

ON-LINE CATALYTIC PHOTODEGRADATION OF ALDICARB

R. PARREÑO ALARCON, A. MORALES-RUBIO and M. DE LA GUARDIA*

Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner St., 46100 Burjassot, Valencia, Spain

ABSTRACT

An on-line catalytic photodegradation procedure has been developed for the detoxification of aqueous solutions containing aldicarb, (2-methyl-2-(methylthio)propanol o-[(methylamine) carbonyl]oxime), a carbamate pesticide which has a lethal oral dose for rats of 0.93 mg Kg^{-1} . The method consist of the light-induced degradation of aldicarb under ultraviolet irradiation in the presence of a TiO_2 slurry, employed as photocatalyst. The effect of different experimental variables on the degradation of aldicarb has been studied and it has been found that an irradiation time of the order of 18 s is sufficient to completely mineralize aldicarb at mg l^{-1} concentrations in the presence of a 0.8 mg l^{-1} of TiO_2 .

INTRODUCTION

Aldicarb is a carbamate pesticide widely used in the treatment of crops but which has a high toxicity for mammalian and, because of that, it is very convenient to develop experimental procedures for the detoxification of aldicarb solutions which could be employed in the treatment of polluted waters.

The degradation of pesticides in waters can be carried out through chemical, thermal, photochemical and microbiological processes. However, most of these procedures

Author to whom correspondence should be addressed

are difficult to apply for the detoxification of waters because they require long periods of time.

Heterogeneous photo-assisted catalytic degradation processes provide an interesting alternative for the fast decomposition of pesticides in waters¹⁻⁵, based on the irradiation of solutions containing the pollutant molecules in the presence of a semiconductor. The use of an irradiation wavelength shorter than the bandgap of the semiconductor induces the formation of electron/hole pairs and subsequently electron transfer reactions occur across the semiconductor/liquid interface providing the formation of oxidizing radicals and molecules which destroy the pollutant⁶⁻⁸.

Most of the reported studies on the photo-assisted catalytic degradation of pesticides have been carried out in batch, using stirred cells containing a suspension of a semiconductor, preferably TiO_2 , and a solar box as light source¹²⁻¹⁵. However, recent analytical works, in which slurries of solid samples have been employed in conventional flow injection analysis (FIA) manifolds^{16, 17}, have evidenced that slurries could be transported without clogging, thus opening the possibility of the use of FIA manifolds to carry out the photodegradation of pesticides in the presence of semiconductors.

There are few precedents on the on-line photodegradation processes but our first papers on this matter have established the basis for the development of this kind of treatments^{18, 19}.

The aim of this work is to study the experimental conditions for the flow injection photo-assisted catalytic degradation of aldicarb by using TiO_2 as semiconductor and ultraviolet light in order to establish a procedure which could be applied for the decontamination of polluted waters.

EXPERIMENTAL SECTION

Apparatus and Reagents

A Hewlett-Packard (HP) Model 8452 A diode-array spectrophotometer, equipped with an HP 89530 A MS-DOS UV-Visible Software, with a response time of 0.1 s, was used for the continuous control of the degradation of aldicarb by means its spectrophotometric determination. A flow cell of 50 μl internal volume and 1 cm pathlength and a quartz cell of 1 cm pathlength were used for carrying out absorbance measurements.

The FIA manifold indicated in Fig. 1 was employed to carry out the photocatalytic decomposition of aldicarb. It is a double channel assembly with a Gilson Minipuls 2 peristaltic pump, two PTFE Reodhyne 50 injection valves and a Y shaped merging zone. Discrete volumes of both, an aqueous solution containing aldicarb, and a TiO_2 slurry, are injected simultaneously into the water carrier stream and merged. In general, a TiO_2 slurry volume 100 μl higher than that of the aldicarb was employed in order to assure that the dispersion of the pesticide takes place, in all cases, in the presence of TiO_2 . A home made teflon filter (see the inset in Fig. 1) with Wathman 42 paper disc filters was employed to separate the suspended TiO_2 before to carry out the absorbance measurements. A directional three way valve (Omnifit) was employed in order to avoid the filter clogging when measurements are unnecessary. All the teflon tubes employed in the manifold were 0.8 mm internal diameter and flexible polyvinyl chloride tubes of 1.52 mm internal diameter were employed to provide a flow rate between 0.45 and 4.35 ml min^{-1} in each channel.

The on-line irradiation of samples was carried out by using a fluorescent lamp Vilberb Lourmat of 220 Volts and 50 Hertz, working at 254, 312 and 365 nm wavelength. As can be seen in the scheme of Fig. 1 the photochemical reactor is a teflon tube wound around the tube of the irradiation lamp.

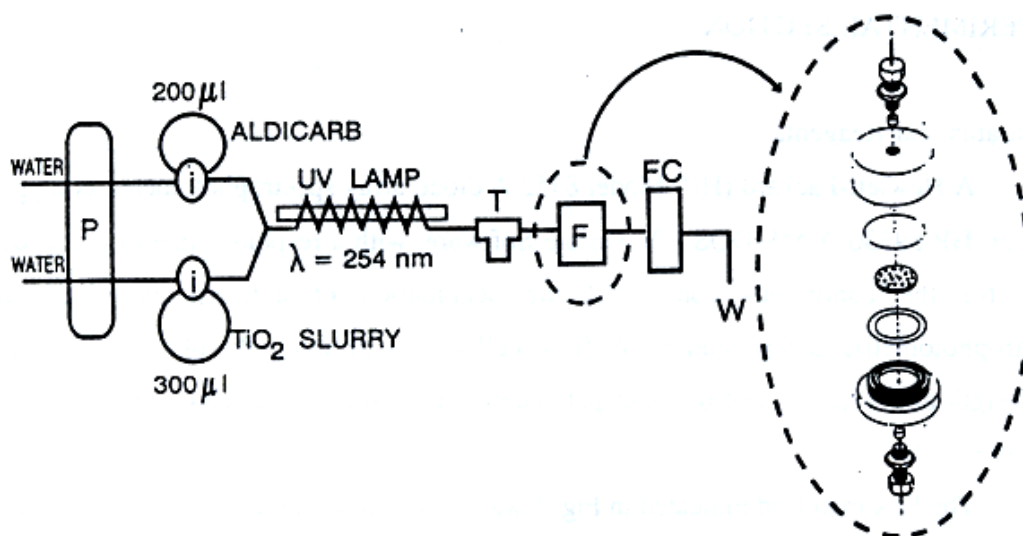


Fig. 1: Manifold employed for the catalytic photodegradation of aldicarb. P: peristaltic pump, I: injection valve, T: directional valve, F: in line filter, FC: flow cell, W: waste.

TiO₂ (Anatasa P25) was obtained from Degussa A.G. (Frankfurt, Germany) and different stock slurries of TiO₂ were prepared by dilution with distilled water until the appropriate concentration.

Aldicarb (99%, C₇H₁₄N₂O₂S) was obtained from Riedel de Haën, and working solutions were weekly prepared by dissolving between 1 to 2 mg in 100 ml of distilled water.

General Procedure

To study the on-line catalytic photodegradation of aldicarb, discrete volumes of an aldicarb water solution were injected in the FIA manifold at the same time than appropriate volumes of a TiO₂ slurry. Both injected solutions were merged, by using a Y-shaped teflon piece and then passed through a teflon coil wound around an UV lamp, in which the photo-assisted catalytic degradation of the pesticide takes place. After that,

solutions were filtered through a filter paper and the degradation yield controlled by UV absorbance measurements, carried out with the diode array.

Alternatively, aldicarb solutions were continuously fed into a water carrier stream and merged with another stream of a TiO_2 slurry, carrying out the on-line photodegradation as previously indicated.

To control the degradation of aldicarb, absorbance measurements at 247 nm were carried out. Fig. 2 shows the UV absorption spectra of different concentrations of aldicarb and the corresponding calibration line obtained in the range from 2 to 100 mg l^{-1} which provides a typical regression line $A = 0.012 + 0.0196 C$ with a regression coefficient of 0.9999.

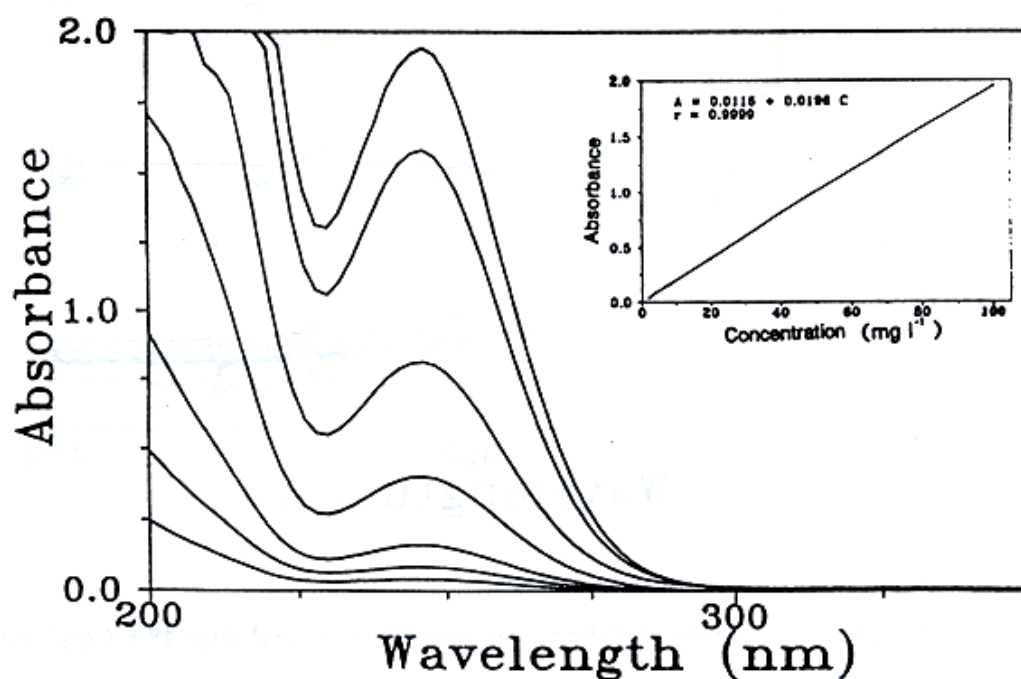


Fig. 2: UV absorption spectra of a series of aldicarb solutions. The inset corresponds to the calibration line obtained.

RESULTS AND DISCUSSION

Stability of aldicarb against the light

Figure 3a shows the UV spectrum of a solution containing 28 mg l^{-1} of aldicarb in distilled water, indicating the presence of a well defined absorption band at 247 nm . This spectrum remains absolutely stable after 48 hours of irradiation with solar light. However when aldicarb solutions are irradiated at 254 nm in the presence of a TiO_2 suspension, the photo-assisted degradation of aldicarb takes place until the total disappearance of the 247 nm maximum (see Fig. 3b)

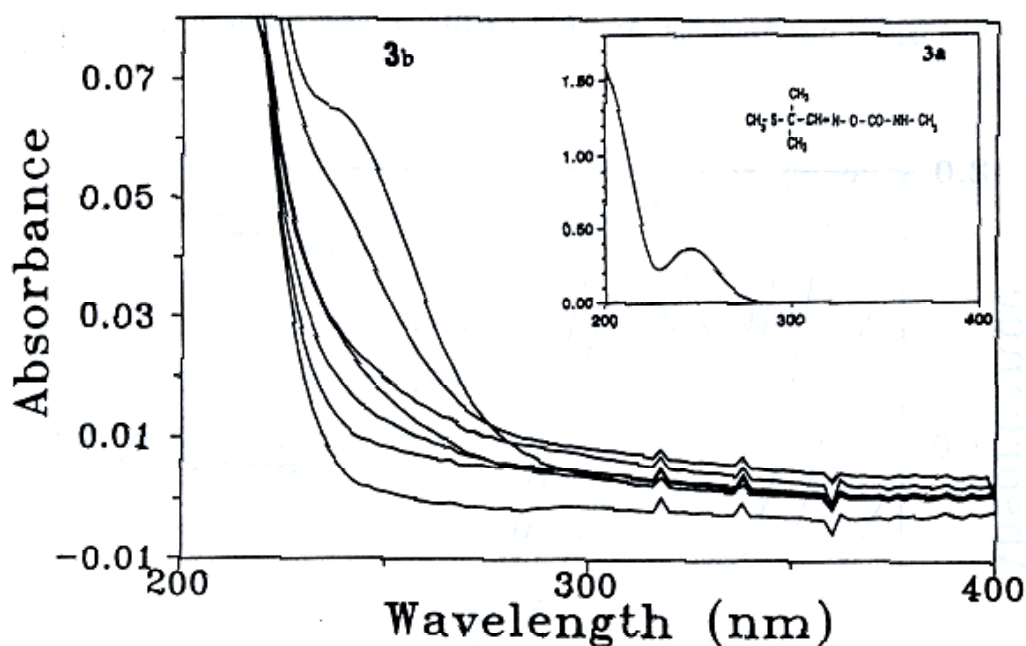


Fig. 3: Stability of aldicarb against the light.

3a: Spectra of a 28 mg l^{-1} solution of aldicarb recorded before and after 48 h (irradiated with solar light in the absence of TiO_2). 3b: Spectra found for a series of measurements carried out on a 15 mg l^{-1} aldicarb solution irradiated at 254 nm in the presence of a 2 mg ml^{-1} TiO_2 slurry. Measurements were taken after 3, 6, 9, 12, 15, 25 and 30 minutes of irradiation.

Flow injection photodegradation of aldicarb

The FIA methodology reduces the handling of samples and saves time and consumables. Thus the application of the FIA concepts to the on-line photo-assisted degradation of pesticides could be the current way for reducing costs and incorporate these treatments to the detoxification of water effluents.

Two alternative methods have been employed in order to automatize the photodegradation of aldicarb, one based on the merging of a water stream with a stream of a TiO_2 slurry, and the second one carrying out the simultaneous injection of aldicarb solutions and TiO_2 slurries in a water carrier stream. The first approach is more appropriate for the treatment of real water effluents but the second one is better for the study of the process variables.

Fig. 4 shows a characteristic FIA recording obtained by injecting $100\ \mu\text{l}$ of a $15\ \text{mg l}^{-1}$ solution of aldicarb into a water stream, which is merged with a stream of a TiO_2 slurry of $0.6\ \text{mg ml}^{-1}$, and, as can be seen, for a fixed concentration of aldicarb the quantity which remains undestroyed diminishes when the carrier flow rate decreases.

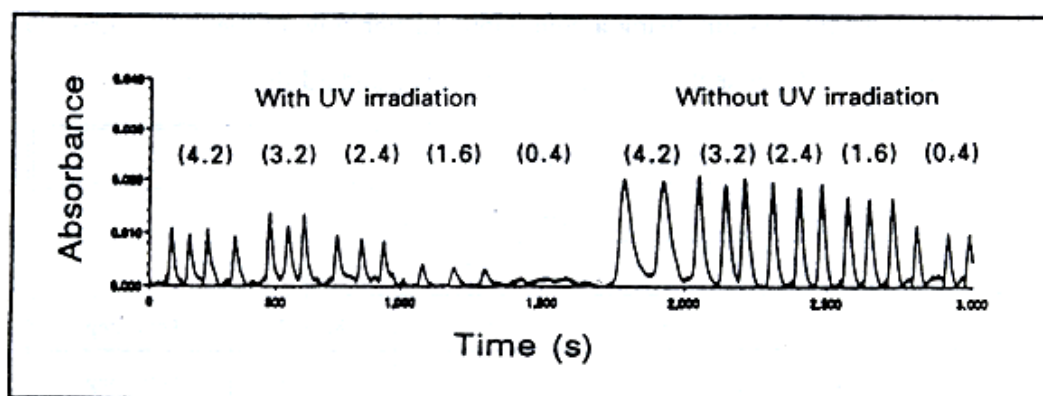


Fig. 4: FIA recording obtained by injecting $100\ \mu\text{l}$ of a $15\ \text{mg l}^{-1}$ solution of aldicarb in a water stream, which is merged with a TiO_2 slurry stream containing $0.6\ \text{mg ml}^{-1}$ of TiO_2 , with, and without UV irradiation at $254\ \text{nm}$, using different carrier flow values in each one of the two channels (values indicated in brackets in ml min^{-1}).

To evaluate the degradation yield of aldicarb, the height of the peaks obtained both, with and without UV irradiation, were compared. On the other hand, it was previously confirmed that aldicarb was not physically adsorbed on the surface of the TiO₂ particles.

Table I summarizes the experimental results found for the degradation yield of an aldicarb solution as a function of the TiO₂ concentration and the carrier flow employed, and, as can be seen, for a fixed carrier flow the degradation yield increases until to reach a maxim value for a concentration of the order of 0.6 mg ml⁻¹. The use of very high TiO₂ concentrations only provides an increase of the degradation yield of aldicarb when very slow carrier flow values are employed, but, in general, the presence of high TiO₂ concentrations reduces the irradiation of samples causing a dark effect which, for high carrier flow values, dramatically reduces the degradation of aldicarb.

Table I: Degradation yield of aldicarb as a function of the TiO₂ concentration and the carrier flow. (Experimental conditions: degradation coil 2.5 m, aldicarb 100 µl of 15 mg l⁻¹, UV wavelength 254 nm, using a continuous carrier flow of the TiO₂ slurry. Data correspond to three independent measurements ± their standard deviation.

DEGRADATION YIELD (%)					
TiO ₂ (mg ml ⁻¹)	Carrier flow (ml min ⁻¹)				
	4.7	3.7	2.7	1.8	0.9
0.2	14 ± 3	18 ± 3	54 ± 3	82 ± 2	Total deg.
0.4	52 ± 4	64 ± 3	76 ± 8	73 ± 8	Total deg.
0.6	65 ± 1	80 ± 3	87 ± 2	90 ± 1	Total deg.
0.8	43 ± 6	69 ± 1	78 ± 2	92 ± 2	Total deg.
1.0	43 ± 5	62 ± 6	83 ± 3	96 ± 2	Total deg.
2.0	23 ± 4	48 ± 5	76 ± 3	96 ± 1	Total deg.

In order to reduce the dark effect of TiO₂, which is partially due to the deposition of the anatase particles inside the degradation coil, both aldicarb solutions and TiO₂ slurries were simultaneously injected as indicated in the manifold of Fig. 1 and the degradation yield of aldicarb studied as a function of TiO₂ concentration and carrier flow employed. Data found are summarized in table II in which it can be seen that the degradation yield increases when the TiO₂ concentration increases and the carrier flow decreases.

Table II: Effect of the TiO₂ concentration and the carrier flow values on the degradation yield of aldicarb. (Experimental conditions: degradation coil 2.5 m, aldicarb 100 µl of 18.5 mg l⁻¹, UV wavelength 254 nm, TiO₂ injection volume 200 µl).

DEGRADATION YIELD (%)					
TiO ₂ (mg ml ⁻¹)	Carrier flow (ml min ⁻¹)				
	4.2	3.2	2.4	1.6	0.9
0.2	24 ± 2	35 ± 4	50 ± 4	68 ± 5	45 ± 7
0.4	37 ± 3	53 ± 2	76 ± 3	83 ± 1	Total deg.
0.6	51 ± 3	65 ± 3	83 ± 3	88 ± 3	Total deg.
0.8	65 ± 5	81 ± 1	88 ± 2	85 ± 4	Total deg.
1.0	68 ± 1	85 ± 1	91 ± 1	Total deg.	Total deg.
2.0	90 ± 1	92 ± 3	Total deg.	Total deg.	Total deg.

Effect of FIA parameters

It has been studied the effect of the main FIA parameters on the degradation yield of aldicarb using the manifold of Fig. 1. The flow rate of the carrier streams was modified from 4.6 to 8.7 ml min⁻¹, the length of the degradation coil from 2 to 5 m and the sample volume injected from 100 to 400 µl.

In general, it has been observed that the increase of the coil length and the decrease of the carrier flow enhances the degradation yield, the volume injected being less important.

Table III summarizes, as an example, the effect of different carrier flow values and different injection volumes on the degradation of an aldicarb solution.

Table III: Effect of the carrier flow and the sample injection volume on the degradation yield of aldicarb. (Experimental conditions: degradation coil 5 m, aldicarb concentration 21 mg l⁻¹, UV wavelength 254 nm, TiO₂ 1mg ml⁻¹. In all cases the volume of the TiO₂ slurry injected was 100 µl higher than that employed for the aldicarb).

DEGRADATION YIELD (%)				
Carrier flow (ml min ⁻¹)	Injection volume of aldicarb (µl)			
	100	200	300	400
8.7	78 ± 2	79 ± 2	84 ± 5	76 ± 2
8.0	86 ± 1	81 ± 2	89 ± 1	85 ± 2
7.3	87 ± 1	83 ± 1	89 ± 1	91 ± 1
6.4	87 ± 2	82 ± 4	90 ± 2	93 ± 1
5.7	82 ± 1	85 ± 2	Total deg.	Total deg.
4.6	Total deg.	82 ± 3	Total deg.	Total deg.

In fact the most important variable seems to be the carrier flow and the degradation coil length, which control the irradiation time of the mixture of both, aldicarb and TiO_2 .

As can be seen in Fig. 5 an irradiation time equal or higher than 30 seconds assures the quantitative degradation of aldicarb, by using a 5 m length irradiation coil, being necessary more than 80 seconds to provide a degradation yield of the order of 80 % by using a coil of 2.5 m length.

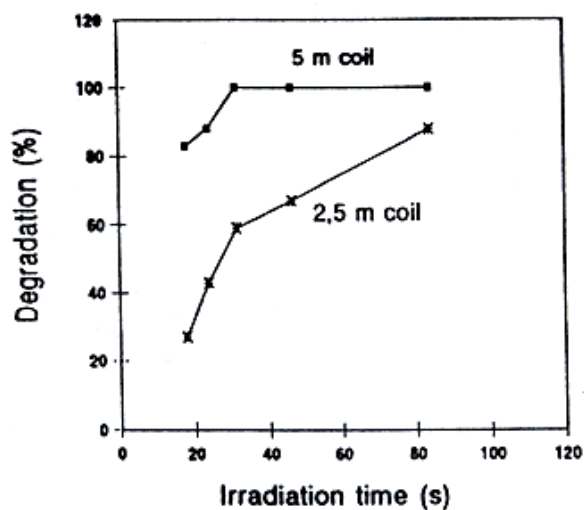


Fig. 5: Effect of the irradiation time on the degradation of 200 μl of an aldicarb solution of 18.5 mg l^{-1} in the presence of 300 μl of 0.8 mg ml^{-1} TiO_2 .

Effect of the aldicarb concentration

It has been studied the effect of the aldicarb concentration (from 12 to 192 mg l^{-1}) on its photodegradation yield, using a TiO_2 concentration of 0.8 mg ml^{-1} , a degradation coil of 2.5 m and different values of the carrier flow. Data obtained in these experiments are summarized in figure 6, which evidences that the increase of the aldicarb concentration requires a decrease of the carrier flow in order to provide the same degradation yield.

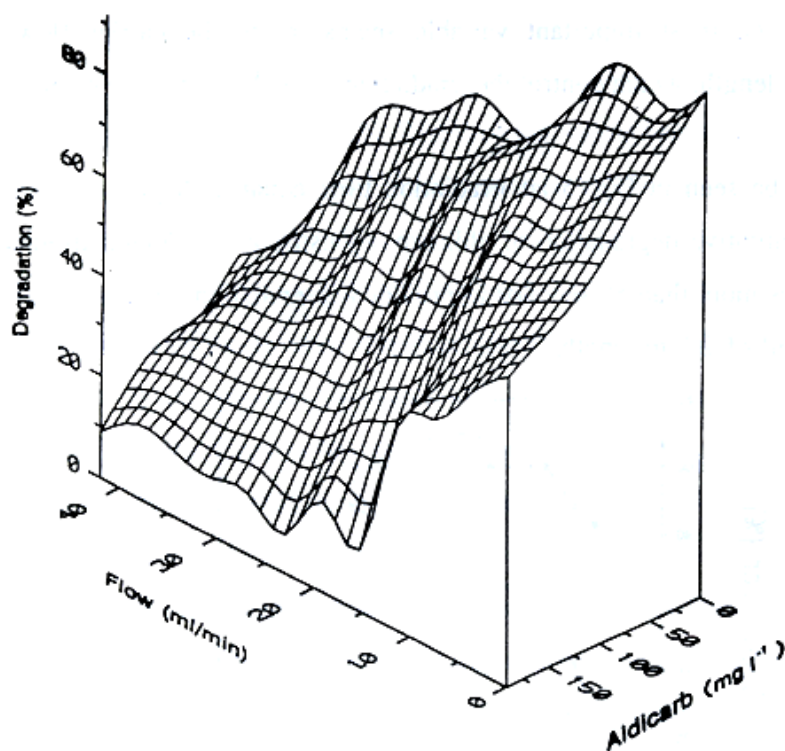


Fig. 6: Variation of the degradation yield of aldicarb as a function of its concentration and the carrier flow rate. Irradiation wavelength employed: 254 nm. Injected volumes of aldicarb and TiO_2 : 200 and 300 μl respectively.

Effect of irradiation wavelength

Three different wavelength radiations were employed, 254, 312 and 365 nm for the degradation of 200 μl of an aldicarb solution of 21 mg l^{-1} in the presence of 300 μl of a 0.8 mg ml^{-1} TiO_2 slurry, using in all cases a degradation coil of 2 m. As it can be seen in table IV the wavelength of the radiation light affects the degradation of aldicarb and when the wavelength increases the degradation yield decreases. This effect is very important for high carrier flow values, which involves a short irradiation time, but, for residence time values of the aldicarb and TiO_2 , under the irradiation light, higher than 40 s it is possible to find degradation yield values equal or higher than the 80 %.

Table IV: Photodegradation yield of aldicarb as a function of the irradiation wavelengths.

DEGRADATION YIELD (%)					
λ (nm)	Carrier flow (ml min ⁻¹)				
	4.2	3.2	2.4	1.6	0.9
254	44 ± 4	59 ± 3	75 ± 2	85 ± 1	85 ± 2
312	25 ± 2	35 ± 3	58 ± 3	80 ± 1	93 ± 1
365	24 ± 2	36 ± 1	45 ± 4	80 ± 2	93 ± 1
	23 ± 1	30 ± 2	59 ± 3	84 ± 1	93 ± 1

CONCLUSIONS

Studies carried out have evidenced that the photo-assisted catalytic degradation of aldicarb can be carried out very fastly in the presence of TiO₂ by using a flow system in which a simple teflon tube can act as a photochemical reactor.

The degradation yield of aldicarb depends on the flow conditions, specially on the irradiation time and also on the TiO₂ and aldicarb concentrations.

The major advantage of the developed procedures is that it can be carried out in flow conditions, by adding TiO₂ to the water effluents to be detoxified, and that the catalyst could be recovered after its use and reutilized.

To scale up the developed methodology, in order to be applied in water treatment plants, it must be taken into account that for this purpose the manifold could be simplified, avoiding the filtration step which is only necessary for the on-line control of

the degradation process, thus improving the amount of waste which can be treated per hour.

The on-line photo-assisted catalytic degradation of aldicarb also opens the door for the development of "clean" analytical methods for the spectrophotometric determination of pesticides, by incorporating a photodegradation unit to the manifold employed for carrying out spectrophotometric measurements after the measurement step. In this sense practical applications have been developed in our laboratory for the determination of resorcinol and propoxur²⁰

REFERENCES

- (1) E. Pelizzetti, C. Minero and V. Maurino, *Adv. Coll. Interface Science*, 217, 32 (1990).
- (2) E. Pelizzetti, E. Pramauro, C. Minero and N. Serpone, *Waste Managements*, 65, 10 (1990).
- (3) M. Halmann, *Photochem. Photophys.*, 75, 5 (1992).
- (4) P.L. Yue, *Process Sof. Environ Prot.*, 145, 70 (B3) (1992).
- (5) W. Aaron, *Chem. Mater.*, 280, 5(3) (1993).
- (6) A.J. Bard, *Science*, 207, 139 (1980).
- (7) A.J. Bard, *J. Phys. Chem.*, 86, 172 (1982).
- (8) M. Grätzel, "Energy resources throught photochemistry and Catalysis", Academic Press, New York (1983).
- (9) T. Nguyen and D.F. Ollis, *J. Phys. Chem.*, 3386, 88, (1984).
- (10) M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello and N. Serpone, *Chemosphere*, 195, 14, (1984).
- (11) R. Borello, C. Minero, E. Pramauro, E. Pelizzetti, N. Serpone and H. Hidaka, *Environ. Toxicol. Chem.*, 997, 8, (1989).

- (12) D.H. Hutson and T.R. Roberts, "Environmental Fate of Pesticides", Wiley, N.Y., 7 (1990).
- (13) C.K. Grätzel, M. Sirousek and M. Grätzel, *J. Mol. Catal.*, 375, 60 (1990).
- (14) J.C. D'Oliveira, G. Al-Sayed and P. Pichat, *Environ. Sci. Technol.*, 990, 24 (1990).
- (15) E. Pelizzetti, V. Carlin, C. Minero and M. Grätzel, *New J. Chem.*, 351, 15 (1991).
- (16) R. Martinez-Avila, V. Carbonell, M. de la Guardia and A. Salvador, *J. Assoc. Off. Anal. Chem.* 73, 389 (1990).
- (17) V. Carbonell, M. de la Guardia, A. Salvador, J.L. Burguera and M. Burguera, *Anal. Chim. Acta*, 238, 417 (1990).
- (18) E. Pramauro and M. de la Guardia, *Tecnologie ambientali*, 63 (1991).
- (19) E. Peris-Cardells, J. Terol, A.R. Maurí, M. de la Guardia and E. Pramauro, *J. Environ. Sci. Health*, B28(4), 431 (1993).
- (20) K.D. Khalaf, B.A. Hasan, A.E. Morales-Rubio, V. Carbonell and M. de la Guardia, *Analyst* (sent to be published).

(Received February 16, 1994)

(Accepted April 5, 1994)