



PHOTOCATALYTIC DEGRADATION OF THE DIMETHOATE FORM INSECTICIDE ARAXION INDUCED BY Fe (III) IN AQUEOUS MEDIUM

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ABSTRACT :

The Photocatalytic degradation of the dimethoate form insecticide "ARAXION" by Fe (III) was investigated. The degradation process was effective and the concentration of the insecticide decreased sharply with time, when Fe (III) catalyst solution was used in the presence of sunlight. In the dark no degradation process has occurred. The method for the degradation process is described within, also the calculated rate of the degradation process (K), and half-life ($t_{1/2}$).

INTRODUCTION:

Catalysts are widely used in industry, and recently they are used effectively for the photodegradation of many hazardous chemicals which can cause damage to the environment and human health. Fe (III) species are known to undergo a redox process in the presence of light^(1,3), giving rise to Fe (II) and $\cdot\text{OH}$ radical.



Hydroxyl radicals are known to be very active species in the advanced oxidation processes (AOP's) and cause the complete mineralisation of the organic, and organometallic pollutants^[1-6].

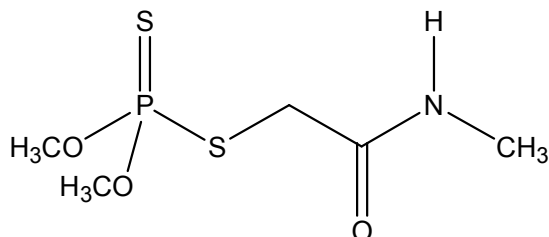
Several organic chemicals that contain halogen and sulfur groups are well known to cause dangerous diseases such as cancer. Many studies were carried out in trying to neutralize or eliminate these hazardous organic

compounds from waste water, and the environment^[7-17] Insecticides and herbicides used in agriculture to fight insects and pests in plants, are organic chemicals that contain halogens, and sulfur. Hence, if methods are developed to cleanse the crops from these insecticides and herbicides^[8]. A major breakthrough could be achieved in minimizing or reducing of the insecticides and herbicides present in crops.

In this research article the photodegradation of the insecticide ARAXION was studied using Fe (III) as the catalyst in an aqueous environment. The reason for using Fe(III), because organic molecules do not significantly absorb solar light, whereas iron (iii) in aqueous solution does absorb, and secondly that the photoredox process taking place upon excitation of iron (iii) in aqueous solution gives rise to iron (ii) and $\cdot\text{OH}$ radicals^[2]. It is important to note that

$\text{FeClO}_4 \cdot 9\text{H}_2\text{O}$, in aqueous form $\text{Fe}(\text{OH})^{2+}$ gives an absorption band centered at 297 nm ($\epsilon_{297\text{nm}} = 2030 \text{ M}^{-1}\text{cm}^{-1}$), and absorbs light till 365 nm^[9].

ARAXION is a dimethoate form insecticide, has the molecular formula $\text{C}_5 \text{H}_{12} \text{NO}_3 \text{PS}_2$, and the structure is as follows:



The dimethoate form insecticide “ARAXION” 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 $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ was analytically pure.

METHOD:

A stock of $1 \times 10^{-3} \text{ M}$ aqueous solution of the insecticide ARAXION was prepared initially. Then, the catalyst solution was prepared by dissolving 2g $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ salt in 1 litre de-ionized water. 1 ml of the $1 \times 10^{-3} \text{ M}$ insecticide solution was added into each of six 500 ml beakers. The beakers were taken to the roof, then the 2g/L catalyst solution were added into 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. Since the insecticide gave a maximum absorbance at 209 nm wavelength, all the

mixtures were measured at 209 nm wavelength. The catalyst solution was used as a blank. To avoid errors the mixtures were filtered before measurements. The measurements were taken by a Beckman UV/VIS spectrophotometer Model DU 7500. The experiment was carried out between 12.00 am and 2.00 pm in the afternoon, in the month of June, which is considered as summer time.

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

Note: for absorbance measurements, the average value of three readings was taken.

RESULTS:

The Absorbance for the insecticide/Fe (III) mixtures decrease with time under sunlight, shown in Figure (1). Using Beer-Lambert law, the concentrations of the dimethoate form insecticide remaining every 15 minutes were calculated, appeared to be decreasing with time, shown in Figure(2). The photodegradation reaction is a first order reaction with respect to the insecticide. Hence, the rate constant K was found to be 0.0116, and the half-life was found to be 59.6 minutes.

For the repeated experiment in which the mixtures contained only the dimethoate form insecticide without the Fe (III) catalyst solution under sunlight, and the repeated experiment in which the insecticide/Fe (III) 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.

Table (1): The Absorbance for the insecticide/Fe (III) mixtures at 209 nm wavelength with time in minutes. The calculated concentrations, rate constants are shown

	Time (minutes)	Absorbance at 209 nm	Conc ⁿ of insect mol/l	Rate constant K
1	0	0.25	1×10^{-4}	-
2	15	0.21	0.84×10^{-4}	0.01163
3	30	0.176	0.70×10^{-4}	0.01170
4	45	0.148	0.59×10^{-4}	0.01165
5	60	0.125	0.5×10^{-4}	0.01155
6	75	0.105	0.42×10^{-4}	0.01157

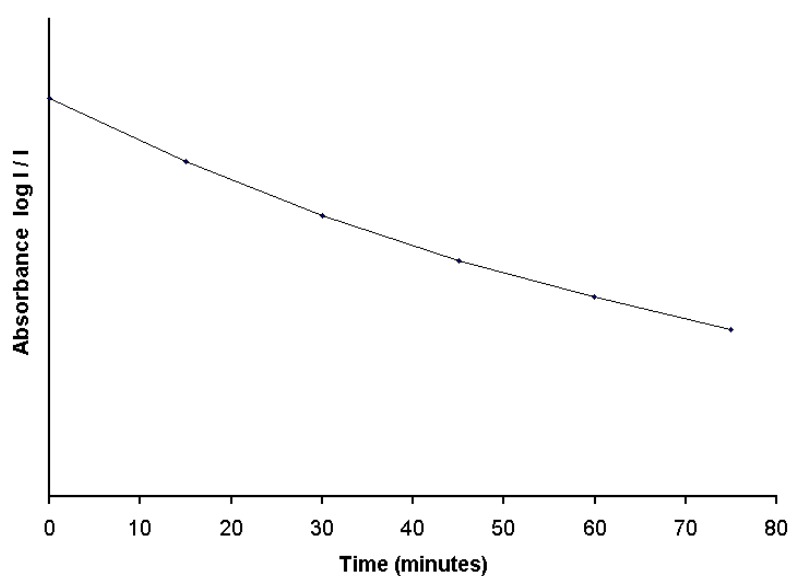


Figure (1): The Absorbance ($\log_{10} I/I_0$) of ARAXION/Fe(iii) mixture at 209 nm with time

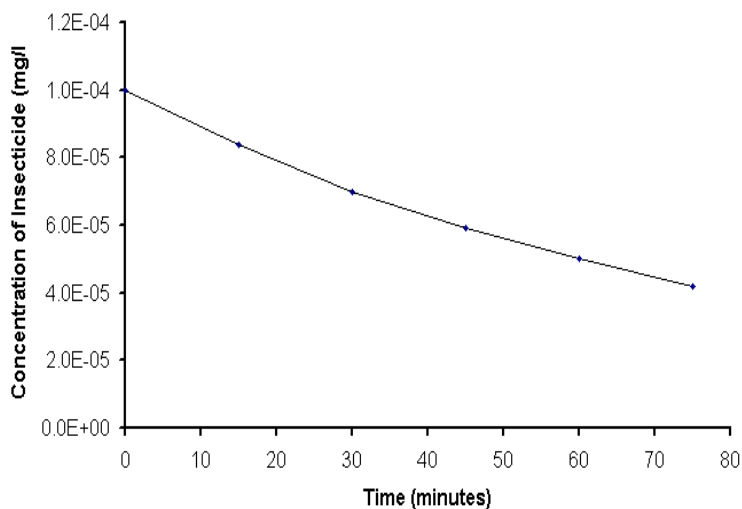


Figure (2) : The concentration (mg/l) of the insecticide ARAXION with time

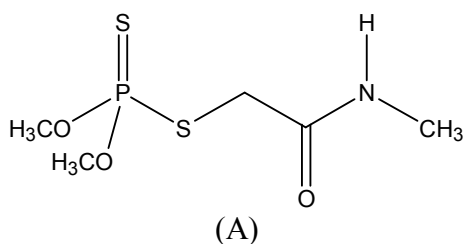
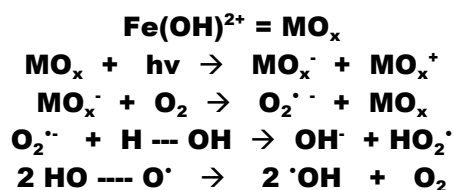
DISCUSSION:

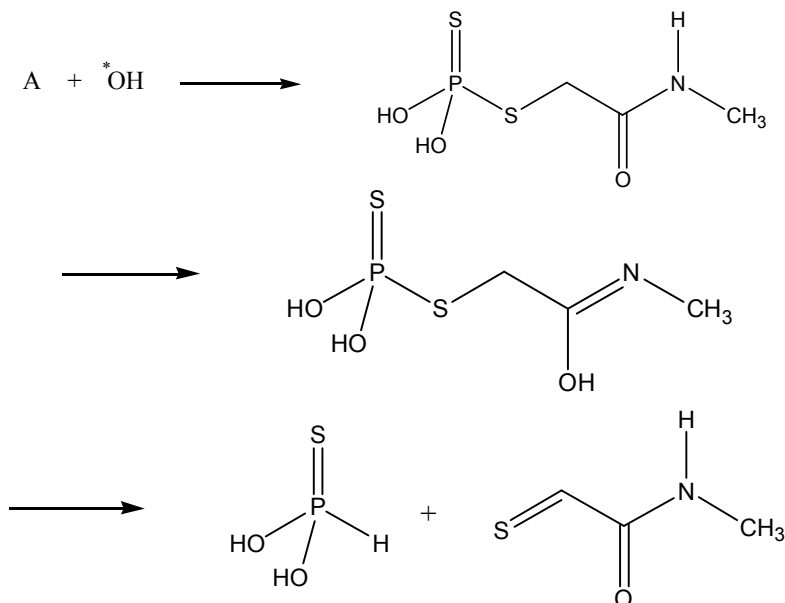
The results show a decrease in absorbance with time. The fact that the absorbance decreased with time at the 209 nm wavelength, maximum absorbance wavelength for the dimethoate form insecticide, indicate the breaking of the structure of the insecticide, and hence a decrease in the concentration of the dimethoate form (ARAXION) insecticide with time. It took 59.6 minutes for the concentration of the insecticide ARAXION to reach half its initial concentration. The Fe (III) catalyst has

proved to be an effective catalyst for the photodegradation process of the insecticide ARAXION in aqueous environment.

In the dark settings the absorbance remained unchanged, this can only prove the importance of sunlight for the degradation. Since, the photolysis of the aqueous Fe (III) needs sunlight. Another point is that the degradation process for the dimethoate form insecticide, did not work without the presence of Fe (III) catalyst solution, an important factor to initiate the degradation.

Possible Degradation Mechanism^[8, 10]:





Comparing the hypothetical mechanism and possible products for the photodegradation in this study with the mechanism and possible products obtained by Mazellier et al⁽⁸⁾, and Tixier et al⁽¹⁰⁾, and referring to reactions of the radical $\cdot\text{OH}$ with organic compounds⁽¹¹⁾. It is assumed that these are the possible products as a result of the photodegradation of the dimethoate insecticide. However, further research studies are needed to verify these suggested products.

CONCLUSION:

The described method has a wide applications in the fight against herbicides and insecticides, that may be present in the vegetables, fruits, green leaves, and crops in general. The use of Fe (III) catalyst makes the method applicable, since the method uses sunlight for its initiation, and carried out in an aqueous environment.

Future research work may concentrate on the pH effects on the rate of the degradation process of the insecticide. It is obvious that some degradation processes of the insecticides will

depend on the functional groups present, and on the pH of the medium.

Nevertheless, this novel method can be applied to study the possible photodegradation of other dangerous complex chemicals, such as dyes, substituted phenols, and other hazardous organic compounds. Also, in the treatment of the waste water, a medium this method worked effeciently in it, in the presence of sunlight.

REFERENCES:

- 1-H. Krysova, J. irkosky, J. Krysa, G. Mailhot, M. Bolte, *Appl. Catal. B. (2003): Environmental*, 40 p1-12.
- 2-B. C. Faust, and J. Hoigne, *Atmos. (1990): Environ.*, 24A, p79-89.
- 3-C. Catastini, S. Rafgah, G. Mailhot, M. Sarakha, *J. Photochem. Photobiol. A. (2004): Chemistry*, 162, p97-103.
- 4-B. Sulzberger, D. Suter, C. Siffert, S. Banwart, and W. Stumm, *Marine Chem.*, 28 (1989) p127-144.
- 5-S. O. Pehkonen, R. Sieffert, Y. Erel, S. Webb, and M. R. Hoffmann, (1993): *Environ. Sci. Technol.*, 27, p2056-2062.

- 6-M. C. Goldberg, K. M. Cunningham, and E. R. Weiner, J. Photochem. Photobiol. A. (1993): Chem, 73, p105-120.
- 7-P. Mazellier, M. Bolte, (2001): Chemosphere 42, p361-366.
- 8-P. Mazellier, M. Bolte, (1998): Intern. J. Environ. Anal. Chem., Vol. 70(1-4), p163-176.
- 9-H. J. Benkelberg, P. Warneck, (1995): J. Phys. Chem., 99, p 5214-5221
- 10-C. Tixier, L. Meunier, F. Bonnemoy, and P. Boule, (2000): Intern. J. Photoenergy, Vol. 2 p 1-8.
- 11-M. A. Malouki, T. Sehili, and P. Boule, (1996): Toxicological and Environmental Chemistry, Vol. 55, p235-246.
- 12-G. Mailhot, M. Astruc, and M. Bolte, (1999): Appl. Organometal. Chem., 13, p53-61.
- 13-N. Brand, G. Mailhot, and M. Bolte (1997): Chemosphere, Vol. 34 (12), p2637-2648.
- 14-S.L. Andrianirinaharivelo, J. F. Pilichowski, and M. Bolte, (1993): Transition. Met. Chem., 18 p37-41.
- 15-N. Brand, G. Mailhot, and M. Bolte, (2000): Chemosphere 40, p395-401.
- 16-F. K. Gunter, S. Hilger, S. Canonica, (1995): Environ. Sci. Technol., 29, p1008-1017.
- 17-E. Mathijs, N. T. D. Oude, M. Bolte, (1989): J. Lemaire, Wat. Res., 23, p845-851.

التحلل الضوئي المحفز للمبيد داميثويت (آراكسن) بواسطة Fe(III) في وسط مائي

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تمت دراسة التحلل الضوئي المحفز للمبيد داميثويت (آراكسن) بواسطة Fe(III)، وقد كانت عملية التحلل فعالة حيث حدث انخفاض حاد لتركيز المبيد مع الوقت، عندما استخدم محلول الحفاز Fe(III) تحت ضوء الشمس. وعندما أجريت التجربة في الظلام أو في غياب Fe(III) لم تحدث عملية التحلل للمبيد. وتم وصف الطريقة المستخدمة لعملية التحلل الضوئي، كما أمكن تعيين معدل التفاعل وفترة نصف العمر.