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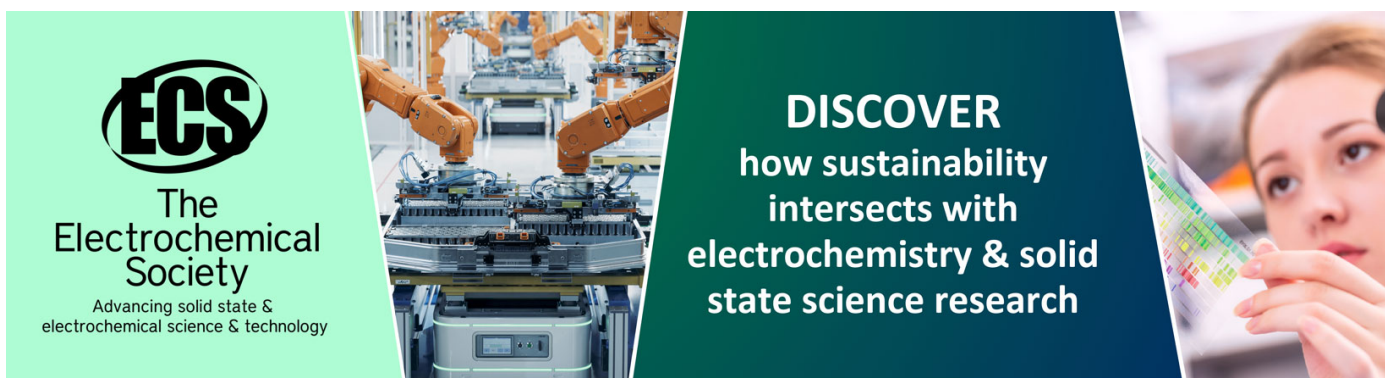
UV Light-Driven Photodegradation of Methylene Blue by Using $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ Nanocomposites

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

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Abstract. The photodegradation activity of nanocomposites for 20 ppm methylene blue solution has been investigated in this work. Nanocomposites $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ have been synthesized using coprecipitation method. The X-ray diffraction (XRD) pattern confirmed the formation of three phases in sample $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ i.e., $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, $\text{Zn}(\text{OH})_2$, and SiO_2 . The appearance of SiO_2 phase showed that the encapsulation process has been carried out. The calculated particles size of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ is greater than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Bonding analysis via vibrational spectra for $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ was smaller (2.70 eV) than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (3.04 eV) due to smaller lattice dislocation and microstrain that affect their electronic structure. The $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ showed high photodegradation ability due to smaller optical gap energy and the appearance of SiO_2 ligand that can easily attract dye molecules. The $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 possess 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_3O_4 , Fe_2O_3 , CuFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , CoFe_2O_4 , MnFe_2O_4 , CaFe_2O_4 , MgFe_2O_4 , $\text{ZnFe}_2\text{O}_4/\text{SnO}_2$, BiFeO_3 , etc [2]. Another type of ferrite nanoparticles is Zn-doped MnFe_2O_4 . The $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is a mixed spinel ferrite which has high magnetic properties and narrow band gap ($E_g < 3.0\text{ eV}$) [3-5]. Polymer coated $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles also showed interesting properties for their biocompatibility. For instance, a remarkable microstructure, morphology, and magnetic properties of silica-coated nanoparticles $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ had reported by [5].

To the best of our knowledge, only small number of researchers reported the photocatalytic activity of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites. The magnetic property of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ is much higher than bare $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The degradation activity of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ for methylene blue without UV light radiation was also investigated.

2. Experimental Method

2.1 Preparation and Characterization of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$

There are many researchers have reported the procedure of preparing ferrite nanoparticle such as $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. In this research, the nanoparticles were prepared by using coprecipitation method such as reported by [4,6]. For an encapsulation, the Si_2O_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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$

The photodegradation testing was carried out for sample $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites and bare $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites and bare $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ and nanoparticles $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ can be shown in Figure 1a. These patterns showed that samples contain two different phases, such as $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (JCPDS card no. 10-0467) and $\text{Zn}(\text{OH})_2$ (card no. 41-1359). A phase of SiO_2 (card no. 45-0131) was investigated in samples of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$. The appearance of $\text{Zn}(\text{OH})_2$ might be caused by an incomplete ferritization reaction of zinc hydroxide compound into ferrite $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Figure 1a shows that both diffraction patterns have four characteristic peaks of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ which represent the mixed spinel cubic FCC structure and space group of $\text{Fd}3\text{m}$. 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ is 20.73 ± 0.24 nm greater than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ of 18.71 ± 0.24 nm. The lattice parameter of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ is approximately close to $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$.

3.2 Structural Morphology and Electron Diffraction

Structural morphology and electron diffraction of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ was performed by using TEM image and SAED (Selected area electron diffraction) such Figure 1b. The structural morphology of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ is lower than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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.

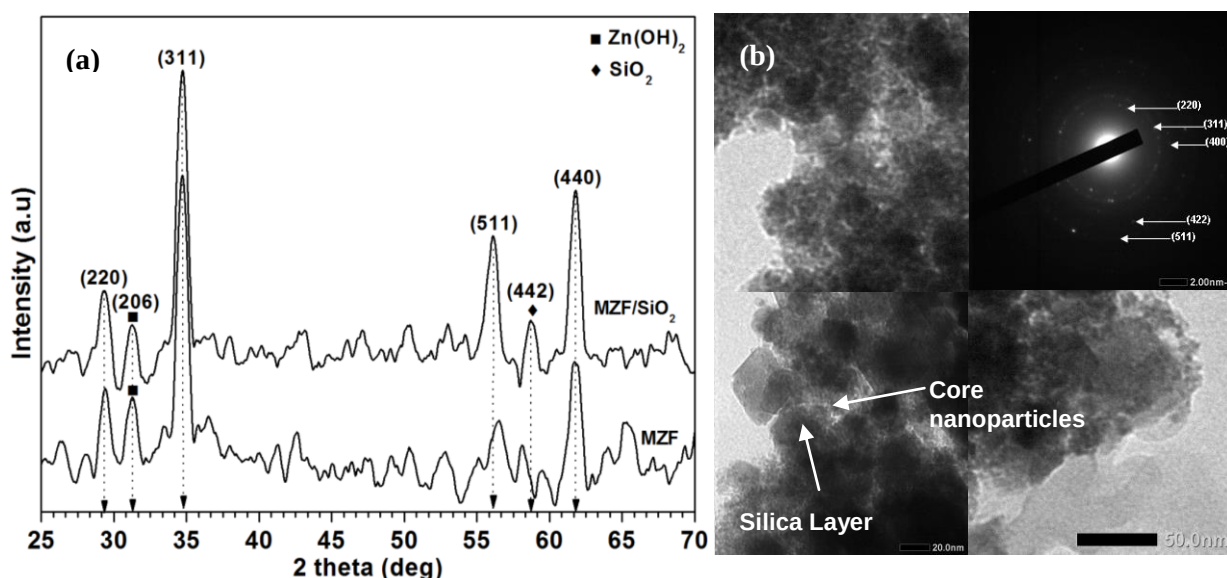


Figure 1. (a) X-ray diffraction patterns of sample nanocomposites and (b) TEM images of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites with its SAED image.

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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 gap energy of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposite is smaller than bare $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ can drive gradually photodegradation reaction of methylene blue dye. Photodegradation rate of dye with only $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle was still lower than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites. A sample of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites is smaller than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. Therefore, the generation of electron-hole pairs will be 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, $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ 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.

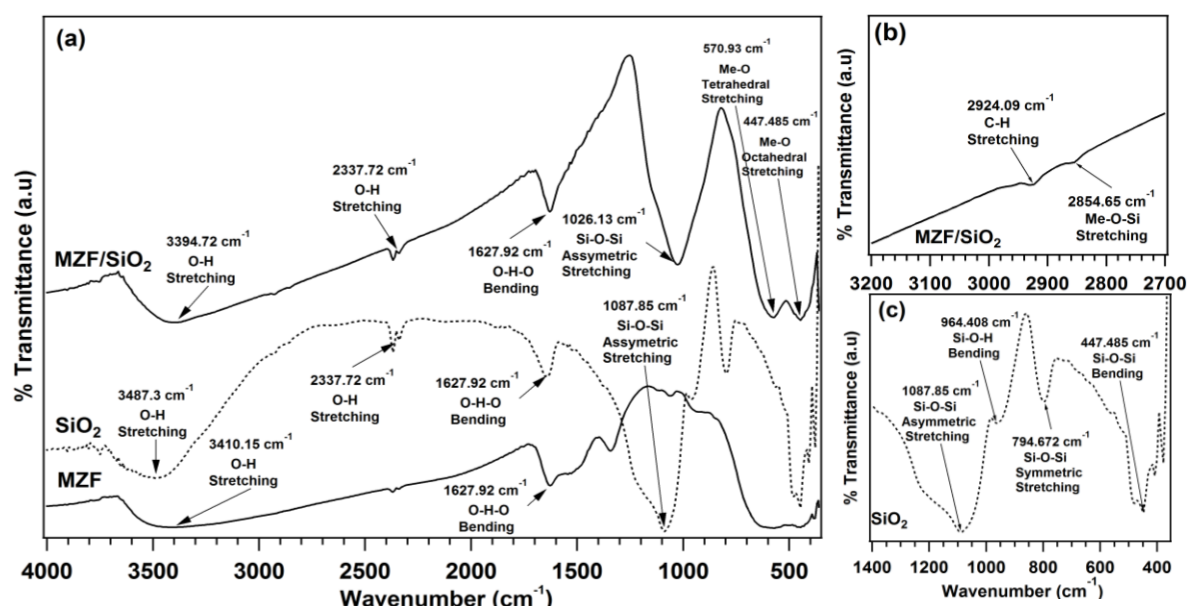


Figure 2. (a) Full vibrational spectra of samples nanocomposites; (b) zoom spectra of nanocomposites $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$; (c) zoom spectra of silica layer.

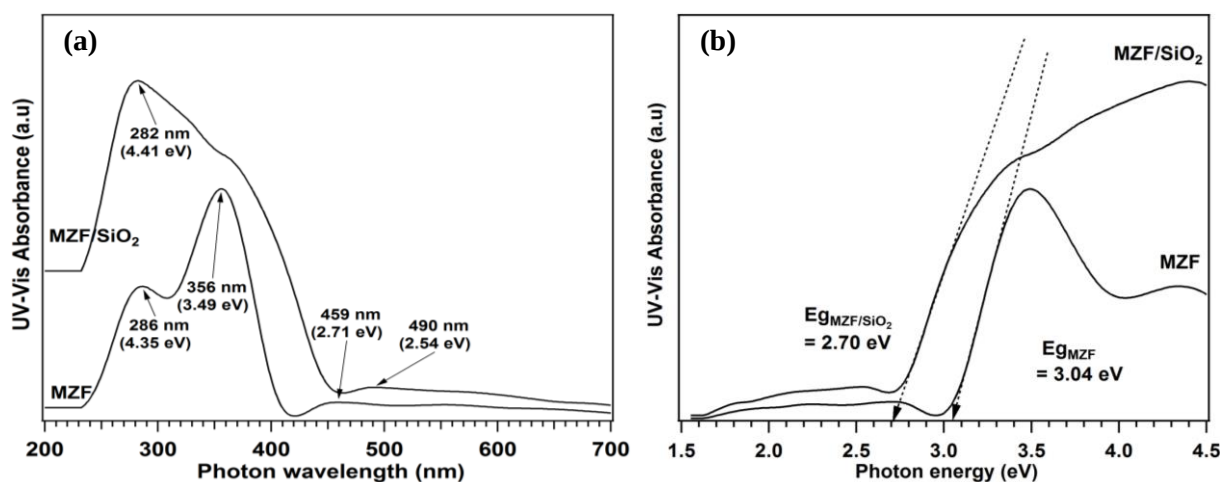


Figure 3. (a) Absorbance spectra vs photon wavelength and (b) the Tauc's plot.

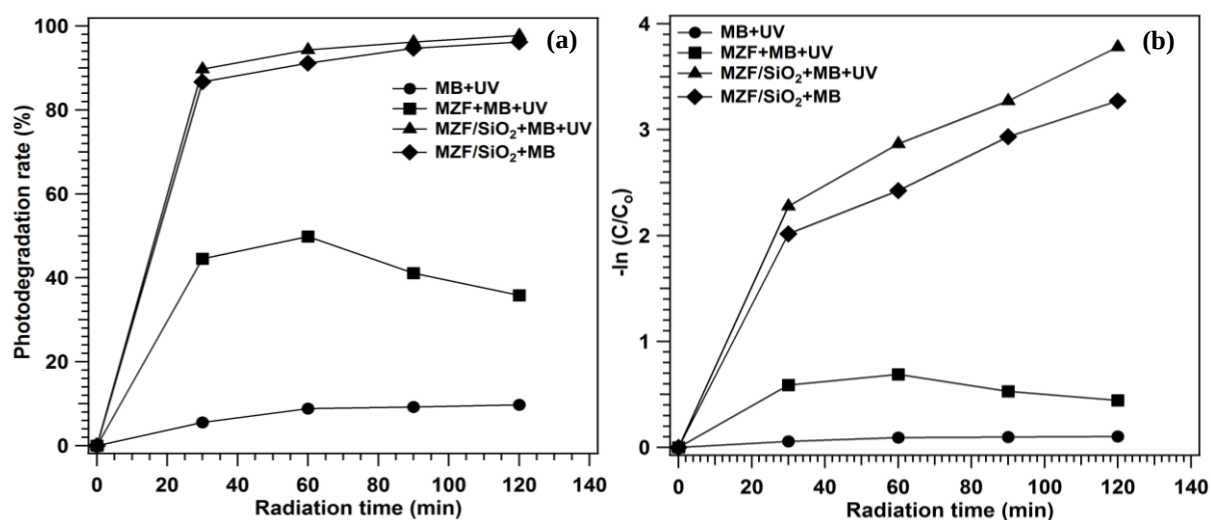


Figure 4. (a) Photodegradation rate of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites under and without UV-light radiation; (b) Photodegradation kinetic of samples.

4. Conclusion

The $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposite have been synthesized using coprecipitation method. The bare nanoparticle $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ has a particles size smaller than $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$. 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ have smaller optical band gap than bare $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$. Nanocomposites $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ also showed a high degradation activity for methylene blue dye even though without UV-light radiation. Nanocomposites $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{SiO}_2$ can be a promising nano-photocatalyst and nano-adsorbent for organic pollutants.

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6. References

- [1] Oliveira L C A, Fabris J D, Rios R R V A, Mussel W N and Lago R M 2004 *Appl. Catal. A* **259** 253–259
- [2] Kharisov B I, Dias H V R and Kharissova O V K 2014 *Arab. J. Chem.* **10** 1–13
- [3] Laohasurayotin K, Pookboonmee S, Viboonratanasri D and Kangwansupamonkon W 2012 *Mater. Res. Bull.* **47** 1500–07
- [4] Indrayana IP T, Siregar N, Suharyadi E, Kato T and Iwata S 2016 *J. Phys.: Conf. Ser.* **776** 012021
- [5] Baykal A, Güner A, Demir A, Esir S, and Genç F 2014 *Ceramics Int.* **40** 13401–13408
- [6] Siregar N, Indrayana IP T, Suharyadi E, Kato T and Iwata S 2017 *J. Phys.: Conf. Ser.* **202** 012048
- [7] Liberman A, Mendez N, Trogler W C and Kummel A C 2014 *Surf. Sci. Rep.* **69** 132 - 158
- [8] Mote V D, Dargad J S, urushotham Y and Dole B N 2015 *Ceramics Int.* **41** 15153–15161
- [9] Ali M B, Bouaifel F B, Elhouichet H, Sieber B, Addad A, Boussekey L, Férid M and Boukherroub R 2015 *J. Colloid Interf. Sci.* **457** 360–369