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Ultrasound Assisted the Degradation of Methylene Blue Using WO_3-Deoiled Spent Bleaching Earth as a catalyst

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Abstract. Spent Bleaching Earth (SBE) that has been impregnated with WO_3 can degrade methylene blue through sonocatalytic. The stages of this research are SBE preparation, activation, WO_3-SBE modification through wet impregnation process and sonocatalytic test. WO_3-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_3-SBE XRD diffraction pattern shows the presence of WO_3 at an angle of 2θ = 28.855°; 34,813°. 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_2 and H_2O. 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_2, ZnO, CdS, Fe_2O_3 and WO_3. TiO_2 has been extensively studied to degrade harmful pollutants but it is only active under ultraviolet radiation. In contrast to Tungsten trioxide (WO_3) is a semiconductor material that can accelerate the degradation process under visible radiation. WO_3 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˚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 50-60°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°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 60-70°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°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°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°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 60-70°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.

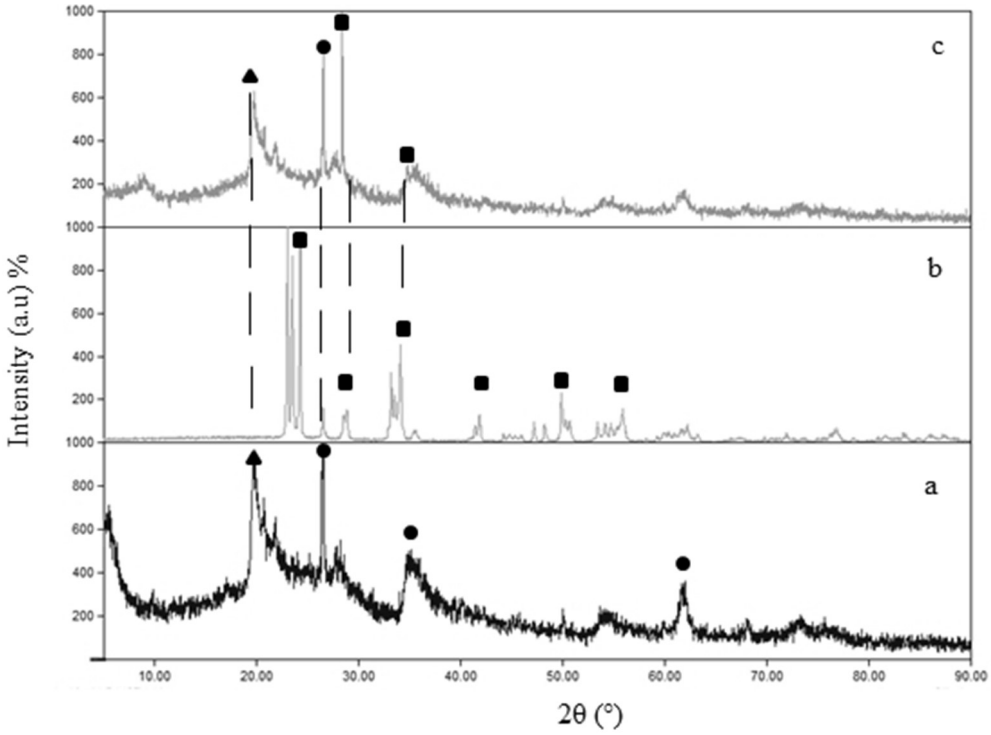

Figure 1. XRD results (a)SBE (b) WO_3dan (c) WO_3-SBE
(WO_3 = ■ ; SiO_2 =▲ ; Al_2O_3 =●).

From the XRD data in figure 1(a) a diffraction pattern is obtained with SiO_2 peak at 2θ = 21.460° and Al_2O_3 peak at 2θ = 26.559°; 35,164°; 62,131°. Based on research by Fadillah [10] there are similarities in diffraction patterns that indicate the mineral is montmorillonite. SiO_2 peaks are found at 2θ = 21,8714˚ and 26,6552˚. Al_2O_3 peaks are at 2θ = 26,6552˚ and 50,1340˚. After conducting WO_3 impregnation, XRD data is obtained in Figure 1(b) showing WO_3 diffraction patterns peak at 2θ = 23.267°; 26,619°; 28,958°; 34,176°; 49,880°; 55,159°. Figure 1(c) shows diffraction patterns of WO_3 peaks are 28,855°; 34,813°. SiO_2 2θ = 21,460° and Al_2O_3 2θ = 26,540°. Based on Putri [11], the similarity of diffraction patterns peak at 2θ = 23,1571˚; 24,4047˚ and 34,2186˚ 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.

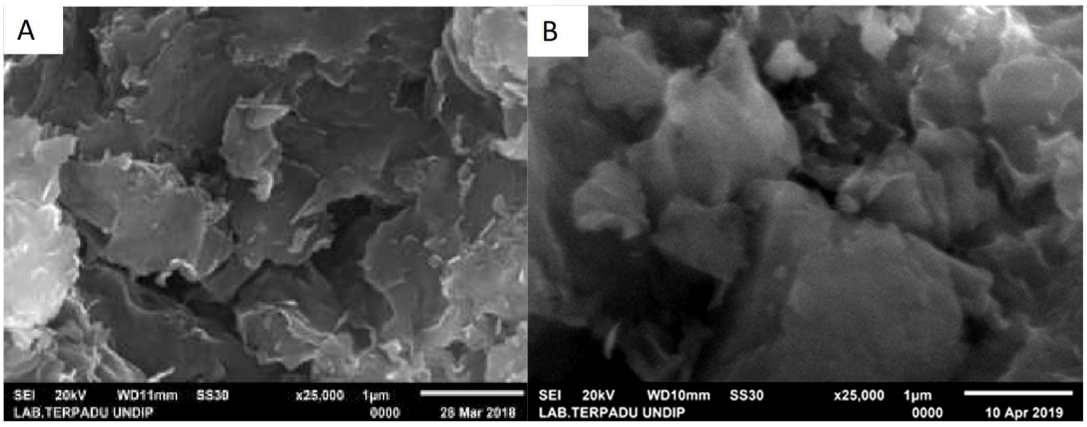

Figure 2. SEM results in 25.000 times magnification (a) SBE after activation, (b) WO_3-SBE.

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).

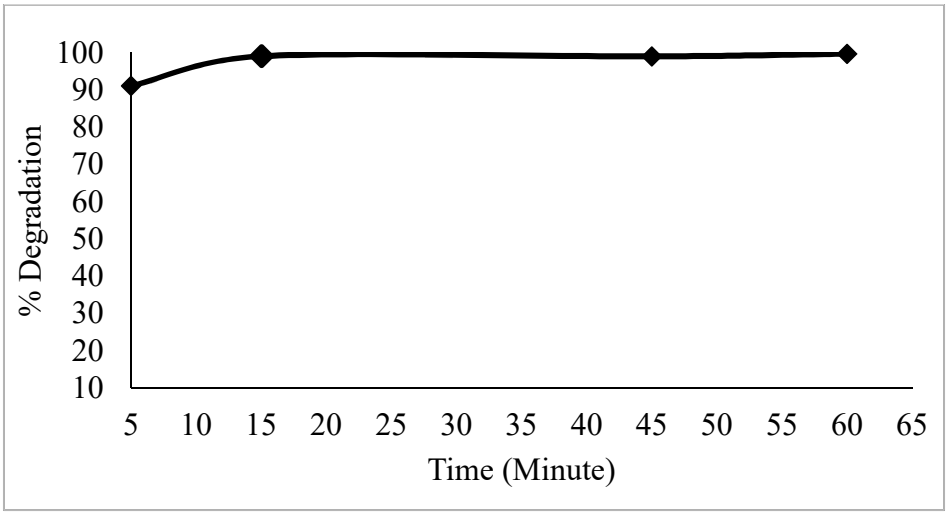

Figure 3. Contact time variations towards methylene blue degradation, 0.15 gram catalyst.

On the graph, the 5th 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).

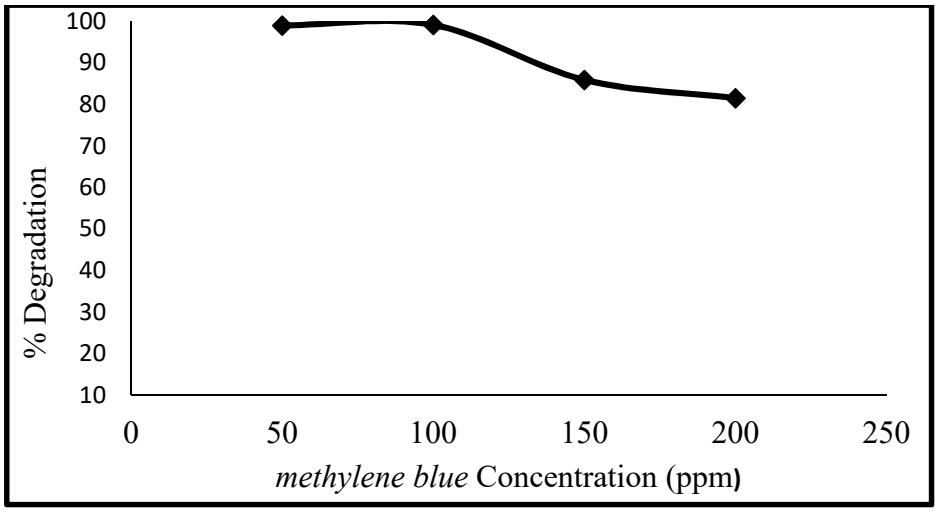

Figure 4. Concentration variations towards methylene blue degradation, 0.15 grams catalyst.

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).

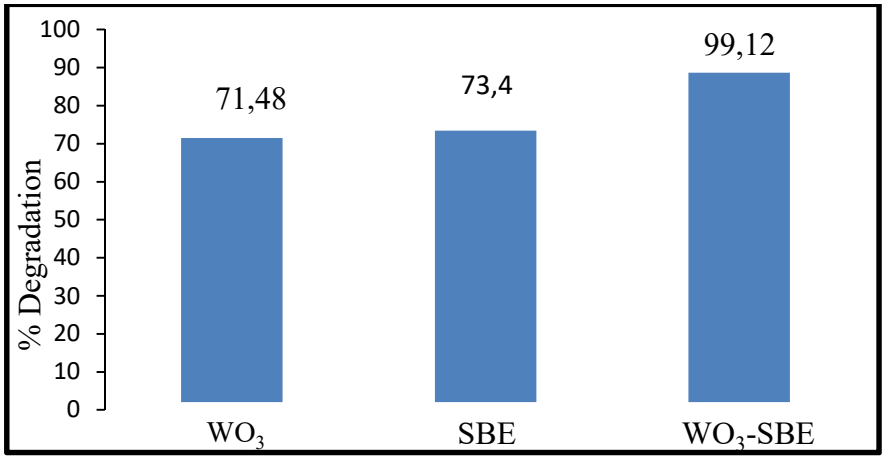

Figure 5. Material types variations towards methylene blue degradation.

The optimum weight is 0.15 gram, the contact time is 15 minutes and the concentration of methylene blue is 100 ppm. At $WO_3$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_3-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_3. 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_3. 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_3 shown the cavities are covered. The XRD results show WO_3 in SBE. The methylene blue degradation percentage with an optimum 0.15 grams WO_3-SBE catalyst, 100 ppm concentration and 15 minutes contact time obtain 99.12%. The degradation percentage of $WO_3$is 71.48%; SBE is 73.45% and WO_3-SBE is 99.12%.

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