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Tremendous Performance Manganese Oxide Via Coprecipitation Method for Degradation of Palm Oil Mill Effluent

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Abstract. Increased production in industries tends to increase burden and complexity of waste produced. For this reason, it was necessary to develop materials that have good degradation capabilities and into environmental products. In this research, the MnO_2 has been synthesized using the strategy of coprecipitation and reducing agents. The as-synthesized MnO_2 is then used for the degradation of methylene blue. The results of this study indicate that different strategy of coprecipitation and reducing agents produce different MnO_2 and has unique properties as nano-hierarchical microstructure. Using citric acid as a reducing agent results in a hierarchical structure of α-MnO_2 and Mn_2O_3, while oxalic acid produces a hierarchical structure of β-MnO_2 and Mn_2O_3. To optimize the degradation of Palm Oil Mill Waste which contains a high concentration of pollutants, it still needs to be improved. From the parameters pH, chemical oxygen demand, oil & grease, and total suspended solids, the best degradation efficiency of each parameter was achieved at pH 8.8, 16.3%, 43.5% and 56.6%.

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1. Introduction

Water pollution due to palm oil mill waste has always been a critical issue and is often a main topic in public and government policy. For this reason, it is necessary to treat waste that can reduce environmental and health impacts (Xueqin Bao; Zhen Qin; Tianshu Zhou; Jingjing Deng;, 2017). Many waste treatment technologies have been developed in the industry (Deliyanni;, 2019). However, with the increasing production, waste load, and complexity, new, more efficient efforts are needed. The physical deposition has caused new problems with the mass transfer of waste to the surface of the adsorbent so further processing is needed (Pan et al., 2019). It is not efficient due to its low adsorption capacities and separation problems (Shayesteh et al., 2017). The adsorbent pores quickly saturate when the waste used is very complex. Biological waste treatment processes still need relatively long retention times and large area requirements. Solutions through the use of chemicals through catalytic reactions are considered more efficient (Zhang et al., 2017). This is because the degradation process is faster, breaking down the molecular structure of the waste into smaller ones, thus facilitating the natural degradation process. The catalyst will also be more easily separated from the post-degradation waste. Several studies have proven the effectiveness of MnO_2 as a catalyst for the degradation of organic wastewater (Pan et al., 2019).

Manganese oxides with variable oxidation states (i.e., +II, +III, and +IV), with the formula MnO_2, are outstanding owing to their structural flexibility. It can exist in different polymorphic phases including the chain-like tunnel-type (α, β, γ, η, and ε-MnO_2 form) (Saputra et al., 2013), the layered type (δ form), and the spinel-type (λ form). The presence of vacant sites and/or Mn (III) in the layers can substantially improve its reactivity (e.g., electron transfer efficiency and adsorption capacity) (Kim et al., 2017). In particular, manganese oxide demonstrated powerful oxidative and catalytic activity (Bibi et al., 2023) for the degradation of dyes and organic compounds from aqueous waste (Saroyan et al., 2019).

It has never been reported before using similar related agents to generate MnO_2 structure. The best results will be tested on a more complex compound, namely POME by observing the environmental parameters pH, COD, TSS, and oil & grease. The hierarchical structure and size of MnO_2 is one solution that needs to be developed to overcome the complexity of organic pollutants in the future (Fu et al., 2019).

2. The Methods

2.1 Material and reagents

The materials used in this study were Potassium Permanganate ($KMnO_4$, Merck), Citric Acid ($C_6H_8O_7$, Merck), Oxalic Acid ($C_2H_2O_4$, Merck), Sodium Hydroxide (NaOH, Merck), Sulfuric Acid (H_2SO_4, Merck), Hydrochloric Acid (HCl, Merck), Potassium Dichromate ($K_2Cr_2O_7$ 0.25 N Solution, Merck), Silver Sulfate (Ag_2SO_4, Merck), Sulfamic Acid (NH_2SO_3H, Merck), Potassium Hydrogen Phthalate (KHP, Merck), Mercury sulfate ($HgSO_4$, Merck), Aquades, Buffer Solution pH 4, 7 and 10. All reactants were reagent grade and used as received without further purification. POME (initial COD ~ 1600 mg. L^{-1}).

2.1 Synthesis of manganese oxide using the coprecipitation method

Manganese oxide was synthesized using the coprecipitation method with several variations. The oxidizing agent and reducing agent were dissolved in deionized water, then homogenized using magnetic stirring at a constant speed. The mixed solution was heated to 70° C for 15 minutes, and 0.2 M NaOH was added dropwise to pH 9. The mixed solution was stirred with a magnetic stirrer for 24 hours at room temperature. The precipitate obtained was washed with deionized water by centrifugation several times and dried at 80 °C for 24 hours.

The synthesized manganese oxide was then calcined at 550 °C for 3 hours. Calcination results will be washed using 1 M HCl and distilled water. The washing results are then dried in an oven. The resulting manganese oxide is characterized and then the optimum conditions for synthesis are known.

2.2 Characterization

The synthesized catalysts were characterized using XRD to see the level of crystallinity and type of material. XRD diffractogram was taken by X-ray diffraction system with Cu Kα radiation (λ=0.154060) from 10° to 90°.

2.3 POME degradation activity

The effectiveness of MnO_2 degradation against POME was determined by comparing the initial data after adding a catalyst for pH, COD, oil & grease, and TSS parameters. The degradation condition uses MB optimization data as a reference. POME was taken 100 mL using a volume pipette. Then put it into a 250 mL beaker and then add a catalyst with an optimum mass and pH. Then stirred using at room temperature after 30 minutes. pH was measured using a calibrated pH meter. COD analysis was carried out using the closed reflux method titrimetrically, oil & grease and TSS were analyzed gravimetrically.

3. Result and Discussion

3.1 Characterization XRD of Manganese Oxide

Figure 2 shows the diffratogram and crystallinity of the synthesized manganese oxide. The different types of substrates tend to produce different MnO_2. A-13, A-14, and A-15 (Citric Acid) produce a hierarchical structure of α-MnO_2 (JCPDS 44-0141) and Mn_2O_3 (JCPDS 41-1442). A-12 (Oxalic Acid) produces a hierarchical structure of β-MnO_2 (JCPDS 24-0735) and Mn_2O_3 (JCPDS 41-1442). The crystal structure hierarchy shown from the diffractogram data is also supported by SEM photos which show that there are two main forms of material. The variation of the precipitation synthesis technique used in this method affects the level of crystallinity. This of course has an impact on the chemical and physical properties as well as their efficiency for the degradation of POME.

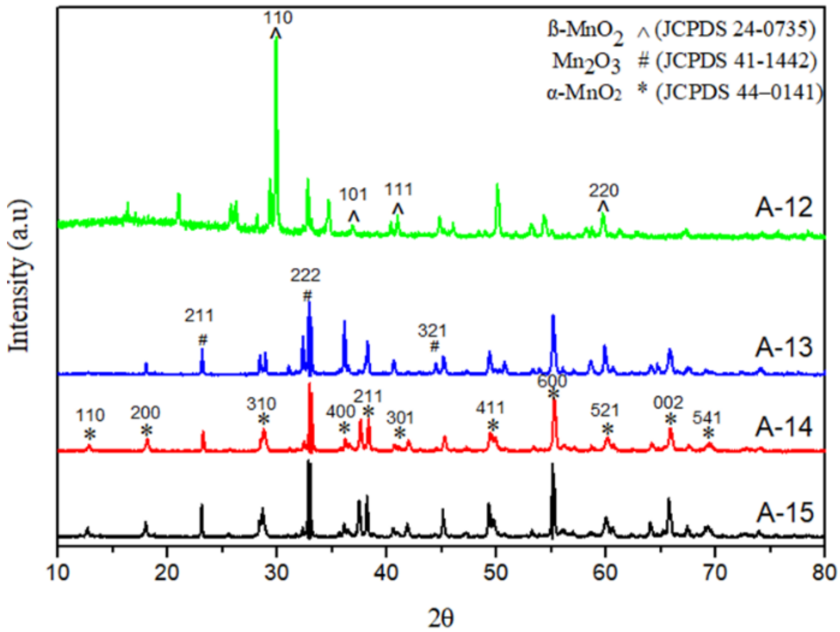

Figure 1. Diffratogram of A-12, A-13, A-14, dan A-15 .

3.2. POME Degradation Activity

POME consists of various compounds, especially fatty acids, cellulose, and etc. Figure 10 shows the effectiveness of A-15 for POME degradation at parameters pH (a), COD (b), oil & grease (c), and TSS (d). The A-15 has demonstrated the ability to degrade POME which has a high loading waste load. There was an increase in the pH solution from about 7.4 (initial pH of POME) to 8.8 after degradation (Figure 2.a).

The effectiveness of POME degradation on COD parameters with initial values of 1.596 mg L^{-1} sequentially from A-14, A-15, A-13, and A-12 were 16.3, 8.2, 6.1, and 5.4%, respectively. The decrease in levels of oil & grease parameters with an initial value of 8.35 mg L^{-1} respectively from A-12, A-14, A-13, and A-15 was 43.5, 41.5, 31.8, and 23.2%. The decrease in TSS parameter levels with an initial value of 563 mg L^{-1} sequentially from A-13, A-12, A-14, and A-15 was 56.6, 56.6, 49.6, and 41.2%.

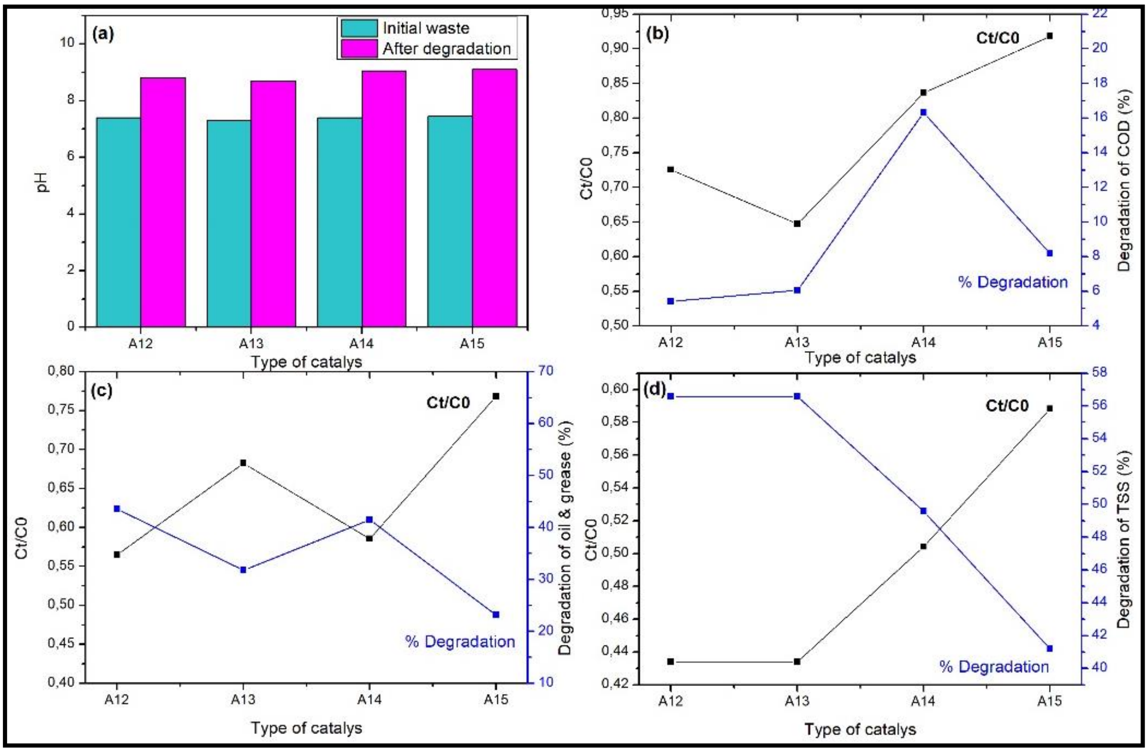

Figure 2. The effectiveness of A-15 for POME degradation in parameters pH (a), COD (b), oil & grease (c), TSS (d) (on COD parameters with initial values of 1.596 mg L^{-1}).

Table 1. The comparison of the effectiveness of COD removal with several types of composite materials

No	Catalyst code	Initial Concentration	Degradation (%)	Add catalyst	Oxidator/ Activator	Ref.
1.	Graphite/MnO_2	COD(25.4 mg L^{-1})	77	1 g L^{-1}	electrolysis	(Teguia Doumbi et al., 2021)
2.	$Mg_{0.1}$-$ZnMn_2O_4$	COD (70 mg L^{-1})	95	1 g L^{-1}	-	(Gherbi et al., 2021)
3.	PKSAC-Fe	COD	85	10 g L^{-1}, pH 3	-	(Tan et al., 2021)
4.	A-12	COD (1,628 mg L^{-1}) O&G (8.5 mg L^{-1}) TSS (530 mg L^{-1})	5.4 43.5 56,6	0.007 g L^{-1}, pH 3		This work
5.	A-13	COD (1,628 mg L^{-1}) O&G (8.5 mg L^{-1}) TSS (530 mg L^{-1})	6.1 31.7 56.6	0.007 g L^{-1}, pH 3		This work
6.	A-14	COD (1,564 mg L^{-1}) O&G (8.2 mg L^{-1}) TSS (595 mg L^{-1})	16.3 41.5 49.6	0.007 g L^{-1}, pH 3		This work
7.	A-15	COD (1,564 mg L^{-1}) O&G (8.2 mg L^{-1}) TSS (595 mg L^{-1})	8.2 23.2 41.2	0.007 g L^{-1}, pH 3		This work

The above conditions show differences in efficiency on various POME waste parameters. This indicates that the complexity of POME waste is much higher than MB waste. There is potential for further development of A-15 applications in the future, for example by increasing the dose of MnO_2 or by using a pre-treatment combination that is able to lower the COD POME value below 1000 mg L^{-1}.

4. Conclusion

The results of this study prove that the coprecipitation method has succeeded in forming MnO_2 with different characteristics due to different treatments. What is more interesting is the formation of a structure and size hierarchy of nanoparticles. This condition affects the degradation efficiency of both MB and POME. The pH condition of the solution also significantly affected the degradation efficiency of all types of MnO_2 used. The best results were achieved at MB degradation with A-15 at a high concentration of 500 mg L^{-1}, pH 1, and a time of 40 minutes with a catalyst mass of 0.007 g L^{-1}. Lifetime using A-15 catalyst can still be used up to 5 repetitions with degradation at 79%. However, for POME degradation optimization, it still needs to be improved. From the parameters pH, COD, oil & grease, and TSS, the best efficiency of each parameter was achieved at pH 8.8, 16.3%, 43.5%, and 56.6%.

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