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Research Article

Photocatalytic Degradation of Methylene Blue by Fe/ZnO/SiO_2 Nanoparticles under Visiblelight

R. M. Mohamed,[1,2] I. A. Mkhalid,[1] E. S. Baeissa,[1] and M. A. Al-Rayyani[1]

[1] *Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia*
[2] *Advanced Materials Department, Central Metallurgical R&D Institute (CMRDI), P.O. Box 87 Helwan, 11421 Cairo, Egypt*

Correspondence should be addressed to R. M. Mohamed, redama123@yahoo.com

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The photocatalytic activity of Fe/ZnO/SiO_2 catalysts under visible-light irradiation for the degradation of methylene blue was evaluated. The effect of pH, illumination time, amount of catalyst loaded, and initial dye concentration on the degradation efficiency of methylene blue was investigated. The results reveal that the optimum photocatalytic oxidation conditions of methylene blue are as follows: pH = 4 and illumination time is 30 min, the amount of catalyst loading is 0.075 g/L and 50 ppm methylene blue dye concentration. Under these conditions, the removal efficiency of methylene blue was 100%.

1. Introduction

Water contamination becomes a serious issue due to the fact that 2% of dyes that are produced from different industries is discharged directly in aqueous effluent [1]. At the present time, the common industry processes are using dyes by textile industry to color their products. Since this industry also uses substantial amount of water in their processes to form highly colored effluent of this industry which generally has hazardous effect in our ecosystem due to the presence of these organic chemicals. So it was necessary to find a new way to remove colored dyes before discharging them into the environment [2, 3]. The various conventional technologies currently employed in the removal of colored effluents in industrial water are classical and do not lead to complete destruction of the dyes. These methods do not work efficiently due to high solubility of dyes as well as their resistance to chemical and biological degradation; also they just transfer the contaminants from one phase to another [4]. Therefore, there is a need to develop a novel treatment method that is more effective in eliminating dyes from the wastewater. Advanced oxidation processes (AOPs) are alternative techniques for destructing dyes in industrial water and these processes are relatively recent. They were developed to meet the increasing demand of an effective wastewater treatment. Semiconductor photocatalysts are newly developed AOPs and can be applied to degrade dyes conveniently [5]. ZnO is one of the most commonly used semiconductors in photocatalytic processes and SiO_2 is characterized by its high surface area. In previous study, we prepared ZnO/SiO_2 xerogel by conventional sol-gel method, in which tetraethyl orthosilicate ($Si(OC_2H_5)_4$) was used as the precursor and zinc nitrate hexahydrated ($Zn(NO_3)_2 \cdot 6H_2O$) was the source of zinc. The prepared xerogel examined as photocatalyst for the degradation of methylene blue dye in aqueous solution under UV-light irradiation [6]. But because the solar spectrum usually contains about 5% UV-light, the solar energy could not be utilized efficiently in the photocatalytic process. Therefore, it was necessary to improve its activities by shifting absorption band gap threshold from the UV-region to the visible-region by loading Fe metal to modify the surface chemical and physical properties of prepared photocatalysts [7, 8]. Fe metal was loaded on the surface of ZnO/SiO_2 nanoparticles by application of a photo-assisted deposition method and the prepared photocatalyst used to degrade the methylene blue under visible light [9]. The aim of the present work is to study the factors effecting on photocatalytic oxidation process of methylene blue using Fe/ZnO/SiO_2 such as pH,

illumination time, amount of catalyst loaded, and initial dye concentration and find out the optimal conditions used in photocatalytic process.

2. Experimental

2.1. Chemicals. All the chemicals used for preparation $Fe/ZnO/SiO_2$ nanoparticles are analytical grade reagents. Zinc nitrate hexahydrated $[Zn(NO_3)_2 \cdot 6H_2O]$, ferric nitrate monohydrate $[Fe(NO_3)_3 \cdot 9H_2O]$, and tetraethyl orthosilicate $[Si(OC_2H_5)]$ "TEOS" are obtained from Sigma-Aldrich.

2.2. Preparation of Fe/ZnO/SiO$_2$ Catalyst. ZnO/SiO_2 nanoparticles were prepared via sol-gel technique by dissolving TEOS and $Zn(NO_3)_2 \cdot 6H_2O$ using optimal conditions as our previous work [6]. Fe-metal was loaded on the surface of ZnO/SiO_2 nanoparticles using photo-assisted deposition method (PAD) to obtain $Fe/ZnO/SiO_2$ nanoparticles as our previous work [9].

2.3. Characterization Techniques. To determine the crystallite sizes and identities of the Fe loaded on ZnO/SiO_2 nanocomposite photocatalyst, X-ray diffraction (XRD) analysis was carried out at room temperature using Rigaku X-ray diffractometer with Cu Kα radiation over a 2θ collection range of 10–80°. The shape of the samples was tested using Hitachi H-9500 Transmission Electron Microscope (TEM), the prepared samples were prepared by suspending the prepared samples in ethanol, followed by ultrasonication for 30 min, then a small amount of this solution onto a carbon-coated copper grid and drying before loading the sample in the TEM. UV-Vis diffuse reflectance spectra (UV-Vis-DRS) were recorded in air at room temperature in the wavelength range of 200–800 nm using Shimadzu UV-2450 spectrophotometer.

2.4. Photocatalytic Activity Evaluation. A set of photocatalytic degradation of methylene blue was carried out using a horizontal cylinder annular batch reactor. A black light-blue florescent bulb (F18W-BLB) was positioned at the axis of the reactor to supply UV illumination. To measure the photocatalytic activity of $Fe/ZnO/SiO_2$ photocatalyst, UV filter was used to cut off the wavelengths shorter than 400 nm. The experiments were performed by suspending photocatalyst into reactor with methylene blue dye solution. The reaction was carried out isothermally at 30°C. The concentration of residual methylene blue in the solution after irradiation was determined by monitoring the absorbance intensity of solution samples at their maximum absorbance wavelength 665 nm by using UV-Vis spectrophotometer which was recorded on a Shimadzu UV-2450 with a 1 cm path length spectrometric quartz cuvette at room temperature. The photodegradation efficiency of methylene blue was calculated by using the following equation:

$$\%\ \text{Photodegradation efficiency} = \frac{C_0 - C}{C_0} \times 100, \quad (1)$$

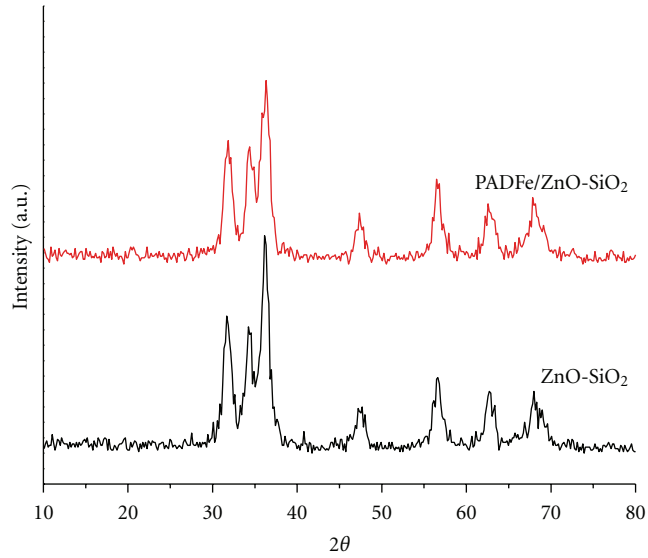


Figure 1: XRD patterns of the $ZnO\text{-}SiO_2$ and PAD:$Fe\text{-}ZnO\text{-}SiO_2$.

where C_0 is the original methylene blue dye concentration, and C is the methylene blue dye residual concentration in solution.

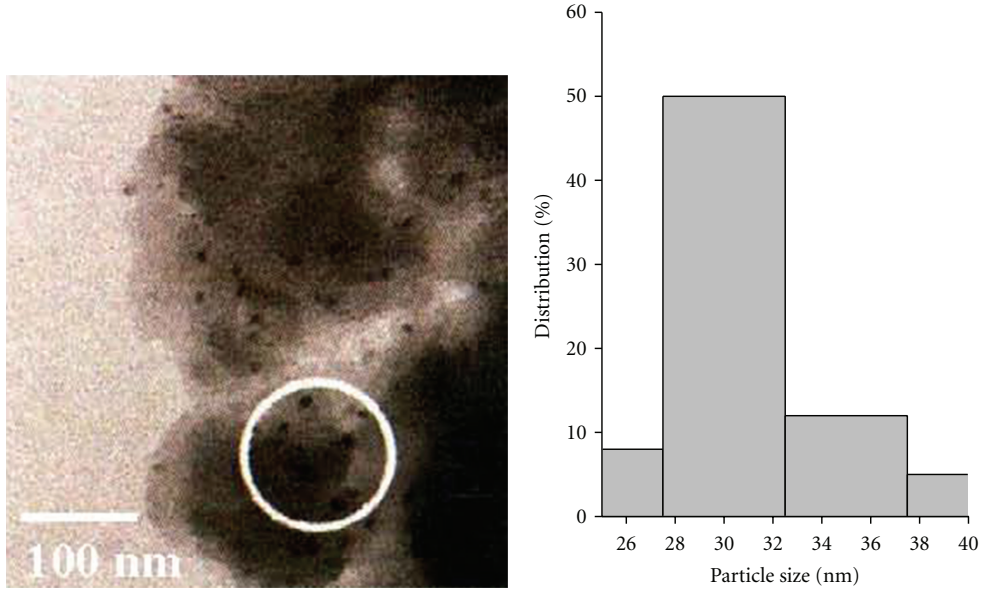
3. Results and Discussion

3.1. Catalyst Characterization. The XRD patterns of the $ZnO\text{-}SiO_2$ and Fe-doped $ZnO\text{-}SiO_2$ nanoparticles prepared by (PAD) route are shown in Figure 1. It can be seen that the diffraction patterns of $ZnO\text{-}SiO_2$ sample and Fe-doped $ZnO\text{-}SiO_2$ are mainly composed of ZnO phase which still exists after applying PAD preparation method. While, in the Fe-doped samples, no diffraction peaks of Fe were observed, this is probably attributed to the low Fe doping content (ca. 2 wt%). Moreover, it is obvious that, Fe is well dispersed within the $ZnO\text{-}SiO_2$ phase.

The grain size of PAD: $Fe\text{-}ZnO\text{-}SiO_2$ nanocomposite photocatalysts are displayed in TEM images as shown in Figure 2(a). The particle size distribution obtained from the analysis of TEM images is shown in Figure 2(b). The results reveal that the nanosized Fe metal with a mean diameter (d) of ca. 30 nm having a narrow size distribution was found on the PAD:$Fe\text{-}ZnO\text{-}SiO_2$ catalyst.

Figure 3 gives UV-Vis-DRS of PAD: $Fe\text{-}ZnO\text{-}SiO_2$. The results show that an increase in absorbency in the visible light region with the iron doping. The results reveal that the value of calculated band gap for PAD:$Fe\text{-}ZnO\text{-}SiO_2$ is 2.7 eV.

3.2. Evaluation of Photocatalytic Activity. The variations in different experimental conditions affecting on photocatalytic oxidation of methylene blue using photo-deposited catalyst $Fe/ZnO/SiO_2$, such as, pH value, illumination time, amount of catalyst loaded, and initial dye concentration, were taken into account to reach to integrated model for the photocatalytic degradation of methylene blue.



(a) (b)

Figure 2: (a) The TEM image of PAD:Fe-ZnO-SiO_2 catalysts after H_2 treatment at 550°C. (b) Size distribution diagrams of Fe metal obtained from the TEM images of the PAD:Fe-ZnO-SiO_2 catalyst after H_2 treatment at 550°C.

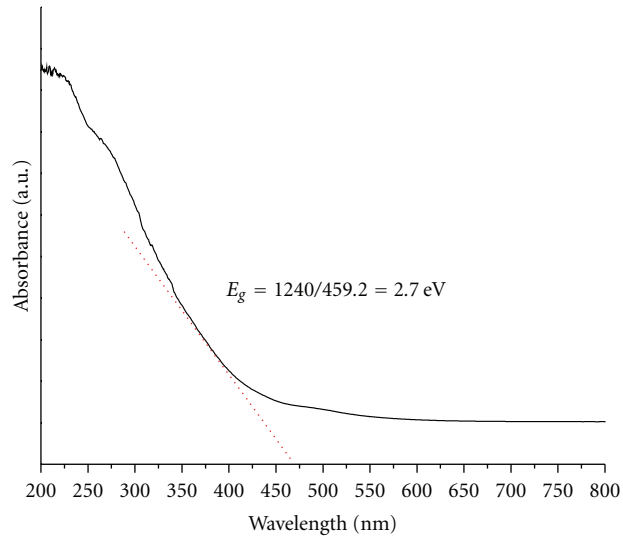


Figure 3: Diffuse reflectance UV-Vis absorption spectra of PAD : Fe-ZnO-SiO_2.

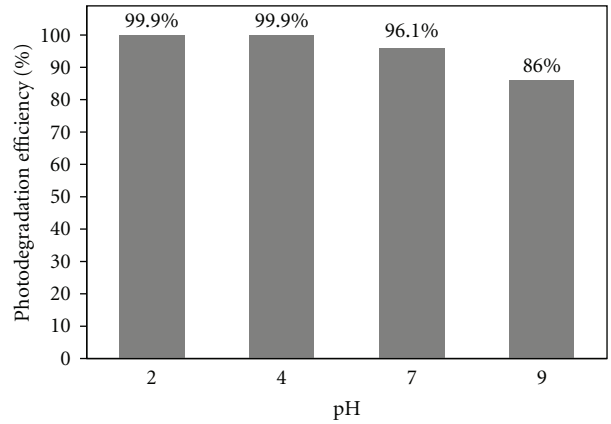


Figure 4: Effect of pH of dye solution on the photodegradation efficiency of methylene blue.

3.2.1. Effect of pH of Dye Solution. It is well known that the pH value influences the rate of photocatalytic degradation of some organic compounds and so it was of interest to study its influence on the photocatalytic degradation of methylene blue. It was also an important operational variable in practical wastewater treatment. Generally, the effect of pH on organic degradation assisted by the semiconductor oxides has been related to the establishment of acid-base equilibrium governing the surface chemistry of metal oxides in water. It can be explained in terms of electrostatic interaction between the catalyst surface and the target substrate. The role of the effect of pH on the photodegradation of methylene blue over Fe/ZnO/SiO_2 catalyst is reported in the pH range of 2–9 using 0.1 gm of catalyst and 300 mL of 50 ppm dye solution under visible light at 30°C for an hour.

Figure 4 demonstrates the results of photodegradation efficiency of methylene blue with different pH values. The results revealed that the photodegradation efficiency decreases with the increase in pH. At low pH value (pH = 2) the photodegradation efficiency reached to 99.90%, when the pH value of methylene blue dye solution increases from 2 to 4, the photodegradation efficiency of methylene blue almost remains unchanged and then the photodegradation efficiency decreased to 96.1 at pH 7. Further increases in pH value of methylene blue dye solution to 9 lead to

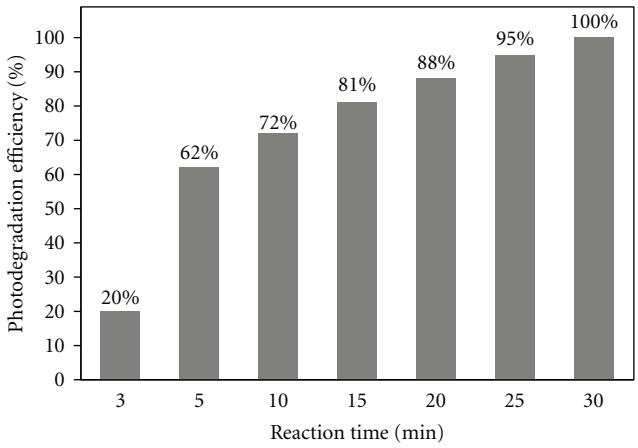


Figure 5: Effect of illumination time on the photodegradation efficiency of methylene blue.

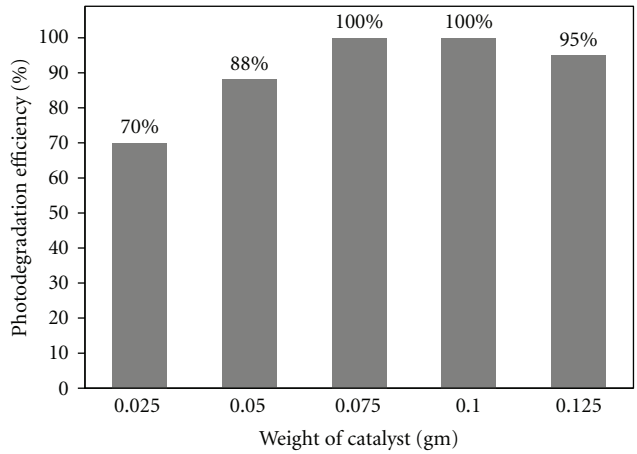


Figure 6: Effect of catalyst loading on the photodegradation efficiency of methylene blue.

further decreasing in photodegradation efficiency from 96.1 to 86%. This is because the methylene blue is negatively charged in acidic medium, whereas ZnO is positively charged below pH 9, which is reported as pH of zero point charge for ZnO [10], so the increasing in pH value tends to change the charge on ZnO to negative charge by adsorbing HO^- ions, which favors the formation of $HO^\bullet$ [11], and consequently, the photocatalytic activity decreased due to the increase of the electrostatic repulsion between ZnO and anionic dye gradually. In addition, the increase of pH may increase e^-/h^+ recombination rate and thus decrease the photocatalytic activity [12]. So, the optimal pH value for the photodegradation of methylene blue is 4 at which the positively charged ZnO and negatively charged methylene blue molecules should readily attract each other and photocatalytic oxidation is maximal.

3.2.2. Effect of Illumination Time. The effect of illumination time on photodegradation efficiency of methylene blue was carried out by measuring the photodegradation efficiency at different periods of time using 0.1 gm of catalyst and 300 mL of 50 ppm dye solution with pH 4 under visible light at 30°C. The results obtained appear in Figure 5. The results revealed that the photocatalytic activity increases with increase of the illumination time and reaches to 100% after 30 min illumination time. Such data reveals the relative high activity of the prepared catalysts which enables the complete degradation of the methylene blue in such short illumination time, and the catalyst has active sites for carrying out the reaction [12].

3.2.3. Effect of Catalyst Loading. The effect of catalyst loading dose on the photodegradation efficiency of methylene blue was observed by taking different amounts of catalyst ranging from 0.025 to 0.125 gm into 300 mL of 50 ppm dye solution with pH 4 under visible light at 30°C for half of an hour. The obtained results are depicted in Figure 6. These results showed that increment of catalyst loading from 0.025

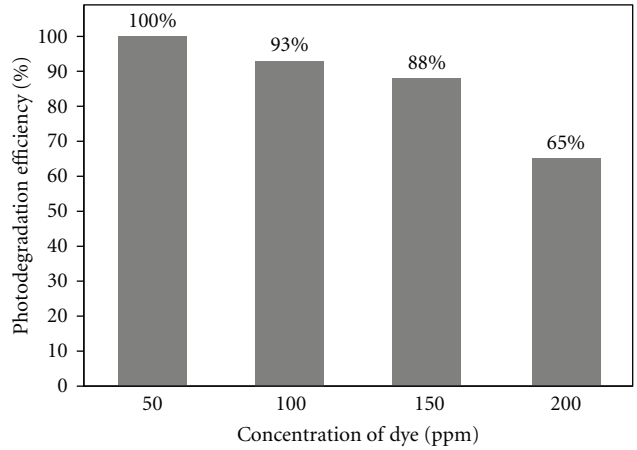


Figure 7: Effect of initial dye concentration on the photodegradation efficiency of methylene blue.

to 0.075 gm increased the photodegradation efficiency of methylene blue from 70 to 100% and after that the further increase in catalyst loading dose above 0.075 gm does not affect on the photodegradation efficiency. This is attributed to the increase in the catalyst loading dose which increased the number of active sites available on the catalyst surface for the reaction, which in turn increased the number of holes and hydroxyl radicals. When the catalyst loading dose increased to above 0.1 gm, the photodegradation efficiency abruptly decreased to 95% due to an agglomeration and sedimentation of the catalyst particles which caused an increase in the particle size and decrease in specific surface area which lead to decrease in the number of surface active sites [13]. Also at high amount of catalyst, the opacity, turbidity of the suspension, and light scattering of catalyst particles are increased. This tends to decrease the passage of irradiation through the sample [14]. Therefore, the most effective photodegradation for methylene blue is observed with 0.075 gm of catalyst-loading dose.

3.2.4. Effect of Initial Dye Concentration. The effect of initial dye concentration was investigated by varying the initial concentration from 50 to 200 ppm using 0.075 gm of catalyst and 300 mL of dye solution with pH 4 under visible light at 30°C for half of an hour. The results obtained are showed in Figure 7. It can be seen that the photodegradation efficiency of methylene blue is inversely proportional to its concentration, which means, the lower of the dye concentration, the higher efficiency of the dye photodegradation. As seen, increasing the initial dye concentration from 50 to 200 ppm decreases the photodegradation efficiency of methylene blue from 100 to 65%. The photodegradation efficiency relates to the formation of hydroxyl radicals, which is the critical species in the degradation process. Hence an explanation to this behavior is that the higher the initial concentration, the higher the adsorbed organic substances on the surface of the catalyst and the solution became more intensely colored. Therefore, there are only fewer active sites for adsorption of HO^- so the generation of $HO^\bullet$ will be reduced. Furthermore, as the concentration of methylene blue increases with constant intensity of light and illumination, the path length of photons entering the solution decreased, so only fewer photons reached the catalyst surface. As a result, the productions of holes or hydroxyl radicals that can attack the pollutants were limited. Therefore, the relative $HO^\bullet$ number attaching the compound decreases and thus the photodegradation efficiency decreases [12, 15]. So, the optimal initial dye concentration is 50 ppm at photodegradation efficiency 100%.

4. Conclusions

The photocatalytic degradation of methylene blue was investigated using prepared $Fe/ZnO/SiO_2$ nanoparticles under visible light. The degree of degradation of methylene blue was obviously affected by the pH of the dye solution, illumination time, amount of catalyst loading, and initial dye concentration. The complete degradation of methylene blue was achieved at these optimal conditions: pH = 4, illumination time is 30 min, and the amount of catalyst loading is 0.075 g/L of 50 ppm methylene blue dye solution.

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