Photocatalytic removal of methylene blue dye from simulated industrial wastewater over neat and methyl orang sensitized zinc oxide

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Abstract:

The current study involves removal of methylene blue dye (MB) from the simulated industrial wastewaters over neat and methyl orange sensitized zinc oxide Sensitization of zinc oxide surface using methyl orange (MO) as a photosensitizer was performed by impregnation method. Surface sensitization with this photosensitizer was studied using Fourier transform infrared spectroscopy (FTIR) and powder x- ray diffraction (XRD). Removal of MB dye from aqueous solution was followed by measuring the absorbance of the supernatant liquid at 665 nm. Sensitized zinc oxide with MO showed higher activity in dye removal in comparison with the neat form under the same reaction conditions.

Keywords: Zinc oxide modification, Removal of methylene blue, surface sensitization.

الخلاصة:

تتضمن هذه الدراسه ازالة صبغة المثيلين الازرق الموجوده في نموذج للمياه الصناعيه باستخدام اوكسيد الزنك المجرد والمحسس بصبغة المثلين البرتقالي كمتحسس ضوئي. تمت عملية التحسيس للسطح باستعمال طريقة الاشباع . تمت دراسة السطح المحسس باستخدام طيف الاشعه تحت المراء وكذلك بواسطة حيود الاشعه السينيه. تم متابعة عملية ازالة الصبغه من المحلول المائي للصبغه من خلال متابعة الامتصاصيه عند الطول الموجي 665 نانومتر. لقد وجد في هذه الدراسه ان الاوكسيد المحسس بالصبغه كان اكثر كفاءة من المجرد في عملية ازالة الصبغه ولنفس ظروف التفاعل المختلفه

الكلمات المفتاحية : اوكسيد الزنك المجرد ، صبغة المثلين الازرق ، تحسيس للسطح

1- Introduction:

Catalytic processes were initiated more than forty years ago when Bard and Frank established heterogeneous photocatalysis systems using a composition of semiconductors photocatalyst and a suitable source of light (R.Grieken,2000and KSayama,2000). In the wide range of the semiconductor photocatalysts, zinc oxide appeared to be a good candidate photocatalyst that can be used for many(U.Stafford,1998). This photocatalyst has promising 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 recovered from reaction mixture (A.Salvador,2002 and R.Li2002). Generally, zinc oxide can be used widely in photocatalytic processes under irradiation with light of a proper photon energy ($h\nu \geq Eg$). It has an excitation bandgap energy of ZnO is ($Eg= 3.30$ eV) (B.Kim 2000) , and this energy fall in range of ultraviolet radiation of solar spectrum (T.Tsuzuki,2001 and Z.Wang2002). From this value of Eg of zinc oxide it can be photoexcited only under irradiation with UV light. The main drawback in this point is that UV light composes only 5% of the solar energy. So that, ZnO canot be excited under solar irradiation and it can work effectively under artificial UV radiation from industrial UV sources (A.Attia,2008). UV light artificial sources are expensive and they can affect negatively on general health of the workers as the UV light is harmful and can cause skin cancer upon long term duration of UV exposure (S.Renagarag,2002 and R.Razado,2005).

In this context, the main challenge is to make a red shift in its absorption to enable this photocatalyst to be photoexcited under visible light of the solar spectrum. To approach this aim, different methods can used to approach this aim. From these methods, sensitization of the surface with photosensitizer can be a good approach towards absorption of visible light with high efficiency (N.Graham,2001). In this method, excited state of photosensitizer can inject electron in to the conduction band of zinc oxide. This electron can participate in the redox reaction for the adsorbed specie on the surface of zinc oxide. Among different applications of photocatalytic reactions, industrial wastewaters treatment seems to be one of the most important applications as there are an increase in the level of environmental pollution especially from industrial wastewaters that are discharged from textile factories to the rivers and other streams. This type of pollutants can affect on water, air and soil and hence can cause massive toxicity to all living organisms and plants. In this type of processes (T.Budinova,2006 and A.Niya,2001) . Zinc oxide can play important role in removal of the colored dyes from industrial wastewaters.

The present study involves removal of methylene blue dye from simulated industrial wastewater using neat zinc oxide . Also the activity of sensitized zinc oxide in dye removal will be investigated.

2- Experimental part

2-1: Used adsorbent:

Methylene blue dye was used in this study as a model of wastewater polluted dye which is widely used in the textile industries , its molecular formula molecular formula ($C_{16}H_{18}N_3SCl$) This dye was purchased from Sigma Aldrich Company (98%) , this dye was used as it was provided without any further purification processes.

2-2 Sensitization of Zinc oxide surface with methyl orange

Zinc oxide that was used in this work, was ZnO (Fluka Company, 99.5%). The used photosensitizer, was methyl orange which was used as a photosensitizer in the modification of ZnO surface. Molecular formula of this dye is ($C_{14}H_{14}N_3NaO_3S$) . The surface of ZnO was sensitized with this dye by impregnation method(F.Hussein2007). In this pocedure, different ratios of ZnO (2-5%) was added into solution of dye in propanol 2 x10^{-5} M under air atmosphere with continuous stirring at 20 □C for three hours. Then, the samples were kept out for one hour under air, then filtered out and the precipitate washed carefully with distilled water for some times to remove weakly adsorbed molecules of the used sensitizer. The resultant samples were dried in vacuumed oven at 3C for overnight.

2-6 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra for both neat ZnO and that sensitized with MO dye was studied using Perkin Elminer Spectrophotometer. All measurements were made in the renge of 400 to 4000 cm^{-1} with scan rate of 1 cm^{-1}. All these samples were mixed with KBr salt, and made as pellets using a suitable pressing with Perkin Elmer hydrolytic pump.

2-8 X-ray powder diffraction (PXRD)

The modes of powder x-rays diffraction were studied for bare zinc oxide and that sensitized with MO dye These patterns were recorded with Simadzu-6000 X-ray diffractometer with a nickel filter using monochromatized CuKα radiation at 40 kV and 30 mA. The scan rate was at 2° (2θ) per min, the range of this scan was 20° 2θ to 60° 2θ.

2-9 Photocatalytic degradation of methylene blue over neat and sensitized ZnO

The photocatalytic activity for both neat ZnO and that sensitized with MO was investigated by following photocatalytic removal of MB dye from the simulated industrial wastewater. To do that, a series of experiments were performed using different mass loading of the used materials in 30 mL of 30 ppm of MB under irradiation with UV light from middle pressure mercury lamp. The optimum conditions for dye removal were conducted using different parameters including of applying different masses of the catalyst, different sensitization ratios of MO dye, different reaction temperatures as well as study the effect of duration time of reaction. Before stating photocatalytic reaction, reaction mixture was kept under stirring for ten minutes for each set of reaction in order to reach adsorption equilibrium. Then for each run and periodically, samples (2 mL) of the reaction mixture were withdrawn and then centerfuged for some times carefully. The optical density of the obtained supenantan liquid was recorded at the 665 nm to follow the amount of the emaining dye in the reaction mixture.

3-Results and Discussion:

3-1 Fourier transform infrared spectroscopy

FTIR spectra for neat zinc oxide and that sensitized with methyl orange are illustrated in Figure 1.

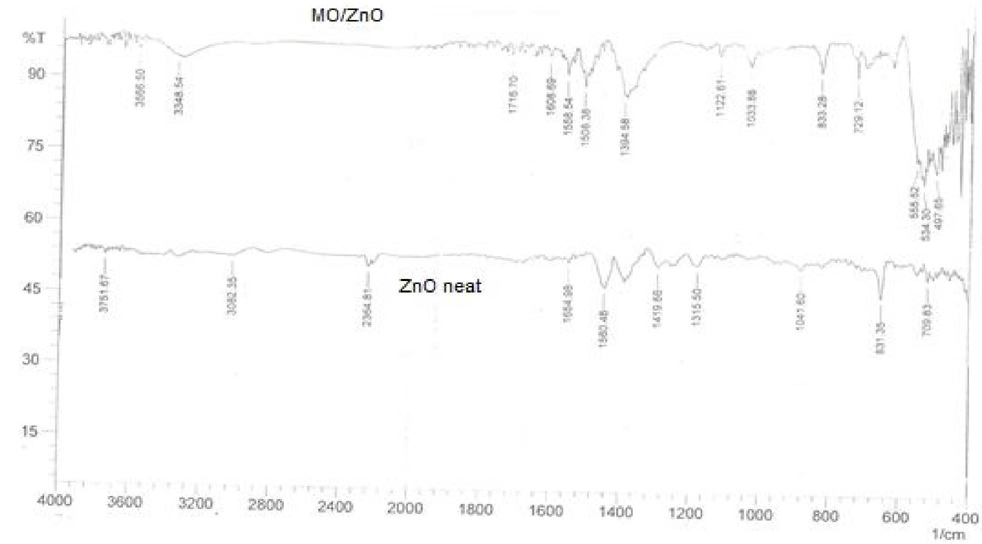


Figure-1: FTIR spectra for neat and MO sensitized zinc oxide

The peak that appears around 450 cm^{-1} and 590 cm^{-1} is related to the stretching vibration mode of zinc oxide (Zn-O) bonds. The characteristic peak of zinc oxide also appears in the modified form of this oxide (MO/ZnO) **(Jun.S.1998).**

The modes of stretching of hydroxyl groups for the catalyst appear around 1630 cm^{-1} and the weak band around 3436 cm^{-1}. These peaks are related to the modes of stretching of hydroxyl groups for the catalyst. The band around 2900 cm^{-1} is assigned to C-H vibration modes. The band that appears around 2350 cm^{-1} is assigned to the adsorption of CO_2 from ambient atmosphere on the surface of zinc oxide (Taps.A.2000) On the other hand modification of ZnO surface with MO can result in formation of new bonding. In this context, peaks appear around 1599 cm^{-1} is assigned to the vibration modes of –C=C- stretching. The peak appears around 1119 cm^{-1} is assigned to the stretching mode of –S=O bonds. The band around 3209 cm^{-1} is assigned to N-H stretching modes. Vibration modes of $–CH_3$ group appear around 1442 cm^{-1}. Weak band at 3080 cm^{-1} relates to the vibration modes of aromatic C-H bonds(R.Nandini,2012)The weak peak that appears around 802 cm^{-1} can be assigned to bending of C-H bonds. Vibration modes of $–CH_3$ group appear around 1442 cm^{-1}.

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

The XRD patterns for both neat ZnO and sensitized with MO were investigated using XRD patterns. From these patterns it can be seen that modification of zinc oxide via sensitization with this dye does not affect significantly on its structure. XRD patterns for these materials are shown in Figure 2**.**

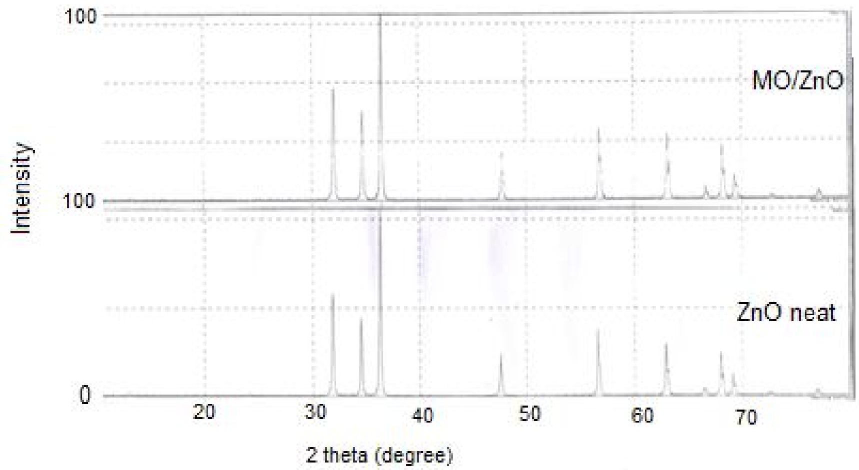


Figure-2: XRD patterns for neat and MO sensitized zinc oxide

It can be seen that, the main features of XRD patterns for neat zinc oxide don't affect by the presence of sensitizer molecules on the surface. Generally, there were very slightly change in the positions of the peaks as well as change in the relative intensities of these peaks. It can be concluded that, the increase in the full width high maxima (FWHM) for MO/ZnO upon sensitization of the surface with MO can result in reduction in particle size for ZnO/MO. In this case, particle size of the catalyst is related to this value in inverse proportionality. These values are summarized in Table1.

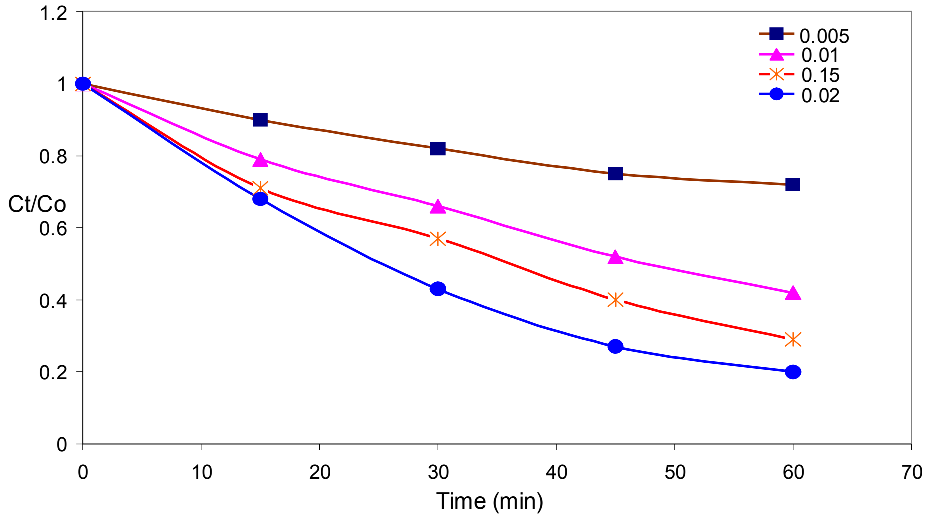
Table 1: XRD data for neat and MO sensitized zinc oxide

Catalyst	2Theta (deg)	FWHM	Intensity (counts)
ZnO	31.8330	0.16870	641
	34.4856	0.16310	486
	36.3191	0.16170	1150
MO/ZnO	32.0628	0.19560	400
	34.7181	0.18530	309
	36.5429	0.19490	701

From the above table, its clear that the main three peaks for MO/ZnO have higher values for FWHM in comparison with those for neat zinc oxide. This means that sensitized zinc oxide has smaller particles size in comparison with the neat form[19]. Beside that the peaks of zinc oxide after sensitization almost have same features with slightly shifting in their positions at sensitized zinc oxide. The activity of the catalyst would increase with the reduction in particle size of catalyst particles.

3-1 The optimization of mass of the used catalyst

The effect of mass of the used catalyst on the photocatalytic activity, a constant dye concentration 30 ppm in 30 mL of reaction mixture at 25 C under ambient atmospheric conditions and continuous stirring for one hour with using different mass of the catalyst for each case. These results are shown in Figure 3.



Figures **3**: Photocatalytic removal of MB from aqueous solution using different masses of the catalyst

From these results, it can be seen that there is a progressive increase in the percentage of dye removal with the increase in the amount of the used catalyst under the same reaction conditions. This observation can be explained according to the first law of photochemistry, in the primary step of photochemical processes one photon of light can be absorbed by one particle of the used catalyst. In this context, increasing number of molecules of the used catalyst under illumination with a constant source of light would lead to increase numbers of the adsorbed photos. This process can increase the photocatalytic activity of the used catalyst via excitation of large numbers of the catalyst, these particles then contribute in the photocatalytic processes at the surface of the catalyst.

3-2 The photocatalytic activity of neat and sensitized ZnO

The photocatalytic activity of neat and sensitized ZnO was conducted by performing, a series of experiments under a controlled reaction conditions. In all experiment, 0.02 g of neat zinc oxide and MO/ZnO at 25 C was suspended in 30 mL of 30 ppm of aqueous solution of MB with continuous stirring for one hour. The photocatalytic removal of this dye was performed by measuring absorbance for the supernatant liquid at 665 nm. These results are shown in Figure 4.

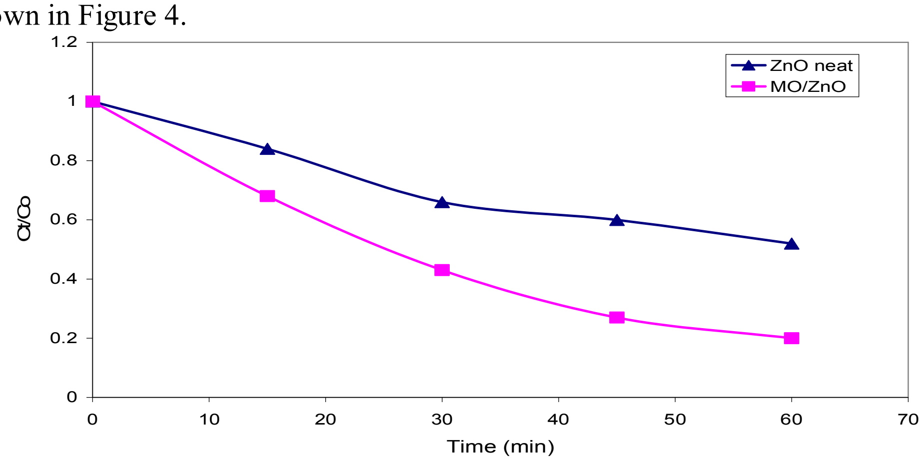


Figure 4**:** Comparison of photocatalytic activity for neat and MO sensitized ZnO

The obtained results showed that sensitization of zinc oxide with MO photosensitizer yielded higher activity in dye removal in comparison with neat zinc oxide under the same reaction conditions. This may result from reduction of rate of back electron transfer which commonly occurs in case of irradiation of neat photocatalyst. Upon photoexcitaion, conduction band electron (e^-_{CB}) and valence band hole (h^+_{VB}) after generation are diffused from bulk into the surface of the catalyst (Yuhas,2006 and D.Edward,1981). At the surface of the catalyst, these redox species can participate in redox reaction with the pre-adsobed species on the surface. These reactive species have very short lifetime around 10^{-8} second, and consequently, if these species ar not consumed quickly by the adsorbed surface species, they can recombine in what so called back electron transfer (Recombination reaction). This process normally reduces the photocatalytic activity of the photocatalyst(H.Kawai,1995). Sensitization of photocatalyst can help in this case in the reduction of the rate of recombination reaction, sensitizer can absorb light with high efficiency to yield singlet or triplet excited state of dye. This excited state of dye then can inject electron into the CB of the photocatalyst which can contribute in redox reaction on the surface with the adsorbed species producing some active radicals suchas OH^-, O^-_2 , and H_2O_2, these active materials can contribute in the photodegradation of dye.

3-4 The effect of level of sensitization of ZnO with dye sensitizer

The effect of loading of photosensitizer on zinc oxide surface was studied by performing photoctalytic reactions using different loading levels of MO on ZnO surface. To do this, a series of samples were prepared with different sensitization level of Zn such as . 0.005%, 0.01%, 0.015%, and 0.02%. In this study, a series of experiments were carried out under different sensitization materials using 0.02 g for each run at 25 C with 30 mL of aqueous solution of MB with continuous stirring for one hour under irradiation with UV light. Photocatalytic removal of dye was followed by following the absorbance of MB dye from the aqueous solution at 665 nm. These results are shown in Figure 5.

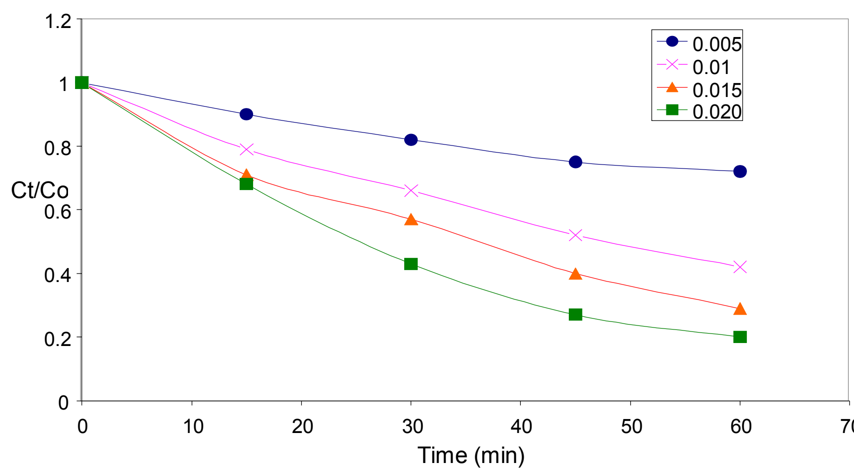


Figure 5**:** Effects of level of sensitization of ZnO with MO on its activity on dye removal

From these results , it is clear that, the efficiency of dye removal was enhanced with increase of sensitization levels of MO on ZnO surface. Increasing in the amount of MO molecules on zinc oxide in the above level can increase the rate of light harvesting of photons and generating excited states of the dye molecules(S.Lakshmi,1995). This process can lead to inject electrons into the CB of zinc oxide and consequently the activity of dye removal would increase under the same reaction conditions.

4. Conclusions

From the obtained results in this study, it was noted that modification of surface of zinc oxide by photosensitization with methyl orange can lead to improve of some of its catalytic properties. From the obtained XRD patterns for neat and sensitized zinc oxide it can concluded that sensitization doesn't alter crystallite structure of ZnO. In addition, particles size of the sensitized form became relatively smaller as it was found from XRD patterns. The photocatalytic activity of MO/ZnO was more efficient than neat zinc oxide under the same reaction conditions.

References:

Attia, A. S. Kadhim, F. Hussein, *E. J. Chem.*, **2008**, 5(2), 219.

Budinova, T. E. Ekinci, F. Yardim, A. Grimm, E. Bjornbom, V. Minikova, and M. Goranova, *Fuel Processing Technology*, **2006**, 87, 899.

Edward, D. J. Googenough, A. Andrew, R. Seddon, R. Wright, *Faraday Disc.*, **1981,** 70, 285.

Graham, N. X. Chen, and S. Jayaseelan, *Water Sci. Technol.*, **2001**, 43, 245.

Grieken, R. J. Guado, M. Lop, J. Marugan, *J. Photochem.* Photobiol. *A: Chem.*, **2002**, 148, 315.

Hussein, F. and A. Alkhateeb, *Desalination*, **2007**, 209, 350.

Jun S., Kim S., Han J., *J. Kor. Ceram. Soc.*, **1998**, 35(3), 209.

Kawai, H.T. Nagamura, *J. Photochem. Photobiol. A: Chem.*, **1995**, 92, 105.

Kim, B. J. Paik, Y. Han, N. Lee, B. Lee, *J. Kor. Ceram. Soc.*, **2000**, 37(1), 1.

Lakshmi, S. R. Rengarathen, S, Fujita, *J. Photochem. Photobiol. A: Chem.*, **1995**, 88, 163.

Li, S. R. Yabe, M. Yamashita, S. Momose, S. Yoshida, S. Yin, T. Sato, *Mater. Chem. Phys.*, **2002,** 72, 39.

Nandini, R. and B. Visholakshi, *E.J. Chem.*, **2012,** 9(1), 1.

Niya, A. W. Duad, F. Mjalli, F. Abnisa, and S. Shafeeyan, *Chemical Engineering Research and Design,* **2011**, 90(6), 776.

Rengarag, S. S. Hyeon, S. Sivabalan, B. Arabindo, and V. Murugesan, *Wastes Management*, **2002**, 22, 543.

Rozado, R. M. Otero, A. Moran, and I. Garcia, *J. Hazardous Materials*, **2005**, 124, 181.

Salvador, A. M. Pascual, J. Adell, A. Requeni, J. March, *J. Pharmaceutical and Biomedical Analysis*, **2002,** 22,301.

Sayama, K. K. Mukasa, R. Yuab, H. Arakawa, *J. Photochem. Photobiol. A: Chem.*, **2002**, 148, 71.

Staffored, U. K. Gray, P. Kamat, *J. Phys. Chem.*, **1998**, 98 (25), 63.

Taps A., Majewaski P., Aldinger F., *J. Am. Ceram. Soc.*, **2000**, 83(12), 2954.

Tsuzuki, T. P. McComick, *Scripta Mater.*, **2001**, 44, 1731.

Wang, Z. H. Li, *Appl. Phys. A*, **2002**, 74, 201.

Yuhas, D. Zitoun, P. Pauzauskie, R. He, P. Yang, *Angew. Chem. Int. Ed.*, **2006,** 45, 420.