE-WO_3 catalyst. As many as 0.75g of DSBE-WO_3photocatalyst were put into 10 mL of dye waste. Contact time was set for 30; 60; 90 and 120 minutes. The mixture of DSBE-WO_3 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_3-DSBE was set as many as 0.5; 0.75; 1 and 1.5 g.

WO3-DSBE Photocatalyst Reusability

WO3-DSBE as a photocatalyst was tested for optimum reusability by separating WO_3-DSBE from the dye and then regenerating WO_3-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.

RESULT AND DISCUSSIONS

Material Preparation and Characterization

The activation process in DSBE was conducted using H_2SO_4 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.

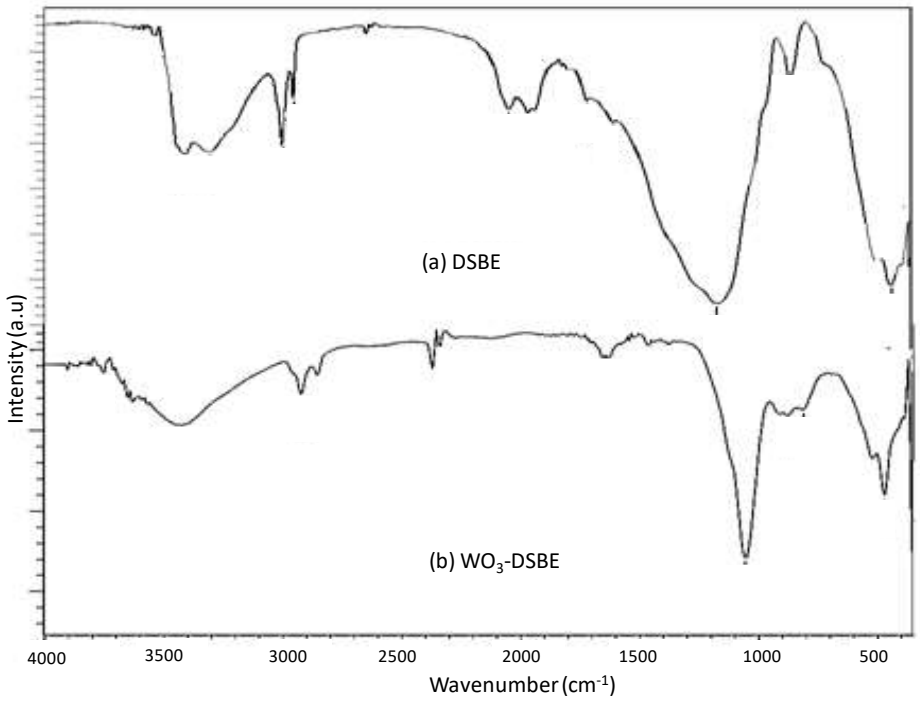

Figure 1 Spectra FTIR of (a) DSBE and (b) WO_3-DSBE

From the FTIR analysis results on DSBE, it can be seen that the wave number 3670.24 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 cm^{-1} shows Si-O-Si bending group and at 796.60 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 cm^{-1}indicates the Si-O-Si bending group and in 810.1 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 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.

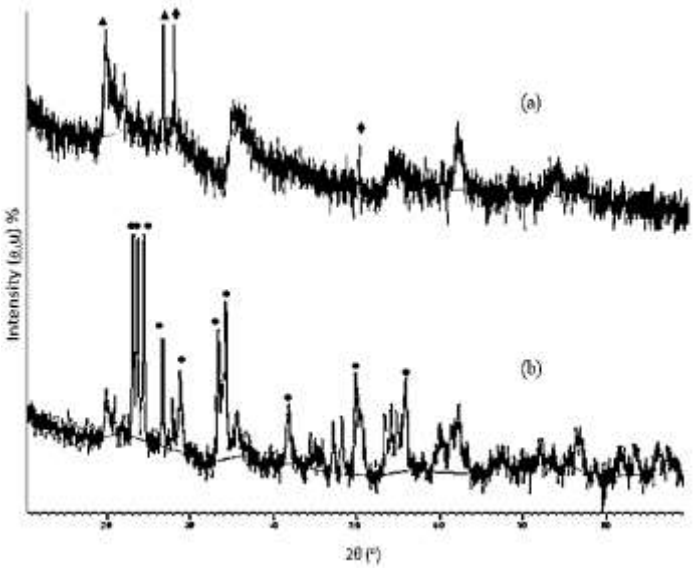

Figure 2. Diffractogram of (a) DSBE after activation and (b) DSBE-WO_3 (WO_3diffraction peak = ●; SiO_2diffraction peak = ▲; Al_2O_3diffraction peak = ♦)

From the XRD results in Figure 2(a), the diffraction pattern peaks are obtained at 2θ = 19.8714° (4.46810 Å); 26,6552° (3,34436 Å); 28.0675° (3.17963 Å) and 50.1340° (1.81963 Å).Based on Fadillah et al (2017), there are some similarities in diffraction patterns indicating the mineral is monmorillonite. Peaks indicating the presence of SiO_2 are found at 2θ = 21.8714° and 26.6552°. While peaks indicating the presence of Al_2O_3 are found at 2θ = 26.6552° and 50.1340°. The same result conducted by Aziz and Shareef (2013), the peak at 2θ = 26° and 50° indicated the Al_2O_3.

After pilarization with WO_3, the XRD results data are shown in Figure 2(b), where the data obtained diffraction patterns peak at 2θ = 23.1571° (3.84102 Å); 24,4047° (3,64742 Å) and 34,2186° (2,62049 Å) 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.

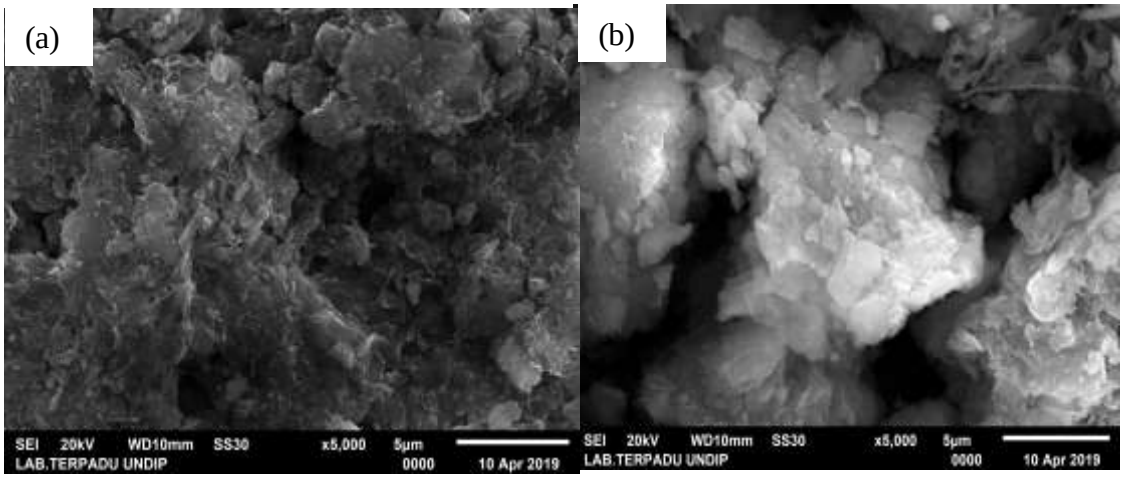

Figure 3. SEM result of (a) DSBE after activation, (b) DSBE-WO_3 (5.000 times magnification)

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 DSBE after pillarization with WO_3, 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 surfaceindicating that WO_3 has successfully doped on the DSBE.

Photocatalitic 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_3 material. Data showing the relationship between percent degradation to time can be seen in Figure 4.

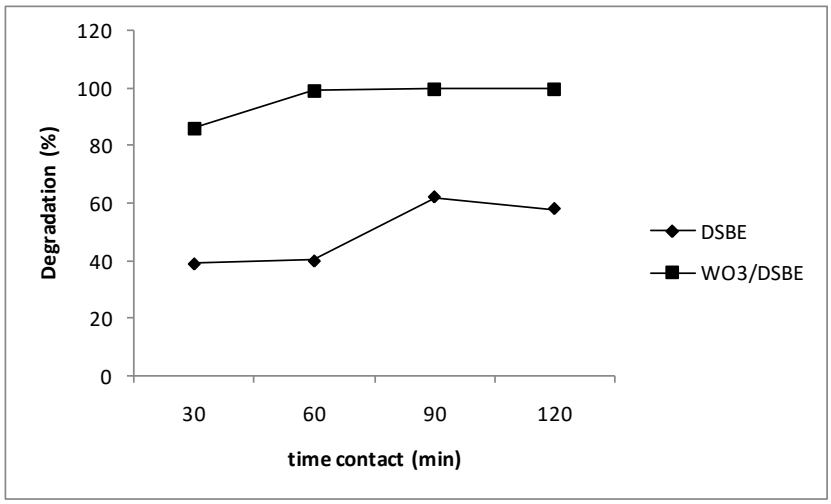

Figure 4 Contact time variations on degradation percentage.

The graph shows that in 30 minutes the percentage of degradation is 84.56%, then in the 60th minute there in 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_3 shows the waste absorption is not as much as DSBE -WO_3

DSBE-WO_3 weight optimization is conducted to determine the optimum weight of DSBE-WO_3 used in the photocatalysis reaction when the waste is contacted with DSBE-WO_3 material. The relationship between percent degradation to DSBE-WO_3 weight is shown in Figure 5.

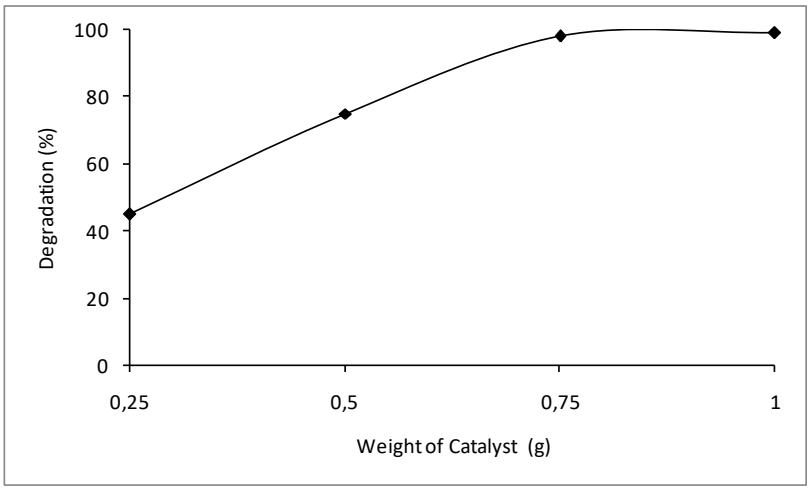

Figure 5 Weight variations on degradation percentage.

The graph shows that there is a significant increase in percent degradation from 48% using 0.25 grams DSBE-WO_3 to 99.8% by using 0.75 gramDSBE-WO3. That is because the more DSBE-WO_3contacted with dyes, the more dye is absorbed in the DSBE-WO_3 cavity (Wismayanti, 2015). The

increase of percent degradation from a mass of 0.25 gram to 0.75 grams is quite bigindicating 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_3 used in the photocatalysis reaction is 0.75 gram.

In order to know the effectiveness of the DSBE-WO_3photocatalyst, light condition variations was conducted. The results of the photodegradation test using various lighting conditions can be seen in Figure 6.

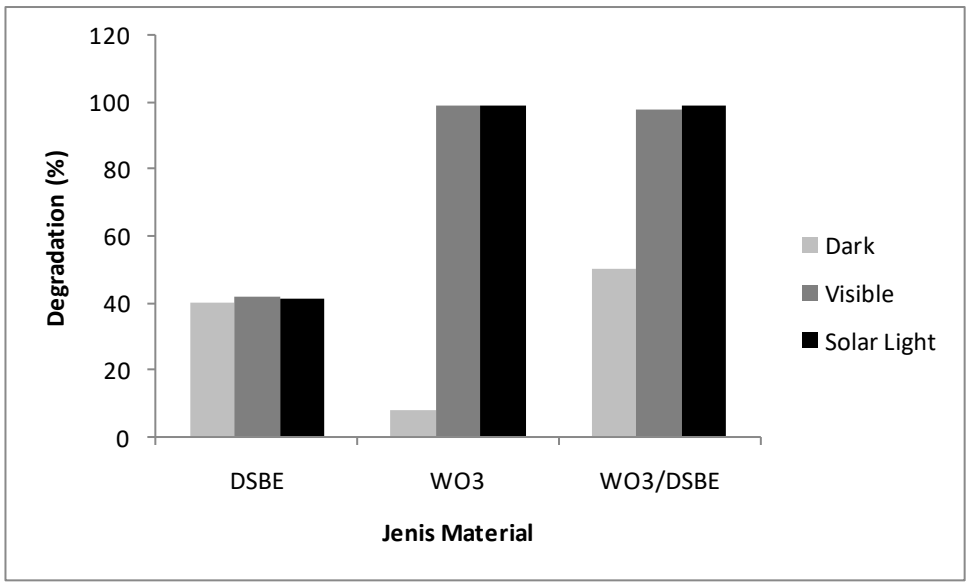

Figure 6. Light source variations on degradation percentage (*methylene blue*dye waste, at 60minutes of contact time and using DSBE-WO_3 1.5 gram)

In Figure 6, it can be seen that thephotodegradation 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_3.

Catalyst Reusability

Reusing DSBE-WO_3 aimed to find out how many times the photocatalyst DSBE-WO3 can be used in the photocatalysis reaction to degrade dye waste. This process was conducted by washing DSBE-WO_3 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_3 can be seen in Figure 7.

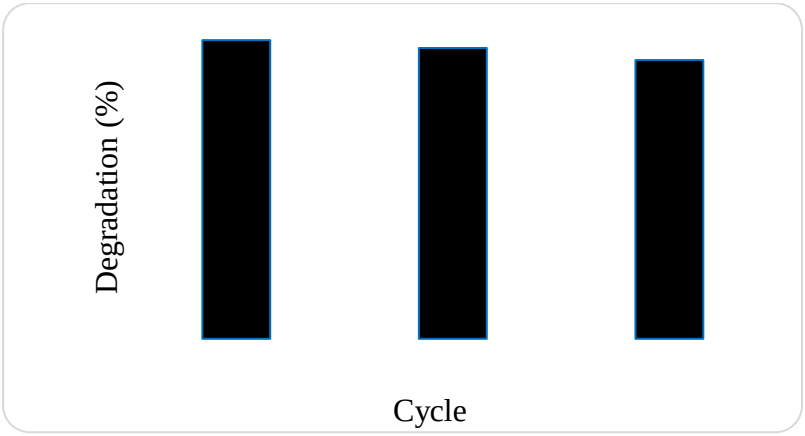

Figure 7. DSBE-WO_3 Reused (*methylene blue*, 1.5 g catalyst,60 minutes contact time)

Figure 7 shows that DSBE-WO3 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_3 being leached after repeatedly usage so that it reduces the effectiveness of radical production •OH and also decreases its photocatalytic ability (Lestari, 2015).

CONCLUSION

In this research, WO_3 has been successfully loaded to DSBE as acatalyst inphotocatalyticreaction to degrade dye waste in producing Sarong Samarinda. Optimum conditions arefound 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%.

AKNOWLEDMENTS

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JBAT Final Decision

From: Jurnal BAT (jurnal.bat@mail.unnes.ac.id)

To: ienwati@yahoo.com

Date: Friday, December 6, 2019 at 09:11 AM GMT+7

Dear Dr. Noor,

Congratulations, your manuscript, entitled "Modification of Spent Bleaching Earth with WO3 and the Application for Photocatalytic Degradation of Waste Dyestuff under Solar Light" Based on the reviewers' recommendations, the manuscript has been **ACCEPTED** to be published in the upcoming JBAT Vol. 8 No 2.

Thank you.

Best Regards,

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Prof. Dr. Megawati S.T., M.T.
Editor in Chief
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