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Photocatalytic Degradation of Methyl Orange Dye using Different Photocatalysts under Solar Light

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Abstract : In the present paper, the degradation of Methyl Orange dye using two commercial photocatalysts (ZnO and TiO_2). These two catalysts have been tested and compared in suspension in a slurry reactor under solar light.

The best values of various transactions such as catalyst concentration, catalyst type and the concentration at the beginning of experiment of that affecting the degradation percentage of Methyl Orange were observed by changing catalyst concentration (0.5 –1.5 g/l), and the elementary dye concentration (50–150 mg/l). The disappearance of colour and substrates together with the abatement of total organic carbon content was monitored. The main sulfonate-containing intermediates were found to be in lower number in respect to those obtained under solar light. The photocatalyst ZnO noticed that was a perfect photocatalyst from TiO_2during the degradation of Methyl Orange.

Keywords : Degradation; Indigo carmine dye; Photocatalysis; Zinc oxide.

1. Introduction

A lot of colored dye effluents which almost making textile industries are poisonous and un-decomposed[1].Almost dyes cause acute environmental contamination troubles by releasing poisonous and potentially risky items into the aquatic phase. Different some processes like deposition, adsorption, air stripping, coagulation, some techniques can be used for color elimination from textile effluents like ultrafiltration and reverse osmosis[2]. However, these processes are non-devastating, so they only transport the un-decomposed item into sludge, donation rise to a new type of pollution, which needs furthermore processing.[3]

The implementation of solar-powered photocatalytic reactors to process wastewater from textile industries keep a promise for areas receiving powerful sunlight over the year, like Iraq[4]. Since dyes absorb highly in the visible zone, the energy gathering efficiency should be sufficiently high to make the photo-assisted processing of dye-polluted wastewater convenient[5,6].

Methyl Orange was considered one of the most important dyes because of it is emotional-state lifetime which was very short and was constant to visible in addition give a useful investigation for the oxidation and reduction of photo reactions[7]. For the oxidation reaction about photo of methyl orange in a slurry reactors and TiO_2immobilized reactors, most studies had been made[8,9]. The experimental data of previous studies would give a good information in estimating the execution of a fluidized bed photocatalytic reactor in a three-phase [10].

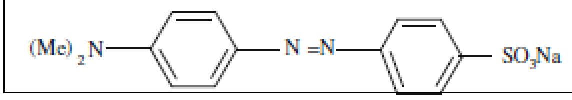
For the present paper, the photocatalytic degradation of methyl orange dye in aquatic solutions using two different photocatalysts has been tested. The major aims of the study were (a) catalyst concentration influence; (b) catalyst type studying; (c) effect of initial concentration of the dye; (d) studies kinetic of reaction.

2. Experimental work

2.1. Materials

In present work, commercial ZnO powder and TiO_2 powder were gained from Merck Company in Germany, Methyl orange was taken up from the same company and was applied out of any purification. Its chemical structure and other property are listed in the below table (Table 1). And at the preparation of various solutions, distilled water was used.

Table (1) shows properties of Methyl Orange dye

Details	**Property**
Anionic Dye	**Nature**
470 Nano meter	λ_{max}
200-800Nano meter	**Spectral Range**
327.34 g/mole	**M. Wt.**
	**Molecular Structure**

2.2. Used Devices

The chemical degradation of photocatalyst was accomplished in specially designed insulation walled reaction containers of 500 ml volume under solar light and by using magnetic stirrers the stirring of the solution was insured stable . Over the reaction time, the temperature was kept steady by spreading water in the photocatalytic reactor vessel. Figure 1 shows the system has been designed.

Figure 1 .Photocatalytic reactor vessel

2.3. UV-Experiments

photocatalyst was addedto150 ml of the dye solution, so the solution was an exhibit to UV ray. All runs were done under solar light. The prepared solution was stirred magnetically over the process, and an aliquot was taken out by using a syringe at various time periods and then Millipore syringe filter was used for filtration.

2.4 Absorption Measurements

The absorption spectrum was recorded using double beam UV-1800 Shmadzo spectrophotometer (Figure 2)compared with distilled water as a reference liquid and the degradation percentage rate was noticed clearly from the change in intensity at λ_{max} of the different dyes during irradiation time. The efficiency of degradation can be estimated as:

% Degradation = ((Abs $_0$– Abs $_t$) / Abs $_0$) * 100

Where :-

% Degradation is a percentage of dye disappearance.

Abs $_0$ is initial absorption of dye (at time = 0 min.)

Abs $_t$ is absorption of dye (at time = t min.)

Similar experiments haveused different catalyst concentration (0.5–1.5 g/l), to select the bestconcentration of both catalyst (ZnO and TiO_2) at the same dye concentration of the solution (50 ppm)

Figure 2.Double beam UV-1800 Shmadzo spectrophotometer

3. Results and Discussion

The used dye (Methyl Orange) has molecular structure and functional groups shown in Table 1. It is an azo dye having sulphonate (SO^{3-}) and azo groups. It has different colour depended on pH (as shown in the Merck company label at pH=3.1 red , at pH=4.4 orang) The experiments of photodegradation were achieved under solar light, two catalysts commercial ZnO and TiO_2were investigated at natural pH for their degradation efficiency. Varying in intensity was represented by a characteristic peaks for the recorded rate of photodegradation and efficiency of catalyst.

3.1 Methyl Orange Visible Spectra

From Figure 3 show UV- visible spectra and for Methyl Orange before photodegradation of dye (time = 0) the main absorption peaks at 470 nm in a visible region and 280 nm in UV region. The degradation rate as calculated proportion to the change in intensity of absorption peaks at 470 nm., Dyes diminished corresponding to the absorption peaks and finally disappeared through the reaction, After that the dyes had been degraded[11,12].

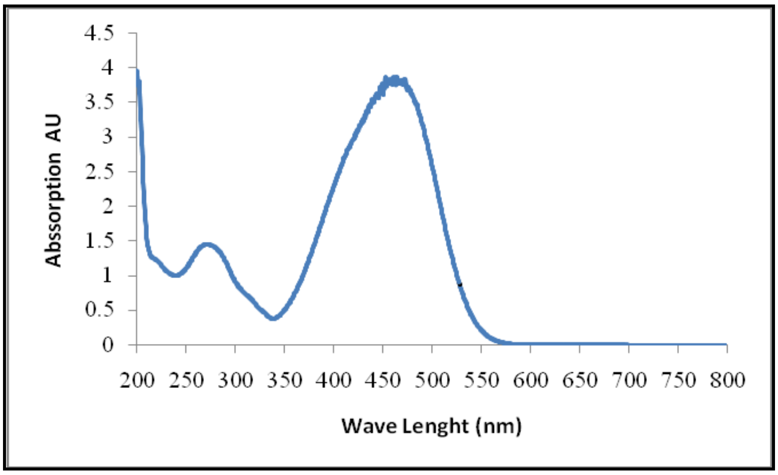


Figure 3 : UV visible spectra of Methyl Orange dye

3.2. Effect ofPhotocatalystsType

Commercial TiO_2 and ZnO were executed with different semiconductors, in order to choose the most active catalyst for dye degradation. Photocatalysed degradation of a dye in solution is started by the semiconductor photoexcitation, then an electron–hole pair was forming on the surface of catalyst (Eq. 1). The direct oxidation of organic matter have the capability to reactive intermediates because of high oxidative potential of the hole (h_{vb}^+) in the catalyst (Eq. 2). On the other hand by the decomposition of H_2O (Eq. (3)) or by the reaction of (h_{vb}^+) with OH^-, very reactive hydroxyl radicals can also be formed (Eq. 4). The degradation of organic chemicals happeninghere because the hydroxyl radical is an extremely strong and non-selective oxidant [13,14]:

Catalyst + $h_v \rightarrow$ Catalyst(e_{CB}^- + h_{VB}^+) (1)

h_{VB}^+ + Methyl Orange$\rightarrow$ oxidation of the Methyl Orange (2)

$h_{VB}^+ + H_2O \rightarrow H^+ + \bullet OH$ (3)

$h_{VB}^+ + OH- \rightarrow \bullet OH$ (4)

Molecular oxygen can be reduced to superoxide anion because of an electron in the conduction band (e_{CB}^-) on the catalyst surface (Eq. 5). In the presence of organic trash, this radical mayform either organic peroxides (Eq. 6) or hydrogen peroxide (Eq. 8):

$e_{CB}^- + O_2 \rightarrow \bullet O^{-2}$ (5)

$\bullet O^{-2}$ + Methyl Orange$\rightarrow$Methyl Orange $^-OO\bullet$ (6)

$\bullet O^{-2} + HO_2\bullet + H^+ \rightarrow H_2O_2 + O_2$ (7)

The main responsible for the production of hydroxyl radicals were electrons in the conduction band, that have been specified as the primary cause of organic matter mineralization (Eq. (8)[15]:

$\bullet OH$ + Methyl Orange$\rightarrow$Degradation of the Methyl Orange (8)

3.3. Influence of PhotocatalystConcentration

The influence of catalyst concentration on the degradation of methyl orange(50 ppm) was investigated using commercialZnO from 0.5 to 1.5 g\l keeping another parameters like (pH, temperature, and dye concentration) constant. The results in theFigures 4, 5,6 , and 7are presented that the degradation percentage increased with an increase in ZnOconcentration up to 1.0 g\l for ZnObut the Figures 8 , 9, 10 , and 11presented the degradation percentage of Methyl Orange increased with an increase in TiO_2commercial concentration up to 1.0g\l,then the degradation does not affected significantly by the increase in catalyst concentration. This can be explained in terms of containing the catalyst surface with active sites and the ability of solarlight to permit in to the suspension. When the catalyst concentration increasing, the total active surface area increases.So, there is a decrease in solar light permeation because of an increase in the turbidity of the suspension, as a result of increased spread effect and hence the photoactivated volume of suspension decreases. Furthermore, there is a difficulty to maintain the suspension homogenous at high catalyst capacity because of particles agglomeration, and these lead to decrease the number of active sites[15-17].

The results also shows the maximum photodegradation for commercial ZnO (1 g/l) achieved after 130 minute (see Figure 5) , but for commercial TiO_2 the maximum photodegradation was after 250 minute (see Figure 9).

The results indicate (see Figure 12) that TiO_2. have lessphotocatalytic activity compared withTiO_2. The quantum efficiency of TiO_2 powder is significantly less than ZnOpowder, Since the band gap of ZnO is 3.17 eV and hence higher efficiencies have been mentioned for ZnO. The fast reassembly of hole and electron permeation due to the minimalband gap and for that reason a lesser photocatalytic activity for degradationcan benoticed[18-22]. Figure 13 shows the UV-instrument image for the progress of degradation during study time.

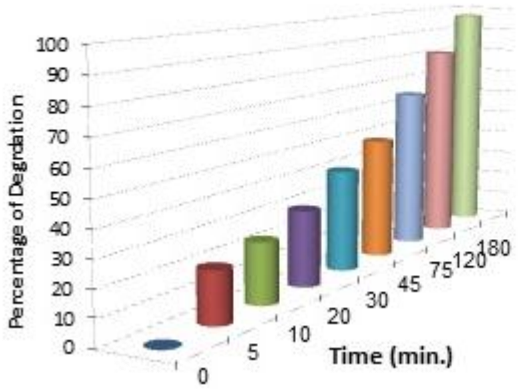


Figure 4 Shows the Percentage Degradation of Methyl Orange for 0.5 g\l ZnO

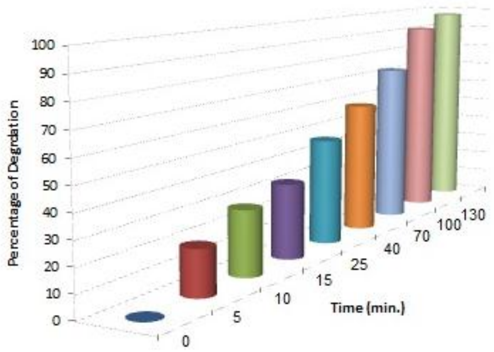


Figure 5 Shows the Percentage Degradation of Methyl Orange for1.0 g\l ZnO

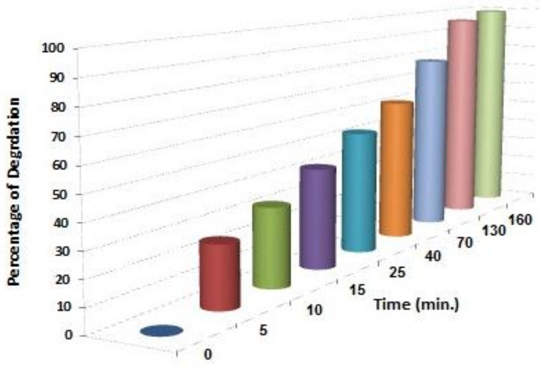


Figure 6 Shows the Percentage Degradation of Methyl Orange using 1.5 g\l ZnO

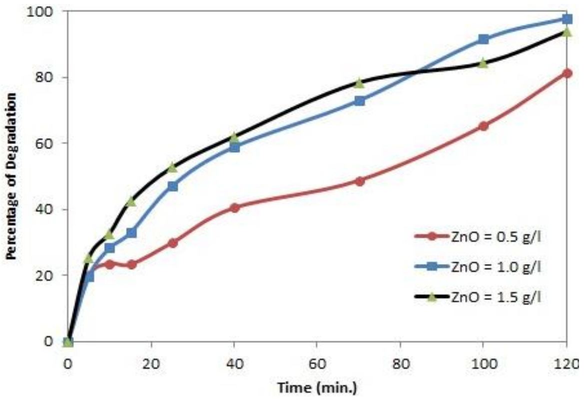


Figure 7 Shows the Comparison of Percentage Degradation of Methyl Orange between (0.5 , 1 , 1.5) g/l

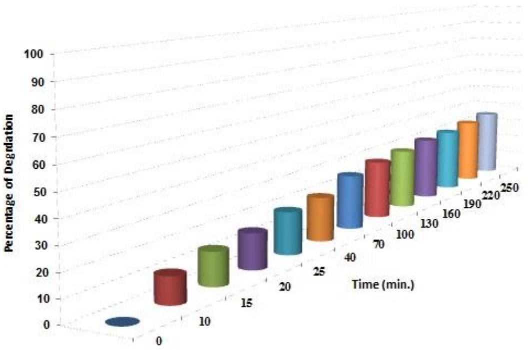


Figure 10 Shows the Percentage Degradation of Methyl Orange using 1.5

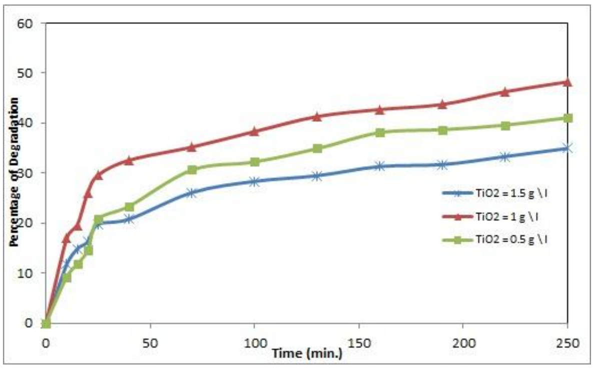


Figure 11 Shows the Comparison of Percentage Degradation of Methyl Orange between (0.5 , 1 , 1.5) g/l

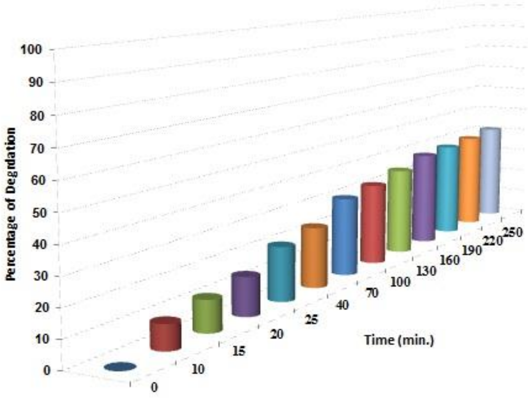


Figure 8 Shows the Percentage Degradation of Methyl Orange using 0.5 g\l

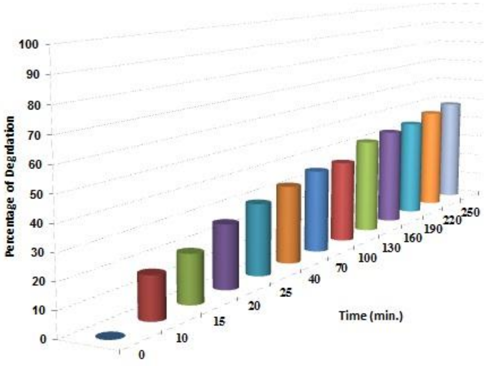


Figure 9 Shows the Percentage Degradation of Methyl Orange using 1.0 g\l

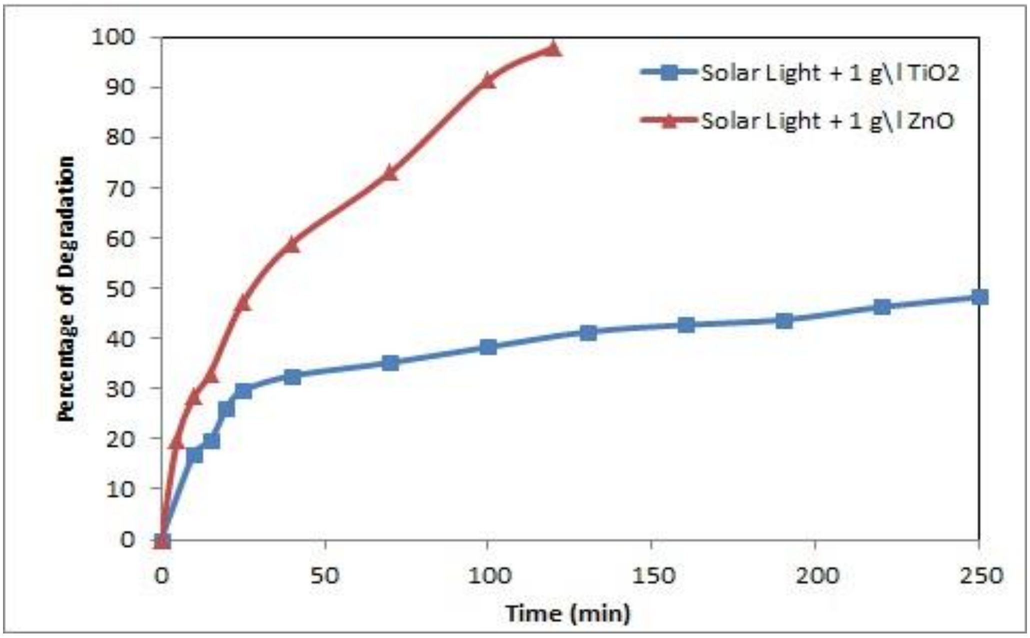
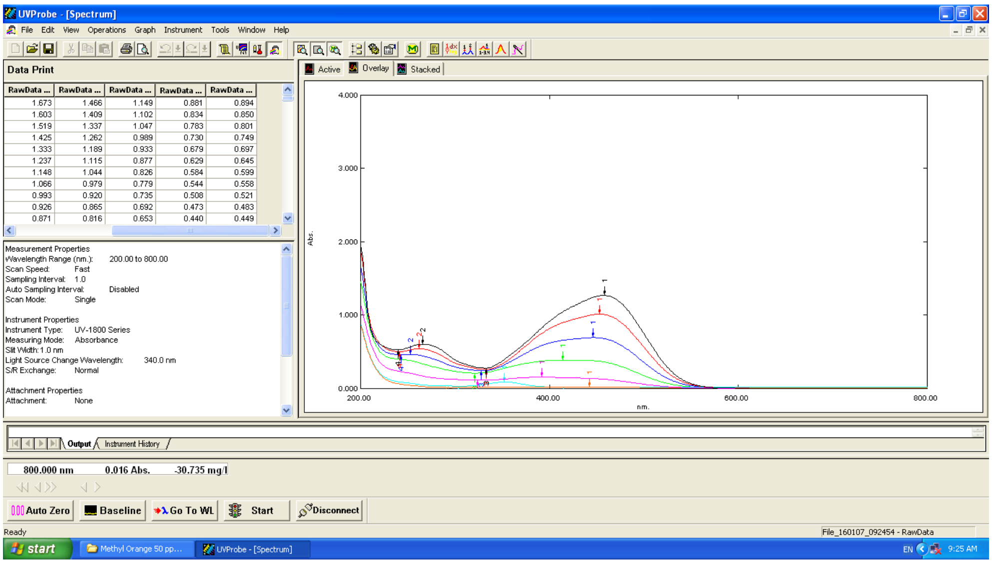


Figure 12 Shows the Comparison of Degradation Percentage of Methyl Orange between best concentration of ZnO and TiO_2



RawData ...	RawData ...	RawData ...	RawData ...	RawData ...
1.673	1.466	1.149	0.881	0.894
1.603	1.409	1.102	0.834	0.850
1.519	1.337	1.047	0.783	0.801
1.425	1.262	0.989	0.730	0.749
1.333	1.189	0.933	0.679	0.697
1.237	1.115	0.877	0.629	0.645
1.148	1.044	0.826	0.584	0.599
1.066	0.979	0.779	0.544	0.558
0.993	0.920	0.735	0.508	0.521
0.926	0.865	0.692	0.473	0.483
0.871	0.816	0.653	0.440	0.449

Measurement Properties
Wavelength Range (nm.): 200.00 to 800.00
Scan Speed: Fast
Sampling Interval: 1.0
Auto Sampling Interval: Disabled
Scan Mode: Single

Instrument Properties
Instrument Type: UV-1800 Series
Measuring Mode: Absorbance
Slit Width: 1.0 nm
Light Source Change Wavelength: 340.0 nm
S/R Exchange: Normal

Attachment Properties
Attachment: None

800.000 nm 0.016 Abs. -30.735 mg/l

Ready
File_160107_092454 - RawData

Figure 13 Shows the instrument picture of Percentage Degradation of Methyl Orange using best concentration of ZnO

3.4.Effect of Dye Concentration

Photodegradation of Methyl Orange was achieved by changing the initial concentration of the dye between 50–150 mg/ldue to determine the effect of initial dye concentration on the best catalyst type and dose (commercial ZnO)., Thedegradation percentage decreased proofing important things for either to increase the concentration of catalyst or time span for the total removal and this happening when the concentration of the dye was increased. Figure 14 depicts graphs of the time-dependent of degradation of Methyl Orange at various concentrations for dye solutions (50–150 mg/l). For the dye solutions of 50 mg/L and 100 mg/L, completelydegradation happenedduring160 and then 240minutes, nowfor150 mg/L duringat least300 minutes for the completelydegradation of dye and the percentage degradation which decreased graduallywhen the concentration of dye increased. The reason for this attitudewasa path length of the photons entering the solution and decreases in highdye concentration that means the photochemical reaction is decreased but some of photons absorbed by catalyst is high at low initial dye concentration absorption for number of photon by the used catalyst in lower[23-28].

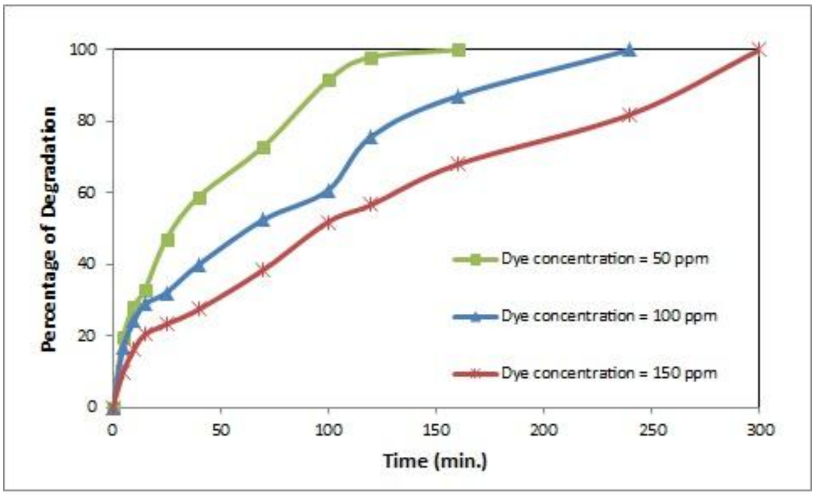


Figure 14 Show the effect of dye concentration on the percentage of photodegradation

3.5 Kinetic Study

Figure 14 states the kinetic of the disappearance of Methyl Orange dye for 50 mg/l concentration at the beginning. The experimental results state that the photocatalyticdegradation of Methyl Orange dye with commercial ZnOconcentration 1 g/l can be represented by the 1st. order kinetic model, ln $(C_0/C) = kt$, where C_0 is the concentration at time equal zero and C is the concentration at time equal t (y=0.0272x). A straight line can be observed fromthe semi-logarithmic plots from the known concentration values. The correlation constant was calculated for the fitted line to be $R^2 = 0.9334$ for commercial ZnO[14].

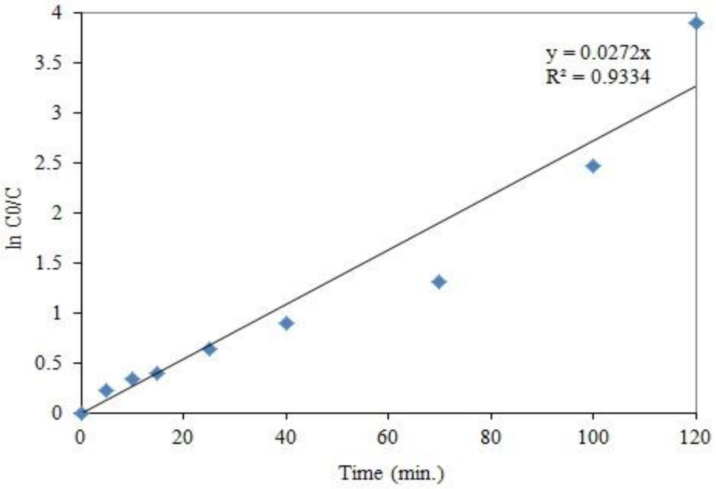


Figure 15 Kinetic study for the degradation of Methyl Orange dye using ZnO

4. Conclusions

It is clearly specified that the ZnO is a better photocatalyst for the degradation of Methyl Orange dye after comprehensive comparison of dye degradation of different semiconductors. The comparison between the commercial of ZnO and $TiO_2$are specified that the ZnOhas ahigh and bestphotocatalytic activity for Methyl Orangedegradation. The photocatalyticdegradation followed pseudo-first order kinetics.

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