

Mn/Carbon Sphere Catalyst For Heterogeneous Activation Of Peroxymonosulfate For Methylene Blue Removal

Yusnimar^{a,1}, Khairat^{a,2}, Chairul^{a,3}, Silvia Reni Yenti^{a,4}, Wisrayetti^{a,5}, Barata Aditya Prawiranegara^{b,6}, Heni Sugesti^{a,7}, Panca Setia Utama^{a,8}, Edy Saputra^{a,9*}

^a Department of Chemical Engineering, Universitas Riau, Pekanbaru, 28293, Indonesia

^b Department of Chemistry, Universitas Riau, Pekanbaru, 28293, Indonesia

¹ yusnisahan@lecturer.unri.ac.id; ² khairat@lecturer.unri.ac.id; ³ chairul@lecturer.unri.ac.id; ⁴ silvia.reni@lecturer.unri.ac.id; ⁵ wisrayetti@lecturer.unri.ac.id; ⁶ barata.p@outlook.com; ⁷ heni.sugesti7193@grad.unri.ac.id; ⁸ panca.setia@lecturer.unri.ac.id; ⁹ edysaputra@unri.ac.id *

* corresponding author

ARTICLE INFO

Article history

Received October 26, 2021

Revised December 23, 2021

Accepted January 03, 2022

Keywords

AOP

Carbon

Catalyst

Manganese

ABSTRACT

One of the latest innovations in textile waste treatment is advanced oxidation processes (AOPs) methods using an oxidizing agent capable of producing sulfate radicals (SO₄[•]). This study aims to determine the activity of the Mn/Carbon sphere catalyst in the oxidation process, reduce the dye content by using a combination of peroxydisulfate (PMS) and Mn/Carbon sphere catalyst as an oxidizing agent, and determine the optimum conditions in the process of reducing dye levels in the water. A hydrothermal process carried out the catalyst synthesis process to produce black carbon from D-glucose solution, then impregnated with variations of 3% and 5% of Mn metal. The degradation of methylene blue (artificial waste) of 25 mg/L (1:10 dilution) was carried out for 120 minutes with variations in the catalyst mass of 0.001, 0.002, 0.003, and 0.004 g and the mass of PMS 0.01, 0.02, 0.03, and 0.04 g in 100 ml sample. Mn/Carbon sphere catalyst was able to activate PMS and degrade methylene blue by 88.16%. The optimum condition for reducing the methylene blue levels in the water is at a concentration of 1 g/L PMS and an Mn/Carbon sphere catalyst (5% Mn metal) 0.5 g/L with an efficiency of 88.16%.

This is an open access article under the [CC-BY-SA](#) license.



1. Introduction

Wastewater from the textile industry not only visually interferes with the quality of water bodies (color) but can also block the passage of light in water, which inhibits biological processes in water bodies [1]. One alternative for processing textile waste with low operational costs is the Advanced Oxidation Process (AOP) method which can degrade hazardous compounds in waste through an oxidative degradation process [2, 3]. Advanced Oxidation Process (AOP) technology is one or a combination of several processes such as ozone (O₃), hydrogen peroxide, ultraviolet light, titanium oxide, photocatalyst, sonolysis, electrical discharge, and several other processes to produce active radicals [4, 5]. These active radicals easily react with any organic compound without exception, especially organic compounds that have been difficult or cannot be decomposed by microbiological methods or membrane filtration. In addition, the final product of the oxidation process is only carbon dioxide and water, so it is less dangerous if discharged into water bodies [6-8].

Therefore, in this study, the AOP process will be carried out on the water that has been added with azo dye, namely Methylene Blue (MB) with a certain concentration, then analyze the results of the process. In the process, the AOP will be applied by combining PMS (2KHS₅.KHSO₄.K₂SO₄) and a catalyst in the form of Mn/Carbon sphere nanoparticles. The combination will produce free radical

sulfate (SO_4^{4-}), breaking the dye molecules in water. This combination is expected to effectively reduce the levels of dyes and organic compounds in wastewater.

Therefore, in this study, the AOP process will be carried out on the water that has been added with azo dye, namely Methylene Blue (MB) with a certain concentration, then analyze the results of the process. In the process, the AOP will be applied by combining PMS ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) and a catalyst in the form of Mn/Carbon sphere nanoparticles. The combination will produce free radical sulfate (SO_4^{4-}), breaking the dye molecules in water. This combination is expected to effectively reduce the levels of dyes and organic compounds in wastewater.

2. Research Methodology

2.1. Materials

The Materials used are D-glucose (Merck), methylene blue (Merck), peroxymonosulfate (oxone®, Dupont's triple salt: $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) obtained from Sigma-Aldrich, Manganese (II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) obtained from Sigma-Aldrich.

2.2. Procedures

2.2.1. Catalyst synthesis

7.24 g of D-Glucose (99.5%) was mixed with 80 ml of water and stirred for 4 hours. Then the mixture was transferred to a Teflon-line autoclave and heated for 18 hours at 180 °C. After that, the black suspension was filtered and washed. The carbon material was then dried at 120 °C for 12 hours. Furthermore, this carbon material is mixed with Manganese (II) nitrate hexahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as much as 3 or 5% of the total mass of black solids, then stirred for 24 hours and dried. Next, the material is calcined in a tube furnace at 500 °C for 4 hours in N_2 . The obtained material is denoted Mn/Carbon.

2.2.2. Catalyst oxidation

The catalytic oxidation of dyes was 100 ml, with a concentration of 25 mg/L, and the catalyst was Mn/Carbon sphere with the variation of 0.001-0.004 g. Samples were taken as much as 5 ml each time interval for 120 minutes. Then the sample was centrifuged at 3000 rpm for 5 minutes to precipitate the catalyst. Then the solution was analyzed by UV-Vis spectrophotometer. Research procedures are written in this part.

3. Results and Discussion

3.1. Characterization of the catalyst

The Mn/Carbon sphere catalyst characterization was carried out using the X-Ray Diffraction (XRD) method. The results of the XRD analysis for the Mn/Carbon sphere catalyst can be seen in Figure 1 below.

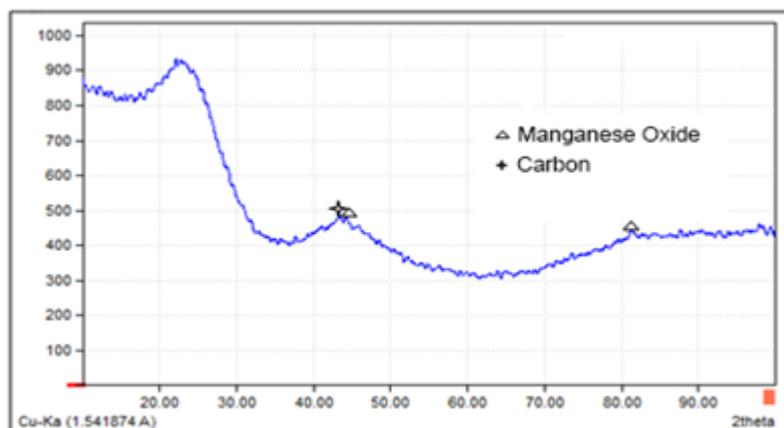


Fig.1. XRD pattern of the catalyst Mn/Carbon sphere Composite.

Based on the XRD analysis that has been carried out, the peak number at 2θ of the compounds contained in the catalyst can be seen in figure 1. Carbon structure is found at position 2θ : $43,453^\circ$ [11, 12]. According to JCPDS no. 41-4187. As for the Manganese oxide compound based on JCPDS no 80-1098, located at 2θ position: $44,411^\circ$, and $81,489^\circ$ [13].

3.2. The effect of the Mn loading of the catalyst

In the AOPs stage, we studied the effect of the metal percentage weight ratio of the catalyst. The catalyst synthesis is the impregnation method, whereby varying the mass percentage of Mn metal as the metalcore. The process is done by varying 3% Mn metal and 5% Mn metal from the total mass of carriers which is carbon material. The effect of the % mass ratio of Mn metal used as a catalyst for the oxidation process can be seen in Figure 2.

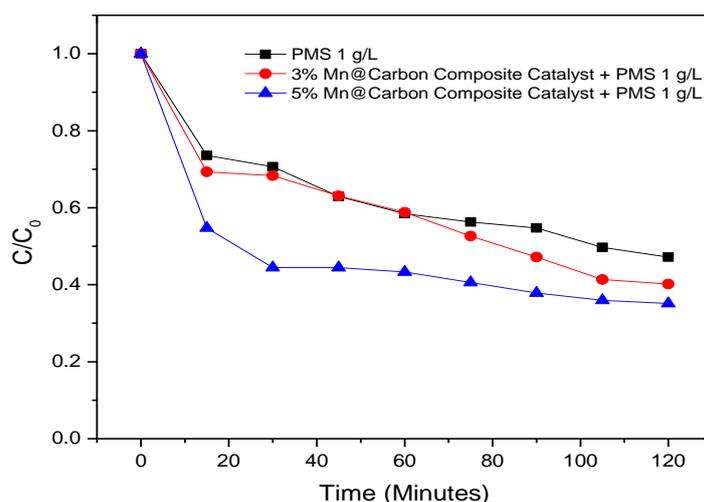
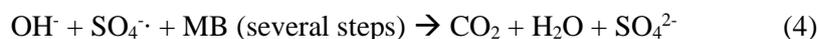
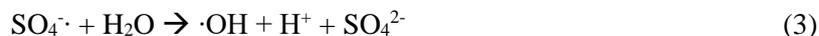
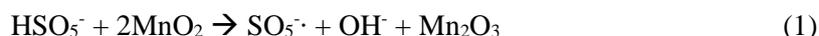


Fig.2. Degradation performance of the Mn/Carbon sphere catalyst at different Mn content. MB = 25 mg/L, catalyst loading = 0.1 g/L, PMS loading = 1.0 g/L, and T = 25 °C.

From Figure 2, it can be seen that there was a decrease in the concentration of methylene blue for each variation of the concentration of the Mn/Carbon sphere catalyst and without a catalyst. The process is assisted by adding additional oxides in the form of oxone (PMS). The 5% Mn/Carbon sphere catalyst variation is more effective than the 3% Mn/Carbon sphere catalyst. The decrease in MB concentration on 5% Mn/Carbon sphere catalyst reached 64.85%. The 3% Mn/Carbon sphere catalyst has an efficiency of 59.81%, while the uncatalyzed process has 50%.

From this data, the addition of metal to the catalyst matrix increases the effectiveness of the catalyst performance. This can be explained because the dominant role of electron charge transfer is metal species in the catalyst matrix (Mn) in this AOP process. As is known, the AOP reaction of PMS activation using Mn metal is as follows [14, 15].



3.3. The effect of the PMS concentration.

To see the performance of the catalyst, an oxidation reaction was carried out at the lowest concentration of PMS, which is at the mass of 0.01 g PMS. The variations in the Mn/Carbon sphere catalyst mass of 0.001 g, 0.002 g, 0.003 g, and 0.004 g for the experiment. Test the catalytic properties of the catalyst used can be seen in Figure 3.

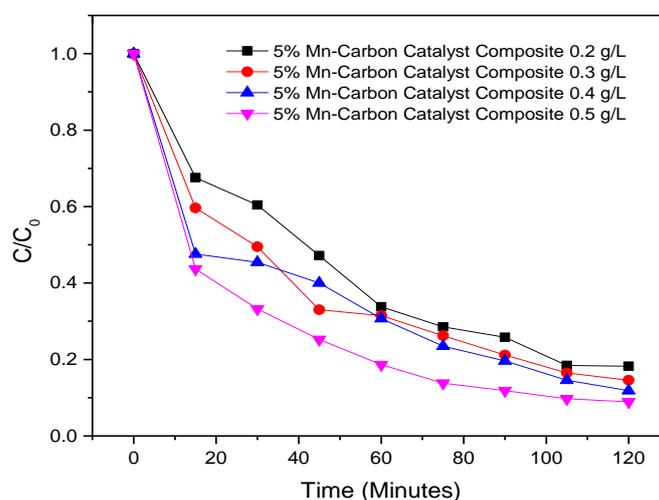


Fig.3. Degradation performance of the Mn/Carbon sphere catalyst at different catalyst mass MB = 25 mg/L, PMS loading = 1.0 g/L, and T = 25 °C.

Based on Figure 3, it can be seen that the effect of variations in the concentration of the Mn/Carbon sphere catalyst is directly proportional to the efficiency of the removal of dye (methylene blue). At 0.001g of Mn/Carbon sphere catalyst in 100 ml of sample, it reduced methylene blue by 64.85%. The addition of a catalyst of 0.002 g was able to reduce methylene blue by 81.75%, the addition of a catalyst of 0.003 g was able to reduce methylene blue by 85.44%. In comparison, the addition of a catalyst of 0.004 g reduced methylene blue by 88.16%. Based on the explanation from Figure 3, it can be concluded that the optimum mass of Mn/Carbon sphere catalyst to degrade or reduce methylene blue dye is 0.004 g with a decrease in concentration from 25 g/L to 2.96 g/L with an efficiency of 88.16%. Adding the amount of catalysts will increase the number of active sites for the radical generation process. This is directly correlated with the increase in efficiency of the photocatalyst process. It is evident from the significant increase in the degradation percentage from 64.85% to 88.16% under the same reaction conditions.

4. Conclusion

In summary, we have prepared a carbon-based catalyst material with Mn metal composites that were varied based on the percentage of catalyst weight. Mn, as much as 3% and 5% of the total percentage of catalyst was added to the carbon matrix by impregnation. These two catalysts were then used to degrade methylene blue (MB) solution by AOP with a PMS oxidant. The results obtained are 5% Mn/Carbon sphere catalyst has an optimum yield of 88.16% with reaction conditions of 1 g/L PMS and 0.5 g/L catalysts. The catalysis process is carried out for 120 minutes.

Acknowledgment

Y.N thank the support of the Indonesian Ministry of Research, Technology, and Higher Education (Ristekdikti), Indonesia

References

- [1] Shen, B., et al., Efficient Fe(III)/Fe(II) cycling triggered by MoO₂ in Fenton reaction for the degradation of dye molecules and the reduction of Cr(VI). *Chinese Chemical Letters*, 2019. **30**(12): p. 2205-2210.
- [2] Ye, Y., et al., Photocatalytic, Fenton and photo-Fenton degradation of RhB over Z-scheme g-C₃N₄/LaFeO₃ heterojunction photocatalysts. *Materials Science in Semiconductor Processing*, 2018. **82**: p. 14-24.
- [3] Utama, P.S., et al., LaMnO₃ Perovskite Activation of Peroxymonosulfate for Catalytic Palm Oil Mill Secondary Effluent Degradation. *Journal of Applied Materials and Technology*, 2020. **2**(1): p. 27-35.
- [4] Cai, Q.Q., et al., Potential of combined advanced oxidation – Biological process for cost-effective organic matters removal in reverse osmosis concentrate produced from industrial wastewater reclamation: Screening of AOP pre-treatment technologies. *Chemical Engineering Journal*, 2020. **389**: p. 123419.
- [5] Saputra, E., et al., Spent Bleaching Earth Supported CeFeO₃ Perovskite for Visible Light Photocatalytic Oxidation of Methylene Blue. *Journal of Applied Materials and Technology*, 2020. **1**(2): p. 81-87.
- [6] Miklos, D.B., et al., Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. *Water Research*, 2018. **139**: p. 118-131.
- [7] Al Amery, N., et al., Removal of methylene blue (MB) by bimetallic- metal organic framework. *Journal of Applied Materials and Technology*, 2020. **2**(1): p. 36-49.
- [8] Al Amery, N., et al., Enhancing Acidic Dye Adsorption by Updated Version of UiO-66. *Journal of Applied Materials and Technology*, 2020. **1**(2): p. 54-62.
- [9] Deng, Y. and R. Zhao, Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Current Pollution Reports*, 2015. **1**(3): p. 167-176.
- [10] Cole-Hamilton, D.J., Homogeneous Catalysis--New Approaches to Catalyst Separation, Recovery, and Recycling. *Science*, 2003. **299**(5613): p. 1702.
- [11] Saputra, E., et al., Manganese oxides at different oxidation states for heterogeneous activation of peroxydisulfate for phenol degradation in aqueous solutions. *Applied Catalysis B: Environmental*, 2013. **142**: p. 729-735.
- [12] Jiang, H., et al., High-rate electrochemical capacitors from highly graphitic carbon-tipped manganese oxide/mesoporous carbon/manganese oxide hybrid nanowires. *Energy & Environmental Science*, 2011. **4**(5): p. 1813-1819.
- [13] Saputra, E., et al., Activated carbons as green and effective catalysts for generation of reactive radicals in degradation of aqueous phenol. *RSC advances*, 2013. **3**(44): p. 21905-21910.
- [14] Guo, R., et al., Sulfamethoxazole degradation by visible light assisted peroxydisulfate process based on nanohybrid manganese dioxide incorporating ferric oxide. *Applied Catalysis B: Environmental*, 2020. **278**: p. 119297.
- [15] Wang, L., et al., Oxidation of bisphenol A by nonradical activation of peroxydisulfate in the presence of amorphous manganese dioxide. *Chemical Engineering Journal*, 2018. **352**: p. 1004-1013.