Orange G degradation by heterogeneous peroxymonosulfate activation based on magnetic $MnFe_2O_4$/α-MnO_2 hybrid

Abstract

Wastewater containing an azo dye Orange G (OG) causes massive environmental pollution, thus it is critical to developing a highly effective, environmental-friendly, and reusable catalyst in peroxymonosulfate (PMS) activation for OG degradation. In this work, we successfully applied a magnetic $MnFe_2O_4$/α-MnO_2 hybrid fabricated by a simple hydrothermal method for OG removal in water. The characteristics of the hybrid were investigated by XRD, SEM, EDX, FT-IR, BET, VSM, and XPS. The effects of operational parameters (i.e., catalytic system, catalytic dose, solution pH, and temperature) were investigated. The results exhibited that 96.8% of OG degradation was obtained with $MnFe_2O_4$/α-MnO_2(1:9)/PMS system in 30 min regardless of solution pH changes. The radical quenching experiments demonstrated that $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and $^1O_2$ were the primary reactive oxygen species responsible for the OG degradation. The hybrid also displayed unusual stability with less than 30% loss in the OG removal after four sequential cycles. Overall, magnetic $MnFe_2O_4$/α-MnO_2 hybrid could be used as a high potential activator of PMS to remove orange G and maybe other dyes from wastewater.

Keywords: $MnFe_2O_4$/α-MnO_2, peroxymonosulfate, Orange G, catalytic degradation, reusability

1. Introduction

Processing industries such as dyeing, printing, textiles, and leather generate a massive amount of polluted wastewater that contains hazardous organic compounds (e.g., orange G, orange II phenol, methyl violet, and methylene blue) (Ejder-Korucu *et al.*, 2015). Orange G (OG) (**Figure 1**), which is an acidic and widely used azo compound in the dyeing of fabrics, has been gained

much attention due to its non-biodegradable, toxic, and potentially carcinogenic nature (Cai *et al.*, 2011). Therefore, the physicochemical treatment of OG-containing wastewater is necessary to reduce its environmental pollution. Treatments of wastewater involved oxidation methods (e.g., photocatalytic oxidation, ozone/hydrogen peroxide-induced oxidation, and Fenton reaction-based oxidation), physical methods (e.g. adsorption and filtration), and biological methods (e.g., aerobic and anaerobic decomposition with fungi, bacteria, and algae) (Javaid and Qazi, 2019; Wang and Zhuan, 2020; Garrido-Cardenas *et al.*, 2019). Recently, advanced oxidation processes (AOPs) have received great interest from researchers since they brought good efficiency in wastewater treatment (M'Arimi *et al.*, 2020). Among the AOPs, sulfate radical-advanced oxidation processes (SR-AOPs) have been widely studied because of their superiorities of (i) greater standard oxidation-reduction potential of sulfate radical ($SO_4^{\bullet-}$) (E_o = 2.5-3.1 V *vs*. normal hydrogen electrode (NHE)) than that of hydroxyl radical ($HO^{\bullet}$) (E_o = 1.8-2.7 V *vs*. NHE), (ii) broader range of reaction pH conditions of $SO_4^{\bullet-}$ (pH 2-8) than that of $OH^{\bullet}$ (pH 2-4, an acidic environment), (iii) longer half-life of $SO_4^{\cdot-}$ ($t_{1/2}$ = 30-40 μs) compared with that of $OH^{\bullet}$ ($t_{1/2} \leq 1$ μs), and (iv) higher oxidation capacity in both carbonate and phosphate buffer solutions (Xia *et al.*, 2020). Sulfate radicals can be effectively produced through the activation of persulfate (PS, $S_2O_8^{2-}$) and peroxymonosulfate (PMS, HSO_5^-), which contain labile peroxide bonds (O-O). In comparison with PS, PMS has been more immensely utilized for its asymmetrical molecular structure, lower peroxide bond dissociation energy, and lesser redox potential (1.77 V *vs*. 2.01 V) (Ma *et al.*, 2021). In general, PMS can be activated to generate sulfate radicals through the presence of physical (e.g., heating, ultraviolet (UV) irradiation, and ultrasonic waves) and chemical activation methods (e.g., transition metal ion-based catalysts (iron (Fe^{2+}), cobalt (Co^{2+})), alkaline, and strong oxidizers) (Peng *et al.*, 2021). Among these agents, the transition metal ion-based catalysts gained the most

interest for their low energy consumption and simplicity of the PMS activation (Li *et al.*, 2021). In particular, heterogeneous systems of these metal ion catalysts were intensively investigated because of their stable structure, high interactive surface area, and easy recovery (Fan *et al.*, 2017). Nevertheless, the major concerns in the utilization of compounds such as Co^{2+} and Fe^{2+} ions were the secondary pollution and potential biological toxicity due to the unexpected release of Co^{2+} and a remarkable reduction in the generation efficiency of sulfate radicals if used in high iron loading quantities, respectively (Hu and Long, 2016). The above-mentioned limitations can partially be surmounted with heterogeneous systems of manganese oxides/ions because of their stability, high catalytic activity, environmental-friendliness, and low cost (Huang and Zhang, 2019). Manganese dioxide (MnO_2) has many different morphologies such as α-, β-, and γ-MnO_2, and each phenotype exhibits unique features (Dong *et al.*, 2014). In this regard, α-MnO_2 presented the highest catalytic activity that can be ascribed to its high surface area and preferable crystalline structure (Xie *et al.*, 2015). However, α-MnO_2 is a heterogeneous catalyst, which interferes with the subsequent catalyst separation and recovery, thereby disturbing its applicability (Uematsu *et al.*, 2016). On the contrary, spinel ferrite $MnFe_2O_4$ has stable, insoluble, and excellent magnetic properties, which make it easy to be separated from the reaction solution (Shao *et al.*, 2012; Yao *et al.*, 2014). These observations suggested the fabrication of a heterogeneous catalyst system via a combination between α-MnO_2 and $MnFe_2O_4$.

In fact, Chen *et al.* (2019) successfully synthesized magnetic MnO_2/$MnFe_2O_4$ nanocomposite by hydrothermal method and applied it to activate PMS for Rhodamine B (RhB) degradation. The study's results displayed that the RhB decomposition efficiency of the MnO_2/$MnFe_2O_4$ nanocomposite (with a molar ratio of 7:1) was 90% within 5 min in the presence of PMS. However, the formation mechanism of the MnO_2/$MnFe_2O_4$ nanocomposite was not

discussed with the lack of TGA and EDX-mapping analyses and the material had a low surface area of 67.2 m^2/g. Besides, the material was strongly affected under alkaline environments but the effect of pH was not thoroughly discussed. For other organic pollutants, $MnFe_2O_4$/δ-MnO_2 (Zhu *et al.*, 2021) and α-MnO_2/$MnFe_2O_4$ (Xu *et al.*, 2021) were fabricated for PMS activation in degradation sulfadiazine and norfloxacin, respectively, in water. However, the results of TGA and EDX-mapping as well as the formation mechanism of $MnFe_2O_4$ were not provided. Also, the role of superoxide radical ($O_2^{\bullet-}$), and especially, singlet oxygen ($^1O_2$) in the reaction mechanism has not been deeply studied. Therefore, a systematic study, which focuses on the formation mechanism of the material and the reaction mechanism in PMS activation for dye, especially popular OG, is needed not only for understanding the formation and activity of the material but also for determining the suitable reaction conditions for further practical application in dye removal by PMS activation.

In this work, we prepared a magnetic $MnFe_2O_4$/α-MnO_2 hybrid via the hydrothermal method and investigated the decomposition efficiency of orange G through the hybrid-catalyzed PMS activation. The physical and chemical properties of the hybrid material were examined by various characterization techniques. The effects of environmental factors such as catalyst dosage, PMS dosage, OG concentration, pH, temperature, and catalyst reusability on the PMS activation were investigated. In addition, the possible degradation mechanisms of the $MnFe_2O_4$/α-MnO_2/PMS system for OG degradation were also determined.

2. Materials and Methods

2.1. Materials

Manganese (II) chloride tetrahydrate ($MnCl_2.4H_2O$), ferric chloride hexahydrate ($FeCl_3.6H_2O$), potassium peroxymonosulfate or PMS ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$, trade name

Oxone®), sodium persulfate ($Na_2S_2O_8$), potassium permanganate ($KMnO_4$), anhydrous sodium acetate (CH_3COONa), ethylene glycol (EG, $(CH_2OH)_2$), polyethylene glycol (PEG), ethanol (CH_3CH_2OH, 99.5%), *tert*-butyl alcohol (TBA, $(CH_3)_3COH$), orange G (OG) were all obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). All reagents used in this work were of analytical grade and used without further purification unless otherwise stated.

2.2. Synthesis of $MnFe_2O_4$/α-MnO_2 hybrid

2.2.1. Synthesis of α-MnO_2 nanoparticles

The α-MnO_2 nanoparticles were prepared by a hydrothermal method (Ma *et al.*, 2011). In brief, 0.363 g of $KMnO_4$ was completely dissolved in 80 mL of deionized water. Then 0.8 mL of concentrated HCl solution (37%) was slowly added to the above aqueous $KMnO_4$ solution and stirred for 1 h. Next, the mixture was transferred into a 100-mL Teflon-lined stainless steel autoclave and treated at 150 ^oC for 12 h. After the reaction, the mixture was cooled down to an ambient temperature. The obtained dark product was consecutively washed three times with deionized water and ethanol before drying in a vacuum oven at 80 °C for 3 h.

2.2.2. Synthesis of magnetic $MnFe_2O_4$ nanoparticles

The $MnFe_2O_4$ nanoparticles were also synthesized by a solvothermal method with slight modification (Reddy and Mohamed, 2015). Briefly, 1.092 g of $FeCl_3.6H_2O$ and 0.254g of $MnCl_2.4H_2O$ were dissolved in 100 mL of EG, and the mixture was stirred for 30 min. After that, 7.242 g of CH_3COONa and 2.0 g of polyethylene glycol (PEG) were sequentially added to the above mixture and stirred for 1 h. The resulting mixture was then transferred into a 100-mL Teflon-lined stainless-steel autoclave and treated at 200 ^oC for 12 h. After the reaction, the mixture was cooled down to an ambient temperature. The black product was separated by a magnet and

consecutively washed three times with deionized water and ethanol, and finally dried in a vacuum oven at 80 °C for 6 h.

2.2.3. Synthesis of magnetic $MnFe_2O_4$/α-MnO_2 hybrid

The $MnFe_2O_4$/α-MnO_2 hybrid was also fabricated using a hydrothermal method (Chen *et al.*, 2019) (**Figure 2**). In detail, 0.5 g of as-prepared $MnFe_2O_4$ was added into 100 mL of deionized water, and the dispersion was sonicated in a water bath for 30 min. Later, 0.856 g of $KMnO_4$ and 1.812 mL of concentrated HCl solution (37%) were serially added into the above dispersion, and the mixed solution was mechanically stirred for 1 h. The mixture was then transferred into a 100-mL Teflon-lined stainless steel autoclave and treated at 150 ^oC for 12h. After the reaction, the mixture was cooled down to an ambient temperature. The resultant product was continuously washed three times with deionized water and ethanol and dried in a vacuum oven at 80 °C for 3 h. To investigate the effective catalytic activity, the hybrids with various mass ratios of $MnFe_2O_4$:α-MnO_2 (i.e., 1:5, 1:7, and 1:9) were prepared.

2.3. Characterization of materials

To confirm the crystalline structure, X-ray diffraction (XRD) patterns of the as-synthesized α-MnO_2, $MnFe_2O_4$, and $MnFe_2O_4$/α-MnO_2 hybrid were recorded on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5418°A), operating at 30 kV and 40 mA. In addition, the size, morphology, and microstructure of these materials were determined using field emission scanning electron microscopy (FE-SEM, Hitachi SU810, Japan) incorporated with an energy-dispersive X-ray (EDX) analyzer (EMAX Energy, Horiba Ltd., Japan). The chemical composition and elemental valence states of the materials were identified by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD). Thermogravimetric analysis (TGA) was carried out by using Pyris 6 TGA Perkin Elmer. The chemical bonds of the materials were confirmed by Fourier

transform infrared spectroscopy (FT-IR, Perkin Elmer BX) with the scanned wavenumber in the range of 4000–400 cm^{-1}. The specific surface area of the materials was examined by a Brunauer–Emmett–Teller method (BET, Micromeritics ASAP 2460) with the degassing process at 300 °C for 4 h before each measurement. The magnetic properties of the synthesized materials were identified by a vibrating sample magnetometer equipped with a 1 T magnet (PMC MicroMag 3900 model).

The isoelectric point of the hybrid material was determined by the titration method. Six 50-mL flasks were added with 25 mL of 0.1 M NaCl solution and initial pH values of the solution (pH_i) were adjusted to range from 3 to 11 using 0.1 M HCl or NaOH solutions. Each flask was then added with 0.05 g of the hybrid material and shaken by a shaker for 48 h. The suspension was then settled and filtered, and the filtrate was sent for final pH measurement (pH_f). A graph was then plotted for the relationship of difference between pH values ($\Delta pH = pH_f - pH_i$) according to pH_i and the pH value at which $\Delta pH = 0$ is determined as the isoelectric pH value (pH_{pzc}) of the material.

2.4. Catalytic activity experiments

At first, stock suspensions of $MnFe_2O_4$/α-MnO_2, orange G (OG), potassium peroxymonosulfate (PMS) with concentrations of 1000, 100, 5000 mg/L, respectively, were prepared by dispersing the pre-weighed amounts of respective chemicals in deionized water using volumetric flasks.

In the typical experiment to determine the catalytic activity of $MnFe_2O_4$/α-MnO_2 in PMS activation, the OG degradation test was performed at room temperature (30±2 ^oC). In a 5-mL volumetric flask, 0.5 mL of $MnFe_2O_4$/α-MnO_2 stock suspension was added into 2.5 mL of OG stock solution and followed by solution pH adjustment using 0.05 M H_2SO_4 or 0.05 M NaOH

solutions. The suspension was then shaken for 30 min until approaching the adsorption-desorption equilibrium. Subsequently, 1.00 mL of PMS stock solution was added to the above mixture under shaking to initiate an oxidation reaction. At pre-determined time points, the mixed solution in the flask was transferred into a quartz cuvette, and the UV/Vis absorbance of the OG solution was measured at 480 nm. The control solutions were also prepared in the same procedure with the absence of OG.

In the specific experiment to investigate the effect of temperature on OG degradation, 10.0 mL of $MnFe_2O_4$/α-MnO_2 suspension was added into 50.0 mL of OG stock solution and followed by the adjustment of initial pH. The mixture was then shaken for 30 min to reach the adsorption-desorption equilibrium. Afterward, 20.0 mL of PMS stock solution was added to the above mixture under shaking. The assigned temperature values (i.e., 20, 30, and 40 ^oC) were set. At pre-determined time intervals, 0.2 mL of Na_2SO_3 (1.0 M, as a reaction terminator) was added into a 4.0 mL aliquot of the sample, and then the UV/Vis absorbance of OG was measured at 480 nm. After the reaction, the hybrid was separated by a magnet, washed three times with deionized water and ethanol, and then dried in a vacuum oven at 80 ^oC for 12 h. The stability and reusability of the $MnFe_2O_4$/α-MnO_2 hybrid were assessed by re-using the recycled catalyst after three consecutive reaction cycles. The quenching tests of reactive radicals were performed by adding a certain amount of TBA, EtOH, and FFA (at 100 mM) and p-BQ (at 10 mM) into the reaction mixtures.

The decomposition efficiency of OG was calculated using the following equation:

$$H\% = \left(1 - \frac{C_t}{C_0}\right).100\ (\%) = \left(1 - \frac{A_t}{A_0}\right).100\ (\%) \quad \text{(Eq. 1)}$$

Where C_o and A_o are the concentration and absorbance, respectively, of OG at the initial time. C_t and A_t are the concentration and absorbance, respectively, of OG at a defined time *t*.

The kinetics of the OG decomposition by the $MnFe_2O_4$/α-MnO_2/PMS system was expressed through a pseudo-first-order model as follows:

$$LnC_t/C_o = -k_{app}.t \quad \text{(Eq. 2)}$$

Where C_o and C_t are the OG concentrations at the initial time and determined time t, respectively and k_{app} is the apparent rate constant (min^{-1}).

3. Results and discussion

3.1. Material characterizations

The morphologies of α-MnO_2, $MnFe_2O_4$, and $MnFe_2O_4$/α-MnO_2 were characterized by SEM. As shown in **Figures 3a and 3b**, the α-MnO_2 was observed in smooth-surfaced and uniformly distributed rod-like structures, with dimensions of 0.5-1 μm in length and 50-100 nm in diameter. (Ma *et al.*, 2011; Huang *et al.*, 2020). The rod structure formation of α-MnO_2 can be explained through its multi-stage synthetic procedure of nucleation - dissolving - anisotropic growth - recrystallization (Zhang *et al.*, 2014). In the early stages, the MnO_2 crystalline seeds were generated by a redox reaction between Cl^- and MnO_4^- in an acidic medium, then developing into MnO_2 with a 1-D rod structure at a low temperature of 120 ^oC and low pressure (Reaction 1). Subsequently, the second stage, which was performed at higher temperature and pressure and prolonged hydrothermal time, made the MnO_2 rods grow longer and larger, and the rods were gradually converted into rod-cluster morphology (Ma *et al.*, 2011; Huang *et al.*, 2020). Zhu *et al.* (2021) showed that a 3-D hierarchical corolla-like structure of δ-MnO_2 was formed at a low synthetic temperature of 100 ^oC. Thus, the temperature played an important role in the formation of structural and morphological forms of MnO_2.

$$2KMnO_4 + 8HCl \xrightarrow[12h]{150^oC} \alpha\text{-}2MnO_2 + 3Cl_2 + 2\,KCl + 4H_2O \quad (1)$$

In addition, $MnFe_2O_4$ were presented as uniform spheres, which possess diameters in the range of 0.1-0.15 μm (**Figures 3c and 3d**). The mechanism for the formation of spherical $MnFe_2O_4$ nanoparticles could be explained in the following steps. First of all, sodium acetate (CH_3COONa) was hydrolyzed to elicit an alkaline medium (Reaction 2). The Fe^{3+} and Mn^{2+} ions then react with the hydroxyl anion (HO^-) to form precipitates of iron (III) and manganese (II) hydroxides, respectively (Reactions 3 and 4). Finally, $Fe(OH)_3$ and $Mn(OH)_2$ were converted to $MnFe_2O_4$ through the dewatering process shown in Reaction 5 (Reddy and Mohamed, 2015). EG not only acts as a solvent but also plays an important role in controlling the size and morphology of the particles in solvothermal systems. Meanwhile, PEG serves as a structure-directing agent, as it can easily self-assemble to form spherical grains, thereby coating the $MnFe_2O_4$ particle surface. Besides, PEG can act as a protective layer that prevents the agglomeration of the particles and minimizes the direct exposure of the ferrite surface to an unexpected environment (Reddy and Mohamed, 2015; Kurtan *et al.*, 2016).

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + HO^- \quad (2)$$

$$Fe^{3+} + 3HO^- \longrightarrow Fe(OH)_3 \quad (3)$$

$$Mn^{2+} + 2HO^- \longrightarrow Mn(OH)_2 \quad (4)$$

$$Mn(OH)_2 + 2Fe(OH)_3 \xrightarrow[200^oC,\ 12h]{EG,\ PEG} MnFe_2O_4 + 4H_2O \quad (5)$$

Uniform spheres

As shown in **Figures 3e** and **3f**, with the combination of $MnFe_2O_4$ and α-MnO_2, the nanorod structure of MnO_2 was retained. However, since $MnFe_2O_4$ has a high tendency to be agglomerated, the aggregation of $MnFe_2O_4$ can be attributed to the magnetic dipole interaction between these particles. A rougher $MnFe_2O_4$/α-MnO_2 surface than α-MnO_2 can also be observed due to the superposition of $MnFe_2O_4$ particles on the α-MnO_2 surface. Thus, in the hybrid materials, α-MnO_2

and $MnFe_2O_4$ alternate with each other, then forming pores, thereby significantly increasing the surface area and the active positions to activate the PMS.

To determine the elemental composition in the magnetic $MnFe_2O_4$/α-MnO_2 hybrid, the EDX spectrum was adopted (**Figures 4a** and **4b**). According to **Figure 4a**, the Fe, Mn, and O elements accounted for 30.16, 58.01, and 11.83%, respectively, in the weight percentage of the hybrid. The results elicited an atomic Mn:Fe ratio of 4.993, which was consistent with the theoretically calculated Mn:Fe ratio of 4.9 for the hybrid. Furthermore, EDX-mapping analysis of Mn, Fe, and O elements (**Figures 4b**) confirmed the good distribution of α-MnO_2 on the $MnFe_2O_4$ surface.

To determine the success in synthesis and the purity of as-prepared materials, the crystal structures of α-MnO_2, $MnFe_2O_4$, and $MnFe_2O_4$/α-MnO_2 materials were investigated through XRD, as shown in **Figure 5**. The synthesized α-MnO_2 displayed typical diffraction peaks at 2θ of 12.8°, 18.12°, 28.84°, 37.52°, 41.96°, 50°, 60.44° and 65.28°, which could be indicated to the 100, 200, 310, 211, 301, 411, 521 and 002 planes, respectively (JCPDS No. 44-141) (Ma *et al.*, 2011; Davoglio *et al.*, 2018). In addition, the prepared $MnFe_2O_4$ presented characteristic peaks at 29.66°, 34.92°, 43.04°, 56.86° and 62.76°, that sequentially attributed to the 220, 311, 400, 511 and 440 lattices of spinel-type $MnFe_2O_4$ nanostructures (JCPDS No. 73-1964) (Cai *et al.*, 2014; Reddy and Mohamed, 2015). Importantly, the $MnFe_2O_4$/α-MnO_2 clearly showed both diffraction peaks of constitutive $MnFe_2O_4$ and α-MnO_2 materials. Of note, in the XRD spectrum of $MnFe_2O_4$/α-MnO_2, all peak intensities were lower than that in separated constituents. Moreover, there was neither the disappearance of characteristic peaks nor the presence of new peaks in the XRD pattern of the hybrid, implying the integrity of $MnFe_2O_4$ and α-MnO_2 crystal structures with high purity. Consequently, these results confirmed the successful synthesis of magnetic $MnFe_2O_4$/α-MnO_2 hybrid by using the hydrothermal treatment.

Figure 6 showed the FT-IR spectra of α-MnO_2, $MnFe_2O_4$, and magnetic $MnFe_2O_4$/α-MnO_2 hybrid. The as-prepared α-MnO_2 presented characteristic peaks at 699.98 and 503.62 cm^{-1}, which could be attributed to Mn-O bending vibrations in MnO_6 octahedra of the α-MnO_2 nanorods (Wang *et al.*, 2007). For the $MnFe_2O_4$ material, the peaks at 3243.80, 1578.10, and 1351.79 cm^{-1} were ascribed to the O-H stretching vibrations (Kurtan *et al.*, 2016). Importantly, the peak at 539.01 cm^{-1} was specifically associated with the Mn-O stretching vibration of spinel-type $MnFe_2O_4$ nanostructures (Chen *et al.*, 2019). Notably, the FT-IR spectrum of $MnFe_2O_4$/α-MnO_2 simultaneously displayed characteristic peaks of α-MnO_2 and $MnFe_2O_4$ at 3243.80, 1578.10, and 1351.79, and 699.98 cm^{-1}. These results further demonstrated the successful synthesis of the hybrid and the maintenance of α-MnO_2 and $MnFe_2O_4$ crystal structures.

Figure 7 displays the XPS spectra of as-synthesized $MnFe_2O_4$/α-MnO_2 hybrid. To minimize the charging effects, the binding energy of the C 1s level at 284.6 eV was adopted as a reference to calibrate the spectrum. As seen from **Figure 7a**, the high-intensity peaks distributed at binding energy (BE) values of 529.9, 641.8-653.9, and 711.2-724.4 eV, corresponding to O 1s, Mn 2p, and Fe 2p levels, respectively. In addition, the high-resolution scans of the O 1s, Mn 2p, and Fe 2p peaks were presented in **Figures 7b–d**. As can be seen from Fe 2p spectrum (**Figure 7b**), the main peaks at 711.2 and 724.4 eV sequentially relate to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ levels, which implied the occurrence of the Fe^{III} compound (Pham *et al.*, 2019). With the regard to Mn 2p spectrum, two main peaks (Mn $2p_{3/2}$ and Mn $2p_{1/2}$) were observed in **Figure 7c**. The first peak including three integrated peaks, which were located at BE values of 641.8, 643.5, and 653.9 eV, indicating the existence of mixed-valent compounds of Mn^{II} (in $MnFe_2O_4$) and Mn^{IV} (in α-MnO_2), respectively (Chen *et al.*, 2019). The O 1s spectrum in **Figure 7d** exhibits three types of the O atom in the material at BE values of about 529.9, 531.4, and 532.8 eV, which were assigned to the presence

of lattice oxygen metal oxides (M-O or M-O-M) and dominates in the O 1s-line, hydrated metal oxides (M-OH or M-O-H), and oxygen of the adsorbed water (H-O-H), respectively (Zhu *et al.*, 2021). These results indicated that the $MnFe_2O_4$/α-MnO_2 hybrid was well-prepared.

To investigate the thermal stability and decomposition of the materials, the thermogravimetric analysis (TGA) was performed (**Figure 8**). As shown in **Figure 8a**, the thermogram curve of α-MnO_2 exhibits three different stages of weight loss. The first stage appeared when the temperature heated up from 100 to 600 ^oC with a weight loss of about 2.50%, which can be ascribed to the evaporation of adsorbed water on the surface of the material. The second stage happened in the temperature range between 600 and 700 ^oC with a weight loss of 4.50%, which can be associated with the structural transformation from α-MnO_2 to Mn_2O_3-bixbite. When the temperature increases to 870 ^oC, an additional weight loss of 0.88% was observed, which can be caused by the transformation from Mn_2O_3-bixbite to Mn_3O_4. The MnO_2 material has different crystalline structures of α-MnO_2, β-MnO_2, and γ- MnO_2, and the TGA thermal analysis scheme can be used to differentiate these types of existence. In this regard, the β-MnO_2 shows thermal stability with only one weight loss (transformation of MnO_2 to Mn_2O_3), the γ-MnO_2 exhibits two weight reductions (surface water loss and transformation of MnO_2 to Mn_2O_3, respectively), and the α-MnO_2 displays three stages in the weight loss process (loss of surface adsorbed water, transformations of MnO_2 to Mn_2O_3, and Mn_2O_3 to Mn_3O_4, respectively) (Pham *et al.*, 2019). With the regard to $MnFe_2O_4$, the thermogram curve presents two main stages of weight loss (**Figure 8b)**. The first stage took place at a temperature of 200 ^oC with a weight loss of around 8.00%, which can be attributed to the water loss. At over 200 ^oC, an additional 2.00% of weight loss was adopted. **Figure 8c** displays the weight decomposition processes of the $MnFe_2O_4$/α-MnO_2 hybrid. At first, when the temperature increased up to 220 ^oC, the weight loss of the material

was about 6.25%, which mainly due to the water evaporation. Subsequently, when the temperature in a range of 220-650 ^{o}C, a further 5.75% of weight loss was obtained, which can be related to the structural transformation from α-MnO_2 to Mn_2O_3-bixbite. At above 650 ^{o}C, an additional weight loss of about 1.01% can be associated with the evolution from Mn_2O_3-bixbite to Mn_3O_4.

Surface area and pore parameters of the catalysts have a tremendous effect on the adsorption and catalytic capability because high surface area evokes more adsorption and active sites on the catalyst to meet oxidant for the pollutant degradation. The N_2 adsorption/desorption isotherm and the pore size distribution of $MnFe_2O_4$/α-MnO_2 are presented in **Figures 9a** and **9b**, respectively. Relied on the IUPAC categorization, the $MnFe_2O_4$/α-MnO_2 hybrid displays a type IV isotherm with a type H3 hysteresis loop at a relative pressure (P/P_0) in the range of 0.4-0.98, which implies a mesoporous structure of the hybrid (**Figure 9a**) (Chen *et al.*, 2019). In addition, as shown in **Figure 9** and **Table 1**, $MnFe_2O_4$/α-MnO_2 exhibits a narrow pore diameter distribution in a range of 2-50 nm, which was in accordance with the changes of the surface area (Sotomayor *et al.*, 2018). Furthermore, as seen in **Table 1**, the specific surface area of the hybrid was 102.12 m^2/g, which was greater than that in $MnFe_2O_4$ (98.58 m^2/g) and other catalysts in previous studies of around 67.0 m^2/g (Chen *et al.*, 2019). Moreover, the pore volume of the hybrid was 0.199 cm^3/g, which was much higher than that of α-MnO_2 (0.036 cm^3/g) and $MnFe_2O_4$ (0.047 cm^3/g) (**Table 1**). The increase in surface area and pore volume could be attributed to the co-existence and interminglement of $MnFe_2O_4$ and α-MnO_2 with different morphologies in the hybrid $MnFe_2O_4$/α-MnO_2. The large specific surface area implies a high number of adsorption and reactive sites on the hybrid, thereby possibly resulting in an enhancement in catalytic capability.

As displayed in **Figure 10**, the magnetic properties of the $MnFe_2O_4$/α-MnO_2 hybrid were examined by the VSM method at room temperature. The results showed that the hybrid presented

a typical S-shaped magnetization curve when applying a magnetic field. In addition, the hybrid displays a low saturation magnetization value of 9.03 emu/g, which results in an easy separation and reusability of the hybrid from the wastewater by applying an external magnetic field and eventually a reduction in the consumption of catalyst as well as the secondary pollution.

3.2. Performance evaluation of the hybrid

3.2.1. Evaluation of catalytic activity and effect of different mass ratio of $MnFe_2O_4$/α-MnO_2

At first, different systems were investigated for determining the catalytic effect of the $MnFe_2O_4$/α-MnO_2 on the PMS activation for OG degradation, including PMS, $MnFe_2O_4$/PMS/OG, α-MnO_2/PMS/OG, $MnFe_2O_4$/α-MnO_2/PMS/OG ($MnFe_2O_4$/α-MnO_2 with different mass ratios of 1:5, 1:7, and 1:9), under the resembled experimental conditions. The conditions for conducting experiments are as follows: [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, initial pH = 3.0, temperature = 30 ^{o}C. As shown in **Figure 11a**, when only PMS was used, the reduction efficiency in OG concentration was approximately 18%. Besides, the addition of the $MnFe_2O_4$/PMS system was observed to induce only 38% in OG degradation. Meanwhile, almost 85% OG removal was adopted for the α-MnO_2/PMS system. These results indicated that the PMS activating capability of α-MnO_2 was much greater than that of $MnFe_2O_4$. On the other hand, the combined utilization of $MnFe_2O_4$/α-MnO_2 catalyst and PMS can elicit a $MnFe_2O_4$/α-MnO_2 mass ratio-dependent OG degradation pattern. In particular, $MnFe_2O_4$/α-MnO_2 (1:5)/PMS and $MnFe_2O_4$/α-MnO_2 (1:7)/PMS systems reduced OG concentration to the extents (sequentially 57% and 82%) less than that of the above-mentioned α-MnO_2/PMS system. The lower efficiencies in OG degradation using $MnFe_2O_4$/α-MnO_2 (1:5)/PMS and $MnFe_2O_4$/α-MnO_2 (1:7)/PMS systems implied that α-MnO_2 possesses a predominant role in PMS activation while $MnFe_2O_4$ mostly accounted for easy separation and reusability of the hybrid and that the $MnFe_2O_4$:α-MnO_2 mass

ratios of 1:5 and 1:7 were insufficient to effectively activate PMS. In contrast, 96.8% of OG was degraded after 30 min treatment with $MnFe_2O_4$/α-MnO_2 (1:9)/PMS system. These results indicated that the OG removal efficiency ascended with the arising of α-MnO_2 content in the composition of $MnFe_2O_4$/α-MnO_2 hybrid. Compared with α-MnO_2/PMS system, the enhancement in $MnFe_2O_4$/α-MnO_2 (1:9)/PMS-induced OG degradation could be ascribed to the increased surface area and active sites for PMS activation that presumably due to the deposition of $MnFe_2O_4$ nanoparticles on the α-MnO_2 nanosheet surface. Moreover, the hybrid might possess a synergistic effect between $MnFe_2O_4$ and α-MnO_2 in overall catalytic ability by reinforcing the relative rates of mass transfer to PMS active sites and the relative rates of chemical reaction at these sites (Chen *et al.*, 2019). Moreover, all results of OG degradation by PMS activation followed pseudo-first-order reaction kinetics with $R^2 \geq 0.990$ (**Figure 11b**). The OG rate constant of $MnFe_2O_4$/α-MnO_2(1:9)/PMS was 1.66, 2, 4, 6.9, and 16 times higher than those of α-MnO_2/PMS, $MnFe_2O_4$/α-MnO_2(1:7)/PMS, $MnFe_2O_4$/α-MnO_2(1:5)/PMS, $MnFe_2O_4$/PMS, and PMS, respectively. To achieve a reasonable decomposition effect and reusability of catalysts, the $MnFe_2O_4$/α-MnO_2 hybrid with a mass ratio of 1:9 was chosen as the optimal catalyst for further experiments. These results are different with those reported in the literature for $MnFe_2O_4$/MnO_2(1:7)/PMS in Rhodamine B removal (Chen *et al.*, 2019), $MnFe_2O_4$/δ-MnO_2(1:4)/PMS for sulfadiazine removal (Zhu *et al.*, 2021), and $MnFe_2O_4$/α-MnO_2(1:5)/PMS for norfloxacin removal (Xu *et al.*, 2021). The difference in $MnFe_2O_4$/α-MnO_2 ratio (i.e., 1:9 for this study) with others in the literature could be due to different material synthesis methods, targeted organic pollutants, and optimum solution pH values.

Time-dependent UV-Vis absorption spectra of OG during the reaction were investigated in the wavelength region of 280-600 nm (**Figure 12**). The result showed that prior to the activation

of PMS by $MnFe_2O_4$/α-MnO_2, the OG contained a weak shoulder near 333 nm and a strong and broad band in the visible region at λ_{max} = 480 nm. The 480 nm peak is attributed to the absorption of π-π^* bond of azo (–N = N–) moiety, while the 333 nm peak is assigned to the naphthalene ring in the structure of OG (Zhou *et al.*, 2018a). Obviously, the results exhibited that the absorbance at wavelengths of 333 and 480 nm steadily decreased over time. After 30 min, the characteristic absorption peaks at 333 and 480 nm were significantly reduced and almost disappeared, indicating that the azo bond and aromatic rings in the OG structure were entirely destroyed. These observations could be ascribed to the attack of generated sulfate radicals to azo bond in the OG after the exposure of $MnFe_2O_4$/α-MnO_2 hybrid to PMS, which is also consistent with those published by Wu *et al.* (2021).

3.2.2. Effect of catalyst dosage

The influence of catalyst dosage in the range of 50-125 mg/mL on the OG decomposition was examined. The kinetics of OG degradation at different catalytic doses followed the pseudo-first-order kinetics model with $R^2 \geq 0.991$ **(Figure 13b)**. As displayed in **Figure 13a** and **13b**, when the dosage of $MnFe_2O_4$/α-MnO_2 hybrid was changed from 50-100 mg/mL, the calculated reaction rate constant *k* values were gradually elevated from 0.024-0.113 min^{-1} and thereby increasing the OG degradation values from 50 to 96.8% after 30 min of treatment. The OG could be entirely degraded when the catalyst dosage was 100 mg/mL. Importantly, there were no notable differences in OG removal (only 2.2% enhancement) and *k* value (from 0.113 to 0.16) when the catalyst dosage elevated from 100 to 125 mg/mL. These results implied that an increase of catalyst dosage elicits more PMS active centers on the catalyst surface, thus leading to an improvement in the capacity of activating PMS to create free radicals such as $SO_4^{\bullet-}$ and $HO^{\bullet}$. However, if the

catalyst dosage increases to a threshold, the number of active centers was not significantly mounted. Therefore, the catalyst concentration of 100 mg/L was adopted for the next experiments.

3.2.3. Effect of temperature

Next, **Figure 14** demonstrates the effect of different reaction temperatures on removing OG, showing that the OG removal was proportionally dependent on the reaction temperature. In particular, the OG decomposition efficiency reached 41.2% at 20 ^{o}C in 30 min, whereas roughly 96.8% of initial OG was decomposed at 30 ^{o}C in the same period. By contrast, $MnFe_2O_4$/α-MnO_2 (1:9)/PMS treatment at 40 ^{o}C exhibited almost complete OG removal within a shorter period (18 min). Moreover, the OG degradation process at different reaction temperatures followed a pseudo-first-order kinetic model with the linear correlation coefficient $R^2 \geq 0.986$ (**Figures 14b**). In particular, when the reaction temperature was elevated from 20 to 40^{o}C, the reaction rate constant ascended remarkably from 0.04 min^{-1} to 0.232 min^{-1}. On the other hand, the relationship between the reaction rate constant and reaction temperature was illustrated through the variant of the Arrhenius equation:

$$k = C/C_0 = Ae^{-\frac{Ea}{RT}} \quad \text{(Eq. 3)}$$

Hence, $$\ln k = \ln(C/C_0) = -\frac{Ea}{R}\frac{1}{T} + \ln A \quad \text{(Eq. 4)}$$

Where k is the reaction rate constant and E_a is the activation energy of OG decomposition. T is the absolute temperature (K) and R is the universal gas constant (8.314 J/(mol.K)). A is the frequency or pre-exponential factor (constant).

As shown in **Figure 14b**, the decomposition rate constant at 40 ^{o}C was about 2.34- and 5.8-folded greater than those at 30 and 20 ^{o}C, respectively. These experimental results were consistent with the kinetics theory, which defines that when temperature increases 10 ^{o}C, the reaction rate

proportionally ascends 2-4 folds (Kralj and Chemistry, 2007). Furthermore, the activation energy (E_a) of 66.90 kJ mol^{-1} was calculated (**Figures 14c)**, which was different from the activation energy values of the previous reports using other experimental systems (e.g., 42.7 KJ mol^{-1} for $MnFe_2O_4$/δ-MnO_2/PMS system and 21.54 KJ mol^{-1} for α-MnO_2/$MnFe_2O_4$/PMS system (Xu *et al.*, 2021; Zhu *et al.*, 2021)). These observations implied that this heterogeneous catalyst system could be monitored by the chemical reaction rate and it would be a potential agent for the PMS activation for the treatment of organic pollutants in water.

3.2.4. Effect of solution pH

In the process of activating PMS by heterogeneous catalyst systems, the solution pH affects the surface functional groups and surface charge of catalysts. Thus, a study on the effect of initial pH on OG degradability was herein conducted in a pH range of 3.0-11.0, as described in **Figure 15**. Overall, the acidic and alkaline pH values had a strong influence on the OG decomposition efficiency while this influence at neutral pH was rather low (**Figures 15a and 15b**). In addition, the data at different pH fitted well with the pseudo-first-order kinetics with $R^2 \geq 0.97$, the *k* value increased steadily in the acidic pH range (pH 3-5), then dropped rapidly at neutral pH (pH 7.0), and eventually reached maxima in the alkaline pH range (pH 9-11) (**Figure 15b**). Evidently, the OG amounts were removed of 96.8 and 97.19% after 30 min of treatment at pH 3 and 5, respectively (**Figures 15a**). The strong degradation of OG in the acidic medium can be explained as follows. The pHzpc of the hybrid material was determined to be 5.25 **(Figure 15c)**. In an acidic environment, the surface of $MnFe_2O_4$/α-MnO_2 is positively charged while HSO_5^- (pK_{a2} = 9.4) is a predominant form of PMS species. Meanwhile, OG has a negative charge due to the existence of anion HL^{2-} (with pH >1) since OG has pKa_1=1 (sulfonic groups (–SO_3H)) and pKa_2=11.5 (hydroxyl group (–OH) (Hsini *et al.*, 2020; Zhou *et al.*, 2018b). Therefore, there is strong

adsorption of PMS and OG on the surface of the catalyst according to the electrostatic attraction mechanism of the opposite ions, leading to an increase in PMS activating ability on the catalytic surface to form active oxygen species for OG decomposition.

In neutral conditions (pH =7), the efficiency of OG decomposition declined to the lowest value of 40.09% after 30 min of reaction. This result was assigned to the reduced electrostatic interaction and adsorption of OG (in HL^{2-} form) and PMS (in HSO_5^- form) on the negatively charged surface of the catalyst, leading to a decrease in the PMS activating ability and the effectiveness of OG degradation. Thus, under acidic conditions, the $MnFe_2O_4$/α-MnO_2/PMS system favorably decomposes OG over neutral conditions (Wu *et al.*, 2021).

In addition, the OG decomposition occurs rapidly when the pH increases to reach an alkaline environment. After 8 min, OG decomposition efficiencies were 97.1 and 97.6% at pH 9 and 11, respectively. In the alkaline environment, PMS and OG correspondingly exist in forms of SO_5^{2-} and HL^{2-}, thus resulting in the reduced electrostatic interaction and absorption of PMS and OG on the negatively charged surface of the catalyst. Theoretically, the OG decomposition efficiency would be drastically reduced. However, in terms of the experiment results, it is observed that the OG decomposition takes place quickly under alkaline conditions, which can be explained as follows. The existence of SO_5^{2-} form leads to the formation of active oxygen species (e.g., $HO^{\bullet}$, $O_2^{\bullet-}$, and $^1O_2$) which hold redox potentials of 2.8, 2.4, and 2.2 V, respectively (Reaction 6-11). These active oxygen types have strong oxidizing properties, thereby rapidly decomposing OG into mineralized products, which was also mentioned in several previous studies (Wu *et al.*, 2021; Xu *et al.*, 2021). However, some studies showed that the α-MnO_2-based hybrid material was negatively affected by the alkaline environment in organics removal (Chen *et al.*, 2019; Huang *et al.*, 2020). Thus, the $MnFe_2O_4$/α-MnO_2/PMS system exhibits high degradability of OG in a wide

range of pH from 3.0 to 11.0, which unveils the potential of using $MnFe_2O_4$/α-MnO_2 as a catalyst to decompose organic pollutants in various industrial wastewaters from tanning, printing, dyeing, pulp/paper, and petrochemical manufacturing.

$$SO_4^{\bullet -} + HO^- \rightarrow HO^{\bullet} + SO_4^{2-} \quad (6)$$

$$HSO_5^- \rightarrow SO_5^{2-} + H^+ \quad (7)$$

$$HSO_5^- + SO_5^{2-} \rightarrow HSO_4^- + {}^1O_2 \quad (8)$$

$$SO_5^{2-} + H_2O \rightarrow H_2O_2 + SO_4^{2-} \quad (9)$$

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

$$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet -} \quad (11)$$

For the $MnFe_2O_4$/α-MnO_2/PMS system with solution pH = 3.0, it does not have to adjust the pH of the solution, and the efficiency of OG degradation was high at this pH (96.8%) after 30 min treatment (Huang *et al.*, 2019; Lyu *et al.*, 2019). Therefore, pH 3.0 was chosen for further studies.

3.2.5. Reusability of magnetic $MnFe_2O_4$/α-MnO_2 hybrid

To evaluate the stability and reusability of $MnFe_2O_4$/α-MnO_2 catalyst, after each OG experimental treatment, the catalyst was adopted by using magnetic separation, washed once with DI water and three times with ethanol, dried at 80 ^oC for 12 hours in a vacuum oven before being continuously reused for a new cycle (of total 4 cycles) under the optimal conditions (i.e., [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, initial pH = 3.0, temperature = 30 ^oC). As shown in **Figure 16**, after four continuous cycles, the $MnFe_2O_4$/α-MnO_2 (1:9)/PMS system presented an approximately 30% decrease in OG removal. This slight reduction in OG degradation could be attributed to either a partial loss of catalyst during recovery processes or residual

contaminants on active sites of the catalyst surface. Overall, the result demonstrated that the catalyst possesses relatively high recyclability and reusability, which contribute to the reduction in expenses for wastewater treatment and used catalyst amount.

3.3. Comparison with other works

Herein, the PMS activation capacity of different heterogeneous catalysts on the basis of the elements Mn and Fe for decomposition of organic pollutants was compared (Zhu *et al.*, 2021; Chen *et al.*, 2019; Huang *et al.*, 2020; Lyu *et al.*, 2019; Fu *et al.*, 2019; Deng *et al.*, 2016). As shown in **Table 2**, OG (50 mg/L) is completely decomposed by the $MnFe_2O_4$/α-MnO_2/PMS system in a short time of 30 min with a high OG degradation rate constant of 0.113 min^{-1} with a low catalyst dosage of 100 mg/L. Different active oxygen types such as $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and $^1O_2$ all contribute to the decomposition of OG. This comparison shows that the performance of the $MnFe_2O_4$/α-MnO_2 /PMS system is excellent and promising for practical applications in wastewater treatment.

3.4. Mechanism of $MnFe_2O_4$/α-MnO_2/PMS system for OG degradation

3.4.1. Identification of reactive oxygen species in the $MnFe_2O_4$/α-MnO_2 /PMS system

The PMS activation process by the $MnFe_2O_4$/α-MnO_2 system can directly form active oxygen types such as $SO_4^{\bullet-}$ and $HO^{\bullet}$. Other active oxygen species such as $O_2^{\bullet-}$ and $^1O_2$ are generated through intermediate reactions. To identify the active oxygen types formed in the $MnFe_2O_4$/α-MnO_2/PMS system, various organic solvents were used as the quenching agents of active oxygen types such as tert-butanol (TBA), ethanol (EtOH), FFA with a concentration of 100mM, and p-BQ with a concentration of 10mM. The basis of solvent selection is as follows. The reaction rate constant of tert-butanol (TBA) with $HO^{\bullet}$ is faster than $SO_4^{\bullet-}$ from 835 to 950 times ($k_{TBA\text{-}HO^{\bullet}}$ = 3.8-7.6×10^8 $M^{-1}.s^{-1}$; $k_{TBA\text{-}SO_4^{\bullet-}}$ = 4.0-9.1×10^5 $M^{-1}.s^{-1}$); therefore, tert-butanol (TBA) was chosen as the decomposing agent of hydroxyl radical ($HO^{\bullet}$). Both reaction rate

498 constants of EtOH with $HO^{\bullet}$ ($k_{EtOH\text{-}HO\bullet}$ = 1.2-2.8×10^9 $M^{-1}.s^{-1}$) and with $SO_4^{\bullet-}$ ($k_{EtOH\text{-}SO4\bullet-}$ = 1.6-
499 7.7×10^7 $M^{-1}.s^{-1}$) are high. Thus, ethanol was selected as the degrading agent of both $HO^{\bullet}$ and $SO_4^{\bullet-}$
500 free radicals. p-BQ was selected for the decomposition of $O_2^{\bullet-}$ radicals due to its high reaction rate
501 constant with $O_2^{\bullet-}$ ($k_{p\text{-}BQ\text{-}O2\bullet-}$= 0.9-1.0×$10^9$ $M^{-1}.s^{-1}$), leading to its capability in radical $O_2^{\bullet-}$
502 quenching. FFA was chosen as decomposing agent of $^1O_2$ and $HO^{\bullet}$ radicals due to its high reaction
503 rate with both $^1O_2$ and $HO^{\bullet}$ ($k_{FFA\text{-}1O2}$ = 1.2×10^8 $M^{-1}.s^{-1}$; $k_{FFA\text{-}HO\bullet}$ = 1.5×10^{10} $M^{-1}.s^{-1}$) (Huang *et al.*,
504 2019).

505 **Figure 17** shows that for a blank sample (no scavengers), 96.8% OG was decomposed by
506 the $MnFe_2O_4$/α-MnO_2/PMS system after 30 min. When adding TBA, FFA, p-BQ, and EtOH with
507 a concentration of 100 mM (for TBA, FFA, and EtOH) and 10 mM (for p-BQ), the decomposition
508 efficiency decreased to 83.8, 36.68, 24.6, and 11.32%, respectively. These results unveiled that the
509 decomposition capability of active oxygen species generated from the $MnFe_2O_4$/α-MnO_2/PMS
510 system is in the order of $SO_4^{\bullet-}$ > $O_2^{\bullet-}$ > $^1O_2$ > $HO^{\bullet}$. Hence, EtOH, p-BQ, and FFA greatly inhibited
511 the OG degradation, indicating that $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and $^1O_2$ in $MnFe_2O_4$/α-MnO_2/PMS have a decisive
512 role in OG removal. This is different from the literature about the $MnFe_2O_4$/MnO_2/PMS and
513 $MnFe_2O_4$/δ-MnO_2/PMS system, where $SO_4^{\bullet-}$ was identified as the key radical for degradation of
514 Rhodamine B (Chen *et al.*, 2019) and Sulfadiazine (Zhu *et al.*, 2021), and α-
515 MnO_2/Palygorskite/PMS and β-FeOOH/MnO_2/PMS systems, where $O_2^{\bullet-}$ and $^1O_2$ are the key
516 radicals for Rhodamine B (Huang *et al.*, 2020) and Orange II (Lyu *et al.*, 2019) degradation. These
517 different conclusions in the role of the key radicals for organics pollutants could be due to the
518 different solution pH, which leads to the formation of different radicals during the PMS activation.

519 **3.2.2. Mechanism of PMS activation by $MnFe_2O_4$ /α-MnO_2 catalyst**

Based on the experimental results, the mechanism of PMS activation by $MnFe_2O_4$/α-MnO_2 catalyst is proposed as follows. First, HSO_5^- in solution is adsorbed on the surface of $MnFe_2O_4$/α-MnO_2. Then, manganese oxides (α-MnO_2) containing Mn active centers with different valences (i.e., Mn^{IV}, Mn^{III}, and Mn^{II}) interact with HSO_5^- to form $SO_5^{\bullet-}$ and $SO_4^{\bullet-}$ radicals (Reactions 12-15). In addition, Fe^{III} and Fe^{II} on the catalytic surface also participate in the formation of $SO_5^{\bullet-}$ and $SO_4^{\bullet-}$ radicals (Reactions 16-17). On the other hand, the reaction between Fe^{2+} and Mn^{4+} to form Fe^{3+} and Mn^{3+} is thermodynamically favorable since the standard potentials of Mn^{IV}/Mn^{III} and Fe^{III}/Fe^{II} are 0.95 and 0.77 V, respectively (Reaction 18) (Chen *et al.*, 2019). The sulfate radical ($SO_4^{\bullet-}$) is partially converted to hydroxyl radical ($HO^{\bullet}$) in the presence of water (Reaction 19). HSO_5^- is destabilized in H_2O, thereby converting to H_2O_2 (Reaction 20). Hydroxyl radical ($HO^{\bullet}$) is decomposed by H_2O_2 to form hydroperoxyl radical ($HO_2^{\bullet}$) (Reaction 10), and then the hydroperoxyl radical decomposes into superoxide radical ($O_2^{\bullet-}$) (Reaction 11). Superoxide radicals can react with both proton (H^+) and hydroxyl radical ($HO^{\bullet}$) to form singlet oxygen ($^1O_2$) (Reaction 21-22).

Among the active oxygen types, $SO_5^{\bullet-}$ and $HO_2^{\bullet}$ have weak oxidizing properties (1.1 V and 1.65V, respectively), while other species including $SO_4^{\bullet-}$ (2.8-3.1 V), $O_2^{\bullet-}$ (2.4 V), and $^1O_2$ (2.2 V) possess stronger oxidizing activities, which mainly account for the decomposition of OG in water. Thus, the mechanism of PMS activation by $MnFe_2O_4$/α-MnO_2 catalyst is proposed in **Figure 18**. This mechanism is determined by the Mn^{IV}/Mn^{III} and Fe^{III}/Fe^{II} redox pairs. Moreover, $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and $^1O_2$ radicals were determined to be the dominant reactive oxygen species in the $MnFe_2O_4$/α-MnO_2/PMS system that are responsible for the decomposition of OG.

$$\equiv Mn^{IV}\text{-}OH + HSO_5^- \rightarrow \equiv Mn^{III}\text{-}OH + SO_5^{\bullet-} + H^+ \quad (12)$$

$$\equiv Mn^{III}\text{-}OH + HSO_5^- \rightarrow \equiv Mn^{IV}\text{-}OH + SO_4^{\bullet-} + OH^- \quad (13)$$

$\equiv Mn^{II}\text{-}OH + HSO_5^- \rightarrow \equiv Mn^{III}\text{-}OH + SO_4^{\bullet-} + OH^-$ (14)

$\equiv Mn^{III}\text{-}OH + HSO_5^- \rightarrow \equiv Mn^{II}\text{-}OH + SO_5^{\bullet-} + H^+$ (15)

$\equiv Fe^{III}\text{-}OH + HSO_5^- \rightarrow \equiv Fe^{II}\text{-}OH + SO_5^{\bullet-} + H^+$ (16)

$\equiv Fe^{II}\text{-}OH + HSO_5^- \rightarrow \equiv Fe^{III}\text{-}OH + SO_4^{\bullet-} + OH^-$ (17)

$\equiv Fe^{II}\text{-}OH + \equiv Mn^{IV}\text{-}OH \rightarrow \equiv Fe^{III}\text{-}OH + \equiv Mn^{III}\text{-}OH$ (18)

$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} + H^+$ (19)

$HSO_5^- + H_2O \rightarrow H_2O_2 + HSO_4^-$ (20)

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

$HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+$ (11)

$2O_2^{\bullet-} + H^+ \rightarrow {}^1O_2 + H_2O_2 + 2HO^-$ (21)

$2O_2^{\bullet-} + HO^{\bullet} \rightarrow {}^1O_2 + H_2O_2$ (22)

$SO_4^{\bullet-}, O_2^{\bullet-}, {}^1O_2 + OG \rightarrow$ Intermediate product + $CO_2 + H_2O + SO_4^{2-}$ (23)

4. Conclusions

In this study, a well-crystallized magnetic $MnFe_2O_4/\alpha\text{-}MnO_2$ hybrid with high purity was successfully synthesized via a new hydrothermal method and characterized by XRD, SEM, EDX, XPS, FT-IR, SEM, and BET. The synthesized hybrid material showed catalytic activity in PMS activation for OG degradation to the extent greater than that of bare $MnFe_2O_4$ and $\alpha\text{-}MnO_2$. The parameters including initial pH, temperature, and catalyst dosage were revealed to be crucial for the OG removal. The results from quenching experiments indicated that $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and $^1O_2$ radicals were responsible for OG degradation. It was unveiled that the OG removal efficiency had less than 30% loss after four consecutive cycles, which implied the good stability of the $MnFe_2O_4/\alpha\text{-}MnO_2$ material. Overall, the heterogeneous $MnFe_2O_4/\alpha\text{-}MnO_2$ hybrid emerges as a promising PMS activator for the treatment of wastewater containing OG and maybe other dyes.

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Figure captions

Figure 1. The molecular structure of Orange G

Figure 2. Schematic illustration for the formation of $MnFe_2O_4$/α-MnO_2

Figure 3. SEM images of (a-b) α-MnO_2, (c-d) $MnFe_2O_4$, and (e-f) $MnFe_2O_4$/α-MnO_2

Figure 4. (a) EDX spectrum and (b) EDX mapping (O, Mn, Fe elements) of the $MnFe_2O_4$/α-MnO_2 hybrid

Figure 5. XRD patterns of α-MnO_2, $MnFe_2O_4$, and $MnFe_2O_4$/α-MnO_2

Figure 6. FT-IR spectra of α-MnO_2, $MnFe_2O_4$, and $MnFe_2O_4$/α-MnO_2

Figure 7. (a) Wide survey XPS spectrum, (b) Fe 2p spectrum, (c) Mn 2p spectrum, and (d) O 1s spectrum of the $MnFe_2O_4$/α-MnO_2 hybrid (Binding energy (BE) values were corrected using the carbon peak at 284.6 eV as a reference)

Figure 8. TGA measurements of (a) α-MnO_2, (b) $MnFe_2O_4$, and (c) $MnFe_2O_4$/α-MnO_2

Figure 9. (a) N_2 adsorption-desorption isotherms of $MnFe_2O_4$/α-MnO_2 and (b) pore size distribution of $MnFe_2O_4$/α-MnO_2

Figure 10. The magnetization curve of magnetic $MnFe_2O_4$/α-MnO_2

Figure 11. (a) Effects of different experimental systems on the decomposition of OG, (b) pseudo-first-order kinetic linear regressions. (Experimental conditions: [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, initial pH = 3.0, and temperature = 30 ^oC)

Figure 12. Time-dependent UV-Vis spectral absorption of OG solution

Figure 13. Effect of different catalyst dosages on the decomposition of OG, (b) pseudo-first-order kinetic linear regressions of different catalyst dosages on OG decomposition. (Experimental conditions: [OG] = 50 mg/L, [PMS] = 1000 mg/L, initial pH = 3.0, and temperature = 30 ^oC)

Figure 14. Effect of different temperature conditions on the decomposition of OG, (b) pseudo-first-order kinetic linear regressions of different temperature conditions on OG decomposition, (c) Arrhenius plot of OG decomposition at different temperature conditions, which determines the activation energy (E_a) of the system. (Experimental conditions: [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, initial pH = 3.0)

Figure 15. Effect of different pH conditions on the decomposition of OG, (b) pseudo-first-order kinetic linear regressions of different pH conditions on OG decomposition, (c) pHpzc plot of $MnFe_2O_4$/α-MnO_2. (Experimental conditions: [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, initial pH = 3.0, and temperature = 30 ^oC)

Figure 16. The reuse efficiency of $MnFe_2O_4$/α-MnO_2 catalyst on the decomposition of OG (Experimental conditions: [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, initial pH = 3.0, and temperature = 30 ^oC)

Figure 17. Influence of different radical scavengers on OG degradation in $MnFe_2O_4$/α-MnO_2/PMS system (Experimental conditions: [OG] = 50 mg/L, [PMS] = 1000 mg/L, [catalyst] = 100 mg/L, [scavenger] = 100 mM, [p-BQ] = 10 mM, pH = 3.0, and temperature = 30 ^oC)

Figure 18. Mechanism of PMS activation by the $MnFe_2O_4$/α-MnO_2 catalyst for radical generation and OG degradation

Table captions

Table 1. Specific surface area, pore size, and pore volume of α-MnO_2, $MnFe_2O_4$, and $MnFe_2O_4$/α-MnO_2

Table 2. Comparison of the decomposition of organic pollutants by PMS activation with heterogeneous catalysts on the basis of Mn and Fe