

**RESEARCH TITLE**

**PHOTO-CATALYTIC DEGRADATION OF METHOMYL IN  
AQUATIC ENVIRONMENT**

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**Abstract**

This research study uses the combination of the catalyst ZnO and sunlight to find the photo-degradation rate of Methomyl "ALFURAT" insecticide. The obtained results were very promising. It was found that the ZnO catalyst has speeded up the degradation very effectively in the presence of sunlight. The conditions of the experiment itself in the dark had no effect, nor did the sunlight have any effect without the presence of the catalyst in the decomposition of the pesticide, as the concentration of the pesticide remained almost constant. Because Methomyl insecticide, give maximum absorbance in the U.V. region at 234 nm wavelength, the absorbance measurements were taken at this wavelength. The absorbance decreased rapidly with time, an indication that the insecticide has underwent a rapid degradation process. The method was described within, the rate constant for the degradation process, and half-life were calculated. This simple method can have wider economical and environmental impacts. It can be applied in the treatment of wastewater.

**Key Words:** Methomyl, photocatalytic degradation, insecticide, sunlight, catalyst, zinc

## 1. Introduction

Methomyl (methyl N (methylcarbamoyloxy) ethanimidothioate) is Carbamates insecticide [1,2]. Its chemical structure is presented in (Figure 1) [3].

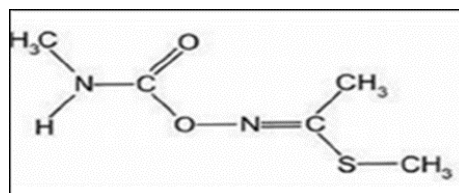


Fig 1: Chemical structure of Methomyl

Methomyl is highly soluble in water (57.9 g/L at 25 °C), has a low sorption affinity to soils and can therefore easily cause groundwater contamination in agricultural areas [4,5]. Methomyl, which has been classified by the World Health Organization, Environmental Protection Agency, USA, and European Commission as a very toxic and hazardous pesticide [5]. Methomyl is produced by reacting *S*-methyl-*N*-hydroxylthio acetamidate (MHTA) in methylene chloride with gaseous methyl isocyanate at 30–35 °C [4,6]. Methomyl is an oxime carbamate insecticide that controls a broad spectrum of arthropods such as spiders, ticks, moths, flies, beetles, aphids, leafhoppers, and spider mites often found on various field crops, ranging from fruits to tobacco [7]. Methomyl is used by farmers in Yemen to fight insects and pests in vegetables, fruits, cotton, citrus, tomatoes, and other crops.

Some work already has been done on degradation studies of Methomyl using ZnO photocatalysis [8,9], TiO<sub>2</sub> photocatalysis [4,6] [8-13]. The aim of this study is to develop a cost-effective and eco-friendly technique by using a zinc oxide catalyst to treat a polluted aqueous environment with Methomyl pesticide.

## 2. Experimental

### 2.1 Apparatus

A Scinco is UV-Vis spectrophotometer, model: S -3100, Serial No S -3100-00-1303005U. Produced by SCINCO CO., LTD, equipped with a Software Version: LabProPlus 2.0 Bulid 5.

### 2.2 Materials

The commercial pesticides Methomyl (ALFURAT), (purity: 90%) was provided by Shanghai Agrofaiith Industial Co.Ltd(China). The commercial pesticide Methomyl —ALFURAT II was supplied form the domestic market in Aden Governorate in the

Republic of Yemen.

Zinc oxide (ZnO) (purity: 99%) was provided by Fizmerk India Chemicals.

### 2.3. Preparation of solutions

Methomyl (ALFURAT) stock solution ( $1 \times 10^{-3}$  M) was prepared by preparing ( $1 \times 10^{-2}$  M) from pesticide in distilled water then 10 ml was taken and diluting it to 100 ml. (the solution was kept in the dark.).

The catalyst solution was prepared by dissolving 0.2g (ZnO) in (100 ml) de-ionized water [14].

### 2.4 Method

A concentration of  $1 \times 10^{-3}$  M of the commercial pesticide Methomyl was prepared initially. Then, the catalyst solution was prepared by dissolving 0.2g ZnO in (100 ml) de-ionized water. 2 ml of the  $1 \times 10^{-3}$  M insecticide solution was added into each of five 500 ml beakers. The beakers were taken to the roof, then the 0.2g/100ml ZnO catalyst solution were added into the five beakers to make up the total volume of 20 ml in each beaker, the mixtures were swirled, subjected to sunlight, and immediately the stopwatch was started. The first beaker (zero minute) was taken down for measurements, and the other mixtures were taken down for measurements every 10 minutes intervals. Since the insecticide gave a maximum absorbance at 234 nm for Methomyl, all the mixtures were measured at 234 nm for Methomyl. The catalyst solution was used as a blank. To avoid errors, the mixtures were filtered before measurements. The measurements were taken by a UV/Vis spectrophotometer. The average absorbance value of three readings was taken.

The same procedure was repeated twice, in the first case all the beakers containing the insecticide were subjected to sunlight without the adding the ZnO catalyst solution, but de-ionized water was added instead. In the second case all the beakers containing the insecticide/ZnO mixtures were placed in the dark [14].

## 3. Results and Discussions

### 3.1. Photocatalytic degradation

Absorbance of the insecticide/ZnO mixtures at 234 nm with time, the calculated concentrations of the insecticide with time, and the rate constants are shown in Table(1).

**Table 1: Absorbance of insecticide /ZnO mixtures at 234 nm with time, the calculated concentrations of the insecticide with time, and the rate constants.**

No.	Time (minutes)	Absorbance at 234 nm	Conc. of insecticide (mol/L)	Rate constant k (min <sup>-1</sup> )
1	0	0.4826	$1.00 \times 10^{-4}$	-
2	10	0.2777	$5.75 \times 10^{-5}$	0.0553
3	20	0.1755	$3.64 \times 10^{-5}$	0.0505
4	30	0.0751	$1.50 \times 10^{-5}$	0.0619
5	40	0.0232	$4.81 \times 10^{-6}$	0.0759

Figure (2), shows the decrease in absorbance of the insecticide/ZnO mixtures at 234 nm with time which indicates that it underwent a photodegradation reaction.

Kinetic analysis of the photocatalytic process of Methomyl “ALFURAT” pesticide was determined, Absorbance of the insecticide/ZnO mixtures at 234 nm with time, the calculated concentrations of the insecticide with time, and the rate constants are shown in Tables (1 and 2). Beer-Lambert law was used to calculate the concentrations of the insecticide remaining at different times.

**Table 2: Absorbance of “ALFURAT” /ZnO mixtures at 234 nm with time, the calculate half-life of the insecticide with time,  $\ln c/c_0$  and percentage of Degradation.**

No.	Time (minutes)	Absorbance at 234 nm	half-life $t_{1/2}$ (min)	$\ln c/c_0$	Degradation %
1	0	0.4826	-	0	-
2	10	0.2777	12.5	-0.55	43
3	20	0.1755	13.72	-1.01	64
4	30	0.0751	11.20	-1.86	85
5	40	0.0232	9.13	-3.03	95

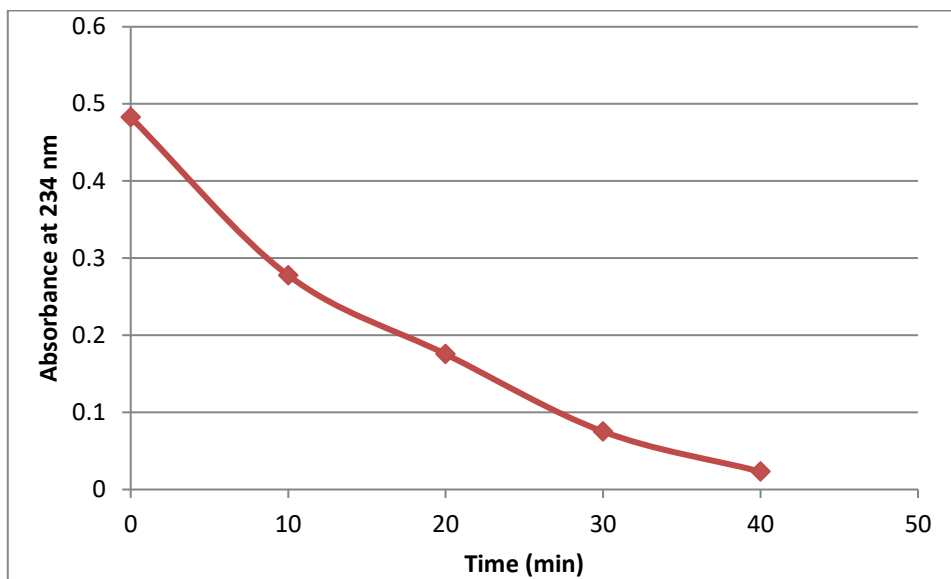


Fig 2: The absorbance of “ALFURAT” /ZnO mixture with time in minutes at 234 nm, showing a decrease in absorbance with time.

A plot of  $\ln(C/C_0)$  versus irradiation time (t) is shown in (figure 3) for Methomyl “ALFURAT” pesticide degradation. It is quite clear that there exists a linear relation between  $\ln(C/C_0)$  and time. The pseudo first order rate constant for photo-degradation process k and R, linear regression coefficient with various con Methomyl “ALFURAT” pesticide centration is given in Table (1). From Tables (1 and 2), the least square fit,  $R^2 = 0.9626$  and rate constant of degradation ( $K = 0.0609 \text{ min}^{-1}$ ) was evaluated as evaluated. The linear relationship between the functions with large  $R^2$  values was observed [15].

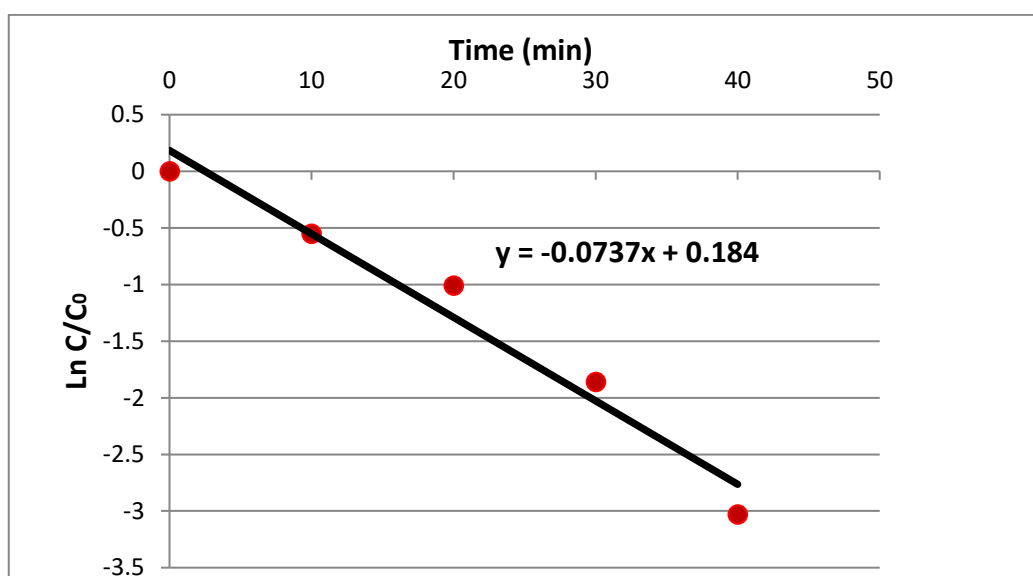


Fig. 3: A plot of  $\ln(C/C_0)$  versus irradiation time of “ALFURAT” the first order model on photocatalysis of with catalyst (ZnO) under sun light, t = (0–40 min)

From Table (1) the percentage of the photocatalytic degradation of Methomyl

“ALFURAT” pesticide with catalyst (ZnO) under sun light at 234 nm has been calculated during the different times (0 - 40 min) per ten minutes using following equation:

$$\text{Degradation \%} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where  $C_0$  is the initial pollutant concentration and  $C$  is the concentration of pollutant at time  $t$  [16,17].

The results showed that the percentage of the photocatalytic degradation of Methomyl “ALFURAT” pesticide was (95%) at (40) minute. the degradation percentage was higher at lower contaminant concentration.

Finally, the results of photocatalytic degradation of pesticide (Methomyl “ALFURAT”) under the influence of direct sunlight with catalyst(ZnO), this method has been carried out during different times of (10- 40) minutes The photocatalytic degradation method was very effective in the removal of pesticide (Methomyl “ALFURAT”).

**Table 3: Comparing results of photocatalytic degradation of pesticide (Methomyl —ALFURAT) /ZnO mixture with time**

pesticide	half-life $t_{1/2}$ ( $\text{min}^{-1}$ )	Degradation %	Rate constant $k$ ( $\text{min}^{-1}$ )	SD	$R^2$
Methomyl “ALFURAT”	11.64	95	0.0609	0.009559	0.9626

SD=Standard deviation,  $R^2$ =Square of the correlation coefficient

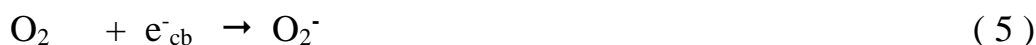
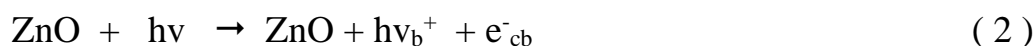
From table (3) The obtained results indicate that the photocatalytic degradation of pesticide (Methomyl “ALFURAT”) is a first order reaction. The calculated values of the rate constant of degradation ( $K$ ) were  $0.0609 \text{ min}^{-1}$  for Methomyl “ALFURAT”. with half-life of 11.64 minutes, this means This pesticide will disappear within one hour in presence of catalyst (ZnO) and under the influence of direct sunlight.

For the settings when the mixtures contained only insecticide without the ZnO catalyst solution, under sunlight, and the settings when the insecticide/ ZnO mixtures were placed in the dark, the absorbance measurements were not consistent and varied slightly up and down, but this did not represent a change in absorbance.

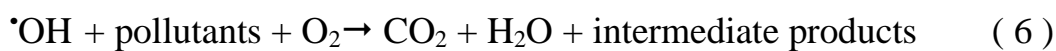
### 3.2. Possible Degradation Mechanism

The photocatalytic degradation of the pesticides take place on the surface of ZnO where  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$  radicals are trapped in the holes of reactive species. Oxygen and water are essential for photocatalytic degradation. The  $\cdot\text{OH}$  radicals are strong enough to break the bonds in the pesticide molecules adsorbed on the surface of ZnO. The amount of ZnO and concentration of pesticides are constant, the number of  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$  radicals increases with the increase in the irradiation period and hence the pesticide molecules are completely degraded into smaller fragments [18-20].

The main possible reactions are presented in equations (2-5) [21,22] and equation (6):



In the water purification by heterogeneous photocatalysis, the pollutants are usually organic. Their reaction in the presence of oxygen is: (equation 5) [23].



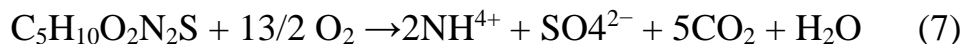
Oxygen is essential for complete degradation and should not be in competition at the level of adsorption with other reactive species on the catalyst.

there is an acceleration of the decrease in the concentration of the pollutant. Other research has shown that the rates and efficiencies of photo-assisted degradation of organic substrates are reported as significantly improved in the presence of oxygen or by the addition of several oxidizing species such as peroxydisulfate or peroxides [24-27]. This acceleration may be related to inhibition of the recombination of electron-hole pair and also by the production of more radicals  $\text{OH}^{\cdot}$  in the middle, so we conclude that oxygen ( $\text{O}_2$ ) here plays the role of a catalyst but since it is not regenerated at the end of the reaction, it affects the performance of the degradation reaction by increasing, so we can conclude that reacts with the pollutant [24].

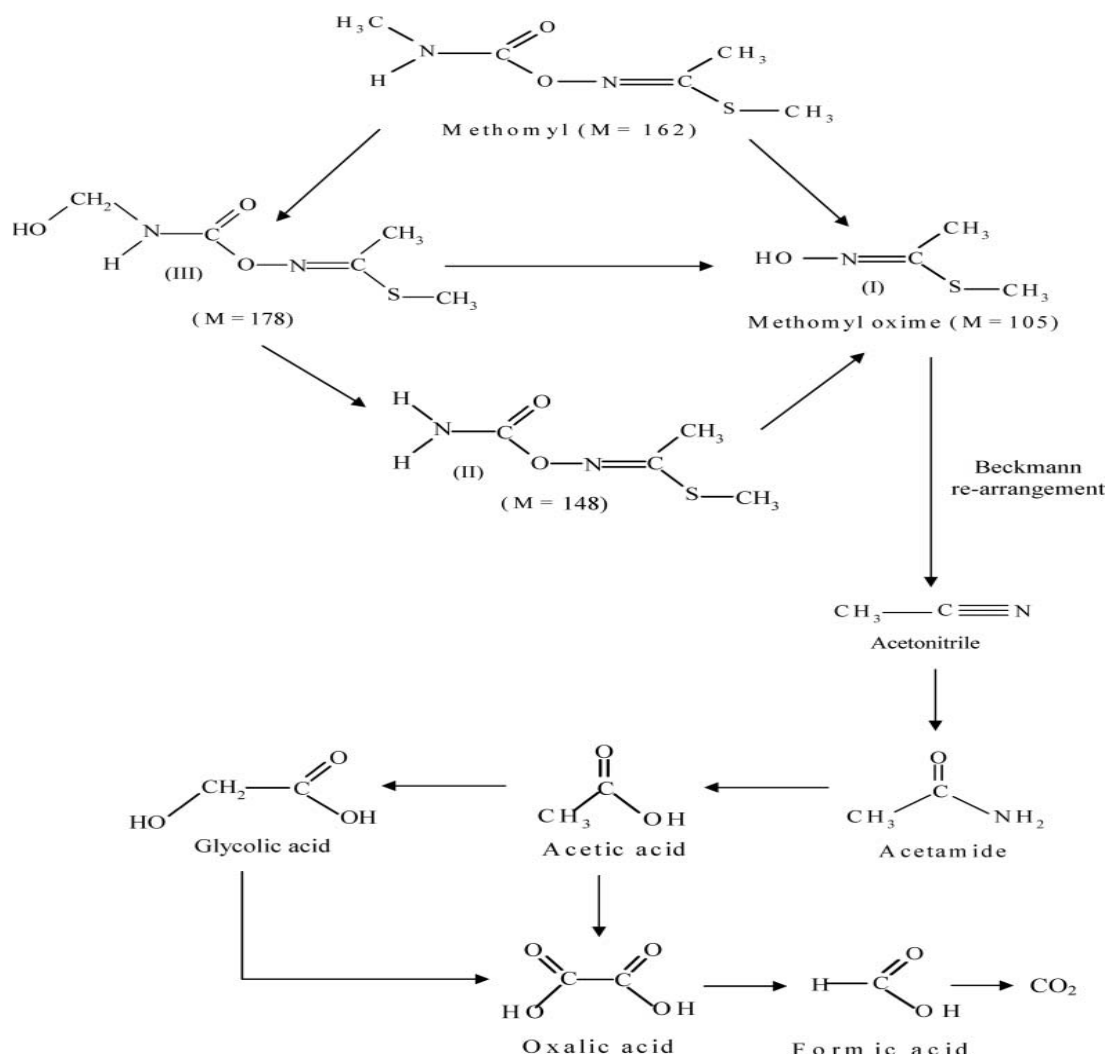
### 3.3. Proposed degradation pathway

In general, Methomyl degradation reaction can be expressed by the following equation which takes into account the absence of significant pH variation during the degradation.





It is noteworthy that in general it is considered that ammonia is oxidized to nitrate after long irradiation time and reactions in which molecules are in their most oxidized state have been proposed [6,7].



**Scheme 1: Tentative pathway for photocatalytic degradation of Methomyl**

After the identification of the various by-products, a pathway of the photocatalytic degradation of Methomyl in water was tentatively proposed (Scheme 1) [6,25].

#### 4. Conclusion

In this work, process was carried out under the influence of direct sunlight with catalyst (ZnO). This process has shown high efficiency in removal this pesticide (Methomyl “ALFURAT”). from this we conclude that the photocatalytic degradation process can not occur and be effective only in existing two factors together (light, catalyst).

The obtained results indicate that the photocatalytic degradation of pesticide is a first



order reaction. The calculated values of the rate constant of degradation (K) was  $0.0609 \text{ min}^{-1}$  for pesticide. with half-life of 11.64 minutes, this means this pesticide will disappear within one hour in presence of catalyst (ZnO) and under the influence of direct sunlight.

Finally, the results of this study showed that the photocatalytic degradation process has high efficiency and effective in removal the pesticides from the aquatic environment, which could be applied to removing many organic pollutants in the sewage, and wastewater systems. This method is a simple, low-cost, safe and easy-to-handle.

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