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## Ultrasound Assisted the Degradation of Methylene Blue Using WO<sub>3</sub>-Deoiled Spent Bleaching Earth as a catalyst

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**Abstract.** Spent Bleaching Earth (SBE) that has been impregnated with WO<sub>3</sub> can degrade methylene blue through sonocatalytic. The stages of this research are SBE preparation, activation, WO<sub>3</sub>-SBE modification through wet impregnation process and sonocatalytic test. WO<sub>3</sub>-SBE is characterized using SEM and XRD. In the SEM results, there are cavities in the surface morphology of SBE after activation and after impregnation, the cavities are covered. WO<sub>3</sub>-SBE XRD diffraction pattern shows the presence of WO<sub>3</sub> at an angle of  $2\theta = 28.855^\circ$ ;  $34.813^\circ$ . The percentage of degradation of methylene blue was 99.12%, using 0.15 grams catalyst, 100 ppm concentration and 15 minutes contact time.

### 1. Introduction

People often complain of various problems, one of them is water pollution caused by textile dye industrial waste. Synthetic dyes often used in batik cloth, paper, office and cosmetic industries. The development of the textile industry has increased the use of dyes that can pollute the environment. The dye that is often used in this industry is methylene blue [1]. Methylene blue (MB) is a very important and relatively inexpensive base dye compared to other dyes. [2] Some alternative technologies are used to treat wastes that contain dyes such as coagulation, flocculation and absorption techniques. Color removal by the process of coagulation, flocculation, and absorption only transforms dyes from the liquid into the solid phase. Those processes do not separate the complex compounds of color. The color particles coagulants need further processing so that it will cause further pollution or new waste. [3] Another alternative that can be developed is the sonocatalytic method to degrade dyes.

One of the more effective methods to degrade dyes is Advance Oxidation Processes (AOPs). [4] AOPs technology is a method of oxidation of a solution phase which is mainly based on the formation and use of hydroxyl radicals (OH) as a by-product that can cause the destruction of pollutant compounds. [5] The Sonocatalytic Method is one of the AOPs that is environmentally friendly because it produces CO<sub>2</sub> and H<sub>2</sub>O. This method works to degrade organic dyes in water media by using ultrasonic vibrations with the help of a catalyst (semiconductor). This method comes from the cavitation effect bubbles produced by liquids under ultrasonic radiation. This can absorb sound energy and collapse to release energy in a very short time, high temperature and pressure. Catalysts that are often used are TiO<sub>2</sub>, ZnO, CdS, Fe<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub>. TiO<sub>2</sub> has been extensively studied to degrade harmful pollutants but it is only active under ultraviolet radiation. In contrast to Tungsten trioxide (WO<sub>3</sub>) is a semiconductor material that can accelerate the degradation process under visible radiation. WO<sub>3</sub> has a narrow bandgap of 2.7-

2.8 eV. [6] The semiconductor catalyst is long-lasting and can be used repeatedly. One of the catalyst support used is Spent Bleaching Earth (SBE). Based on the background described above, research of  $WO_3$  impregnation in Spent Bleaching Earth (SBE) as a sonocatalytic to degrade methylene blue is conducted.

## 2. Experimental Procedure

### 2.1. Spent Bleaching Earth Preparation

At first, the SBE is weighed as many as 300 grams using an analytical scale. Then the SBE is sieved using 140 sized mesh and then put in an oven at a temperature of  $120^\circ\text{C}$  for 2 hours.

### 2.2. SBE Activation

Spent Bleaching Earth (SBE) is a mixed with  $H_2SO_4$  1N solution with a ratio of 1:10 (b/v) and then homogenized. The mixed container is tightly closed. The mixture is then treated with ultrasonic wave irradiation at the optimum irradiation temperature of  $50\text{-}60^\circ\text{C}$  in 60 minutes of activation time. After that, the sample is filtered and the SBE obtained is washed using distilled water to neutralize the pH. Then the SBE is dried in an oven at  $110^\circ\text{C}$  for 3 hours and sifted in 140 mesh. [7]

### 2.3. $WO_3$ Impregnation on SBE

SBE weighed as many as 50 grams and mixed into 20 grams of  $WO_3$ , then added 400 mL of 7 M  $NH_4OH$  solution. The mixture is refluxed for 5 hours at  $60\text{-}70^\circ\text{C}$ . After that, the sample is filtered and the  $WO_3$ -SBE obtained is washed using distilled water to neutralize the pH. Then put it in the oven at  $110^\circ\text{C}$  in 3 hours. After drying,  $WO_3$ -SBE is crushed and then sieved using a 140 mesh sieve. Furthermore the solid is calcined at  $500^\circ\text{C}$  for 2 hours. [8]

### 2.4. Sonocatalytic Test on Methylene Blue Using $WO_3$ -SBE

Sonocatalytic tests are performed using variations in contact time and concentration of methylene blue. 0.15 grams of  $WO_3$ -SBE is added to 50 mL of 100 ppm methylene blue. Then put into an ultrasonic cleaner at a temperature of  $60^\circ\text{C}$  with a time variation of 5, 15, 45 and 60 minutes. Then it is filtered. Furthermore, absorbance is measured using a UV-Vis spectrophotometer. Then the degradation percentage is calculated. This is also conducted at variations in the concentration of 50, 100, 150 and 200 ppm.

### 2.5. Material Type Variation Test

In order to find out the performance of  $WO_3$ -SBE, a comparison of material types is conducted using the previous optimum condition with variations of  $WO_3$ , SBE and  $WO_3$ -SBE material.

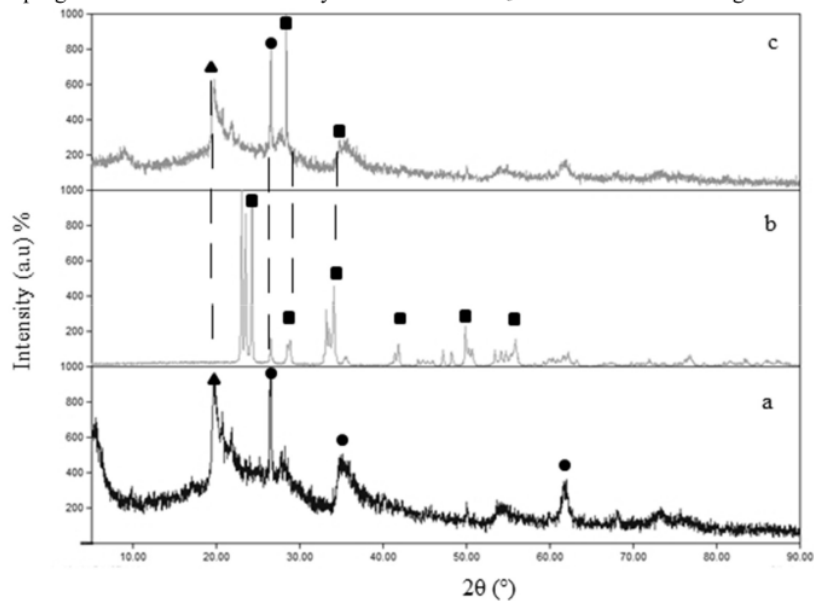
## 3. Results and Discussions

### 3.1. Impregnation and Characterization of $WO_3$ -SBE

SBE is activated by using  $H_2SO_4$  1N that can increase the surface area by exchanging  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Mn^{2+}$  and others contained in the interlayer into  $H^+$  ion.  $H_2SO_4$  1N is the optimum concentration; using concentrations above 1N can damage the *montmorillonite* structure. This is because  $Al^{3+}$  can dissolve  $H_2SO_4$ . Meanwhile, the concentration under 1 N makes the activation process takes longer. [9]

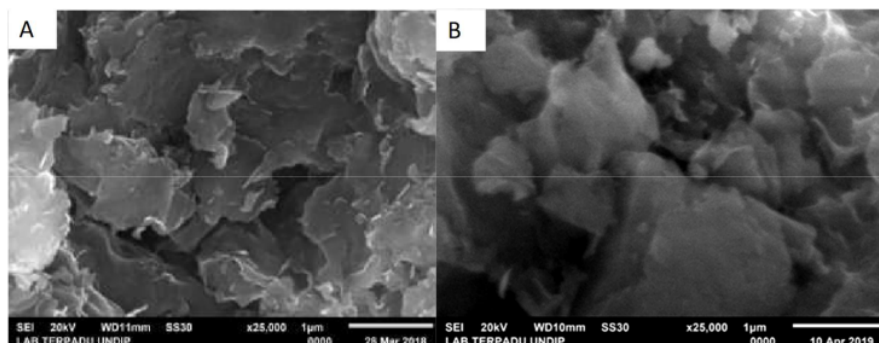
The base impregnation is conducted by using  $NH_4OH$  as a solvent that can dissolve  $WO_3$ . Because the material modification is shorter, the cost is relatively cheap and the success of modification is greater. At first,  $WO_3$ -SBE is refluxed and assisted by constant heating and stirring at the optimum temperature of  $60\text{-}70^\circ\text{C}$ . Then the  $WO_3$ -SBE obtained is washed using distilled water to reach pH 7. Furthermore, calcination is performed to tighten the distribution of the particles so that they are not easily separated, remove the remaining impurities and convert metals to their oxides.

Then the  $WO_3$ -SBE characterization is conducted using XRD to find out the peak of  $WO_3$  diffraction on the impregnated SBE. The XRD analysis results for  $WO_3$ -SBE can be seen in Figure 1.



**Figure 1.** XRD results (a)SBE (b)  $WO_3$ -dan (c)  $WO_3$ -SBE  
 ( $WO_3$  = ■ ;  $SiO_2$  = ▲ ;  $Al_2O_3$  = ●).

From the XRD data in figure 1(a) a diffraction pattern is obtained with  $SiO_2$  peak at  $2\theta = 21.460^\circ$  and  $Al_2O_3$  peak at  $2\theta = 26.559^\circ$ ;  $35.164^\circ$ ;  $62.131^\circ$ . Based on research by Fadillah [10] there are similarities in diffraction patterns that indicate the mineral is montmorillonite.  $SiO_2$  peaks are found at  $2\theta = 21.8714^\circ$  and  $26.6552^\circ$ .  $Al_2O_3$  peaks are at  $2\theta = 26.6552^\circ$  and  $50.1340^\circ$ . After conducting  $WO_3$  impregnation, XRD data is obtained in Figure 1(b) showing  $WO_3$  diffraction patterns peak at  $2\theta = 23.267^\circ$ ;  $26.619^\circ$ ;  $28.958^\circ$ ;  $34.176^\circ$ ;  $49.880^\circ$ ;  $55.159^\circ$ . Figure 1(c) shows diffraction patterns of  $WO_3$  peaks are  $28.855^\circ$ ;  $34.813^\circ$ .  $SiO_2$   $2\theta = 21.460^\circ$  and  $Al_2O_3$   $2\theta = 26.540^\circ$ . Based on Putri [11], the similarity of diffraction patterns peak at  $2\theta = 23.1571^\circ$ ;  $24.4047^\circ$  and  $34.2186^\circ$  which show the typical  $WO_3$  diffraction. Then the SEM analysis is performed to determine the morphological form of SBE after activation and  $WO_3$ -SBE which can be seen in Figure 2.



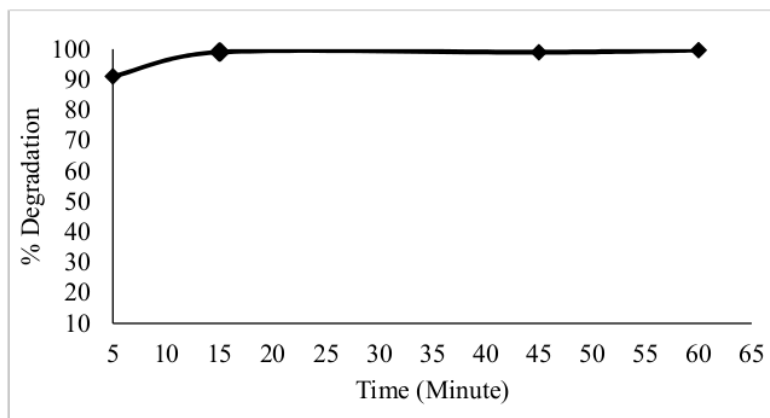
**Figure 2.** SEM results in 25.000 times magnification (a) SBE after activation, (b)  $WO_3$ -SBE.

In figure 2(a) SBE after activation of the morphological form shows the presence of pore and heterogeneous shape of the particle. While in figure 2(b)  $WO_3$ -SBE, shows some of the pores has been covered with the suspected entry of  $WO_3$  in SBE.

### 3.2. Sonocatalytic Test on Methylene Blue using $WO_3$ -SBE

#### 3.2.1. Contact Time Variation towards Methylene Blue Degradation

In this research, the variation of contact time is conducted in order to find out the optimum contact time needed by  $WO_3$ -SBE to degrade Methylene Blue. The following graph shows the relationship between contact time and degradation percentage as follows (Figure 3).



**Figure 3.** Contact time variations towards methylene blue degradation, 0.15 gram catalyst.

On the graph, the 5<sup>th</sup> minute obtains 91.14% degradation. Then the percent degradation is increased in the 15 min to 99.12%, indicating that it is the optimum contact time of  $WO_3$ -SBE in degrading methylene blue. Then the 45 min is 99.08% and 60 min is 99.81%, which indicates the percent degradation is running constantly. According to Zhou et al. [12] in general, the semiconductor catalyst ( $WO_3$ ) will produce sonocatalytic electrons ( $e^-$ ) and holes ( $h^+$ ). After that, it will cause the electrons in the valence band to be excited towards the conduction band. This has been explained in the mechanism of sonoluminescence. Sonoluminescence involves light entering through the recombination of free radicals formed from the bubbles of cavitation effects. The cavitation effect gives emission of light, so

that energy can move electrons [13]. Then OH radicals are formed which can degrade methylene blue. The longer the time needed for  $WO_3$ -SBE, the more OH radicals are formed. It is causing a greater catalyst ability to degrade methylene blue. The more OH radicals produced, the more methylene blue is degraded.

### 3.2.2. Optimum Concentration Variation towards Methylene Blue Degradation

In this research, variations in concentration are conducted in order to determine the optimum concentration required by  $WO_3$ -SBE to degrade methylene blue. The following graph shows the relationship of concentration with degradation percentage of methylene blue (Figure 4).

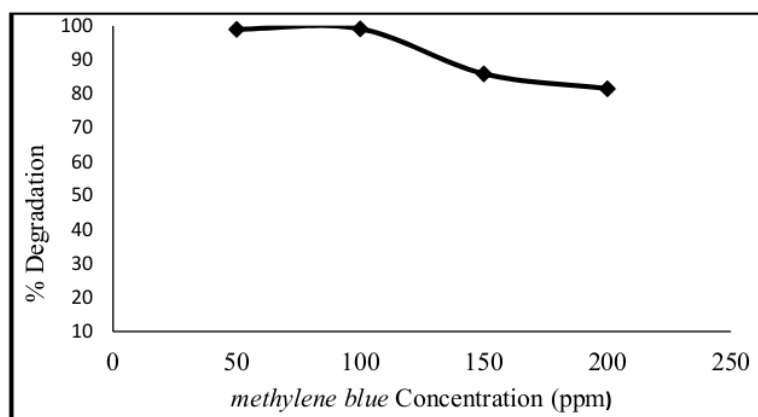


Figure 4. Concentration variations towards methylene blue degradation, 0.15 grams catalyst.

Based on the graph, the use of 50 ppm concentration obtains 99.02% degradation. Then the degradation percentage has increased at 100 ppm to 99.12% which indicates that it is the optimum concentration of  $WO_3$ -SBE in degrading methylene blue. When the concentration of methylene blue gets smaller the adsorption rate and the degradation rate will be directly proportional. This is because SBE and  $WO_3$  have the same performance. At a concentration of 150 ppm decreases to 85.91% as well as a concentration of 200 ppm gets 81.51%. At high concentrations, it is possible that the adsorption rate is getting smaller because the methylene blue that is absorbed is not in accordance with the SBE capability. It causes the degradation process in  $WO_3$  to be hampered. [14]

### 3.2.3. Variations on Type of Material

In this research, variations in material type aim to determine the process of adsorption or degradation of  $WO_3$ -SBE. The following is a graph of the relationship of variations in material types with degradation percentage of methylene blue (Figure 5).



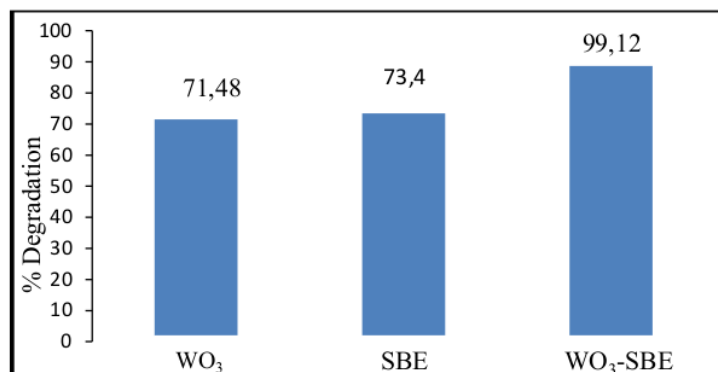


Figure 5. Material types variations towards methylene blue degradation.

The optimum weight is 0.15 gram, the contact time is 15 minutes and the concentration of methylene blue is 100 ppm. At WO<sub>3</sub> the degradation percentage is 71.48%, this is considered as the process of degradation. The SBE degradation percentage is 73.45%, this is due to the adsorption process. Then the WO<sub>3</sub>-SBE percentage is 99.12% this is due to the existence of two processes, adsorption and degradation. The first is the adsorption process on SBE then the second is the degradation process at WO<sub>3</sub>. SBE which has a large surface area causes the active adsorbent to be greater so that methylene blue is absorbed on the surface simultaneously and is degraded with WO<sub>3</sub>. Then the degraded methylene blue causes the active adsorbent to return vacant. Then the process of adsorption and degradation continues. This is a possible greater synergistic effect. If the adsorption rate is greater means the rate of degradation will be greater.

#### 4. Conclusion

In the SEM results, the surface morphology of SBE after impregnation with WO<sub>3</sub> shown the cavities are covered. The XRD results show WO<sub>3</sub> in SBE. The methylene blue degradation percentage with an optimum 0.15 grams WO<sub>3</sub>-SBE catalyst, 100 ppm concentration and 15 minutes contact time obtain 99.12%. The degradation percentage of WO<sub>3</sub> is 71.48%; SBE is 73.45% and WO<sub>3</sub>-SBE is 99.12%.

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