Fe$_3$O$_4$/MMT Fenton-like heterogeneous catalyst for the methylene blue degradation

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**Abstract**

Modified clay materials constitute a unique series of materials for effective and efficient heterogeneous catalytic oxidation applied to environmental remediation. In this work, magnetite-decorated montmorillonite catalyst (Fe$_3$O$_4$/MMT) was prepared by co-precipitation method and then characterized by Fourier-transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy and UV-visible spectroscopy. Montmorillonite show interesting properties in adsorption and catalysis. Moreover the Fe$_3$O$_4$ nanoparticles mainly existed on the surface of the MMT, thus exhibiting improved dispersion and lower levels of aggregation. The catalytic activity of Fe$_3$O$_4$/MMT was interrogated in advanced oxidation process using methylene blue (MB) as a model pollutant. The catalyzed degradation of MB was conducted in the presence of H$_2$O$_2$. Fe$_3$O$_4$/MMT showed a higher degradation efficiency compared to MMT and Fe$_3$O$_4$. This survey was optimized by a change in initial H$_2$O$_2$ concentration and temperature; the results obtained show a quasi-complete removal of the MB color. This study confirmed the catalytic efficiency of Fe$_3$O$_4$/MMT material for MB removal by heterogeneous Fenton oxidation. In addition, the synthesized material was easily recovered by simple magnetic separation which accounts for good reusability and remarkable catalytic stability.

**Keywords:** Heterogeneous Fenton catalysts; Methylene blue; Fe$_3$O$_4$; Montmorillonite decolonization ratio

**1. Introduction**

Tackling water pollution is an important issue that requires strict control at the global level. Various chemicals that exist in nature or released from anthropogenic activities are the main resources of water pollution. Residual effluents of industry often contain a variety of contaminants. Organic dyes are one of the pollutants that threaten the environment. Each year, more than 700,000 tonnes of dyes are produced worldwide while about 12% of the dyes are directly released into waters compartment [1].
They are characterized by their complex structures and higher molecular weights, which make them recalcitrant and persistent in the environment [2–5]. Numerous types of dyes are toxic, carcinogenic and mutagenic to a broad selection of living species [6,7].

The various water treatment and purification technologies have been widely discussed in literature, but the design and operation of the methods remains a challenge to date. It should be stressed here that every method has its own technical or economic limits for tangible applications [8,9].

Recent developments in the chemical water treatment field have led to an improvement in oxidative degradation processes of organic compounds in aqueous media; this is through the application of catalytic and photochemical methods. In the course of the last twenty years, new treatment processes have emerged including advanced oxidation processes (AOPs), which have proven to be very useful for the treatment of high-organic loading and non-biodegradable in the wastewater [10,11].

Fenton’s reagent is commonly used in AOPs processes because it has several advantages such as high efficiency of oxidation, mild reaction conditions, environmentally friendly materials and simple operation [12,13]. H2O2/Fe2+ mixtures have very powerful oxidizing properties in an acidic medium due to the generation of hydroxyl radicals (HO•). These radical species are well known to be very efficient and non-selective in the degradation of persistent organic pollutants. The production of hydroxyl radicals can be explained by the following equations [14,15].

\[
\begin{align*}
\text{Fe}^{3+} + H_2O_2 & \rightarrow \text{Fe}^{2+} + HO^- + HO^+ & k_1 &= 76 \text{ M}^{-1} \cdot \text{s}^{-1} \\
\text{HO}^+ + \text{Fe}^{3+} & \rightarrow \text{Fe}^{2+} + HO^- & k_2 &= 3 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}
\end{align*}
\]

Under acidic environments where pH is between 2.7 and 2.8, Fe2+ is reduced to Fe3+:

\[
\text{Fe}^{3+}(aq) + H_2O_2 \rightarrow \text{Fe}^{2+}(aq) + HO^- + H^+ & k_3 = 3.1 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}
\]

The combination of clays such as montmorillonite with magnetite nanoparticles and a peroxo-oxidant provides a new composite material exhibiting synergic behavior or complementary to the constituents. This can be explained by the fact that montmorillonite has interesting properties in adsorption and catalysis, while Fe3O4 contains the on the other hand the formation of reactive HO• radicals when it is coupled to H2O2.

Some heterogeneous catalysts with low iron dissolution, such as nanoparticulate zero-valent iron, iron oxides and immobilized iron on clays have replaced Fe2+/Fe3+ solutions to avoid accumulation and precipitation of soluble iron [19].

Heterogeneous Fenton oxidation has proven to be an efficient and economical method, where iron is immobilized on solid supports such as clays and carbon nanotubes [20]. In the presence of a suitable oxidant, these composite materials can remove organic contaminants over a wide pH range and reduce the loss of iron catalyst.

Particular attention has been given to magnetite, Fe3O4 in the treatment of recalcitrant organic compounds for two reasons; on the one hand for its excellent chemical stability and on the other hand the formation of reactive HO• radicals when it is coupled to H2O2.

Indeed, magnetite-based catalysts are easily recovered and reused for several cycles in the heterogeneous Fenton process. The dissolution of iron ions in the aqueous phase is very limited or even insignificant; a very small quantity of iron ions is released from the catalyst during the degradation of organic pollutants. At this stage hydrogen peroxide oxidizes ferrous ions to produce hydroxyl radicals rapidly, leading to a rapid decrease in ferrous ions in solution [23].

In this work, we synthesized a nanocomposite Fe3O4/MMT for Fenton-like decoloration an azo dye which is methylene blue (MB). It is used in several sectors such as chemistry, pharmacology, medicine, biology and textiles. The use of this dye presents a potential risk to the environment and human health. This is why, it is imperative to be concerned about the impact of these substances on this environmental compartment.

The catalyst Fe3O4/MMT was prepared using the co-precipitation method. The Fenton-like catalytic performance of this catalyst to decolorize MB was been evaluated. Similar studies has been conducted on degradation of some persistent pollutants such as antibiotics (Ofloxacin) and pesticides (phenol) [24].

Features mentioned previously made us excited for the synthesis and characterization of a composite material based on magnetite and montmorillonite by co-precipitation route. The elaborated composite was evaluated in the removal of methylene blue by the heterogeneous Fenton-like process.

2. Experimental

2.1. Materials

Anhydrorous ferric sulfate (Fe2(SO4)3), ferrous sulfate (FeSO4·7H2O) and hydrogen peroxide (H2O2 25% wt.) were
purchased from BIOCHEM. Montmorillonite K10, was purchased from Sigma-Aldrich (Germany).

Methylene blue (cationic dye) taken as a pollutant model was used without any prior purification. The solutions were prepared by dissolving the amounts of the dye in distilled water.

2.2. Preparation of the modified montmorillonite

Magnetite/montmorillonite (Fe$_3$O$_4$/MMT) composite was synthesized by co-precipitation method [25]. Initially, in a three-necked round-bottomed flask (500 mL), the MMT (4.0 g) was dispersed into 200 mL of an aqueous solution in which Fe$_2$(SO$_4$)$_3$ (4.9 g, 12.25 mmol) was dissolved. The mixture was stirred for 12 h in order to obtain a stable suspension. Once the 12 h of stirring reached, FeSO$_4$·7H$_2$O (1.72 g 6.18 mmol) was added in the flask under N$_2$ atmosphere. This solution was heated till 90°C and then NH$_4$OH (6.0 mL, 25%, wt./wt.) was added rapidly. A black precipitate appeared immediately and the mixture was kept under stirring for another hour. After cooling to room temperature, the precipitate of modified montmorillonite was separated by centrifugation and washed successively with distilled water. The obtained product was finally dried at 80°C and has been ready for use. For comparison study, pure Fe$_3$O$_4$ NPs were also prepared via an analogous method but in the absence of any MMT. The relevant chemical reaction can be expressed as follows:

$$2\text{Fe}^{3+} + \text{Fe}^{2+} + 8\text{OH}^- + \text{MMT} \rightarrow \text{MMT} - \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$

(7)

2.3. Characterization methods

The montmorillonite and its magnetic composite were characterized by X-ray diffraction (XRD) using an X’pert-Pro panalytical powder diffractometer. The data recording were carried out within an angle range from 20° to 80° with a step of 0.013° using a 0.154056 nm wavelength radiation of copper anode (CuK$_\alpha$ radiation, 45 kV, 40 mA). The diffraction data were analyzed with a PanalyticalX’Pert High Score Plus software. The crystalline phases were determined compared to registered models of the PDF3 database. The morphology of the composite was observed using a scanning electron microscope JEOI JCMA 5000 Neoscope scanning electron microscopy (SEM). Fourier-transform infrared (FTIR) spectra were recorded between 400 and 4,000 cm$^{-1}$ using a spectrometer Thermo Scientific Model Nicolet IS10 equipped with an ATR measuring device (Attenuated Total Reflection) Golden Gate Model, with a Specac Model Diamond Crystal.

X-ray photoelectron (XPS) spectra were recorded using a Thermo Fisher K-Alpha spectrometer using a monochromatic AlK$_\alpha$X-ray beam (1486.6 eV, 300 µm spot size). The samples were outgassed before they were introduced into the analysis chamber at about 2 x 10$^{-4}$ Pa. Pass energy was 200 eV for survey and 20 eV for high-resolution spectra. The Thermo Scientific Advantage Software (version 5.943) was used for collecting and processing the spectra. The binding energy shifts were calibrated relative to the adventitious carbon C1s position fixed at 284.6 eV and the BE accuracy was ±0.1 eV.

3. Results and discussion

3.1. Infrared spectroscopic characterizations

The Fourier-transform infrared spectra of montmorillonite and modified composite are shown in Fig. 1. The absorption band at about 3,404 cm$^{-1}$ can be attributed to the water molecule vibration [26]. Furthermore, the three absorption bands located at 1,040, 792 and 526 cm$^{-1}$ are the characteristic peaks of Si–O stretching vibrations. As can be observed, the intensity of the Si–O bands in the Fe$_3$O$_4$/MMT composite is lower than that of MMT, indicating an interaction between Fe–O and Si–O bands on the surface of Fe$_3$O$_4$/MMT [25,27]. This means that Fe–O was probably bound to the surface of MMT during the synthesis procedure.

3.2. XRD analysis

XRD analysis of MMT and Fe$_3$O$_4$/MMT are shown in Fig. 2. The patterns confirm the presence of magnetite in the obtained composite, with the appearance of new characteristic peaks of magnetite at 20 = 30.89°, 35.64° and 62.94°.
corresponding to (220), (311) and (440) reflections, respectively (ICDD-PDF No 00-019-0629). The other diffraction peaks at 2θ = 26.73°, 29.99°, 35.07°, 54.23°, 40.37° and 61.93° are clearly attributed to MMT (ICDD-PDF No 00-029-1498).

3.3. XPS analysis

Survey spectra are displayed in Fig. 3 with Al2p, Si2p, O1s and Fe2p major peak assignments; C1s is due to unavoidable hydrocarbon contamination.

High-resolution spectra are used to verify the chemical nature of the elements present at the surface of MMT and Fe3O4/MMT composite, particularly O1s and Fe2p. As shown in Fig. 4a, the O1s peak is fitted with four components centered at 529.4, 531.0, 532.0 and 534.1 eV assigned to Fe3O4, possibly hydroxides, Al–O–Si and organic contamination. The Fe2p region (Fig. 4b) exhibits spin-orbit coupling which resulted in Fe2p3/2 and 2p 1/2 peaks located at 710.8 and 724.4 eV respectively, which account for Fe3O4 oxide [28–30].

3.4. SEM analysis

The MMT and Fe3O4/MMT micrographs (Fig. 5) obtained by scanning electron microscopy (SEM) shows clear and visible contrast in the morphology between MMT and Fe3O4/MMT. The MMT surface has an aggregated morphology with an irregular plate like shape (Fig. 5a). After the modification of MMT with magnetite, the particle size is slightly reduced as seen in Fig. 5b.

3.5. Magnetic properties

The magnetic properties of the Fe3O4/MMT composite were studied by vibrating sample magnetometry (VSM) at 298 K. Fig. 6, shows the magnetic hysteresis loop of Fe3O4/MMT. It can be seen that the values of magnetization (Ms) are 35 emu/g, compared to the theoretical Ms value of magnetite [31] which is generally 92 to 100 emu/g, the Ms of the composite is relatively low. This may be due to the introduction of the non-magnetic MMT particles. However the saturation magnetization of as-prepared composite material is sufficient to meet the needs of magnetic separation. In the presence of an external magnetic field, the catalyst was attracted to the wall of the flask in a short time compared to a homogeneous dispersion without an extrinsic magnetic magnet (Inset of Fig. 6).

3.6. Catalytic performances of Fe3O4/MMT in the catalyzed MB degradation

The catalytic performances of Fe3O4/MMT were evaluated through the heterogeneous Fenton degradation of MB under the assistance of H2O2 (MB: 50 mg/L, catalysts: 0.5 g/L, pH: 3.0, H2O2: 6.65 g/L, T: 20°C). Batch experiments were performed in order to investigate the removal efficiency of MB dye. All the reactions were carried out in the darkness to avoid the effect of light onto the degradation. The results obtained are shown in Fig. 7.

Fig. 7 clearly shows that discoloration of MB is negligible with H2O2 only (Fig. 7a). Nearly 15% of MB was removed...
in 120 min in the presence of Fe₃O₄ (Fig. 7b). The combination of Fe₃O₄ with H₂O₂ returned better results, yet leveling off at 22% removal of MB within 120 min. In contrast, the removal efficiency of MB increased to 60% in the presence of Fe₃O₄/MMT (Fig. 7d) and jumped to 90% when the catalyzed reaction was conducted in the presence of both Fe₃O₄/MMT and H₂O₂ (Fig. 7e).

These results indicated that the higher removal efficiency of MB dye from aqueous medium is obtained with Fe₃O₄/MMT catalyst in the presence of H₂O₂. This can be explained by the production of the hydroxyl radicals from the reaction of H₂O₂ with the iron oxide immobilized on the surface of the composite. The dye removal efficiency by this catalyst is probably due to a synergy effect of adsorbed peroxide and Fe₃O₄/MMT composite, which improves the degradation of the organic compounds. Indeed, previous studies show that the presence of iron oxide, Fe(II) and Fe(III), immobilized on the composite surface promotes the adsorption of H₂O₂ and the conversion of H₂O₂ to OH• radicals [32].

3.7. Optimization of H₂O₂ concentration

The concentration of hydrogen peroxide plays an important role in the effectiveness of Fenton oxidation on the degradation of methylene blue.

The reaction rate constants are described by Eq. (8),

\[
-\frac{[\text{MB}]}{[\text{MB}]_0} = k_{\text{app}} \cdot t
\]

where \([\text{MB}]_0\) is the concentration of the methylene blue at time \(t = 0\), \([\text{MB}]_0\) is the initial concentration of the dye at time \(t = 0\), and \(k_{\text{app}}\) is the apparent rate constant of the methylene blue degradation reaction. The calculated apparent
rate constants and the coefficients of determination $R^2$ are reported in Table 1.

The results reported in Table 1 clearly show that the degradation of MB is effective with a hydrogen peroxide concentration equal to 6.65 g/L. In this case the calculated rate constant $k_{app}$ is equal to $1.60 \times 10^{-2}$ min$^{-1}$ and the determination coefficient $R^2$ is very close to 1. An increase in the concentration of $H_2O_2$ improves the rate of MB discoloration. However we have noted that a higher concentration of $H_2O_2$ on the order of 8.46 g/L implies a decrease in the rate of discoloration of MB ($29.1 \times 10^{-3}$). This is due to the excess of $H_2O_2$ which favours the recombination between the hydroxyl radicals on the one hand and the reaction between the hydroxyl radicals and hydrogen peroxide on the other hand according to the following reactions (9) and (10):

$$\text{OH}^* + \text{OH}^* \rightarrow H_2O_2 \quad (9)$$

$$\text{OH}^* + H_2O_2 \rightarrow H_2O + HO^*_2 \quad (10)$$

3.8. Influence of temperature on MB removal efficiency

MB removal was investigated in the temperature range of 10°C–60°C with 10°C increments. The tests were carried out by adding 50 mg of Fe$_3$O$_4$/MMT composite to 100 mL of MB solution with concentration of 50 mg/L at pH = 3 and in the presence of $H_2O_2$ at 6.65 g/L.

As noted from Fig. 8, the rate of MB degradation is notably improved with increasing reaction temperature. It was observed that the color removal rate of MB was quasito-tal at $T = 50^\circ$C. The increase of the temperature shortened the time of the reaction where about 99.5% of MB is eliminated after 30 min.

The initial removal rate at 50°C is higher than that observed at 60°C, this can be explained by the fact that when temperatures increase, it leads to the thermal decomposition of hydrogen peroxide into $O_2$ and $H_2O$, which prevents the formation of hydroxyl radicals and reduce the removal rate of dye [23,33].

From the calculated values of reaction rate (Table 2), an increase was observed when the temperature raised.

This can be explained by the fact that between 10°C and 50°C the heterogeneous Fenton process is endothermic reaction [34]. Besides, an increase in temperature could also facilitate the activation of the hydrogen peroxide and the diffusion of the reagents to the surface of the catalyst. The determined activation energy was 38.50 kJ/mol for Fe$_3$O$_4$/MMT/$H_2O_2$. This value indicated that the degradation of MB by Fe$_3$O$_4$/MMT/$H_2O_2$ catalyst through heterogeneous Fenton reaction in temperature range between 20°C and 50°C did not require a very high energy [35].

Table 3 shows the comparison of $k_{app}$ values of MB degradation obtained in our study with those described in the literature for other types of catalytic nanocomposites. We observed that the value of apparent rate constant calculated under optimum conditions is $11.0 \times 10^{-2}$ min$^{-1}$ which is higher than reported in the literature.

3.9. Catalytic stability of the Fe$_3$O$_4$/MMT

The reusability of a heterogeneous catalyst is crucial for its practical application and the resilience of a catalyst to reaction conditions is often expressed by its ability to be reused. For this purpose and to evaluate the

<table>
<thead>
<tr>
<th>$[H_2O_2]$ (g/L)</th>
<th>0</th>
<th>1.66</th>
<th>3.32</th>
<th>4.99</th>
<th>6.65</th>
<th>8.32</th>
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<tr>
<td>$k_{app}$ (min$^{-1}$)</td>
<td>$8.82 \times 10^{-3}$</td>
<td>$1.26 \times 10^{-2}$</td>
<td>$1.29 \times 10^{-2}$</td>
<td>$1.32 \times 10^{-2}$</td>
<td>$1.60 \times 10^{-2}$</td>
<td>$2.95 \times 10^{-3}$</td>
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<tr>
<td>$R^2$</td>
<td>0.994</td>
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<td>0.988</td>
<td>0.959</td>
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<td>0.958</td>
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<th>$T$ (°C)</th>
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<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
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<tr>
<td>$k_{app}$ (min$^{-1}$)</td>
<td>$8.7 \times 10^{-3}$</td>
<td>$1.61 \times 10^{-2}$</td>
<td>$2.27 \times 10^{-2}$</td>
<td>$5.35 \times 10^{-2}$</td>
<td>$11.0 \times 10^{-2}$</td>
<td>$7.60 \times 10^{-2}$</td>
</tr>
<tr>
<td>$R^2$</td>
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<td>0.975</td>
<td>0.984</td>
<td>0.982</td>
<td>0.986</td>
<td>0.830</td>
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</table>
The evaluation of the capacity and the stability of the composite via the Fenton reaction were tested for three successive cycles (Fig. 9). MB discoloration efficiency was around 99% after the third use.

4. Conclusion

In this study, the composite material Fe₃O₄/MMT was prepared and used as a catalyst for the degradation of methylene blue in a heterogeneous Fenton-like process. XRD, FTIR, SEM and XPS characterization results confirmed the presence of magnetite in the modified montmorillonite. Optimal reaction conditions for the degradation of MB were found to be an initial pH of 3, an initial H₂O₂ concentration of 6.65 g/L and a reaction temperature of 50°C. Under these conditions the rate of discoloration of the MB solution is almost total (about 99%), which confirms the catalytic effect of the material developed. This removal efficiency by this catalyst is probably due to the effective contribution of the adsorbed peroxide on to Fe₃O₄/MMT composite, which improves the degradation of organic compounds.

It should also be noted that this process allows easy recovery of the catalyst due to the magnetic properties of the composite.

The tests of the reusability of the composite showed a catalytic behavior which could be reproduced in consecutive experiments without significant drop recovery.

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