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Research Article

Redox-driven formation of hausmannite-type manganese oxide and its catalytic performance

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ABSTRACT: Various manganese oxides have been reported as active catalysts for dye degradation. Synthetic manganese oxides can be produced using several methods, yielding products with different physicochemical properties and structures. This research focuses on the synthesis of hausmanite-type manganese oxide (Mn_3O_4) via the hydrothermal method, using different mole ratios of $KMnO_4$/glucose (3:1 and 2:3), and its application as a Fenton catalyst for methylene blue (MB) degradation. The as-synthesized manganese oxides were characterized by XRD to determine their structure and crystallinity, and by FTIR and Raman spectroscopy to analyze lattice vibrations. The average oxidation state (AOS) of manganese in the synthesized oxide was determined using the back titration method. XRD results indicated the presence of mixed phases, with hausmanite as the major component, alongside cryptomelane and birnessite as minor phases. FTIR spectroscopy revealed O-Mn vibrations at wavelengths of 468 cm^{-1}, 487 cm^{-1}, and 726 cm^{-1}. Additionally, Raman spectroscopy clearly identified the specific vibrations of hausmanite at 655 cm^{-1} and 653 cm^{-1}, respectively. A lower Mn AOS value was observed when the oxide was synthesized with a lower $KMnO_4$/glucose ratio and a shorter reaction time. The synthesized hausmanite was tested as a Fenton catalyst for MB degradation. Despite variations in mole ratio and reaction time, the catalysts exhibited similar catalytic activity, with the highest MB removal efficiency reaching 89.97%.

Keywords: *Haussmanite, Hydrothermal, Redox-reaction, Catalyst, Methylene blue*

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1. INTRODUCTION

Manganese oxides have been proposed for various applications due to their economic value and environmental friendliness. They are widely used as sensors and catalysts in various chemical reactions, with their catalytic performance largely dependent on physicochemical properties and structures. A wide range of synthetic techniques and synthesis conditions has been reported to influence the structure, surface characteristics, and catalytic efficiency of these materials [1]. Manganese oxide compounds exhibit different stoichiometric ratios of manganese to oxygen, including rock-salt MnO (manganosite), Mn_3O_4, Mn_2O_3, and layered or tunnel-structured MnO_2.

Various synthesis methods have successfully produced manganese oxides with diverse structures and morphologies. Synthetic techniques such as solid-state reactions, hydrothermal synthesis, microwave irradiation, sol-gel processing, and chemical vapor deposition (CVD) have been employed to fabricate these materials [2]. The layered birnessite-type manganese oxide has been successfully synthesized via the ceramic method using $KMnO_4$ and glucose precursors at a 3:1 ratio, achieving methylene blue (MB) degradation up to 95.67% within 120 minutes [3]. Wang et al. (2015) synthesized mixed-phase Mn_3O_4 via the hydrothermal method using $MnSO_4$, CTAB, and urea as reactants. The resulting product was tested for MB degradation using the Fenton method and UV radiation, yielding degradation efficiencies of 34.7%, 52.3%, and 75.6% over 180 minutes, respectively. The synthesis

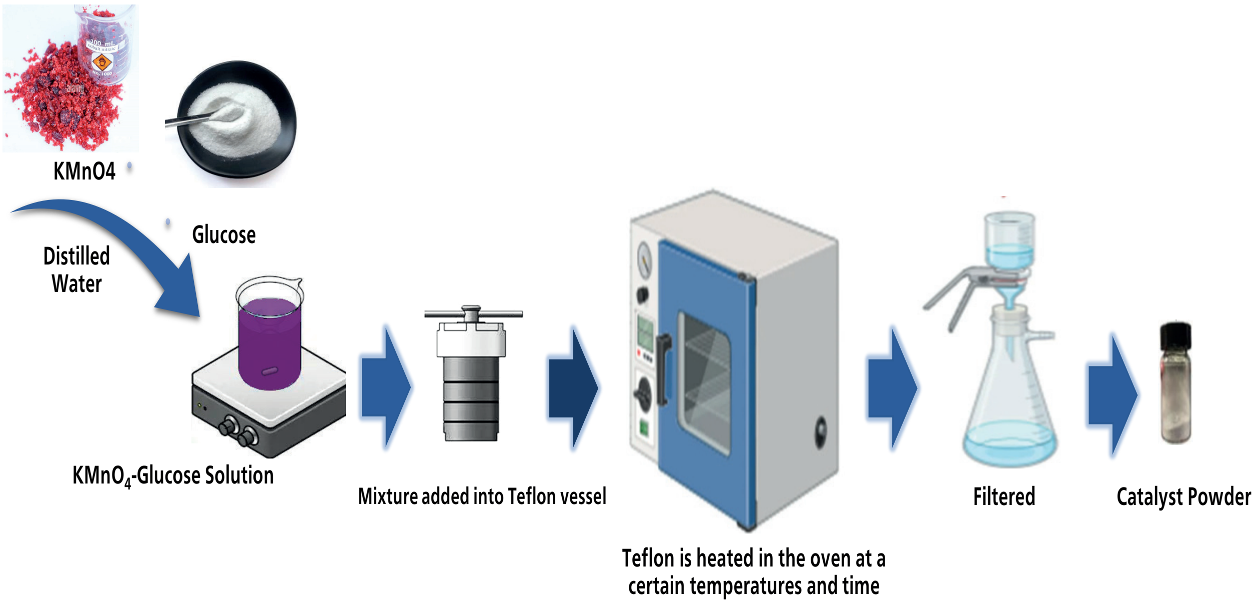

Figure 1. Schematic representation of catalyst synthesis via the hydrothermal method.

of manganese oxides using glucose and $KMnO_4$ via hydrothermal methods via hydrothermal methods has never been reported previously. This approach is expected to yield manganese oxides with unique physicochemical properties and structural characteristics [4].

Over the past two decades, manganese oxides have been applied as catalysts for the degradation of textile waste. Untreated waste from textile industries can cause adverse environmental effects, particularly in aquatic ecosystems. Residues of dyes, such as methylene blue (MB), generated during the coloring process, are produced in large quantities [5]. MB has been reported to cause health issues in humans, including eye, respiratory, digestive, and mental disorders [6]. Additionally, MB exhibits high toxicity to aquatic organisms due to its persistent nature and bright coloration, making it difficult to degrade in water [7].

Various methods for dye removal include biological techniques using microbes, as well as physical methods such as coagulation, electrocoagulation, and adsorption. However, these methods are often ineffective in addressing recalcitrant textile waste substances, which can severely impact aquatic environments. Some drawbacks of these methods include high operational costs and implementation challenges in Indonesia. While adsorption is considered a simple and widely used approach for dye waste treatment, it is often inefficient. The primary issue is that adsorbed organic waste continues to accumulate in the adsorbent, potentially causing secondary environmental pollution [8].

Advanced Oxidation Processes (AOPs) are considered the most effective and efficient chemical methods for treating color waste, particularly those containing high organic compound concentrations. AOP technology comprises several processes involving ozone, hydrogen peroxide (H_2O_2), ultraviolet (UV) light, titanium dioxide (TiO_2), photocatalysis, sonolysis, electron beams, electrical discharges (plasma), and other techniques, all of which generate hydroxyl radicals ($OH^{\cdot}$) [9]. All the aforementioned methods have been reported to decompose organic compounds into CO_2 and water through complete oxidation. In this study, hausmanite-type manganese oxide (Mn_3O_4) was synthesized via redox reaction using the hydrothermal method and applied as a Fenton catalyst for methylene blue (MB) degradation. The Fenton method is regarded as a simple, safe, and cost-effective approach for environmental applications in Indonesia.

In this research, hausmannite will be synthesized using a one-step hydrothermal method from $KMnO_4$ and glucose. Variations in reaction time and mole ratio will be conducted to study the catalyst's activity. The catalyst's performance will be tested in methylene blue (MB) degradation using the Fenton method. It is expected that differences in mole ratio and synthesis time will result in distinct characteristics, leading to variations in catalytic activity.

2. MATERIALS AND METHODS

2.1. Materials. The materials used in this research were Potassium Permanganate (KMnO4) (pa Merck), hydrochloric acid (pa Merck), glucose (pa Merck), methylene blue (pa Merck) without further purification, Whatman filter paper No. 42, distilled water.

2.2. Synthesis of Mn_3O_4 using the hydrothermal method. Hydrothermal synthesis was conducted using $KMnO_4$/glucose mole ratios of 2:3 and 3:1. The synthesis of manganese oxide with a $KMnO_4$/glucose ratio of 2:3 was performed as follows: 2.68 grams of $KMnO_4$ was dissolved in 50 mL of demineralized water (aqua DM), followed by the addition of 4.68 grams of glucose. The mixture was stirred for approximately 2 minutes, then transferred to an autoclave and heated in an oven at 120°C for 6 hours. The resulting product was filtered and washed twice with 25 mL of aqua DM, then dried at 110°C. The final product was pulverized and washed with 0.1 M HCl and 10 mL of aqua DM, three times each, then dried at 110°C and stored in a desiccator. The same protocol was applied for the synthesis of manganese oxide using the $KMnO_4$/glucose mole ratio of 3:1. The schematic of catalyst synthesis is illustrated in Figure 1.

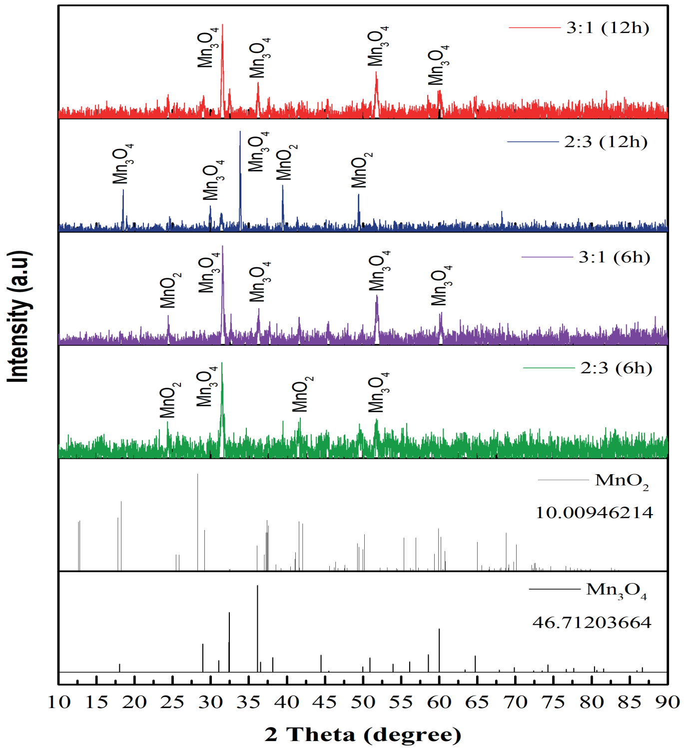

Figure 2. The XRD patterns of the catalysts synthesized under different reaction times and precursor molar ratios.

2.3. Characterization of the as-a synthesized hausmanite Mn_3O_4. The as-synthesized manganese oxides were characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and Raman spectroscopy. The average oxidation state (AOS) of manganese in the synthesized oxides was determined using the back titration method.

2.4. Catalytic performance of hausmanite Mn_3O_4. About 100 mL of a 12.5 ppm methylene blue (MB) solution was placed into a beaker glass. The solution was then added with 50 mg of the as-synthesized manganese oxide. The mixture was stirred using a magnetic stirrer at 400 rpm for 30 minutes, followed by the addition of 15 mL of H_2O_2 solution. A 10 mL portion of the solution was taken every 10 minutes, up to 120 minutes, and centrifuged at 3000 rpm for 10 minutes to separate the solid oxide catalyst from the remaining MB solution. The remained MB solution was then analyzed using a UV-Vis spectrophotometer at its optimum wavelength. The influence of hydrogen peroxide concentration on methylene blue degradation was examined following the same methodology, but with different volumes of H_2O_2: 0, 5, 10, and 15 mL. The optimal peroxide concentration was then used as a constant variable for further studies, such as the effect of catalyst concentration on MB degradation.

In this study, the amount of catalyst was varied as follows: 25 mg, 50 mg, and 75 mg, including a control sample without the catalyst. Thus, the optimal concentrations of hydrogen peroxide and catalyst were determined for maximum MB degradation and were then used as constant variables to examine the effect of initial MB concentrations: 4, 8, and 12.5 ppm.

3. RESULT AND DISCUSSION

3.1. Analysis of the synthesized catalyst. Manganese oxide catalysts were synthesized via the hydrothermal method using a $KMnO_4$/glucose mole ratio of 2:3. The synthesis was conducted in an autoclave, followed by calcination at 120°C for either 6 or 12 hours to study the effect of reaction time on composition and crystallinity. The The precursor solution, prepared by mixing $KMnO_4$ and glucose, underwent redox reactions in which $KMnO_4$ functioned as an oxidizing agent and glucose as a reducing agent, as shown in Equation 1.

$$3KMnO_4\,(aq) + C_6H_{12}O_6\,(s) \rightarrow Mn_3O_4\,(s) + 6CO_2\,(g) + 6H_2O\,(aq) + 3K^+(aq) \quad (1)$$

After synthesis, the obtained product was washed with demineralized water (aqua DM) to remove impurities, followed by filtration and drying. The catalyst was further washed with 0.1 M HCl and aqua DM (10 mL) to eliminate residual K^+ and Cl^- ions. The final product was dried at 110°C, ensuring moisture removal, and subsequently characterized using XRD, FTIR, and Raman spectroscopy. XRD analysis confirmed the presence of hausmannite (Mn_3O_4) peaks, indicating successful formation of the targeted manganese oxide phase.

3.2. Characterization of catalyst. The as-synthesized catalysts were characterized using X-ray diffraction (XRD) to determine their crystal structure, size, and degree of crystallinity. The XRD diffractograms (Figure 2) reveal diffraction peaks corresponding to various manganese oxide crystal phases, including hausmannite (Mn_3O_4) and MnO_2. For the 2:3 (6h) catalyst, hausmannite-type manganese oxide was observed at a 2θ angle

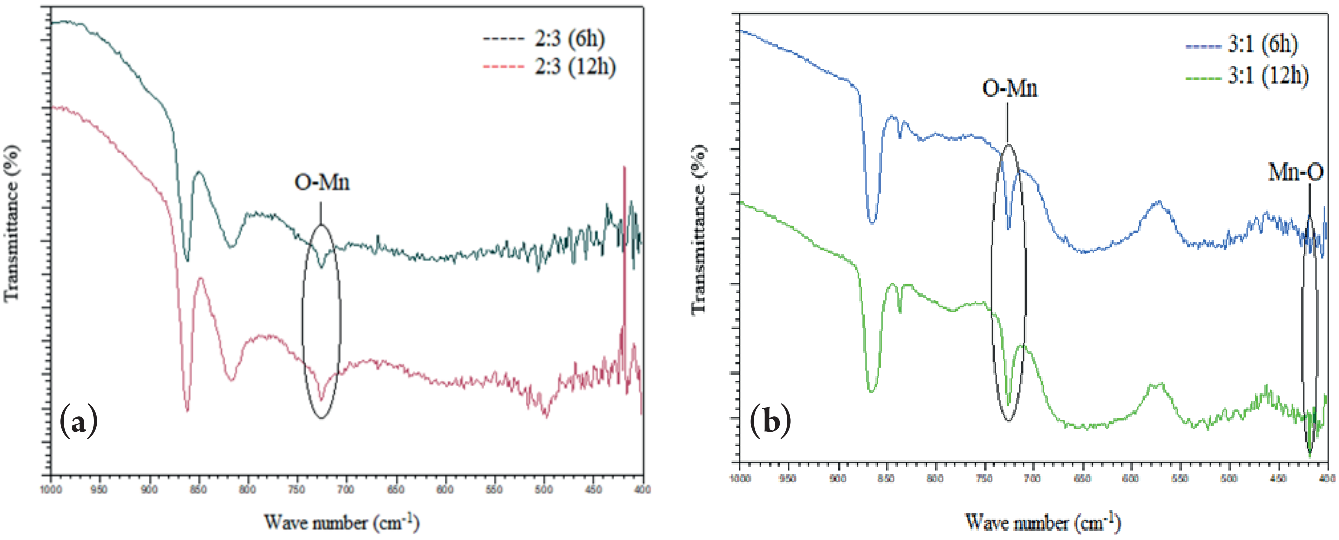

Figure 3. The IR spectra of as-synthesized catalyst at (a) 2:3 mole ratio (b) 3:1 mole ratio.

of 32.42° with a diffraction plane of (103). Additionally, a hausmannite peak appeared at 50.90°, along with two MnO_2 peaks at 25.85° and 41.60° with diffraction planes of (105), (202), and (310), respectively. When the reaction time was extended to 12 hours (2:3 (12h)), two additional hausmannite peaks emerged at 18.04° (101) and 31.04° (200), while two additional MnO_2 peaks appeared at 41.03° (402) and 49.49° (411).

Similarly, for the 3:1 mole ratio, a strong hausmannite peak at 32.42° (103) was observed at 6 hours (3:1 (6h)), which remained stable even at 12 hours (3:1 (12h)). The 3:1 (12h) catalyst exhibited Bragg peaks corresponding to hausmannite at 2θ angles of 32.42°, 36.13°, 50.90°, and 59.99°, with diffraction planes of (103), (211), (105), and (224), respectively. The 3:1 (6h) catalyst displayed a similar diffractogram pattern, with an additional MnO_2 peak at 25.85° (202).

These results suggest that prolonged reaction times lead to the formation of additional hausmannite peaks, whereas a higher $KMnO_4$/glucose ratio stabilizes the hausmannite phase. Furthermore, previous studies using sol-gel and co-precipitation methods have reported the formation of cryptomelane-type manganese oxides under similar synthetic conditions, reinforcing the influence of synthesis techniques on the resulting crystal phase.Additionally, the crystallinity of the 2:3 (6h) catalyst was significantly lower compared to the other catalysts, indicating that reaction time and precursor ratio strongly affect phase stability and crystalline properties.

Figure 3 displays the FTIR spectra of hausmannite-type manganese oxide synthesized at different $KMnO_4$/glucose mole ratios and reaction times. The O-Mn lattice vibration was observed at 726 cm^{-1}. For the 3:1 (6h) sample, an additional peak appeared at 468 cm^{-1}, which shifted to 468 cm^{-1} for 3:1 (12h), also assigned to O-Mn lattice vibrations.

Figure 4 presents the Raman spectra of 2:3 (6h) and 3:1 (12h), clearly indicating the characteristic features of spinel structures [10]. The 655 cm^{-1} and 653 cm^{-1} peaks are associated with O-Mn strain vibrations. Furthermore, the Raman spectra of the synthesized manganese oxides (Figure 4) support the formation of the hausmannite phase, in agreement with the XRD results and previous findings by Hou [11]. The 655 cm^{-1} Raman peak corresponds to symmetrical O-Mn stretching vibrations, characteristic of hausmannite-phase manganese oxide.

Table 1 presents the Mn average oxidation state (AOS) of synthesized hausmannite, prepared at different mole ratios and reaction times. It is evident that the 2:3 ratio has a significantly lower AOS value than the 3:1 ratio. Additionally, hausmannite synthesized at longer reaction times exhibits higher AOS values.

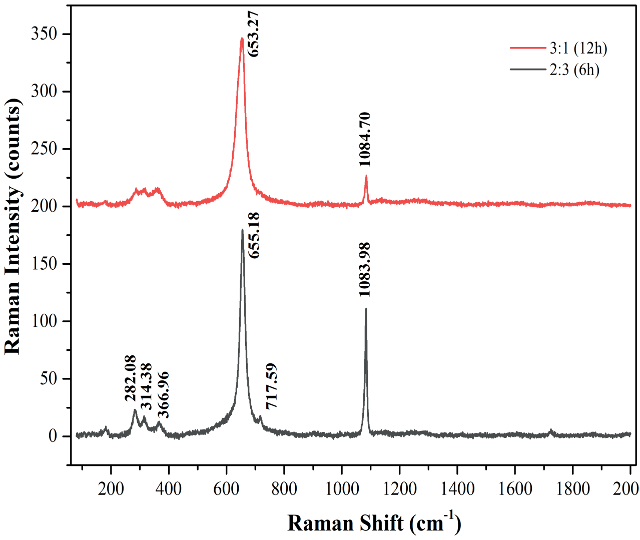

Figure 4. Comparison of the selected Raman spectra of as-synthesized MnOx catalysts at mole ratios of 3:1 (12h) and 2:3 (6h).

These data indicate that both mole ratio and reaction time influence Mn AOS in the as-synthesized hausmannite. A lower Mn AOS suggests a higher defect density, likely due to an increase in Mn^{3+} concentration or the presence of oxygen vacancies. Moreover, the effect of mole ratio on Mn AOS appears to be more significant than that of reaction time.

Table 1. The Mn AOS of the as-synthesized hausmannite.

Catalyst	Average oxide state (AOS) of Mn
2:3 (6h)	3.16
2:3 (12h)	3.29
3:1 (6h)	3.45
3:1 (12h)	3.51

3.3. Catalytic performance of catalysts in methylene blue removal. The MnOx catalyst has been utilized for methylene blue degradation, with its catalytic activity influenced by several parameters, including the volume of H_2O_2 addition, catalyst weight variation, and methylene blue concentration.

The degradation of methylene blue follows a Fenton-like mechanism, which is a modification of the Fenton method based on the formation and utilization of hydroxyl radicals ($HO^\bullet$) a strong oxidizing agent capable of breaking down organic pollutants into harmless substances [12].

Hausmannite (Mn_3O_4 or $MnO{\cdot}Mn_2O_3$) consists of Mn^{2+} in a tetrahedral structure and Mn^{3+} in an octahedral structure [13]. The methylene blue degradation mechanism occurs through adsorption, oxidation, and desorption processes. The first stage involves the adsorption of H_2O_2 on the manganese oxide surface, followed by its decomposition into free radicals, such as HO, $O_2^\bullet$, and $HOO^\bullet$, which exhibit high oxidative ability to decompose dye molecules into CO_2, H_2O, or other small molecules. The degradation mechanism is represented in equations 2-7 [14, 15] .

$$Mn_2+ + H_2O_2 \rightarrow Mn^{3+} + HO^\bullet + OH^- \quad (2)$$

$$Mn^{3+} + H_2O_2 \rightarrow Mn_2+ + HO_2^\bullet + H^+ \quad (3)$$

$$Mn^{3+} + H_2O_2 \rightarrow Mn^{4+} + OH^\bullet + OH^- \quad (4)$$

$$Mn^{4+} + H_2O_2 \rightarrow Mn^{3+}\ HO_2^\bullet + H^+ \quad (5)$$

$$HO_2^\bullet \rightarrow H^+ + O_2^{\bullet -} \quad (6)$$

$$(HO^\bullet, O_2^{\bullet -}) + MB \rightarrow \text{degradation products} \quad (7)$$

All synthesized catalysts were tested under identical conditions for methylene blue degradation, as illustrated in Figure 5. Among the tested samples, the 2:3 (6h) catalyst demonstrated the highest catalytic performance, achieving a methylene blue removal efficiency of 58.01% after 120 minutes of contact time. In comparison, the 3:1 (6h), 3:1 (12h), and 2:3 (12h) catalysts exhibited slightly lower removal efficiencies of 54.27%, 55.10%, and 55.51%, respectively.

These results are align with the AOS values presented in Table 1. A higher AOS value corresponds to lower MB removal efficiency. When the AOS value is close to 3, it suggests that the Mn^{3+} content in MnOx is greater than Mn^{4+}.

The superior performance of the 2:3 (6h) catalyst can be attributed to its optimized Mn^{3+} concentration, which enhances H_2O_2 decomposition efficiency. The electron configuration of Mn^{3+} is spin d^4, where one electron occupies the highly reactive e_{91} antibonding orbital. These reactive electrons readily decompose H_2O_2 to generate HO• radicals [16]

Additionally, the presence of Mn^{3+} facilitates the formation of oxygen vacancy defects (OVDs), which further enhance MB removal efficiency, as demonstrated in Equation 8 [17]. Thus, the 2:3 (6h) catalyst will be used to examine the effects of H_2O_2 volume, catalyst weight, and initial MB concentration on its catalytic performance. Due to the high activity of the 2:3 (6h) catalyst, further investigations were conducted to examine the effects of additional operating conditions.

$$-Mn^{4+}\text{-}O^{2-}\text{-}Mn^{4+} \rightarrow -Mn^{3+}\text{-}\square\text{-}Mn^{3+}\text{-} + \tfrac{1}{2}\, O_2 \quad (8)$$

Figure 6 illustrates the significant impact of H_2O_2 addition on methylene blue (MB) removal. Without H_2O_2, the MB removal efficiency was only 32.65% after 120 minutes of contact time. In contrast, the addition of 5 mL of H_2O_2 increased MB removal to 47.20% within 10 minutes, further rising to 58.01% after 120 minutes.

However, excessive H_2O_2 resulted in a decline in MB removal efficiency. As shown in Figure 6, the MB removal decreased to 45.95% and 38.89% with the addition of 10 mL and 15 mL of H_2O_2, respectively, after 120 minutes of contact time. This decrease is attributed to an imbalance between the rate of $HO^\bullet$ formation and the rate of MB oxidation by $HO^\bullet$. Excess H_2O_2 can induce a scavenging effect, inhibiting $HO^\bullet$ radical formation, as demonstrated in Equations 9–11 [17–19]:

$$H_2O_2 + H_2O_2 \rightarrow H_2O + O_2 \quad (9)$$

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \quad (10)$$

$$HO_2^\bullet + HO^\bullet \rightarrow O_2 + H_2O \quad (11)$$

Excess H_2O_2 reacts with itself (Equation 9) without generating HO• radicals. Additionally, it can react with pre-formed $HO^\bullet$ radicals, producing the less reactive $HO_2^\bullet$ species (Equation 10), which subsequently reacts with $HO^\bullet$, forming O_2 and H_2O (Equation 11).

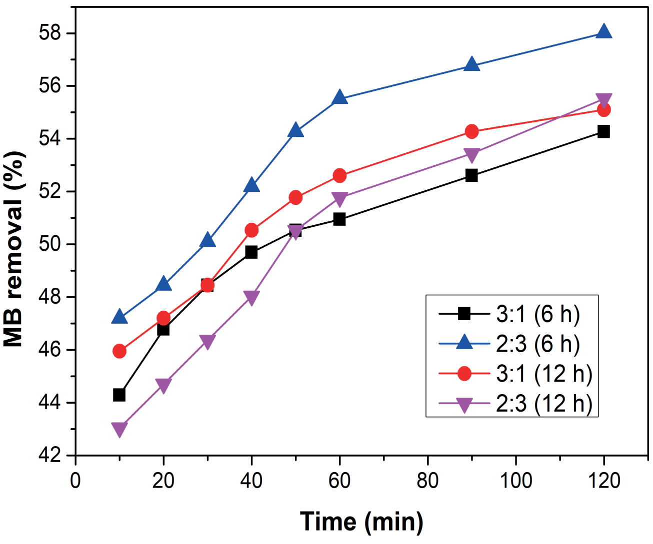

Figure 5. Effect of catalyst type on MB degradation (constant variables: 5 mL of H_2O_2; 12.5 ppm MB concentration; 50 mg MnOx.

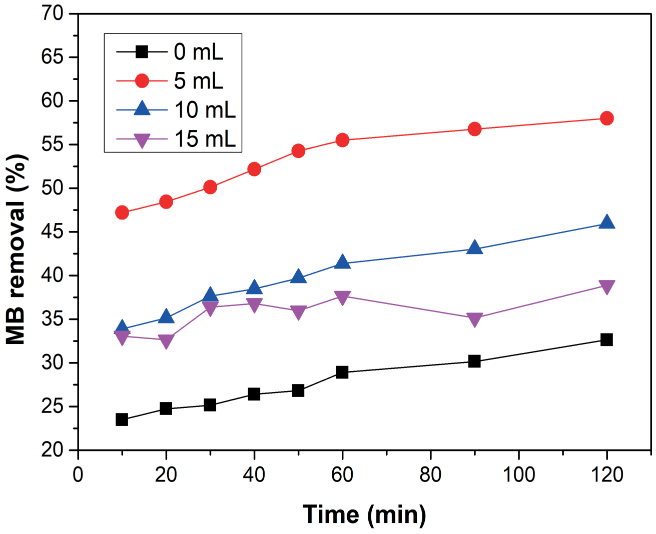

Figure 6. The effect of H_2O_2 concentration on the degradation of MB (Constant variables: 12.5 ppm MB; 50 mg of MnOx (2:3) (6h)).

The next parameter studied for its influence on MB removal efficiency was the catalyst weight. The experiment analyzed the effect of varying catalyst amounts, specifically 0 mg (without catalyst), 25 mg, 50 mg, and 75 mg. The results in Figure 7 show that catalyst addition led to a noticeable increase in MB removal efficiency compared to the absence of a catalyst (0 mg). The addition of the 2:3 (6h) catalyst from 0 mg to 50 mg exhibited a directly proportional relationship with MB removal efficiency, higher catalyst weight resulted in increased MB removal. However, at 75 mg, the removal efficiency declined.

These findings indicate the presence of an optimum catalyst weight, identified as 50 mg, for effective MB degradation. Excessive catalyst loading can lead to agglomeration, where catalyst particles cluster together, reducing the available surface area for the reaction and potentially trapping impurities

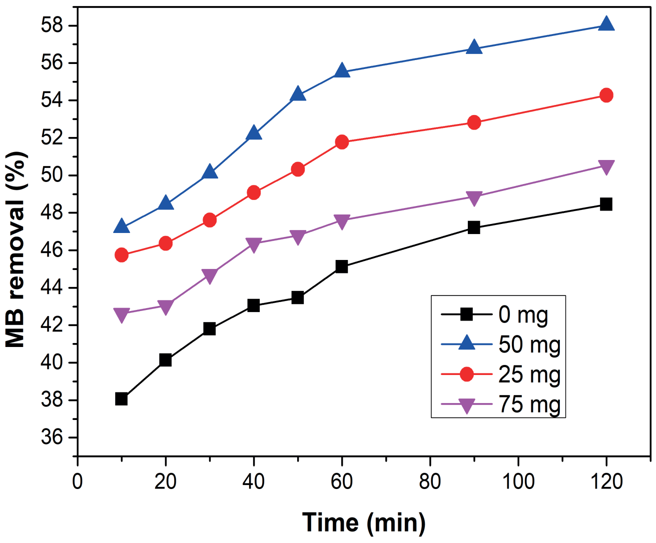

Figure 7. The effect of catalyst concentration on the degradation of MB using the MnOx (2:3) (6hr) (Constant variables: 12.5 ppm MB; 5 mL H_2O_2).

The parameter studied was the effect of initial methylene blue (MB) concentration on MB removal efficiency. The previously low MB removal efficiency prompted the research team to lower the initial MB concentration. The results in Figure 8 indicate an inverse relationship between MB removal efficiency and initial MB concentration. At an initial concentration of 4 ppm, MB removal reached 89.97%, decreasing to 87.99% at 8 ppm and further to 58.01% at 12.5 ppm after 120 minutes of contact time.

These findings align with previous research. A higher initial MB concentration increases the number of MB molecules requiring oxidation by HO• radicals, thereby reducing MB removal efficiency. This effect can be attributed to catalyst surface saturation, where MB and H_2O_2 adsorption sites become occupied, limiting further oxidation [20].

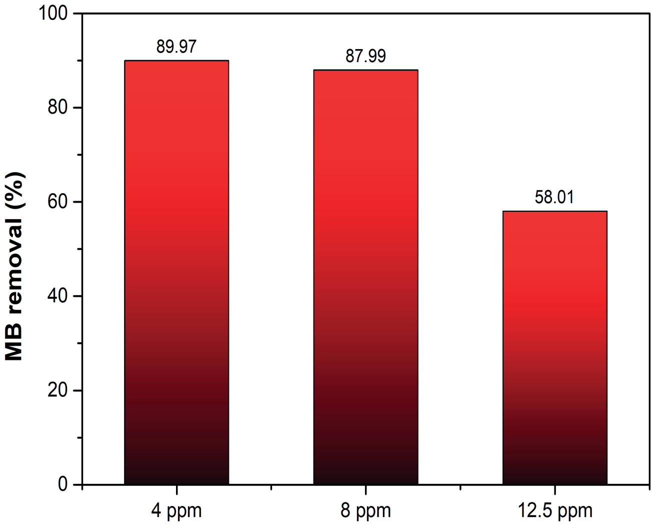

Figure 8. Effect of initial MB concentration on MB removal (Constant variables: 5 mL of H_2O_2; 50 mg MnOx (2:3) (6h)).

4. CONCLUSION

Hausmannite-type manganese oxides were successfully synthesized via the hydrothermal method through a redox reaction between $KMnO_4$ and glucose. A higher $KMnO_4$/glucose mole ratio (3:1 vs. 2:3) facilitated the formation of the hausmannite phase with fewer defects. The synthesis conditions significantly influence the resulting AOS value, directly affecting MB removal efficiency. The catalyst with the best catalytic performance, 2:3 (6h), achieves 89.97% MB removal under conditions of 5 mL of H_2O_2, 50 mg of catalyst, and an initial MB concentration of 4 ppm after 120 minutes of contact time.

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CREDIT AUTHOR STATEMENT

Amir Awaluddin: Supervision, Conceptualization, Methodology, Writing-Original draft preparation, Formal analysis. **Aulia Nur Ilahi**: Writing-Original draft preparation, Writing-Reviewing and Editing, Visualization, Formal analysis. **Ivano Fachran Putra Deraf**: Investigation, Data curation, Formal analysis. **Siti Saidah Siregar**: Methodology, Data curation, Writing-Reviewing and Editing. **Edy Saputra**: Writing-Reviewing and Editing, Visualization.

DECLARATIONS

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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