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RESEARCH PAPER

Degrading colour with magnets: degradation of methylene blue MnOx-Fe_3O_4 using the photo-fenton method

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Abstract: One practical approach to reducing methylene blue (MB) levels is through the Advanced Oxidation Processes (AOPs) method, which utilizes hydroxyl radicals (•OH) to degrade the colored compounds. AOPs have proven to be a highly efficient technology in treating coloured wastewater, with the ability to produce strong oxidants that break down molecules that are difficult to decompose naturally. One of the widely used AOP technologies is the Fenton heterogeneous catalyst, which is known for its affordable price, ease of reuse, and the fact that it does not produce solid sludge. In this study, MnOx-Fe_3O_4 composites were synthesized using the hydrothermal method with variations in the addition of Fe_3O_4 in ratios of 1:5 and 1:10. Several variables tested in the MB degradation process included the volume of H_2O_2 used (5, 10, and 15 mL), composite contact time, and the effect of pH on degradation efficiency. The results showed that the addition of 5 mL of H_2O_2 to the MnOx-Fe_3O_4 composite significantly increased the degradation efficiency of methylene blue up to 92.54% within 120 minutes, with an optimal pH of 9. The addition of H_2O_2 was shown to accelerate the degradation process, which shows great potential in wastewater treatment applications. In addition, the magnetic properties of the MnOx-Fe_3O_4 composite allow easy separation of the catalyst after the treatment process, thus accelerating and facilitating the recovery and reuse of the catalyst. This degradation process involves the formation of hydroxyl radicals (•OH), which are highly reactive and can efficiently break down MB molecules. Thus, this study demonstrates that the MnOx-Fe_3O_4 composite has the potential to be a highly efficient and environmentally friendly catalyst for treating coloured wastewater. This catalyst is also expected to be reusable in several cycles, making it a sustainable and effective choice in industrial wastewater treatment.

Keywords: MnOx-Fe_3O_4, fenton heterogeneous catalyst, methylene blue, UV light.

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INTRODUCTION

Methylene blue (MB) is a dye known for its resistance to natural decomposition, which can cause environmental damage. To mitigate this, one promising solution is to enhance natural photodegradation using photocatalysts, which can help reduce environmental damage. A highly effective, efficient, and environmentally friendly method for wastewater treatment is the Fenton reaction, which utilizes catalysts. Recently, the development of composite catalysts has received attention due to their larger surface area compared to single catalysts. One such composite can be formed by combining Manganosite (MnOx) with Fe_3O_4.

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The addition of Fe_3O_4 as a magnet in the MnOx-Fe_3O_4 composite offers the advantage of facilitating the summation process, allowing the catalyst to be reused. [7].

Using materials based on metal oxides is one possible technique for methylene blue degradation. Manganese oxide exhibits strong catalytic activity throughout the oxidation process, whereas magnetite (Fe3O_4), a magnetic substance, offers advantages in separation following catalytic events. Through modified Fenton reactions or photocatalytic processes, manganese oxide and magnetite can combine to create materials with complementary qualities that improve the efficiency of methylene blue breakdown.

Previous studies have successfully synthesized MnO_2/Fe_3O_4 composites using various methods, including ultrasonic, precipitation, and sol-gel. Dubey et al. synthesized an α-MnO_2/Fe_3O_4 nanocomposite using the hydrothermal method and found that this nanocomposite was able to degrade nearly 100% of 2,4-dichlorophenol within 80 minutes at pH 9. Additionally, this nanocomposite photocatalyst can be easily recycled using a magnet at room temperature, exhibiting high stability.

The addition of MnO_2 to the Fe_3O_4/CuO catalyst (MnO_2-Fe_3O_4/CuO) increased the decolourization rate of dye wastewater through the Fenton oxidation process, with a methylene blue removal efficiency of 90% in 45 minutes, higher than that of Fe_3O_4/CuO (79%). This hybrid catalyst showed high efficiency and could be recycled more than six times (efficiency >90%). In addition, Mn-doped Fe_3O_4/RGO was also effective as a photo-Fenton catalyst for decomposing RhB, with high efficiency. It could be separated using an external magnetic field, indicating its chemical stability and potential for economical wastewater treatment applications.

Researchers are interested in synthesizing MnOx/Fe_3O_4 composites by adding Fe_3O_4 to manganese oxide to facilitate separation using a magnetic field, thereby enabling recycling. This study employed a one-step hydrothermal method, involving the mixing of $KMnO_4$, glucose, and Fe_3O_4 in a closed autoclave. This method has the advantage of being carried out at low temperatures, producing homogeneous crystal products quickly and maintaining the purity of the material. The synthesis of MnOx-Fe_3O_4 composites using this hydrothermal method has not been reported previously, so it is expected to serve as a new reference in manganese oxide composite research.

MATERIALS AND METHODS

Composite synthesis using the hydrothermal method was carried out by mixing 2.765g of $KMnO_4$ with 4.725g of glucose ($C_6H_{12}O_6$), then stirring until dissolved, after which Fe_3O_4 was added with variations (1:5 and 1:10). Then, the mixture was put into a Teflon-coated stainless steel autoclave at a temperature of 110 ^oC for 6 hours. The product formed was washed with 0.1 M HCl and distilled water. The product was dried at 120 ºC for 2 hours. Then it was used to degrade methylene blue by varying pH and adding H_2O_2 for 120 minutes.

This research examines three parameters: the effect of catalyst contact, the effect of adding H_2O_2 at varying concentrations (5, 10, and 15 mL), and the effect of pH at different levels (2, 4, 7, and 9). Take 100 mL of the MB liquid waste solution using a volume pipette. Then, place it in a 250 mL beaker and add the catalyst (under optimum conditions). Then, the mixture was stirred using a hotplate stirrer at room temperature for 10, 20, 30, 40, 60, 80, 100, and 120 minutes, and subsequently centrifuged for 20 minutes at 2000 rpm to separate the catalyst. Next, testing was carried out with a UV-Vis spectrophotometer with a wavelength of 663 nm.

RESULTS AND DISCUSSION

In this research, a MnOx-Fe_3O_4 composite was synthesized using the hydrothermal method as a catalyst for the degradation of methylene blue. MnOx-Fe_3O_4 was synthesized using potassium permanganate ($KMnO_4$) and glucose ($C_6H_{12}O_6$) as precursors, supported by Fe_3O_4 with variations in the Fe_3O_4-to-KMnO4 weight ratio (1:5 and 1:10). The MnOx-Fe_3O_4 composite is qualitatively characterized by black particles that can interact with magnetic fields, as seen in Figure 1.

When brought close to an external magnetic field, the MnOx-Fe_3O_4 composite interacts with the magnet and is completely attracted. The magnetic properties of the MnOx-Fe_3O_4 composite appear when it is brought close to an external magnetic field and then disappear when the magnetic field is removed. It shows that the MnOx-Fe_3O_4 composite has paramagnetic properties.

Figure 1. Composite Contact Time Degradation Results

The synthesized manganese oxide catalyst was characterized using X-Ray Diffraction (XRD), which aims to determine its crystal phase. The characterization results are presented in the form of diffractograms in Figure 2. The diffraction peaks obtained from the synthesis results are adjusted to match the International Centre for Diffraction Data (ICDD) database, which corresponds to the synthesis catalyst. From the results obtained, it can be seen that sharp peaks indicate a high level of crystallinity, while peaks that are not sharp or high indicate that the peak has less crystallinity and is amorphous. In this study, the expected results obtained were the types of manganese oxides, manganosite and cryptomelane. However, using the hydrothermal method, different manganese oxide results were obtained, as shown in Figure 2.

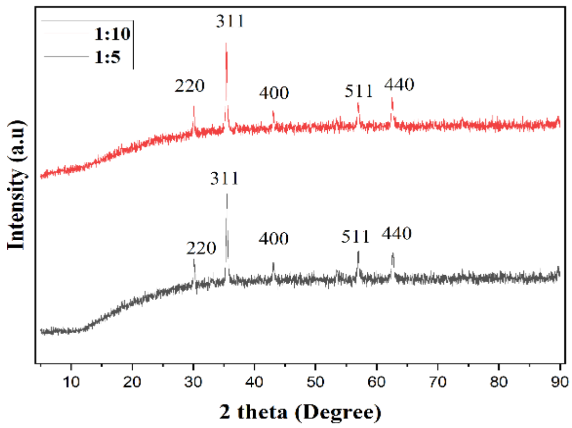

Figure 2. XRD characterization results of samples 1:5 and 1:10

The XRD results show that the peaks formed correspond to those of Fe_3O_4, in accordance with JCPDS No. 19-0629. Based on the image above, the peaks that appear in the MnOx-Fe_3O_4 composite synthesized using the hydrothermal method are typical peaks of magnetite characteristics, as evidenced by the presence of peaks that appear at diffraction angles of around 30, 35, 43, 57 and 62° with Miller indices respectively [220], [212], [400], [511], and [440]. The results of the study are consistent with those of previously reported studies [15, 17]. Magnetite has been successfully synthesized using the hydrothermal method. The more Fe_3O_4 is added, the higher the resulting peak is.

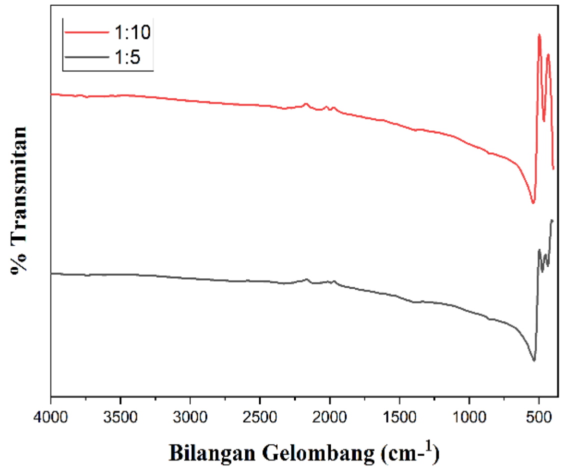

Figure 3. FTIR characterization results

Fourier transform infrared spectroscopy (FTIR) describes information about chemical bonds in the infrared spectrum of the absorption of the synthesized material in the range of 400–4000 cm^{-1} (Figure 3). The FTIR characterization results show that with the addition of Fe_3O_4, the MnOx peak overlaps with the Fe_3O_4 peak. The wave number 1640-3462 cm^{-1} is the stretching and bending vibration of the H-O-H bond. The wave number at 450–700 cm^{-1} shows the stretching vibration of Fe-O-Fe. This band is quite divided due to the overlap of the Fe–O peak together with Mn–O, which indicates the attachment of Fe_3O_4 to the MnOx surface. This study is in accordance with research [15]. The band in the range of 400 - 650 cm^{-1} is a characteristic of the Fe-O bond [18].

From the SEM image, MnOx is observed to have an irregular grain or particle morphology, characterized by a rough and dense overlapping surface. Then, after the addition of 1:1 Fe_3O_4, the image shows smaller grains (Fe_3O_4 nanoparticles) that are bound together to form agglomerations or larger groups. This agglomeration is a collection of nanoparticles that combine due to interactions between particles. The more Fe_3O_4 is added, the more irregular the particle shapes appear, tending to be rounded to slightly angular. The particle sizes vary, but in general, they appear quite uniform within each group. The presence of aggregation or clumping between particles suggests a fairly strong interaction force between them. The SEM results show that Fe_3O_4 initially adhered to the surface of MnOx, then merged and formed a larger surface, indicating that Fe_3O_4 had been thoroughly mixed and effectively covered the surface of MnOx.

MnOx-Fe_3O_4 1:5 **MnOx-Fe_3O_4 1:10**

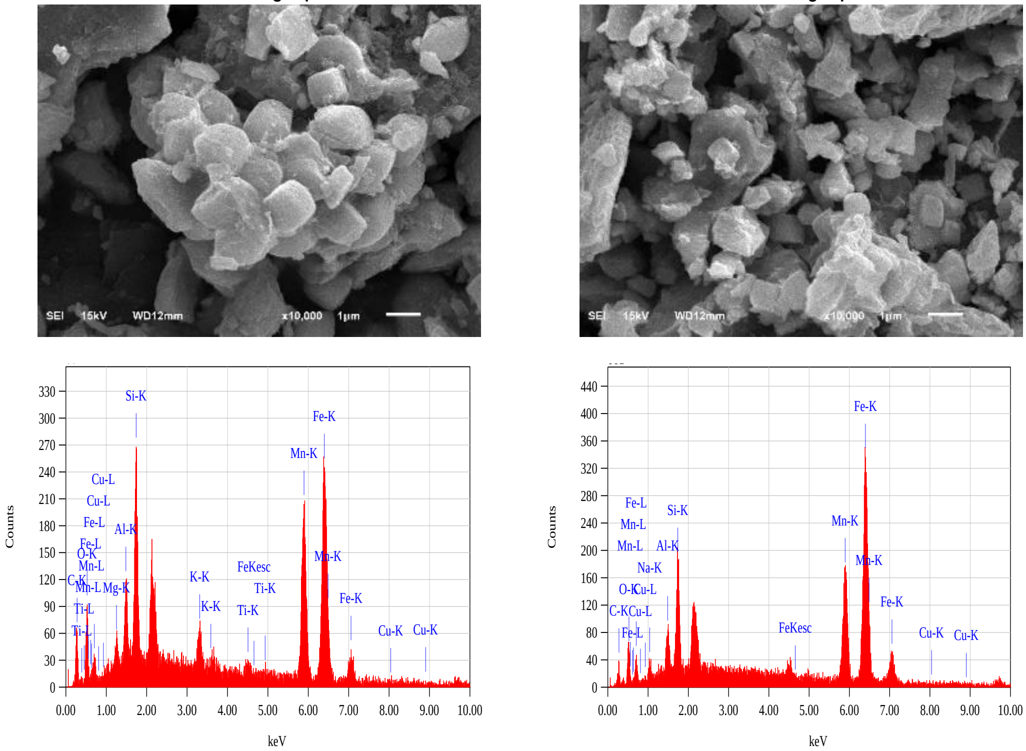

Figure 4. SEM-EDX MnO_x- Fe_3O_4 results

The EDX results show that the MnOx-Fe_3O_4 contains the elements Fe, Mn, O which are the constituent elements of the MnOx-Fe_3O_4 material and indicate that Fe_3O_4 has been well bound to the surface of Manganosite (MnOx) so that MnOx-Fe_3O_4 can be formed according to the desired variation.

Table 1. Elemental Content in MnOx- Fe_3O_4

No	Element Name	Variation	
		MnOx-Fe_3O_4 1:5	**MnOx-Fe_3O_4 1:10**
1.	Mn	29.7474	25.6989
2.	Fe	48.4109	62.9223
3.	Si	5.0340	3.5254
4.	C	3.5080	1.5428
5.	O	6.3459	4.4611
6.	Mg	0.5582	-
7.	Al	1.7339	1.0995
8.	Ti	1.2858	-
9.	Cu	1.2650	0.2461
10.	K	2.1107	-
11.	Na	-	0.5038
Total = 100			

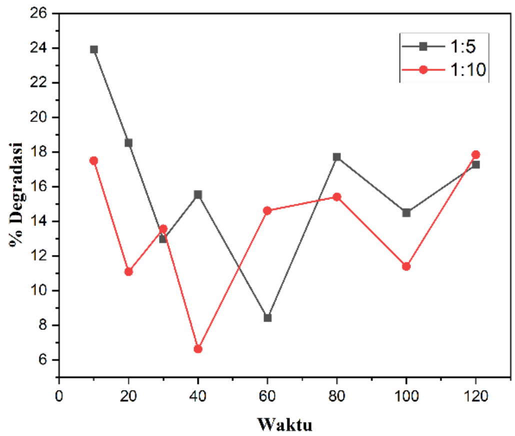

Figure 5. Composite Contact Time Degradation Results

The contact time of the MnOx-Fe_3O_4 catalyst is an important factor influencing the efficiency of methylene blue degradation. Increasing contact time generally increases degradation efficiency; however, it is essential to note that there is an optimal contact time that yields the best degradation efficiency. Apart from contact time, other factors such as catalyst concentration, methylene blue concentration, solution pH, temperature, and type and dose of oxidant also need to be considered to optimize the degradation process [10].

Figure 5 shows the contact time for the composite in degrading methylene blue, without the addition of H_2O_2 or pH adjustment. In this process, researchers aim to determine the optimal composite contact time. The contact times used are 10, 20, 30, 40, 60, 80, 100 and 120 minutes. The results showed that the MnOx-Fe_3O_4 composite with a 1:5 variation exhibited the best contact time, with 24% degradation of Methylene Blue after 10 minutes. Meanwhile, for the MnOx-Fe_3O_4 composite, the optimal contact time variation of 1:10 was 120 minutes, resulting in 18% degradation of methylene blue.

Hydrogen peroxide (H_2O_2) plays a very crucial role in the Fenton degradation process. In the Fenton system, H_2O_2 reacts with iron ions (Fe^{2+}) to produce hydroxyl radicals (•OH). This hydroxyl radical is a highly reactive and non-selective species, capable of oxidizing various organic compounds, including methylene blue, into simpler and less hazardous compounds.

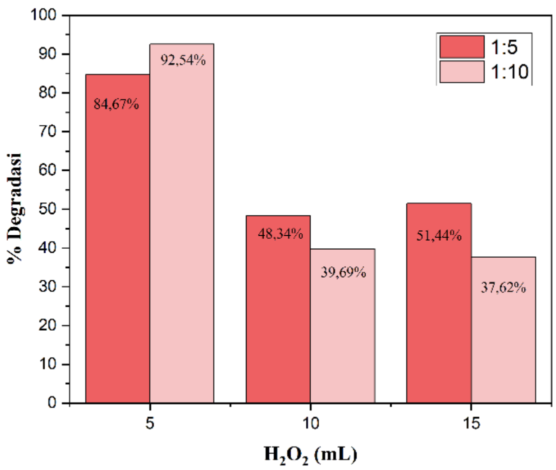

Figure 6. Morphol Degradation of MB Variations in the Addition of H_2O_2

In the research, we aimed to determine whether the addition of more H_2O_2 would improve its ability to degrade methylene blue. In Figure 3, it is shown that the more H_2O_2 added, the smaller the resulting degradation. At concentrations of H_2O_2 that are too high, the formation of superoxide radicals (•O_2^-) can occur, which can compete with hydroxyl radicals in reactions with methylene blue, thereby reducing degradation efficiency. Too high concentrations of H_2O_2 can lead to excessive consumption of H_2O_2 without a significant increase in the formation of hydroxyl radicals.

In this research, the best results were obtained when 5 mL of H_2O_2 was added; the MnOx-Fe_3O_4 composite variation 1:5 was able to degrade methylene blue by 84.67%, while the MnOx-Fe_3O_4 composite variation 1:10 was able to degrade methylene blue by 92.54%.

pH is one of the important parameters that can influence the photocatalytic rate. However, interpreting the effect of pH is challenging due to its dual role, which includes electrostatic interactions between the catalyst surface, solvent molecules, and substrate, as well as the formation of radicals during the reaction [18]. In this study, methylene blue at pH 2, 4, 7 and 9 was used. The results of pH variations in Figure 4 show an increase in the degradation rate as the pH increases. The optimum pH is obtained at alkaline pH, namely pH 9, which is 82.77% for the 1:5 composite variation, while 87.62% for the 1:10 composite.

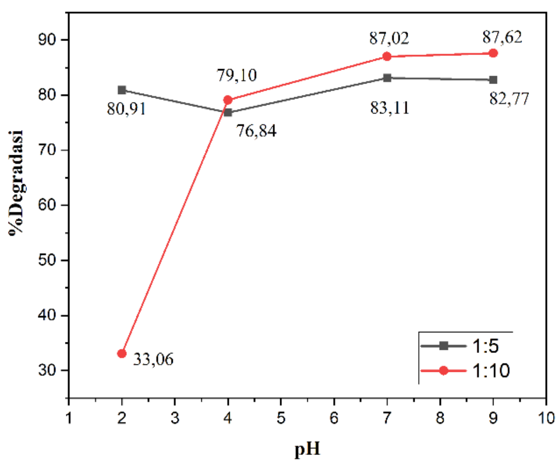

Figure 7. Effect of pH on MB degradation by MnOx-Fe_3O_4 composite

At low pH, the catalyst surface is generally positively charged. If the methylene blue molecule is also positively charged, electrostatic repulsion will occur, which inhibits adsorption and degradation. At high pH, the catalyst surface is generally negatively charged. If the methylene blue molecule is positively charged, an electrostatic attraction will occur, resulting in increased adsorption and degradation. However, a pH that is too high can cause the deposition of catalysts or metal species that can inhibit the degradation process. Neutral pH often provides good degradation results because at this pH, the interaction between the catalyst and methylene blue molecules tends to be optimal.

Based on this figure, the most optimal results are shown in the 1:10 Composite variation treatment, using 0.05 g of H_2O_2 and 100 ml of methylene blue. In the Fenton system, the addition of composite and H_2O_2 must be balanced to produce optimum processing. In the combination process, either OH, OH^- · O_2^-, or HO_2 is an oxidizing agent that is very efficient in oxidizing organic materials and decomposing them into CO_2 and H_2O. High colour degradation occurs because the colour molecules have been oxidized. By increasing the molar ratio of Fenton's reagent, the number of hydroxyl radicals will increase [19].

The decrease in degradation rate at acidic pH may be due to the high adsorption at low pH. The catalyst surface is covered by dye molecules, which causes the absorption of UV radiation on the catalyst surface to decrease. In low pH environments, the system is also considered saturated with excess H+ ions, thereby inhibiting MB from being adsorbed. Consequently, in acidic conditions, the amount of positive charge on the catalyst surface is reduced, which facilitates the formation of hydroxyl radicals from the active catalyst. Meanwhile, at higher pH, there is an excess of OH anions, which facilitates photodegradation of OH radicals. Changes in pH shift the redox potential of the valence and conduction bands, which can affect transfer [18].

CONCLUSION

The conclusion obtained in this study is that the synthesis of MnOx - Fe_3O_4 composite has been successfully carried out using the hydrothermal method at a temperature of 110 °C for 6 hours. The optimized MnOx-Fe_3O_4 catalyst achieved a degradation efficiency of 92.54% for 100 mL of 25 ppm methylene blue, indicating its potential for wastewater treatment, with a catalyst concentration of 0.05 g/l and the addition of 5 mL of H_2O_2 using the Fenton method.

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