

## **Sunlight Photocatalytic of dazomet herbicides in aqueous solution**

### **الأكسدة الضوئية لمبيد العشبى الدازومت بواسطة ضوء الشمس**

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#### **Abstract**

The solar photocatalytic of an aqueous dazomet were carried out under natural weathering conditions. Photocatalytic of 50 µg/ml dazomet solution degraded 93.5. % of the solution after one hour of solar irradiation, by using 40 mg of zinc oxide as a catalyst . The effect of various parameters such as amount of catalyst and illumination time on the degradation of dazomet has been studied The degradation percentages were investigated by monitoring the dazomet mineralization spectrophotometrically. The mineralization rate of dazomet is calculate. .

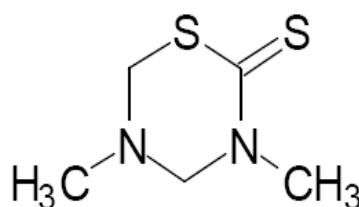
#### **الخلاصة**

أجريت الأكسدة الضوئية للمحلول المائي للمبيد العشبى الدازومت بتركيز 50 مايكرغرام/مل تحت الظروف الطبيعية والذي تجزأ بمعدل 93.5% بعد ساعة من الأكسدة الشمسية وباستخدام 40 ملغرام من اوكسيد الزنك كعامل محفز. وتمت دراسة تأثير بعض العوامل ككمية العامل المحفز ووقت التشعيع وتم تتبع التفاعل مطيافيا. وقد حسب معدل سرعة التجزئة

#### **Introduction**

Dazomet Granular (Basamid) is a soil fumigant that controls fungi, bacteria, nematodes, and weed seeds in soils <sup>(1, 2)</sup>. Formulated Basamid contains 99% of the active ingredient dazomet (tetrahydro-3, 5-dimethyl-2H-1, 3, 5-thiadiazine-2-thione) and is formulated as a solid microgranule. When incorporated into moist aerated soil, dazomet is degraded into several volatile intermediate products including methylisothiocyanate (MITC). Methylisothiocyanate is toxic to many soil borne organisms <sup>(1, 3,4)</sup>. The degradation end products include bicarbonate, nitrate, and sulfate compounds <sup>(1)</sup>.

The pesticide dazomet belongs to the class of chemicals called thiadiazines. Its chemical structure consists of a heterocyclic ring containing carbon, nitrogen, sulfur, and hydrogen <sup>(5)</sup>. As shown below:



Environmental pollution is concerned problem all around world due to rapid increase of industrialization and urbanization. Especially, the intensive pesticide use has caused some environmental problems in many countries. The major problem occurred in water resources. Therefore, these resources need to be protected from the contamination of pesticides for future sustainable use <sup>(6-8)</sup>.

Solar photocatalysis aims at mineralizing the contaminants into carbon dioxide, water and inorganics, and treatment of industrial waste water <sup>(9, 10)</sup>. The photocatalytic oxidation of organic compounds in water is the subject of a large body of research that has been performed in

laboratories all over the world <sup>(11-13)</sup>. A lesser but rapidly increasing amount of work has been devoted to the oxidation of volatile organic or inorganic compounds in the gas phase. Photocatalytic reduction of both organic compounds and metal-containing ions is also receiving increasing attention <sup>(14)</sup>.

Photocatalytic effects of semiconductors have been of much interest from the viewpoint of solar energy utilization. They have been applied not only to produce useful chemicals, but also to convert pollutants in waste streams to innocuous or less harmful form <sup>(15)</sup>. ZnO is a well-known semiconducting oxide under solar irradiation time and its photodegradation mechanism has been proven to be similar to that of TiO<sub>2</sub> although it shows less vigorous oxidation states <sup>(16)</sup>.

The present work, aims to study the solar photocatalytic degradation of dazomet using ZnO under natural weathering conditions.

## **Experimental**

### ***Materials and methods***

The commercial dazomet Trade Name (basamid) obtained from (Unifert) company (by Lebanon) license from PASF Germany with purity of 98% the photocatalyst ZnO was purchased from E.Merck (99%) purity. All other chemicals were used without further purification.

Dazomet degradation was identified by UV-Visible Spectrophotometer (UV-Visible 1650, spectrophotometer, Shemadzu, Japan and High performance liquid chromatographic (HPLC),Knauer ,Germany.). The determined wavelength was 283 nm, which is the maximum absorption wavelength..

Experiments were carried out in clear sunny days during august 2009; All experiments have been performed at the floor of chemistry department building in baghdad University, in an open atmosphere between 11.00 a.m.-1.00 p.m. Sunlight illumination was accomplished in a 250 ml conical flask containing 75 ml of the 50 µg/ml. dazomet solution.

In all experiments, 40 mg of the catalyst zinc oxide was suspended using a magnetic stirrer in dazomet solution, during the irradiation of the reaction mixture, 5 ml samples of the reaction mixture were, periodically, withdrawn using a syringe with a long pliable needle. These were centrifuged to separate the solid catalyst .In each case, 1 ml of the supernatant was drawn to measure the absorbance at 283 nm, using ultraviolet-visible spectrophotometer. To minimize the possible dark reactions, all samples were kept in the refrigerator in the dark. The effect of temperature on photolytic reaction was monitored by adjusting the temperature of the circulating water between (20-25) C°.The absorption spectra of dazomet is presented in Fig. 1.

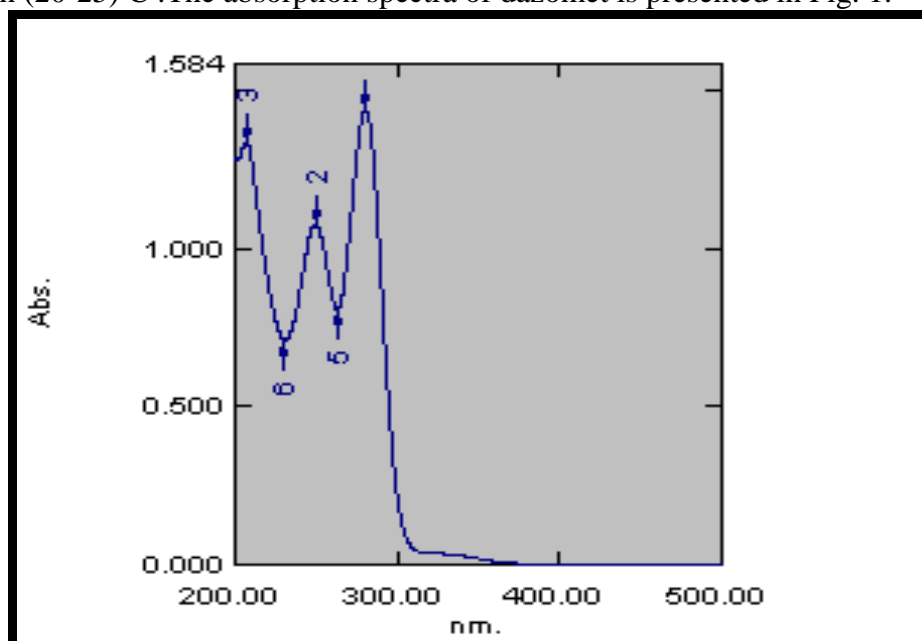


Fig. 1. The absorption spectra of dazomet

## **Results and Discussion**

Dazomet is extensively used in Iraqi country for the control of worms' roots contract in several different crops and especially in eggplant, tomato<sup>(17)</sup>.

No report in literature has been observed for solar photo catalytic behavior of dazomet in aqueous solution. Only little formation was given about the photochemical activity for the intermediate MITC in aqueous solution by Geddes et al<sup>(18)</sup>.

Solar photodegradation of dazomete using ZnO us catalyst was performed ,the Influence of various reaction parameters like amount of the catalyst, concentration of the dazomet and reaction time, are investigated to select an appropriate condition for comparison of activity.

Efficiency of photocatalytic degradation process was investigated as in Eq. 1.

$$\text{Efficiency of degradation (\%)} = (C_0 - C) / C_0 \times 100 \quad (1)$$

Where  $C_0$  is the initial concentration value of dazomet of at time  $t = 0$  min and  $C$  is final concentration value of dazomet solution in different time intervals photocatalytic treatment in the presence of ZnO and sunlight irradiation.

### **Effect of catalyst loading**

The effect of photo-catalyst loading on the degradation of dazomet in aqueous solution under sunlight illumination was investigated .For determine the optimization of the minimum amount of ZnO catalyst suspension concentration required to degradation of dazomet . .

The results are illustrated in Fig. 2. With increasing the catalyst amounts up to 40 mg, the degradation efficiency increased.

The increase in the amount of photocatalyst increased the total surface area, namely number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased.

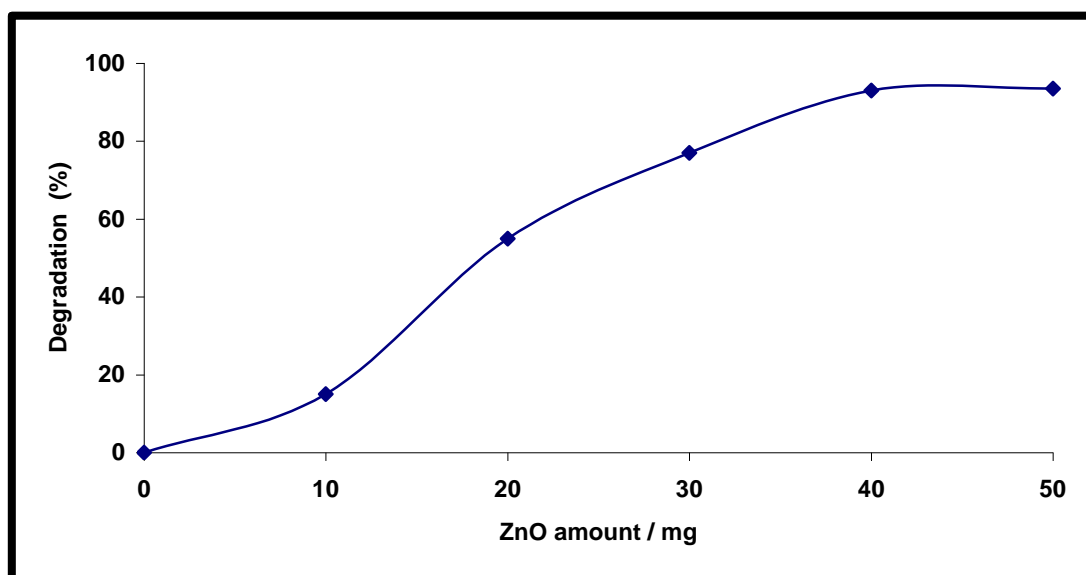


Figure 2: Effect of ZnO amount on the solar photocatalytic degradation of dazomet in aqueous solution of dazomet 50 µg/ml.

This indicates the increase in the number of hydroxyl and superoxide radicals. However, the suspension of ZnO catalyst increased above the limiting value, the number of active sites on the ZnO surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle-particles interactions) at high solid concentration<sup>(19)</sup>.

When a blank experiment without ZnO photocatalyst was performed until one hour illumination, the degradation efficiency increased , it could be concluded that the degradations was attributed to the photocatalytic reaction, not to thermal one. As a consequence, 40 mg of ZnO was chosen as the optimal amounts of photocatalyst for the sequential experiment.

**Effect of illumination time**

The effect of illumination time on the photocatalytic degradation of dazomet in water with ZnO was investigated. The results are illustrated in Fig. 3. The photo-catalytic decomposition process proceeded rapidly until 30 min. At 60 min illumination time, dazomet disappeared and degraded in aqueous solutions.

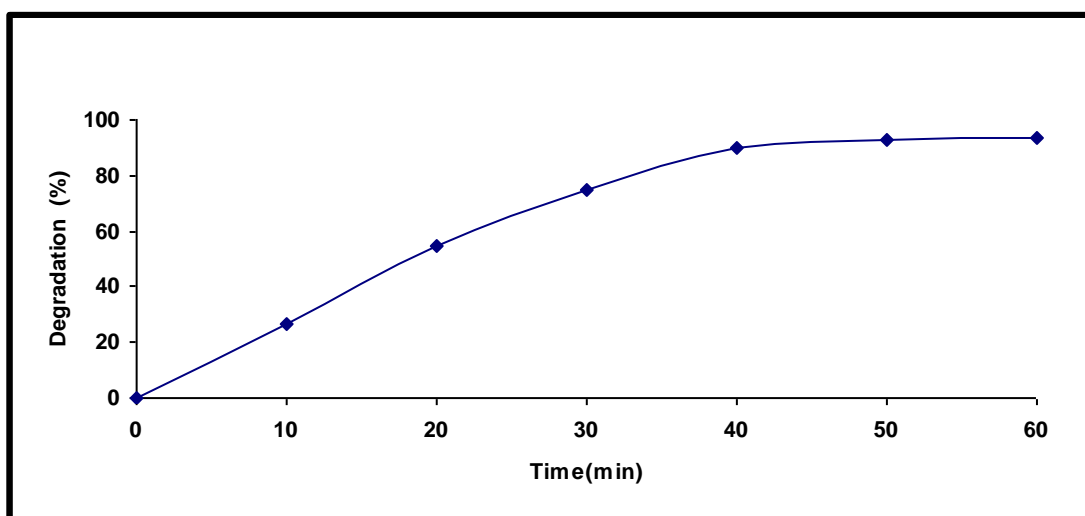
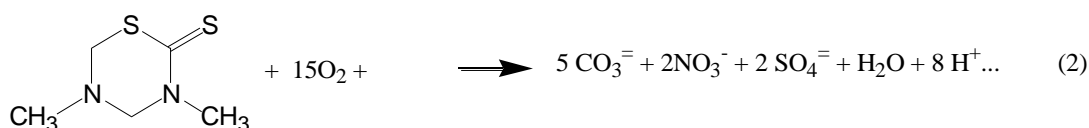


Figure 3: Effect of illumination time on the solar photocatalytic degradation of dazomet in aqueous solution using ZnO.: 40 mg ,dazomet : 5 µg/ml.

**Kinetic Degradation**

The rate of photodegradation of dazomet on ZnO catalyst was monitored under the optimum conditions employed for dazomet (ZnO loading is 40 mg and starting initial concentration 5 µg/ml in aqueous solution. We suggest the following mineralization by Eq. 2.



Graphical methods were also employed to predict the order of reaction spectrophotometrically. The decreases in concentration of dazomet in aqueous solution was monitored by the absorption at λ<sub>max</sub> 283 nm with different irradiation time.

The plot of the ln (A<sub>t</sub>-A<sub>∞</sub>) versus the sun irradiation time shows a straight line behavior. This suggests also the first - order kinetics of the photocatalst process.

From the slope of straight line, the degradation of dazomet and the value of the first order specific rate constant k<sub>phot.</sub> in aqueous solution was plotted in Fig. 4.

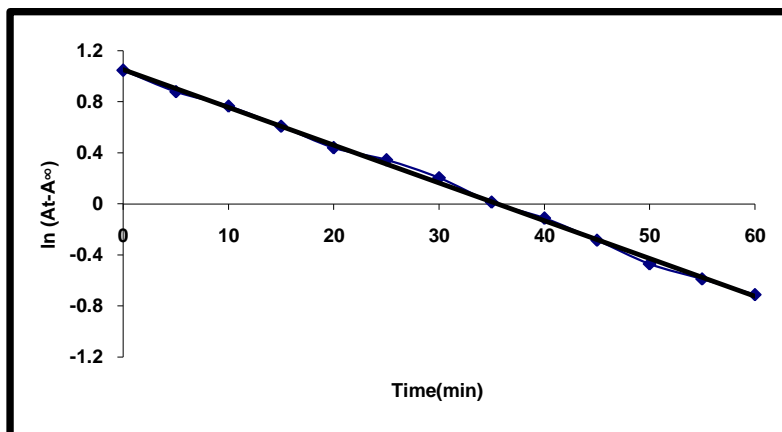


Figure 4: The Relation Between  $\ln (A_t - A_\infty)$  and the Irradiation Time for Dazomet Degradation in aqueous solution.

From the slope of straight line, the value of the first order specific rate constant  $k_{\text{phot}}$  is to be equal to  $2.96 \times 10^{-2} \text{ min}^{-1}$ .

### Identification of Dazomet Photocatalyst Products

Ultraviolet-Visible spectroscopy technique was used to monitor the formation of photodegradation products of dazomet with ZnO suspension in aqueous solution.. Fig. 5 shows the absorption spectrum of dazomet degradation in aqueous solution at different irrerradation time in the spectral range between (200-500) nm.

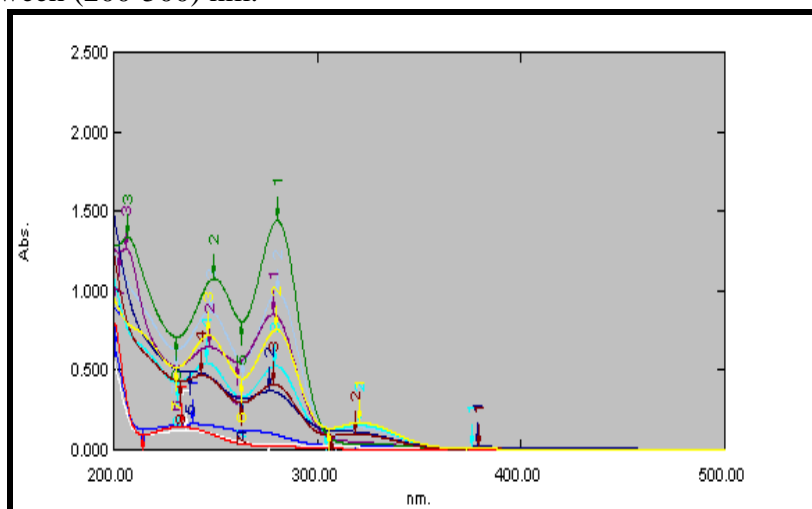


Figure 5: UV-Visible Spectral Change of Degradation for solar photocatalytic degradation of dazomet in aqueous solution using ZnO.: 40 mg ,dazomet : 5 µg/ml.

The photocatalytic process of on ZnO suspension was also monitored by HPLC chromatogram of Dazomet degradation, Fig. 6a illustrated the HPLC chromatogram and showed the absorbance peak, which appeared at retention time of 6.5minutes before irradiation .After the sun irradiation the intensity of this peak is gradually decreased with sun irradiation time Fig. 6b and. a new absorbance peaks start to appear after one 30 min sun irradiation time and this peaks located at retention time ( $R_t = 1.9, 2.0, 3.4$ ) minutes. Test analysis of authentic compound reveals that this new peaks was related to methyl amine ( $R_t = 1.9$ ) minutes, formaldehyde ( $R_t = 2.0$ ) minutes and  $\text{CS}_2$  ( $R_t = 3.4$ ) minutes.

Fig. 6c shows no HPLC peaks were detected and completed mineralization of dazomet under sunlight were happened.

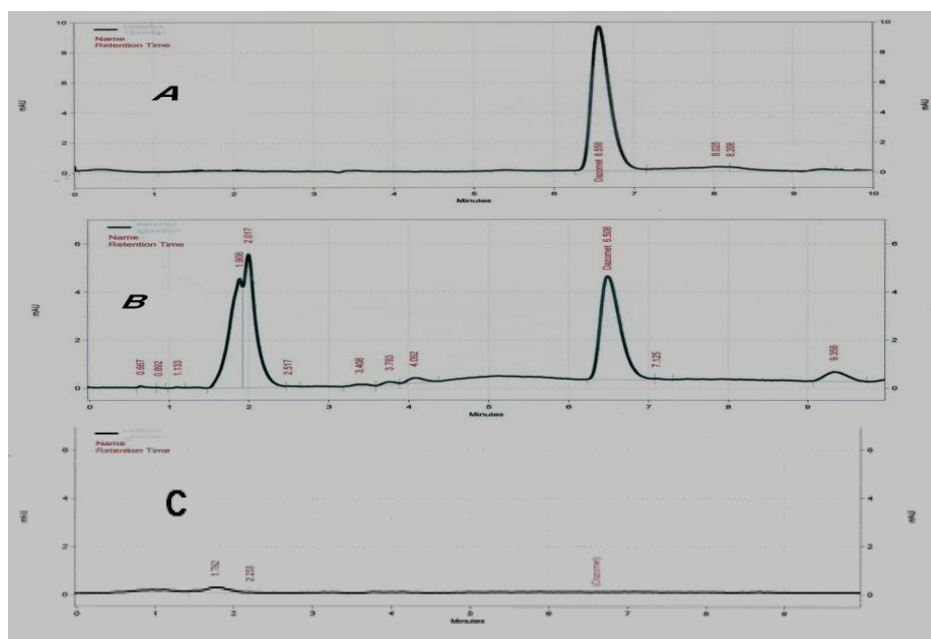
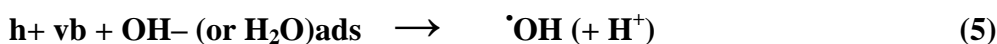
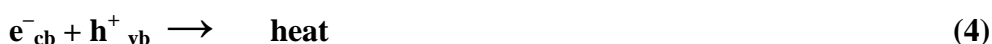
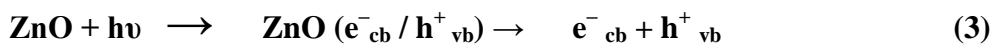


Figure 5: HPLC Chromatogram of Dazomet Solution [(A) Before Photolysis (B) after 30 min (C) after 60 min using ZnO.: 40 mg ,dazomet : 5 µg/ml. The HPLC Condition are: Mobile Phase Acetonitril: Water (30/70V/V) Column C<sub>8</sub> (5µm, 25 x0.4cm)and UV.Detector at283nm.

### Photodegradation mechanism

A general ZnO photocatalytic mechanism is proposed <sup>(20)</sup> under the irradiation of energy greater than the band gap, valence band electrons are promoted to the conduction band leaving a hole behind Eq. (3). These electrons ( $e^-_{cb}$ ) - hole ( $h^+_{vb}$ ) pairs can either recombine Eq. (4) or interact separately with other molecules. The holes at the ZnO valence band can oxidize adsorbed water or hydroxide ions to produce  $\cdot\text{OH}$  radicals Eq. (5). Electron in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion Eq. (6). This radical may form hydrogen peroxide or hydroperoxy radical  $\cdot\text{OOH}$  Eqs. (7) and (8). The hydroxyl radical is a powerful oxidizing agent and attacks to dazomet, and intermediate products are formed. These intermediates react with more hydroxyl radicals to produce final products  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , Eq. (9).



### Conclusion

The optimization of solar photocatalytic degradation conditions of dazomet in water using zinc oxide was investigated. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In Iraqi country, sunlight energy is available and it could be effectively used for the photocatalytic degradation of pollutants in waste water. .

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