

A STUDY OF PHOTO DEGRADATION KINTICS AND TOXITY EFFECT ON THE BIOLOGICAL ACTIVITY OF NOGOS IN CONTROLLING OF APHIDS (*Myzus persicae*) ON CUCUMBER

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ABSTRACT:

to investigate the effect of photo This experiment was conducted at AL-Ramadi distinct / AL-Anbar province, Iraq in 2008 degradation kinetics of 50% (w/v) Nogos (which belongs to the family of organo phosphorus compounds, of molecular formula (Di Methyl 2,2 – di chlorovinyl phosphate)) on the biological activity of this insecticide in controlling aphids (*Myzus persicae*) on cucumber.

The insecticide was exposed to three different wavelengths in the laboratory (253.7, 365 and 623.5nm) for four different periods of time (1, 2, 4, 6 and 8 h) at temperature 25 C⁰, before field application for infestation % of aphids and productivity of cucumber were estimated. Results showed that Nogos activity was decreased at low wavelengths treatment, whereas infestation % were (24 and 22 %) at (253.7, 365 nm) treatments respectively. While it was (15 %) for (623.5 nm) treatment decreased productivity of plant with decreasing wavelengths , was also recorded, the average yield was (2893 and 2939 kg/D) recorded for plants treated with nogos exposed to (253.7, 365 nm) wave lengths respectively , compared to (3154 kg/D) obtained under (623.5 nm) treatment . The results also showed that photo degradation of Nogos which was measured by ion phosphorus increased while pH reduced by increasing light wavelength . The kinetic studies indicated that the rate of reaction is Ln (P₀ / P_t) with time of light which showed a linear relation, which was of the first order to drawing the relation between highly effect by light.

على فعاليته الحيويه في NOGOS دراسة حركية التحلل الضوئي والتأثير السمي لمبيد النوكوز (على نبات الخيار *Myzus persicae* مكافحة حشرة المن)

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الكلمات المفتاحية : التحلل الضوئي ، المبيد ، النوكوز.

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المستخلص

نقد البحث في احد الحقول الزراعية التابعة لمدينة الرمادي / محافظة الانبار – العراق للموسم ٢٠٠٨ بهدف دراسة تأثير حركية التحلل الضوئي لمبيد Nogos (w/v) 50% أحد المبيدات الحشرية الهامة ينتمي الى مجموعة مركبات الفسفور العضوية Organo Phosphorus Compounds والصيغة الجزيئية له هي (Di Methyl 2,2 – dichlorovinyl phosphate) على فعاليته الحيوية في مكافحة حشرة المن (*Myzus persica*) على نبات الخيار وتأثير ذلك بالمقابل على الإنتاجية .

حيث تم تعريض المبيد مختبرياً للاشعة فوق البنفسجية بأطوال موجيه مختلفة (٢٥٣.٧ و ٣٦٥ nm) والأشعة المرئية بطول موجي (٦٢٣.٥ nm) ولفترات زمنية مختلفة (١، ٢، ٤، ٦، ٨ ساعة) ، وبدرجة حرارة 25 C⁰ ومن ثم اختبرت فعالية المبيد لكافة المعاملات أعلاه حقلياً لأجل دراسة نسبة الإصابة والإنتاجية في نباتات الخيار .

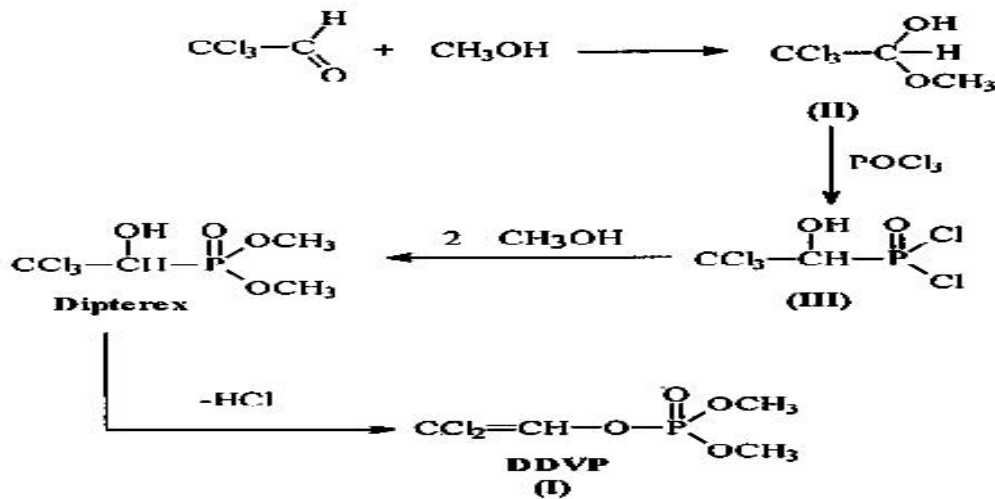
تبين من نتائج الدراسة إن نسبة الإصابة تناسبت عكسيا مع زيادة الطول الموجي حيث بلغت أذناها (١٥ %) وذلك عند تعرض المبيد للطول الموجي (٦٢٣.٥ nm)، وقد اختلفت معنويا عن الأطوال الموجية الأخرى (٣٦٥ و ٢٥٣.٧ nm) والتي تسببت في رفع نسبة الإصابة عند تعريض المبيد لها وبلغت (٢٢ و ٢٤ % على التوالي) . والسبب في ذلك ربما يعزى إلى تحلل المبيد ضوئيا بشكل أسرع لدى تعرضه للأطوال الموجية القصيرة لكون شدة الإضاءة (طاقة الأشعة) الصادرة من هذه الأطوال الموجية يكون اكبر من الأطوال الموجية العالية.

اظهر تعرض المبيد للأطوال الموجية القصيرة الأثر الواضح في خفض الإنتاجية اذ بلغت (٢٨٩٣ و ٢٩٣٩ كغم/دونم) عند التعرض للأطوال الموجية (٣٦٥ و ٢٥٣.٧ nm) ، في حين ارتفعت الإنتاجية معنويا عند تعرض المبيد للطول الموجي (٦23.5nm وبلغت (٣١٥٤ كغم/دونم) . وقد بينت الدراسة أيضاً أن التجزئة الضوئية للمبيد الفسفوري العضوي النوكوز والمقاسة بدلالة تركيز أيونات الفسفور [P] المتحررة تزداد في حين تقل قيمة الأس الهيدروجيني [pH] للمحلول مع زيادة زمن تأثير الأضاءة وقد أوضحت الدراسة الحركية أن سرعة التفاعل هي من المرتبة الأولى برسم العلاقة اللوغارتمية بين $\ln(P_0/P_t)$ مع أزمنة الأضاءة فكانت العلاقة خطية وكان للضوء تأثير كبير في قيمها .

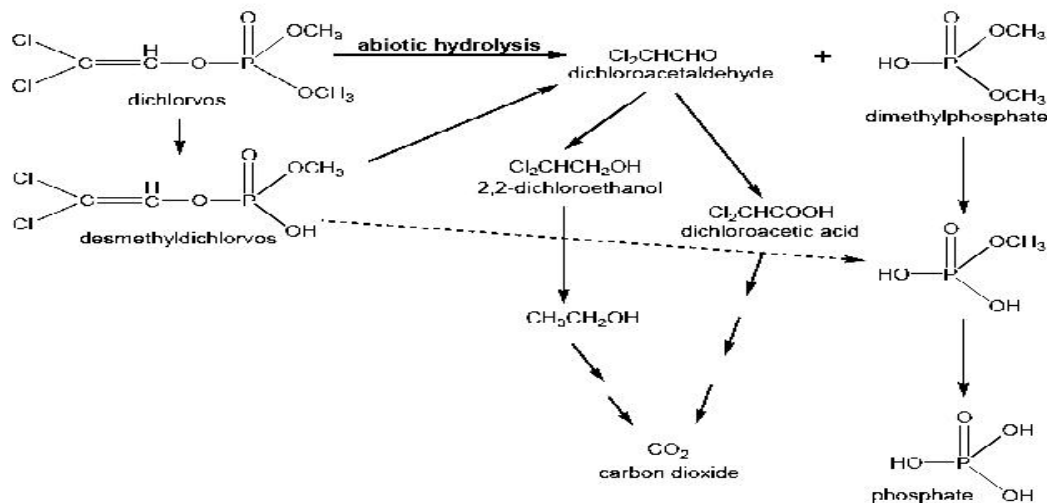
INTRODUCTION:

Nogos is one of pesticides in phosphorus group which is produced by the following reaction (Muhlmann and Schrader, 2005).

Nogos is very soluble in water, alcohol, zylene and acetone. The photochemical processes are used in the completion of different reactions and follow up these reactions at different stages (Horspool, 1976).



Synthesis of dichlorvos insecticide



Proposed pathway for the breakdown of dichlorvos in soil and in water / sediment systems, including a biotic hydrolysis and microbial degradation steps (Howard and Bayer, 2008).

Chemical insecticides participated actively in the increase of the agricultural production, and the limitation of the diseases that transplant to both humans and animals. Some studies showed that it's difficult to obtain a highly economical and viable production without the use of insecticides in the production process. (Qunfer, 1984, Al Malah and Shaban, 1993).

Insecticides are usually stored until the need emerges. It may be stored for years which could make them useless. This may be attributed to many reasons:

- 1-Accuracy in the estimation of their real need and their kinds.
- 2-Absence of an equilibrium policy of consumption besides the deficiency in their distribution.
- 3-The difficulty that emerge from the fact, its impossible getting the right weather predictions from one agricultural season to another, moreover the area that hits differs seasonally. The yield of these variations conduct to the decomposition and destruction of these chemical compounds (Mansoor *etal*, 1983). especially in stores which miss the standards conditions of storage.

Undoubtedly insecticides were affected by many factors such as heat, illumination and the time of storage, this will cause the transformation of them to another compounds that differ from the original ones in many aspects such as toxicity and the rest of chemo-physical properties.

The packed insecticides exposed to two kinds of variation:

- 1-Chemical changes in the active material transforming insecticides to other products; which may be more or less toxicants (Mansoor *etal*, 1983).
- 2-Physical changes represented by the separation of the catalysts, precipitation and crystallization (Marer *etal*, 1988).

Chemical processes depend on the intensity of the absorbed light causing the break of the

molecular bonds, which depend on the density of insects, from these processes, photo reduction, Photo oxidation, photo polymerization, photo addition and photo rearrangement (Omar and Sayyed, 1986).

There are two kinds of reactions that promoted by radiation especially the u.v light which effect the chloro organic compounds.

1-Photo dechlorination which occurred during the exposure to radiation especially that of micro waves u.v light leading to the removal of the chloroatom (Smith, 1972).

2-Inter molecular rearrangement, this process forms the isomers of the original compound via photo-chemical reactions (Al Malah and Shaban, 1993).

Photo oxidation of insecticides caused by radiation especially that u.v of solar source that may initiate and also chemical and physical changes (Connell and Publishers, 1997). The most probable change is that of the destruction of the active material forming new compounds of less toxicity or may be intoxic (Simons, 1971, Wanyne, 1970).

The rate of degradation of an insecticide depends on light intensity, wavelength, acidity of solution, dissolved oxygen quantity, nature of the solvent used and the reaction medium (Crosby, 1976).

Another study on diazinone (Al-Kubaysi, 2002). and peromethrin (Green *etal*, 1977). Found the irradiation of such insecticides lead to photo degradation inversely and proportionally to wavelength.

Due to the fact that noxos, of wide range usage in dealing with many epidemic insects, effect the agricultural crops.

This work had been carried out aiming to showing the effect of different u.v wavelengths on its biological efficiency to control (*Myzus persicae*) in cucumber plant.

EXPERIMENTAL PART:

The Noxos was irradiated by three different wavelengths of (253.7, 365 and 623.5 nm) for different periods of time (1, 2, 4, 6 and 8 hours) at temperature 25 °C. In order to find the effect of light on this pesticide the following equipments

were used:

1-Reading - photo reactor type 31 produced by applied photo physics Ltd. (London). This instrument contains:

A-Two low pressure mercury lamps which are faced to face to each other and each lamp is in M form and emission of light at (253.7 nm).

B-Two medium pressure mercury lamps which are face to face, each lamp is in a cylindrical form and with emission light of (365 nm).

2-Fluorescent lamp (usual candle) which contains neon gas and has an intensity of (623.5nm). This lamp is used in the research because it is usually used in the pesticide store room. These lamps were left lightening for long period as a result of carelessness.

A bio test was performed in the field on aphids (*Myzus persicae*) which were distributed on cucumber plant. An agricultural part of field was selected and prepared in rows according to the typical method of gaps between the plants (Mohammed, 1983). The agricultural practices were implanted equally for all plants. Three rows were used for each treatment on a condition that each row represents experiment of unit with a length of 40 meters. A suitable distance was left between treatments to prevent mixing during spray or mist.

The infected plants with aphids were treated with nogos insecticide at the beginning of the appearance of infection. The used insecticide was treated with different light intensities with different periods mentioned above to find the effects of all the above treatments on the following requirements:

1-Infection Percentage (%):

The number of the infected plants was counted from the following relation:

Infection percentage = number infected plants / total number of plants × 100.

2-Production (kg / Donam)

The quantity of cucumber (kg) for each treatment was calculated from the net of each

experimental unit (one row) and comparing it with the total area of all treatments.

(RCBD) design was used in this experiment and the results were verified by (LSD) test in a probability level of 5% (Al-Rawi and Khalaf, 1980).

3-Many experiments were implemented in order to identify the essential variables to get fractionation process of the Nogos pesticide and following photo fractionation by:

A-Phosphorus Concentration Measurements by Spectrophotometric Method (APHA; AWWA, and WPCF, 1975). Spectrophotometer was used in this method (25) ml of standard Nogos sample solution and exposed Nogos to light with addition of (4) ml of combined reagent (prepared from 50 ml of 5N (H₂SO₄), 5ml of 0.27% Antimony potassium tartrate, 15ml of 4% Ammonium molybdate and 30ml of 1.76% of Ascorbic acid) Absorbance's were measured with (10-30) minutes by spectrophotometer at 880 nm.

The standard solutions of potassium dihydrogen ortho phosphate (*KH₂PO₄*) were prepared in the range of concentration of (**0.01 - 0.8 M**) in order to get the calibration curve and from it the concentration of phosphorus was picked up during the photo fractionation process.

B-pH Change Measurements of the Solution was estimated by regular method.

The rate of pesticide decomposition constant (**K**) is obtained from the slope of the calibration graph. The decomposition rate constant had identified the first order reaction for the pesticide from application the following relation:

$$\ln P_0 / P_t = Kt$$

Modified to the following relation according to the requirements of the research:

$$\ln P_\infty / P_\infty - P_t = Kt$$

Where P_∞ = the produced phosphorus concentration in the final reaction which equivalent to P_0

P_t = concentration of phosphorus produced after photolysis exposure.

t = time of exposure of the pesticide sample to light.

RESULTS AND DISCUSSION:

1- Infection Percentage (%) :

It is clear from the results compiled on table (1) that there was a decrease in infection percentage significantly when nogos insecticide was exhibited to light intensity at wavelength of (623.5nm) which approached (15%), on other hand, the infection percentage was increased with two treatments when the insecticide was exposed to u.v light intensity at wavelengths (253.7 and 365 nm) being (24 and 22%) respectively. The increase in infection percentage may be due to the photo decomposition of the insecticide by the high energy of the short wavelengths which resulted in physical and chemical changes which destroyed the active part of the insecticide and the formed materials had less poison effects than the original insecticide (Simons, 1971, Wanyne, 1970, Al-Kubaysi, 2002, Green *etal*, 1977).

For the effect of different periods of the exposing the insecticide for the light intensity, an increase of infection percentage was observed which approached the maximum levels (23%) when it was exposed for one hour. The percentage of infection was decreased to (18%) for six hours of exhibition. When the mixed two factors of light intensity and period of exhibition were run, an increase of infection percentage to maximum level (29%) was obtained when the insecticide was irradiated by light intensity at (253.7 nm) for one hour.

The infection percentage was reduced to the minimum level (13%) when the insecticide was exposed to light intensity of (623.5nm) for 4 hours.

2-Production:

The exhibition of nogos insecticide to light intensity at (253.7 and 365nm) has shown significant effect in reduction of production of cucumber plant which approached (2893 and 2939 kg/Donam), respectively but when the insecticide was exposed to light intensity at (623.5nm) it offered significant increase of production reached (3154 kg/Donam) table(2). Therefore the production reduction when the

insecticide was exhibited to short wavelengths may be due to the photo decomposition attainment which destroys the active material of the insecticide and forming new compound that are less poison than the original one (Simons, 1971, Wanyne, 1970, Al-Kubaysi, 2002, Green *etal*, 1977).

Mean while, the exhibition period has raised the production to (3139 kg/Donam) which the insecticide was exhibited for one hour, while it was reduced to minimum level (2824 kg/Donam) when the insecticide was exhibited for 8 hours both factors have shown a production decrease reached (2620 kg/Donam) when the insecticide was exhibited to light intensity at (253.7nm) for 8 hours while an increase of production was obtained to maximum levels which reached (3464 kg/Donam) when the insecticide was exhibited to light intensity at (623.5nm) for one hour.

3-The changes in phosphate concentrations and pH of Nogos solutions irradiated for different periods of time were shown in tables (3 to 5). There was an increase in phosphate ion concentrations with time for wavelengths. The phosphate ion concentrations approached a maximum of 15.0×10^{-2} ppm, 23.5×10^{-2} ppm and 28.7×10^{-2} ppm at 8 h for (623.5, 365 and 253.7 nm) respectively. These results were in agreement with some of pervious investigations (Shi- Fu and Xue- Li, 1998).

Dramatic decrease in pH values was occurred at irradiation processes especially for 253.7 nm due to the formation of ions in solution (Allwi, 1998).

The results of reaction rate for three wavelengths showed that a first-order is matching very well with the decomposition processes, Figs. (1 to 3). However, the constant rate of the decomposition processes showed a value of 0.1835 h^{-1} by using a light of 623.5 nm. While a value of 0.2525 h^{-1} and 0.2544 h^{-1} was obtained with light of (365 and 253.7 nm) which focus up the importance of this wavelength.

CONCLUSIONS:

The following conclusions were recognized on the basis of the results of the research:

1-There is high effect of the light intensity at short

wavelength (253.7 and 365nm) to destroying the active material of the nogos insecticide. As a result of photo decomposition of the insecticide followed by reduction of its activity on the *Myzus persicae*, the products of the destroyed insecticide are less poisonous from the original one.

2-The treatment of cucumber plants with nogos insecticide irradiated at 623.5nm (fluorescent lamp) have shown infection by *Myzus persicae* but less than when the insecticide was exhibited to light intensity at (253.7 and 365 nm).

RECOMMENDATIONS:

1-Insecticides should be reserved in dark stores in order to keep them far from the light intensity; otherwise they will be decomposed and destroyed. The light is not used unless it is necessary.

2-Regulation of a balanced consumption Policy to use the oldest insecticides and then the more recent ones.

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Table-1: Effect of different wavelengths on Nogos upon casualty percentage of cucumber of aphids (*Myzus persicae*)

Exposure periods (hours) Wavelengths	Infection percentage (%)					
	1	2	4	6	8	Mean
Wavelength						
253.7 nm	29	23	25	19	22	24
365	24	24	20	22	22	22
623.5 nm	16	16	13	14	17	15
Mean	23	21	19	18	20	
LSD 0.05 for a= 3.6 b= 2.1 a*b=4.0						

a=Wavelengths

b=Exposure periods

a*b=Interference between wavelengths and exposure times

Table-2: Effect of different wavelengths on Nogos on the productivity of cucumber casualed by aphids (*Myzus persicae*)

Exposure periods (hours)	Production (kg / Donam)					
	1	2	4	6	8	Mean
Wavelength						
253.7 nm	2942	3037	2986	2882	2620	2893
365 nm	3011	3011	2939	2843	2891	2939
623.5 nm	3464	3188	3340	2816	2962	3154
Mean	3139	3079	3088	2847	2824	
LSD 0,05 for a =56.3 b =134.7 a × b =116.1						

Table-3: Phosphate ion concentrations and pH of Nogos products during photo decomposition of 623.5 nm light at temperature 25 C⁰

Irradiation by 623.5 nm		
Irradiation time (h)	[P] Ppm ×10 ⁻²	pH
0	19.1	2.27
1	5.8	2.21
2	6,1	2.16
4	10.2	1.97
6	13.1	1.84
8	15.0	1.63

Table-4: Phosphate ion concentrations and pH of Nogos products during photo decomposition of 365 nm light at temperature 25 C⁰

Irradiation by 365 nm		
Irradiation time (h)	[P] Ppm ×10 ⁻²	pH
0	27.4	2,27
1	6.7	2.17
2	10.4	2.04
4	17.9	1.88
6	22.1	1.57
8	23.5	1.52

Table (5): Phosphate ion concentrations and pH of Nogos products during photo decomposition of 253.7 nm light at temperature 25 C⁰

Irradiation by 253.7 nm		
Irradiation time (h)	[P] Ppm ×10 ⁻²	pH
0	32.6	2.27
1	8.8	2.08
2	14.2	1.77
4	19.8	1.47
6	25.2	1.19
8	28.7	1.11

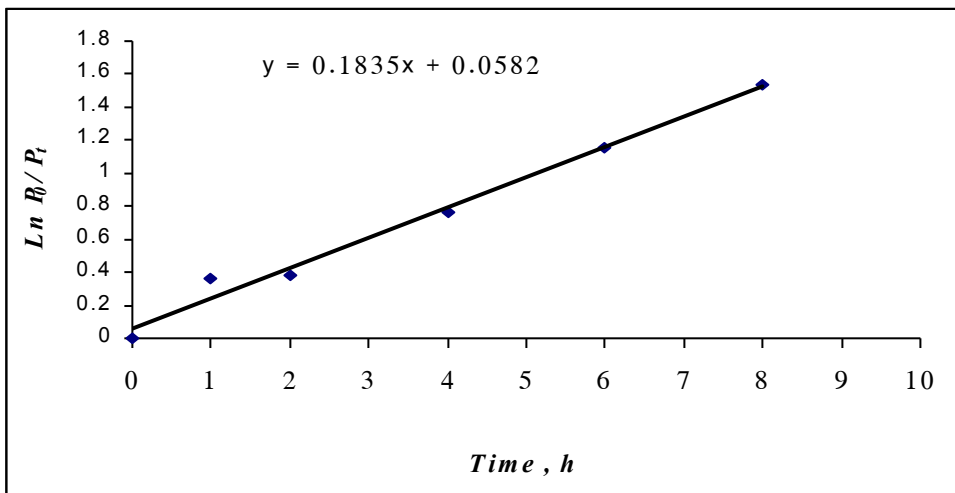


Fig-1: Decomposition rate of Nogos irradiated by 623.5 nm

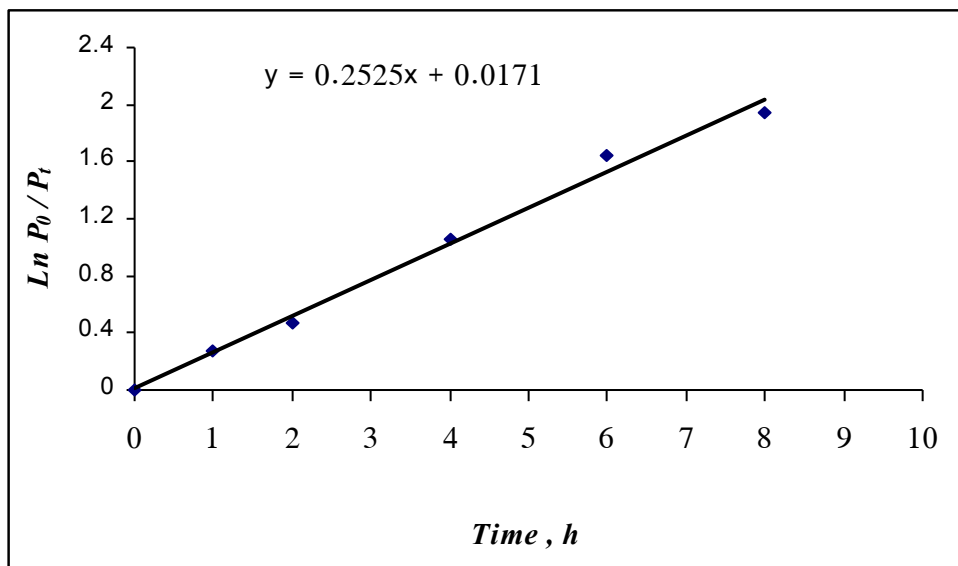


Fig-2: Decomposition rate of Nogos irradiated by 365 nm

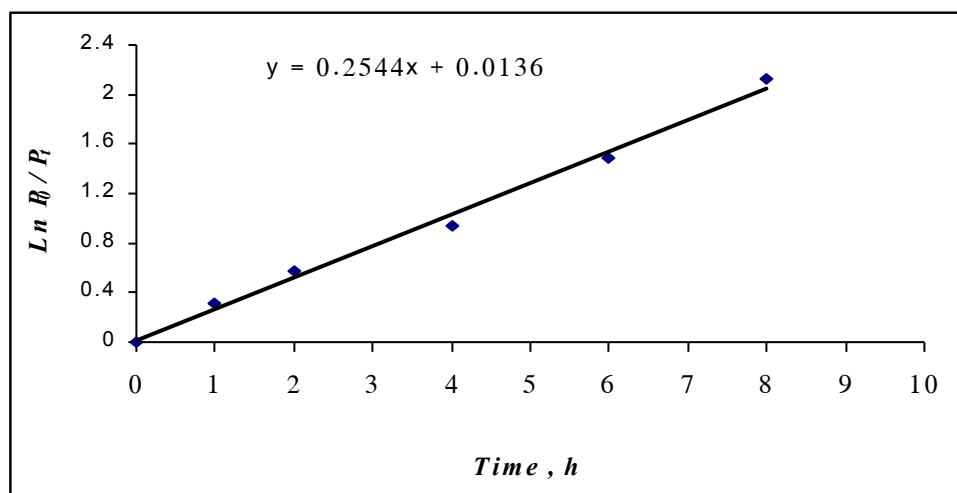


Fig-3: Decomposition rate of Nogos irradiated by 253.7 nm

References:

- 1-Al Malah, N. M. and Shaban, A. ,1993. Pesticides. Mousel. Univ., PP. 81,3,321,09.
- 2-Al-Kubaysi, A.M. ,2002. Kinetics of Photo and thermal degradation of organo phosphorus pesticide (diazinon), M.S.c. Thesis. Al-Anbar univ., Iraq.
- 3-Allwi, S. ,1998. M. Sc. Thesis. Mustansiriah Univ., Iraq.
- 4-Al-Rawi, K. M.and Khalaf, A. A. ,1980. Design and Analysis of agricultural experiments, Dar Al-Kutob for Press and Publication, Mousel univ.
- 5- APHA; AWWA, and WPCF ,1975. Methods of water and wastewater analysis. WHO.
- 6-Connell, D. and Publishers, L. ,1997. Basic concepts of Environmental Chemistry. Bocorato, New York, PP. 188,339.
- 7-Crosby, D.G. ,1976. Pesticides Chemistry degradation and mode of action. In: P.C. Kearney (Ed.), PP. 835.
- 8-Green, M. B; Hrttey, G.S. and West, T.F. ,1977. Chemical crop protection and pest control, Pergamon Press Ltd., London, PP. 291.
- 9-Horspool, W. M. ,1976. Aspects of organic photochemistry . Academic press Inc.London.
- 10-Howard, G. S. and Bayer, C. N. ,2008. Australian Pesticides and veterinary medicines Authority .PP. 14
- 11-Mansoor, S. A; Intisar, M. N. and Muntaha, S.,1983. The effect of temperature on the stability of Insecticides, Annual Book for crops protection, Vol.3, 2nd part, PP.113 -120.
- 12-Marer, P. J. ; Flint, M.L. and Stmmann, M.W.,1988. The safe and effective use of pesticides, Academic press. California, U.S.A., PP. 465.
- 13-Mohammed, I. S. ,1983.Vegetables seeds production, Mousel. Univ. press, Iraq.
- 14-Muhlmann, R. and Schrader, G. Z. (2005). *Arab Journal of Nuclear Sciences and Applications*, 38 (3), 277.
- 15-Omar, S.S. and Sayyed , A.A. ,1986. Physical Chemistry. Basra Univ., PP.300, 387.
- 16-Qunfer, R. ,1984. Insect infection control and special refer to agriculture in Africa, Al-Hikma house for press, Basra univ., PP.339.
- 17-Shi- Fu, C. and Xue- Li, C. ,1998. *J. Environ. Sci.* 10:43.
- 18-Simons, J.P. ,1971. Photo Chemistry and Spectroscopy. John Wiley and Sons, Ltd. London, PP. 110.
- 19-Smith, D.B. ,1972.Photo Chemistry. John Wiley and Sons, Ltd. PP. 3,538.
- 20-Wanyne, R. P. ,1970. Photo Chemistry. London. Butter worth, PP.10.