Improving Photocatalytic Performance in Degradation of Methylene Blue using Magnetite Fe-doped ZnO/Montmorillonite Nanocomposite

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Abstract. In this work, we have successfully synthesized Fe:ZnO/Montmorillonite (MMT) nanocomposite with various loading of magnetite (Fe₃O₄) using co-precipitation method. The as-prepared samples were characterized by some measurements such as X-ray Diffraction (XRD), Burneaur-Emment-Teller (BET) surface area analysis, and Fourier Transform Infrared Spectroscopy (FTIR). The XRD result shows that the diffraction pattern of nanocomposites exhibit characteristic from hexagonal wurtzite structure of ZnO and cubical spinel structure of Fe₃O₄. However, the diffraction pattern from MMT could not be detected using XRD measurement. The presence of MMT in the nanocomposite was further confirmed in the FTIR spectra. Furthermore, the photocatalytic performance of the samples was also checked for degrading methylene blue (MB) under UV light irradiation. The result shows that incorporation of Fe₃O₄ in Fe:ZnO/MMT has better photocatalytic efficiency than Fe:ZnO/MMT alone. Stability of the nanocomposites was also monitored after several cycle processes.

1. Introduction
Photocatalysis has been a popular technique to degrade organic dyes for the past few years. Moreover, photocatalysis is low cost and environmental friendly [1]. One of many tools that is used in the photodegradation of dyes is semiconductor catalyst. We had studied photocatalytic performance of Fe-doped ZnO (Fe:ZnO) and Fe:ZnO modified with montmorillonite in our previous works [2,3,4]. Doping method is advantageous for inhibiting the recombination rate of electron-hole pairs because the dopant acts as the electron trap [5]. In addition, modifying the catalyst with MMT could increase the specific surface area of the catalyst. Therefore, the contact probability between irradiated light and the catalyst increases, resulting in enhanced photocatalytic activity.

Stability of catalyst has attracted so much interest among scientists. It is known that incorporation of magnetite (Fe₃O₄) nanoparticle could stabilize and increase the magnetic saturation of the non-magnetic catalyst [6]. So an external magnetic field could be used to separate the catalyst that has been used in the first cycle of phototocatalytic activity from the aqueous solution. The separated samples was then reused in the next runnings. Therefore, in this work, we synthesized Fe:ZnO/MMT/Fe₃O₄ nanocomposite by using co-precipitation method with five weight ratio of the magnetite in Fe:ZnO/MMT by 0.05, 0.1, 0.3, 0.5, and 1. Some characterizations were conducted in this work such as Diffuse Reflectance Spectroscopy, X-Ray Diffraction, Burneaur-Emment-Teller and Fourier Transform Infrared Spectroscopy.

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2. Experimental Details

2.1. Materials
Zinc (II) sulfate hepta hydrate (ZnSO$_4$.7H$_2$O), iron (II) sulfate hepta hydrate (FeSO$_4$.7H$_2$O), ethylene glycol, acetic acid, and sodium hydroxide (NaOH) were purchased from Merck while montmorillonite from Nanocor. They were analytical grade and used without further purification. Distilled water was used throughout the experiment.

2.2. Synthesize of the Fe:ZnO/MMT/Fe$_3$O$_4$ nanocomposites
The Fe:ZnO/MMT nanocomposites were prepared using co-precipitation method as described in our previous work [4]. The Fe:ZnO/MMT/Fe$_3$O$_4$ nanocomposites were synthesized five times with weight ratio of Fe:ZnO/MMT to Fe$_3$O$_4$ by 1:0.05, 1:0.1, 1:0.3, 1:0.5, and 1:1. These are the following steps: first, the Fe:ZnO/MMT and Fe$_3$O$_4$ were dissolved into ethanol. Then, the solution was mixed with distilled water and ultrasonicated for two hours. Next, a centrifugation process was conducted to separate the solutions and precipitations. After that, the precipitations were allowed to stand under room temperature for 18 hours before being dried in the oven at 100°C in vacuum condition for one hour.

2.3. Characterization
The optical, structure, magnetic, and surface area of the samples were characterized using X-ray diffraction (Rigaku Miniflex 600) operated at 30 kV and 15 mA, vibrating sample magnetometer (Oxford type 1.2 T), infrared spectroscopy (FTIR) and Burneur-Emment-Teller (BET).

2.4. Catalytic activity
The photodegradation of methylene blue (MB) was investigated using Fe:ZnO/MMT/Fe$_3$O$_4$ for two hours at the interval of 15 minutes. The dye’s degradation rate was monitored by using UV-Vis Hitachi UH5300 spectrophotometer. A 40 W UV lamp was used as light irradiation source. The effect of pH was also examined in this work. The catalyst was run for four cycle processes to check its stability.

3. Result and Discussion
The XRD was used to characterize the crystal structure of the nanocomposites. The diffraction patterns of the nanocomposites are shown in Figure 1. The magnetite, pure ZnO, and Fe:ZnO/30 wt% MMT diffraction patterns are also pointed out as comparisons. As can be observed in the figure, diffraction peaks of Fe:ZnO/MMT/Fe$_3$O$_4$ at 2θ = 30.25° (220), 35.55° (311), 43.13° (400), 53.64° (442), 57.20° (511), and 62.81° (440) represent the cubic spinel structure of the magnetite [7], while at 2θ = 31.82° (100), 34.55° (002), 36.29° (101), 47.57° (102), 56.65° (110), 62.85° (103), 66.49° (200), 67.99° (112), and 69.13° (201) represent the hexagonal wurtzite structure of ZnO [8]. It means that the samples were successfully produced. As can be shown in the figure, the magnetite intensity increases as its load increases in Fe:ZnO/MMT. The lattice parameter obtained by the Rietveld refinement technique using the program MAUD and crystal size of the nanocomposites calculated using Debye-Scherer formula [9] are tabulated in Table 1. Specific surface area of nanocomposites were calculated using BET, as shown in Table 2. It indicates that the addition of magnetite nanoparticle into Fe:ZnO/MMT could decrease the surface area value of the nanocomposites.
Absorption spectra of Fe:ZnO/MMT/Fe$_3$O$_4$ nanocomposites with various weight of the magnetite are displayed in Figure 2. The existence of MMT in the samples can be confirmed by the Si-O-Al bending vibration and Si-O-Si stretching vibration found at wave number about 970 cm$^{-1}$ and 1090 cm$^{-1}$, respectively [10,11]. Moreover, there is also absorption peak assigned to stretching vibration of Fe-O at wave number 594 cm$^{-1}$ [12], which derive from the dopant ion Fe and Fe$_3$O$_4$. Furthermore, the absorption peaks at wave numbers 1049, 1384, and 1723 cm$^{-1}$ derive from the stretching vibrations of C=O, O-H, and C=O [13]. Then, the broad absorption peak at wave numbers range 3000-3500 cm$^{-1}$ is attributed to vibration mode of the O-H bond [14].

The photodegradation of methylene blue has been examined using Fe:ZnO/MMT/Fe$_3$O$_4$ nanocomposites as photocatalysts. Figure 3 exhibits the rapid degradation rate of MB using the photocatalyst with various weight of the magnetite. The MB degradation rate using Fe:ZnO/MMT without Fe$_3$O$_4$ is also shown. As can be seen in the figure, the photocatalyst with ratio of 1:0.05 performs the best photocatalytic activity. This result is corresponding to their surface area, where the nanocomposite with higher surface area could interact with MB more effectively when irradiated.

| Sample                  | Weight Ratio | Lattice Parameter | Crystallite Size (nm) | Unit Cell Volume (Å$^3$) |
|-------------------------|--------------|-------------------|-----------------------|-------------------------|
| ZnO                     | -            | a=b (Å)           | c (Å)                 | ZnO | Fe$_3$O$_4$ | ZnO | Fe$_3$O$_4$ |
| Fe$_3$O$_4$             | -            | -                 | -                     | 8.365 | - | 16 | - | 45 | 585.326 |
| Fe:ZnO/3 MMT            | 0 wt.%       | -                 | 3.261                 | 5.225 | - | - | 14 | 18 | 47.361 | 605.281 |
| Fe:ZnO/MMT/Fe$_3$O$_4$  | 1:0.05       | 3.244             | 5.196                 | 8.459 | 14 | 11 | 10 | 29 | 47.076 | 621.961 |
|                         | 1:0.1        | 3.237             | 5.196                 | 8.461 | 11 | 22 | 10 | 29 | 47.163 | 607.110 |
|                         | 1:0.3        | 3.244             | 5.197                 | 8.536 | 10 | 11 | 22 | 12 | 47.163 | 607.110 |
|                         | 1:0.5        | 3.213             | 5.207                 | 8.586 | 9  | 9  | 22 | 12 | 47.163 | 607.110 |
|                         | 1:1          | 3.192             | 5.217                 | 8.61  | 7  | 7  | 22 | 12 | 46.05  | 638.277 |
The reduced degradation may also due to increased magnetite loading which can cover the active sites of ZnO nanoparticles.

It was [15] reported that ZnO has zero point charge of 9±0.3. It causes the surface of ZnO positively charged when the pH is below this value and negatively charged above this value. Moreover, MB is cationic dye and positively charged when dissolved into water. When the pH value of the aqueous solution of MB increases, its degradation is further increased, as presented in Figure 4. The explanation is as follows. In acidic and neutral condition, both catalyst surface and MB are positively charged, resulting repulsive force and reducing photocatalytic activity because MB cannot provide hydroxyl group to form hydroxyl radical [16]. In contrast, opposite charge on the surface of the catalyst and MB in alkaline condition are attracted to each other so that the MB degradation increases.

**Table 2. Surface Area of the Samples.**

| Sample                     | Weight Ratio | Surface Area (m²/g) |
|----------------------------|--------------|---------------------|
| Fe:ZnO/MMT/Fe₃O₄          | 1:0.05       | 39.326              |
|                            | 1:0.1        | 34.242              |
|                            | 1:0.3        | 28.502              |
|                            | 1:0.5        | 25.196              |
|                            | 1:1          | 21.702              |

**Figure 3. MB Degradation Curve Using Fe:ZnO/MMT and Fe:ZnO/MMT with Various Weight Ratio of Fe₃O₄.**

**Figure 4. MB Degradation under different pH Value.**
Reusing the photocatalyst for four times processes results in great MB purification in aqueous solution, as shown in Figure 5. It can be seen that the photocatalytic activity exhibits 100% MB degradation for the first and second cycle, 98% for the third and 97% for the fourth. It indicates that Fe:ZnO/MMT/Fe$_3$O$_4$ nanocomposite is a stable photocatalyst.

4. Conclusion
The Fe:ZnO/MMT/Fe$_3$O$_4$ nanocomposites had been synthesized successfully by using co-precipitation method. The XRD patterns showed that the incorporation of magnetite nanoparticle could change the structure of ZnO. Maximum discoloration of methylene blue was performed by Fe:ZnO/MMT/0.05Fe$_3$O$_4$ sample. After four cycle processes of photocatalytic activity, the sample exhibited good stability in degrading methylene blue.

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