Article

Synthesis of Petal-Like MnO$_2$ Nanosheets on Hollow Fe$_3$O$_4$ Nanospheres for Heterogeneous Photocatalysis of Biotreated Papermaking Effluent

Yangliu Du $^{1,2}$, Fuqiang Li $^{1,2}$, Yecan Peng $^{1,2}$, Shaowu Jia $^{1,2}$, Lei Lan $^{1,2}$, Jinghong Zhou $^{1,2,*}$ and Shuangfei Wang $^{1,2}$

$^1$ School of Light Industry and Food Engineering, Guangxi University, Nanning 530004, China
$^2$ Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning 530004, China
* Correspondence: jhzhoudou@gxu.edu.cn; Tel.: +86-134-7100-2595

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Abstract: Owing to the implementation of increasingly stringent water conservation policies and regulations, the pulp and paper mill industry must make increased efforts to meet the limits for pollutant emissions. The primary pretreatment and secondary biochemical treatment methods used currently generally fail to meet the country-specific environmental regulations, and the wastewater must be processed further even after being subjected to secondary biochemical treatments. In this work, we synthesized Fe$_3$O$_4$/MnO$_2$ nanocomposites (FMNs) with a flower-like structure for use in the heterogeneous photocatalytic treatment of biotreated papermaking wastewater. FMNs1.25, which were formed using a KMnO$_4$/Fe$_3$O$_4$ molar ratio of 1.25, could be separated readily using an external magnetic field and exhibited higher photocatalytic activity than those of the other samples as well as MnO$_2$ and Fe$_3$O$_4$. The effects of various experimental parameters on the photocatalytic activity of FMNs1.25, including the initial pH of the wastewater and the catalyst dosage, were determined. The common chemical oxygen demand (COD$_{Cr}$) reduction rate in the case of this sample reached 56.58% within 120 min at a pH of 3, the COD$_{Cr}$ of effluent after treatment was 52.10 mg/L. Further, even under neutral conditions, the COD$_{Cr}$ of the treated effluent was below the current limit for discharge in China. Moreover, the nanocomposites exhibited good recyclability, and their catalytic activity did not decrease significantly even after five usage cycles. This study should serve as a platform for the fabrication of effective photocatalysts for the advanced treatment of biotreated papermaking effluent and refractory organic wastewater.

Keywords: Fe$_3$O$_4$/MnO$_2$ nanocomposites; magnetic catalyst; photocatalysis; advanced treatment; bio-treated effluent of papermaking

1. Introduction

The effective treatment of wastewater plays an important role in maintaining the ecological balance of the natural environment [1–7]. Pulp and paper mills consume a lot of water and, at the same time, emit a considerable amount of wastewater [8,9]. Primary pretreatments and secondary biochemical treatments are the main steps in wastewater treatment [10,11]. Owing to the problems related to the scale, papermaking materials and bleaching methods used, wastewater recycling rate, wastewater treatment technology employed, and equipment renewal, some pollutants inevitably remain in the final discharged wastewater. In China, because of the increasingly strict environmental protection guidelines and the implementation of stricter regulations, it has become essential to subject wastewater to additional treatments. However, these advanced treatments for wastewater pose an urgent problem in case of the pulp and paper industry [12]. It is very important to remove the organic pollutants
present in pulp and papermaking wastewater, as these compounds are refractory, toxic, mutative, and carcinogenic and can have long-term harmful effects on the ecological environment [13]. Photocatalytic oxidation techniques have many advantages. For instance, they involve mild and controllable reaction conditions, allow for the oxidative degradation of organic matter, and do not result in the secondary pollution of the environment. As a result, they are being studied widely [14–16].

MnO$_2$, a typical transition metal oxide, is used extensively in batteries [17–19], supercapacitors [20–22], and photocatalysts [23–27] because of its special physical and chemical properties. Moreover, C$_3$N$_4$/MnO$_2$ nanocomposites have been synthesized and used for the photocatalytic degradation of phenol and dye during water treatment [28]. Further, films of CuO/MnO$_2$ nanorod arrays have been synthesized and used for the efficient catalytic oxidation of acid fuchsin dye [29]. Similarly, mesoporous MnO$_2$ has been fabricated and utilized in the catalytic ozonation of 4-nitrophenol [30] while hierarchically structured MnO$_2$@SiO$_2$ nanofibrous membranes have been employed for the degradation of methylene blue [31]. These studies have shown that MnO$_2$ has wide applicability as an efficient catalytic material. Nevertheless, MnO$_2$ alone or nonmagnetic MnO$_2$-containing heterogeneous catalysts cannot be separated and recycled readily after the treatment reaction. This increases the cost associated with their industrial use and also causes additional pollution [32]. Therefore, the development of novel catalysts with high separability and recyclability is essential. The magnetic separation technique provides a practical solution to this problem [33]. Loading MnO$_2$ nanosheets onto the surfaces of Fe$_3$O$_4$ nanoparticles is an easy way of producing nanocomposite catalysts that can be removed and recycled readily using an external magnetic field. The durability of these catalysts is also high [34,35]. Zhang et al. [27] prepared a magnetic recyclable thin-layer MnO$_2$ coated Fe$_3$O$_4$ nanocomposite by hydrothermal method combined with a mild ultrasonic means and used it in the photocatalytic decolorization of model pollutant MB (methylene blue) under ultraviolet irradiation. The results showed that the maximum photodegradation rate was 98.2% after UV-vis light irradiation for 3h. However, few studies have been done on the treatment of industrial wastewater by MnO$_2$/Fe$_3$O$_4$ nanocomposite, especially in the advanced treatment of the biotreated effluent of papermaking wastewater, which has a complex composition, containing lignin, hemicellulose, residual alkali, sugars, inorganic salts, volatile acids, organic chlorides, etc.

In this study, hollow Fe$_3$O$_4$ nanospheres (HFNs) and flower-like Fe$_3$O$_4$/MnO$_2$ nanocomposites (FMNs) based on these HFNs were synthesized through a simple process. First, the HFNs were fabricated through a hydrothermal method using different initial (NH$_4$)$_2$CO/C$_6$H$_5$Na$_2$O$_7·2$H$_2$O molar ratios. Next, the FMNs were fabricated via the coprecipitation method using different K$\text{MnO}_4$/Fe$_3$O$_4$ molar ratios. The fabricated HFNs had a raspberry-like surface, which allowed for a high catalyst surface area as well as the ready growth of the MnO$_2$ nanosheets. The synthesized FMNs were subsequently used for the treatment of the biotreated effluent of papermaking wastewater. The effects of the molar ratios of the reactants on the morphologies of the HFNs and FMNs were evaluated. In addition, the effects of several other factors on the efficiency of the heterogeneous photocatalytic reaction were also studied in detail. Finally, the decrease in the common chemical oxygen demand (COD$_w$) after the heterogeneous photocatalysis process and the recyclabilities of the photocatalysts were also investigated.

2. Materials and Methods

2.1. Materials Used

Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), potassium permanganate (KMnO$_4$), and urea ((NH$_4$)$_2$CO) were purchased from Guangdong Guanghua Sci-Tech Co. Ltd (Guangzhou, China). Sodium citrate (C$_6$H$_5$Na$_2$O$_7·2$H$_2$O), sulfuric acid (H$_2$SO$_4$, 95%–98%), fuming hydrochloric acid (HCl, 37%), and ethanol (CH$_3$CH$_2$OH, ≥99.7%) were purchased from Tianjin Zhiyuan Chemical Co. Ltd. (Tianjin, China). Polyacrylic acid (30% solid, average $M_w$: 3000) was purchased from Shanghai Macklin Biochemical Co. Ltd (Shanghai, China). All the reagents were analytical grade. Deionized water with
a resistivity of 18.0 MΩ·cm⁻¹ was obtained from a Milli-Q apparatus (Millipore, Bedford, MA, USA) and was used throughout the study. The wastewater used was the biotreated effluent from a factory of the Guangye Guitang Sugar Group Co., Ltd (Guigang, China). The pH of the wastewater was 6.58 and its CODCr was 120 mg·L⁻¹.

2.2. Synthesis of Hollow Fe₃O₄ Nanospheres (HFNs)

The HFNs were synthesized by the conventional hydrothermal method [27], different reactant molar ratios were used in the synthesis experiment. First, 4 mmol of FeCl₃·6H₂O, different amounts (16, 18, and 20 mmol) of (NH₄)₂CO, and different amounts (8 and 12 mmol) of C₆H₅Na₃O₇·2H₂O were dissolved in 60 mL of deionized water and stirred continuously for 30 min at room temperature. Then, 0.75 mL of polyacrylic acid was added to the resulting dispersion. After being constantly stirred for 30 min, the mixture was transferred to a 100 mL Teflon-lined autoclave and kept at 200 °C for 12 h. Next, the autoclave was cooled to room temperature, the products were washed with deionized water and ethanol three times, and finally dried at 60 °C in a vacuum oven. The HFN samples obtained were labeled as HFNs1, HFNs2, HFNs3, HFNs4, HFNs5, and HFNs6. The experimental parameters used to fabricate these samples are listed in Table 1.

Table 1. Experimental parameters used for synthesis of hollow Fe₃O₄ nanospheres (HFNs).

| Sample  | FeCl₃·6H₂O (mmol) | (NH₄)₂CO (mmol) | C₆H₅Na₃O₇·2H₂O (mmol) | PAA (mL) | H₂O (mL) |
|---------|------------------|-----------------|------------------------|----------|----------|
| HFNs1   | 4                | 16              | 8                      | 0.75     | 60       |
| HFNs2   | 4                | 18              | 8                      | 0.75     | 60       |
| HFNs3   | 4                | 20              | 8                      | 0.75     | 60       |
| HFNs4   | 4                | 16              | 12                     | 0.75     | 60       |
| HFNs5   | 4                | 18              | 12                     | 0.75     | 60       |
| HFNs6   | 4                | 20              | 12                     | 0.75     | 60       |

2.3. Synthesis of Fe₃O₄/MnO₂ Nanocomposites (FMNs)

The FMNs were synthesized through a modified coprecipitation process. First, KMnO₄ (0.75, 1.5, 1.875, 2.25, or 3 mmol) was dissolved in 75 mL of deionized water. Then, 1 mL of fuming hydrochloric acid was added to the solution in a dropwise manner. After the mixture had been stirred for 30 min, 1.5 mmol of the as-prepared HFNs was dispersed evenly in the solution. Next, the mixture was stirred for 30 min at room temperature and heated to 90 °C and kept at that temperature for 90 °C for 3 h. The obtained brownish-black product was sequentially washed with deionized water and ethanol. Finally, the product was dried at 60 °C for 24 h in a vacuum oven. The synthesized FMN samples were labeled as FMNs0.5, FMNs1, FMNs1.25, FMNs1.5, and FMNs2, and the experimental parameters used to produce them are listed in Table 2.

Table 2. Experimental parameters used for synthesis of Fe₃O₄/MnO₂ nanocomposites (FMNs).

| Sample  | KMnO₄ (mmol) | Fe₃O₄ (mmol) | HCl (mL) | H₂O (mL) |
|---------|--------------|--------------|----------|----------|
| FMNs0.5 | 0.75         | 1.5          | 1        | 75       |
| FMNs1   | 1.5          | 1.5          | 1        | 75       |
| FMNs1.25| 1.875        | 1.5          | 1        | 75       |
| FMNs1.5 | 2.25         | 1.5          | 1        | 75       |
| FMNs2   | 3            | 1.5          | 1        | 75       |

2.4. Characterization

The X-ray diffraction (XRD) patterns of the FMNs were acquired using a Rigaku MiniFlex600 X-ray diffractometer (Rigaku, Tokyo, Japan) with a Cu-Kα radiation source. The measurements were performed at 40 kV × 15 mA and 2θ values of 5–80°. X-ray photoelectron spectroscopy (XPS)
was used to determine the surface chemical compositions of the samples. The XPS analyses were performed using a Thermo ESCALAB 250XI spectrometer (Thermo Scientific, Waltham, MA, USA) with an Al-Kα radiation source. The C1s peak at 284.6 eV was used as the internal reference peak for calibration. Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor II, Bruker, Karlsruhe, Germany) was also performed on the samples; KBr was used to form the tablets for the measurements. The surface morphologies of the samples were characterized using a ZEISS SIGMA HD field-emission scanning electron microscopy (FESEM) system (Zeiss, Oberkochen, Germany) and a FEI Tecnai G2 F20 transmission electron microscopy (TEM) system (FEI, Hillsboro, OR, USA). An LDJ 9600 vibrating sample magnetometer (LDJ Electronics, Dayton, OH, USA) was used to determine the magnetic properties of the as-prepared samples. The Brunauer–Emmett–Teller (BET) surface areas (m² g⁻¹) of the samples were measured at 77 K using a Micromeritics TriStar II 3flex automatic specific surface and porosity analyzer (Micromeritics Instruments Corporation, Norcross, GA, USA). The zeta potential of the suspension was recorded on a Malvern Panalytical NANO ZS90 (Malvern Ltd, Malvern, UK). The 3D-excitation-emission-matrix (3D-EEM) spectra of the treated wastewater samples were obtained using a Horiba FluoroMax-4 fluorescence spectrophotometer (Horiba, Kyoto, Japan). The excitation wavelengths were 220–440 nm, while the emission wavelengths were 300–600 nm. The CODCr values of the treated wastewater samples were measured using a COD/ammonia nitrogen double-parameter rapid tester (5B-3C(V8), Beijing Lianhua Technology Co. Ltd, Beijing, China).

2.5. Heterogeneous Photocatalytic Tests

The heterogeneous photocatalytic treatment of the secondary biotreated effluent of pulp and paper mill wastewater was performed in a GHX-V photochemical reactor (Shanghai Jiapeng Technology Co., Ltd., Shanghai, China); a schematic of the device is shown in Figure 1. The light source used was a 200 W high-pressure mercury lamp (wavelengths of 350–450 nm), and the reaction temperature was adjusted to 25 ± 2 °C. During each run, 250 mL of the wastewater was added to the reactor, and the initial pH of the reaction was adjusted using a 0.1 M NaOH or H₂SO₄ solution. Next, a certain amount of the FMNs sample in question was added to the solution. The suspension was stirred continuously and exposed to light. The CODCr value was determined by taking water samples at regular intervals. All the experiments were performed for same duration (180 min) in order to elucidate the effects of the photocatalytic treatment. Each group of samples was tested thrice, and the average CODCr was calculated. The CODCr removal rate of wastewater (α) can be calculated from the initial CODCr (C₀) and the CODCr during sampling (Cₜ) as follows:

\[ \alpha = \frac{(C₀ - Cₜ)}{C₀} \times 100\% \] (1)

Figure 1. Schematic of reactor used for heterogeneous photocatalytic reaction.
3. Results and Discussion

3.1. Characterization of Hollow Fe₃O₄ Nanospheres and Fe₃O₄/MnO₂ Nanocomposites

Figure 2a shows the XRD patterns of FMNs0.5, HFNs1, HFNs1.25, HFNs1.5, and HFNs2. The diffraction peaks at 2θ of 30.08°, 35.43°, 37.02°, 43.08°, 53.42°, 56.95°, and 62.68° correspond to the (220), (311), (222), (400), (422), (511), and (440) reflection planes, respectively, and are consistent with the standard pattern of magnetite Fe₃O₄ (JCPDS Card No. 19-0629). Further, the diffraction peak appearing at 2θ of 65.98° is in keeping with the standard spectrum of γ-MnO₂ (JCPDS Card No. 12-0714) and corresponds to MnO₂ [36–38].

![Figure 2. (a) XRD patterns and (b) FT-IR spectra of synthesized FMNs.](image)

The FTIR spectra of the as-synthesized nanocomposites are shown in Figure 2b. In the cases of FMNs0.5 and FMNs1, the absorption peak at 574 cm⁻¹ can be assigned to the Fe-O stretching vibrations that occur in iron oxide. Further, the characteristic peak at 3420 cm⁻¹ is related to the stretching vibrations of the O-H bond and may be ascribable to the hydroxyl groups present on the sample surfaces. The peak at 1635 cm⁻¹ corresponds to COO-stretching in citrates or peroxyacetic acid, while the peak at 1395 cm⁻¹ can be attributed to the stretching of the C-O bond in citrates [39]. The peak at 458 cm⁻¹ can be ascribed to the stretching of the Mn-O bond in MnO₂ [40]. In addition, a peak related to the Fe-O stretching vibrations was also observed in the cases of FMNs1.25, FMNs1.5, and FMNs2 but at a lower wavenumber (541 cm⁻¹), owing to an increase in the Mn-O bond strength [41].

The chemical compositions and oxide states of the FMN samples were studied by XPS. The integral survey spectrum of FMNs1.25 is displayed in Figure 3a, which shows the binding energies of the Fe(2p), Mn(2p), O(1s), and C(1s) peaks of the nanocomposite. Figure 3b shows that two high-intensity bands with binding energies of 711.1 and 724.9 eV were present; these were the Fe₂p₁/₂ and Fe₂p₃/₂ peaks, respectively, and corresponded to the Fe²⁺ (FeO) and Fe³⁺ (Fe₂O₃) states, respectively, of Fe and were characteristic of the Fe₃O₄ structure [38–40]. Further, as can be seen from Figure 3c, the binding energies of the Mn₂p₃/₂ and Mn₂p₁/₂ peaks were 642.5 and 654.1 eV, respectively, indicating the presence of Mn⁴⁺ in the sample. These results were in keeping with previous reports [40,42]. Hence, these characterization data confirmed that the FMNs had been synthesized successfully.
The dosages of (NH\textsubscript{2})\textsubscript{2}CO and C\textsubscript{6}H\textsubscript{5}Na\textsubscript{3}O\textsubscript{7}·2H\textsubscript{2}O determined both the morphology and the size of the HFNs. Figure 4 shows FESEM images of the HFNs synthesized using the different initial (NH\textsubscript{2})\textsubscript{2}CO/C\textsubscript{6}H\textsubscript{5}Na\textsubscript{3}O\textsubscript{7}·2H\textsubscript{2}O molar ratios. Figure 4a–c show the images of the HFNs produced using 8 mmol of C\textsubscript{6}H\textsubscript{5}Na\textsubscript{3}O\textsubscript{7}·2H\textsubscript{2}O. It can be seen from Figure 4a that the nanoparticles of sample HFNs\textsubscript{1} had diameters of 20–30 nm. With an increase in the amount of (NH\textsubscript{2})\textsubscript{2}CO added, as shown in Figure 4b,c, nanoparticles with rough surfaces and a diameter of approximately 200 nm were formed, as in the cases of HFNs\textsubscript{2} and HFNs\textsubscript{3}. Moreover, a few incompletely formed spherical structures were also observed, indicating that the formed nanospheres were hollow. Figure 4d–f show FESEM images of the HFNs formed using 12 mmol of C\textsubscript{6}H\textsubscript{5}Na\textsubscript{3}O\textsubscript{7}·2H\textsubscript{2}O. It can be seen clearly that the HFNs had diameters of 200–300 nm and were well dispersed and fully formed. In summary, it can be concluded that the amount of C\textsubscript{6}H\textsubscript{5}Na\textsubscript{3}O\textsubscript{7}·2H\textsubscript{2}O used had a determining effect on the morphology and size of the HFNs formed. According to the molding conditions of the hollow nanospheres, HFNs\textsubscript{6} sample was selected as the raw material for the subsequent experiments.

Next, the as-synthesized HFNs\textsubscript{6} sample and different amounts of KMnO\textsubscript{4} were used to prepare the various FMN samples by the coprecipitation method. The morphologies and microstructures of the fabricated FMNs can be seen from the FESEM and TEM images shown in Figures 5 and 6, respectively. Figure 5 shows that, with an increase in the amount of KMnO\textsubscript{4} added, the growth of the MnO\textsubscript{2} nanosheets on the surfaces of the HFNs also increased. When the KMnO\textsubscript{4}/Fe\textsubscript{3}O\textsubscript{4} molar ratio was increased to two, the MnO\textsubscript{2} nanosheets turned into petal-like structures and completely covered...
were completely coated with nanosheets. It can be seen from Figure 6b–e that the nanospheres had a black edge and a grayish-white central region. This confirmed that they were hollow.

![Figure 5. FESEM images of (a) FMNs0.5, (b) FMNs1, (c) FMNs1.25, (d) FMNs1.5, and (e) FMNs2.](image)

![Figure 6. Transmission electron microscopy (TEM) images of FMNs1.25 at (a) 10,000×, (b) 15,000×, (c) 25,000×, (d) 30,000×, (e) 40,000× and (f) 50,000× magnification.](image)

The TEM images (Figure 6) also showed that FMNs1.25 consisted of nanospheres whose surfaces were completely coated with nanosheets. It can be seen from Figure 6b–e that the nanospheres had a black edge and a grayish-white central region. This confirmed that they were hollow.

The BET surface areas and pore characteristics of HFNs6 and the various FMNs are presented in Figure 7a. The BET surface area of pure Fe3O4 (HFNs6) was 63.69 m2/g, much lower than the value of MnO2 nanosheet. Further, with an increase in the loading rate of MnO2, the BET surface area of the nanocomposites (from FMNs0.5 to FMNs1.25) increased from 201.76 m2/g to 214.36 m2/g, much higher than the values of pure Fe3O4 due to the amount of MnO2 nanosheet. FMNs1.25 had the largest BET surface area at 214.36 m2/g. However, when the KMnO4/Fe3O4 molar ratio was increased to two, the BET surface area of FMNs2, was low at 192.00 m2/g, suggesting that excess KMnO4 solution could not increase the BET. The trend in the Barrett–Joyner–Halenda (BJH) pore volume of the
nanocomposites was the same as that in the BET surface area, with FMNs1.25 exhibiting the highest BJH pore volume at 0.45 cm³/g.

**Figure 7.** (a) Brunauer–Emmett–Teller (BET) surface areas and pore characteristics of HFNs6 and synthesized FMNs and (b) N₂ adsorption-desorption isotherm and (c) pore size distribution of FMNs1.25.

The N₂ adsorption–desorption isotherm of FMNs1.25 and its pore size distribution are shown in Figure 7b,c. There is significant hysteresis between the adsorption and desorption arms of the isotherm for P/P₀ values between 0.4 and 1.0 (see Figure 7b); this was indicative of a typical mesoporous structure [43]. The pore size distribution of FMNs1.25 is given in Figure 7c. The distribution contains a sharp peak at 6 nm and a smaller peak at 22 nm. The average pore diameter was determined to be 8.32 nm. These data suggest that the fabricated catalysts had a high BET surface area and a mesoporous structure, which would result in the presence of a large number of active sites for the adsorbate. This, in turn, would promote the mass transfer of free radicals and hence dramatically improve the catalytic performance of the nanocomposites with respect to the organic pollutants present in wastewater [44,45].

The zeta potential and (b) diameter of FMNs1.25 were observed with the PH. As seen in Figure 8a, the Zeta potential of FMNs1.25 decreased with the rise of PH, the point of zero charge (PZC) of FMNs1.25 appeared between 3–5 of the initial PH of the reaction system, indicating the surface of FMNs1.25 was positively charged in solutions at PH below the PZC [46]. Therefore, the electrostatic attraction forces predominated at pH 3, leading to more organic pollutants adsorbing on the surface of catalysts and the COD Cr removal rate reached higher. The average diameter varied as a function of pH between 3 and 9, and the results are shown in Figure 8b. The highest diameter of FMNs1.25 was 1801.1 nm at the PH of 3, when the PH of the solution was 9, the diameter reached its lowest point at 649.5 nm. These results show that the dispersion of catalyst in solution was getting better with the increases of PH.

**Figure 8.** (a) Zeta potential and (b) diameter of FMNs1.25 as a function of PH.
3.2. Effects of Fe$_3$O$_4$/MnO$_2$ Nanocomposites on Treatment of Wastewater Through Heterogeneous Photocatalysis

A series of synthetic samples were applied to determine the COD$_{Cr}$ removal efficiency, and the results are shown in Figure 9a. The areas of the curves before an elapsed time of 20 min represent the adsorption phase. It was obviously found that HFNs6 (pure Fe$_3$O$_4$) has lower COD$_{Cr}$ removal efficiency compared with the Fe$_3$O$_4$/MnO$_2$ nanocomposites under the same tested conditions. Control experiments performed using FMNs1.25 in the absence of UV-vis light showed that, on its own, the absorption of FMNs1.25 was 25.03%, the COD$_{Cr}$ of effluent after treatment was 89.96 mg/L. There was no appreciable degradation of COD$_{Cr}$ without light irradiation. The observed decreases in the COD$_{Cr}$ in the case of the FMNs were principally attributable to the catalytic generation of radicals and the adsorption of organic pollutants by Fe$_3$O$_4$/MnO$_2$ was limited. In contrast, after UV-vis light irradiation for 120 min, the maximal COD$_{Cr}$ removal rates of FMNs0.5, FMNs1, FMNs1.25, FMNs1.5 and FMNs2 (reaction temperature of 25 °C, catalyst dosage: 1.75 g/L) were 43.58%, 45.57%, 56.58%, 50.66% and 47.83%, respectively. At the same time, the COD$_{Cr}$ of effluent after treatment was 67.70 mg/L, 65.32 mg/L, 52.10 mg/L, 59.21 mg/L and 62.60 mg/L, respectively. The best COD$_{Cr}$ removal rates (56.58%) were achieved by FMNs1.25, as indicated by the decreased COD$_{Cr}$ concentrations from 120 mg/L to 52.10 mg/L, less than the prescribed level for discharge standard of water pollutants for pulp and paper industry in China. Previous studies have shown that under UV–vis light irradiation, the maximal degradation efficiency of methylene blue treated with a thin-layer MnO$_2$ nanosheet-coated Fe$_3$O$_4$ nanocomposite could reach 98.2% [27] and the maximum adsorption capacities of As(III) and As(V) were 76.73 mg/g and 120.50 mg/g, respectively [47]. This means the Fe$_3$O$_4$/MnO$_2$ nanocomposites have great potential, not only in the treatment of refractory industrial wastewater, but also in the treatment of heavy metal wastewater.

![Figure 9](image-url)

**Figure 9.** Effects of (a) FMNs sample, (b) initial PH, and (c) catalyst dosage on decrease in chemical oxygen demand (COD$_{Cr}$) of wastewater.
During the photocatalytic reaction, MnO₂ plays a more important role than Fe₃O₄ [48]. The BET surface area and BJH pore volume of the FMNs increase with the growth of the MnO₂ nanosheets. This, in turn, results in more active sites being present on the surfaces of the catalyst particles. Thus, the greater the amount of MnO₂ in the nanocomposites, the higher their catalytic activity will be (as seen in the cases of FMNs0.5 to FMNs1.25). However, when the MnO₂ loading amount was increased further (i.e., for FMNs1.25 to FMNs2), the BET surface area and BJH pore volume decreased, causing a decrease in the catalytic efficiency. Moreover, when MnO₂ and Fe₃O₄ were used individually as catalysts for the heterogeneous photocatalytic reaction, the COD₇ of the effluent remained higher than the current discharge standard in both cases.

Next, the effects of the pH and catalyst dosage on the decrease in the COD₇ were investigated using FMNs1.25 as the photocatalyst. Figure 9b showed that the rate of decrease in the COD₇ reduced as the pH was increased from 3.0 to 9.0. The highest decrease in the COD₇ (57.63%) was achieved at a pH 3, the COD₇ of treated wastewater was 50.84 mg/L. Further, the COD₇ of effluent after treatment was 77.78 mg/L at a pH of 7 and 81.60 mg/L at a pH of 9. Hence, the efficiency of the catalytic reaction was significantly affected by the initial pH of the treated wastewater. As can be seen from Figure 8b, during the first 20 min, the adsorption capacity under acidic conditions (pH values of 3–5) was larger than that under alkaline conditions (pH values of 7–9). These results agreed with Zhang’s analysis [27], in that at acidic conditions, the surface of MnO₂ nanosheet-coated Fe₃O₄ nanocomposite is positively charged, and then •OH production is accelerated. •OH production is greatly advantageous for the photocatalytic degradation of MB. The reactions involved in the above-described process are as follow [49]:

\[
e^- + O_2 \rightarrow O_2^- \quad (2)
\]
\[
e^- + H^+ + O_2^- \rightarrow HO_2^- \quad (3)
\]
\[
HO_2^- + H^+ \rightarrow H_2O_2 \quad (4)
\]
\[
O_2^- + H_2O \rightarrow HO_2^- + OH \quad (5)
\]

The lower pH of reaction system, the higher concentration of H⁺ ions in the solution, causing the surfaces of the solid-phase catalyst particles to be positively charged. As a result, a greater number of the photogenerated electrons in the system migrate to the surfaces of the catalyst particles. This results in the combination of the electrons and the O₂ that is adsorbed on the catalyst surfaces, leading to the generation of H₂O₂, this is consistent with Equations (2)–(4). Eventually, more •OH is generated: Equation (5) represents the reaction process, resulting in an improvement in the efficiency of the catalytic reaction [49–51].

Thus, a pH of 3 was taken to be the optimal pH for the subsequent experiments to explore the effect of catalyst dosage on COD₇ removal. Figure 9c shows the effects of the catalyst dosage on the rate of decrease in the wastewater COD₇. When the catalyst dosage was increased from 1.25 g/L to 1.75 g/L, the decrease in the COD₇ removal rate of wastewater increased from 49.97% to 57.63%. Further, when the catalytic dosage was increased to 2 g/L, the COD₇ of the wastewater decreased by 54.67%. The particle size of the synthesized catalysts was small and the particles were well dispersed in the wastewater, resulting in an increase in the turbidity for the solution. Hence, some of the incident light was scattered and did not participate in the photocatalytic reaction. This adversely affected the catalytic efficiency [52,53].

From the above results, the as-synthesized catalyst shows high efficiency in the advanced treatment of wastewater from the pulp and paper mill. Moreover, it has been proved that a magnetically recyclable thin-layer MnO₂ nanosheet-coated Fe₃O₄ nanocomposite performs well in the simulated dye wastewater [27]. In result, the Fe₃O₄/MnO₂ nanocomposites in this study have great potential for the advanced treatment of biotreated papermaking effluent, dye wastewater and other refractory organic wastewater.
3.3. Kinetics of Heterogeneous Photocatalytic Reaction

The kinetics of the heterogeneous photocatalytic reaction were also studied. The software Origin 9.0 was used to fit the data corresponding to the relationship between the COD\textsubscript{Cr} decrease rate and the reaction time. The reaction for the measurements was performed under optimized conditions, which were as follows: A reaction temperature of 25 °C, contact time of 180 min, with the following catalyst used: FMNs1.25, with an initial pH of 3, and a catalyst dosage of 1.75 g/L. Figure 10a,b show the pseudo-first-order-kinetics and pseudo-second-order-kinetics models obtained after multiple fittings. The fitting equation for the pseudo-first-order-kinetics model is \( Y = 0.24539 + (8.06311 \times 10^{-4})X \), with the pseudo-first-order-kinetics rate constant being \( 8.06311 \times 10^{-4} \) and \( R^2 = 0.87718 \). In addition, the fitting equation for the pseudo-second-order-kinetics model is \( Y = 0.21099 + 0.00175X - (4.75151 \times 10^{-6})X^2 \), with the pseudo-second-order-kinetics rate constant being \( -4.75151 \times 10^{-6} \) and \( R^2 = 0.9506 \). In the figures, the y-axis represents \( \ln(C_0/C_t) \) while the x-axis represents the reaction time (min). These results indicated that the catalytic reaction was primarily driven by pseudo-second-order kinetics.

![Figure 10.](image)

3.4. Recyclability of \( \text{Fe}_3\text{O}_4/\text{MnO}_2 \) Nanocomposites

With respect to heterogeneous photocatalytic reactions, the recyclability and reusability of the catalyst used are important parameters for evaluating its industrial applicability. The magnetic properties of the nanocomposites fabricated in this study had a significant effect on their reusability. As shown in Figure 11a, after each reaction, the photocatalyst used was separated for solid-liquid separation within 30 s. The MS value of FMNs1.25 was 56.22 emu/g and 31.34 emu/g, respectively, when subjected to an external magnetic field. This allowed for solid-liquid separation within 30 s. However, in spite of having a lower MS value, FMNs1.25 could be readily separated from an aqueous solution at a low magnetic field gradient (Figure 11a).

![Figure 11a](image)

Reusability tests were performed, again under optimized conditions: Reaction temperature of 25 °C, the COD\textsubscript{Cr} of the wastewater of 120 mg/L, contact time of 180 min, catalyst used: FMNs1.25, initial pH of 3, and catalyst dosage of 1.75 g/L. After each reaction, the photocatalyst used was separated from the wastewater sample being treated using an external magnetic field, and the collected catalyst was washed three times with water and ethanol respectively and dried at 60 °C for 24 h before the next experiment. The COD\textsubscript{Cr} of the wastewater as measured after each test is shown in Figure 11b. It can be seen that, with an increase in the number of reaction cycles, the COD\textsubscript{Cr} of wastewater after reaction decreased gradually. After the 5th cycle, COD\textsubscript{Cr} reduced from the initial value of 120 mg/L to

![Figure 11b](image)
approximately 67 mg/L, which achieved 80% of the initial use effect. This confirmed that the catalyst exhibited good recyclability and reusability.

![Figure 11](image)

**Figure 11.** (a) Hysteresis loop of FMNs1.25 and (b) effect of number of reaction cycles on COD$_{Cr}$ (optimized reaction conditions: Initial COD$_{Cr}$ of 120 mg/L, FMNs1.25 concentration of 1.75 g/L, contact time of 180 min, solution pH of 3, and temperature of 25 °C).

### 3.5. Degradation of Organic Pollutants

3D-EEM spectroscopy is a useful technique of analyzing the chemical properties of the organic compounds present in the wastewater, which can be evaluated based on the position, shift, and intensity of the fluorescence peaks present in the obtained spectrum [34]. Figure 12a shows the 3D-EEM spectrum of an untreated wastewater sample while Figure 12b shows the 3D-EEM spectrum of the wastewater sample after the heterogeneous photocatalytic reaction. In this case too, the reaction was performed under optimized conditions: Reaction temperature of 25 °C, contact time of 180 min, with the following catalyst used: FMNs1.25, with an initial pH of 3, and a catalyst dosage of 1.75 g/L. As can be seen from Figure 12a, two distinct fluorescence peaks (A and B) were present in the spectrum of the untreated wastewater sample. Peak A was centered at E$_m$/E$_m$ = 322 nm/435 nm and was the humic-related fluorescent peak in the visible region [55]. Furthermore, peak B was centered at E$_m$/E$_m$ = 246 nm/425 nm and displayed the fulvic-related fluorescent peak in the visible region [56]. After the photocatalytic reaction under optimized conditions, the center of peak A changed to E$_m$/E$_m$ = 318 nm/425 nm, while that of peak B moved to E$_m$/E$_m$ = 246 nm/440 nm (see Figure 12b). Moreover, the changes in the peak intensities were used to determine the differences in the contents of the various fluorescent components of the wastewater sample before and after the photocatalytic reaction. The intensity of peak A in the untreated sample was $3.88 \times 10^5$ (a.u.) while that of peak B was $2.55 \times 10^5$ (a.u.). After the heterogeneous photocatalytic reaction, the intensity of peak A decreased to $1.78 \times 10^5$ (a.u.) while that of peak B decreased to $1.77 \times 10^5$ (a.u.), indicating that the removal rate of the humic-like substance was 54.12% while that of the fulvic-like substance was 30.60%. In conclusion, while the heterogeneous photocatalytic reaction could remove more of the humic-like material than the fulvic-like material present in the wastewater sample, both components were degraded to a high degree.
4. Conclusions

To summarize, a series of magnetic, flower-like nanocomposites consisting of petal-like MnO₂ nanosheets coated on hollow Fe₃O₄ nanospheres were synthesized by way of a simple hydrothermal method and a subsequent coprecipitation process. Sample FMNs₁.₂₅, which was fabricated using a KMnO₄/Fe₂O₃ molar ratio of 1.25, exhibited higher photocatalytic activity than those of the other FMN nanocomposites as well as those of MnO₂ and Fe₂O₃; this was the case even under neutral reaction conditions. The use of FMNs₁.₂₅ reduced the COD Cr in the effluent to less than the prescribed level for discharge standard of water pollutants for pulp and paper industry in China, indicating that it is highly suitable for the photocatalytic treatment of wastewater. Further, because of their magnetic properties, the fabricated nanocomposite catalysts also showed good recyclability and reusability when used repeatedly in the treatment reaction. Thus, the Fe₃O₄/MnO₂ nanocomposites fabricated have great potential for use as stable, efficient, environmentally friendly, and low-cost catalysts for the advanced treatment of refractory organic wastewater.

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