

**PHOTODEGADATION OF TRIAZOPHOS COMPLEXES OF IRON(III) AND  
COBALT(III)  
USING ZINC OXIDE AND TITANIUM DIOXIDE AS CATALYSTS**

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**ABSTRACT** : In this study, zinc oxide and titanium dioxide are used as photocatalysts to degrade triazophos pesticide complexes with iron(III) and cobalt(III) , under natural weathering conditions. The blank experiments for either illuminated solutions of triazophos complexes , or the suspensions containing ZnO or TiO<sub>2</sub> and triazophose complexes in the dark, showed that both illumination and the catalyst were necessary for the destruction of the pesticide. The rate of the decolorization of the suspensions was followed spectrophotometrically by measuring the maximum absorption at 400 and 514 nm for iron complex and cobalt complex respectively. The color disappearance was achieved within 200 min for both ZnO and TiO<sub>2</sub> catalysts.

## INTRODUCTION

The intensive increase and widespread use of pesticides has resulted in significant contamination of the surface and ground water. As a result, it is important to evaluate the ways by which pesticides enter runoff water, to reduce the environmental risk. Effective purification methods for eliminating pesticides in natural water have been in urgent demand. In recent years, research for new methods has led to processes that involve light and semiconductors, to produce OH radicals in aqueous media. These radicals show little selectivity and are able to oxidize the pollutants due to their high oxidative capacity (Espulgas *et al.* 2002, Andreozzi *et al.* 1999, Legrini *et al.* 1993).

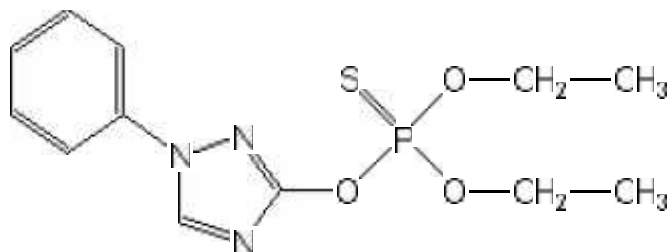
Agricultural pesticides treatment can cause a dispersed pollution usually at  $\mu\text{gL}^{-1}$  levels, on the other side, the disposal of unused portions of pesticides or the contaminated rinse water from washing pesticides containers or applicators can lead to well defined sites with concentration of pesticides at  $\text{mgL}^{-1}$  levels. These contaminations are usually

toxic, non-biodegradable and quite persistent in the environment (Floesser-Mueller and Schwack 2001).

The photocatalytic degradation of pesticides using  $\text{TiO}_2$  has already been studied. Harada *et al.* 1990, examined the rate of photocatalytic oxidation of dichlorvos using rutile  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Pt}$  as catalyst. Naman *et al.* 2002, Lu *et al.* 1993 and Balkaya 1999, examined the effect of various parameters like the initial concentration of the dichlorvos (organophosphorous insecticide), the addition of salts, the addition various sensitizers, etc. However, only a single report, concerning the photocatalytic efficiency of ZnO on dichlorvos degradation (Naman *et al.* 2002), and no such reports found for the photocatalytic degradation for triazophos.

The organophosphorus insecticides are widely used overall the world. They are extremely toxic, acting on acetylcholinesterase activity (Ragnarsdottir 2000, Mileson *et al.* 1998). Triazophos (O,O-diethyl-O-1-phenyl-1H-1,2,4-triazol-

3-yl-phosphorothioate) used for insect control in food storage areas, green houses



It is a yellowish stable liquid, soluble in most organic solvent, but has only slightly soluble (30-40 mg/Kg) in water. In this study, photocatalytic decolorization of triazophos complexes of iron(III) and cobalt(III) using  $\text{TiO}_2$  and  $\text{ZnO}$  has been investigated to evaluate the degree of mineralization of the pesticide.

## **EXPERIMENTAL**

Triazophos analytical grade was purchased from Sinochem- Ningbo (China) and used without any further purification. Iron(III) and cobalt(III) complexes of triazophos were prepared according to literature methods, by reacting aqueous solution of iron(III) chloride or cobalt(II) chloride with triazophos in 1:3 mole ratio (Al-Fartoosy et al. 2008). Titanium dioxide

and barns (Mennear 1998). Triazophos has the following structure:

powder (BDH) and zinc oxide powder (Dentam) were used as supplied.

Solutions of triazophos complexes in distilled water ( $10 \text{ mgL}^{-1}$ ) with the appropriate amount of catalyst were magnetically stirred before and during the illumination. The suspension were left for 30 min in the dark, prior to illumination in order to achieve the maximum absorption of the pesticide onto catalyst surface.

Experiments were carried out in June 2011 over a continuous 20 days period. All experiments were done at the floor of the Chemistry Department building in Basrah University, in an open atmosphere at temperatures around  $45^\circ\text{C}$ , between 10-12am. Sun light illumination was collected using converging lens with a focal length of 5 cm.

At specific time intervals, samples were withdrawn from the suspensions using a syringe with a long pliable needle. These were centrifuged to separate the solid catalyst. The absorbance of the clear samples were measured at the time intervals at  $\lambda_{max}$  using Cintra 5 UV-VIS spectrophotometer. The percentage of

photodegradation of triazophos complexes was followed spectrophotometrically by comparing the absorbance at specific intervals of time with a calibration curves conducted by measuring the absorbance at known wavelengths with different concentration of the colored complexes.

$$\% \text{ photocatalytic degradation} = \frac{A_0 - A}{A_0}$$

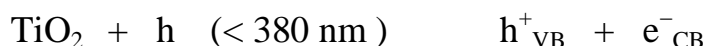
$A_0$  = the initial absorbance of the sampled solution

$A$  = the absorbance at specific intervals of time

## RESULTS AND DISCUSSION

The ability of semiconductors to act as sensitizers and consequently to enhanced the photodegradation of the organic pollutants is attributed to their electronic structure which is characterized by filled

valence band and an empty conduction band. When semiconductors are illuminated with energy greater than their energy band gap,  $E_g$ , excited high energy states of electron and hole pairs are produced :

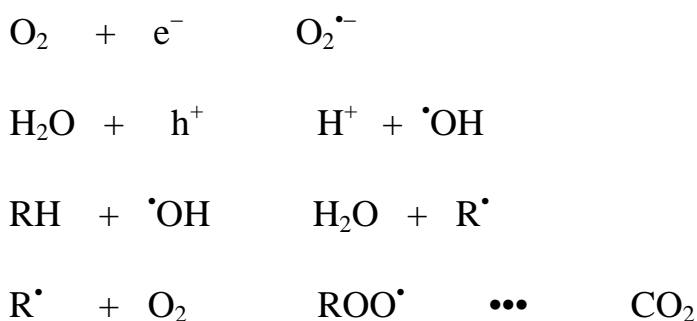


These generated species can either recombine and dissipate the input energy as heat, or react with the electron donors or electron acceptors which are adsorbed on

the semiconductor surface, or trapped within the surrounding. The general scheme of the photocatalytic destruction of an organic compounds (Ollis 1998,

Hoffmann et al. 1995, Kabra et al. 2004,

Al-Khateeb et al. 2005) is:

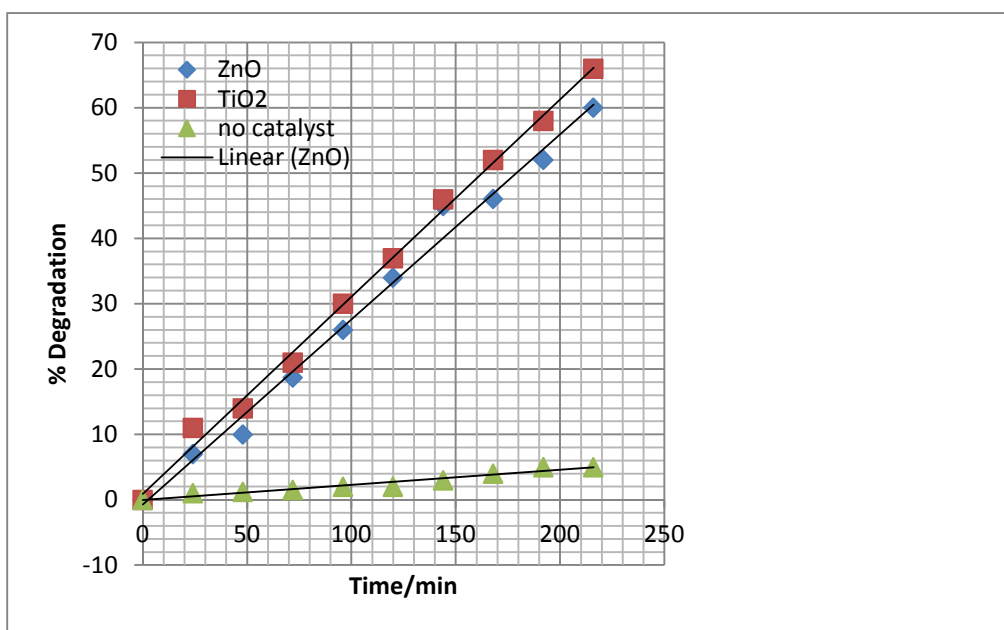


However, only 5% of the solar energy reaching the earth surface could be used in the photocatalytic reaction on TiO<sub>2</sub> (E<sub>bg</sub>= 3.2 eV) and ZnO (E<sub>bg</sub> = 3.17 eV), because only light below 380 nm is absorbed and capable of transferring an electron from the valence band to the conducting band of the semiconductor.

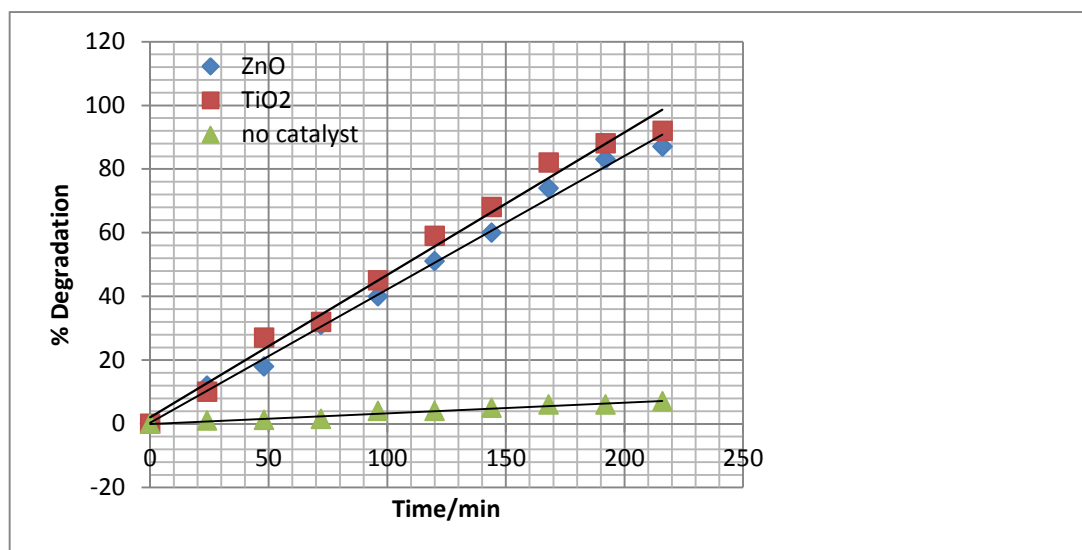
Because, only spectrophotometric methods depend on the color change to follow photocatalytic degradation, so our

study concerned on the degradation of triazophos complexes which are colored compounds( λ<sub>max</sub> at 400 and 514 nm for iron and cobalt complexes) rather than the pesticide itself which has only λ<sub>max</sub> at 300 nm.

The photocatalytic degradation of triazophos complexes of iron(III) and cobalt(III) in the presence or in the absence of catalyst are presented in Figure below (a) and (b).



(a) iron (III) complex



(b) cobalt (III) complex

Fig. Photocatalytic degradation of triazophos complexes on TiO<sub>2</sub> and ZnO under natural weathering conditions. (a) iron (III) complex . (b) cobalt (III) complex

It is clear that the decolorization of the solutions of triazophos complexes in the presence of TiO<sub>2</sub> is more active than in the presence of ZnO catalyst .This result is in good agreement with previous findings (Naman *et al.* 2002, Hussein *et al.* 2003) .

Illumination of solutions in the absence of a catalyst, showed that the photolytic decomposition of the complexes occurs at much slower rates. Furthermore , blank experiments showed that the addition of the catalyst without UV radiation have a negligible effect on the complex initial concentration.

By comparing the degradation rates of iron(III) and cobalt(III) complexes in Figure 1, it seems that the decomposition of cobalt(III) complex is faster than that for iron(III) complex. This may reflect that iron(III) complex is kinetically more stable than cobalt(III) complex.

In a recent study (Evgenidou *et al.*2005) , the photocatalytic degradation of the insecticide ,dichlorvos, alone using TiO<sub>2</sub> and ZnO has been investigated. It shows that dichorvos disappeared within 20 min when treated with TiO<sub>2</sub> and in~120 min with illuminated ZnO. The similarity

of dichlorvos with triazophos indicate that complexation of these pesticides increase their stability towards photocatalytic degradation as the decolorization of the triazophos complexes occurred within ~

200 min. The influence of the pH upon the photocatalytic degradation was not concerned in this project, and the pH values of the solutions were adjusted to 7.0 .

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التحلل الضوئي لمعقدات تراي ايزو فورس للحديد الثلاثي والكوبلت الثلاثي باستخدام اوكسيد

الزنك و اوكسيد التيتانيوم كعوامل تحلل ضوئي

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### المستخلص

في هذه الدراسة استعمل اوكسيد الزنك و اوكسيد التيتانيوم كمحفزات ضوئية للانحلال لمعقدات الحديد والكوبلت لمبيد تراي ايزوفوس تحت اسم تحت ظروف الجو الاعتيادية .

التجارب الاولية لكلا معقدات المحاليل تراي ايزوفوس في الضوء او معلقات هذه المحاليل المحتوية على اوكسيد الزنك او اوكسيد التيتانيوم في الظلام ، اظهرت بان كل من وجود الضوء و المحفز الضوئي هما ضروريان لتحطيم معقدات المبيد.

تم متابعة سرعة التحلل للمعلقات بواسطة قياس اطيف الامتصاص الضوئية عند الاطوال الموجية 400 514 نانومتر لكل من معقدي الكوبلت والحديد على التوالي . انجزت عملية تلاشي اللون بزمن يقارب من 200 دقيقة محفز اوكسيد الزنك و اوكسيد التيتانيوم .