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Modification of Surface of Zinc Oxide by Sensitization with Methyl Orange Photosensitizer

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ABSTRACT

This study involves removal of methylene blue dye (MB) from its aqueous solution using the concept of the photocatalytic reaction. Removal of this dye was conducted using neat zinc oxide nanopowder as a photocatalyst. Also the removal of this dye was performed via using modified photocatalyst by sensitization surface of the photocatalyst. Sensitization of ZnO surface using methyl orange sensitizer was conducted by impregnation method. Surface sensitization with this photosensitizer was investigated using powder X- ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). Removal of MB dye from aqueous solution was conducted by following the absorbance of the supernatant liquid at 665 nm. Sensitized zinc oxide with MO was more efficient than neat form in removal of MB from aqueous solution.

Keywords: Zinc oxide, Methylene blue, Photosensitizer.

INTRODUCTION

Photocatalysis processes were used more than forty years ago in many types of applications. The first pioneers in this field were Bard and Frank who established heterogeneous photocatalysis systems based on using semiconductors as photocatalysts [1,2] . Among different types of these photocatalysts, zinc oxide has been used widely in different applications including industrial and environmental applications [3]. This probably arises from its perfect properties such as high thermal stability, high resistance towards acids and bases, non-toxicity, high surface area, high refractive index, relatively low cost and it can be recovered from reaction mixture. Due to these properties, zinc oxide can be used in some modern fields such as UV protection material, field emission displays, thermoelectric materials and functional devices [4-6]. In addition to all these potential applications, it was used widely in photocatalytic processes under irradiation with light of a proper photon energy ($h\nu \geq Eg$). The bandgap energy of ZnO is ($Eg= 3.30$ eV), this amount of energy fall in range of ultraviolet radiation of solar spectrum [7-8]. Additionally, it ratio in solar radiation does not exceed 5% of whole solar energy and accordingly ZnO is inactive under solar irradiation and it can work effectively under artificial UV radiation from industrial UV sources [9]. Using these artificial sources for UV light is not effective from cost view beside that it 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 [10-12]. So that the key point is made a red shift in its absorption to enable it to be photoexcited under visible light of the solar spectrum. Different methods can applied to approach this goal, one of them is the sensitization of its surface with photosensitizer that can absorb visible light with high efficiency [13]. Excited state of photosensitizer inject electron in conduction band of zinc oxide, this then can participate in redox reaction on the surface. Recently, and as a result of different industrial activities there was 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, decolorization is the essential step in the treatment of wastewaters [14,15] . Zinc oxide can play important role in removal of the colored dyes from wastewater.

The present work is to investigate effect the modification of ZnO surface by sensitization with MO in its ability in the removal of MB from simulated industrial wastewater.

MATERIALS AND METHODS

Used Dye: The dye that is used in this study as a model of polluted dye methylene blue (MB), its molecular formula is ($C_{16}H_{18}N_3SCl$). This dye used as a model of polluted dyes in this study. This dye was provided by Sigma Aldrich Company (98%) and it was used without further purification.

Modification of Zinc oxide surface by sensitization: The used zinc oxide in this study was ZnO (Fluka Company, 99.5%)**.** Methyl orange dye is used as a photosensitizer in the modification of ZnO surface, its molecular formula is ($C_{14}H_{14}N_3NaO_3S$) . The surface of ZnO was sensitized with this dye by impregnation method [16]. According to this method, 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. After that the samples was keep out for one hour then filtered out and the precipitate was washed with distilled water number of times to remove from weakly adsorbed dyes. Then these samples were dried in vacuumed oven at 30 C for overnight. These dried samples were investigated using powder X-rays diffraction (PXRD), Fourier infrared spectroscopy (FTIR).

Fourier transform infrared spectroscopy (FTIR): Each of bare ZnO and that sensitized with MO dye was investigated using Perkin Elminer Spectrophotometer. Measurements were performed in the ranged from 450 to 4000 cm^{-1}. All these samples were grounded with KBr salt, then, these mixed samples were made as pellets using a suitable pressing with Perkin Elmer hydrolytic pump. All FTIR spectra were conducted in from range of 450- 4000 cm^{-1} with a resolution of 1 cm^{-1} for each run.

X-ray powder diffraction (PXRD): The patterns for each neat zinc oxide and that sensitized with MO dye were studied using Powder X-ray diffraction (PXRD). 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.

Photocatalytic degradation of methylene blue over neat and sensitized ZnO: In order to investigate the photocatalytic activity for each of neat ZnO and that sensitized with MO dye was performed. The photocatalytic removal of MB dye from aqueous solutions was followed. A series of experiments were undertaken 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. To obtain optimum conditions for dye removal different parameters were involved including 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 was withdramn 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.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy: FTIR spectra of both neat zinc oxide and that sensitized with methyl orange are illustrated in figure 1.

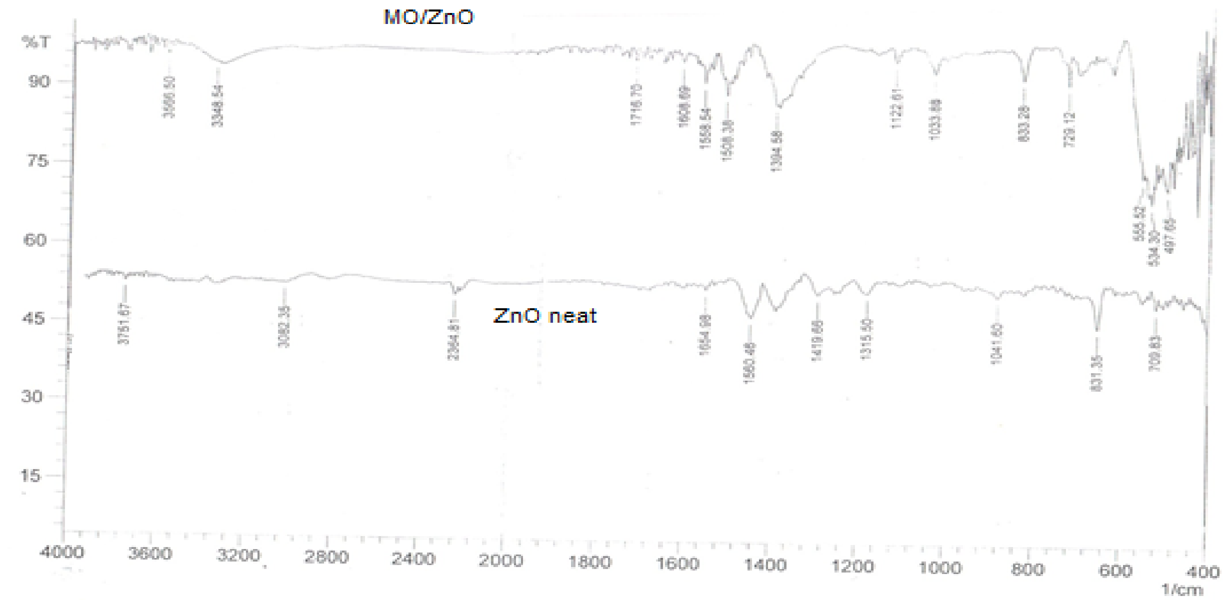


Figure-1: FTIR spectra for neat and MO sensitized zinc oxide

From this figure, 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. This characteristic peak of zinc oxide also appears in the modified form of this oxide (MO/ZnO) [17]. The bands that appears around 1630 cm^{-1} and the weak band around 3436 cm^{-1} are related to the modes of stretching of hydroxyl groups for the catalyst. The weak band that appears around 3400 cm^{-1} is related to O-H group vibration modes. The band around 2900 cm^{-1} is related to C-H vibration modes. 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 MO photosensitizer results in formation of new bonding in comparison with bare ZnO. These peaks appear around 1599 cm^{-1} and is assigned to the vibration modes of –C=C- stretching. The peal 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. The weak band around 802 cm^{-1} is relates to bending of C-H bonds. Vibration modes of $–CH_3$ group appears around 1442 cm^{-1}. Weak band at 3080 cm^{-1} is relates to the vibration modes of aromatic C-H bonds [19].

X-ray diffraction for neat and sensitized zinc oxide: The crystallite structure for both neat a MO sensitized zinc oxide was investigated using XRD. From XRD patterns for neat and sensitized zinc oxide it can be seen that sensitizing ZnO with methyl orange doesnot affect significantly on its structure. The patterns of XRD for these materials are shown in Figure 2**.**

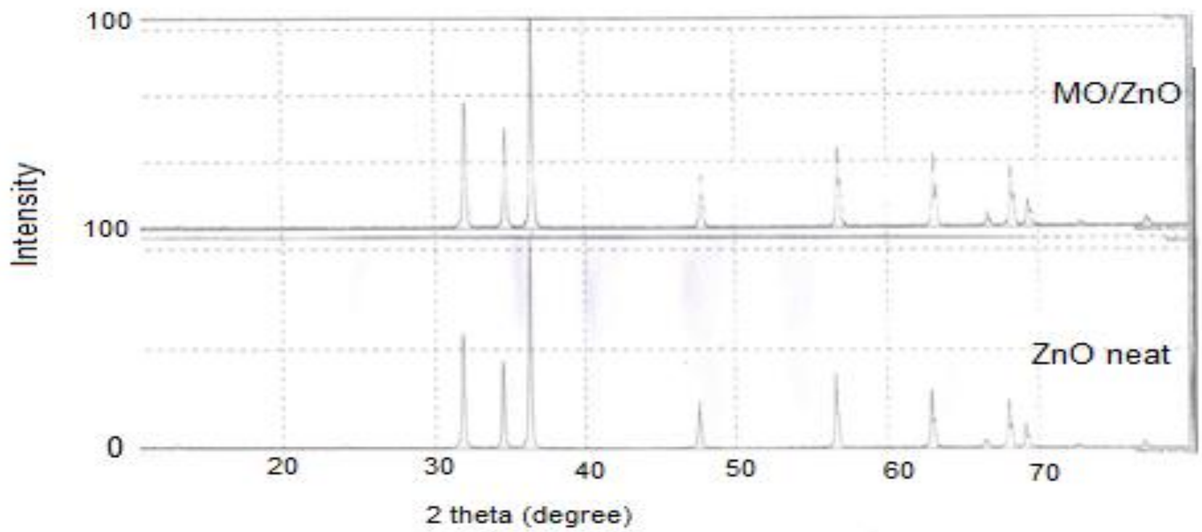


Figure-2: XRD patterns for neat zinc oxide and that sensitized with MO

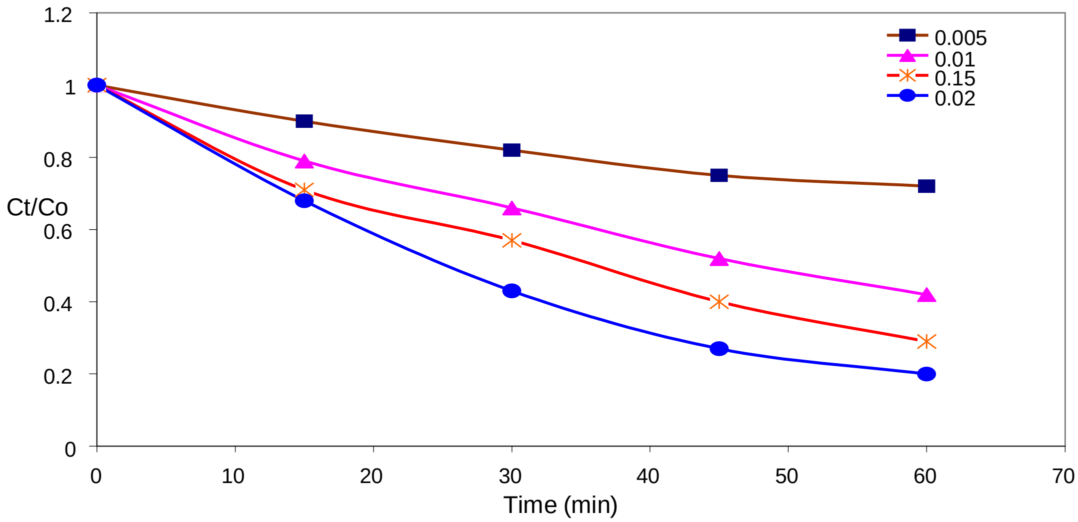
From above patterns, the main features of XRD for neat zinc oxide don't affect by the presence of sensitizer molecules on the surface. After sensitization of zinc oxide surface there were very slightly change in the positions of the peaks as well as change in the relative intensities of these peaks. The most important thing in this context is the increase in the full width high maxima (FWHM) for MO/ZnO upon sensitization of the surface will for neat zinc oxide they were slightly smaller. The particle size of the catalyst is related to this value in inverse proportionality i.e this means that as the value of FWHM was smaller, then the particle size will be larger. In this study, sensitization of zinc oxide with this dye results in reduction of particle size. These values are summarized in table 1.

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

CFrom the listed results in the above table, it is 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 [20]. Beside that the peaks of zinc oxide after sensitization almost have same features with slightly shifting in their positions at sensitized zinc oxide. It is well known that the activity of the catalyst would increase with decease size of its particle.

The optimization of mass of the used 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 dye concentration 30 ppm in 30 mL of reaction mixture at 25 □ C underambient 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 the above, it can be seen that there is an increase in the percentage of dye removal with the increase in the amount of the used MO/ZnO at the reaction conditions. This can be explained by considering the first law of photochemistry which states that, in the primary photochemical processes only one photon is absorbed by one molecule of the catalyst. So that 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 [21]. This process can increase the photocatalytic activity of the used catalyst.

The photocatalytic activity of neat sensitized ZnO: In order to investigate the effect of sensitization of ZnO with MO sensitizer on its photocatalytic activity, a series of experiments were performed using 0.02 g of both neat zinc oxide and that sensitized with MO at 25 C. In each experiment 30 ppm of MB was suspended in 30 mL with continuous stirring for one hour. Photocatalytic MB removal was followed by measuring the optical density for the supernatant liquid at 665 nm. These results are shown in figure 4.

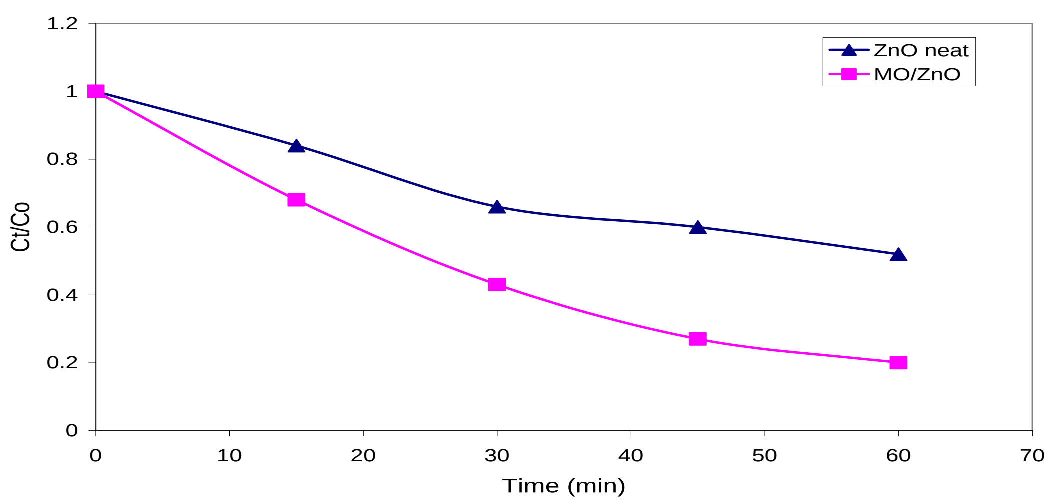


Figure 4: Comparison of photocatalytic activity for neat and MO sensitized ZnO

From the above results we can conclude that MO sensitized zinc oxide was more efficient than neat zinc oxide in the dye removal from aqueous solution**.** This can may result from reduction of rate of recombination reaction that is occurred normally when irradiation of neat photocatalyst. Conduction band electron (e^-_{CB}) and valence band hole (h^+_{VB}) after generation upon photoexcitation are diffused from bulk into the surface of the catalyst[22]. At the surface they participate in redox reaction with the pre-adsorbed species on the surface. The lifetime of these surface species are too short 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 challenge goal in this point is how to separate $e-_{CB}$ from $h+_{VB}$ for long time. Sensitization of photocatalyst can help in this case, 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. In this case there isnot 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.

The effect of level of sensitization of ZnO with dye sensitizer: In order to investigate the effect of level of sensitization on the photocatalytic activity of ZnO, a series of samples were prepared with different sensitization level of ZnO. This was 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 25^0 C with 30 mL of aqueous solution of MB with continuous stirring for one hour under irradiation with UV light. Photocatalytic removal of MB dye was followed by monitoring absorbance at 665 nm. The results are shown in figure 5.

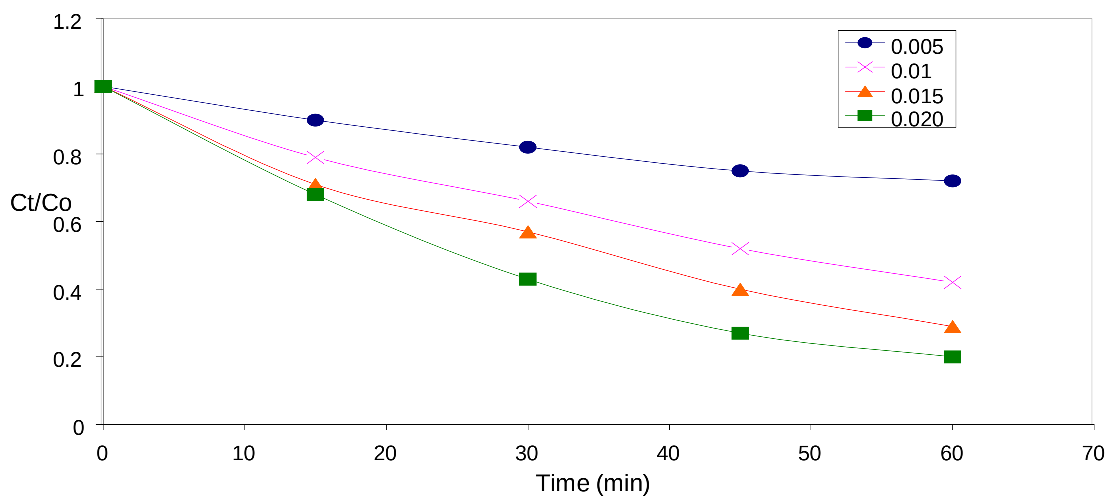


Figure 5: Effects of level of sensitization of ZnO with MO on its activity on dye removal

From this figure, it can be seen that the percentage of dye removal was increased 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 above level can increase the rate of light harvesting of photons and generating excited states of the dye molecules [24,25]. This process can lead to inject electrons into the CB of zinc oxide, this observation can yield high efficiency for dye removal.

APPLICATIONS

The modification of surface of zinc oxide by photosensitization with methyl orange can be useful to enhance some catalytic properties of it.

CONCLUSIONS

This study showed that modification of surface of zinc oxide by photosensitization with methyl orange can enhance some catalytic properties of it. Sensitization of zinc oxide does not alter its crystallite structure, beside that its particles after sensitization became relatively smaller as it was found from XRD patterns for neat and sensitized ZnO. The photocatalytic activity of MO/ZnO was more efficient than neat zinc oxide under the same reaction conditions.

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