

Photocatalytic degradation of rohdamine B by modified zinc oxide catalysts

A.G. Abd-El-Hameed¹, S.A. El-Hakam², Z.A.El-Samia¹

¹Basic Science Department, Nile Higher Institute for Engineering and Technology, Egypt

²Chemistry Department, Faculty of Science, Mansoura University, Egypt

Abstract

Aqueous solutions of organic contaminant like rhodamine B) is photodegraded under ultraviolet - visible light using modified ZnO by MCM-41 as photocatalyst, due to its low costs, use of sunlight, mild reaction conditions, high photochemical reactivity, low environmental toxicity and stability to photocorrosion. ZnO and MCM-41/ZnO photocatalysts with different percentage of MCM-41/ZnO (1%, 3%, 5%, and 8%) were prepared by precipitation method. Nanocomposites was synthesized and characterized by X-ray diffraction (XRD).

1. Introduction

Water treatment can be achieved by physical method such as flocculation and filtration or by biological treatment. These processes are easy and low coast. But not effective in low concentration of organic and inorganic contaminates and usually used at the beginning of the purification process to remove solids from the water [1-5]. Where, Chemical methods had been improved to remove low concentration of contaminates such as photocatalytic degradation of the organic pollutants using semiconductors such as TiO₂ and ZnO. Most organic pollutants escape from traditional wastewater treatment but photocatalytic degradation method evolved from

research works has been considered to overcome many limitations of traditional wastewater treatment process.

Photocatalysis processes are classified homogeneous and heterogeneous system. Visible-light-driven Heterogeneous photocatalysis is an advanced oxidation processes (AOP) it could successfully solve the problem of the removal of toxic and bio-resistant organic and inorganic compounds from waste water by their total conversion into species that are non-toxic [6-11]. It gives a good chance of offering a technology well suited to the above requirements.

2. Materials

All organic and inorganic chemicals used in preparation of catalysts are zinc acetate dihydrate $Zn(CO_2CH_3)_2 \cdot (H_2O)_2$, ethanol (C_2H_5OH), sodium hydroxide (NaOH), MCM-41, methylene blue dye and rhodamine B dye. All reagents used in this study were in analytical grade.

3. Preparation of the catalysts:

3.1 preparation of ZnO nanocatalyst.

Synthesise of ZnO nanocrystalline particle was suggested by precipitation method. Where, 2.701g of zinc acetate dehydrate dihydrate $Zn(O_2CCH_3)_2 \cdot (H_2O)_2$ was dissolved in 50ml ethanol at room temperature until clear solution is obtained, sufficient amount of NaOH is added drop by drop to reach pH(8:9), the formed product was then filtered off and dried in a rotary at 60°C, the nanocrystalline material was finally obtained by calcination of hydroxide structure at 400 °C, 500 °C and 600 °C for 2 hr.

3.2 Preparation of MCM-41/ ZnO nanocatalyst.

MCM-41 supported on ZnO by impregnation method. Where, 0.01, 0.03, 0.05 and 0.08 g calcined MCM-41 dispersed under vigorous stirring into solution contain 2.701g of zinc acetate dehydrate dihydrate $Zn(O_2CCH_3)_2 \cdot (H_2O)_2$ was dissolved in 50ml ethanol to obtain 1 wt.%, 3 wt.%, 5 wt. % and 8 wt. % MCM-41, respectively. The stoichiometric amount of NaOH is added drop by drop with vigorous stirring to reach pH (8:9) for 12 hr. The formed product was then filtered off and dried in a rotary at 60°C. The catalyst was finally obtained by calcination at 400 °C, 500 °C and 600 °C for 2 hr. the catalyst was given name as (X-MCM-41/ZnO) where X (1%, 3%, 5% and 8 wt. %)

4. Photocatalytic experiments

The photocatalytic activity of ZnO and wt. %MCM-41/ZnO was studied by the degradation of RB under visible light. Photocatalytic degradation of dyes studies were carried out with 0.05g of activated catalyst introduced into 50 ml of RB dye solutions with initial dye concentration 10 mg/l. The degradation equilibrium of RB by the prepared materials was reached after 1hr of stirring under visible light by using UV/visible mercury lamp (400 watt). The suspensions were filtered by centrifuge. [12] The percentage degradation of dyes was calculated by the following equation.

$$\text{Degradation (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$(C/C_o) = \frac{C_t}{C_{\text{initial}}} \quad (2)$$

where;

C_o : is the initial concentration of the dye (mg/L)

C_i : is the concentration of dye at any t_{minute} (mg/L).

5. Result and discussion

5.1 X-ray diffraction

5.1. 1 X-ray diffraction of zinc oxide catalyst.

The X-Ray Diffraction patterns were measured for ZnO prepared by sol gel method. Fig. (1) Shows the XRD patterns of ZnO calcined at 500 °C. It represents high angle powder XRD patterns of pure ZnO. Pure ZnO sample exhibit peaks at $2\theta = 31.6, 34.2, 36.3, 47.4, 56.76, 62.9, 68.1$ nm. Which are characteristic for ZnO nanostructures with hexagonal crystal type, and with nanosize 55.0-77.2 nm. This results agree with literature XRD pattern for hexagonal wurtzite ZnO according to literature [13-15]. These diffraction peaks are in a good agreement with the standard joint Committee on powder diffraction standards the JCPDS (card No.36-1451).

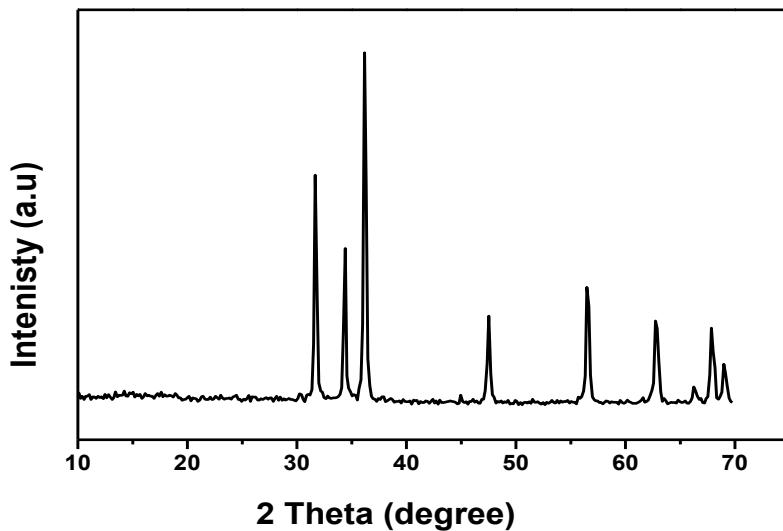


Fig.(1): X-ray diffraction patterns for pure ZnO calcined at 500 °C.

5.1.2 X-ray diffraction of MCM-41/ ZnO.

The XRD patterns of pure zinc oxide, 1 wt. %, 3 wt. % and 5 wt. % MCM-41/ ZnO calcined at 500°C are shown in fig. (2). the peaks appear at $2\theta = 31.6, 34.2, 36.3, 47.4, 56.76, 62.9, 68.1$ nm, were confirmed hexagonal structure of MCM-41/ZnO, The products exhibited sharp and narrow peaks at 30-40° for all samples, [16-21] indicate high degree of crystallinity.

The results indicates that % MCM-41 supported on ZnO does not affect the structure of ZnO crystals, expect only a slight decrease its major x-ray diffraction peak at $2\theta = 31.6, 34.2$ and $2\theta = 36.3$ nm, which indicate the crystallinity of hexagonal ZnO, peaks intensity decrease by increasing MCM-41 content. the crystallite size of hexagonal ZnO phase increases with increasing MCM-41 content until 3 wt.% and then decrease at 5 wt.%. 3 wt.%MCM-41 sample was the best nanosize and photodegradation activity. The crystallite size of samples are summarized in table (1)

The degree of crystallinity of the ZnO/MCM-41 samples increased with amount MCM-41 content accordance to nanosize.

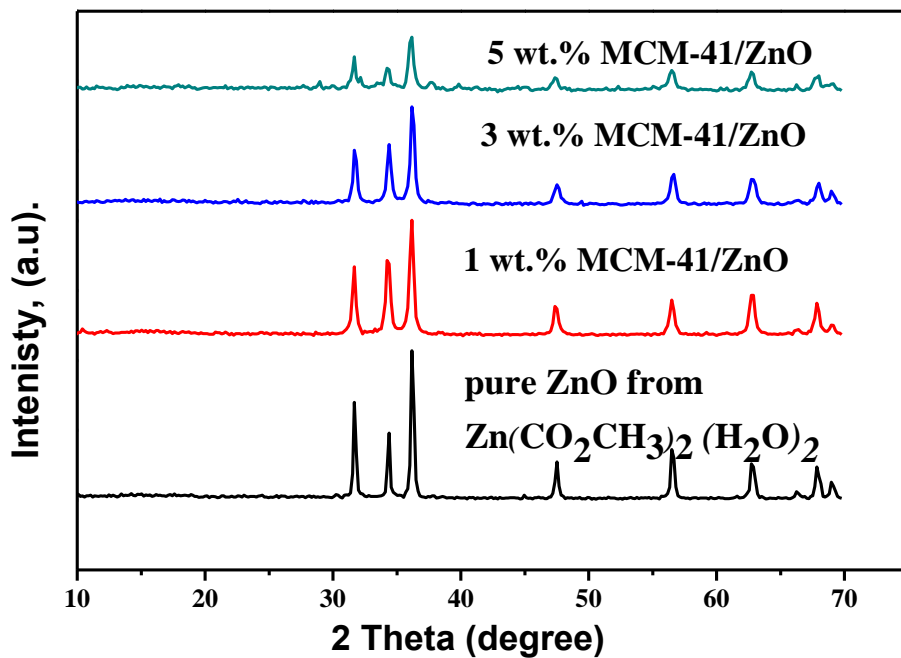


Fig.(2): XRD patterns of ZnO, 1%MCM/ZnO, 3%MCM/ZnO and 5%MCM/ZnO.

Table (1): Effect of calcination temperatures on crystallite size of ZnO, 1%MCM/ZnO, 3%MCM/ZnO and 5%MCM/ZnO.

Sample name	Crystallite size L (nm)
Pure ZnO from Zn (acetate)	55 - 77.2
1wt% MCM-41/ZnO	23.4– 38.4
3wt% MCM-41/ZnO	19.7-37.6
5wt% MCM-41/ZnO	22-39.8

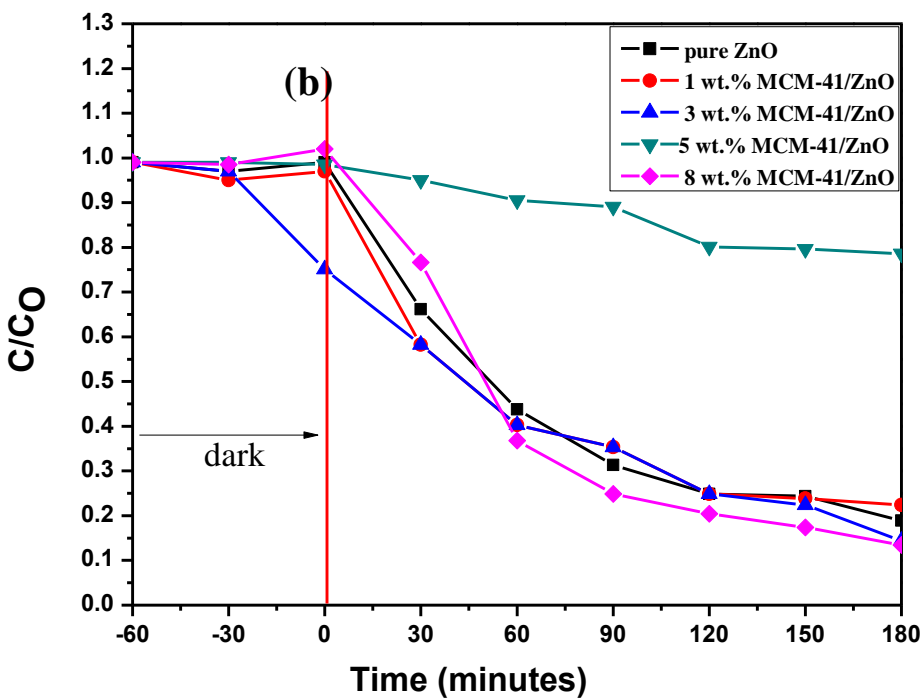
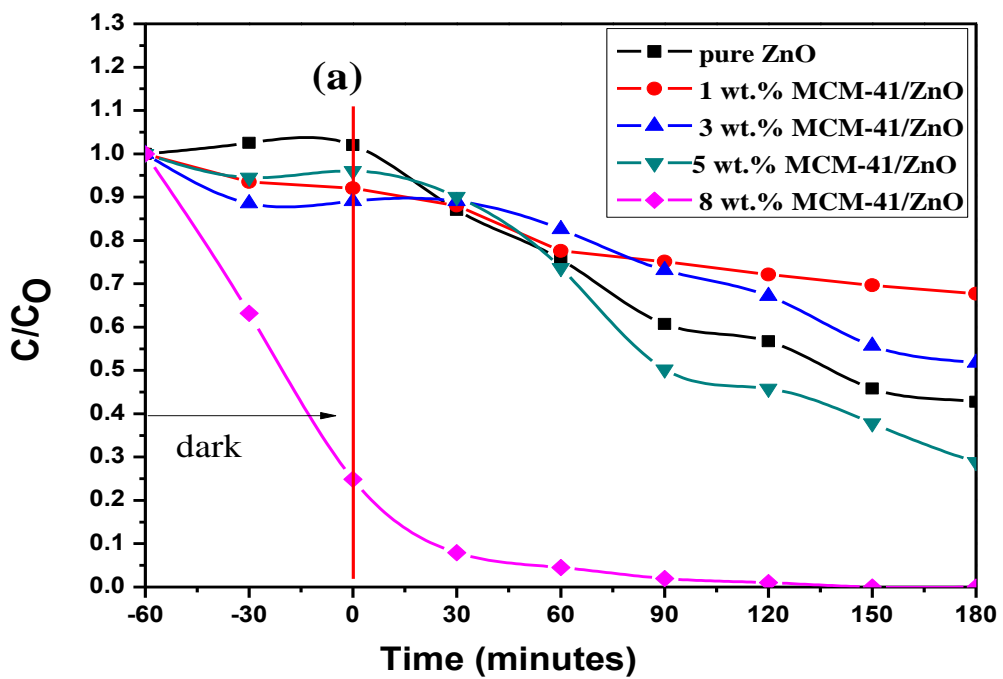
Photocatalytic degradation of rohdamine B by MCM-41/ ZnO from zinc acetate.

5.2.1 Effect of MCM-41 weight percentage of MCM-41/ZnO nanocomposites.

The photocatalytic degradation of RB dye [22-24] was studied at different time by using 0.05 g of photocatalyst, and 10 ppm dye solution. Firstly we studied the adsorption activity in dark for 60 minutes, before the study of its photocatalytic activity.[45-48]

The photocatalytic activity of ZnO samples[25] supported with different amount of MCM-41 were first increasing with MCM-41 content, reaching maximum at 5wt.% MCM-41 /ZnO then decreasing with increasing MCM-41 content. Activity decreases at higher MCM-41 contents due to the increased scattering of photons and absorbance through excess MCM-41 in the photosystem. Increasing MCM-41 content can therefore shield the light from reaching the surface of ZnO nanocatalyst. But suitable amount of MCM-41 doped with ZnO nanostructure has effects on the surface area of the photocatalyst and the separation of photogenerated electron-hole pairs.

The results indicate that the adsorption activity for 1 wt. %, 3 wt. %, and 5 wt. % MCM-41/ZnO nanocomposites were insignificant, it did not exceed 10% adsorption after 60 minutes, while on 8 wt. % MCM-41/ZnO nanocomposite was 40% adsorption. We found that the adsorption activity of 1 wt. %, 3 wt. %, and 5 wt. % MCM-41/ZnO nanocomposites showed improvement in photocatalytic activity due to the adsorption of the dye on the surface of the photocatalysts, thus photocatalytic degradation activity occurs easily. While, 8 wt. % MCM-41/ZnO nanocomposites has high adsorption activity and the photocatalytic degradation was low. Fig.(3) show the effect of contact time from 0-150 minutes on the photocatalytic degradation efficiency of MB and RB dyes respectively with different loading MCM-41 weight percentage content. Result shows that, the adsorption part in dark after 60 minutes is small due to the low concentration of MCM-41. The most effective content was 3 wt. % MCM-41 which degraded MB dye after 90 minutes by high percentage reaches to 99.42%, and RB after 180 minutes by 85.57%. The photocatalytic degradation of two dyes displays quick increase during the first 30 minutes, and then gradually increases during 30 to 60 mins, and thereafter the degradation becomes slight. The maximum photocatalytic degradation efficiency of RB is shown in table (3). The experimental data, XRD confirm that the 3 wt. % MCM-41/ZnO nanocomposites was the best photocatalytic activity due to the low nanosize.



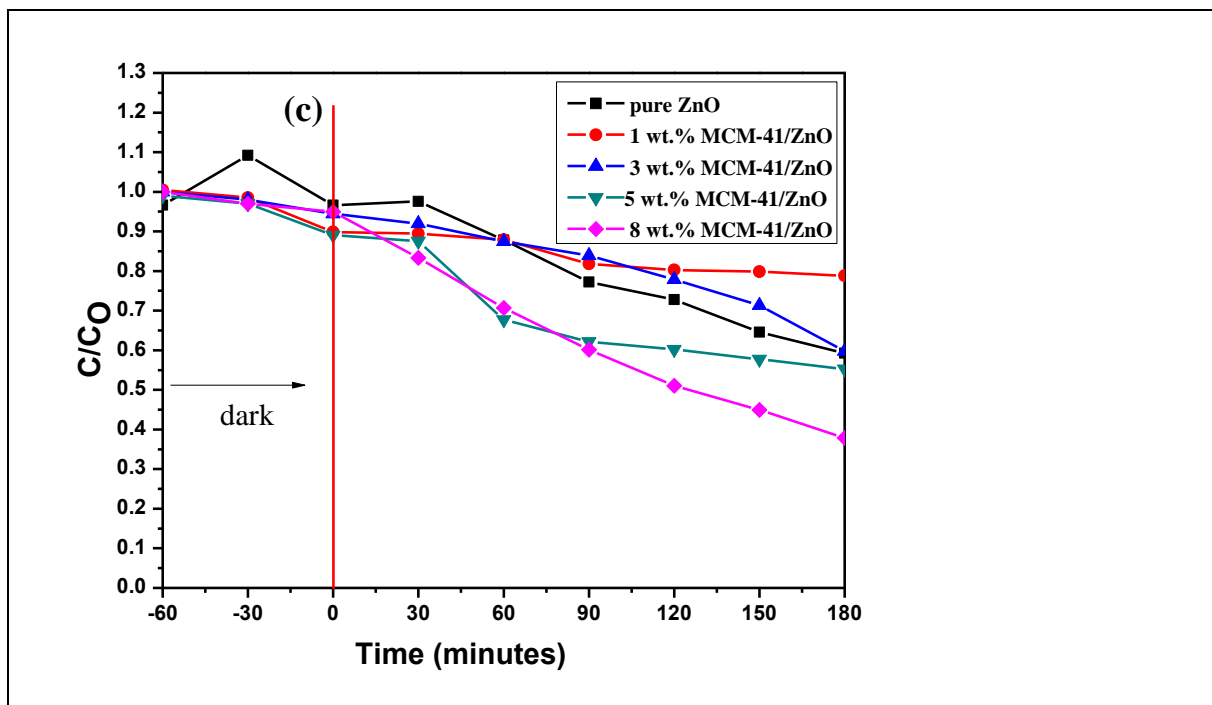


Fig. (3): Effect of contact time on photocatalytic degradation of RB by MCM-41/ ZnO nanocomposites calcined at (a)400 °C, (b) 500°C and (c) 600 °C

Table (2): The percentage degradation of rhodamine B after 180 mins.

The samples	Calcination temperatures		
	400 °C	500 °C	600 °C
Pure ZnO	62.6	81.02	40.7
1 % MCM-41/ZnO	23.2	79.1	21.2
3 % MCM-41/ZnO	51.7	85.57	40.2
5 % MCM-41/ZnO	71.1	21.39	42.7
8 % MCM-41/ZnO	100	86.5	62.1

6. Conclusion

In the present study ZnO was prepared by precipitation method and modified by MCM-41. The morphology and crystallization of the films as-obtained were characterized by XRD. From the results The ZnO nanoparticles were efficiently crystallized in hexagonal phase. The prepared composites powders were used as catalysts to degrade rohdamine B effectively under UV-visible light irradiation.

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