Semiconductor-sensitized photodegradation of dichlorvos in water using TiO$_2$ and ZnO as catalysts

E. Evgenidou [a], K. Fytianos [a,*], I. Poulios [b]

[a] Environmental Pollution Control Laboratory, Chemistry Department, Aristotle University of Thessaloniki, Greece
[b] Laboratory of Physical Chemistry, Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Abstract

In the present study, the photocatalytic degradation of an organophosphorous insecticide, dichlorvos, using two different photocatalysts (TiO$_2$ and ZnO) has been investigated. The blank experiments for either illuminated dichlorvos solution or the suspension containing TiO$_2$ or ZnO and dichlorvos in the dark showed that both illumination and the catalyst were necessary for the destruction of the pesticide. Dichlorvos disappearance is achieved in $\sim$20 min when treated with illuminated TiO$_2$ and in $\sim$120 min with illuminated ZnO. The degradation of the organic molecule follows first-order kinetics according to the Langmuir–Hinshelwood model. It was observed that the initial rate increases linearly with an increase in the amount of catalyst up to a level where it reaches a plateau. Temperature and pH also affect the rate of the reaction. The addition of an oxidant (H$_2$O$_2$ or K$_2$S$_2$O$_8$) to the TiO$_2$ suspensions leads to an increase in the rate of photooxidation. On the contrary, the addition of hydrogen peroxide in ZnO suspensions caused a decrease in the reaction rate. Moreover, illuminated TiO$_2$ suspensions were proved to be quite effective in mineralizing dichlorvos. Measurements of chlorine and phosphate ions gave valuable information about how this process is achieved. On the other hand, ZnO suspensions could not lead in complete mineralization of the insecticide. Addition of the oxidants enhances mineralization for both photocatalytic systems. Finally, toxicity measurements showed that toxicity increases during treatment independently from the type of catalyst or the oxidant that has been used, indicating the inefficient detoxification capacity of the processes.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Photocatalysis; Dichlorvos; TiO$_2$; ZnO; Mineralization; Toxicity

1. Introduction

The increasingly intensive and widespread use of pesticides has resulted in significant contamination of surface and ground water. Thus, in order to reduce the environmental risk, it is important to evaluate the ways by which pesticides enter runoff water. Agricultural pesticide treatment practices can cause a dispersed pollution usually at μg L^{-1} levels, on the other hand the disposal of unused portions of pesticides or the contaminated rinse water from washing pesticide containers or applicators can lead to well-defined sites with concentrations of pesticides at mg L^{-1} levels. These contaminants are usually non-biodegradable, toxic and quite persistent in the environment [1].

As a result, effective purification methods for eliminating pesticides in natural waters have been in urgent demand. The already existing methods like adsorption or biological treatment appear to have many drawbacks since the former involves only phase transfer of the pollutants without degradation and the latter cannot be applied to contaminants which are toxic to the bacteria. In the recent years, research for new methods that can overcome these disadvantages has led to processes that involve light, which are called Advanced Oxidation Processes (AOP's). Although processes based on combinations like UV-B/H$_2$O$_2$ and UV-B/O$_3$ or with semiconductors like UV-A/TiO$_2$ and UV-A/ZnO make use of different reacting systems, they are all characterized by the same chemical feature: production of

* Corresponding author. Tel.: +30 231 099 7873; fax: +30 231 099 7873.
 E-mail address: fyti@chem.auth.gr (K. Fytianos).

OH radicals ($^\bullet$OH). These radicals show little selectivity of attack and are able to oxidize the pollutants due to their high oxidative capacity (reduction potential of OH$^\bullet$ $E_0 = 2.8$ V) [2–4].

The organophosphorous insecticides are comprised within the 10 most widely used pesticides all over the world. They are extremely toxic acting on acetylcholinesterase activity [5,6]. Dichlorvos (2,2-dichlorovinyl-o,o-dimethyl phosphate) was commercially manufactured in 1961 and it is used for insect control in food storage areas, greenhouses and barns [7]. It is also used for controlling parasites and insects in houses, aircraft and outdoor areas (as aerosols, liquid sprays):
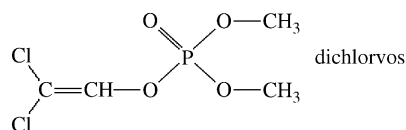
In this study, the photocatalytic degradation of dichlorvos using TiO$_2$ and ZnO as catalysts has been investigated. The objectives were: (i) to evaluate the kinetics of pesticide disappearance; (ii) to compare the photocatalytic efficiency of the two catalysts; (iii) to examine the influence of various parameters such as the mass of the catalyst, the initial concentration of dichlorvos, the addition of oxidants, pH, temperature; (iv) to evaluate the degree of mineralization and finally (v) to examine the toxicity during and at the end of the treatment.

The photocatalytic degradation of dichlorvos using TiO$_2$ has already been studied by other researchers. Harada et al. examined the rate of the photocatalytic oxidation of dichlorvos using rutile TiO$_2$ and TiO$_2$/Pt as catalysts [8]. Naman et al. [9], Lu et al. [10] and Balkaya [11] examined the effect of various parameters like the initial concentration of dichlorvos, the addition of salts, the addition of various sensitizers, etc. However, only a single report exists concerning the photocatalytic efficiency of ZnO on dichlorvos degradation comparing only the dechlorination rate of the insecticide under illuminated TiO$_2$ and ZnO suspensions [9]. No significant effort has been made, from previous researchers, in order to study the photocatalytic efficiency of ZnO on dichlorvos oxidation and the factors affecting it.

The effect of the addition of oxidants on the photocatalytic oxidation has already been studied for a variety of organic compounds [8,9,12–19]. Both hydrogen peroxide and peroxydisulfate were examined and have been proven to enhance the oxidation and mineralization rate of the pollutants. However, the effect of various oxidants on ZnO photocatalytic capacity was not thoroughly examined. Finally, although mineralization has been proven to be enhanced, there is no information provided from previous researchers concerning the effect of the addition of oxidants on the toxicity of the treated solution. Most studies were focused on the examination of the toxicity under illuminated TiO$_2$ suspensions without the presence of oxidants [20–22].

In the present study, various parameters that may affect the photooxidation of dichlorvos in the presence of TiO$_2$ and ZnO suspensions has been conducted, in order to obtain a more complete knowledge of ZnO photocatalytic efficiency providing additionally a comparison with the TiO$_2$ photocatalytic system under the same experimental conditions. Moreover, an effort has been made in order to compare the effect of two oxidants on the photocatalytic degradation of dichlorvos. New information is presented in this study concerning not only the effect of the addition of peroxydisulfate on the illuminated ZnO suspensions but also the examination of five different reacting systems based on combinations between two photocatalysts with two oxidants, in order to evaluate their ability to mineralize dichlorvos and to detoxify the treated solution.

2. Experimental

2.1. Reagents and materials

Dichlorvos analytical grade (99.9% purity) was purchased from Riedel-de-Haen (Germany) and was used without any further purification. HPLC-grade solvents (acetonitrile and water) were supplied by Merck. Hydrogen peroxide (30%) was obtained from Panreac. K$_2$S$_2$O$_8$ was purchased from Merck. Titanium dioxide P-25 Degussa (anatase/rutile: 65/35, non-porous, mean size 30 nm, surface area 56 m^2 g^{-1}) and ZnO (mean size 110 nm, surface area 9.5 m^2 g^{-1}) were used as received. HCl, NaOH and phosphate buffer pH 7 were used to adjust the pH when necessary. Doubly distilled water was used throughout the work. Stock solutions of dichlorvos (1000 mg L^{-1}) were prepared in water, protected from light and stored at 5 °C.

2.2. Irradiation procedure

Irradiation experiments were carried out in a 500 ml Pyrex UV reactor equipped with a diving Philips HPK 125 W high-pressure mercury lamp. The lamp was jacked with a water-cooled Pyrex filter restricting the transmission of wavelengths bellow 290 nm. The tap water cooling circuit was used to remove IR radiation preventing any heating of the suspension (30–35 °C).

Dichlorvos solution (10 mg L^{-1}, unless otherwise stated) with the appropriate amount of catalyst was magnetically stirred before and during the illumination. The suspension was left for 30 min in the dark, prior to illumination, in order to achieve the maximum adsorption of the pesticide onto semiconductors surface. The pH was not adjusted unless otherwise stated.

2.3. Analysis

At specific time intervals samples where withdrawn from the reactor. To remove TiO$_2$ or ZnO particles the solution

samples were filtered through a 0.45 μm filter. Dichlorvos concentrations were determined by a Shimadzu 10AD liquid chromatograph equipped with a variable wavelength UV detector using a reversed phase, 250 mm × 4.6 mm, C18 nucleosil 100-S column. The mobile phase was a mixture of acetonitrile and water (50/50, v/v) with a flow rate of 1 mL min^{-1}. The detection was realized at 210 nm. Standard solutions of pure compounds were used for quantitative analysis.

In order to evaluate the extend of mineralization, DOC (dissolved organic carbon) measurements were carried out by a Shimadzu V-csh TOC analyzer. Chlorine and phosphate ions were analyzed spectrophotometrically according to the ferricyanide and the molybdenum blue/ascorbic acid method, respectively [23].

For the examination of the toxic properties of the samples collected at specific time intervals throughout the photocatalytic treatment, the luminescent bacteria *V. ficheri* were used. Luminescent bacteria emit light as a by-product of their cellular respiration and metabolic processes. During direct contact with the target compounds, the reduction of the light emission indicates a decreased rate of respiration caused by the presence of toxic compounds. The inhibition of *V. ficheri* was measured by the Microtox test system (Microtox 500 Analyzer, SDI) within short time exposure, 5 and 15 min. The bacteria were in freeze-dried form and were activated prior to use by a reconstitution solution provided by SDI. Since *V. ficheri* is a marine organism an adjustment of the osmotic pressure of the samples was applied, in order to obtain samples with 2% salinity, using a concentrated salt solution (22% NaCl). Toxicity measurements of the samples were conducted using the 82% Microtox screening test protocol (sample concentration 82%) [24]. The pH value of the samples was adjusted to 7 ± 1, prior to the toxicity tests, by the addition of 0.1N HCl or 0.1N NaOH solutions.
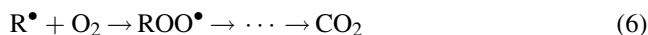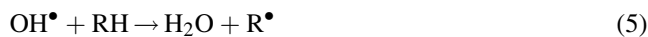
3. Results and discussion

3.1. Primary degradation

The ability of the semiconductors to act as sensitizers and consequently to enhance 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 the semiconductors are illuminated with energy greater than their bandgap energy E_g, excited high-energy states of electron and hole pairs are produced:

$$TiO_2 + h\nu(<380nm) \rightarrow h^+ + e^- \tag{1}$$

$$ZnO + h\nu(<380nm) \rightarrow h^+ + e^- \tag{2}$$
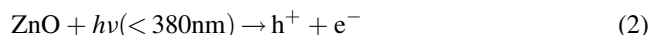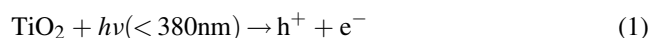
These generated species can either recombine and dissipate the input energy as heat or react with electron donors or electron acceptors which are adsorbed on the semiconductor surface or trapped within the surrounding electrical double layer of the charged particles (Eqs. (3) and (4)) to produce strong oxidizing hydroxyl radicals which can promote the oxidation of organic compounds (Eqs. (5) and (6)) [25,26]:

$$O_2 + e^- \rightarrow O_2^{\bullet -} \tag{3}$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet \tag{4}$$

$$OH^\bullet + RH \rightarrow H_2O + R^\bullet \tag{5}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \rightarrow \cdots \rightarrow CO_2 \tag{6}$$

The photocatalytic degradation of dichlorvos in the presence or in the absence of the two catalysts is presented in Fig. 1. It is clear that in the presence of TiO$_2$ the disappearance of dichlorvos is achieved within 20 min of illumination while in the presence of ZnO complete disappearance is achieved after 120 min of light exposure. Illumination of the solution in the absence of a catalyst showed that the photolytic decomposition of the insecticide occurs at a much slower rate. Furthermore, blank experiments showed that the addition of the catalysts without UV radiation had a negligible effect on dichlorvos initial concentration. Titanium dioxide appears to be more effective on dichlorvos oxidation than ZnO probably due to its larger surface area. This result is in agreement with other studies [9].

3.2. Kinetics

According to many researchers, the influence of the initial concentration of the solute on the photocatalytic degradation rate of the most organic compounds is described by pseudo-first-order kinetics which is rationalized in terms of the Langmuir–Hinshelwood model, modified to accommodate reactions occurring at a solid–liquid interface [12,27,28]. On the assumption of no competition with reaction byproducts, the simplest representation for the rates of disappearance of dichlorvos is given by

$$r_0 = -\mathrm{d}C/\mathrm{d}t = k_r K C_0/(1 + K C_0)$$

where r_0 is the initial rate of disappearance (mg L^{-1} min^{-1}) of dichlorvos and C_0 (mg L^{-1}) its initial concentration. K represents the equilibrium adsorption constant of dichlorvos and k_r reflects the limiting reaction rate at maximum coverage for the experimental conditions. A standard means of
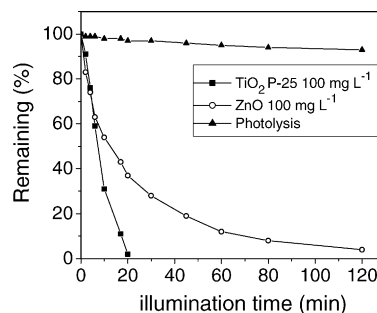

Fig. 1. Photodegradation of dichlorvos (10 mg L^{-1}) as function of irradiation time in the presence of TiO$_2$, ZnO or UV light only, pH ~7.
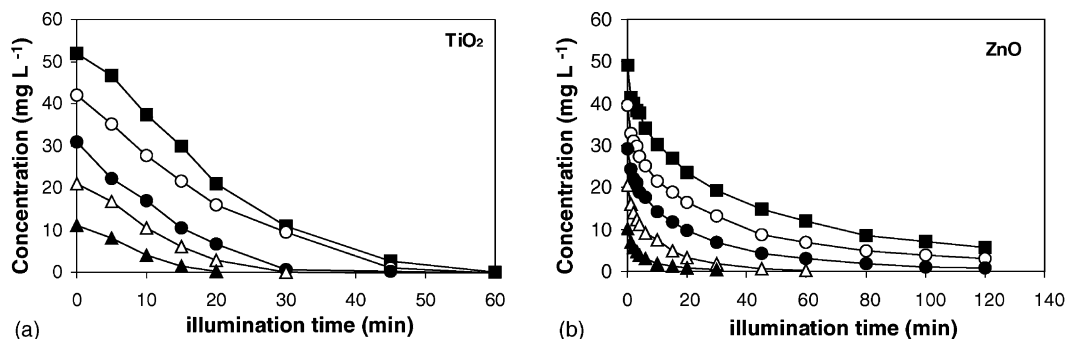
Fig. 2. Plot of the photodegradation of dichlorvos vs. irradiation time at various initial concentrations in the presence of: (a) $TiO_2 = 100$ mg L^{-1}, pH 6.5 and (b) ZnO = 500 mg L^{-1}, pH 7.2.

using this equation is to demonstrate linearity of data when plotted as the inverse initial rate versus inverse initial concentration:

$$1/r_0 = 1/k_r + 1/k_r K \times 1/C_0$$

Fig. 2a and b present plots from experiments carried out using various initial concentrations of dichlorvos (10–50 mg L^{-1}) versus time of irradiation for TiO_2 and ZnO suspensions, respectively.

The r_0 values where independently obtained from these curves, by the linear fit using only the experimental data obtained during the first min of illumination until 20% reduction was achieved, in order to minimize variations as a result of competitive effects of intermediates, pH changes, etc. [12].

As indicated in Fig. 3 the plot of the reciprocal initial rate r_0^{-1} as a function of the reciprocal initial concentration C_0 yields a straight line. The linear transform of this expression yields $k_r = 4.29$ mg L^{-1} min^{-1} (1.94×10^{-5} M min^{-1}) and $K = 0.02$ mg^{-1} L (4.45×10^3 M^{-1}) for the TiO_2 and $k_r = 7.34$ mg L^{-1} min^{-1} (3.32×10^{-5} M min^{-1}) and $K = 0.03$ mg^{-1} L (6.77×10^3 M^{-1}) for the ZnO.

3.3. Effect of catalyst concentration

The influence of the photocatalyst concentration on the disappearance kinetics of dichlorvos has been investigated employing different concentrations of TiO_2 and ZnO
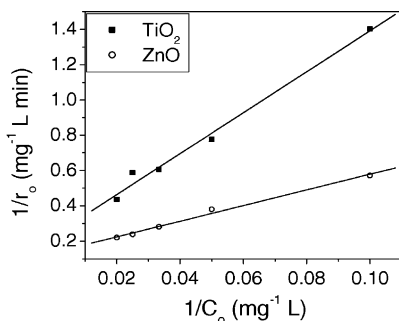
varying from 10 to 1000 mg L^{-1} and from 50 to 1000 mg L^{-1}, respectively (Fig. 4).

It is obvious that the rate increases with an increase of the amount of catalyst up to a level corresponding to the optimum of light absorption. Above this value the suspended particles of the catalysts block the UV-light passage and increase the light scattering [29–32]. Thus, any further increase of the amount of the catalyst will have no effect on the photodegradation efficiency [13].

As can be seen in Fig. 4 ZnO appears to give higher photodegradation rates than TiO_2 especially at high concentrations (above 200 mg L^{-1}). In small concentrations titanium dioxide appears to be more effective probably due to its larger surface area, but as concentration increases, the light scattering, which is greater in the TiO_2 suspensions due to the small particle size, reduces the photocatalytic efficiency, while ZnO is able to absorb more light quanta without provoking great scattering of light [33].

However, these initial photodegradation rates are misleading concerning the overall photocatalytic efficiency of ZnO because the r_0 values are calculated from the experimental data obtained in the first 10 min of irradiation. After the first minutes of illumination, due to the drop of pH, dissolution of ZnO takes place and the photocatalytic efficiency of the semiconductor oxide drops dramatically, thus requiring longer irradiation time in order to achieve complete disappearance of dichlorvos comparing to TiO_2. This phenomenon is obvious in Fig. 1 where the initial
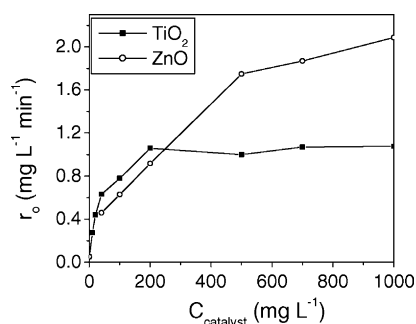

Fig. 3. Linearized reciprocal kinetic plot for the photocatalytic degradation of dichlorvos in the presence of $TiO_2 = 100$ mg L^{-1}, pH 6.5 and ZnO = 500 mg L^{-1}, pH 7.2.

Fig. 4. Dependence of the initial rate r_0 on the concentration of the catalyst ([dichlorvos] = 10 mg L^{-1}): (i) TiO_2, pH 6.5; (ii) ZnO, pH 7.4.
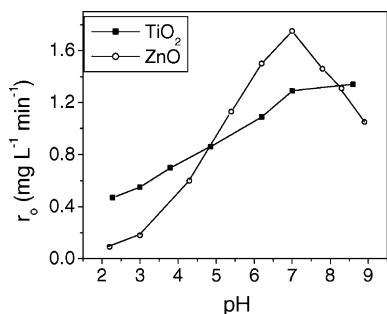
Fig. 5. Effect of pH on the initial photodegradation rate of dichlorvos (10 mg L^{-1}) in the presence of 100 mg L^{-1} TiO$_2$, 500 mg L^{-1} ZnO.

Fig. 6. Effect of the H$_2$O$_2$ on the photocatalytic degradation of dichlorvos (10 mg L^{-1}) in the presence of 100 mg L^{-1} TiO$_2$, pH 6.2.

photodegradation rate of dichlorvos is almost the same for both photocatalysts but after the first 10 min of illumination, a great retardation is observed in the case of ZnO.

3.4. Effect of the pH

According to previous studies, pH appears to play an important role in the photocatalytic process of various pollutants [12,14,29,33–36]. The influence of the initial pH value on the initial photodegradation rate of dichlorvos for the TiO$_2$ and ZnO suspensions is demonstrated in Fig. 5.

In the illuminated TiO$_2$ system, the degradation rate of the pesticide is higher at alkaline pH values and a three-fold increase is observed as pH increases from 2 to 9. The effect of pH on the photocatalytic reaction is generally attributed to the surface charge of TiO$_2$ (point of zero charge, pzc, of TiO$_2$ ∼5–6) and its relation with the ionic form of the organic compound (anionic or cationic). Electrostatic attraction or repulsion between the catalyst's surface and the organic molecule is taking place and consequently enhances or inhibits, respectively, the photodegradation rate. Since dichlorvos is an unionizable compound the observed increase of the reaction rate at alkali pH can be ascribed to the high hydroxylation of the catalyst's surface due to the presence of a large quantity of OH$^-$ ions. Consequently, higher concentration of OH$^\bullet$ species are formed and the overall rate is enhanced [33].

For the ZnO system a sharper increase is observed as pH is increased from 2 to 7 (nine-fold increase). At pH 7 the maximum initial rate is achieved and increasing further the pH values the photodegradation rate of dichlorvos decreases. The low initial reaction rates at acidic or at alkali pH values are due to dissolution and photodissolution of ZnO (see Fig. 14) [37]. The semiconductor oxide presents an amphoteric behavior. At acidic pH, ZnO can react with acids to produce the corresponding salt and at alkalic pH, it can react with a base to form complexes like [Zn(OH)$_4$]$^{2-}$.

3.5. Effect of oxidants

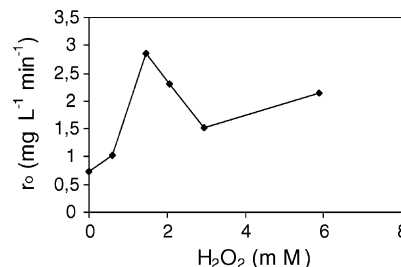The addition of an oxidant into a semiconductor suspension has been proven to enhance the rate of

photooxidation of the organic pollutants [8,9,12–19]. The photocatalytic degradation of dichlorvos at different H$_2$O$_2$ and K$_2$S$_2$O$_8$ concentrations has been studied. In Fig. 6 the initial rates of reaction versus the concentration of hydrogen peroxide are presented.

It is obvious that small concentrations of the oxidant enhance the process. As it is mentioned before the photogenerated electrons and holes can recombine in the absence of a suitable scavenger. The role of hydrogen peroxide is dual. It can act as an electron acceptor and consequently promotes the charge separation and secondly it can produce OH$^\bullet$ radicals according to the following equations:

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \qquad (7)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^- + OH^\bullet + O_2 \qquad (8)$$

At high concentrations, the addition of hydrogen peroxide causes a decrease (Fig. 6) to the reaction rate because it can act as a hole or OH$^\bullet$ scavenger. According to previous researchers that the effect of hydrogen peroxide depends on the H$_2$O$_2$/contaminant molar ratio [18,38]. In our study the optimal concentration of hydrogen peroxide corresponds to a molar ratio: ∼32. Above this ratio the reaction rate decreases.

An opposite effect is observed in the case of zinc oxide (Fig. 7). The addition of the oxidant causes a decrease to the rate of photooxidation of dichlorvos. This is probably due to its low adsorption on the zinc oxide's surface. When TiO$_2$ and ZnO are illuminated hydrogen peroxide is produced. In the case of titanium dioxide small concentrations of

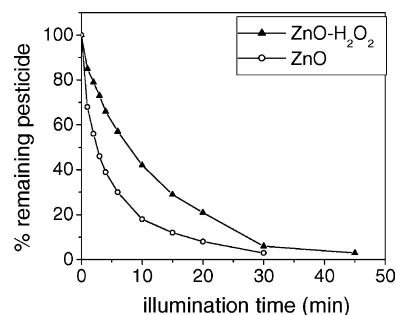Fig. 7. Effect of the addition H$_2$O$_2$ (1.47 M) on photocatalytic degradation of dichlorvos (10 mg L^{-1}) in the presence of 500 mg L^{-1} ZnO, pH 7.2.
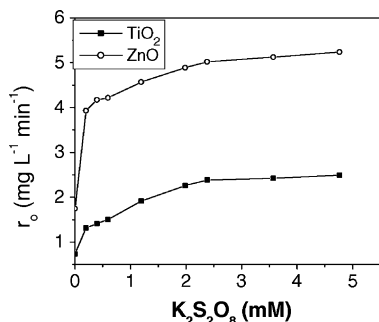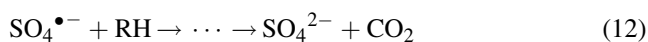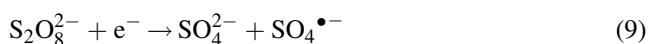
Fig. 8. Effect of the $K_2S_2O_8$ on the photocatalytic degradation of dichlorvos (10 mg L^{-1}) in the presence of: 100 mg L^{-1} TiO$_2$, pH 6.2; 500 mg L^{-1} ZnO, pH 7.4.

hydrogen peroxide have been detected because the latter can be easily adsorbed on TiO$_2$ surface and consequently is degraded more efficiently. On the other hand, an increasing concentration of peroxide has been measured during illumination of ZnO suspensions due to its low adsorption on ZnO surface [38–40]. In this case, addition of peroxide will have no effect or moreover, it may cause a negative effect because, as previously noted, an excess of peroxide can act as a radical or a hole scavenger. For this reason the system ZnO–H$_2$O$_2$ was not further investigated.

The effect of adding another electron scavenger (peroxydisulfate) that has been used with promising results [18,22] is presented in Fig. 8. Increase of $K_2S_2O_8$ concentration causes a rapid increase of the reaction rate for both TiO$_2$ and ZnO suspensions. The reactions where $K_2S_2O_8$ is involved and responsible of its efficiency are the following:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \tag{9}$$

$$SO_4^{\bullet-} + e^- \rightarrow SO_4^{2-} \tag{10}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^\bullet + H^+ \tag{11}$$

$$SO_4^{\bullet-} + RH \rightarrow \cdots \rightarrow SO_4^{2-} + CO_2 \tag{12}$$

$K_2S_2O_8$ traps the photogenerated electron, preventing the recombination with the positive hole and at the same time produces the sulfate radical, which is a very strong oxidizing agent (reduction potential of $SO_4^{\bullet-}$ $E_0 = 2.6$ V).

Increasing the concentration of peroxydisulfate an increase on the reaction rate is observed until it reaches a plateau. In contrast to hydrogen peroxide, peroxydisulfate addition is not detrimental at very high concentrations and consequently it does not cause a reduction to the reaction rate. This is in agreement with other studies which support that peroxidisulfate is not depended on the oxidant/contaminant molar ratio [18]. Comparing the effect of the two oxidants on the photocatalytic degradation of dichlorvos, it is observed that in the TiO$_2$ system, they cause more or less the same effect to the photodegradation rate of dichlorvos. On the other hand, in the illuminated ZnO suspension, $K_2S_2O_8$ appears to be more effective since it is

able to enhance the degradation efficiency of ZnO where H$_2$O$_2$ fails to do.

However it must be noted that the activity of the oxidants is not only due to the entrapment of the photogenerated electrons but, also due to their own ability to absorb light and act as sensitizers through the production of hydroxyl and sulfate radicals (for H$_2$O$_2$ and $K_2S_2O_8$, respectively). Experiments with UV light and the oxidants, without the photocatalyst, were performed and showed that both oxidants are able to cause photooxidation of the insecticide. In Table 1 the initial reaction rates and the percentage of dichlorvos degradation after 10 min of treatment are presented. Consequently, the improvement of the photo-catalytic degradation of dichlorvos by the addition of oxidants is not only due to prevention of the recombination of the e$^-$/h$^+$ pair but also due to the photolytic activity of the oxidant. Blank experiments with the oxidants without the presence of the catalyst or UV light showed a negligible degradation of the insecticide.

3.6. Effect of temperature

The dichlorvos degradation rate as a function of temperature was also studied for both illuminated TiO$_2$ and ZnO suspensions. Fig. 9 shows the Arrhenius plot of k versus T^{-1} from which the activated energy of dichlorvos degradation was calculated. The E_a for TiO$_2$ is 36 kJ mol^{-1} and for ZnO 13.3 kJ mol^{-1}. It is obvious that the increase of the temperature causes an increase to the reaction rate. The enhancement of the photooxidation is probably due to the increasing collision frequency of molecules. Irradiation is believed to be the primary source of e$^-$/h$^+$ pairs at ambient temperature because the band gap is too high to overcome by thermal excitation [10].

Table 1
Dichlorvos initial degradation rates (r_0) and percentage of degradation (after 10 min of illumination), in the presence of TiO$_2$, ZnO, H$_2$O$_2$, $K_2S_2O_8$, TiO$_2$ + H$_2$O$_2$, TiO$_2$ + $K_2S_2O_8$, ZnO + H$_2$O$_2$ and ZnO + $K_2S_2O_8$

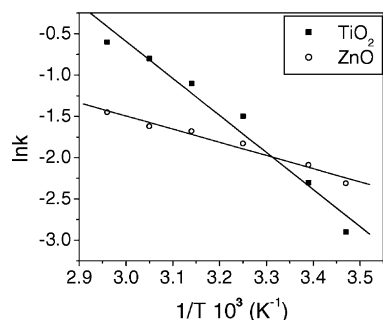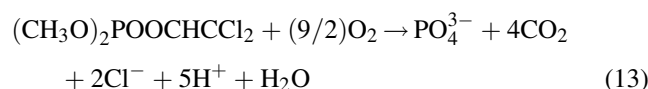| Catalyst or oxidant added	r_0 (mg L^{-1} min^{-1})	% degradation (after 10 min of irradiation)
TiO$_2$ (100 mg L^{-1})	0.91	69
ZnO (500 mg L^{-1})	1.75	82
H$_2$O$_2$ (1 mM)	0.35	27
$K_2S_2O_8$ (1 mM)	0.91	51
TiO$_2$ + H$_2$O$_2$ (100 mg L^{-1} + 1 mM)	2.26	92
TiO$_2$ + $K_2S_2O_8$ (100 mg L^{-1} + 1 mM)	1.50	95
ZnO + H$_2$O$_2$ (500 mg L^{-1} + 1 mM)	0.73	58
ZnO + $K_2S_2O_8$ (500 mg L^{-1} + 1 mM)	4.22	100

Fig. 9. Effect of temperature on photocatalytic degradation of dichlorvos (10 mg L^{-1}) in the presence of: 100 mg L^{-1} TiO$_2$, pH 6.2; 500 mg L^{-1} ZnO, pH 7.4.

Fig. 11. Dichlorvos/DOC reduction and chlorine/phosphate ions release as a function of irradiation time in the presence of TiO$_2$ = 100 mg L^{-1} and H$_2$O$_2$ = 3.12 mM (pH 6, dichlorvos = 22 mg L^{-1}).

3.7. Photodegradation products

In order to study the extent of mineralization of dichlorvos over illuminated TiO$_2$ and ZnO suspensions DOC measurements were carried out. Previous studies have shown that the photocatalytic degradation of dichlorvos using titanium dioxide as catalyst leads to the formation of H$^+$, Cl$^-$, PO$_4^{3-}$ and CO$_2$ as final products [8,10]:

$$(CH_3O)_2POOCHCCl_2 + (9/2)O_2 \rightarrow PO_4^{3-} + 4CO_2$$
$$+ 2Cl^- + 5H^+ + H_2O \qquad (13)$$

In Fig. 10a and b DOC reduction and formation of chlorine and phosphate ions is presented. For the TiO$_2$ system we have complete disappearance of the insecticide within 60 min while DOC is only 20% reduced. DOC is 96% reduced after 6 h of illumination. This lag of time indicates the formation of intermediates. The release of chlorine ions is a rapid process and probably responsible for dichlorvos disappearance since almost the 80% of the expected amount is observed in 60 min. From 60 min to 6 h dechlorination proceeds at a slower rate and reaches the maximum concentration after 6 h of irradiation. The release of phosphate ions is a slower process, which indicates the formation of phosphate containing intermediates. The rate of their release is almost the same with the rate of DOC reduction and the expected amount is observed in 240 min.
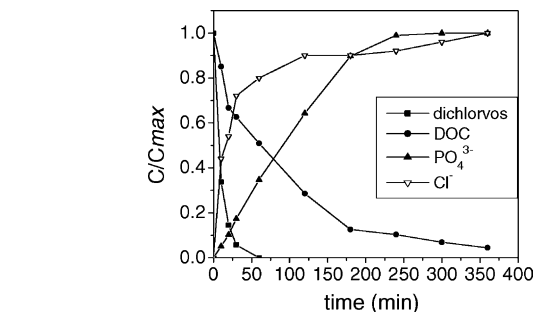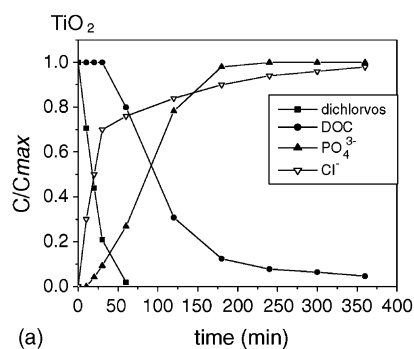
On the other hand, for the ZnO system complete disappearance of dichlorvos is achieved after 3 h of illumination while DOC was only 32% reduced after 6 h of illumination. Dechlorination proceeds at a slower rate comparing to the TiO$_2$ system reaching the 75% of the maximum amount after 6 h, but still remains the primary process in the photooxidation. No release of phosphate ions is observed indicating the formation of phosphate containing intermediates which are persistent under the illumination of ZnO suspensions. On the other hand, it is possible to have a release of phosphate ions but not be able to measure as they may be trapped by ions of zinc (from dissolution of ZnO) to form Zn$_3$(PO$_4$)$_2$ which is insoluble in water.

For the TiO$_2$–H$_2$O$_2$ system (Fig. 11) the whole process shows a negligible difference from that observed at the TiO$_2$ system. As it was previously noted, the oxidant enhances the photooxidation of organic pollutants and consequently promotes dichlorvos disappearance and the DOC reduction especially in the first minutes of illumination. Yet, the outcome is almost the same since DOC is 96% reduced after 6 h of treatment. Moreover, a limited acceleration of the ions release is observed, only in the first minutes of treatment.

On the other hand the addition of peroxydisulfate in the illuminated TiO$_2$ strongly affects the photooxidation and mineralization of dichlorvos (Fig. 12a). It is obvious that enhances dichlorvos disappearance, which is achieved within 30 min of irradiation while DOC needs only 2 h to be 94% reduced. Chlorine ions release proceeds very
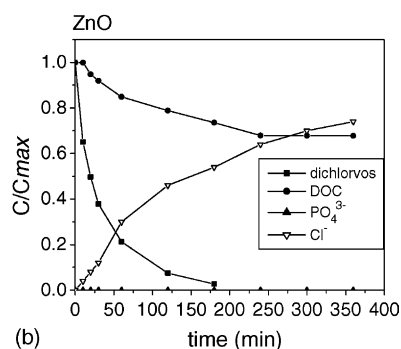

Fig. 10. Dichlorvos/DOC reduction and chlorine/phosphate ions release as a function of irradiation time: (a) dichlorvos = 22 mg L^{-1}, TiO$_2$ = 100 mg L^{-1}, pH 6.5; (b) dichlorvos = 22 mg L^{-1}, ZnO = 500 mg L^{-1}, pH 7.4.
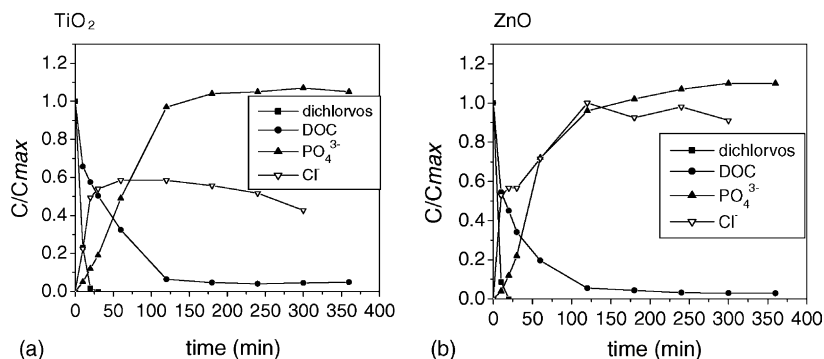
Fig. 12. Dichlorvos/DOC reduction and chlorine/phosphate ions release as a function of irradiation time in the presence of: (a) $TiO_2 = 100$ mg L^{-1} and $K_2S_2O_8 = 3.1$ mM; (b) $ZnO = 100$ mg L^{-1} and $K_2S_2O_8 = 3.1$ mM (pH 6, dichlorvos = 22 mg L^{-1}).

quickly in the first 30 min reaching only the 50% of the expected amount. This phenomenon indicates that a different reaction mechanism takes place producing different intermediates and final photooxidation products. Phosphate ions are released very quickly reaching almost their maximum value after 120 min of treatment.

In Fig. 12b, dichlorvos oxidation and mineralization under illuminated $ZnO/K_2S_2O_8$ is presented. It is obvious that addition of peroxydisulfate strongly accelerates dichlorvos disappearance and DOC reduction under illuminated ZnO suspension, since the former is completed in 20 min instead of 3 h and the latter reaches a 95% reduction in 2 h instead of 32% in 6 h. Moreover, a very rapid phosphate ions release is achieved indicating the involvement of a different reaction mechanism. Since $Zn_3(PO_4)_2$ is soluble in acids, it cannot be formed under illuminated peroxydisulfate because of the production of H_2SO_4. Finally, chlorine ions are also rapidly released in the first minutes achieving the maximum amount in 2 h.

3.8. Toxicity measurements

The photocatalytic degradation of the organic compounds is a promising method for eliminating these compounds from water. However, the question of partial versus total oxidation is quite important since some incompletely oxidized compounds can be more toxic than the parent contaminants. In our study, toxicity measure-

ments of the treated solutions were carried out in order to give a more complete evaluation of the efficiency of the technologies that have been used. The toxicity of the samples collected from different stages of the treatment was measured using the Microtox test. The results obtained after 15 min exposure of the bacteria to the samples are presented to Fig. 13.

It is obvious that mineralization of dichlorvos is not followed by reduction of the toxicity in all systems studied. Under the illuminated TiO_2 suspensions toxicity appears a slight drop in the first 2 h from 45 to 29% inhibition. After the 2 h although DOC is still reducing and we observe an almost stoichiometric release of chlorine and phosphate ions, toxicity is increasing and finally reaches a 63% of inhibition which is in agreement with previous studies [20]. The addition of the oxidants in the system appears to cause a negative effect in toxicity evolution in contrast with their effect to mineralization. Although they enhance dichlorvos disappearance and DOC reduction, they cause an increase to the toxicity especially $K_2S_2O_8$, where the toxicity reaches the 99% inhibition after 2 h of treatment. This increase to the toxicity can be attributed to the photocatalytic products that are produced throughout the applied processes and may be more toxic than the parent compound. Moreover, synergistic effects between the photoproduced compounds can also cause an increase to the toxicity.

The increase of the toxicity in the illuminated ZnO and $ZnO/K_2S_2O_8$ systems is attributed to the dissolution of ZnO.
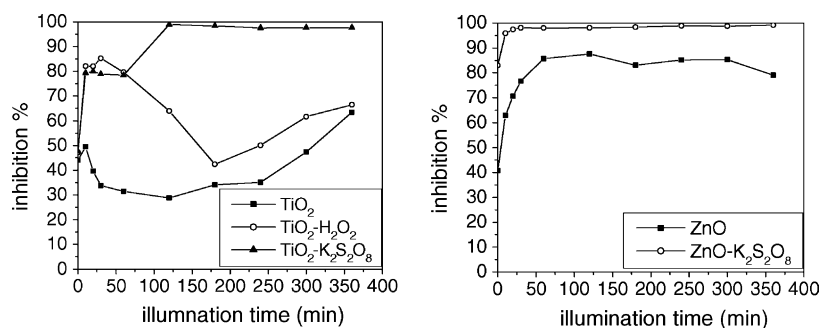

Fig. 13. Toxicity evolution as a function of irradiation time in the presence of $TiO_2 = 100$ mg L^{-1}, $TiO_2 = 100$ mg $L^{-1} + H_2O_2 = 3.12$ mM, $TiO_2 = 100$ mg $L^{-1} + K_2S_2O_8 = 3.1$ mM, 500 mg L^{-1} ZnO, ZnO = 100 mg $L^{-1} + K_2S_2O_8 = 3.1$ mM.
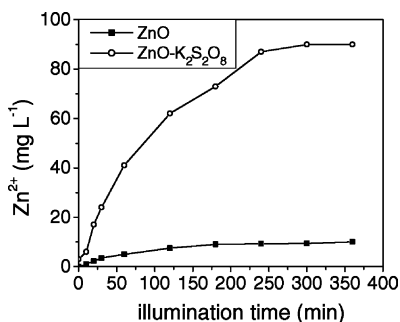
Fig. 14. Concentration of zinc in the solution as a function of irradiation time in the presence of: (a) ZnO = 500 mg L^{-1} and (b) ZnO = 100 mg L^{-1} and K$_2$S$_2$O$_8$ = 3.1 mM.

This is confirmed by measurements of Zn^{2+} presented in Fig. 14 (EC$_{50}$ of zinc is 1.62 mg L^{-1} [41]) and by the difference in the toxic response between the 5 and 15 min exposure, which is characteristic of the metal ions [42]. This makes impossible any conclusion concerning the toxicity of the photoproducts.

4. Conclusions

The photocatalytic oxidation of dichlorvos has been studied using TiO$_2$ and ZnO as catalysts. Titanium dioxide proved to be more efficient photocatalyst since the oxidation of the insecticide proceeded at higher reaction rates and almost complete mineralization was achieved. On the other hand illumination of zinc oxide suspensions could lead to the disappearance of dichlorvos but mineralization was not achieved leading to the formation of intermediates.

The photooxidation of dichlorvos followed first order kinetics according to the Langmuir–Hinshelwood model. Parameters such as pH, temperature and concentration of the catalyst play an important role affecting the reaction rate. With the addition of oxidants into illuminated TiO$_2$ and ZnO suspensions a synergistic effect was observed leading to an enhancement of the process except of the addition of hydrogen peroxide into ZnO suspension which causes a decrease to the rate of the reaction.

Finally the toxicity of the treated samples increased in all the systems that were studied, indicating the inefficient detoxification capacity of the processes. Probably, longer irradiation times or higher concentrations of catalysts could cause a decrease of the initial toxicity of the treated solution.

References

[1] H. Floesser-Mueller, W. Schwack, in: G.W. Ware (Ed.), Reviews of Environmental Contamination and Toxicology, vol. 172, Springer, 2001p. 129.

[2] S. Espulgas, J. Giménez, S. Contreras, E. Pascual, M. Rogríguez, Water Res. 36 (2002) 1034.

[3] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Catal. Today 53 (1999) 51.

[4] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.

[5] K.V. Ragnarsdottir, J. Geol. Soc. 157 (2000) 859.

[6] B.E. Mileson, J.E. Chambers, W.L. Chen, W. Dettbarn, M. Ehrich, A.T. Eldefrawi, D.W. Gaylor, K. Hamernik, E. Hodgson, A.G. Karczmar, S. Padilla, C.N. Pope, R.J. Richardson, D.R. Saunders, L.P. Sheets, L.G. Sultatos, K.B. Wallace, Toxicol. Sci. 41 (1998) 8.

[7] J.H. Mennear, Reg. Toxicol. Pharmacol. 27 (1998) 265.

[8] K. Harada, T. Hisinaga, K. Tanaka, Water Res. 24 (1990) 1415.

[9] S.A. Naman, Z.A.-A. Khammas, F.M. Hussein, J. Photochem. Photobiol. A: Chem. 153 (2002) 229.

[10] M.-C. Lu, G.D. Roam, J.-N. Chen, C.P. Huang, J. Photochem. Photobiol. A: Chem. 76 (1993) 103.

[11] N. Balkaya, Environ. Technol. 20 (1999) 617.

[12] I. Poulios, A. Avranas, E. Rekliti, A. Zouboulis, J. Chem. Technol. Biotechnol. 75 (2000) 205.

[13] N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem. Photobiol. A: Chem. 162 (2004) 317.

[14] I. Poulios, M. Kositzi, A. Kouras, J. Photochem. Photobiol. A: Chem. 115 (1998) 175.

[15] S. Malato, J. Blanco, A.R. Fernández-Alba, A. Agüera, Chemosphere 40 (2000) 403.

[16] M. Muneer, D. Bahnemann, Appl. Catal. B: Environ. 36 (2002) 95.

[17] T. Chen, R. Doong, W. Lei, Water Sci. Technol. 37 (1998) 187.

[18] S. Malato, J. Blanco, M.I. Maldonado, P. Fernández-Ibánez, A. Campos, Appl. Catal. B: Environ. 28 (2000) 163.

[19] S. Malato, J. Blanco, C. Richter, B. Braun, M.I. Maldonado, Appl. Catal. B: Environ. 17 (1998) 347.

[20] M.-C. Lu, G.D. Roam, J.-N. Chen, C.P. Huang, Chemosphere 27 (1993) 1637.

[21] J.-M. Herrmann, C. Guillard, M. Arguello, A. Agüera, A. Tejedor, L. Piedra, A. Fernández-Alba, Catal. Today 54 (1999) 353.

[22] A.R. Fernández-Alba, D. Hernando, A. Agüera, J. Cáceres, S. Malato, Water Res. 36 (2002) 4255.

[23] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Waste Water, 16th ed., 1985.

[24] Microbics Corporation, Microtox Manual, A Toxicity Testing Handbook, vol. 1–5, Carlsbad, CA, USA, 1992.

[25] D.F. Ollis, Catal. Technol. 2 (1998) 149.

[26] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[27] C.S. Turci, D.F. Ollis, J. Catal. 122 (1990) 178.

[28] J. Cunningham, G. Al-Sayyyed, S. Srijaranai, in: G. Helz, R. Zepp, D. Crosby (Eds.), Aquatic and Surface Photochemistry, CRC Press, 1994, p. 317.

[29] A.B. Prevot, M. Vincenti, A. Bianciotto, E. Pramauro, Appl. Catal. B: Environ. 22 (1999) 149.

[30] D. Robert, B. Dongui, J.-V. Weber, J. Photochem. Photobiol. A: Chem. 156 (2003) 195.

[31] J.-M. Herrmann, C. Guillard, C.R. Acad. Sci. Paris, Série Iic, Chimie/Chemistry 3 (2000) 417.

[32] J.P. Percherancier, R. Chapelon, B. Pouyet, J. Photochem. Photobiol. A: Chem. 87 (1995) 261.

[33] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Sol. Energy Mater. Sol. Cells 77 (2003) 65.

[34] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Catal. Today 76 (2002) 235.

[35] A. Piscopo, D. Robert, J.V. Weber, Appl. Catal. B: Environ. 35 (2001) 117.

[36] D.S. Bhatkhande, V.G. Pangarkar, A. Beenackers, J. Chem. Technol. Biotechnol. 77 (2001) 102.

[37] P. Spathis, I. Poulios, Corros. Sci. 37 (1995) 673.

[38] P. Pichat, C. Guillard, L. Amarlie, A.-C. Renard, O. Plaidy, Sol. Energy Mater. Sol. Cells 38 (1995) 391.

[39] J.R. Harbour, J. Tromp, M.L. Hair, Can. J. Chem. 63 (1985) 204.

[40] A.H. Boonstra, C.A.H.A. Mutsaers, J. Phys. Chem. 79 (1975) 1940.

[41] N.H. Ince, N. Dirilgen, I.G. Apikyan, G. Tezcanli, B. Üstün, Arch. Environ. Contam. Toxicol. 36 (1999) 365.

[42] K. Kaiser, Palabrica, Water Pol. Res. J. Canada 26 (1991) 361.