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Article

Photocatalytic Activity of Nano Modified ZnO

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Abstract: In this work, ZnO photocatalyst and ZnO with different percentage of MCM-41 (1 wt. %, 3 wt. %, 5 wt. % and 8wt. %MCM-41) was synthesized by precipitation method. The photocatalytic activity of ZnO loaded MCM-41 was studied by the degradation of methylene blue in presence of UV/visible mercury lamp. The effects of preparation conditions such as MCM-41 weight percentage of MCM-41/ZnO nanocomposites and calcination temperature on the photocatalytic activity of % MCM-41/ZnO nanocomposites were examined. In addition to the influences of UV light irradiation time, pH of dye solution, dye initial concentration and % MCM-41/ZnO amount as well as organic dyes on the photocatalytic degradation were also investigated. Kinetic study indicates that the photocatalytic degradation of methylene blue by MCM-41/ZnO nanocomposites is pseudo-first order reaction.

Keywords: photocatalysis; ZnO; MCM-41; Methylene blue

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

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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 TiO_2 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.

Metal semiconductors act as photocatalysts for the light induced photochemical reactions due to their unique electronic band structure, comprising filled valence band (VB) and empty conduction band (CB). The excitation of semiconductor with photon energy ≥ Eg generates an electron in (CB) and hole in (VB)[12-14]. The excited charge carriers (electrons and holes) are highly reactive radicals with robust reducing and oxidizing capacity respectively. The band gap excitation of zinc oxide involves excitation, bulk diffusion and surface transfer of photo-induced charge carriers, where the carrier's life time is vital in determining the photocatalytic activity. Heterogeneous photocatalysis with nanostructured ZnO has been successfully applied to degrade organic pollutants due to the dispersion and surface area of zinc oxide, which depend on the synthesis method. Various techniques have been used to synthesize ZnO nanoparticles such as, alkali precipitation, thermal decomposition, hydrothermal synthesis, organo-zinc hydrolysis .spray pyrolysis, and microwave irradiation [15-18]. ZnO is a unique semiconductor material with relatively wide band gap (Eg ~3.0 eV) at room temperature. ZnO photocatalyst is preferred due to its attractive properties, such as high chemical stabilizations, nontoxicity, and abundance in nature. Its conductive band edges are more positive potentials than the oxidation potentials needed for many organic contaminants [19-22]. In present article we are reporting photocatalytic activity of zinc oxide synthesized by precipitation method and MCM-41 supported with ZnO by precipitation method and effect of calcination temperature on photocatalytic degradation of methylene blue.

2. Experimental

2.1. Materials

All organic and inorganic chemicals used in preparation of catalysts are zinc acetate dihydrate

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$Zn(CO_2CH_3)_2 (H_2O)_2$, ethanol(C_2H_5OH), sodium hydroxide (NaOH), MCM-41, methylene blue dye . All reagents used in this study were in analytical grade.

2.2. Preparation of the Catalysts

2.2.1. Preparation of ZnO nanocatalyst

Synthesis of ZnO nanocrystslline particle was suggested by precipitation method. Where, 2.701g of zinc acetate dehydrate dihydrate $Zn(O_2CCH_3)_2$ $(H_2O)_2$ 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 arotary 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.

2.2.2. 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 $Zn(O_2CCH_3)_2$ $(H_2O)_2$ 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 arotary 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. %)

2.3. Photocatalytic Experiments

The photocatalytic activity of ZnO and wt. %MCM-41/ZnO was studied by the degradation of MB under UV/visible mercury lamp. Photocatalytic degradation of dyes studies were carried out with 0.05g of activated catalyst introduced into 50 ml of dye (MB) solutions with initial dye concentration 10 mg/l. The degradation equilibrium of MB 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. Then methylene blue equilibrium concentrations were determined by spectrophotometer at λ=666 nm [23].

The percentage degradation of dyes was calculated by the following equation.

$$Degradation\ (\%) = \frac{Co - Ce}{Co} x100 \qquad (\mathbf{1})$$

$$(C/C_o) \quad = \frac{C_t}{C_{intial}} \qquad \mathbf{(2)}$$

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where

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

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

3. Result and Discussion

3.1. Effect of MCM-41 Weight Percentage of MCM-41/ZnO Nanocomposites

The photocatalytic degradation of dyes (MB) [26-29] 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 [24-26].

The photocatalytic activity of ZnO samples[30] supported with different amount of MCM-41 were first increasing with MCM-41 content, reaching maximum at 3wt.% MCM-41/ZnO then decreasing with increasing MCM-41content. 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.

Figure 1 shows the effect of contact time from 0-150 minutes on the photocatalytic degradation efficiency of MB dye with different loading MCM-41 weight percentage content. Result shows 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 which show improvement in photocatalytic activity due to the adsorption of the dye on the surface of the photocatalyts, thus photocatalytic degradation activity occurs easily, while on 8 wt. % MCM-41/ZnO nanocomposites was 40% adsorption and the photocatalytic degradation was low. The most effective content was 3 wt. % MCM-41 which degraded MB dye after 90 minutes by high percentage reaches to 99.42%. The maximum photocatalytic degradation efficiency of MB is shown in table 1 [31-36].

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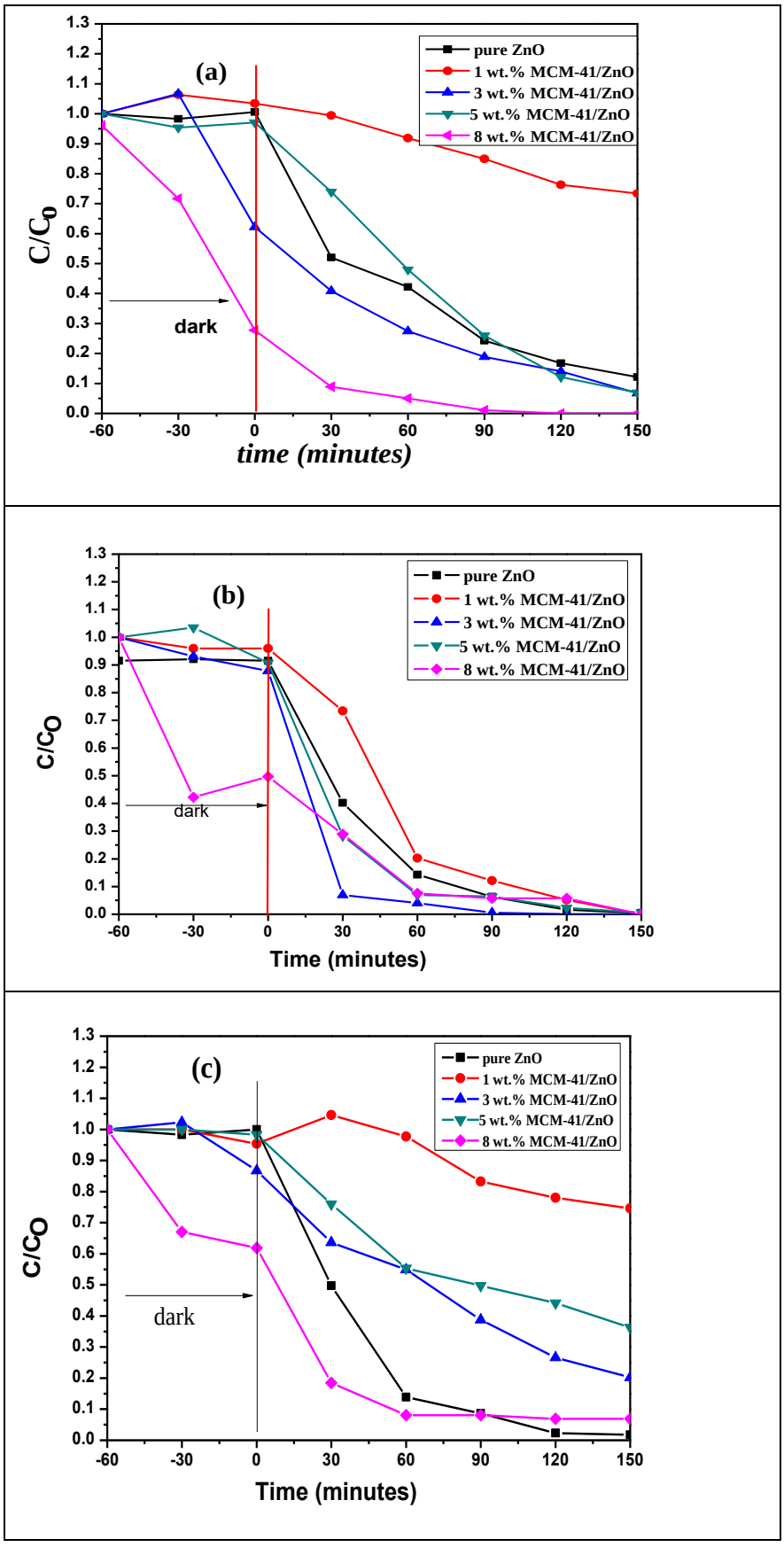

Figure 1: Effect of contact time on photocatalytic degradation of MB by MCM-41/ ZnO nanocomposites calcined at (a)400 ºC, (b) 500ºC and (c) 600 ºC

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Table 1: The percentage degradation of methylene blue after 120 mins

The samples	Calcination temperatures		
	400 ºC	500 ºC	600 ºC
Pure ZnO	83.2	98.2	97.11
1 % MCM-41/ZnO	23.6	99.2	27.16
3 % MCM-41/ZnO	81.02	100	73.14
5 % MCM-41/ZnO	87.8	97.68	55.86
8 % MCM-41/ZnO	100	94.2	93.06

3.2. Effect of Solution's pH

Effect of pH on photocatalytic degradation of methylene blue at different pHs 2, 4, 8 and10 by 3%MCM-41/ZnO calcined at 500ºC are shown in figure 2. The optimum pH for degradation of MB was 8, photocatalytic degradation of MB increase as pH increased from 2 to 10, which indicate that photo-degradation efficiency increased were at pH 8 the maximum photodegradation was achieved.

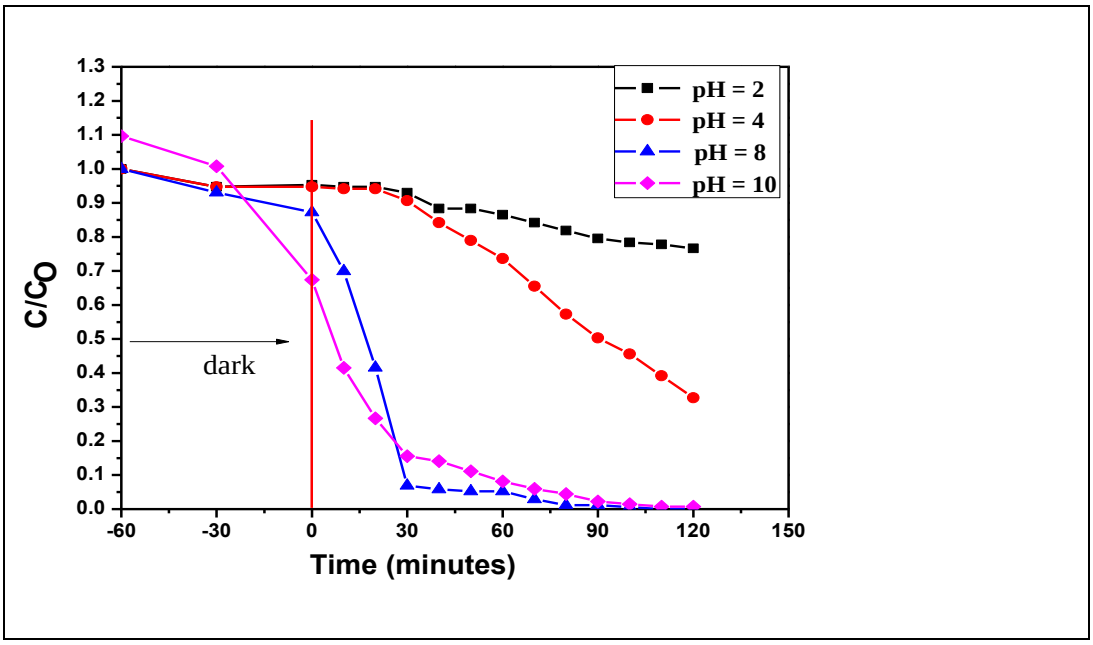

Figure 2: Effect of pH change on degradation of MB using 3 wt. % MCM-41/ZnO calcined at 500ºC.

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3.3. Effect of Catalyst Weight on the Catalyst Activity

The photocatalytic degradation of methylene blue dye by 3 wt.% MCM-41/ZnO nanocomposites calcined at 500°C was studied by changing of the catalyst weight 0.025, 0.05, 0.075 and 0.01g with keeping initial dye concentration 10 mg/L and at pH = 8. The effect of catalyst dosage on photocatalytic degradation of dyes is shown in figure 3 and table 2 which indicate that the photocatalytic degradation of day increases with the increase in the catalyst weight. The maximum photocatalytic degradation efficiency was 100%. This indicates that as the weight of the catalyst increases, the photodegradation increases, where the ability of the catalysts to create electron-hole pairs increases, thus the generated free radicals increase. This may be due to the increase of the exposed active sites increase with catalyst weight [13-14].

Table 2: The maximum photocatalytic degradation efficiency of MB at different catalyst weights after 50 mins.

Weight of the catalyst (g)	0.025	0.05	0.075	0.1
% photocatlytic degradation of MB	94.3	97.7	98.3	100

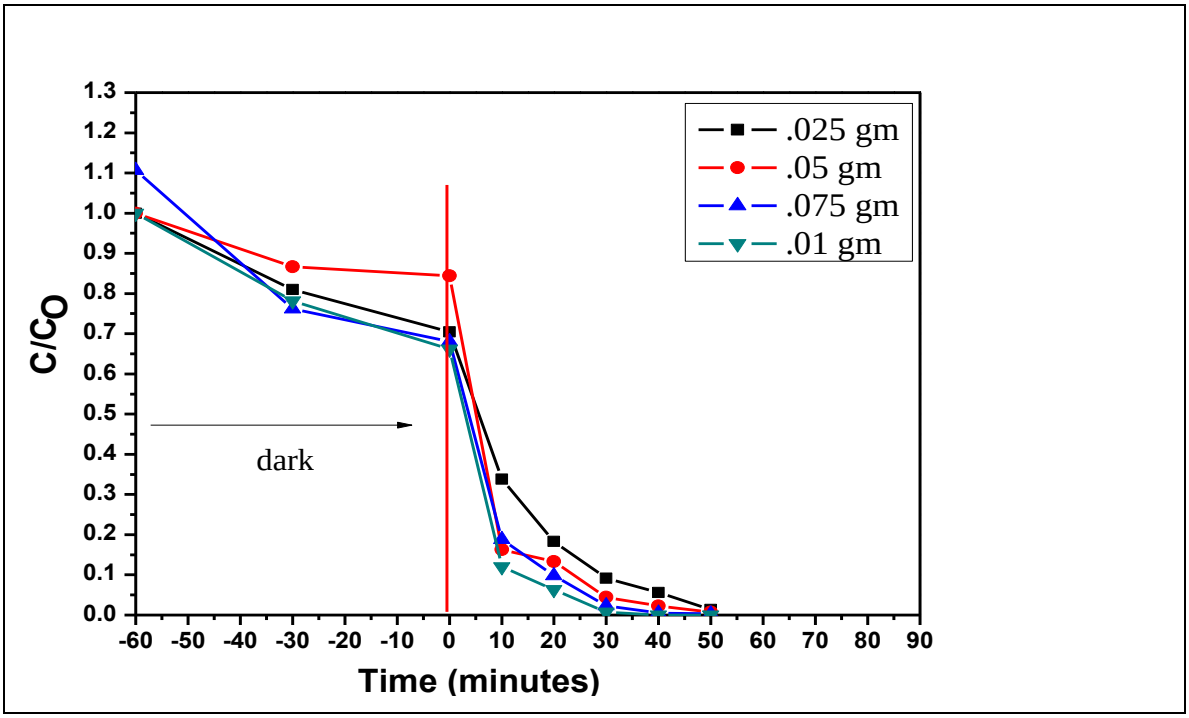

Figure 3: Irradiation time for methylene blue by 3 wt.% ZnO/MCM-41 calcined at 500 ^{o}C using different catalyst weight.

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3.4. Effect of Initial Dye Concentration

Effect of initial dye concentrations on the photocatalytic degradation rate was studied at initial dye concentrations 10, 20, 30, 40 and 50 mg/L by using 0.1g of 3 wt. %MCM-41/ZnO nanocomposites and at pH = 8. Figure 4 indicates that the photocatalytic degradation efficiency of methylene blue decreases with initial dye concentrations from 10 to 50 mg/L respectively, due to that the increasing of concentration of dye blocking the active sites on surface as shown in table 3.

Table 3: The maximum photocatalytic degradation efficiency of methylene blue after 40 minutes at different initial dyes concentrations.

C_i (mg/L)	10	20	30	40	50
% photocatalytic degradation of methylene blue.	100	94.9	82.05	74.7	73.18

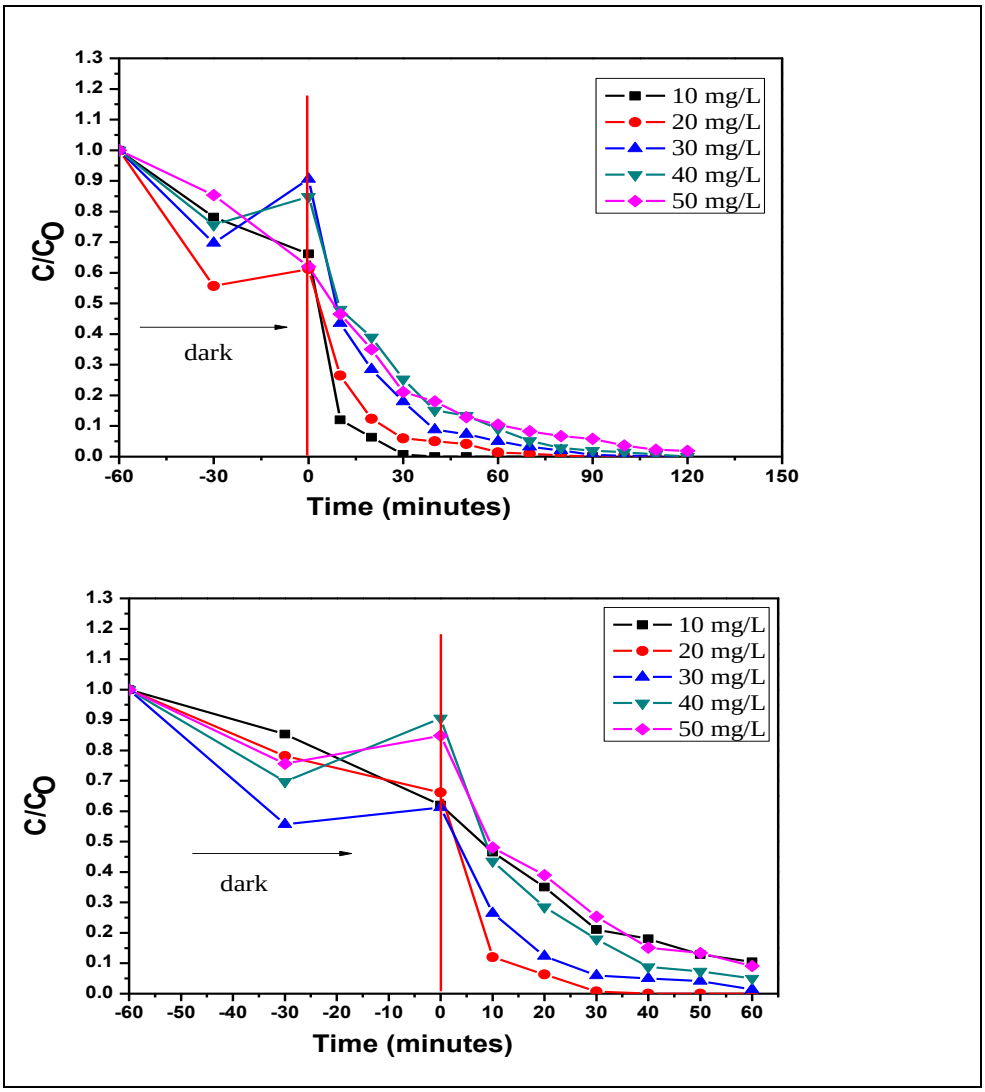

Figure 4: Effect of initial MB concentrations on the photocatalytic degradation activity by 3 wt. % MCM-41/ZnO nanocomposites at optimum conditions.

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3.5. Kinetic Study

Kinetic photocatalytic degradation data of pure ZnO and MCM-41/ZnO nanocomposites was carried out to understand the mechanism of photocatalytic degradation. Most of the photocatalytic degradation reactions follow Langmuir-Hinshelwood kinetic In (C_0/C_t) = kt, which belong to the first-order kinetics, where C_0 is the initial concentration of dye, C_t is the concentration of dye at the reaction time of t, t is the reaction time and k is the apparent reaction rate constant, this is confirm by a nearly linear plot of ln (C_0/C_t) with t. Figure 5 shows the kinetic of photocatalytic degradation of methylene blue over pure ZnO and MCM-41/ZnO nanocomposites. The kinetic parameters were calculated and listed in the inset table 4. We found that the photocatalytic degradation of methylene blue by MCM-41/ZnO nanocomposites is pseudo-first order reaction kinetics.

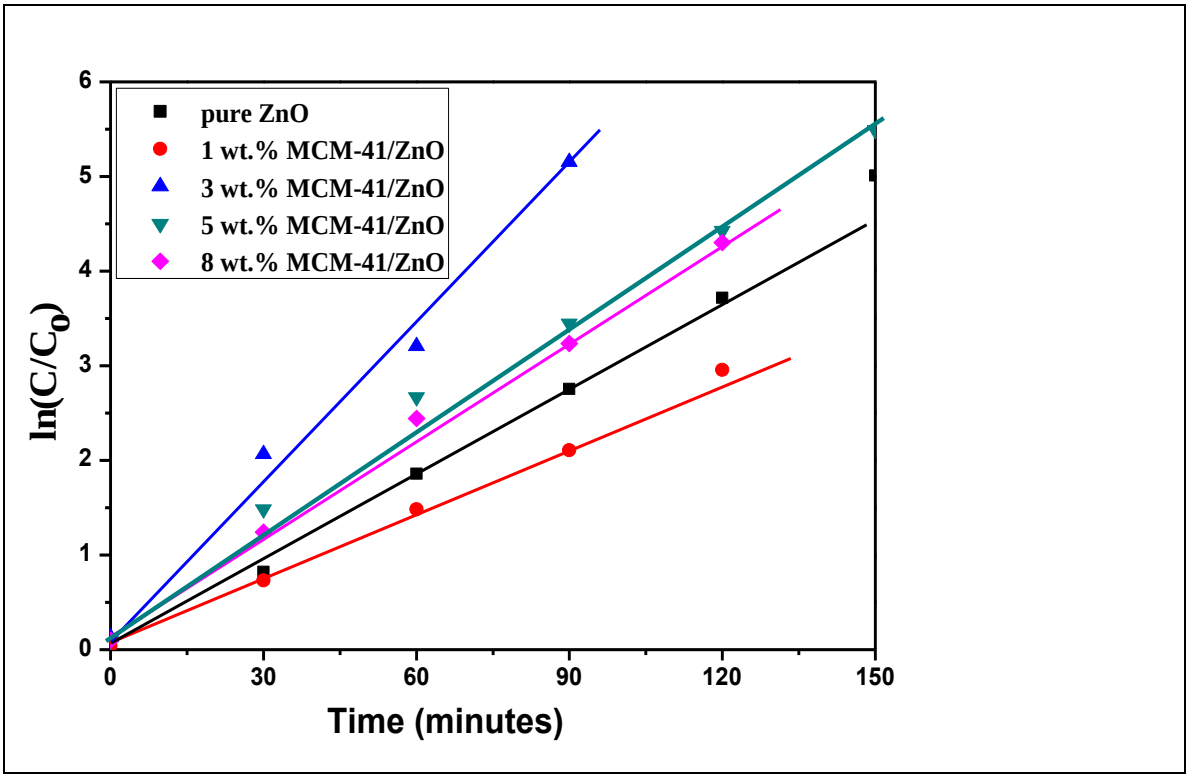

Figure 5: kinetic of photocatalytic degradation of MB by pure ZnO, 1 wt. %, 3 wt. %, 5 wt. % and 8 wt. % MCM-41/ZnO nanocomposites.

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Table 4: Kinetic model parameters (Langmuir-Hinshelwood kinetic-pseudo 1st order) for photocatalytic degradation of MB by MCM-41/ZnO photocatalyst

The samples	Methylene blue	
	K_1	R^2
Pure ZnO	0.024	0.9489
1 wt.%MCM-41/ZnO	0.017	0.9896
3 wt.%MCM-41/ZnO	0.035	0.9944
5 wt.%MCM-41/ZnO	0.028	0.9964
8 wt.%MCM-41/ZnO	0.022	0.778

4. Conclusion

In the present study ZnO was prepared by precipitation method and modified by MCM-41. The prepared composites powders were used as photocatalysts to degrade methylene blue effectively under UV-visible light irradiation. The experimental results indicated that 3 wt. % MCM-41/ZnO nanocomposites photocatalytic activity was much superior to that of ZnO under the same condition.

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