Article

Fenton Degradation of Ofloxacin Using a Montmorillonite-Fe$_3$O$_4$ Composite

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Abstract: In this work, FeM composites consisting of montmorillonite and variable amounts of Fe$_3$O$_4$ were successfully synthesized via a facile co-precipitation process. They were characterized using X-ray photoelectron spectroscopy (XPS), a field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX), a transmission electron microscope (TEM), N$_2$ adsorption–desorption, and Fourier transform infrared spectroscopy (FTIR) techniques to explain the effect of Fe$_3$O$_4$ content on the physicochemical properties of the Fe$_3$O$_4$–montmorillonite (FeM) composites. The FeM composites were subsequently used as heterogeneous Fenton catalysts to activate green oxidant (H$_2$O$_2$) for the subsequent degradation of ofloxacin (OFL) antibiotic. The efficiency of the FeM composites was studied by varying various parameters of Fe$_3$O$_4$ loading on montmorillonite, catalyst dosage, initial solution pH, initial OFL concentration, different oxidants, H$_2$O$_2$ dosage, reaction temperature, inorganic salts, and solar irradiation. Under the conditions of 0.75 g/L FeM-10, 5 mL/L H$_2$O$_2$, and natural pH, almost 81% of 50 mg/L of OFL was degraded within 120 min in the dark, while total organic carbon (TOC) reduction was about 56%. Although FeM composites could be a promising heterogeneous catalyst for the activation of H$_2$O$_2$ to degrade organic pollutants, including OFL antibiotic, the FeM-10 composite shows a significant drop in efficiency after five cycles, which indicates that more studies to improve this weakness should be conducted.

Keywords: Fenton degradation; ofloxacin; Fe$_3$O$_4$; montmorillonite; wastewater

1. Introduction

For the past few years, the high consumption of antibiotics has resulted in their continuous detection in surface, ground, drinking, and wastewater around the world [1]. Their presence is a threat to the ecological environment due to their chemical stability and slow biodegradation since antibiotics are harmful to microorganisms [2,3]. Among the antibiotics, ofloxacin (OFL) is an extensively used 2nd-generation fluoroquinolone due to its efficiency in degrading and even mineralizing persistent organic contaminants [4,5]. It is commonly used to treat bronchitis, infectious diarrhea, pneumonia, pelvic inflammatory disease, eye infections, ear infections, gonorrhea, respiratory tract infections, urinary tract infections, gastrointestinal infections, and skin infections [6–8]. However, approximately 90% is excreted via urination in its original form 48 h after administration [7]. The presence of OFL in water results in unpleasant odors and may also present a significant risk to aquatic species due to its toxicity [9,10]. Unfortunately, OFL is still being detected in wastewater even after conventional treatment [11]. Thus, the development of an effective method for the removal of OFL from wastewater becomes imperative.

The Fenton reaction is an effective process that has gained widespread acceptance due to its efficiency in degrading and even mineralizing persistent organic contaminants with the highly reactive hydroxyl radicals (•OH) generated from H$_2$O$_2$ using Fe$^{2+}$ from a Fenton reagent [12]. However, to overcome the shortcomings of the homogeneous Fenton process, various heterogeneous Fenton catalysts, including Fe$_3$O$_4$ nanoparticles [13], Fe-Mn
oxide [14], and Cu-Fe oxide [15], have been proposed. Among the catalysts, Fe$_3$O$_4$ nanoparticles have received significant attention due to their low toxicity and biocompatibility properties [16]. Moreover, another type of potential heterogeneous catalyst that has gained attention involved the immobilization of Fe$_3$O$_4$ on inorganic or organic solid supports [17]. Although such immobilization prevents agglomeration and enhances the dispersibility of Fe$_3$O$_4$, the choice of appropriate support is critical [18].

Montmorillonite is a silicate mineral with a nanolamellar structure [19]. It is among the most abundant clay minerals on earth, is cheap, has a large surface area, is nontoxic, and abundant with many other excellent properties [20–22]. All these imply that montmorillonite is a good candidate that could be used as a support for Fe$_3$O$_4$.

In the present study, a heterogeneous catalyst (Fe$_3$O$_4$–montmorillonite (FeM)) was synthesized via a facile co-precipitation process and used to activate green oxidant (H$_2$O$_2$) for the subsequent degradation of ofloxacin (OFL) antibiotic. The efficiency of the FeM composites was studied by varying various parameters of Fe$_3$O$_4$ loading on montmorillonite, catalyst dosage, initial solution pH, initial OFL concentration, different oxidants, H$_2$O$_2$ dosage, reaction temperature, inorganic salts, and solar irradiation. Reusability and stability studies were also conducted.

2. Results and Discussion

2.1. Characterization of Bare Montmorillonite and Fe$_3$O$_4$–Montmorillonite Composites

XPS spectra of bare montmorillonite and FeM composites are shown in Figure 1. In the case of bare montmorillonite, the spectrum indicates that Mg, O, C, Ca, Si, and Al existed on the surface of bare montmorillonite. In the case of FeM composites, in addition to Mg, O, C, Ca, Si, and Al of bare montmorillonite, the spectra confirm the existence of Fe. For instance, Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks appeared at binding energies of about 710 and 725 eV. The Fe $2p_{3/2}$ at a binding energy of about 710 eV confirmed the existence of octahedral Fe$^{3+}$ species [23]. Meanwhile, the Fe $2p_{1/2}$ peak at a binding energy of about 725 eV indicates the presence of octahedrally coordinated Fe$^{2+}$ species or Fe$_3$O$_4$ [24]. Such results have confirmed the presence of Fe$^{2+}$ and Fe$^{3+}$ in the Fe$_3$O$_4$/montmorillonite (FeM) composites. Furthermore, the peak at about 94 eV is attributed to the existence of Fe$_3$O$_4$ [25]. This indicates that the iron oxide in the FeM composites is Fe$_3$O$_4$.

![Figure 1. Cont.](image-url)
Figure 1. Cont.
Figure 1. Cont.
The surface morphology of bare montmorillonite and FeM composites was studied using a field emission scanning electron microscope (FESEM), and the results are shown in Figure 2. Based on the images, the surface of bare montmorillonite is smooth with irregular flake-like particles. In contrast, the FESEM images of FeM composites showed the presence of Fe$_3$O$_4$. Nevertheless, in the case of FeM-3, FeM-5, and FeM-8 composites, montmorillonite remained visible due to the low amount of Fe$_3$O$_4$ immobilized in the composite. However, the surface of montmorillonite in FeM-10 and FeM-15 composites is wholly covered due to the large amount of Fe$_3$O$_4$ immobilized in the composites [8]. This makes the surfaces of FeM-10 and FeM-15 composites coarser than that of bare montmorillonite. Such results have confirmed the successful immobilization of Fe$_3$O$_4$ onto a montmorillonite support, forming Fe$_3$O$_4$/montmorillonite composites.
Figure 2. Field emission scanning electron microscope (FESEM) images of montmorillonite (a), FeM-3 (b), FeM-5 (c), FeM-8 (d), FeM-10 (e), and FeM-15 (f).

Furthermore, from the energy-dispersive X-ray spectroscopy (EDX) data presented in Table 1, the percentage of iron on the surface of the FeM composites kept on increasing as we increased the amount of Fe salts. Such a change in the amount of iron on the surface of the FeM composites could lead to a substantial increase in catalytic activity due to modifications to the nature of the active sites available for reactions to take place [26]. Compared to bare montmorillonite, the absence of K\(^+\) and Mg\(^{2+}\) in the FeM composites is due to the exchange of these ions with Fe\(^{2+}\) and Fe\(^{3+}\) ions in the interlayer of montmorillonite [27].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al %</th>
<th>Si %</th>
<th>K %</th>
<th>Mg %</th>
<th>O %</th>
<th>Fe %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>9.21</td>
<td>33.06</td>
<td>4.10</td>
<td>1.11</td>
<td>52.52</td>
<td>-</td>
</tr>
<tr>
<td>FeM-3</td>
<td>1.61</td>
<td>17.76</td>
<td>-</td>
<td>-</td>
<td>37.36</td>
<td>43.19</td>
</tr>
<tr>
<td>FeM-5</td>
<td>1.31</td>
<td>10.17</td>
<td>-</td>
<td>-</td>
<td>36.92</td>
<td>51.60</td>
</tr>
<tr>
<td>FeM-8</td>
<td>0.83</td>
<td>6.58</td>
<td>-</td>
<td>-</td>
<td>33.93</td>
<td>58.66</td>
</tr>
<tr>
<td>FeM-10</td>
<td>0.47</td>
<td>5.24</td>
<td>-</td>
<td>-</td>
<td>33.73</td>
<td>60.54</td>
</tr>
<tr>
<td>FeM-15</td>
<td>0.18</td>
<td>2.71</td>
<td>-</td>
<td>-</td>
<td>32.96</td>
<td>64.15</td>
</tr>
</tbody>
</table>

The morphology of bare montmorillonite and FeM composites was further studied using TEM and the results are shown in Figure 3. Based on the images presented, bare montmorillonite (Figure 3a) has a porous-like surface. The immobilization of the Fe\(_3\)O\(_4\) particles onto the surface of montmorillonite produces rod-like particles (Figure 3b–f) which confirm the fact that the Fe\(_3\)O\(_4\) particles have been deposited and form agglomerates on the surface of montmorillonite. However, compared to FeM composites loaded with a low amount of Fe\(_3\)O\(_4\), the surfaces of FeM-10 and FeM-15 composites contain more agglomerations. Such an effect could be attributed to the larger amount of Fe\(_3\)O\(_4\) in the FeM-10 and FeM-15 composites.
Particle sizes of bare montmorillonite and the FeM composites calculated from TEM images by using ImageJ software are shown in Table 2 and the particle size distributions are given in the Supplementary Materials. Based on the values, the particle size follows the trend of FeM-15 > FeM-10 > FeM-8 > FeM-5 > FeM-3 > bare montmorillonite. This implies that bare montmorillonite has a smaller particle size than Fe$_3$O$_4$-loaded montmorillonite composites. Such an effect is attributed to the filling up of the bare montmorillonite pores by Fe$_3$O$_4$. Furthermore, the larger particle sizes in the case of FeM-15 and FeM-10 composites are due to agglomeration of Fe$_3$O$_4$.

Table 2. Surface area, pore volume, and particle size of bare montmorillonite and FeM composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Brunauer–Emmett–Teller BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>258.108</td>
<td>0.423</td>
<td>8.092</td>
</tr>
<tr>
<td>FeM-3</td>
<td>247.944</td>
<td>0.634</td>
<td>32.532</td>
</tr>
<tr>
<td>FeM-5</td>
<td>192.118</td>
<td>0.602</td>
<td>48.290</td>
</tr>
<tr>
<td>FeM-8</td>
<td>163.552</td>
<td>0.384</td>
<td>66.101</td>
</tr>
<tr>
<td>FeM-10</td>
<td>161.800</td>
<td>0.365</td>
<td>69.735</td>
</tr>
<tr>
<td>FeM-15</td>
<td>113.186</td>
<td>0.312</td>
<td>69.735</td>
</tr>
</tbody>
</table>

Figure 3. TEM images of montmorillonite (a), FeM-3 (b), FeM-5 (c), FeM-8 (d), FeM-10 (e), and FeM-15 (f).
Chemical bonds on the surface of bare montmorillonite and FeM composites were studied using FTIR, and the spectra are presented in Figure 4.

![FTIR spectra of bare montmorillonite and FeM composites.](image)

**Figure 4.** FTIR spectra of bare montmorillonite and FeM composites.

In the case of bare montmorillonite, bands at about 450 and 523 cm$^{-1}$ are attributed to Al-O-Si and Si-O-Si deformations [28]. The absorption band at about 798 cm$^{-1}$ corresponds to Si-O in SiO$_2$ [29]. The band at about 916 cm$^{-1}$ is attributed to Al-Al-OH bending vibration, while that at 1050 cm$^{-1}$ is due to the Si-O stretching [29,30]. Furthermore, the bands at about 1650, 3450, and 3630 cm$^{-1}$ correspond to OH group stretching vibration [31]. In the case of the FeM composites, the peaks within 1090–400 cm$^{-1}$ are less intense compared to those of bare montmorillonite. This indicates that Fe could link with Al-O and Si-O in montmorillonite [32].

The nitrogen adsorption–desorption isotherms and Barrett-Joyner-Halender (BJH) pore size distribution of bare montmorillonite and FeM composites are shown in Figure 5.

![N2 adsorption-desorption isotherms and BJH pore size distribution.](image)

**Figure 5.** Cont.
Figure 5. N₂ adsorption–desorption isotherms and the corresponding pore size distribution (insets) for montmorillonite (a), FeM-3 (b), FeM-5 (c), FeM-8 (d), FeM-10 (e), and FeM-15 (f) composites.

The isotherms are identified as type IV with an H₃ hysteresis loop in the range of 0.5–0.98, a characteristic of mesoporous materials [33]. Furthermore, Brunauer–Emmett–Teller (BET) surface areas and pore volumes of bare montmorillonite and FeM composites are presented in Table 2. Based on the values obtained, FeM composites have a lower BET surface area compared to bare montmorillonite. This could be attributed to the Fe₃O₄ in pores or on the surface of montmorillonite. In terms of the pore volume, FeM-3 and FeM-5 composites have higher volumes compared to bare montmorillonite. Such an increase in pore volume is due to the secondary pore structures formed during the Fe₃O₄ precipitation [34]. In contrast, FeM-8, FeM-10, and FeM-15 composites with larger amounts of Fe₃O₄ have lower pore volumes compared to the bare montmorillonite due to the agglomeration of Fe₃O₄ particles on the support. It is also believed that some of the Fe₃O₄ particles clogged the pores, thus reducing the pore volume.

2.2. Fenton Reaction
2.2.1. OFL Removal in Different Processes

As a control, the performance of (i) bare montmorillonite + OFL, (ii) H₂O₂ + OFL, (iii) Fe₃O₄-montmorillonite + OFL, (iv) montmorillonite + H₂O₂, (v) Fe₃O₄ + OFL, and (vi) Fe₃O₄ + H₂O₂ + OFL in the removal of OFL from aqueous solution was also studied, and the results are shown in Figure 6. Due to the low oxidation potential of H₂O₂, the percentage of removal in the presence of H₂O₂ was negligible [17]. In contrast, bare montmorillonite could remove more than 50% of OFL (50 mg/L) within 120 min. However, the percentage of removal was almost maintained even after the introduction of H₂O₂. This implies that bare montmorillonite did not activate H₂O₂. For bare Fe₃O₄, the percentage
of OFL removal via adsorption (Fe$_3$O$_4$ + OFL) and via Fenton degradation in the dark (Fe$_3$O$_4$ + H$_2$O$_2$ + OFL) was found to be 47% and 64%, respectively. In the case of FeM composite, the percentage of removal recorded in the presence of H$_2$O$_2$ was much higher than the removal in the absence of H$_2$O$_2$. Hence, this finding confirms the fact that FeM could activate H$_2$O$_2$.

![Figure 6. Ofloxacin (OFL) removal in different processes.](image)

2.2.2. Influence of Process Variables

The catalytic ability of FeM composite was further studied by investigating the degradation efficiencies under different conditions. Figure 7a shows the effect of Fe$_3$O$_4$ loading on montmorillonite on the degradation of OFL. Such a parameter was studied by varying the amount of Fe$_3$O$_4$ loading on montmorillonite from 3–15 mmol. It was observed that as the amount of Fe$_3$O$_4$ loading increases from 3–10 mmol, the percentage of removal also increases systematically. Such an effect is attributed to the increased production of hydroxyl radicals by a larger amount of iron ions. Beyond 10 mmol (in the case of FeM-15 composite), the percentage of removal decreases. This is because a large amount of iron ions serves as a hydroxyl radical scavenger [35]. Furthermore, the smaller particle size of the FeM-10 composite plus the fact that it has a larger surface area and larger pore volume (Table 2) compared to the FeM-15 composite could lead to more reactive surface and accelerate mass transfer in the FeM-10 composite, which enhanced the Fenton oxidation process and its efficiency [36]. Thus, the FeM-10 catalyst was selected and used for the rest of the study.

The effect of catalyst dosage shown in Figure 7b revealed that, as the dose of FeM-10 composite increases from 0.025–0.1 g, the percentage of removal also increases. This is due to the increase in surface area or active sites for pollutant reactions [37]. However, the percentage of removal recorded using 1 g/L of FeM-10 composite is not very much different from the removal using 0.75 g/L. Such a performance is attributed to the hydroxyl scavenging effect by the large amount of iron ions in 1 g/L of the FeM-10 composite.

Figure 7c shows the effect of initial solution pH of the Fenton degradation of OFL using the FeM-10 composite as the heterogeneous activator for H$_2$O$_2$. Based on the results obtained, the performance was favorable at a low pH and kept on retarding with an increase in pH. Various reasons have been attributed to such performance. For instance, hydroxyl radicals have lower redox potential in basic medium and H$_2$O$_2$ may be consumed without the production of hydroxyl radicals [37]. Moreover, at a higher solution pH, the H$_2$O groups are replaced by OH$^-$ groups, and more Fe(OH)$_6$$^-$ is formed [38]. This affects the reaction between the catalytic species and H$_2$O$_2$ [39].

The effect of initial OFL concentration (50, 75, 100, and 150 mg/L) on the efficiency of the FeM-10 composite was studied and the results are presented in Figure 7d. It was observed that the percentage of removal keeps on decreasing with increases in initial
concentration. Such an effect is due to the unavailability of the active sites of FeM-10 composites, which have been occupied by OFL and its intermediates [38].

Figure 7. Effects of (a) Fe₃O₄ loadings on montmorillonite, (b) catalyst dosage, (c) initial solution pH, (d) initial OFL concentration, (e) different oxidants, (f) H₂O₂ dosage, (g) reaction temperature, and (h) inorganic salts. Unless stated otherwise, reaction conditions are based on: [OFL] = 50 mg/L, pH = 9, (FeM-10) = 0.75 g/L, (H₂O₂) = 5 mL/L.
Figure 7e presents the effect of different oxidants peroxydisulfate (PDS), peroxomonomosulfate (PMS), and $\text{H}_2\text{O}_2$ on the Fenton degradation of OFL. The percentage of removal in the presence of PDS and $\text{H}_2\text{O}_2$ was higher than the removal in the presence of PMS. However, the percentage of removal recorded upon the introduction of either $\text{H}_2\text{O}_2$ or PDS was approximately similar. In the case of PMS, the low performance recorded could be attributed to the inherent pH of aqueous OFL solution (pH = 9). Previously, Ji et al. [40] reported that the self-dissociation of PMS occurs at elevated pH through non-radical pathways, and may partly account for the reduced degradation of OFL.

The effect of $\text{H}_2\text{O}_2$ dosage on the Fenton degradation of OFL using the FeM-10 composite was also studied, and the results are presented in Figure 7f. The percentage of removal increases with an increase in dosage from 1–5 mL/L. However, beyond 5 mL/L, the percentage of removal decreases. It was reported by Khodadadi and co-workers [37] that the surplus amount of $\text{H}_2\text{O}_2$ might consume hydroxyl radicals, resulting in a decrease in degradation efficiency.

Figure 7g shows the effect of temperature on the Fenton degradation of OFL using the FeM-10 composite. It is observed from the figure that while the temperature varied from 25 to 60 °C, the percentage of removal remained virtually unchanged. This indicates that the effect of temperature was insignificant. As such, higher reaction temperatures were not useful for increasing the degradation of OFL by FeM-10.

Due to the possibility of the existence of organic pollutants with inorganic ions, the effect of inorganic salts on the Fenton degradation of OFL using FeM-10 composites was studied, and the results are shown in Figure 7h. Based on the results obtained, there was a minor decrease in the percentage of OFL removed in the presence of the inorganic salts used. Such a decrease was attributed to the adsorption of $\text{Cl}^-$ on the active sites of the FeM-10 composite or because $\text{Cl}^-$ serves as a hydroxyl radical scavenger [41,42].

2.2.3. Total Organic Carbon (TOC) Removal of the OFL Solution

Following the establishment of the adsorption–desorption equilibrium and Fenton degradation for 120 min, the catalytic activity of the FeM-10 catalyst was further investigated by evaluating the total organic carbon (TOC) concentration of the OFL solution and the results are shown in Figure 8. The TOC value decreased to 34.1 mg/L and subsequently to 20.92 mg/L after 30 min of the adsorption–desorption equilibrium and 120 min of the Fenton degradation reaction compared to the fresh OFL solution (50 mg/L), which is 46.95 mg/L. In terms of efficiency, the percentages of TOC removal were found to be 27% and 55%, respectively. The lower mineralization efficiency compared to the removal efficiency (~81%) is an indication that the mineralization of the organic pollutant is a slow process and that intermediates still exist in the solution.

Figure 8. Total organic carbon (TOC) removal using FeM-10, reaction conditions are based on: [OFL] = 50 mg/L, pH = 9, (FeM-10) = 0.75 g/L, (H$_2$O$_2$) = 5 mL/L.
2.2.4. Photo-Fenton Catalytic Activity

The photo-Fenton activity of the FeM-10 composite towards the degradation of OFL antibiotic was studied using optimized conditions, under solar irradiation, and the results are shown in Figure 9.

![Figure 9. Degradation of OFL under different conditions.](image)

From the figure, the amount of OFL oxidized under solar irradiation after 120 min was minimal. However, the percentage increased upon the introduction of H$_2$O$_2$. Such an increase is due to the formation of hydroxyl radicals through the direct photolysis of H$_2$O$_2$ [43]. Furthermore, the percentage of OFL removed via adsorption by the FeM-10 composite was about 56%. However, the percentage increased further to 76% upon exposure to solar irradiation, due to the photocatalytic effect of the FeM-10 composite. Finally, compared to the percentage of removal recorded via the Fenton process (about 81%), the performance via photo-Fenton degradation was higher (about 92%).

2.2.5. Reusability and Stability Studies

The recyclability of the FeM-10 composite was also studied to determine its chemical stability for up to five cycles, and the results are shown in Figure 10a. It can be seen that the efficiency of the catalyst continued to drop with the number of cycles and after the fifth cycle, the efficiency dropped to ~59%. This could probably be explained by the loss of the active sites required for the catalytic reaction to take place. It could also be due to the leaching of the Fe$_3$O$_4$ from the surface of the FeM composite. Meanwhile, the FTIR spectrum of the FeM-10 composite (Figure 10b) after the fifth cycle is in good agreement with that of the fresh FeM-10 composite, as no additional peaks were detected.
3. Materials and Methods

3.1. Materials

All chemicals and reagents were of analytic grade and used without further purification. Iron (II) sulfate heptahydrate (FeSO₄·7H₂O) and montmorillonite were obtained from Sigma-Aldrich (Saint Louis, MO, USA). Hydrogen peroxide (H₂O₂), nitric acid (HNO₃), sodium hydroxide (NaOH), and ethanol (CH₃CH₂OH) were obtained from Acros Organics (Morris, NJ, USA), while potassium chloride (KCl) was supplied by Fluka (St. Gallen, Switzerland). Deionized water was used throughout the study.

3.2. Synthesis of Fe₃O₄–Montmorillonite (FeM) Composites

Fe₃O₄–montmorillonite (FeM) composites were synthesized via a facile co-precipitation process [25]. Initially, a solution of equimolar amounts of ferric salt and ferrous salt was prepared by dissolving 3, 5, 8, 10, and 15 mmol of FeCl₃·6H₂O and FeSO₄·7H₂O in 60 mL of 10 mmol L⁻¹ aqueous HCl solution and heated to 80 °C. Then, 0.5 g of montmorillonite (precipitant) were slowly added and stirred for 2 h. After that, the product was collected and washed several times with distilled water and absolute ethanol. Finally, the product was dried in an oven at 60 °C overnight and labeled FeM-3, FeM-5, FeM-8, FeM-10, and FeM-15, based on the equimolar amount of iron salts used in synthesis.

3.3. Characterization Techniques

The chemical states of bare montmorillonite and FeM composite measurements were analyzed using an ULVAC-PHI Quantera II X-ray photoelectron spectroscopy (XPS) system with a monochromatic Al K-Alpha source (Chigasaki, Japan). The morphology of the samples was examined by a transmission electron microscope (TEM) and field emission scanning electron microscope (FESEM) using a Technai G2 F20 (Eindhoven, The Netherlands) and Leo Supra 50 VP FESEM (Eindhoven, The Netherlands) accompanied with an energy dispersive X-ray detector (EDX) to determine their elemental composition. FTIR spectra were recorded with a Perkin Elmer 2000 spectrometer (Beaconsfield, England) within the range of 4000–400 cm⁻¹ using the KBr pellet technique. Brunauer–Emmett–Teller (BET)
surface area and porosity analyses were carried out by N₂ adsorption–desorption analysis at 77.2 K using an ASAP 2020 V4.01 surface area analyzer (Norcross, GA, USA).

3.4. Fenton Reaction

OFL was selected to evaluate the catalytic performance of bare montmorillonite and Fe₃O₄–montmorillonite composites. Typically, 0.075 g of the catalyst were placed into 100 mL of 50 mg/L OFL solution, and the suspension was stirred in the dark for 30 min to establish adsorption/desorption equilibrium. Subsequently, 0.5 mL of H₂O₂ (30% w/w) were added to activate the Fenton reaction. After a certain period, 5 mL of the supernatant were collected for centrifugation, and the concentration of OFL was then analyzed using a Shimadzu UV 2600 spectrophotometer (version 1.03 operated using UV probe 2.42) at an absorption wavelength of 286 nm. Using the same experimental procedure, the effects of Fe₃O₄ loading on montmorillonite, catalyst loading, initial solution pH, initial OFL concentration, different oxidants, H₂O₂ dosage, reaction temperature, inorganic salts, and solar irradiation were studied. Reusability and stability studies were also conducted. The removal efficiency of OFL was calculated as follows:

\[
\% \text{ Removal} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \%
\]

where \(C_0\) and \(C_t\) are the initial and the concentration of OFL solution at different reaction times \(t\). Total organic carbon (TOC) was determined using a Shimadzu TOC-L analyzer.

4. Conclusions

Fe₃O₄–montmorillonite composites have been synthesized via facile co-precipitation process. The effect of Fe₃O₄ loading on montmorillonite was characterized using X-ray photoelectron spectroscopy (XPS), a field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX), a transmission electron microscope (TEM), N₂ adsorption–desorption, and Fourier transform infrared spectroscopy (FTIR) techniques. The FeM composites were subsequently used as heterogeneous Fenton catalysts to activate green oxidant (H₂O₂) for the subsequent degradation of ofloxacin (OFL) antibiotic. The effects of various operational parameters, such as Fe₃O₄ loading on montmorillonite, catalyst dosage, initial solution pH, initial OFL concentration, different oxidants, H₂O₂ dosage, reaction temperature, and inorganic salts, were analyzed. Under the conditions of 0.75 g/L FeM-10, 5 mL/L H₂O₂, and natural pH, almost 81% of 50 mg/L of OFL was degraded within 120 min in the dark. Although FeM composites could be a promising heterogeneous catalyst for the activation of H₂O₂ to degrade pollutants, including OFL antibiotic, they showed a drop in efficiency after five cycles.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/2/177/s1, Figure S1: The corresponding pore size distribution for montmorillonite (a), FeM-3 (b), FeM-5 (c), FeM-8 (d), FeM-10 (e), and FeM-15 (f) composites.

Author Contributions: Conceptualization, methodology, resources, and writing—review and editing, R.A.; writing—review and editing, W.D.O. and S.S.I.; investigation and writing—original draft preparation, A.R.D.A. All authors have read and agreed to the published version of the manuscript.

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37. Khodadadi, M.; Panahi, A.H.; Al-Musawi, T.J.; Ehrampoush, M.; Mahvi, A. The catalytic activity of FeNi$_3$@SiO$_2$ magnetic nanoparticles for the degradation of tetracycline in the heterogeneous Fenton-like treatment method. *J. Water Process Eng.* **2019**, *32*, 100943. [CrossRef]


