

Fe-doped ZnO Supported with Montmorillonite: Synthesis, Characterization, and Photocatalytic Activity

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Abstract. In this study, Fe-doped ZnO/MMT has been prepared by using co-precipitation method with the various amount of MMT (10, 20, 30, and 40 wt%). The samples were characterized by using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy, and (FTIR), Brunauer-Emmett-Teller (BET) surface area analysis. The crystallite structure of ZnO did not change with the additional of dopant and MMT. The presence of MMT could be confirmed by using FTIR, which showed the bending vibration and stretching vibration of Si-O-Al and Si-O-Si. The degradation of methylene blue and methyl orange were examined by using montmorillonite (MMT) modified Fe-doped ZnO catalyst in photocatalytic process under UV light irradiation. The photocatalytic results indicated that certain amount of MMT could increase photocatalytic performance in degrading methylene blue and methyl orange. Methylene blue degradation increased with the increasing of pH value while the opposite trend occurred for methyl orange degradation.

1. Introduction

Chemical, textile, and paint industries have played a big role in dye-contaminated water. Some methods have been used to eliminate dyes from wastewater including adsorption [1], activated carbon [2], and photocatalysis [3]. In the last decades, photocatalysis has been a promising way to degrade dyes in aqueous solution because it is low cost, highly efficient, and less polluting.

Zinc oxide (ZnO) nanoparticle is a popular photocatalyst beside TiO₂. ZnO has a direct bandgap of 3.37 eV which is in the ultra violet (UV) region. However, pure ZnO still performs the low photocatalytic activity. Doping ZnO with transition metal iron (Fe) and modifying it with montmorillonite (MMT) clay are good ways to enhance the photocatalytic performance[4,5]. Moreover, MMT is a good supporter in nanoparticle because of its high surface area and excellent adsorption ability[6].

In our previous work [7], we had studied the photodegradation of methylene blue (MB) and methyle orange (MO) by using Fe:ZnO/MMT nanocomposite. In expectation to obtain better dyes' photodegradation, we varied the amount of MMT in nanocomposites and studied their photocatalytic activity in this work. The effects of dosage concentration and pH in the photocatalytic activity were also examined.



2. Experimental Method

2.1. Materials

FeSO₄·7H₂O (Merck), ZnSO₄·7H₂O (Merck), NaOH (Merck), and MMT clay (Nanocor) were analytical grade and used without further purification. Distilled water was used in the whole experiment.

2.2. Synthesis of the Fe:ZnO/MMT nanocomposites

The Fe:ZnO/MMT nanocomposites were prepared through co-precipitation method as described in our previous work [7]. The nanocomposite was synthesized four times with the amount of montmorillonite 10-40%.

2.3. Characterization

The specific surface area, optical properties, and structural properties of the samples were characterized by using Burneur-Emmett-Teller (BET; Nova Quantachrome 2000) surface area analysis, X-ray diffraction (XRD; Rigaku Miniflex 600), and fourier transform infrared spectroscopy (FTIR; FEI Spectrophotometer Shimadzu IR Prestige-21).

2.4. Catalytic performance

The photocatalytic performance of Fe:ZnO/MMT nanocomposites was examined by using methylene blue (MB) and methyl orange (MO) as the models of organic pollutant under a 40 W UV lamp as light irradiation source. The degradation rate of MB and MO was observed in 15 minutes intervals for two hours by using UV-Vis Hitachi UH5300 spectrophotometer. To obtain the optimal condition in the photocatalytic activity, the effect of pH was also studied.

3. Results and Discussion

The crystal structure of the samples were studied by using XRD spectroscopy. Table 1 summarizes the lattice parameter value, obtained by the Rietveld refinement technique by using the program of MAUD, and the crystallite size that was calculated through the Debye-Scherrer formula [8]. Figure 1 shows the diffraction patterns of Fe:ZnO with various amount of MMT. The diffraction pattern of MMT and ZnO was also displayed as comparison. The diffraction patterns of Fe:ZnO/MMT nanocomposites show the existence of diffraction peaks at $2\theta = 31.54^\circ, 34.34^\circ, 36.13^\circ, 47.46^\circ, 56.44^\circ, 62.77^\circ, 66.02^\circ, 67.81^\circ, \text{ and } 68.91^\circ$ which represent the areas of (100), (002), (101), (102), (110), (103), (200), (112), and (201) which are from the hexagonal wurtzite structure of ZnO [19]. They indicated that the nanocomposites were successfully synthesized without changing the structure of ZnO after doping with metal iron. Furthermore, the intensity of MMT in four samples does not increase significantly as its loading increases. There were also no impurities detected from the XRD patterns. Specific surface area of the synthesized samples were characterized by using Burneur-Emmett-Teller (BET) and summarized in Table 1. It shows that the increasing amount of MMT in Fe:ZnO could increase the surface area of the nanocomposite.

Table 1. Lattice Parameters, Unit Cell Volumes, Crystal Size, and Specific Surface Area of Nanocomposites

Sample	MMT Ammount	Lattice Parameter		Unit cell volume ($\text{\AA}^3$)	Crystal Size (nm)	Surface Area (m^2/g)
		a = b ($\text{\AA}$)	c ($\text{\AA}$)			
Fe:ZnO/MMT	10%	3.259	5.222	47.695	17	23.64
	20%	3.261	5.221	48.097	18	35.58
	30%	3.261	5.225	48.126	19	42.85
	40%	3.263	5.226	48.156	20	48.31

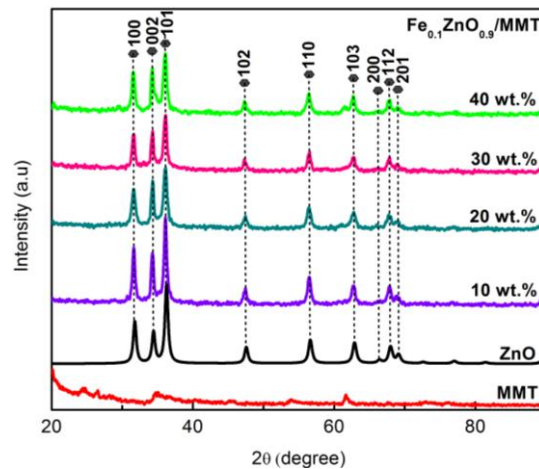


Figure 1. XRD Patterns of MMT, ZnO, and Fe:ZnO/MMT Nanocomposites

FTIR spectroscopy was used to confirm the existence of the MMT in the nanocomposites. Figure 2 shows the absorption spectra of montmorillonite and the nanocomposites with percentage of MMT from 10-40%. Respectively, the Si-O-Al bending vibration and Si-O-Si stretching vibration were found at wave number of 970 cm^{-1} and 1090 cm^{-1} , confirming the existence of MMT in the sample [10,11]. There are also stretching vibrations of C-O, O-H, and C=O at the absorption peaks of wave numbers of 1049, 1384, and 1723 cm^{-1} [12]. The spectroscopy also detected a vibration mode of the O-H bond from the broad peak at wave numbers of $3000\text{--}3500\text{ cm}^{-1}$ [13]. The photodegradation of methylene blue and methyl orange were observed under UV light irradiation for 2 hours. Figure 3 shows the degradation of MB and MO using nanocomposites with various amount of MMT. It shows that increasing amount of MMT to 30% results in improved photocatalytic degradation efficiency of MB and MO. The increase of photocatalytic efficiency may be due to the increasing num of the specific surface area value. Therefore, the surface active site also increased, which yielded to a higher interfacial charge carrier transfer for photocatalysis [14]. However, when the amount of MMT further increased to 40%, the photocatalytic efficiency decreased. It may be due to the active sites get blocked by the over maximum content of MMT.

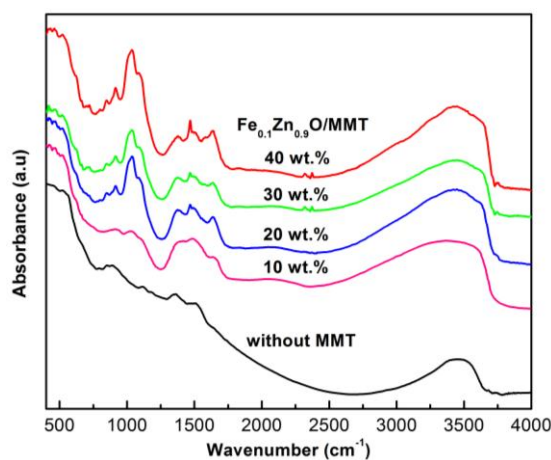


Figure 2. Infrared Spectra of Fe:ZnO Nanoparticle and Fe:ZnO/MMT Nano composites

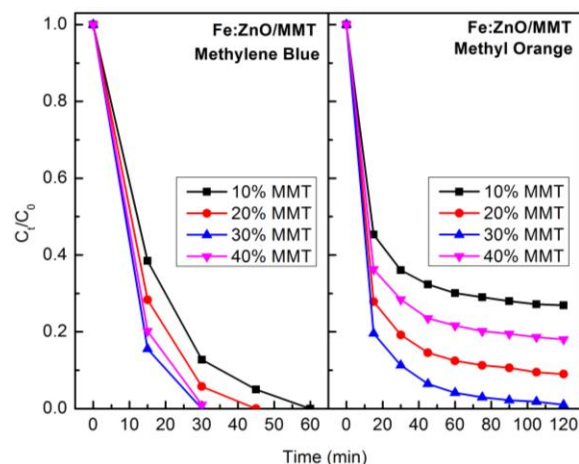


Figure 3. Photodegradation Percentage of MB and MO using Fe:ZnO with various amount of MMT.

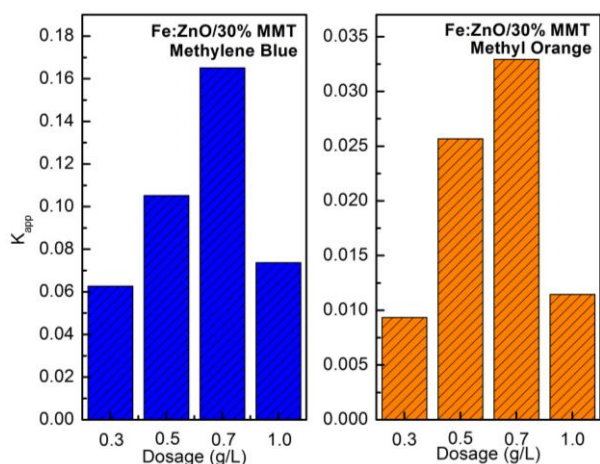


Figure 4. The apparent reaction rate constant (k_{app}) of MB and MO degradation with different catalyst

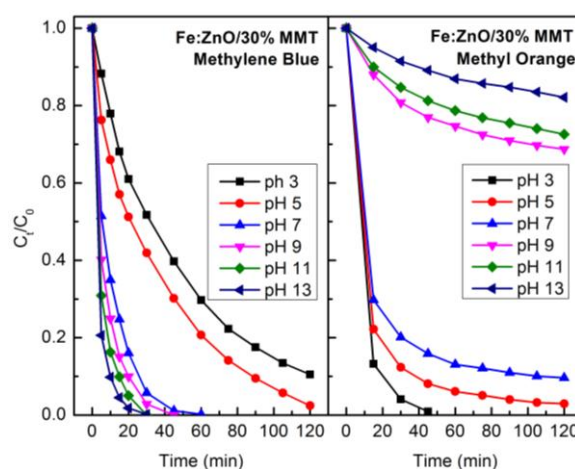


Figure 5. The degradation curve of MB and MO under different pH value.

Figure 4 shows the apparent rate constant (k_{app}) of MB and MO with the effect of catalyst dosage which varied from 0.3 g/L to 1.0 g/L. Increasing catalyst dosage from 0.3 g/L to 0.7 g/L led to enhancing degradation of both dyes but decreasing degradation when the dosage was further loaded to 1.0 g/L. These results indicate that the increasing catalyst amount can add the number of active sites to interact with dye molecules. However, the excessive amount of catalyst can decrease the photocatalytic efficiency due to the opacity of the suspension increasing [5].

Figure 5 shows the photocatalytic performance of Fe:ZnO/30% MMT under acidic, neutral, and alkaline conditions. As can be seen in the figure, the MB photodegradation rate increased rapidly in alkaline conditions but decreases in acidic conditions while MO photodegradation rate exhibits the opposite trend, like had been observed in our previous works [7]. The mechanism is described as follows. ZnO was reported to have zero point charge of 9 ± 0.3 [15] which makes it will be positively charged under acidic and neutral condition and negatively charged under alkaline condition. Since MB is a cationic dye, it is positively charged in aqueous solution. In the acidic condition, the Coulomb repulsive force occurs between positive charges of ZnO and MB, which can decrease the photocatalytic efficiency because MB cannot provide hydroxyl group to form hydroxyl radicals ($\bullet OH$) formation [16]. However, in alkaline condition, the opposite charges of ZnO and MB attract each other so they can interact to decompose MB molecules from the water by providing a higher concentration of hydroxyl ions that can react with holes to form $\bullet OH$ [17].

The degradation of MO under different pH condition can be described similarly to the degradation of MB above. MO is an anionic dye, resulting positively charged ZnO's surface in pH value, which is acidic condition, lower than its zero point charge can enhance the photocatalytic activity in degrading MO. Meanwhile, the pH value which is higher than its zero point charge cannot decompose MO's complex molecule effectively.

4. Conclusion

The Fe:ZnO nanocomposites with various amount of montmorillonite have been successfully synthesized by using co-precipitation method. The results show that the amount of 30% MMT plays important role in enhancing the photocatalytic activity of Fe:ZnO. The pH value of 13 and 3 are the best condition for degrading MB and MO, respectively.

5. References

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