Mn$_3$O$_4$ Catalysts for Advanced Oxidation of Phenolic Contaminants in Aqueous Solutions

Syaifullah Muhammad$^{1,2,*}$, Muhammad Wahyu Nugraha$^{3}$, Edy Saputra$^{3,*}$ and Nasrul Arahman$^{1,2}$

$^1$ Department of Chemical Engineering, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia; nasrular@unsyiah.ac.id
$^2$ ARC-PUIPT Nilam Aceh Universitas Syiah Kuala, Banda Aceh 23111, Indonesia
$^3$ Department of Chemical Engineering, Universitas Riau, Pekanbaru 28293, Indonesia; muhammad_18000003@utp.edu.my
* Correspondence: syaiful.muhammad@unsyiah.ac.id (S.M.); edysaputra@unri.ac.id (E.S.)

Abstract: Water-soluble organic pollutants, such as phenolic compounds, have been exposed to environments globally. They have a significant impact on groundwater and surface water quality. In this work, different Mn$_3$O$_4$ catalysts were prepared for metal oxide activation of peroxymonosulfate (PMS) to remove the phenolic compound from the water environment. The as-prepared catalysts were characterized using thermogravimetric-differential thermal analysis (TG-DTA), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface area analysis. Furthermore, the effect of temperature and reusability of the as-prepared Mn$_3$O$_4$ catalysts is also investigated. The Mn$_3$O$_4$ nanoparticles (NPs) catalyst reveals an excellent performance for activating PMS to remove phenol compounds. Mn$_3$O$_4$ NPs exhibits 96.057% efficiency in removing 25 ppm within 60 min. The kinetic analysis shows that Mn$_3$O$_4$ NPs fitted into pseudo-first order kinetic model and exhibited relatively low energy activation of 42.6 kJ/mol. The reusability test of Mn$_3$O$_4$ NPs displays exceptional stability with 84.29% efficiency after three-sequential cycles. The as-prepared Mn$_3$O$_4$ NPs is proven suitable for phenolic remediation in aqueous solutions.

Keywords: catalysts; phenolic remediation; emerging contaminants; water treatment

1. Introduction

Rapid economic growth has benefited socio-economic development, but has increased the risk of environmental issues [1]. One of the most severe environmental problems is water pollution. The limited availability of freshwater, which only accounts for 2.5% of the planet’s water, faces water security threats that can affect 80% of the world’s population [2]. The emerging contaminants (ECs), such as organic pollutants, pesticides, and pharmaceuticals, have been increased through the mismanagement of industrial wastewater. Water-soluble organic pollutants, mainly phenolic compounds, are particularly widespread, with approximately 3 million tonnes identified in the environment globally [3]. The phenolic effluents come mostly from coal conversion processes, petroleum refineries, phenolic resin manufacturing, herbicide manufacturing, phenolic resin manufacturing, herbicide manufacturing, pharmaceuticals, pulp and paper, and petrochemicals [3,4]. Phenolic compounds are extremely harmful to humans due to their acute toxicity, mutagenicity, and bio-recalcitrant characteristic [3,5].

Different biological, chemical, and physical processes have been applied to remove organic pollutants from an aqueous solution, such as adsorption, biodegradation, coagulation-flocculation, ion exchange, photocatalytic, membrane electrodialysis and filtration, and solvent extraction. These strategies are incapable of completely removing phenolic compounds, require more extended time, and are not cost-effective [3,6–11]. Advanced oxidation processes (AOPs) have been proven to be a promising alternative to water treatment due to their compelling oxidation potential for the mineralization of organic pollutants [12].
This process generates radical species, such as the hydroxyl radical (•OH) and the sulfate radical (SO₄•⁻) [13]. Among those reactive radicals, the SO₄•⁻ radical has higher reduction potential (E₀ = 2.5–3.1 V vs. •OH radical with E₀ = 1.8–2.7 V), possesses a better half-life, better reaction stoichiometric efficiency than •OH, and can be utilized in wider pH range [14,15].

SO₄•⁻ radicals generally reproduce from the activation of peroxymonosulfate (PMS) or persulfate (PS) through heating, light irradiation, ultrasonication, or transition metals [14]. The activation through transition metals exhibits a distinguished advantage because it does not require external energy, unlike the other activations [16]. Various transition metals have been studied for phenolic compounds oxidation degradation, i.e., BiFeO₃ magnetic nanoparticles [17], ZnO [18], Co-TiO₂ [19], nano-Ag, Mn₃O₄-g-C₃N₄ [16], α-Mn₂O₃ [20], and dipicolinic acid-functionalized- Fe₂O₃ [21]. Of the various transition metals, Mn has superiority due to its abundance in nature, low toxicity, multivalence, inexpensiveness, and environmental friendly [16].

Moreover, the efficiency of Mn is influenced by different characteristics such as crystallinity, oxidation state and species, morphology, and specific surface area [16,22]. The effect of crystallinity demonstrated the most influence compared to other characteristics, e.g., MnO₂ (146 m²/g) achieved an approximately eight times better performance compared to amorphous MnO₂ (179 m²/g) [12].

In this present study, the evolution of morphology and degree of crystallinity of manganese oxides are investigated. The as-prepared transition metal oxide catalyst is used for sulfate radical generation using PMS, where the effect of morphology and degree of crystallinity for phenolic compound degradation is exhibited thoroughly. The investigation of the temperature effect and reusability is also presented using a kinetic analysis, where the estimated activation energy is a key parameter.

2. Materials and Methods

2.1. Materials

Potassium permanganate (CAS 7722-64-7), OXONE® (CAS 70693-62-8), polyethylene glycol (PEG200) (CAS 25322-68-3), and ethanol (CAS 64-17-5) were purchased from Sigma Aldrich, USA. All materials were used without any further purification.

2.2. Mn₃O₄ Catalysts Preparation

Mn₃O₄ 950 °C was synthesized from as-prepared spherical MnO₂ using the sonochemical method from Sankar et al., study [23]. Firstly, 0.8 g of potassium permanganate was dissolved in 50 mL of deionized water (DI water), then 10 mL of PEG200 was added to the aqueous solution. Afterward, the mixture was subjected to ultrasonication with a 20 kHz frequency for 15 min, where the reaction reached around 80 °C. The resulting brown precipitate was vacuum filtered using 0.45 µm Merck Millipore PVDF membrane and washed, firstly using DI water, and subsequently using ethanol. The obtained MnO₂ was dried at 80 °C for 8 h. Finally, the as-prepared MnO₂ was calcined at 950 °C. The as-prepared catalyst was denoted as Mn₃O₄ 950 °C.

Secondly, the Mn₃O₄ NPs and octahedral catalysts were prepared using a hydrothermal method described by Li et al. [24], with some modifications. Firstly, Mn₃O₄ NPs was prepared using 0.105 g of potassium permanganate precursor, dispersed into 30 mL of DI water. Subsequently, 15 mL of PEG200 was added to the solution. The mixture was mixed for 30 min at ambient temperature before being put into a Teflon-line stainless steel autoclave. The mixture then underwent a hydrothermal process for 8 h at 120 °C. The as-prepared products were collected using vacuum filtration and washed several times using DI water and ethanol before drying at 60 °C for 12 h. The as-prepared catalyst was denoted as Mn₃O₄-NPs.

Lastly, octahedral Mn₃O₄ was prepared using a similar hydrothermal method with higher PEG200 concentrations. Five mol of potassium permanganate was dissolved into
30 mL of DI water with the addition of 30 mL of PEG200. Then, the as-prepared catalyst was denoted as octahedral Mn$_3$O$_4$.

2.3. Characterizations

The thermogravimetric analysis (TGA) (TGA/DSC1, Mettler Toledo, Columbus, OH, USA) was used to analyze the thermogravimetric profile of the MnO$_2$. As-prepared catalysts were characterized for powder X-ray diffraction (XRD) using the Bruker-AXS D8 model (Bruker, Hannover, Germany) equipped with filtered Cu Kα radiation with a wavelength of 1.54178 Å and a scan range of 2θ of 5–70°. The surface morphology of the samples was examined using the NEON 40EsB model (ZEISS, Oberkochen, Germany). The average length and diameter of the samples were calculated using the image processing program ImageJ from 50 individual structures. Micromeritics Tristar 3000 (Micromeritics, Norcross, GA, USA) was used to acquire Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and average pore radius.

2.4. Phenolic Degradation Performance

The typical catalytic oxidation of phenol was conducted in a 500 mL reactor containing 0.2 g/L as-prepared catalysts and immersed in 25 ppm, 250 mL phenol solutions. The reactor was dipped in a water bath, which had an attached temperature controller and stirring rod with a rotational speed of 400 rpm. Subsequently, after adsorption-desorption equilibrium is achieved, 2 g/L OXONE® was added to begin the oxidation process. At certain time intervals, 1 mL liquid solution was withdrawn from the reactor using a PVDF syringe filter of 0.45 µm. The liquid was then added to 0.5 mL methanol to prevent further reaction. The liquid concentrations were analyzed using high-performance liquid chromatography (HPLC), which is equipped with a UV detector at λ = 270 nm. The C-18 HPLC column was used with the mobile phase of 30% CH$_3$CN and 70% ultrapure H$_2$O with flowrate 1 mL/min. For chosen samples, total organic carbon (TOC) was defined applying a Shimadzu TOC-5000 CE analyzer.

The phenolic compound degradation efficiency was calculated using the following Equation (1):

\[
\text{Degradation efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100
\]

where $C_0$ and $C_e$ is the initial and remaining phenol concentrations, respectively.

Furthermore, the kinetic analysis of the as-prepared samples were calculated using Langmuir-Hinshelwood (L-H) pseudo first-order kinetic equation as follow in Equation (2) [25]:

\[
-\ln \left(\frac{C_t}{C_0}\right) = k \times t
\]

where $C_0$ and $C_t$ are the initial and final phenol concentration, respectively, $k$ is rate constant (min$^{-1}$), and $t$ is time (min).

Additionally, the activation energy of the as-prepared catalysts was calculated at different temperatures (25–45 °C) using the Arrhenius equation. The Arrhenius equation, which correlated the relationship between the observed rate constant ($k_{obs}$) and temperature, was presented in the following Equation (3) [26,27]:

\[
\ln k_{obs} = \ln A - \frac{E_a}{RT}
\]

where A is the pre-exponential factor which can be calculated from the intercept of the Arrhenius plot, $E_a$ is activation energy (Kj.mol$^{-1}$), $T$ is temperature (K), and $R$ is the gas constant (8.314 J/mol K).

Moreover, the reusability test was done with the solid catalyst from the previous experimental run. Before the next experimental run, the solid catalyst was washed thoroughly with DI water and dried at 60 °C for 12 h.
3. Results and Discussion

3.1. Thermogravimetric Profile of MnO$_2$

The thermal stability and evolution profile of MnO$_2$ are presented in Figure 1. The initial weight loss of 4.3361% in the range of 30–200 °C corresponds to the evaporation of adsorbed water content on the surface of MnO$_2$ [28,29]. Moreover, observable two-phase weight losses were observed at 550 °C and 940 °C with 12.0075% and 16.2841% reduction, respectively. The first phase of weight loss at 550 °C is attributed to the evolution of MnO$_2$ to Mn$_3$O$_4$ due to the oxygen release and reduction of Mn$^{4+}$ ions into Mn$^{3+}$ ions [30,31]. The second phase of weight loss at 940 °C correlates with the sustained oxygen loss resulting in the conversion of Mn$_2$O$_3$ to Mn$_3$O$_4$ [30]. The TGA profile of Mn$_3$O$_4$ concurrence with previous studies that reported the thermal stability of MnO$_2$ materials [30,32]. Furthermore, the transformation of as-prepared samples was examined further with XRD analysis. This TGA finding led to the choice of temperature for the hydrothermal synthesis of Mn$_3$O$_4$ catalysts at 950 °C.

![Figure 1. TGA profile of MnO$_2$.](image-url)

3.2. Crystallinity Structure, Morphology, and Surface Area Analysis

The crystallinity of as-prepared Mn$_3$O$_4$ is observed in Figure 2a,b for Mn$_3$O$_4$ 950 °C, Mn$_3$O$_4$ NPs, and octahedral Mn$_3$O$_4$. All 2θ diffractions of the as-prepared samples exhibit peaks at 18.13°, 29.03°, 31.14°, 32.41°, 36.21°, 38.12°, 44.56°, 50.94°, 54.06°, 56.18°, 58.64°, 60.01°, and 65.24° correspond to (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (224), and (400) planes, respectively. The standard diffraction is matched with JCPDS card No. 80–0382 correlated with the hausmannite spinel structure [24]. The broad diffraction of the as-prepared samples possesses nanostructure dimensions, as seen in previous work [24]. Subsequently, Figure 2c exhibited different peak intensities of XRD spectra for the as-prepared samples. The Mn$_3$O$_4$ 950 °C sample reveals the lowest intensity, followed by octahedral Mn$_3$O$_4$ and Mn$_3$O$_4$ NPs. The difference in peak intensity can be associated with different crystallite sizes and dislocation densities. The higher intensities correspond to larger crystallite sizes and better crystallinity. It is found that a larger crystallite size and higher crystallinity induced better degradation of organic compounds, as seen in a previous study [33]. Moreover, the determination of morphology of as-prepared Mn$_3$O$_4$ is presented using SEM imaging.
Figure 2. XRD pattern of (a) Mn$_3$O$_4$ 950 °C (b) Mn$_3$O$_4$ NPs and octahedral Mn$_3$O$_4$. (c) combined XRD pattern of as-prepared Mn$_3$O$_4$ samples.

Figure 3a–c shows the SEM imaging of three as-prepared Mn$_3$O$_4$ samples. Figure 3a of Mn$_3$O$_4$ 950 °C image shows clustered nanoparticles forming a quasi-spherical shape. The average diameter of the quasi-spherical shape of Mn$_3$O$_4$ 950 °C is around 122.290 ± 43.0 nm. Moreover, the Mn$_3$O$_4$ NPs SEM image (Figure 3b) exhibits an agglomerated nanoplatelet with a length of approximately 85.211 ± 23.4 nm. These nanoplatelets clustered, forming pre-octahedral shapes. Finally, octahedral Mn$_3$O$_4$ SEM image (Figure 3c) reveals more dispersed nanoparticles with octahedral shapes, and slight nanorod shapes can be observed. The length of octahedral Mn$_3$O$_4$ is 0.65 ± 0.1 μm. Octahedron shapes could be formed utilizing accelerated reduction, and nucleation growth. However, the nanorod shapes could occur with excess PEG as a reducing agent and shape-directing agent [34].
Figure 3. Morphology of (a) Mn$_3$O$_4$ 950 °C (b) Mn$_3$O$_4$ NPs (c) octahedral Mn$_3$O$_4$ catalysts.

Figure 4 illustrates the morphological evolution of Mn$_3$O$_4$ from nanoplatelet to octahedral architecture. Firstly, Mn$_3$O$_4$ forms a nanoplatelet-like shape. Afterward, the Mn$_3$O$_4$ is agglomerated, forming a pre-octahedral shape, depicted in Figure 3b highlighted with the red circles. Then, the Mn$_3$O$_4$ formed dispersed octahedral shapes (Figure 3c). The morphological evolution happened due to higher PEG200 concentrations. The polymer acts as a reducing agent and shape-directing agent [34]. The morphological evolution is followed by a self-assembly mechanism and then an Ostwald ripening mechanism [24].

The BET surface area, and N$_2$ adsorption-desorption of each catalyst was analyzed to determine surface area, pore volume, and average pore radius. Table 1 lists the summary of the BET analysis. It reveals Mn$_3$O$_4$ 950 °C possesses $S_{\text{BET}}$ 156.0 m$^2$/g with a pore volume of 0.24 cm$^3$/g and an average pore radius of 31.1 Å. The calculated surface area of Mn$_3$O$_4$ at 950 °C exhibited a higher BET surface area compared to other quasi-spherical Mn$_3$O$_4$ from previous studies, e.g., chemical leached Mn$_3$O$_4$ from manganese ore with a surface area of 9.32 m$^2$/g [34], Mn$_3$O$_4$ synthesized using a precipitation method from potassium permanganate with a surface area of 21.2 m$^2$/g [35], and solvothermal Mn$_3$O$_4$ from manganese(II) acetate tetrahydrate with a surface area of 131.49 m$^2$/g [36]. Furthermore, different concentrations of the PEG200 alters the surface area of Mn$_3$O$_4$. Mn$_3$O$_4$ NPs exhibited higher surface area of 184.6 m$^2$/g with an agglomerated platelet-like shape. With higher PEG200 concentrations, the Mn$_3$O$_4$ NPs transform from agglomerated nanoplatelets that resemble pre-octahedra into more polished octahedral shapes. Octahedral-shape controlled Mn$_3$O$_4$ was also exhibited in Li’s study, where the Mn$_3$O$_4$ formation evolution is exhibited through different reaction times [24]. The as-prepared octahedral Mn$_3$O$_4$ possesses a lower surface area compared to Mn$_3$O$_4$ NPs. This is due to the smaller size of individual nanoplatelets of Mn$_3$O$_4$ NPs compared to octahedral shapes of octahedral Mn$_3$O$_4$. This phenomenon can be seen from previous transformation morphology studies of Mn$_3$O$_4$ [24,34]. The calculated $S_{\text{BET}}$ of octahedral Mn$_3$O$_4$ is 122.4 m$^2$/g is proven to be higher than octahedral Mn$_3$O$_4$ from previous works, i.e., hydrothermal Mn$_3$O$_4$ from KMnO$_4$ with $S_{\text{BET}}$ of 23 m$^2$/g [37] and hydrothermal Mn$_3$O$_4$ from manganese(II) acetate with $S_{\text{BET}}$ of 57.7 m$^2$/g [38]. Moreover, all three as-prepared catalysts observed micropore-type pore size. This classification is determined by IUPAC classification with
pore diameter of <2 nm, 2–50 nm, and >50 nm classified as micropore, mesopore and macropore, respectively.

| Catalyst          | Surface Area (SBET, m²/g) | Total Pore Volume (cm³/g) | Average Pore Radius (Å) |
|-------------------|---------------------------|---------------------------|-------------------------|
| Mn₃O₄ 950 °C      | 156.0                     | 0.24                      | 31.1                    |
| Mn₃O₄ NPs         | 184.6                     | 0.77                      | 8.01                    |
| Octahedral Mn₃O₄ | 122.4                     | 0.33                      | 18.16                   |

3.3. Phenolic Degradation Performance

The catalytic activity of the as-prepared Mn₃O₄ catalysts is evaluated from phenolic degradation using PMS presented in Figure 5. The initial PMS degradation without transition metal activation is performed to identify the contribution of PMS to phenolic degradation. It is found that PMS without activation degraded 2.465% phenolic compound, which has a negligible effect on the overall performance. This is because, with PMS alone, the sulfate radicals cannot be produced for phenolic oxidation [39]. Similar PMS without activation performance was also reported from previous work. Liu and Huang reported the role of PMS without activation is negligible, with only <5% oxidation for the phenolic compound [40]. Furthermore, the preliminary performance of Mn₃O₄ without the presence of PMS is investigated using a Mn₃O₄ NPs sample. It is shown that the adsorption performance of Mn₃O₄ adsorbed 9.242% phenolic compound within 60 min. The low adsorption capacity of Mn₃O₄ is also recorded in previous studies. This occurs because phenol molecules easily penetrate through pores larger than 1 nm, while most NPs have pores smaller than this. Wang et al. reported no to little adsorption of phenol with only <5% adsorption using Mn₃O₄ 2D nanosheet after 2 h reaction time [5]. The higher adsorption rate we achieved in comparison to Wang et al. is due to the as-prepared Mn₃O₄ having a higher calculated surface area than in their work (65.2 m²/g).

![Figure 5](image-url) - Phenolic degradation efficiency in catalytic oxidation using manganese oxide catalysts. Reaction condition: phenol concentration = 25 ppm, catalyst = 0.4 g/L, PMS = 2 g/L, and t = 25 °C.

The oxidation performance of PMS with different Mn₃O₄ catalyst activations is observed. All Mn₃O₄ catalysts are shown to efficiently activate PMS for phenol removal. Mn₃O₄ 950 °C exhibited 49.730% efficiency within 60 min reaction time. While octahedral Mn₃O₄ reached 71.362% removal, the Mn₃O₄ NPs exhibited the best performance with 96.057% phenolic compound removal. This phenomenon occurred because the Mn₃O₄ NPs possess the most surface area and pore volume of the three catalysts, and these are
the active sites where PMS activation occurs [12]. Additionally, octahedral Mn$_3$O$_4$ has the second-best oxidative degradation performance because it has a higher pore volume with a tighter pore radius, and therefore more active sites, compared to Mn$_3$O$_4$ 950 °C. The greater availability of active sites for PMS activation is attributed to the fast-generating rate of sulfate radicals [39,41].

The two best-performing catalysts underwent investigation of different temperatures toward phenolic compound removal. Figure 6a shows octahedral Mn$_3$O$_4$ phenol removal performance at 25, 35, and 45 °C reaction temperatures. Moreover, the Langmuir-Hilselwood pseudo-first order kinetic model is fitted to determine the reaction rate [42]. Table 2 shows all the constant rates and the correlation coefficient of 0.99. The degradation result of octahedral Mn$_3$O$_4$ at 45, 35, and 25 °C all achieved 100% removal within 40, 120, and 190 min with k$_{obs}$ of 0.128, 0.073, and 0.030 min$^{-1}$, respectively. Additionally, Figure 6b shows Mn$_3$O$_4$ NPs results at 45, 35, and 25 °C achieved 100%, 99.408%, and 96.057% removal within 40, 60, and 60 min with k$_{obs}$ of 0.186, 0.073, and 0.043 min$^{-1}$, respectively. The result shows that higher temperature ensued better oxidation of phenol compounds. Higher temperature stimulates the chemical bond breakage and accelerates the decomposition of the persulfate, which leads to increased phenol removal [43–45]. TOC removal in Mn$_3$O$_4$ NPs/PMS systems was also measured and the results showed that roughly 78% of TOC removal was obtained for Mn$_3$O$_4$ NPs/PMS, at 190 min.

![Figure 5. Phenolic degradation efficiency in catalytic oxidation using manganese oxide catalysts.](image)

**Figure 6.** Effect of temperature on phenolic degradation in catalytic oxidation using (a) octahedral Mn$_3$O$_4$ (b) Mn$_3$O$_4$ NPs. Reaction condition: phenol concentration = 25 ppm, catalyst = 0.4 g/L, PMS = 2 g/L.

| Catalyst       | Temperature (°C) | k$_{obs}$ (min$^{-1}$) | $R^2$ | $E_a$ (kJ/mol) |
|----------------|------------------|------------------------|-------|----------------|
| Mn$_3$O$_4$ NPs| 25               | 0.043                  | 0.98  |                |
|                | 35               | 0.076                  | 0.99  |                |
|                | 45               | 0.186                  | 0.99  |                |
| Octahedral     | 25               | 0.030                  | 0.99  | 42.60          |
| Mn$_3$O$_4$    | 35               | 0.073                  | 0.99  | 71.23          |
|                | 45               | 0.128                  | 0.99  |                |

The correlation between temperature and reaction rate is further studied using the Arrhenius equation plot. Figure 7a,b show the Arrhenius plot for the as-prepared catalysts with a correlation coefficient of 0.99. It is found that octahedral Mn$_3$O$_4$ has an energy
activation of 71.23 kJ/mol, which is much higher than Mn$_3$O$_4$ NPs with $E_a$ of 42.6 kJ/mol. The energy activation of both catalysts is higher than diffusion-controlled reaction, which is in the range of 10–13 kJ/mol. This higher value indicates that the reaction rate is predominantly an intrinsic chemical reaction on the surface of oxide rather than a rate of mass transfer [46].

Figure 7. Arrhenius plot of phenol degradation on (a) octahedral Mn$_3$O$_4$ (b) Mn$_3$O$_4$-NPs catalyst.

In addition, the comparison of PMS activation using several related catalysts for phenolic compound degradation is presented in Table 3. The as-prepared Mn$_3$O$_4$ NPs catalyst has relatively lower energy activation than several catalysts from previous works. Activation energy gives an insight into the minimum energy required for a chemical reaction to occur. The degradation of catalysts with lower activation energy starts faster compared to catalysts with higher activation energy [47].

Table 3. Comparison of PMS activation using related catalysts for phenolic removal.

| Catalyst                        | Operation Condition                              | $E_a$ (kJ/mol) | Ref.  |
|---------------------------------|-------------------------------------------------|----------------|-------|
| Mn$_3$O$_4$ nanorods            | Phenol cons. 20 ppm, catalyst dosage 0.2 g/L, PMS dosage 6.5 mM | 59.7           | [5]   |
| Cubic $\alpha$-Mn$_2$O$_3$      | Phenol cons. 25 ppm, catalyst dosage 0.4 g/L, PMS dosage 2 g/L | 61.2           | [19]  |
| MnO$_2$/ZnFe$_2$O$_4$           | Phenol cons. 20 ppm, catalyst dosage 0.2 g/L, PMS dosage 2 g/L | 49.4           | [31]  |
| Mesoporous biochar with modified KOH and CaCl$_2$ (Ca/BS-800-KOH) | Phenol cons. 20 ppm, catalyst dosage 0.066 g/L, PMS dosage 1 g/L | 68.3           | [43]  |
| CoMnAl mixed metal oxide (CoMnAl-MMO) | Phenol cons. 10 ppm, catalyst dosage 0.02 g/L, PMS dosage 1.5 g/L | 76.83          | [46]  |
| CoMgAl layered double hydrotalcite (CoMgAl-LDH) | Phenol cons. 0.1 mM, catalyst dosage 0.3 g/L, PMS dosage 0.3 mM | 65.19          | [48]  |
| $\alpha$$_3$O$_4$-reduced graphene oxide (Mn$_3$O$_4$-rGO) | MO cons. 30 ppm, catalyst dosage 0.5 g/L, PMS dosage 1.5 g/L | 49.5           | [49]  |
| Magnetic core/shell carbon nanosphere supported manganese (Mn/Air-MCS) | Phenol cons. 20 ppm, catalyst dosage 0.2 g/L, PMS dosage 2 g/L | 59.5           | [50]  |
| Octahedral Mn$_3$O$_4$           | Phenol cons. 25 ppm, catalyst dosage 0.4 g/L, PMS dosage 2 g/L | 71.23          | This work |
| Mn$_3$O$_4$ NPs                | Phenol cons. 25 ppm, catalyst dosage 0.4 g/L, PMS dosage 2 g/L | 42.60          | This work |

Figure 8a,b depict the reusability test of octahedral Mn$_3$O$_4$ and Mn$_3$O$_4$ NPs evaluated in three sequential cycles. Both catalysts observed a decline in the efficiency trend. Mn$_3$O$_4$
NPs maintained an efficiency of 84.29% within 60 min after the third recycling, with only an 11.81% decline. On the other hand, octahedral Mn$_3$O$_4$ exhibited a 9.29% decrease in degradation performance with 87.35% efficiency within 150 min reaction time after the third recycle. The decline in efficiency can be attributed to the surface deactivation of the catalysts with intermediates on their surface [51]. However, the results of both catalysts show a considerably good performance after the third cycle since no additional purification is performed, except for simply washing them with water. Nevertheless, the best way to remove the intermediates from the catalyst surface is to calcinate and wash with ammonia solution, as Sun et al. reported [52].

![Figure 8](image1.png)  
**Figure 8.** Phenol degradation efficiency of recycled (a) octahedral Mn$_3$O$_4$ (b) Mn$_3$O$_4$ NPs catalyst. Reaction condition: phenol concentration = 25 ppm, catalyst = 0.4 g/L, PMS = 2 g/L.

3.4. Proposed Mechanism of PMS Activation by Mn$_3$O$_4$ Catalyst

The oxidation of organic compounds started when PMS contacted the active sites on the surface of Mn$_4$. Then the active sites transferred a donor electron via a reduction-oxidation reaction, both Mn(III) and Mn(IV). Mn(IV) was reduced to Mn(III) and afterward oxidized to Mn(IV) using HSO$_3^-$,. Subsequently, Mn(IV) activated PMS to produce SO$_4^{2-}$, then released into the bulk solution and interacted with H$_2$O and OH to produce *OH. The generated SO$_4^{2-}$ and *OH would target phenol and produce numerous intermediates until the phenol is broken down into CO$_2$ and H$_2$O. The full step by step mechanism is illustrated in the following Equation (4) and Figure 9.

![Figure 9](image2.png)  
**Figure 9.** Schematic mechanism of PMS activation by Mn$_3$O$_4$ catalyst.
Equation (4) [5,41,53]:

\[\begin{align*}
\text{Mn}^{(4+)} + \text{HSO}_5^- & \rightarrow \text{Mn}^{(3+)} + \text{SO}_4^{2-} + \cdot \text{OH} \\
\text{Mn}^{(3+)} + \text{HSO}_5^- & \rightarrow \text{Mn}^{(4+)} + \text{SO}_5^{2-} + \text{H}^+ \\
\text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} + \text{H}^+ \\
\cdot \text{OH} + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-} \\
\text{SO}_4^{2-} + \text{OH}^- & \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} \\
\cdot \text{OH} + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-}
\end{align*}\]

4. Conclusions

Three different MnO4 catalysts with different crystallinity, morphology, and specific surface areas were successfully synthesized using a simple hydrothermal method. The MnO4 NPs exhibit excellent performance in activating PMS for phenol removal with high efficiency and relatively low energy activation compared to other related catalysts. MnO4 NPs has an efficiency of 96.057% with \( E_a = 42.6 \text{ kJ/mol} \), followed by octahedral MnO4 with an efficiency of 71.362% with \( E_a = 71.23 \text{ kJ/mol} \), and MnO4 950 °C with the efficiency of 49.73%. The three-stage sequential recycling of MnO4 NPs shows a high degree of reusability, with only an 11.81% reduction in performance. This work provides a facile preparation of MnO4 NPs for the advanced oxidation process in water remediation applications.

Author Contributions: Conceptualization, S.M.; Data curation, S.M. and M.W.N.; Formal analysis, M.W.N.; Investigation, M.W.N.; Project administration, E.S.; Supervision, E.S.; Writing—original draft, S.M.; Writing—review & editing, E.S. and N.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to gratefully thank to the Chemical Engineering Department, Universitas Syiah Kuala and Chemical Engineering Department, Universitas Riau – Indonesia.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fan, Y.; Fang, C. A Comprehensive Insight into Water Pollution and Driving Forces in Western China d Case Study of Qinghai. J. Clean. Prod. 2020, 274, 129950. [CrossRef]
2. Tang, W.; Pei, Y.; Zheng, H.; Zhao, Y.; Shu, L. Twenty Years of China’s Water Pollution Control: Experiences and Challenges. Chemosphere 2022, 295, 133875. [CrossRef] [PubMed]
3. Zulfiqar, M.; Fakhrlul, M.; Samsudin, R.; Sufian, S. Modelling and Optimization of Photocatalytic Degradation of Phenol via TiO2 Nanoparticles: An Insight into Response Surface Methodology and Artificial Neural Network. J. Photochem. Photobiol. A Chem. 2019, 384, 112039. [CrossRef]
4. Franchi, O.; Rosenkranz, F.; Chamy, R. Key Microbial Populations Involved in Anaerobic Degradation of Phenol and P-Cresol Using Different Inocula. Electron. J. Biotechnol. 2018, 35, 33–38. [CrossRef]
5. Wang, Q.; Li, Y.; Shen, Z.; Liu, X.; Jiang, C. Facile Synthesis of Three-Dimensional MnO4 Hierarchical Microstructures for Efficient Catalytic Phenol Oxidation with Peroxymonosulfate. Appl. Surf. Sci. 2019, 495, 143568. [CrossRef]
6. Ye, R.; Çetinkaya, S. MnO4/p(DCPD) HIPE Nanocomposites as an Efficient Catalyst for Oxidative Degradation of Phenol. J. Nanoparticle Res. 2020, 22, 198.
7. Saputra, E.; Utama, P.S.; Daniel, M.; Simatupang, V.; Prawiranegara, B.A.; Abid, H.R.; Muraza, O. Spent Bleaching Earth Supported CeFeO3 Perovskite for Visible Light Photocatalytic Oxidation of Methylene Blue. J. Appl. Mater. Technol. 2020, 1, 81–87. [CrossRef]
8. Al Amery, N.; Abid, H.R.; Wang, S. Enhancing Acidic Dye Adsorption by Updated Version of UiO-66. J. Appl. Mater. Technol. 2020, 1, 54–62. [CrossRef]
9. Takagi, R.; Mulyati, S.; Arahan, N.; Ohmukai, Y.; Maruyama, T.; Matsuura, H. Time Dependence of Transport Number Ratio during Electro dialysis Process. Desalination Water Treat. 2011, 34, 25–31. [CrossRef]
10. Arahman, N.; Mulyati, S.; Fahrina, A.; Muchtar, S.; Yusuf, M.; Takagi, R.; Matsuyama, H.; Nordin, N.A.H.; Bilad, M.R. Improving Water Permeability of Hydrophilic PVDF Membrane Prepared via Blending with Organic and Inorganic Additives for Humin Acid Separation. *Molecules* **2019**, *24*, 4099. [CrossRef]

11. Al Amery, N.; Abid, H.R.; Wang, S.; Liu, S. Removal of Methylene Blue (MB) by Bimetallic-Metal Organic Framework. *J. Appl. Mater. Technol.* **2020**, *2*, 36–49. [CrossRef]

12. Saputra, E.; Muhammad, S.; Sun, H.; Ang, H.; Tadé, M.O.; Wang, S. A Comparative Study of Spinel Structured MnO<sub>2</sub>, CO<sub>3</sub>O<sub>4</sub> and FeO<sub>3</sub>Nanoparticles in Catalytic Oxidation of Phenolic Contaminants in Aqueous Solutions. *J. Colloid Interface Sci.* **2013**, *367*, 467–473. [CrossRef] [PubMed]

13. Yalili, M.; Abdelraheem, W.H.; He, X.; Kestioglu, K. Photochemical Treatment of Tyrosol, a Model Phenolic Compound Present in Olive Mill Wastewater, by Hydroxyl and Sulfate Radical-Based Advanced Oxidation Processes (AOPs). *J. Hazard. Mater.* **2019**, *367*, 734–742. [CrossRef]

14. Yang, Q.; Ma, Y.; Chen, F.; Yao, F.; Sun, J.; Wang, S.; Yi, K. Recent Advances in Photo-Activated Sulfate Radical-Advanced Oxidation Process (SR-AOP) for Refractory Organic Pollutants Removal in Water. *Chem. Eng. J.* **2019**, *378*, 122149. [CrossRef]

15. Utama, P.S.; Widayatno, W.B.; Azhar, M.R.; Abid, H.R.; Peng, W.; Muraza, O.; Saputra, E. LaMnO<sub>3</sub> Perovskite Activation of Peroxymonosulfate for Catalytic Palm Oil Mill Secondary Effluent Degradation. *J. Appl. Mater. Technol.* **2020**, *2*, 27–35. [CrossRef]

16. Fan, J.; Wang, Q.; Yan, W.; Chen, J.; Zhou, X.; Xie, H. MnO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> Composite to Activate Peroxymonosulfate for Organic Pollutants Degradation: Electron Transfer and Structure-Dependence. *J. Hazard. Mater.* **2022**, *434*, 128818. [CrossRef]

17. Soltani, T.; Lee, B. Enhanced Formation of Sulfate Radicals by Metal-Doped BiFeO<sub>3</sub> under Visible Light for Improving Photocatalytic Degradation of 2-Chlorophenol. *Chem. Eng. J.* **2017**, *313*, 1258–1268. [CrossRef]

18. Shukla, P.; Fatimah, I.; Wang, S.; Ang, H.M.; Tadé, M.O. Photocatalytic Generation of Sulphate and Hydroxyl Radicals Using Zinc Oxide under Low-Power UV to Oxidise Phenolic Contaminants in Wastewater. *Catal. Today* **2020**, *157*, 410–414. [CrossRef]

19. Chen, Q.; Jì, F.; Guo, Q.; Guan, W.; Yan, P.; Pei, L.; Xu, X. Degradation of Phenol by Vis/Co-TiO<sub>2</sub>/KHSO<sub>5</sub> Hybrid Co-SR—Photoprocess at Neutral PH. *Ind. Eng. Chem. Res.* **2013**, *1*, 12540–12549. [CrossRef]

20. Saputra, E.; Muhammad, S.; Sun, H.; Ang, H.; Tadé, M.O.; Wang, S. Shape-Controlled Activation of Peroxymonosulfate by Single Crystal-MnO<sub>2</sub> for Catalytic Phenol Degradation in Aqueous Solution. *Appl. Catal. B Environ.* **2014**, *154–155*, 246–251. [CrossRef]

21. Oh, W.; Lua, S.; Lim, T. High Surface Area DPA-Hematite for eFl Cient Detoxification of Bisphenol A via Peroxymonosulfate Activation. *J. Mater. Chem. A* **2014**, *2*, 15836–15845. [CrossRef]

22. Oh, W.; Dong, Z.; Lim, T. Generation of Sulfate Radical through Heterogeneous Catalysis for Organic Contaminants Removal: Current Development, Challenges and Prospects. *Appl. Catal. B Environ.* **2016**, *194*, 169–201. [CrossRef]

23. Sankar, S.; Inamdar, A.I.; Im, H.; Lee, S.; Kim, D.Y. Template-Free Rapid Sonochemical Synthesis of Spherical α-MnO<sub>2</sub> Nanoparticles for High-Energy Supercapacitor Electrode. *Ceram. Int.* **2018**, *44*, 17514–17521. [CrossRef]

24. Li, Y.; Tan, H.; Yang, X.Y.; Goris, B.; Verbeeck, J.; Bals, S.; Colson, P.; Cloots, R.; Van Tendeloo, G.; Su, B.L. Well shaped Mn3O4 nano-octahedra with anomalous magnetic behavior and enhanced photodecomposition properties. *Small* **2011**, *7*, 475–483. [CrossRef] [PubMed]

25. Nugraha, M.W.; Dzul, M.; Wirzal, H.; Ali, F.; Roza, L.; Sambudi, S. Electrosynsp Polylactic Acid/Tungsten Oxide/Amino-Functionalized Carbon Quantum Dots (PLA/WO<sub>3</sub>/N-CQDs) Fibers for Oil/Water Separation and Photocatalytic Decolorization. *J. Environ. Chem. Eng.* **2021**, *9*, 106033. [CrossRef]

26. Amasha, M.; Baalbaki, A.; Ghauch, A. A Comparative Study of the Common Persulfate Activation Techniques for the Complete Degradation of an NSAID: The Case of Ketoprofen. *Chem. Eng. J.* **2020**, *350*, 395–410. [CrossRef]

27. Zhang, H.; Liu, X.; Ma, J.; Lin, C.; Qi, C.; Li, X.; Zhou, Z.; Fan, G. Activation of Peroxymonosulfate Using Drinking Water Treatment Residuals for the Degradation of Atrazine. *J. Hazard. Mater.* **2018**, *344*, 1220–1228. [CrossRef]

28. Gupta, S.P.; Gosavi, S.W.; Late, D.J.; Qiao, Q.; Walke, P.S. Temperature Driven High-Performance Pseudocapacitor of Carbon Nano-Onions Supported U Minh like Structures of a MnO<sub>2</sub> Nanorod. *Electrochim. Acta* **2020**, *354*, 136626. [CrossRef]

29. Zia, J.; Aazam, E.S.; Riaz, U. Facile Synthesis of MnO<sub>2</sub> Nanorods and ZnMn<sub>2</sub>O<sub>4</sub> Nanohexagons: A Comparison of Microwave-Assisted Catalytic Activity against 4-Nitrophenol Degradation. *Integr. Med. Res.* **2020**, *9*, 9709–9719. [CrossRef]

30. Saputra, E.; Muhammad, S.; Sun, H.; Ang, H.; Tadé, M.O.; Wang, S. Manganese Oxides at Different Oxidation States for Heterogeneous Activation of Peroxymonosulfate for Phenol Degradation in Aqueous Solutions. *Appl. Catal. B Environ.* **2013**, *142–143*, 729–735. [CrossRef]

31. Wang, Y.; Sun, H.; Ang, H.M.; Tadé, M.O.; Wang, S. Facile Synthesis of Hierarchically Structured Magnetic MnO<sub>2</sub>/ZnFe<sub>2</sub>O<sub>4</sub> Hybrid Materials and Their Performance in Heterogeneous Activation of Peroxymonosulfate. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19914–19923. [CrossRef]

32. Zhu, H.T.; Luo, J.; Yang, H.X.; Liang, J.K.; Rao, G.H.; Li, J.B.; Du, Z.M. Birensite-Type MnO<sub>2</sub> Nanowalls and Their Magnetic Properties. *J. Phys. Chem. C* **2008**, *112*, 17089–17094. [CrossRef]

33. Amara, M.A.; Larbi, T.; Mahdhi, N.; Saadallah, F.; Amlouk, M. Enhancement of photocatalytic degradation of MB by recyclable Li/MnO<sub>2</sub> thin films. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 10963–10976. [CrossRef]

34. Sukhdev, A.; Challa, M.; Narayani, L.; Somashekhar, A. Synthesis, Phase Transformation, and Morphology of Hausmannite MnO<sub>4</sub>Nanoparticles: Photocatalytic and Antibacterial Investigations. *Heliyon* **2020**, *6*, e03245. [CrossRef] [PubMed]

35. Shabanloo, A.; Salari, M.; Shabanloo, N.; Hadi, M.; Pittman, C.U.; Mohan, D. Heterogeneous Persulfate Activation by Nano-Sized Mn<sub>3</sub>O<sub>4</sub> to Degradate Furfural from Wastewater. *J. Mol. Liq.* **2020**, *298*, 112088. [CrossRef]
36. Yang, Y.; Huang, X.; Xiang, Y.; Chen, S.; Guo, L.; Leng, S. Mn₃O₄ with Different Morphologies Tuned through One-Step Electrochemical Method for High-Performance Lithium-Ion Batteries Anode. *J. Alloys Compd.* 2019, 771, 335–342. [CrossRef]

37. Huang, S.Z.; Jin, J.; Cai, Y.; Li, Y.; Tan, H.Y.; Wang, H.E.; Van Tendeloo, G.; Su, B.L. Engineering single crystalline Mn₃O₄ nano-octahedra with exposed highly active [011] facets for high performance lithium ion batteries. *Nanoscale* 2014, 6, 6819–6827. [CrossRef]

38. Wang, F.; Xiao, M.; Ma, X.; Wu, S.; Ge, M.; Yu, X. Insights into the Transformations of Mn Species for Peroxymonosulfate Activation by Tuning the Mn₃O₄ Shapes. *Chem. Eng. J.* 2021, 404, 127097. [CrossRef]

39. Zhao, X.; Niu, C.; Zhang, L.; Guo, H.; Wen, X.; Liang, C. Co-Mn Layered Double Hydroxide as an Effective Heterogeneous Catalyst for Degradation of Organic Dyes by Activation of Peroxymonosulfate. *Chemosphere* 2018, 204, 11–21. [CrossRef]

40. Liu, S.; Zhang, Z.; Huang, F.; Liu, Y.; Feng, L.; Jiang, J.; Zhang, L. Carbonized Polyarilime Activated Peroxymonosulfate (PMS) for Phenol Degradation: Role of PMS Adsorption and Singlet Oxygen Generation. *Appl. Catal. B Environ.* 2021, 286, 119921. [CrossRef]

41. Yu, J.; Tang, L.; Pang, Y.; Zeng, G.; Wang, J.; Deng, Y.; Liu, Y.; Feng, H.; Chen, S.; Ren, X. Magnetic Nitrogen-Doped Sludge-Derived Biochar Catalysts for Persulfate Activation: Internal Electron Transfer Mechanism. *Chem. Eng. J.* 2019, 364, 146–159. [CrossRef]

42. Othman, I.; Hisham, J.; Abu, M.; Banat, F. Catalytic Activation of Peroxymonosulfate Using CeVO₄ for Phenol Degradation: An Insight into the Reaction Pathway. *Appl. Catal. B Environ.* 2020, 266, 118601. [CrossRef]

43. Zhang, H.; Tang, L.; Wang, J.; Yu, J.; Feng, H.; Lu, Y. Enhanced Surface Activation Process of Persulfate by Modified Bagasse Biochar for Degradation of Phenol in Water and Soil: Active Sites and Electron Transfer Mechanism. *Colloids Surf. A* 2020, 599, 124904. [CrossRef]

44. Sun, H.; Kwan, C.; Suvorova, A.; Ming, H.; Tadé, M.O.; Wang, S. Catalytic Oxidation of Organic Pollutants on Pristine and Surface Nitrogen-Modified Carbon Nanotubes with Sulfate Radicals. *Appl. Catal. B Environ.* 2014, 154–155, 134–141. [CrossRef]

45. Wang, Y.; Sun, H.; Duan, X.; Ang, H.M.; Tadé, M.O.; Wang, S. A New Magnetic Nano Zero-Valent Iron Encapsulated in Carbon Spheres for Oxidative Degradation of Phenol. *Appl. Catal. B Environ.* 2015, 172–173, 73–81. [CrossRef]

46. Li, W.; Wu, P.; Zhu, Y.; Huang, Z.; Lu, Y.; Li, Y.; Dang, Z. Catalytic Degradation of Bisphenol A by CoMnAl Mixed Metal Oxides Catalyzed Peroxymonosulfate: Performance and Mechanism. *Chem. Eng. J.* 2015, 279, 93–102. [CrossRef]

47. Xu, F.; Wang, B.; Yang, D.; Hao, J.; Qiao, Y.; Tian, Y. Thermal Degradation of Typical Plastics under High Heating Rate Conditions by TG-FTIR: Pyrolysis Behaviors and Kinetic Analysis. *Energy Convers. Manag.* 2018, 171, 1106–1115. [CrossRef]

48. Liao, Z.; Zhu, J.; Jawad, A.; Muzi, J.; Chen, Z.; Chen, Z. Degradation of Phenol Using Peroxymonosulfate Activated by a High Efficiency and Stable CoMgAl-LDH Catalyst. *Materials* 2019, 12, 968. [CrossRef]

49. Yao, Y.; Xu, C.; Yu, S.; Zhang, D.; Wang, S. Facile Synthesis of Mn₃O₄–Reduced Graphene Oxide Hybrids for Catalytic Decomposition of Aqueous Organics. *Ind. Eng. Chem. Res* 2013, 52, 3637–3645. [CrossRef]

50. Wang, Y.; Sun, H.; Ang, H.M.; Tadé, M.O.; Wang, S. Synthesis of Magnetic Core/Shell Carbon Nanosphere Supported Manganese Catalysts for Oxidation of Organics in Water by Peroxymonosulfate. *J. Colloid Interface Sci.* 2014, 433, 68–75. [CrossRef]

51. Barzegar, G.; Jor, S.; Zarezade, V.; Khatebasreh, M. 4-Chlorophenol Degradation Using Ultrasound/Peroxymonosulfate/Nanoscale Zero Valent Iron: Reusability, Identification of Degradation Intermediates and Potential Application for Real Wastewater. *Chemosphere* 2018, 201, 370–379. [CrossRef] [PubMed]

52. Sun, H.; Liang, H.; Zhou, G.; Wang, S. Supported Cobalt Catalysts by One-Pot Aqueous Combustion Synthesis for Catalytic Phenol Degradation. *J. Colloid Interface Sci.* 2013, 394, 394–400. [CrossRef] [PubMed]

53. Xiao, Y.; Wang, Y.; Xie, Y.; Ni, H.; Li, X.; Zhang, Y.; Xie, T. Shape-controllable synthesis of MnO₂ nanostructures from manganese-contained wastewater for phenol degradation by activating peroxymonosulfate: Performance and mechanism. *Environ. Technol.* 2018, 41, 2037–2048. [CrossRef] [PubMed]