



Modification of Photocatalytic Activity of Zinc Oxide Photocatalyst by Sensitization with Riboflavin as a Photosensitizer

**Hussein Adrees¹, Noor A. Nema², Abbas Jassim¹, O. Karar Abdali^{2,*},
Salih Kahdum¹, Abdulazeez O. Mousa²**

¹Department of Chemistry, College of Science, University of Babylon, Iraq

²Department of Physics, College of Science, University of Babylon, Iraq

*E-mail address: karar_ali9@yahoo.com

ABSTRACT

This project involves modification of the photoresponse of zinc oxide by sensitization with riboflavin (RF) as a photosensitizer. Sensitization of the surface of zinc oxide with RF was performed using impregnation method. Modification of zinc oxide surface with this photosensitizer was investigated using different techniques such as XRD, FTIR, SEM and UV-Visible spectroscopy. The photocatalytic activity of both neat and sensitized zinc oxide was investigated by removal of methylene blue dye (MB) from the simulated industrial wastewater. Removal of this dye from the aqueous solutions was conducted by measuring the absorbance of this dye at 665 nm.

Keywords: ZnO, riboflavin, industrial wastewater, photosensitizer, sensitization, photosensitizer

1. INTRODUCTION

In our modern life catalytic processes have played a crucial role in all aspects of humankind, these processes were initiated more than forty years ago when Bard and Frank

established heterogeneous photocatalytic systems using a composition of semiconductor photocatalysts and a suitable source of light. Early reported work in this field was the photocatalytic splitting of water into oxygen and hydrogen gas over an electrode of TiO₂ and under irradiation with UV light^(1,2).

These photocatalytic semiconductors have a bandgap energy ranged from 2-4 eV, and among a wide range of the semiconductor photocatalysts, zinc oxide (ZnO) is appeared to be a good candidate photocatalyst that can be used for wide range of photocatalytic reactions and it can be photoexcited under both UV and visible light irradiation⁽³⁾. This photocatalyst has some excellent photocatalytic properties such as, high resistance towards acids and bases, non-toxicity high refractive index, high thermal stability, high surface area, relatively low cost and it can be cyclized from reaction mixture to be used in further photocatalytic reactions⁽⁴⁻⁶⁾. Generally, zinc oxide can be used widely in photocatalytic processes under irradiation with light of a proper photon energy ($h\nu \geq E_g$).

It has an excitation bandgap energy of ZnO is ($E_g = 3.30$ eV), and this energy fall in range of ultraviolet radiation of solar spectrum⁽⁷⁻⁸⁾. From this value of E_g of zinc oxide it can be photoexcited effectively only under irradiation with UV light of the solar spectrum. This point represents the main drawback in the use of ZnO, as UV light composes only 5% of the total solar energy. So that, ZnO can't be excited effectively under solar irradiation and it can work effectively under artificial UV radiation from industrial UV sources⁽⁹⁾. Generally, artificial sources of UV light are expensive and they can affect negatively on general health of the workers. In General, this type of light is harmful to human, plants and other living organisms and can cause severe harms for living species in case of long term duration of UV exposure⁽¹⁰⁻¹²⁾.

So that the key point in this context, is how to make a red shift in its absorption of this semiconductor to enable this photocatalyst to be photoexcited under visible light of the solar spectrum. However, this aim can be approached via surface modification and currently different methods can be used to approach this ultimate goal. Different methods can be used in surface modification and among these methods surface sensitization using a suitable photosensitizer can be a good approach towards absorption of visible light with high efficiency⁽¹³⁾.

For sensitized photocatalysts, photosensitizer can absorb light in visible region of solar spectrum, then excited state of photosensitizer can inject electron in to the conduction band of the desired photocatalyst. This electron can participate in the redox reaction with the adsorbed specie on the surface of zinc oxide or any other photocatalyst. Among different applications of photocatalytic reactions, environmental applications are important type of these applications and photocatalytic treatment of industrial wastewaters seems to be one of the most important application as there are a significant increment in the levels of environmental pollution especially from industrial wastewaters that are discharged from textile factories to the rivers and other streams. This type of pollutants can effect on water, air and soil and hence can cause massive toxicity to all living organisms and plants. In this type of processes^(14,15).

Among different types of the used photocatalysts, zinc oxide can play important role in removal of the colored dyes from industrial wastewaters due to above mentioned catalytic properties and its activity under solar spectrum can be increased upon sensitization using suitable photosensitizers.

The present study involves removal of methylene blue dye from simulated industrial wastewaters using over both neat and riboflavin sensitized zinc oxide.

2. EXPERIMENTAL PART

2. 1. Removed dye

In our current study the photocatalytic activity of neat and sensitized ZnO was investigated via using MB dye as a model of dye polluted industrial wastewater as this dye is widely used in many modern industries. It is molecular formula (MF: $C_{16}H_{18}N_3SCl$), and its molecular weight (MM = 319.85 g/mol). This dye was purchased from Sigma Aldrich Company (98%), and it was used as it was provided without any additional purification processes.

2. 2. Sensitization of Zinc oxide surface with riboflavin

In this work, zinc oxide was provided by (Fluka Company, 99.5%), and the used photosensitizer was RF which was used as a photosensitizer in the sensitization of ZnO surface. Its molecular formula (MF: $C_{17}H_{20}N_4O_6$) and its molecular weight (MW: 376,36 g/mol). Surface sensitization was performed using impregnation method⁽¹⁶⁾. According to this method, different ratios of ZnO (2-5%) was added into solution of RF in propanol (2×10^{-5} M) under air atmospheric conditions with continuous stirring at 20 C for four hours. The resulting samples was kept aside for two hours under air at room temperature, the obtained samples were filtered out and the obtained precipitates were washed with DW carefully for some times to remove weakly adsorbed molecules of RF sensitizer. Then the resultant samples were dried in a vacuumed oven at 30 °C for overnight to give RF sensitized ZnO (RF/ZnO).

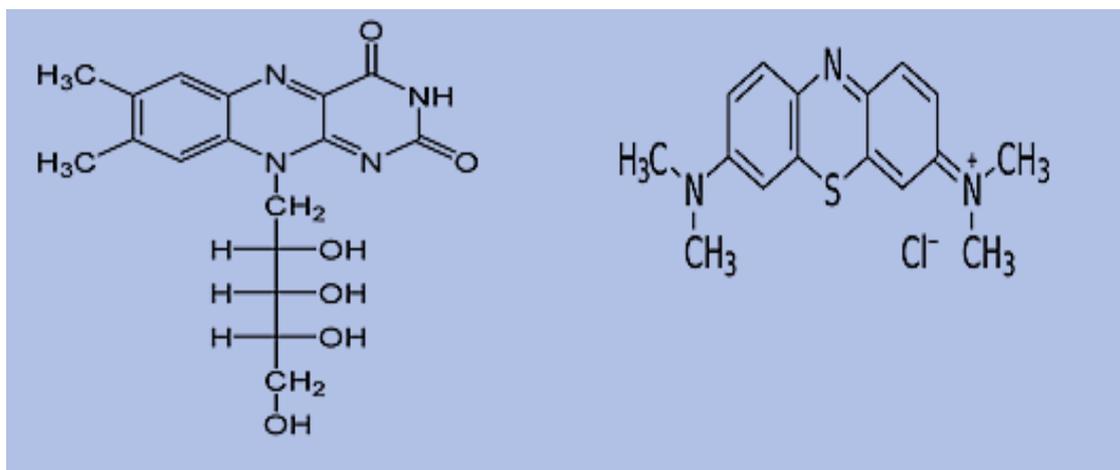


Figure 1. Chemical structure of Riboflavin photosensitizer (left) and methylene blue (right).

2. 3. Fourier transform infrared spectroscopy (FTIR)

Functional groups at the surface of both neat ZnO and RF/ZnO were investigated with FTIR spectroscopy using Perkin Elmer Spectrophotometer. All measurements were recorded in the range from 400 to 4000 cm^{-1} with scan rate of 1 cm^{-1} . Prior to run samples, all of them were mixed with KBr salt, and were made as pellets using a suitable pressing with Perkin Elmer hydrolytic pump.

2. 4. X-ray powder diffraction (PXRD)

Crystal structure for both for neat zinc oxide. The modes of powder x-rays diffraction and RF/ZnO was investigated using powder X-rays diffraction (PXRD). XRD patterns modes were recorded with Simadzu-6000 X-ray diffractometer with a nickel filter using monochromatized $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. For all runs, scan rate was at 2° (2θ) per min, and the range of this scan was recorded from ($2\theta = 20^\circ - 60^\circ$).

2. 5. Photocatalytic removal of methylene blue over neat and sensitized ZnO

The photocatalytic activity of neat ZnO and RF/ZnO was conducted via following photocatalytic removal of MB dye from the simulated industrial wastewaters samples. To perform that, a series of experiments were undertaken using different mass loading of the used materials in MB solution (30 mL, 30 ppm). Before starting illumination, the dark reaction was studied by following the adsorption of MB dye over the photocatalyst under dark conditions until reaching equilibrium time for dye adsorption. This time of dark reaction which was 10 minute for RF/ZnO and 12 minutes for neat ZnO will be considered for all reactions. After dark reaction time irradiation was started using UV light from middle pressure mercury lamp.

The optimum conditions for dye removal were investigated using different reaction conditions such as using different masses of the catalyst, different sensitization ratios of RF photosensitizer, different reaction temperatures as well as study the effect of duration time of reaction. Upon stating illumination of reaction mixture with continuous stirring under normal air conditions. Then for each run, periodically, samples (2 mL) of the reaction mixture was withdrawn and then centrifuged for sometimes to separate any solid materials. The optical density of the obtained supernatant liquid was recorded at the 665 nm to follow the amount of the remaining MB dye in the irradiated reaction mixture.

3. RESULTS AND DISCUSSION

3. 1. Fourier transform infrared spectroscopy

Fourier transform infrared spectra for ZnO and RF/ZnO were recorded and these are shown in Figure 2.

From these spectra, it can be seen that there are peaks in the range of $400- 590 \text{ cm}^{-1}$ which are related to the stretching vibration mode of zinc oxide (Zn-O) bonds in the surface of both ZnO and RF/ZnO. Generally, these are characteristic peaks that confirm the presence of metal-oxygen bond at the surface of these materials⁽¹⁷⁾.

The peaks that appear around 1640 cm^{-1} and the weak peak around 3440 cm^{-1} are attributed to the modes of stretching of hydroxyl groups at the surface of the catalyst.

The weak band that appears around 3410 cm^{-1} is assigned to vibration modes of O-H groups at the surface of both ZnO and RF/ZnO. The band around 2980 cm^{-1} is assigned to C-H vibration modes at the surface of RF/ZnO and this peak doesn't appear at the spectrum of neat ZnO. The band that appears around 2350 cm^{-1} is related to the CO_2 adsorption from ambient atmosphere on the surface of zinc oxide⁽¹⁸⁾.

Interaction between ZnO surface and RF photosensitizer results in formation of new bonding in comparison with bare ZnO. These peaks appear around 1600 cm^{-1} and is assigned to the vibration modes of $-\text{C}=\text{C}-$ stretching. The peak appears around 1130 cm^{-1} is attributed to the stretching vibrations modes of $-\text{N}=\text{O}$ bonds.

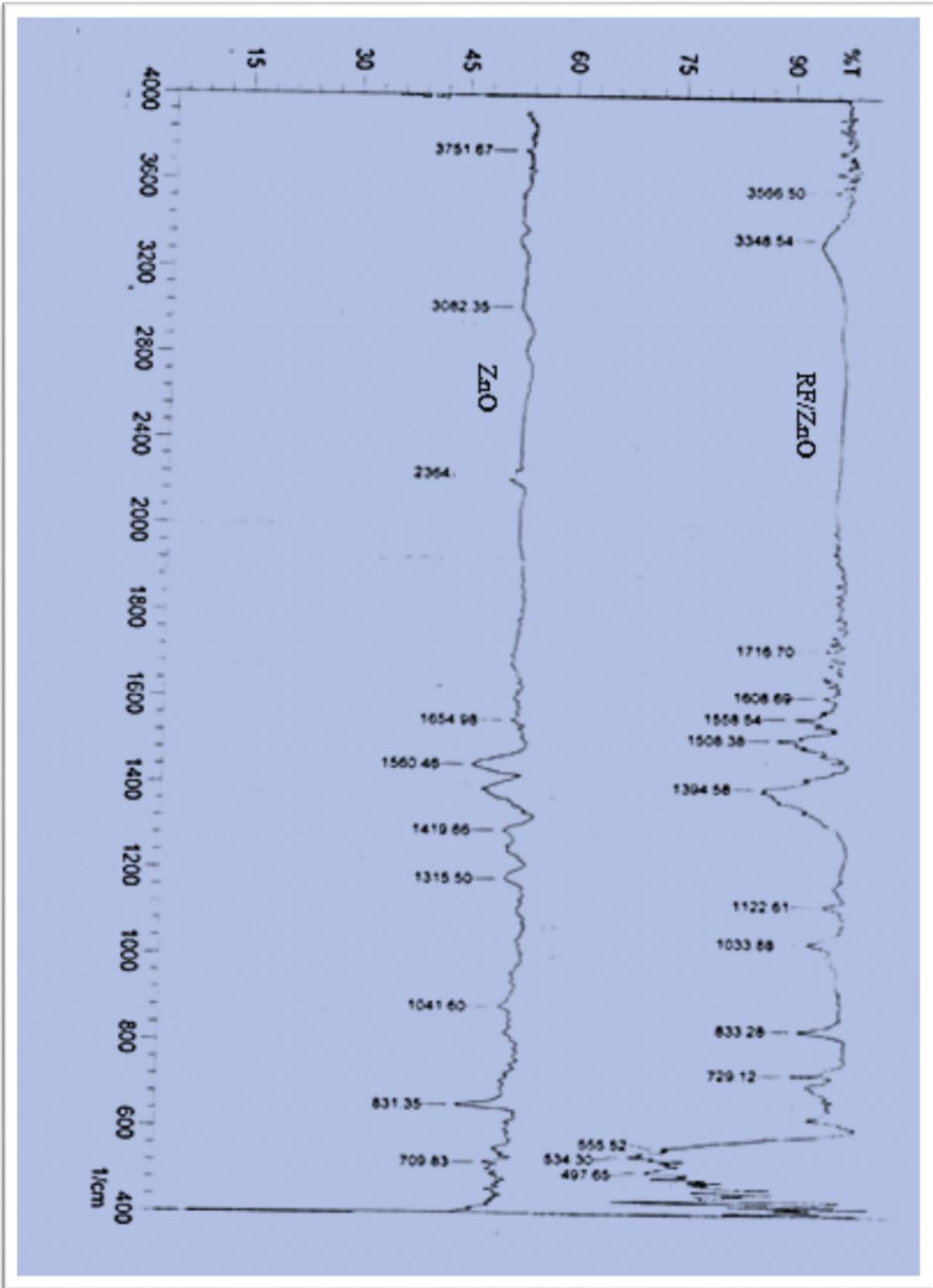


Figure 2. FTIR spectra for neat ZnO and RF/ZnO.

The band around 3210 cm^{-1} is assigned to N-H stretching modes. The weak band around 810 cm^{-1} is relates to bending of C-H bonds. Vibration modes of $-\text{CH}_3$ group appears around 1445 cm^{-1} . Weak band at 3080 cm^{-1} is relates to the vibration modes of aromatic C-H bonds⁽¹⁹⁾.

3. 2. X-ray diffraction for neat and sensitized zinc oxide

The XRD patterns of crystallite structure for both ZnO and RF/ZnO was investigated using XRD analysis. From the recorded XRD patterns for neat and sensitized zinc oxide it can be found that modification surface of ZnO by sensitizing with RF doesn't affect significantly on its crystal structure and its XRD patterns for neat and sensitized form are almost the same. XRD patterns for neat and sensitized ZnO are summarized in Figure 3.

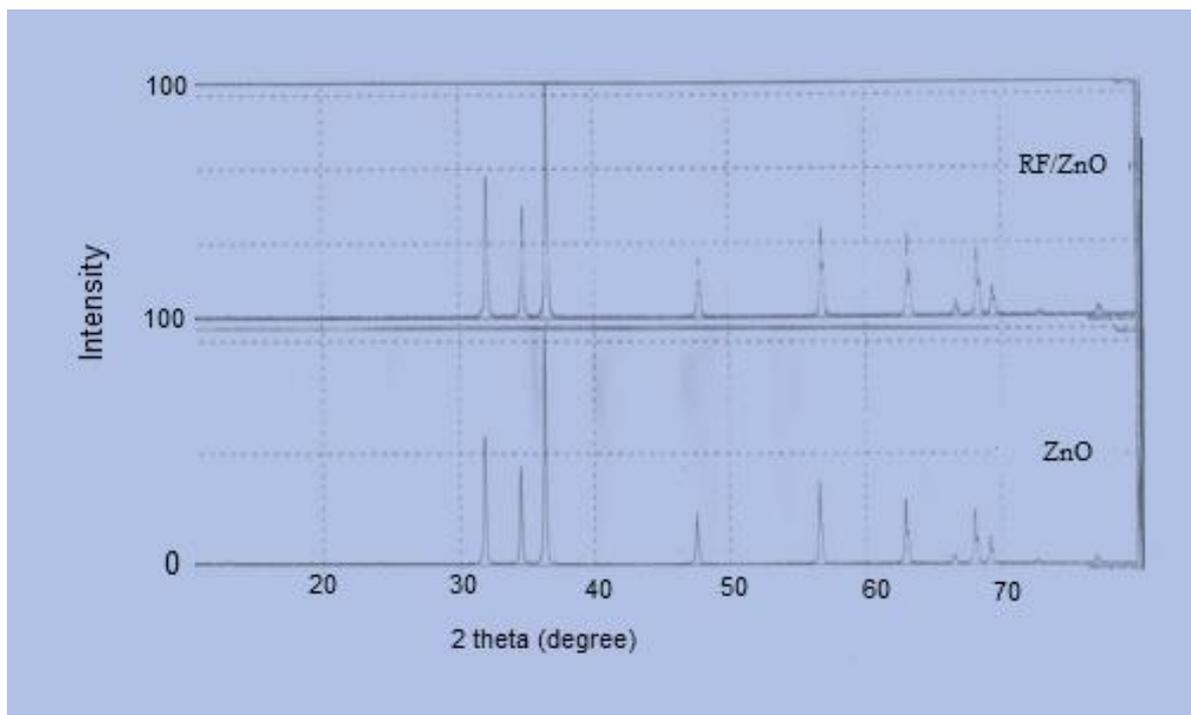


Figure 3. XRD patterns for neat and RF sensitized zinc oxide.

From the above XRD patterns that were recorded for neat and RF sensitized zinc oxide it can be concluded that, the main features of XRD for neat zinc oxide don't affect by the presence of sensitizer molecules on the surface and the patterns for two cases are almost similar to each other. Upon surface sensitization there were very slightly changes in the positions of the peaks as well as changes in the relative intensities of these peaks. Also from the obtained results it can be found that, the main peaks of zinc oxide after sensitization almost have same features with slightly shifting in their positions at sensitized zinc oxide. The most important thing in this point is the increase in the full width high maxima (FWHM) for RF/ZnO upon sensitization of the surface while FWHM for neat zinc oxide they were slightly smaller. The particle size of the catalyst is related to this value in inverse proportionality. This means that as the value of FWHM was smaller, then the particle size will be larger. From the

obtained results in this study, sensitization of zinc oxide with RF results in reduction of particle size. The obtained values for neat and doped zinc oxide are summarized in Table 1.

Table 1. XRD data for neat and RF sensitized zinc oxide.

Catalyst	2Theta (deg)	FWHM	Intensity (counts)
ZnO	31.8330	0.16860	640
	34.4856	0.16300	485
	36.3191	0.16160	1148
RF/ZnO	32.0628	0.19542	411
	34.7181	0.18528	305
	36.5429	0.19485	705

From the above results, it's clear that the main three peaks for RF/ZnO have higher values for FWHM in comparison with those for neat zinc oxide. This gives indication to report that sensitized zinc oxide in these ratios with RF has smaller particles size in comparison with that of bare ZnO⁽²⁰⁾. It is well known that the activity of the catalyst would increase with decrease size of its particle and with the increase of its surface area²⁰.

3. 3. The optimization of mass of the used catalyst

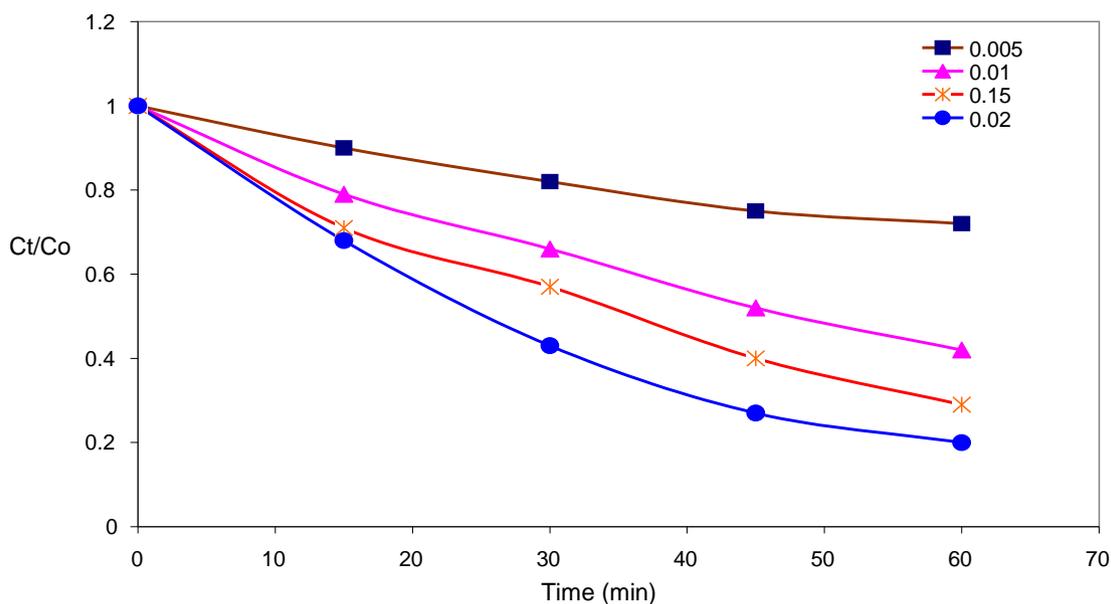


Figure 4. Photocatalytic removal of MB from aqueous solution using different masses of the catalyst.

In order to use the catalytic material in a perfect concentration loading in the suspension of reaction, a series of experiments were undertaken at other constant reaction conditions. This can be achieved using a constant MB dye concentration (30 ppm, 30 mL) of reaction mixture at 25 °C under normal air conditions and continuous stirring for one hour with using different mass of the catalyst for each case under irradiation with UV light and the activity of the photocatalytic dye removal was investigated by following the absorbance of supernatant liquid periodically at 554 nm. The obtained results was presented as C_t/C_0 versus irradiation time as shown in in Figure 4.

From the above results, it is clear that there was a progressive increase in the percentage of MB removal from reaction mixture with increase in the amount of the used RF/ZnO under the same reaction conditions. This observation can be explained according to the second law of photochemistry which states that, in the primary photochemical processes only one photon ($h\nu$) can be absorbed by one particle of the catalyst, this process is called photochemical equivalent.

So that increasing number of particles of the used catalyst under a constant illumination rate with a constant source of light would lead to increase numbers of the absorbed photos⁽²¹⁾. Then these particles will be photoexcited and then participated in redox processes on the surface of the photocatalyst. This process can lead to increase the photocatalytic activity of the used catalyst.

3. 4. The photocatalytic activity of neat and RF sensitized ZnO.

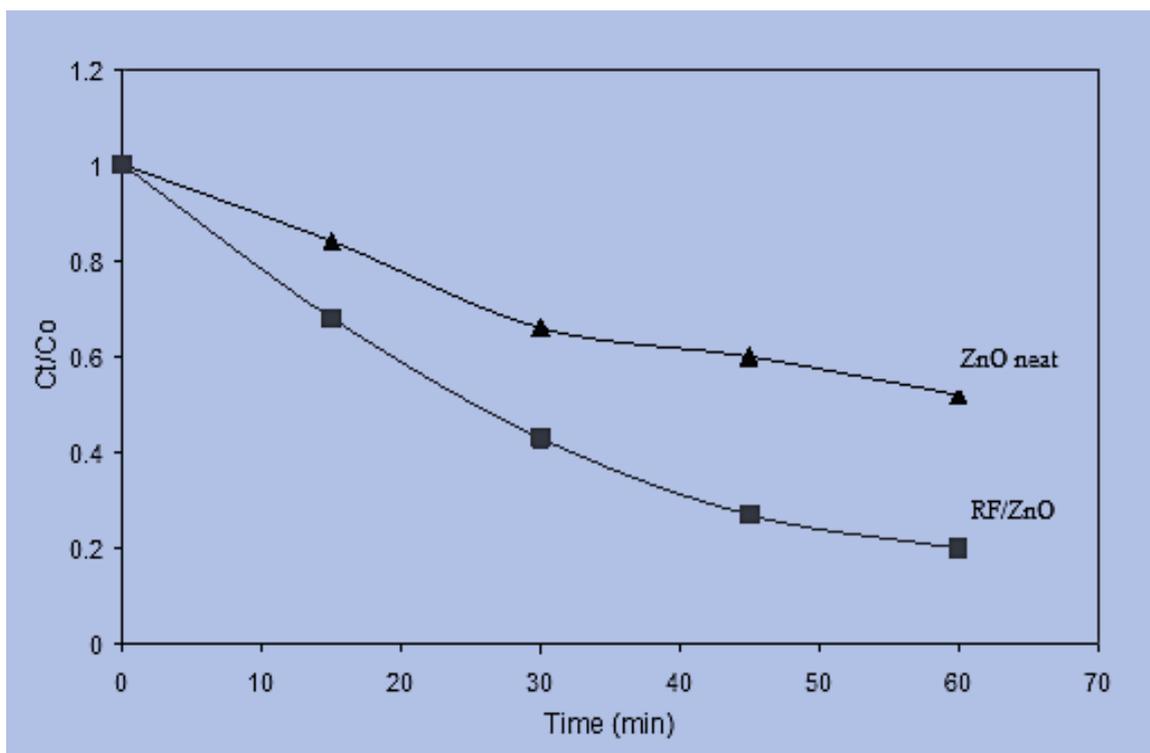


Figure 5. Comparison of photocatalytic activity for neat and RF sensitized ZnO.

In order to investigate the effect of sensitization of ZnO with RF sensitizer on its photocatalytic activity, a series of experiments were performed using 0.02 g of both neat zinc oxide and that sensitized with RF at 25 °C. In each experiment (30 ppm, 30 mL) of MB aqueous solution was suspended under irradiation with UV light with continuous stirring for one hour. The photocatalytic was investigated by following MB dye removal and the absorbance of supernatant liquid was recorded at the 665 nm. The obtained results were reported as dye removal (Ct/Co) as a function of irradiation time as summarized in Figure 5.

From the above results, it can be found that RF/ZnO was more efficient than neat ZnO in the dye removal from aqueous solution under the same reaction conditions. This observation may result from reduction of rate of back electron transfer (recombination reaction). This process normally occurs with neat photocatalyst upon irradiation with radiation of a proper energy ($h\nu \geq E_g$). Upon irradiation of the photocatalyst with light with a sufficient energy that is equal to or greater it band gap energy. Valence band hole (h^+_{VB}), and Conduction band electron (e^-_{CB}) would be generated at valence and conduction band respectively. After generation of these redox species upon photoexcitation, these are diffused from bulk into the surface of the catalyst⁽²²⁾.

Both of h^+_{VB} , and e^-_{CB} at the surface would participate in redox reactions with the pre-adsorbed species on the surface. The lifetime of these surface species are too short and its around 10^{-8} second, consequently, these species can recombine in what so called back electron transfer (Recombination reaction). This process can affect negatively on the activity of photocatalyst⁽²³⁾. The important point here is how to separate e^-_{CB} from h^+_{VB} for long time to give them a sufficient time to react with the surface adsorbed species. Sensitization of photocatalyst can help in this case, sensitizer can absorb light with high efficiency to yield singlet or triplet excited state of dye. Then this excited state of dye then can inject electron into the CB of the ZnO photocatalyst which can contribute in redox reaction on the surface with the adsorbed. This process can minimize the rate of recombination reaction and/or sometimes no recombination reaction at all. In this case there is not recombination reaction as only e^-_{CB} will be available without h^+_{VB} . This observation can give a higher photocatalytic activity in dye removal when use MO. ZnO in comparison with using neat ZnO species producing some active radicals such as OH^\cdot , O^{2-} , and H_2O_2 . Generally, these reactive species can contribute in the photodegradation of dye to yield smaller fragmentation species and these can produce inorganic final products such as CO_2 and H_2O .

3. 5. The effect of level of sensitization of ZnO with RF sensitizer

To study the effect of level of sensitization on the photocatalytic activity of RF/ZnO, a series of samples were prepared with different sensitization level of RF/ ZnO. These concentration levels were 0.005%, 0.01%, 0.015%, and 0.02%. A series of experiments were performed using different sensitization materials using 0.02 g for each run at 25 °C with 30 mL of aqueous solution of MB (30 ppm) with continuous stirring under irradiation with UV light for one hour. Photocatalytic dye removal was followed by recording the absorbance at 665 nm. The obtained results are presented in Figure 6.

From these above results, it can be seen that the percentage of MB dye removal was improved with increase of sensitization loading of the sensitizer over surface of zinc oxide. Increasing in the amount of sensitizer molecules on zinc oxide in the range of these above levels can increase the rate of light harvesting of photons and producing excited states of the sensitizer molecules^(24,25).

This process can lead to increase the efficiency of electron injection electrons into the CB of zinc oxide, this process can lead to increase the efficiency of MB dye removal under these circumstances.

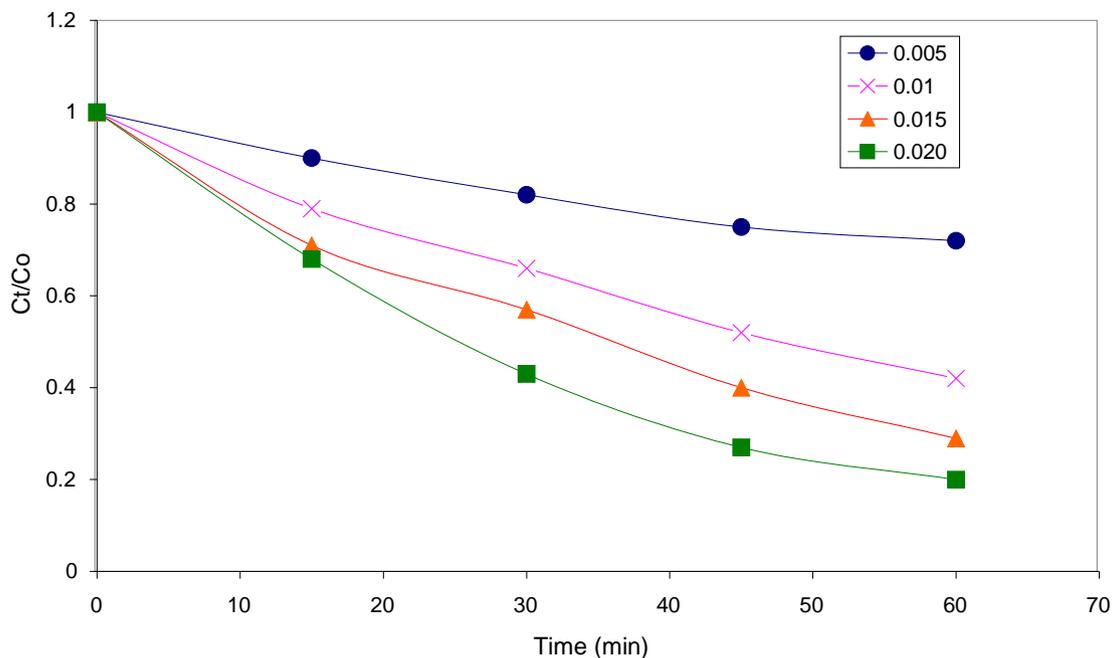


Figure 6. Effects of level of sensitization of ZnO with RF on its activity on dye removal.

4. CONCLUSIONS

This work showed that modification of surface of zinc oxide by photosensitization with riboflavin can enhance its catalytic activity. It was found that sensitization of zinc oxide doesn't alter its crystallite structure significantly. Also, its particle size after sensitization became relatively smaller as it was found from XRD patterns for neat and RF/ ZnO. The photocatalytic activity of RF/ZnO was more efficient than neat zinc oxide under the same reaction conditions.

References

- [1] R. Grieken, J. Guado, M. Lop, J. Marugan, *J. Photochem. Photobiol. A: Chem.* 2002, 148, 315.
- [2] K. Sayama, K. Mukasa, R. Yuab, H. Arakawa, *J. Photochem. Photobiol. A: Chem.* 2002, 148, 71.
- [3] U. Staffored, K. Gray, P. Kamat, *J. Phys. Chem.* 1998, 98 (25), 63.

- [4] Salvador, M. Pascual, J. Adell, A. Requeni, J. March, *J. Pharmaceutical and Biomedical Analysis*, 2002, 22, 301.
- [5] R. Li, S. Yabe, M. Yamashita, S. Momose, S. Yoshida, S. Yin, T. Sato, *Mater. Chem. Phys.* 2002, 72, 39.
- [6] B. Kim, J. Paik, Y. Han, N. Lee, B. Lee, *J. Kor. Ceram. Soc.* 2000, 37(1), 1.
- [7] T. Tsuzuki, P. McComick, *Scripta Mater.* 2001, 44, 1731.
- [8] Z. Wang, H. Li, *Appl. Phys. A*, 2002, 74, 201.
- [9] Attia, S. Kadhim, F. Hussein, *E. J. Chem.* 2008, 5(2), 219.
- [10] S. Rengarag, S. Hyeon, S. Sivabalan, B. Arabindo, and V. Murugesan, *Wastes Management*, 2002, 22, 543.
- [11] R. Rozado, M. Otero, A. Moran, and I. Garcia, *J. Hazardous Materials*, 2005, 124, 181.
- [12] K. Imamura, E. Ikeda, T. Nagayasu, T. Sakiyamo, and K. Nakanishi, *J. Colloid Interface Sci.* 2002, 245, 50.
- [13] N. Graham, X. Chen, and S. Jayaseelan, *Water Sci. Technol.* 2001, 43, 245.
- [14] T. Budinova, E. Ekinci, F. Yardim, A. Grimm, E. Bjornbom, V. Minikova, and M. Goranova, *Fuel Processing Technology*, 2006, 87, 899.
- [15] Niya, W. Duad, F. Mjalli, F. Abnisa, and S. Shafeeyan, *Chemical Engineering Research and Design*, 2011, 90(6), 776.
- [16] F. Hussein, and A. Alkhateeb, *Desalination*, 2007, 209, 350.
- [17] Jun S., Kim S., Han J., *J. Kor. Ceram. Soc.* 1998, 35(3), 209.
- [18] Taps A., Majewaski P., Aldinger F., *J. Am. Ceram. Soc.* 2000, 83(12), 2954.
- [19] R. Nandini, and B. Visholakshi, *E. J. Chem.* 2012, 9(1), 1.
- [20] 20-B. Yuhas, D. Zitoun, P. Pauzauskie, R. He, P. Yang, *Angew. Chem. Int. Ed.* 2006, 45, 420.
- [21] M. Hirds, *J. Coatings Technol.* 1976, 48, 75.
- [22] H. Gerischer, M. Beverly, F. Tributsch, *Electrochem. Acta* 1968, 13, 1509.
- [23] D. Edward, J. Googenough, A. Andrew, R. Seddon, R. Wright, *Faraday Disc.*, 1981, 70, 285.
- [24] H. Kawai, T. Nagamura, *J. Photochem. Photobiol. A: Chem.* 1995, 92, 105.
- [25] S. Lakshmi, R. Rengarathen, S. Fujita, *J. Photochem. Photobiol. A: Chem.* 1995, 88, 163.