



Photocatalytic oxidation technique using TiO₂ for detoxification of fenitrothion and diazinon residues in water.

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ABSTRACT

An oxidation photo catalytic technique in the presence and absence of titanium dioxide (TiO₂) as photo catalysts was used for the detoxification of diazinon and fenitrothion in water. Both insecticides were used at 5 ppm where TiO₂ at 50 ppm under artificial light source. The results showed that photodegradation rate of diazinon and fenitrothion was increased in the presence of TiO₂. Disappearance of these insecticides was achieved within 4.5 and 3.5 hr, respectively. While in the absence of TiO₂ the disappearance was not achieved and photodegradation percentages of diazinon and fenitrothion were 27.4 and 25 %, respectively. Complete mineralization of diazinon and fenitrothion residues was attained in the presence of TiO₂ after 22 and 18 hr, respectively. While in the absence of TiO₂ complete mineralization was not achieved and the percentages of released phosphate ions were 20.5 and 19.3 only, respectively. Bioassay of the treated water on the 4th larval instar of *Culex pipens* was conducted in order to evaluate the toxicity of the intermediate photodegradation products. Data revealed that percentages of *Culex pipens* larvae mortality for diazinon and fenitrothion residues after 26 and 22 hr of starting irritation were 45 and 40 % respectively. While in the presence of TiO₂ the irritated solutions of diazinon and fenitrothion residues were not toxic for *Culex pipens* larvae at the same periods. Some Bolti fish enzymes activities were determined after rearing for 30 days in water treated with 1/10 LC₅₀ of both insecticides and exposed to the previous techniques for insecticide detoxification. Data revealed generally that there were no significant differences recorded in the activities of tested enzymes as affected by the photocatalytic oxidation process.

INTRODUCTION

The increasing uncontrolled use of synthetic pesticides has led to several problems concerning environmental pollution and dangerous risk for human and animal health. Diazinon and fenitrothion insecticides are recommended for combating rice stem borers. They have quite persistence and toxicity against aqueous organisms especially fish (Al Said 2002). Drainage water which is polluted with hazardous levels of residues is used as a water supply for fish cultures.

Pesticide elimination or reduction of pesticide residues from drainage water or water supplies in general, to reach the rational registered levels of residues is of valuable concept. Advanced oxidation processes for pesticide detoxification are alternatives to conventional methods which have many disadvantages. The use of photons (light energy) in the presence of semiconductors (like titanium dioxide (TiO₂)) involve the generation of the hydroxyl radical ([•]OH) in sufficient quantity to affect water purification. The hydroxyl radical is a powerful, non-selective chemical oxidant which acts very rapidly with most organic compounds. This in the presence of oxygen initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound. (Rein 2001, Mahvi *et al.* 2007 and Masih *et al.*, 2007). So the present study includes photo oxidation of diazinon and fenitrothion residues in water in the presence and absence of TiO₂. Bioassay experiment using a susceptible 4th larval instar of mosquito strain is used to insure the toxicity of the intermediate degradation products. To estimate the possible effects of the used technique biochemical effects of the treated water on some Bolti fish enzymes were estimated.

MATERIALS AND METHODS

1) Tested Insecticides:

Technical grade of: Diazinon (98 %) and Fenitrothion (95 %) were supplied by Kafr El-Zayat Company.

2) Tested organisms :

Mosquito larvae (*Culex pipiens*): A susceptible strain of *Culex pipiens* was obtained from the Institute of Medical and Veterinary Entomology Dokki, Cairo, Egypt.

Boliti fish (*Tilapia nilotica*):

Fish weighting 10 ± 2 gm were obtained from Fish Hatchery at EL-Hamul culture, Kafrelsheikh. fish were acclimatized to laboratory conditions for four weeks prior to experiment.

3) Photocatalytic oxidation of diazinon and fenitrothion insecticides in the presence of TiO_2 :

Two treatments were carried out for each insecticide, in the presence and in the absence of TiO_2 . TiO_2 was used at 50 ppm. All treatments are exposed to irradiation, in Pyrex beakers which were covered with Pyrex glass in order to prevent any contamination and extensive evaporation (Bandala *et al.*, 2002). These beakers transferred into solar simulator box. The distance between the solution and sun radiation lamp was 50 cm. The pH value of the tested solution was adjusted to 6 using hydrochloric acid 1 M the solutions were magnetically stirred for 10 min for uniform distribution of TiO_2 particles then were left for 30 min prior to irradiation to achieve maximum adsorption of pesticides on photo catalyst surface (Evgenidou *et al.*, 2005). The solution were magnetically stirred and supplied with atmospheric oxygen throughout the irradiation process using a normal compressor (it is necessary for complete mineralization, (Konstantinou and Albanis, 2004). At specific time intervals, samples were withdrawn and centrifuged to remove the precipitated TiO_2 before extraction.

4) Extraction of samples:

10 ml. of the irradiated samples were extracted according to the method of Sakkas *et al.*, 2004 using 10 ml. of n.hexane. This step was repeated 10 times. Diazinon and fenitrothion concentrations were determined using Gas chromatography (Hewlett Packard GC Model 6890) equipped with a flame photometric detector (FPD) with phosphorus filter. A fused silica capillary (PAS-1701), column containing 14 % cyanopropylsiloxane was conducted as stationary phase (30 m length X 0.23 mm internal diameter X 0.25 μm film thickness). Injector and detector temperatures were 240 and 250 $^{\circ}\text{C}$ respectively, initial oven temperature, 160 $^{\circ}\text{C}$ for 2 min, raised at 5 $^{\circ}\text{C}/\text{min}$ and then hold at 240 $^{\circ}\text{C}$ for 2 min. The carrier gas was nitrogen at 4 ml/min, and hydrogen, and air were used for the combustion at 75 and 100 ml/min, respectively.

Complete mineralization of diazinon and fenitrothion:

Measurement of phosphate ions, released during photo degradation of organophosphorus insecticides gave valuable information about complete mineralization of photoproducts (Evgenidou *et al.*, 2005). Irradiated samples were taken from solar simulator at regular time intervals and pH values were adjusted to 12 by adding NaOH (3N) to avoid phosphate ions adsorption on TiO_2 surface at acidic medium (Konstantinou and Albanis, 2003 and Kormali *et al.*, 2004). Samples which were Photolysis withdrawn from solutions

containing TiO_2 were centrifuged to remove the precipitated TiO_2 after that phosphorus solutions supernatant were analyzed spectrophotometrically (880 nm.) according to the method of A. O. A. C. (1975).

4) Bioassay of diazinon and fenitrothion photoproducts:

This experiment was performed based on WHO (1963) method for testing insecticides diazinon and fenitrothion on mosquito larvae. The percent mortalities were corrected according to Abbott's formula 1925 and data were statistically analyzed according to Litchfield and Wilcoxon method 1949. Water treated with LC_{50} from diazinon or fenitrothion then exposed to the previous treatment with TiO_2 . Samples were taken at the same intervals and pH values were adjusted to 7 prior to toxicity tests and TiO_2 particles were removed by centrifugal process (Fernandez-Alba *et al.*, 2002, Konstantinou and Albanis, 2003 and Malato *et al.*, 2003).

5) Side effects on some Bolti fish enzymes:

Biochemical changes of some Bolti fish enzymes such as acetylcholinesterase, alkaline phosphatase, aminotransferase, when fish reared in treated water were recorded.

At the beginning, the LC_{50} values after 24 hrs of diazinon and fenitrothion were calculated against fingerlings of Bolti fish, *Tilapia nilotica* using dechlorinated tap water. The percent mortalities were corrected according to Abbott's formula 1925, and data were statistically analyzed according to Litchfield and Wilcoxon, 1949.

Water samples received $1/10 \text{LC}_{50}$ were exposed to photo catalytic oxidation and pH value was adjusted to 7 (Isoelectric point) of TiO_2 suspension. Few hours are necessary for all TiO_2 particles to settle in tanks bottom after that photocatalysed solutions can be discharge directly. Fish were transferred to the aquarium and the experiment was conducted for 30 days and the tested solution were renewed three times in a week and mechanically aerated. The fish samples were taken randomly at periods of 1, 3, 7, 15 and 30 days and homogenized in a cold solution of 0.25 M sucrose. The homogenate was centrifuged at 4000 rpm (1430xg) for 20 min. and kept frozen for biochemical analyses.

Determination of some Bolti fish enzymes activity:

Some Bolti fish enzymes activities were determined according to standard methods such as; acetylcholinesterase Ellman *et al.*, 1961, alkaline phosphatase Kind and King, 1954 and transaminases AST (Aspartate aminotransferase) and ALT (Alanine aminotransferase) Schmidt and Schmidt, 1963). All the obtained data are statistically analyzed using Duncan's multiage rang test Duncan, 1955.

RESULTS AND DISCUSSION

Photocatalytic oxidation of diazinon and fenitrothion insecticides in presence of TiO_2 :

Disappearance of the parent compounds; diazinon and fenitrothion was determined in the presence and the absence of TiO_2 . The percent recoveries of the tested method were 87.56 and 95.94 %, for diazinon and fenitrothion respectively. Comparing the obtained data, (Fig 1 and 2), it can be concluded that; the rate of photocatalytic degradation of diazinon was increased sharply in the presence of the catalyst TiO_2 to reach its maximum (100 %) after 4.5 hrs while, it was slower without completely disappearance in the absence of the catalyst. The corresponding values were; 69.0, 78.0, 96.4, 97.5, 98.6 and 100 % (in the presence of TiO_2) comparing to 6.8, 11.2, 15.8, 17.2 and 27.4 % (in the absence of TiO_2) after 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 hrs respectively after exposure to radiation.

The current results are in agreement with those obtained by Kouloumbos *et al.*, 2003 and Sakkas *et al.*, 2004 they indicated that diazinon disappearance was achieved in the presence of TiO₂ short time of irradiation whereas in the absence of TiO₂ the disappearance was not achieved at the same time of irradiation, as well as the photodegradation rate was very slow.

Regarding photo catalytic degradation of fenitrothion, data in Fig (2) revealed nearly the same trend previously obtained with diazinon.

These results were supported by the finding of Kerzhentsev *et al.*, 1996 and Kormali *et al.* 2004 who stated that disappearance of fenitrothion was negligible in the absence of TiO₂ but in the presence of TiO₂ the disappearance was achieved after time of irradiation.

The complete and rapid disappearance of diazinon and fenitrothion in the presence of TiO₂ is due to the highly reactive ([•]OH) free radicals introduced by illumination TiO₂ in the aqueous media that oxidize the insecticide residues rapidly (Irmak *et al.*, 2004, Evgenidou *et al.*, 2005 and Perez *et al.*, 2006).

Complete mineralization of diazinon and fenitrothion photoproducts in the presence of TiO₂:

Complete mineralization was determined by the photocatalytic process which achieved with phosphate ions as final products in organophosphorus insecticide photo degradation (Konstantinou and Albanis, 2003 and Kormali *et al.*, 2004). Comparing the obtained data of Fig (3) one can notice that the percentage of phosphate ion release from diazinon photodegradation in the presence of TiO₂ under simulated sunlight was increased sharply to reach 100 % after 22 hrs, comparing to 20.5 % only in the absence of the photocatalyst.

The current results are in a good harmony with those obtained by Tapalov *et al.*, (2003) and Kormali *et al.*, 2004 who found that stoichiometric quantities of released phosphate ions from organophosphorus insecticides in the case of TiO₂ were obtained after short time of exposure to UV and near visible light. It could be concluded that photo oxidation catalyst (TiO₂) is able to achieve complete mineralization of diazinon after 22 hrs. of irradiation

The same trend was noticed with fenitrothion as exhibited in Fig (4) which showed phosphate ions released in 100% from fenitrothion photodegradation with TiO₂ in 18 hrs but without TiO₂ the phosphate ions were 20 % during the same period. It was confirmed by the finding of Kormali *et al.*, 2004) who reported that the complete disappearance of fenitrothion is followed by 100 % recovery of carbon as CO₂, sulphur as sulphate and phosphorous as phosphate ions with illuminated TiO₂.

It can be concluded that illumination of diazinon and fenitrothion residues in the presence of TiO₂ lead to the complete mineralization. This can be explained on basis of the ability of illuminated TiO₂ for producing very reactive and oxidizing ([•]OH) free radicals able to achieve the complete mineralization of insecticides to inorganic phosphate ions.

Effect on mosquito larvae:

The mortality percentages of the 4th larval instar were recorded after 24 hrs when the larvae were transferred to water solutions of both insecticides that exposed to photolysis (after the same intervals) in the presence and the absence of TiO₂ which were showed in Fig (5 and 6) that as for diazinon water solutions, a very interested results were obtained in which at zero time percent mortality was 50 (since water was treated with LC₅₀) which increased to reach

100 % after 8 and 10 hrs then declined to be non toxic after 26 hrs (in the presence of TiO_2). These results may be due to the presence concentration of diazinon or fenitrothion during 10 hrs were enough to cause 100 % mortality for mosquito larvae then the photodegradation of the compounds was increased and the remained concentration were unable to cause high mortality. So the effect on larvae decreased with increasing the irradiation periods. These results are coincided with the previously obtained data that complete mineralization was attained after 26 hrs interpret the following data. The same trend of results was exhibited also with fenitrothion. These results are confirmed by those obtained by (Mahvi *et al.*, 2007).

Side effects on some Bolti fish enzymes:

The side effects were measured as the effects on AChE, ALP, AST and ALT.

A) Effect on AChE:

Data in Table (1) reflected that there were no significance differences in the specific activities of AchE among the control and groups which were exposed to photocatalytic oxidation degradation in the presence of TiO_2 . In contrast there were significant depressions in the groups which received both insecticides without photolysis. Both diazinon and fenitrothion inhibited the activity of AchE enzymes with 60-80 % inhibition during the time of experiment (1-30 days). The presence of TiO_2 completely prevents the inhibitory effect of both compounds. AChE is considered a good diagnostic tool for organophosphorous pollution (Dembele *et al.*, 2000).

B) Effect on alkaline phosphatase (ALP):

The use of TiO_2 didn't significantly affect ALP activities while highly significant stimulation was recorded with fish exposed to 1/10 LC_{50} of both insecticides without catalytic photolysis Table (2). This increase suggests an increase in lysosomal mobilization and cell necrosis due to pesticides toxicity (Rao, 2006).

C) Effect on aminotransferase activities:

The exposure to both insecticides without catalytic degradation resulted in highly significant stimulation of the activities of both of AST and ALT. These results are a good harmony with those of Oluah 1999 and Rao 2006. On the other hand there was no recorded significant difference between the activities the enzymes in fish exposed to water which received catalytic oxidation at all intervals. The recorded exceptions were noticed on ALT enzyme after 15 and 30 days of exposure in which the activity of the enzyme was also simulated to become significant comparing with control. This induction might to due to the presence of some photo products which was affected liver function (Table 3 and 4).

As a conclusion the obtained results reflect the efficiency of the tested technique for detoxification of the used insecticides in water at the used concentration of both the insecticide and the catalyst. More studies are required in order to judge in the safety of the this method on more fish species and under different circumstances.

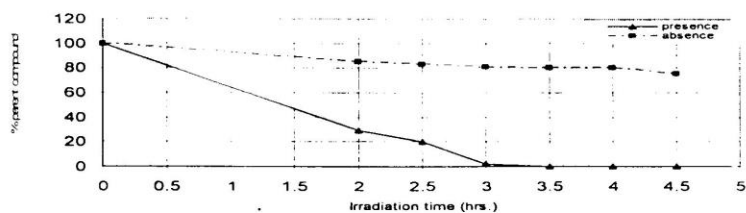


Fig (1) Photodegradation of diazinon insecticide in the presence and absence of TiO₂

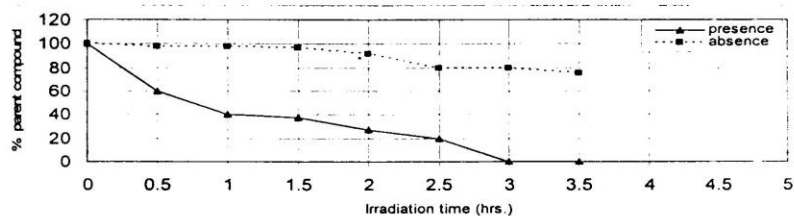


Fig (2) Photodegradation of fenitrothion insecticide in the presence and absence of TiO₂

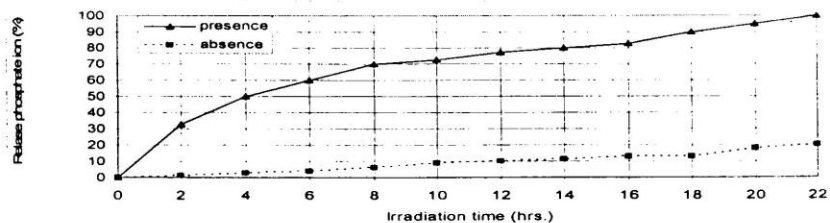
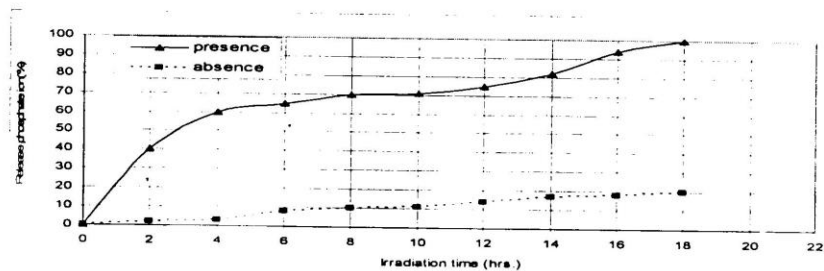
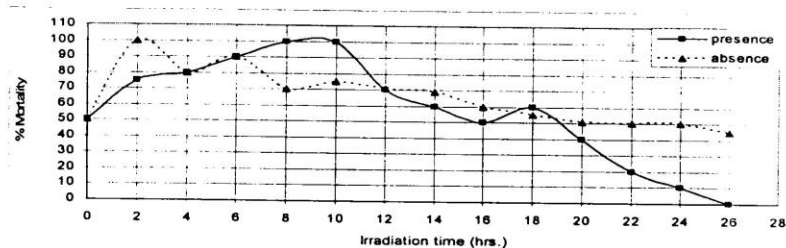


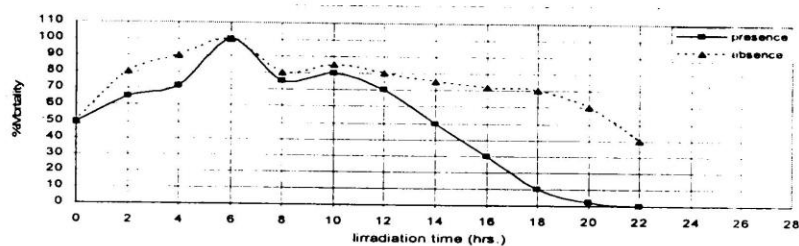
Fig (3) Complete mineralization of diazinon insecticide in the presence and absence of TiO₂



Fig(4) Complete mineralization of fenitrothion insecticide in the presence and absence of TiO_2



Fig(5) Toxicity measurements of diazinon photoproducts on mosquito larvae in the presence and absence of TiO_2



Fig(6) Toxicity measurements of fenitrothion photoproducts on mosquito larvae in the presence and absence of TiO_2

Table (1) Specific activities of AChE in whole homogenates of Bolti fish in presence and absence of TiO₂ photodegradation of diazinon and fenitrothion .

Treatments	Time (days)				
	1	3	7	15	30
	S.A	S.A	S.A	S.A	S.A
Control	10.31 c	10.02 c	9.93 c	9.61 c	9.85 c
Diazinon	4.12 b	3.91 b	3.11 b	3.01 b	2.03 b
Fenitrothion	3.82 a	3.01 a	2.70 a	2.52 a	2.79 a
Diazinon + TiO ₂	10.29 c	9.99 c	9.90 c	9.50 c	9.53 c
Fenitrothion + TiO ₂	10.27 c	9.89 c	9.91 c	9.54 c	9.51 c
TiO ₂	10.30 c	10.01 c	9.92 c	9.60 c	9.55 c

S.A = Specific activity = μ mole ASCh / min / mg.protein .
Values followed by the same letters are not significantly different .

Table(2) Specific activities of alkaline phosphatase in whole homogenates of Bolti fish in presence and absence of TiO₂ photodegradation of diazinon and fenitrothion .

Treatments	Time (days)				
	1	3	7	15	30
	S.A	S.A	S.A	S.A	S.A
Control	8.85 a	8.94 a	9.05 a	9.58 a	9.70 a
Diazinon	15.90 b	16.58 b	18.79 b	18.31 b	20.42 c
Fenitrothion	17.23 c	17.87 c	17.98 c	19.80 c	20.44 c
Diazinon + TiO ₂	8.89 a	8.96 a	9.08 a	9.60 a	9.75 a
Fenitrothion + TiO ₂	8.91 a	8.99 a	9.09 a	9.66 a	9.73 a
TiO ₂	8.79 a	8.73 a	9.07 a	9.42 a	9.69 a

S.A = Specific activity = μ mole IU/1/ min / mg protein.
Values followed by the same letters are not significantly different.

Table(3) Specific activities of AST in whole homogenates of Bolti fish in presence and absence of TiO₂ photodegradation of diazinon and fenitrothion .

Treatments	Time (days)				
	1	3	7	15	30
	S.A	S.A	S.A	S.A	S.A
Control	2.22 a	2.32 a	2.27 a	2.29 a	3.21 a
Diazinon	4.01 b	5.02 b	5.51 b	6.00 c	6.89 c
Fenitrothion	4.81 c	5.91 c	6.00 c	6.59 d	6.90 c
Diazinon + TiO ₂	2.24 a	2.25 a	2.29 a	4.03 b	4.51 b
Fenitrothion + TiO ₂	2.25 a	2.27 a	2.28 a	4.05 b	4.59 b
TiO ₂	2.23 a	2.25 a	2.27 a	2.28 a	3.23 a

S.A = Specific activity = IU/1/ min / mg protein.
Values followed by the same letters are not significantly different.



Table(4) Specific activities of ALT in whole homogenates of Bolti fish in presence and absence of TiO₂ photodegradation of diazinon and fenitrothion .

Treatments	Time (days)				
	1	3	7	15	30
	S.A	S.A	S.A	S.A	S.A
Control	1.21a	1.49a	1.72a	1.95a	2.11a
Diazinon	4.01b	4.12b	4.51b	5.01b	5.91b
Fenitrothion	4.03b	4.13b	4.53b	5.04b	5.95c
Diazinon + TiO ₂	1.27a	1.51a	1.74a	1.97a	2.14a
Fenitrothion + TiO ₂	1.25a	1.50a	1.77a	1.99a	2.16a
TiO ₂	1.23a	1.47a	1.74a	1.98a	2.13a

S.A = Specific activity = IU/1/ min / mg protein.

Values followed by the same letters are not significantly different.

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الملخص العربي

اختبرت فاعلية تكنولوجيا الأكسدة الضوئية المتقدمة وتعتمد هذه الطريقة على إنتاج أصول حرة مؤكسده قوية في ضوء الشمس الطبيعي أو الصناعي (في وجود عوامل مساعدة مثل ثاني أكسيد التيتانيوم) . في إزالة وتحطيم مبيدات الديازينون والفينثروثيون تحطيمًا كاملاً إلى عناصرها الأولية في المياه الملوثة.

وقد استخدم المبيدين بتركيز 5 جزء في المليون بينما استخدم ثاني أكسيد التيتانيوم بتركيز 50 جزء في المليون . وقد استخدم جهاز الغاز الكروماتوجرافي لتقدير تلك المبيدات كما قدرت نسبة أيونات الفوسفات غير العضوية كدليل على التحطم الكامل للمبيدين الفوسفوريين . وقد استخدم التقييم الحيوي على العمر اليرقي الرابع لبعوض الكيولكس كدليل على سمية نواتج التحطم كما استخدم التأثير على بعض إنزيمات السمك كمؤشر على إمكانية استخدام الماء المعالج بالتقنية المذكورة في مزارع السمك .

أظهرت النتائج ما يلي :-

- 1- تم اختفاء الديازينون والفينثروثيون بعد حوالي 4.5 ، 3.5 ساعة على التوالي من بداية التعرض للأشعة في حين كان معدل التحطم الضوئي في غياب ثاني أكسيد التيتانيوم 27.4 ، 25 % على التوالي لكلا المبيدين
- 2- حدوث تحطم كامل لمبيدات الديازينون والفينثروثيون في حالة وجود ثاني أكسيد التيتانيوم بعد 22 ، 18 ساعة من بداية التعرض للأشعة بينما في حالة غياب ثاني أكسيد التيتانيوم لم يسجل التحطم الكامل لهذه المبيدات وكانت نسبة أيونات الفوسفات المنطلقة من التحطم الضوئي للمبيدين على الترتيب 20.5 ، 19.3 % من بداية التعرض للأشعة .
- 3- اختبار سمية متبقيات مبيدات الديازينون والفينثروثيون ليرقات البعوض كانت نسبة الموت كانت 45 ، 40 % بعد 26 ، 22 ساعة من بداية التعرض للأشعة في حالة غياب ثاني أكسيد التيتانيوم بينما لم ترصد سمية بعد نفس الفترة في حالة استخدام ثاني أكسيد التيتانيوم .
- 4- كما أشارت إختبارات الإنزيمات إلى عدم وجود أي فروق معنوية بين مجموعات الكنترول والمجموعات التي تعرضت لثاني أكسيد التيتانيوم وأيضاً المجموعات التي تعرضت لمحاليل مبيدات الديازينون والفينثروثيون بعد تحطيمها الضوئي الكامل بفعل ثاني أكسيد التيتانيوم باستثناء إنزيم جلوتاميك أوكسالو ترانس امينيز في اليوم الخامس عشر واليوم الثلاثون.

وفي ضوء هذه الدراسة يمكن القول أن تكنولوجيا الأكسدة الضوئية المتقدمة في وجود ثاني أكسيد التيتانيوم

تعتبر من الطرق الواعدة والتي تحتاج إلى مزيد من الدراسة لاستخدامها في إزالة التلوث بمبيدات في

مياه الصرف الزراعي مما يحسن من جودتها لاستخدامها بأمان في المزارع السمكية