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pH EFFECT ON THE PHOTOCATALYTIC DEGRADATION OF THE CHLORPYRIFUS FORM INSECTICIDE MORISBAN4 BY ZNO IN AQUEOUS MEDIUM

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ABSTRACT :

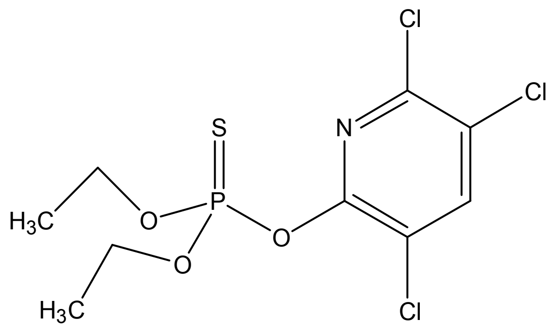
The effect of pH on the photodegradation of the chlorpyrifus form insecticide "MORISBAN4" in an aqueous environment, using ZnO catalyst was studied. It was found that the rate of the photodegradation process of the insecticide was dependent on the pH values. A photodegradation processes at three different pH values 4, 7, and 10 were studied. A rapid degradation process for the chlorpyrifus form insecticide was obtained when the pH value was 4, in other words in moderate acidic medium. The rate constant (K), half-life ($t_{1/2}$) for the degradation processes at different pH values were calculated. The method for the photocatalytic degradation process in the presence of sunlight is described within.

INTRODUCTION:

The insecticides are widely used for the protection of crops from harmful insects. However, there is a negative impact for their use on the environment, beside their effects on human health. Insecticides are hazardous chemical compounds, because they are carcenogenous, and bioaccumulative. Hence, there presence in the food-chain are indeed a major risk to human health. Many studies were carried out in trying to minimize dangerous chemical substances, such as chlorophenols and dyes using catalysts in an aqueous environment[1—3]. Phenolic derivatives are involved in the synthesis of many chemical compounds and are frequently found as pollutants of natural waters[4—6]. Photochemical transformation can be useful to eliminate phenolic compounds(7—8). The photocatalytic transformation of a phenyl-urea herbicide was investigated using TiO_2 and ZnO[9-11]. Many researches were carried out in trying to find ways to photodegrade organic pollutants[11–18] .

In this research the insecticide MORISBAN4 was used to study the effect of pH on the degradation rate using ZnO catalyst in an aqueous medium, in the presence of sunlight. MORISBAN4 is a Chlorpyrifus form insecticide widely used in Yemen, to fight insects of crops such as citrus, coffee, cotton, and maize. Also used against household pests, mosquitoes, and the control of parasites on cattle and sheep.

Its molecular formula $C_9H_{11}Cl_3NO_3PS$, its chemical name phosphorothioic acid o, o-diethyl o-(3,5,6-trichloro-2-pyridinyl) ester[18]. Its structure is as follows:



The chlorpyrifus form insecticide "MORISBAN4" was supplied by the Agriculture Research Center in Sana'a. The research was carried out in the Pharmaceutical Quality Control Lab, at the Ministry of Health. All chemicals and glassware were supplied by the Chemistry Dept., College of Science, Sana'a University. The catalyst ZnO was analytically pure.

METHOD:

To start with a 1 x 10^{-3} M solution of the chlorpyrifus form insecticide "MORISBAN4" was prepared. Also, the catalyst solution (a suspension) was prepared by dissolving 2g of ZnO in 1 litre de-ionized water. Into six 500 ml beakers,1.00 ml of the 1 x 10^{-3} M insecticide solution were added into each beaker, followed by 10.00 ml of the appropriate buffer (4, 7, and 10). The beakers were taken to the roof , then the 2g/l ZnO catalyst solution were added (about 89 ml) into each of the six beakers to make up the total volume of 100 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 measurement, the other mixtures were taken down for measurements every 15 minutes intervals. The chlorpyrifus form insecticde "MORISAN4" gave a maximum absorbance at 290 nm wavelength. The absorbance measurements for the insecticide/ZnO mixtures at different times, were taken at 290 nm wavelength in the U.V. spectrum, using a Beckmann UV/VIS spectrophotometer Model DU 7500. The blank was the catalyst solution plus 10 ml of the required buffer solution. To avoid errors all the mixtures were filtered before taken the measurements of absorbance, this included the blank, for absorbance measurements, the average value of three readings was taken.

Since, the purpose of the experiment is to see the effect of pH on the photocatalytic degradation, the experiment was done three times for the three pH values 4, 7, and 10.

The same procedure was repeated twice for each pH value, 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.

RESULTS :

Figure (1) shows the absorbance of the chlorpyrifus MORISBAN4 at pH 4 with time, clearly the absorbance decrease with time, indicating the concentration of the insecticide has decreased with time. Using Beer-Lambert law, the concentrations of the insecticide remaining in the mixture at different time were calculated, and used to plot concentration of insecticide versus time, shown in Figure (2). Since the degradation reaction is a first order reaction with respect to the insecticide, the rate constant K was calculated and found to be 0.01669, and the half-life for the degradation process was found to be 41 minutes.

For the settings when the mixtures contained only insecticide without the ZnO catalyst solution then were placed 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.

Here in Figure (3) the absorbance of the mixtures at pH =7 with time shows clearly the absorbance decreases with time. Again using Beer-Lambert law the concentrations of the insecticide remaining in the mixture at different times was calculated, and used to plot the concentration of insecticide with time, Figure (4). The rate constant was found to be 8.356 x 10^{-3}, with half-life of 83 minutes.

Again, when the mixtures contained only insecticide without the ZnO catalyst solution then were placed under sunlight, and 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.

At pH=10, the absorbance of the insecticide was not consistent and did not decrease with time. Therefore, at pH = 10, the insecticide did not undergo photodegradation under this conditions. The absorbance measurements were not consistent and varied slightly up and down with time, but this did not represent a change in absorbance with time. The same inconsistency occurred when the experiment was repeated in the dark, and the repeated experiment without adding ZnO catalyst solution.

Table (1): Absorbance of the insecticide/ZnO mixtures at 290 nm with time in minutes, calculated concentrations, and rate constants, at pH = 4.

	Time in minutes	Absorbance at 290 nm	Conc. of insect. mol/l	Rate constant K
1	0	0.127	1 x 10^{-5}	-
2	15	0.098	7.7 x 10^{-6}	0.01728
3	30	0.077	6.06 x 10^{-6}	0.01668
4	45	0.060	4.72 x 10^{-6}	0.01666
5	60	0.046	3.62 x 10^{-6}	0.01693

Table (2): Absorbance of the insecticide/ZnO mixtures at 290 nm with time in minutes, calculated concentrations, and rate constants, at pH = 7

	Time in minutes	Absorbance at 290 nm	Conc. Of insec. mol/l	Rate constant K
1	0	0.109	1 x 10^{-5}	-
2	15	0.096	8.81 x 10^{-6}	8.47 x 10^{-3}
3	30	0.085	7.79 x 10^{-6}	8.29 x 10^{-3}
4	45	0.075	6.88 x 10^{-6}	8.31 x 10^{-3}

Table (3): The absorbance of the insecticide/ZnO mixtures at 290 nm and 230 nm with time, at a pH = 10.

Time in minutes	Absorbance at 290 nm	Absorbance at 230 nm
0	0.398	0.464
15	0.297	0.377
30	0.419	0.393
45	0.688	0.716
60	0.474	0.804

75	**0.884**	**0.751**

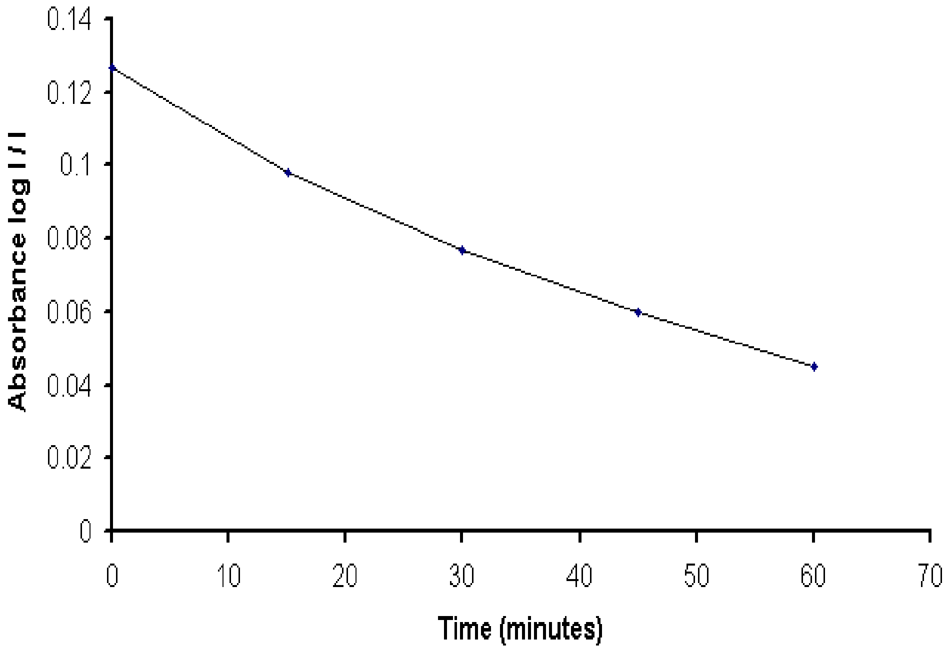


Figure (1): The Absorbance (log_{10} I/I_0) of the insecticide MORISBAN4/ZnO mixture at λ=290 nm and pH=4 with time

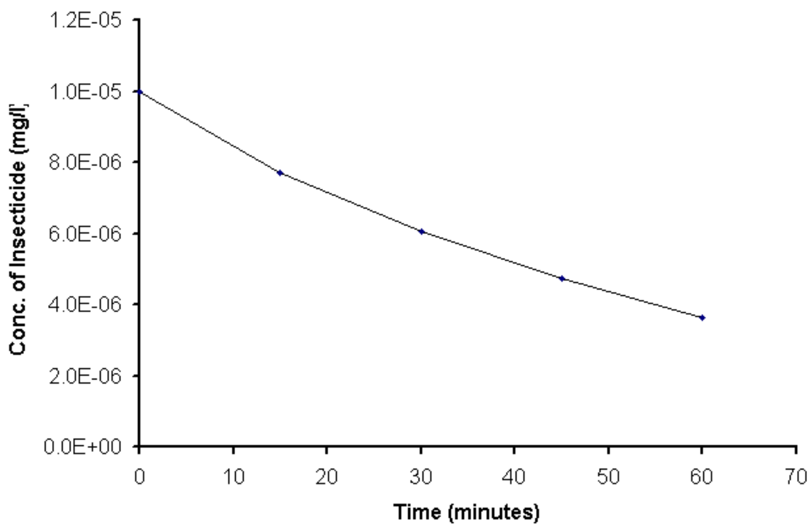


Figure (2) :The concentration (mg/l) of the insecticide "MORISBAN4" at λ= 290 nm and pH = 4 with time

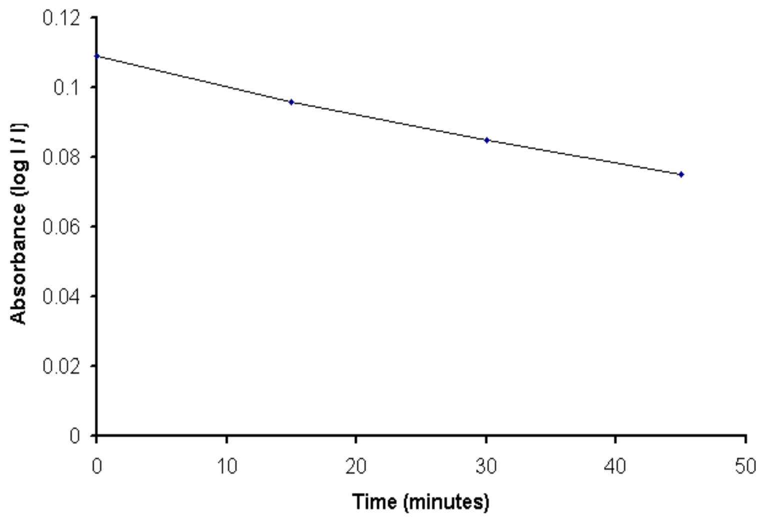


Figure (3): The Absorbance (log_{10} I/I_0) of the insecticide MORISBAN4/ZnO mixture at λ=290 nm and pH=7 with time

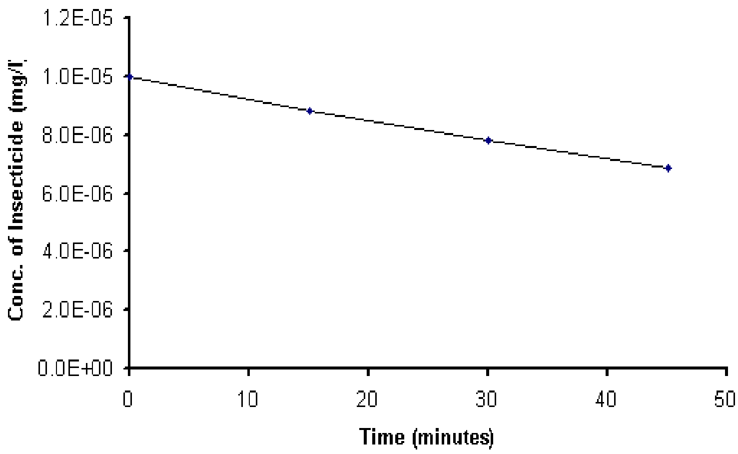


Figure (4): The concentration of the insecticide MORISBAN4 at λ= 290 nm and pH=7 with time

DISCUSSION:

The results show clearly that the photocatalytic degradation of the chlorpyrifus form insecticide "MORISBAN4", was at its greatest at pH = 4, with a rate constant of 0.017, and half-life for the reaction of 41 minutes, this indicates that the photocatalytic degradation was effective in acidic environment. At pH = 7, the rate constant for the degradation process was found to be 8.36 x 10^{-3}, and a half-life of 83 minutes, here in the neutral medium the reaction was slower. But, at pH=10, the reaction did not proceed, and hence no photodegradation occurred. It is concluded that for the chlorpyrifus form insecticide "MORISBAN4", the photocatalytic degradation worked more effectively in acidic environment. Also, the ZnO catalyst proved to work in acidic medium, and gave the desired photodegradation process of the insecticide.

Possible Degradation Mechanism[13, 14]:

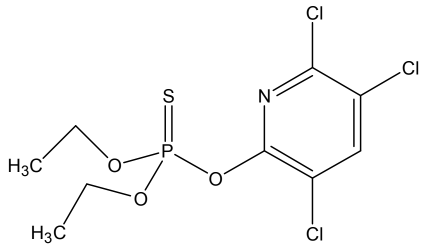
$$ZnO = MO$$

$$MO + hv \rightarrow MO^{-} + MO^{+}$$

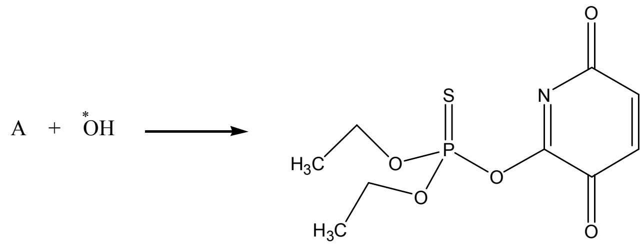
$$MO^{-} + O_2 \rightarrow O_2^{\bullet -} + MO$$

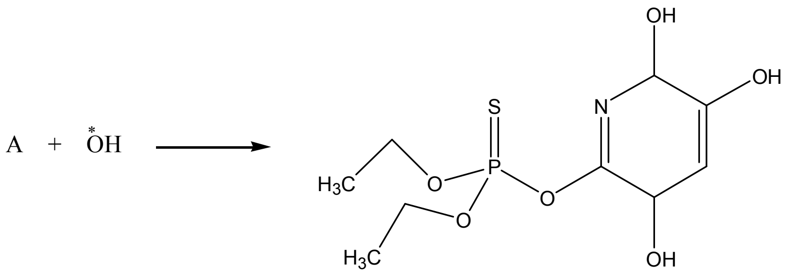
$$O_2^{\bullet -} + H --- OH \rightarrow OH^{-} + HO_2^{\bullet}$$

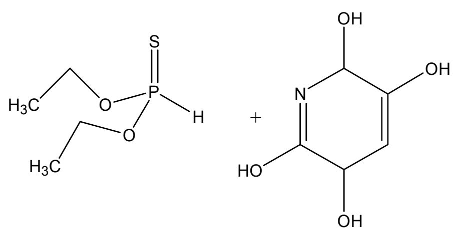
$$2\ HO ---- O^{\bullet} \rightarrow 2\ {}^{\bullet}OH + O_2$$

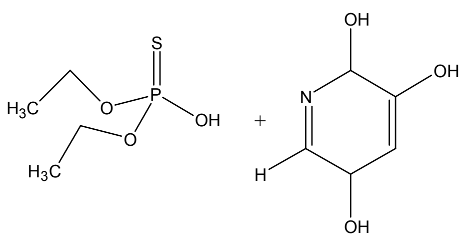


(A)









These suggested products of the photodegradation process of the chlorpyrifus insecticide MORISBAN4 were assumed, after referring to the possible mechanism and possible products put in previous work done by Mazellier *et al*[13], and Tixier *et al*[14], and reactions of the $^{\bullet}$OH radicals with organic compounds[4]. However, further research studies are needed to verify the photodegradation products qualitatively and quantitatively.

CONCLUSION:

A photodegradation process of the chlorpyrifus form insecticide is achieved, using the ZnO catalyst solution, in the presence of sunlight. The fastest degradation process for the insecticide occurred at pH = 4, in the acidic medium, slowed down slightly at pH = 7, in the neutral medium, and did not function at pH = 10, in the alkaline medium. These tell us that for a particular insecticide, a photodegradation process will work at a pH medium which facilitates the photodegradation reaction..

However, the catalyst also requires certain conditions for it to work effeciently. These conditions are pH range, temperature, pressure, and light. In this study beside the pH range, sunlight played an important role, since it starts the photodegradation process, by initiating the photolysis process of the ZnO catalyst solution, which produces the very reactive *OH radicals, responsible for attacking the insecticide and degrading it.

The chlorpyrifus form insecticide underwent degradation in an aquatic medium, an environment which could open a wide scope of applications. This method can be used to treat crops from the remains of any insecticide, by spraying the catalyst solution on the crops before removing from the field under sunlight. Hence, eliminating any amount of insecticides from the crops. Also, this method can be used to treat waste water (sewage), and removing any dangerous organic compounds, such as chlorophenols, textile dyes, and insecticides from the treated water, to be recycled for useful purposes.

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تأثير قيمة الأس الهيدروجيني (pH) على التحلل الضوئي المحفز لمبيد الكلوربايريفوس (مورسبان 4) بواسطة ZnO في وسط مائي

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تم دراسة تأثير الأوس الهيدروجيني على التحلل الضوئي لمبيد الكلوربايريفوس (مورسبان 4) في الوسط المائي بأستخدام الحفاز ZnO . حيث وجد أن معدل التفاعل لعملية التحلل الضوئي للمبيد معتمدة على قيمة الأس الهيدروجيني، حيث تم دراسة عمليات التحلل الضوئي عند ثلاث قيم مختلفة للأوس الهيدروجيني هي 4، 7، 10. وجد أن عملية التحلل كانت سريعة لمبيد الكلوربايريفوس عند الأس الهيدروجيني 4 (وسط حمضي). وتم الحصول على معدل سرعة التفاعل ونصف العمر لعمليات التحلل عند قيم الأس الهيدروجيني المختلفة. كما تم وصف الطريقة لعملية التحلل الضوئي المحفز تحت ضوء الشمس.