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Solar photocatalytic degradation of Aldrin

Erick R. Bandala [a,*], Silvia Gelover [a], Maria Teresa Leal [a],
Camilo Arancibia-Bulnes [b], Antonio Jimenez [b], Claudio A. Estrada [b]

[a] *Instituto Mexicano de Tecnologia del Agua, Paseo Cuauhnahuac 8532, Jiutepec, Morelos 62550, Mexico*
[b] *Centro de Investigacion en Energia—UNAM, Privada Xochicalco S.N. A.P. 34, Temixco, Morelos 62580, Mexico*

Abstract

Photocatalytic degradation of the pesticide Aldrin dissolved in water was carried out, in one case, using concentrated solar radiation and, in another case, using non-concentrated solar radiation. In these experiments, the effects of catalyst concentration, oxidant agent concentration, and solar irradiation were tested. In experiments without irradiation, strong adsorption of the pesticide over titanium dioxide was observed in the first few minutes of contact in the presence of titanium dioxide (TiO_2). These results can be explained by means of Coulombic interactions between the catalyst surface and the pesticide molecules. During the photodegradation process, results show a residual degradation (photolysis) in both the cases, when no catalyst was added. In the case of the non-concentrated solar system, the achieved results suggest that the use of H_2O_2 increased the degradation rate. For concentrated sunlight, an increase of the Aldrin concentration was observed during the first few minutes of irradiation. This can be explained as a desorption process that is triggered by a change in surface charge of the catalyst in the presence of hydrogen peroxide (H_2O_2) during irradiation. When photocatalysis was performed with TiO_2 alone, no Aldrin was detected in the water solutions throughout the entire experiment. This result was unexpected; however, it might be explained by the adsorption of the pesticide on the catalyst surface and by the absence of the oxidant's effect. Three transformation products (TPs) of the degradation process were identified: dieldrin, chlordene and 12-hydroxy-dieldrin. The results presented here are in agreement with previously reported results for photocatalytic degradation of other chlorinated pesticides using lamps as radiation sources.

Keywords: Photocatalysis; Photocatalytic oxidation; Pesticide treatment; Aldrin photodegradation; Solar photocatalysis

1. Introduction

There has been a steady increase in the production and use of chemicals for agricultural activities in the past decades. This trend has generated an increase in public awareness of the effects of these compounds on the earth and in water ecosystems. Due to their chemical characteristics, pesticides, in general, are a type of pollutant that demonstrate variable persistence to photochemical, chemical, and biochemical degradation. The environmental lifetime of some of these pesticides tends to be long [1]. The application of synthetic pesticides to control weeds, insect pests, and fungal diseases has been routine in agriculture for the past century [2]. It has been shown that residues of these synthetic pesticides are the cause of many adverse health effects. Moreover, several kinds of pesticides have been used in many indiscriminate and haphazard ways in the past [3].

The United Nations has reported that from the total amount of pesticides used in agriculture, less than 1% actually contacts the crops. The rest ends up in the soil or in the air, but mostly, in the water. The lack of these

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[*] Corresponding author. Tel./fax: +52-73-194-281.
E-mail address: ebandala@tlaloc.imta.mx (E.R. Bandala).

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pollutants' biodegradability, along with their continuous accumulated use, is a considerable problem and a critical issue with potentially detrimental and unpredictable consequences for the future. Despite the undesirable characteristics of pesticides, the global sale of these products increases each year, and predominantly in developing countries, which contribute to more than 70% of the total pesticide consumption. Included among these developing countries, Mexico has its own environmental problems regarding the presence of pesticides in its water bodies and in its underground water as well. Although the pesticide production has decreased in this country, a sizeable amount of 6000 t from just four pesticides alone was produced in 1999. Furthermore, the apparent pesticide consumption during the same year exceeded 6700 t [4]. In total, the volume of all pesticides used in Mexico, only for agricultural use, has raised from 16,400 t in 1995 to 23,300 t in 1999 [5], an increase in consumption of 36% in just 4 years.

The widespread presence of these organic chemicals in water has motivated interest to find alternative environmental-friendly solutions for the treatment and/or removal of their residues. Many technologies for pesticide removal have been studied and reported. These include adsorption, filters, biological treatment, and advanced oxidation processes (AOPs). Nevertheless, tertiary treatment of drinking water as done in treatment plants, such as inverse osmosis or adsorption with activated carbon, seems not to be efficient and effective enough for the removal of these highly persistent pollutants. In the last few years, solar photodegradation processes have been proven to be an excellent alternative for pesticide degradation in the field of AOP. This technology degrades the pesticides in polluted water; however, the efficiency of the process is heavily dependent on the chemical nature of the pesticides being treated [6].

Aldrin belongs to the organochloride pesticide group. Although it is included in the list of restricted pesticides in Mexico, it is one of the most widely occurring pesticides in surface water in this country. Photocatalysis of other pesticides from this same family have already been investigated [6,7–9]. Nevertheless, to the best of our knowledge, no studies concerning the solar photocatalytic degradation of Aldrin have yet been published [15]. Due to the environmental importance, as well as the extensive presence of Aldrin in surface and underground water, the proposal of new alternatives for the removal of this xenobiotic is an important issue that calls for extensive investigation and needs to be solved. The purpose of this work is to demonstrate the application of concentrated and non-concentrated solar radiation on the photocatalytic degradation of Aldrin in water.

2. Experimental method

2.1. Materials and reagents

Chemicals used in this work, such as the catalyst titanium dioxide (TiO_2) (>99% anatase, particle size 180 Å, specific surface area 23 m^2/g) and hydrogen peroxide (H_2O_2) (30%, stabilized), were obtained from Aldrich and Baker, respectively, as reactive grade products. Aldrin (95% purity) was obtained from Chem Service. Methylene chloride, hexane, and acetone of Burdick and Jackson pesticide grade were used as received.

2.2. Procedure

2.2.1. Adsorption over TiO_2

Adsorption tests were performed using a Philips and Bird 7790-400 test apparatus. Synthetic samples were prepared adding 2.5 mg of Aldrin to 500 ml of water in flasks protected from light. Different quantities of TiO_2 were added to each flask: 0.0, 0.5, 1.0, 2.0, and 3.0 g/l. The suspensions were mixed at 100 rpm over a 48 h period. The experiments were run with monitoring of the Aldrin concentration at the intervals of 0, 1, 3, 5, 24 and 48 h.

2.2.2. Irradiation experiments

Experiments were carried out using two different solar collectors. First, a parabolic trough solar concentrator (PC), able to concentrate radiation to a level of 41 suns, as described by Jiménez et al. [10]. Secondly, a tubular flat plate collector (FPC) for the non-concentrated sunlight experiments. See Fig. 1 for schematic diagrams of these devices. The FPC was tilted 18° (equal to local latitude), and a set of six Pyrex tubes was affixed to the plate. Each tube was 5.0 cm inner diameter, 0.45 m in length, with a UV transmissivity of 85%.

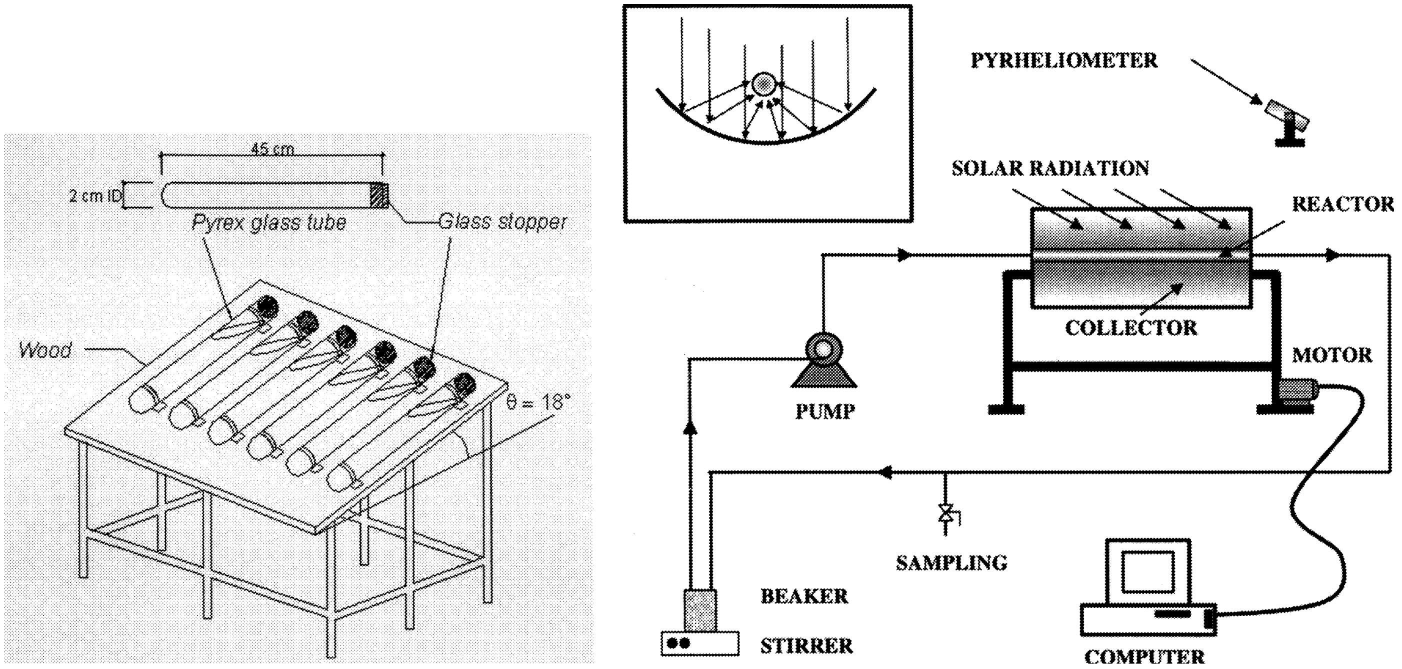

Fig. 1. Schematic representation of the FPC and the PC used in this work.

Table 1
Experimental conditions (FPC)

Experimental run	Aldrin (mg/l)	TiO_2 (g/l)	H_2O_2 (%)
E1	5	–	–
E2	5	0.2	–
E3	5	0.2	3.00
E4	5	0.2	6.00

When using the PC system, the working suspension was prepared as follows: 2.5 l of water was spiked with Aldrin [$C_0 = 5$ mg/l, determined by GC–ECD (electron capture detector) analysis], additionally, 2.0 g/l of TiO_2 was added. For some of the experiments 3 g/l of hydrogen peroxide were added. The mixture was kept in the dark for 48 h prior to irradiation, and then circulated through the PC system. The suspension was allowed to be in contact with air during irradiation.

For the FPC system, the experimental conditions are summarized in Table 1. Each mixture was homogenized in the dark for 5 min. Each tube was covered with a glass stopper in order to prevent contamination and extensive evaporation of the sample. The tubes were then exposed to sunlight. During irradiation they were stirred every 60 min to reduce TiO_2 deposition. All the experiments were performed two times.

2.3. *Sample handling*

Samples were taken every 4 h, in the case of the FPC setup, and every 30 min or less, in the case of the PC experiments. Once taken, samples were immediately filtered using a 0.22 μm Millipore membrane to separate the catalyst. Then the samples were analyzed for Aldrin concentration after performing a liquid–liquid extraction using methylene chloride. Extracts were concentrated under reduced pressure at a temperature below 45 °C in a rotatory evaporator. These concentrates were filled to a level of 1.0 ml by a gentle nitrogen flow. The solution was then injected in a gas chromatograph Hewlett-Packard 5890 series II, which was coupled to an ECD. A 30 m × 0.25 mm × 0.33 μm capillary RTX-5 column was employed. Additionally, any catalyst remaining after filtration was extracted with methylene chloride. Then, that extract was concentrated and analyzed for the presence of Aldrin using the same conditions as described above in order to complete the mass balance of the system.

During the Aldrin analysis, quality-control assurance was performed by means of spiked and surrogated samples. The surrogate used was 4,4-dichlorobiphenyl, as required by the USEPA method 8081B. The quality-control criteria adopted for the acceptance of the experimental results were those recommended in the USEPA standard method mentioned above.

The identification of transformation products (TPs) from the final effluent was carried out by means of gas chromatography–mass spectrometry (GC–MS). A Hewlett-Packard 5890 series II gas chromatograph was used coupled with a quadrupole mass spectrometer, Hewlett-Packard 5971 series. A 30 m × 0.25 mm × 0.33 μm capillary ultra 2 column was employed. The sample injection was carried out with a 3 min solvent delay. The MS analysis was carried out with ionization by electron impact (70 eV), and the spectra were recorded within the interval of 40–600 amu. Identification of the products was done with the aid of the Wiley (275,000 spectra) and the NIST (130,000 spectra) database library.

2.4. *Evaluation of solar radiation*

Global solar ultraviolet (UV) data sets were obtained using a total UV radiometer (Eppley, TUVR), which is able to measure in a wavelength range between 295 and 385 nm. Direct solar radiation was determined using an Eppley pyrheliometer. Accumulated energy is defined as the total amount of radiative energy reaching the reactor since the beginning of a experiment up to a given time by unit volume. This quantity was determined by means of Eq. (1) as proposed by Malato et al. [11]:

$$Q_{\mathrm{UV},n} = Q_{\mathrm{UV},n-1} + \Delta t_n \mathrm{UV}_{\mathrm{G},n}[A/V], \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

where t_n is the experimental time for each sample, $\mathrm{UV}_{\mathrm{G},n}$ the average solar UV irradiation UV_G during the time interval Δt_n, A the collector area, V the total volume, and $Q_{\mathrm{UV},n}$ the accumulated energy (kJ/l). When Q_{UV} is used as the variable describing the process, the reaction rate is expressed in units of mg/kJ of UV incident on the collector surface.

The resulting data were used to obtain the value of incoming energy through a factor (Φ_{ef}), which was obtained for each device by means of actinometrical procedures as previously published in Sánchez et al. [16].

3. Results and discussion

3.1. Aldrin adsorption in experiments without irradiation

Fig. 2 shows the behavior of pollutant concentration in batch tests in the presence of different titanium dioxide (TiO_2) concentrations.

As shown, an important adsorption occurs as soon as the pesticide and the TiO_2 make contact. Other results, not included in Fig. 2, revealed that complete adsorption was achieved within 15 min. Afterwards, the Aldrin concentration, in solution, remained relatively constant for the remainder of the experiment. Further changes, such as changes in pH (10) or changes in ionic strength (by applying NaCl 0.1 M) did not cause Aldrin desorption, as it was not detected in the aqueous phase. When samples of TiO_2 were extracted with methylene chloride, only 70% of the initial Aldrin was recovered.

These results could be explained by the electronic interaction between the pesticide molecules and the active sites on the titanium dioxide surface. Aldrin is an organic compound, whose chemical structure includes six chlorine atoms per molecule (see Fig. 5). Each one of these halogen atoms possesses three pairs of non-bonding electrons in its valence band. Therefore, a high electronic density is caused around the carbon structure that can promote strong electrostatic bonding between the halogen atoms and the positive active sites on the catalyst surface.

A behavior similar to the above has been observed for amino acids by Horikoshi et al. [12], who analyzed L-alanine, L-serine, and L-phenylalanine. They found that there is a high correlation between each amino acid's adsorption on TiO_2 and the electronic density due to the chemical structure of the amino acid. These authors propose that this association is due to Coulombic interactions between the carboxylic group in the amino acid (the part of the structure with the highest electronic density) and the solid surface.

3.2. Solar photocatalytic degradation

Fig. 3 shows the behavior of pesticide concentration as a function of the energy reaching the photo-reactor ($Q^*_{UV,n}$) for the experiments using non-concentrated solar radiation. $Q^*_{UV,n}$ is the accumulated energy including the efficiency factor associated with the collector geometry (Φ_{ef}) previously described by Curcó et al. [17]. As can be seen, even though the solution received around 100 kJ/l of sun energy, no significant Aldrin concentration reduction was observed when the pollutant was irradiated without use of the

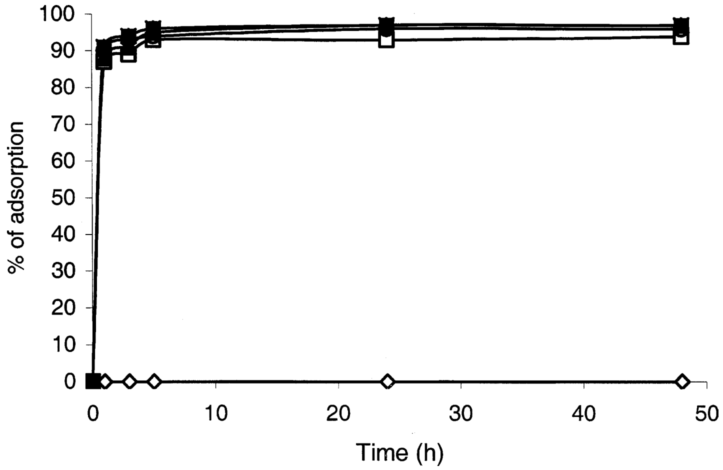

Fig. 2. Pesticide adsorption in titanium dioxide in non-irradiated experiments for several catalyst concentrations: 0.0 g/l TiO_2 (diamonds); 0.5 g/l TiO_2 (open squares); 1.0 g/l TiO_2 (closed triangles); 2.0 g/l TiO_2 (open circles); 3.0 g/l TiO_2 (closed squares).

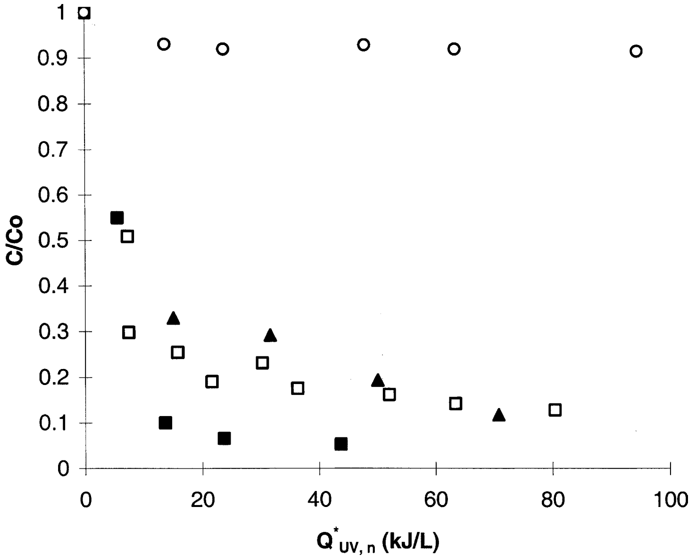

Fig. 3. Aldrin disappearance as a function of energy reaching the photo-reactor under non-concentrated sunlight for tested conditions: without TiO_2 (open circles); TiO_2 alone (open squares); $TiO_2 + H_2O_2$ (3 g/l) (closed triangles); $TiO_2 + H_2O_2$ (6 g/l) (closed squares).

photocatalyst. Fig. 3 also illustrates the effect upon the rate of solar photocatalysis at different concentrations of hydrogen peroxide. When only titanium dioxide was used with no hydrogen peroxide added, a degradation of around 80% was achieved using nearly 80 kJ/l of accumulated energy.

The use of 3.0 g/l of the oxidant agent H_2O_2 seemed to improve the degradation process, as it required 70 kJ/l to reach the same degradation as obtained when using TiO_2 alone. The trend was confirmed by using a higher concentration of hydrogen peroxide as indicated in Fig. 3. The best performance was achieved when using 6.0 g/l of oxidant: 90% degradation was reached with just 43 kJ/l of energy. This amounts to a reduction of 12% in the energy requirements, in the first case, and 54% in the latter case. In other words, the use of hydrogen peroxide allows a reduced irradiation time or, perhaps, the use of additional technologies in conditions of poorer irradiation. The obtained results agree with previous reports of the improvement of photocatalytic reaction when using electron acceptors. As it has been stated earlier [19], one of the practical problems with using TiO_2 as a photocatalyst is the electron–hole recombination (e^-/h^+), which could represent a major energy-wasting step in order to achieve a high quantum yield. One strategy for inhibiting e^-/h^+ recombination is to introduce irreversible electron acceptors within the reaction. The use of inorganic peroxides has been demonstrated to enhance the rate of degradation because they trap the photo-generated electrons more efficiently than O_2 [18]. Previous studies have shown that H_2O_2 can act both, as an efficient electron scavenger and as an efficient hole trap as well [20]:

$$H_2O_2\,(\text{ads}) + 2e^- \rightarrow 2OH^- \tag{2}$$

$$H_2O_2\,(\text{ads}) + 2h^+ \rightarrow O_2 + 2H^+ \tag{3}$$

Some authors [21] have proposed that H_2O_2 photodecomposition involves the formation of radical species, which can react with adsorbed organic molecules:

$$H_2O_2\,(\text{ads}) + h^+ \rightarrow HO_2{}^{\bullet} + H^+ \tag{4}$$

$$H_2O_2\,(\text{ads}) + e^- \rightarrow OH^{\bullet} + OH^- \tag{5}$$

It is a common practice to exhibit the reduction of concentration *versus* irradiation time as in Table 2. In the case of the experiments using non-concentrated light, since all runs were done simultaneously, the comparison is valid. Nevertheless, when the experiments are done on different days this is not true. An Aldrin concentration reduction of 85% was observed after nearly

Table 2
Decrease of Aldrin concentration as a function of irradiation time for non-concentrated solar radiation

Irradiation time (h)	C/C_0			
	Without TiO_2	TiO_2 alone	$TiO_2 + H_2O_2$ (3 g/l)	$TiO_2 + H_2O_2$ (6 g/l)
0	1	1	1	1
4	0.93	0.5		0.5
8	0.92	0.29	0.32	0.1
12		0.25	0.29	
16	0.93		0.19	0.065
20		0.19		0.052
24	0.92	0.16	0.078	
28		0.14	0.063	
32	0.91	0.12	0.06	

28 h of irradiation with titanium dioxide alone. When 3.0 g/l of hydrogen peroxide were applied, a degradation of 90% was obtained in the same time frame. Moreover, a pesticide degradation of 93% was reached in only 20 h when using 6.0 g/l of H_2O_2, i.e. 7 h less than in the experiment with no hydrogen peroxide.

Fig. 4 shows the behavior of Aldrin concentration under concentrated solar energy irradiation. As can be seen, the effect of solar energy without any catalyst, i.e. photolysis, is more significant under concentrated sunlight conditions when compared with experiments with non-concentrated radiation. In the latter case, only a slight variation was observed in the pesticide concentration. The Aldrin concentration was reduced by 15% after nearly 360 kJ/l of accumulated energy were applied within the PC system.

In the case of photocatalytic experiments, where no H_2O_2 was added to the system, no pesticide was detected within the aqueous samples. Surrogate recovery levels for these samples were between 40 and 120%, which are considered acceptable. Therefore, the failure of pesticide detection cannot be associated with the sample extraction procedure. The strong adsorption of the pesticide onto the catalyst is one way to explain the unexpected behavior. The catalyst was recovered and extracted with methylene chloride without any Aldrin detection.

A significant decrease in the amount of dissolved Aldrin was observed before irradiation, when 3.0 g/l of H_2O_2 were used. However, after 120 min of irradiation (262 kJ/l of accumulate energy), 90% degradation of Aldrin was achieved. The amount of Aldrin detected was only around 5% in the aqueous phase. An important item to note is that an increase in

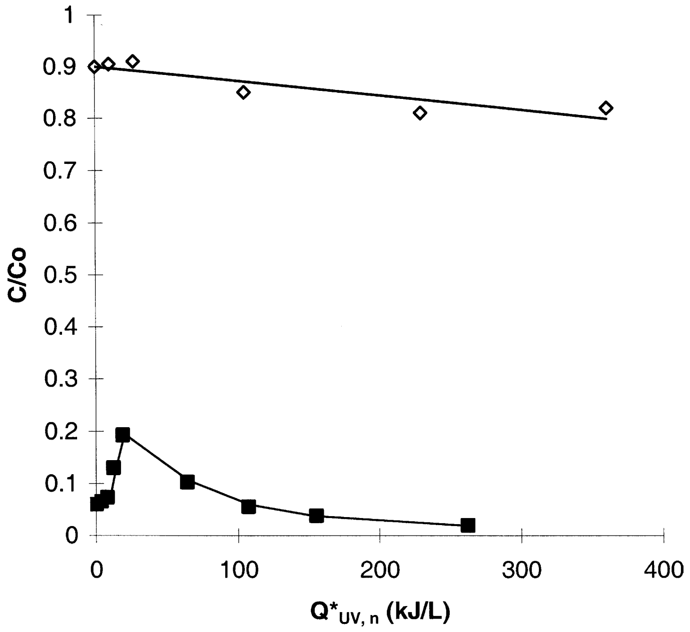

Fig. 4. Aldrin disappearance under concentrated sunlight: without TiO_2 (diamonds); $TiO_2 + H_2O_2$ (3 g/l) (squares).

dissolved Aldrin reached around 20% of the initial concentration within the earliest stages of the experiment. The increase could be explained by a process of desorption of Aldrin from the catalyst surface. As soon as irradiation starts, the surface charge changes due to the interaction between the radiation and the catalyst. These surface changes may trigger the desorption process, with a consequent increase in the concentration of dissolved Aldrin, to the point where the C/C_0 rate reaches its maximum value. After this point, the photocatalytic degradation process seems to play the dominant role.

The behavior described above must take place due to the effect of the oxidant agent used. We think that the H_2O_2 may become associated with active sites on the TiO_2 surface and with pesticide molecules. Once this association occurs, the photocatalytic reaction can proceed through hole scavenging methods initiated by the hydroxyl groups that are generated on the surface. Subsequently, the process is followed by an attack on the pesticide molecules by the $OH^\bullet$ radicals as proposed by Regazzoni et al. [22] for the photocatalysis of salicylic acid that is adsorbed by TiO_2.

In order to confirm the observed process of adsorption, an additional set of experiments was carried out. The experimental conditions tested are shown in Table 3. In this table, t represents the amount of time during which mixtures remained in contact prior to performing the catalyst separation and extraction with methylene chloride for Aldrin determination. As for the UV column, an asterisk (∗) indicates irradiation of the mixture with UV radiation under controlled conditions (40 W) for the duration of 40 min prior to performing the catalyst separation.

As proposed, the presence of the oxidant has some effect on the pesticide adsorption. As can be seen from Table 3, when TiO_2, Aldrin, and hydrogen peroxide are together, the last two compounds are adsorbed on the semiconductor surface. Probably, preference is given to hydrogen peroxide over Aldrin adsorption due to a higher oxygen–TiO_2 affinity *versus* the chlorine–TiO_2 affinity. Without an oxidant, no Aldrin was detected in the solution (the same as observed in the photocatalytic experiments using concentrated radiation). In contrast, when hydrogen peroxide was added to the mixture, the pesticide was detected in solution. In fact, the higher is the oxidant concentration, the higher is the detection of dissolved Aldrin in the sample.

Time is another important variable to take into account. Refer to test runs 3 and 4 shown in Table 3. For samples under the same conditions but with different time of contact, the sample with the shorter contact period, test 3, showed a pesticide chromatographic response three times higher than the sample with the longer time of contact. For the experiment without the oxidant but extracted after 10 min, as shown in test 2, a low concentration of Aldrin was detected, whereas for experiments without H_2O_2, Aldrin was neither detected after 24 h of contact nor after irradiation.

When the mixture was irradiated, hydrogen peroxide homolysis started. The equilibrium of the proposed TiO_2–peroxide–Aldrin interaction changed and released the Aldrin molecules to the aqueous phase. When no oxidant was added, this effect could not be achieved, and only a poor Aldrin concentration was released to the aqueous phase. After hydrogen peroxide homolysis, then the photo-generated hydroxyl

Table 3
Experimental conditions and results for adsorption experiments

Experiment	Aldrin	TiO_2	H_2O_2[a]	Time (t)	UV	Aldrin (CR[b])
1	Yes	No	No	–	No	4.5×10^6
2	Yes	Yes	Yes	10 min	No	0.5×10^6
3	Yes	Yes	Yes	10 min	*	1.0×10^6
4	Yes	Yes	Yes	24 h	*	0.3×10^6
5	Yes	Yes	6%	24 h	*	0.5×10^6
6	Yes	Yes	No	24 h	*	ND[c]

[a] H_2O_2 concentration was 3%, except when otherwise is indicated.

[b] Chromatographic response.

[c] Not detected.

Table 4
Variation of Aldrin concentration under concentrated sunlight

Circulation time (min)	C/C_0		
	Without TiO_2	TiO_2 alone	$TiO_2 + H_2O_2$ (3 g/l)
0	0.9	ND[a]	0.064
5		ND	0.064
10	0.905	ND	0.072
15			0.13
20	0.91		0.192
25		ND	0.086
30	0.85	ND	0.102
60		ND	0.054
90	0.81	ND	0.038
120		ND	0.018
180	0.82	ND	

[a] Not detected.

radicals could react with Aldrin molecules and produce different kinds of intermediates: those generated by the hydroxyl insertion, and those produced by dehalogenation of the pesticide. Whereas, the $^{\bullet}OH$ insertion produces hydrophilic intermediates, dechlorination of Aldrin may produce hydrophobic intermediates that could remain adsorbed on the TiO_2 surface. Chloride determination in the samples (qualitative data not included) confirms significant dechlorination; nevertheless, no dehalogenated intermediates were identified by GC–MS.

Table 4 shows the Aldrin behavior as a function of circulation time, for concentrated sunlight at different titanium dioxide and hydrogen peroxide concentrations. As stated before, without the oxidant addition, no Aldrin was detected; whereas, a 90% degradation of Aldrin was obtained when 3.0 g/l of oxidant was added for 120 min of irradiation. As can be seen in both Fig. 4 and Table 4, an increase of the C/C_0 ratio is observed in the initial minutes of the experimental run.

The degradation determined for Aldrin agrees with previous reports for other organochloride pesticides. Zaleska et al. [13] reported that the degradation of lindane, DDT, and methoxychlor ranged between 50 and 99% in aqueous solutions containing 40 mg/l of each pesticide, when treated separately. The authors described the elimination of the pesticides after 150 min of irradiation time, using a 150 W mercury lamp. In the same way, a degradation of 84% of lindane was observed in 1 day tests using sunlight-concentration systems [14]. The authors reported the use of PCs, similar to the one used in this work, for a lindane concentration of up to 35.9 mg/l.

3.3. *Transformation products*

The GC–MS technique indicates the presence of the parent compound and three TPs, by means of spectral comparison. The mass spectra of these compounds are listed in Table 5, and their structures are shown in Fig. 5. At the end of the experimental runs, low concentrations of Aldrin were identified by mass spectrometry. The other TPs identified were dieldrin, chlordene and 12-hydroxy-dieldrin.

The first two compounds have also been identified as Aldrin derivative products in biological degradation processes [3]. The toxicity of most of these identified TPs is lower than that reported for Aldrin, which could allow biological treatment after the photocatalytic process. This could be an interesting subject for future study. Although a high degradation rate of Aldrin was observed within the photocatalytic process, no dehalogenated TPs were identified, instead, only highly oxidized structures. This result could

Table 5
Mass spectrum data of identified TPs

Name	Retention time (min)	Molecular weight	Main fragments, *m*/*z* (relative abundance)
Aldrin	43.6	361	66 (100), 79 (40.4), 101 (28.2), 154 (17.4), 170 (3.9), 186 (6.5), 220 (4.3), 258 (11.2), 263 (31.7), 293 (8.6), 298 (10)
Dieldrin	44.0	377	79 (100), 81 (42), 108 (20), 237 (8.6), 261 (10.8), 263 (11.7), 265 (10.8), 345 (6.5), 349 (3.9)
12-Hydroxy-dieldrin	39.75	393	37 (13), 62 (39), 196 (32.6), 206 (20.8), 232 (100), 267 (39.5), 303 (67.4), 307 (15.2), 338 (17.4)
Chlordene	40.6	334	78 (100), 95 (62.5), 196 (13.15), 237 (42.7), 272 (39.4), 315 (4)

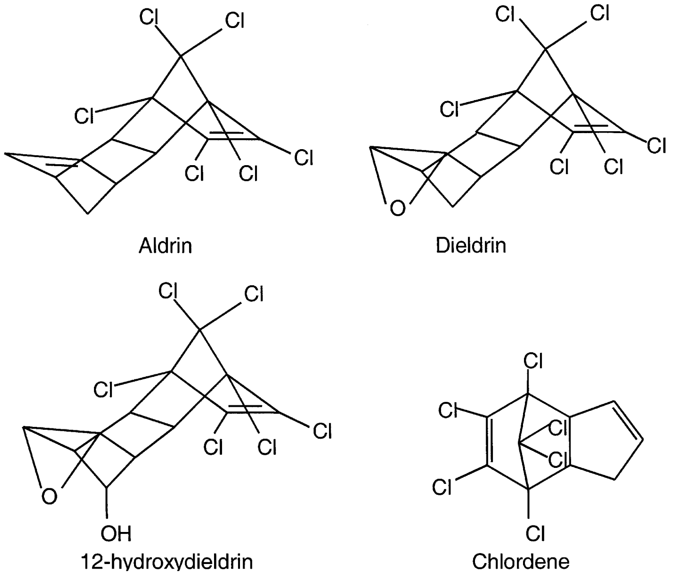

Fig. 5. Chemical structure of identified TPs.

mean that, at the actual irradiation conditions, Aldrin degradation is highly efficient, but longer irradiation times are necessary to obtain the mineralization of the pollutant.

4. Conclusions

Degradation of Aldrin was performed using titanium dioxide as a catalyst in one case, using concentrated solar radiation and, in another case, using non-concentrated solar radiation. A residual degradation (photolysis) was observed, in both the cases, when no catalyst was added. An important adsorption of the pesticide on the catalyst was observed.

The addition of hydrogen peroxide as an oxidant agent improved the reaction rate in both the cases, as has been reported for photocatalysis of other organic and inorganic pollutants. The results obtained for Aldrin degradation are comparable to literature reports for photodegradation of other organochloride pesticides using lamp cylindrical reactors.

Although the addition of hydrogen peroxide reduces the energy requirements, and thus permits the utilization of such a system under low solar radiative levels, there is no information concerning the quality of the degradation for each case. This points out to the need of further research to clarify this subject.

Each one of the tested solar collectors was capable of similar degradation of Aldrin; however, they differ in their applicability. The non-concentrated system is cheaper and simpler but needs larger collection areas. In contrast, the concentrated system is capable of quicker degradation with smaller collection areas, but it requires additional technical knowledge, as well as higher operation and maintenance costs.

The GC–MS analysis of final samples allowed the identification of trace concentrations of the parent pesticide and three TPs, dieldrin, 12-hydroxy-dieldrin and chlordene, which are common degradation products of Aldrin with lower toxicity values (in the case of the first two products.) So far, no dehalogenated TPs have been identified, despite the high degradation rates that were observed during the experimental runs. This could mean that higher accumulated energy is necessary to complete the mineralization of the pesticide.

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References

[1] L.A. Albert, Proceedings of the Second International Symposium on Sustainable Agriculture, México, D.F., 1998 (in Spanish).

[2] A.B. Lawrence, B. Williams, A. Fairbrother, Environ. Toxicol. Chem. 15 (4) (1996) 427.

[3] E.R. Bandala, J.A. Octaviano, V. Albiter, L.G. Torres, in: G.B. Wickramanayake, R.E. Hinchee (Eds.), Designing and Applying Treatment Technologies, Battelle Press, Columbus, OH, USA, 1998, p. 177.

[4] Mexican Association of Chemical Industry (ANIQ), Annual Report of the Mexican Chemical Industry, México, D.F., 2000 (in Spanish).

[5] National Institute of Statics, Geography and Informatics (INEGI), Monthly Industrial Report, México, D.F., 2000 (in Spanish).

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

[7] H. Hidaka, K. Nohara, J. Zhao, N. Serpone, E. Pelizzetti, J. Photochem. Photobiol. A 64 (1992) 247.

[8] A. Bianco-Prevot, E. Pramauro, M. de la Guardia, Chemosphere 39 (3) (1999) 493.

[9] A. Bianco-Prevot, M. Vicenti, A. Bianciotto, E. Pramauro, Appl. Catal. B 22 (1999) 149.

[10] A.E. Jiménez, C. Estrada, A.D. Cota, A. Roman, Solar Energy Mater. Solar Cells 60 (2000) 85.

[11] S. Malato, J. Blanco, C. Richter, B. Milow, M.I. Maldonado, Chemosphere 38 (5) (1999) 1145.

[12] S. Horikoshi, N. Serpone, J. Zhao, H. Hidaka, J. Photochem. Photobiol. A 118 (1998) 123.

[13] A. Zaleska, J. Hupka, M. Wiergowski, M. Biziuk, J. Photochem. Photobiol. A 135 (2000) 213.

[14] S. Malato, J. Blanco, C. Richter, M. Vincent, Solar Energy 56 (5) (1996) 401.

[15] D.M. Blake, National Renewable Energy Laboratory, Technical Report NREL/TP-510-31319, November 2001.

[16] M. Sánchez, E.R. Bandala, M.T. Leal, C. Estrada, Proceedings of the XXV National Association of Solar Energy Meeting, México, D.F., 2001, p. 477 (in Spanish).

[17] D. Curcó, S. Malato, J. Blanco, J. Gimenez, P. Marco, Solar Energy 56 (5) (1996) 387.

[18] S. Malato, J. Blanco, C. Richter, B. Braun, M.I. Maldonado, Appl. Catal. B 17 (1998) 347–356.

[19] E. Pelizzetti, V. Carlin, C. Minero, M. Grätzel, New J. Chem. 15 (1991) 351.

[20] I. Ilisz, Z. László, A. Dobi, Appl. Catal. A 180 (1999) 25.

[21] V. Augugliaro, E. Davi, L. Palmisano, M. Schiavello, A. Scalfani, Appl. Catal. 65 (1990) 101.

[22] A. Regazzoni, P. Mandelbaum, M. Matsuyoshi, S. Schiller, S.A. Bilmes, M.A. Blesa, Langmuir 14 (4) (1998) 868.