UV Light-Driven Photodegradation of Methylene Blue by Using Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ Nanocomposites

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Abstract. The photodegradation activity of nanocomposites for 20 ppm methylene blue solution has been investigated in this work. Nanocomposites Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ have been synthesized using coprecipitation method. The X-ray diffraction (XRD) pattern confirmed the formation of three phases in sample Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$, i.e., Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, Zn(OH)$_2$, and SiO$_2$. The appearance of SiO$_2$ phase showed that the encapsulation process has been carried out. The calculated particles size of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ is greater than Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. Bonding analysis via vibrational spectra for Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ confirmed the formation of bonds Me-O-Si stretching (2854.65 cm$^{-1}$) and Si-O-Si asymmetric stretching (1026.13 cm$^{-1}$). The optical gap energy of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ was smaller (2.70 eV) than Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (3.04 eV) due to smaller lattice dislocation and microstrain that affect their electronic structure. The Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ showed high photodegradation ability due to smaller optical gap energy and the appearance of SiO$_2$ ligand that can easily attract dye molecules. The Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ also showed high degradation activity even without UV light radiation. The result showed that photodegradation reaction doesn’t follow pseudo-first order kinetics.

1. Introduction

Heterogeneous photocatalyst has remarkable properties, both photocatalytic and magnetic properties. Among all alternative heterogeneous photocatalysts, ferrite nanoparticles have gained a great interest of researchers. Ferrite nanoparticles offer many advantages of having narrow band gap which capable of absorbing visible light radiation. Ferrites posses’ spinel crystal structure which is able to improve the efficiency because of the availability of extra catalytic sites [1]. Some types of ferrite materials that have been used for photocatalyst are Fe$_3$O$_4$, Fe$_2$O$_3$, CuFe$_2$O$_4$, NiFe$_2$O$_4$, ZnFe$_2$O$_4$, CoFe$_2$O$_4$, MnFe$_2$O$_4$, CaFe$_2$O$_4$, MgFe$_2$O$_4$, ZnFe$_2$O$_4$/SnO$_2$, BiFeO$_3$, etc [2]. Another type of ferrite nanoparticles is Zn-doped MnFe$_2$O$_4$. The Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ is a mixed spinel ferrite which has high magnetic properties and narrow band gap ($E_g < 3.0$ eV) [3-5]. Polymer coated Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles also showed interesting properties for their biocompatibility. For instance, a remarkable microstructure, morphology, and magnetic properties of silica-coated nanoparticles Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ had reported by [5].

To the best of our knowledge, only small number of researchers reported the photocatalytic activity of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ nanocomposites. The magnetic property of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ is useful for the separation between nanocomposites and the solution only by using external magnetic field after the photodegradation process was conducted. Herein, we predominantly focus on reporting the photodegradation activity of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ for 20 ppm methylene blue dye with a driven of UV light radiation. Further, microstructural and optical properties of nanocomposites were also investigated for main consideration in explaining the photodegradation phenomena. The reaction mechanism during photodegradation was also studied. It was found that the photodegradation activity...
of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} is much higher than bare Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}. The degradation activity of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} for methylene blue without UV light radiation was also investigated.

2. Experimental Method

2.1 Preparation and Characterization of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2}

There are many researchers who have reported the procedure of preparing ferrite nanoparticle such as Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}. In this research, the nanoparticles were prepared by using coprecipitation method such as reported by [4,6]. For an encapsulation, the Si_{2}O_{3} solution was used as the starting material for the formation of SiO_{2} layer. The encapsulation process was conducted by using Ströber method as reported by [7]. The nanocomposites were characterized by their microstructural parameters by using XRD technique. The FTIR measurement was performed to study the vibrational mode of functional group bonds within samples. Particles’ morphology and electron diffraction image of samples were investigated by using Transmission electron microscope (TEM). The optical properties of samples were investigated by using diffuse reflectance UV-visible spectrophotometer.

2.2 Photodegradation Testing of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2}

The photodegradation testing was carried out for sample Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} nanocomposites and bare Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}. Each sample was tested for their photodegradation activity for 120 minutes. The measurement of absorbance spectra was performed in every 30 minutes using UV-visible light spectrophotometer with a wavelength of 664.095 nm. The Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} degradation activity was also investigated in condition without UV light radiation. The 10W UV source of 275 nm in wavelength was used in this testing. Powder Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} nanocomposites and bare Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} of each mass 20 mg were used to degrade 30 ml of 20 ppm methylene blue dye. Each prepared powder was added into methylene blue solution in Erlenmeyer flask. The mixer was stirred at room temperature with and without UV light radiation.

3. Result and Discussion

3.1 XRD Analysis

The X-ray diffraction pattern of samples nanocomposite Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} and nanoparticles Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} can be shown in Figure 1a. These patterns showed that samples contain two different phases, such as Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} (JCPDS card no. 10-0467) and Zn(OH)_{2} (card no. 41-1359). A phase of SiO_{2} (card no. 45-0131) was investigated in samples of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2}. The appearance of Zn(OH)_{2} might be caused by an incomplete ferritization reaction of zinc hydroxide compound into ferrite Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}. Figure 1a shows that both diffraction patterns have four characteristic peaks of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} which represent the mixed spinel cubic FCC structure and space group of Fd3m. Peak of Miller plane (311) has the highest intensity. The formation of sharp peaks indicates that samples have high crystallinity. The calculated particles size by using Scherrer’s method [5,6] of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} is 20.73 ± 0.24 nm greater than Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} of 18.71 ± 0.24 nm. The lattice parameter of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} is approximately close to Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}.

3.2 Structural Morphology and Electron Diffraction

Structural morphology and electron diffraction of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} was performed by using TEM image and SAED (Selected area electron diffraction) such Figure 1b. The structural morphology of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} couldn’t be determined. Although the encapsulation with SiO_{2} layer has been carried out, the sample of nanocomposites still exhibited agglomeration. Hence, the specific layer of SiO_{2} on the surface of bare nanoparticles definitely difficult to be investigated of its size. The SAED image shows that the formation of polycrystalline materials. These are indicated by the dotted rings appear in electron diffraction images. The SAED image also confirmed the appearance Miller planes of (220), (311) and (511) that could be diffracted by the electron in the crystal lattice of the sample. Somehow, the intensity of electron diffraction of Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}/SiO_{2} is lower than Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} nanoparticles. The diffraction rings of (220), (311) and (511) were consistent with result presented by X-ray diffraction pattern (Figure 1). Among these rings, the diffraction ring of Miller plane (311) has the sharpest intensity in agreement with the highest intensity shown by X-ray diffraction pattern.
3.3 Vibrational Spectra

Bonding analysis of samples can be performed based on spectra provided by FTIR in Figure 2. The bands at 570.93 cm\(^{-1}\) and 447.49 cm\(^{-1}\) of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/SiO\(_2\) spectra are assigned as Me-O tetrahedral stretching and Me-O octahedral stretching vibration consecutively. These two characteristic bands show the formation of a bond between metal salt and oxygen in entire spinel ferrite structure. Sample Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/SiO\(_2\) nanocomposites show some absorption bands. Peaks at 1026.13 cm\(^{-1}\) are assigned as Si-O-Si asymmetric stretching vibration. This vibrational frequency shifted toward lower value due to a higher bond length between Si-O after interacting with the metal ion of bare nanoparticles. The appearance band at 2854.65 cm\(^{-1}\) is assigned as Me-O-Si stretching which definitely shows the formation of a bond between bare nanoparticles and the silica layer [5]. It implicates that the encapsulation of silica layer on the surface of bare nanoparticles was successfully carried out. Further, bands at 1627.92 cm\(^{-1}\), 2337.72 cm\(^{-1}\) and 3394.72 cm\(^{-1}\) also confirmed the existence of hydroxyl group bonds within sample Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/SiO\(_2\) nanocomposites.

3.4 Optical Properties

The optical properties of samples were studied in accordance to the diffuse reflectance UV-visible spectra. The absorbance spectra vs photon wavelength can be shown in Figure 3. The calculated optical band gap energy of sample Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) and Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4)/\text{SiO}_2\) in this result are bigger than reported by [5]. The optical band gap energy shows the energy that required by an electron to excite from valence band to conduction band. Nevertheless, in this case, we specifically can’t determine the type of inter-band excitation whether direct or indirect optical band gap energy. The optical band gap energy of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4)/\text{SiO}_2\) nanocomposite is smaller than bare Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) due to two reasons. First, surface encapsulation of bare nanoparticle with SiO\(_2\) layer might cause a change in microstrain and lattice density of the sample. These changes will affect the electronic band structure of the material that makes smaller optical gap energy. Second, the decrease of the optical band gap is caused by the increase of particle size as an effect of quantum confinement [8].

3.5 Photodegradation Activity

Photodegradation activity of samples was carried out with variation of irradiation time such Figure 4a. For a pure methylene blue solution, the dye degradation actually run very slow due to the absent of photocatalyst which drives the reduction-oxidation reaction. The existence of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) can drive gradually photodegradation reaction of methylene blue dye. Photodegradation rate of dye with only Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticle was still lower than Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4)/\text{SiO}_2\) nanocomposites. A sample of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4)/\text{SiO}_2\) nanocomposites has the highest photodegradation rate up to 97.72%.
First, the existence of SiO$_2$ layer on the surface of bare nanoparticles increases the surface reactivity of samples. The ligand of vicinal silanols group that is resulted by SiO$_2$ layer increases the adsorption ability of nanocomposites to attract dye molecules to the surface of particles. Further, the SiO$_2$ layer is a good adsorbent to address several organic molecules such methylene blue dye. This fact enhances the adsorption ability of nanocomposites toward methylene blue molecules on the surface of nanocomposites [9]. Second, the optical band gap energy of sample Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ nanocomposites is smaller than Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles. Therefore, the generation of electron-hole pairs wills more effective than larger optical band gap energy materials for the same photon energy radiation. Studying the photodegradation rate of each sample can give chance to understand the photodegradation kinetic. The photodegradation kinetic was displayed in Figure 4b. All samples do not follow the pseudo-first order kinetic reaction. Somehow, it is difficult to decide what model of kinetic reaction the samples follow for this case. Furthermore, it needs to be studied in more detail about the mechanism of reaction and possibly to carry out an experiment by using appropriate probes such as GC-MS and photoluminescence spectrophotometer. Moreover, Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ can be considered as a candidate for nanophotocatalyst or nano-adsorbent for organic pollutant because of their potential that has been proven even though without UV-light radiation.

![Figure 2](image_url)

**Figure 2.** (a) Full vibrational spectra of samples nanocomposites; (b) zoom spectra of nanocomposites Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$; (c) zoom spectra of silica layer.

![Figure 3](image_url)

**Figure 3.** (a) Absorbance spectra vs photon wavelength and (b) the Tauch’s plot.
Figure 4. (a) Photodegradation rate of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ nanocomposites under and without UV-light radiation; (b) Photodegradation kinetic of samples.

4. Conclusion
The Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ nanocomposite have been synthesized using coprecipitation method. The bare nanoparticle Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ has a particles size smaller than Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$. The FTIR spectra confirmed the formation of the nanoferrites structure and the appearance of vibration band Si-O-Si stretching and Me-O-Si stretching. Nanocomposites Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ have smaller optical band gap than bare Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ due to smaller surface defect and larger particles size. The encapsulation of SiO$_2$ layer on the surface on bare nanoparticles enhances photodegradation activity of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$. Nanocomposites Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ also showed a high degradation activity for methylene blue dye even though without UV-light radiation. Nanocomposites Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/SiO$_2$ can be a promising nano-photocatalyst and nano-adsorbent for organic pollutants.

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