Application of solid-phase microextraction to the study of the photochemical behaviour of five priority pesticides: "on-fiber" and aqueous photodegradation[☆]

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Abstract

Solid-phase microextraction (SPME) is applied to study the photochemical degradation of five priority pesticides: atrazine, alachlor, aldrin, dieldrin, endrin. Analyses were carried out by gas chromatography–mass spectrometry. The possibility of studying the photochemical degradation of the target compounds in solid-phase microextraction fibers, "photo-SPME", is evaluated employing different SPME coatings. The target analytes were extracted from aqueous solutions using different commercial coatings and then, the fibers were exposed to UV light. Results indicated that on-fiber photodegradation takes place in a considerably major extent using PDMS coating for an irradiation time of 30 min. On-fiber photodegradation kinetics of each analyte were determined by UV irradiation of the PDMS for different times. A large number of photoproducts were generated and they were tentatively identified by means of their mass spectra and with the aid of literature. In this way, main photodegradation mechanisms could be postulated. Aqueous photodegradation studies followed by SPME were performed and compared with photo-SPME. All the photoproducts detected in the aqueous experiments were previously found in the photo-SPME experiments. This study shows the potential of photo-SPME to evaluate the photo-transformation of organic pollutants.
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Keywords: Solid-phase microextraction; Photodegradation; Pesticides; Atrazine; Alachlor; Aldrin; Dieldrin; Endrin

1. Introduction

Pesticide is any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. This term is applied to herbicides, fungicides and various other substances used to control pests. Pesticides can cause harm to humans, animals or the environment because they are designed to kill or otherwise adversely affect living organisms. The health effects of pesticides depend on the type of pesticide.

Atrazine (*s*-triazine herbicides member) is one of the most frequently used pesticides in agriculture in the United States and is the most commonly detected in ground and surface water due to its wide use, and its ability to persist in soil and to move into water. The US Environmental Protection Agency (EPA) has categorised atrazine as a possible human carcinogen. Alachlor, a chloroacetamide herbicide, is a restricted used pesticide considered a likely carcinogen at high doses. Studies indicate chronic effects including hepatotoxicity and eye degeneration with secondary cataract formation. Aldrin, dieldrin and endrin (chlorinated cyclodiene insecticides) are

the common names for three closely related chemicals that have been widely used for controlling soil insects. They are considered highly toxic, specially endrin and some of its metabolites, and have been banned in most developed countries.

To evaluate the fate of pesticides in the environment, the influences of both abiotic and biotic factors should be considered. Among the abiotic factors affecting the behaviour of pesticides, photodegradation processes are important and they are involved in the dissipation of these compounds in water, soils and plants. Also it is important to identify photoproducts, which could have biological and toxical properties completely different from those of the original pesticide. Several authors have carried out studies of the photochemical behaviour of these compounds in water [1–7].

Solid-phase microextraction (SPME) [8] has demonstrated to be a suitable technique for the determination of several groups of pesticides in water samples and other matrices [9–13].

In this work, the photochemical behaviour of the five priority pesticides is studied, employing SPME fibers as photoreaction support. "Photo-SPME" has been recently introduced and applied to study the photodegradation of polychlorinated biphenyls (PCBs) and DDT [14–16]. In this procedure, analytes are exposed to light irradiation after being sorbed in SPME fibers. This powerful tool makes possible to study kinetics of photodegradation of organic compounds. Besides, the generation of photoproducts takes place "in situ" in the SPME fiber, which allows their study, without the need of any additional extraction step. Aqueous photodegradation studies were also performed and compared with photo-SPME to confirm the potential of this new approach.

2. Experimental

2.1. Reagents and materials

Atrazine [1912-24-9], alachlor [15972-60-8], and endrin [72-20-8] were purchased from Sigma–Aldrich (Seelze, Germany). Aldrin [309-00-2], and dieldrin [60-57-1] were supplied by Supelco (Bellefonte, PA, USA). The chemical structures are shown in Table 1.

Analytical grade acetone was supplied by Merck (Mollet del Vallés, Barcelona, Spain). Water solutions were prepared by addition of acetone standard solutions of the compounds.

2.2. Solid-phase microextraction and photodegradation procedures

Commercially available 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB), 85 μm polyacrylate (PA) and 74 μm Carboxen–polydimethylsiloxane (CAR–PDMS) fibers housed in a manual SPME holder were used (Supelco).

A 5 mL aliquot of a water sample containing the target compounds was placed in a 10 mL headspace vial and SPME was performed (30 min). Different extraction conditions have been tested: direct SPME and headspace (HS) SPME both at room temperature and at 100 °C. In experiments performed at 100 °C, vials were immersed in a water bath and allowed to equilibrate for 5 min before extraction. After SPME, the fibers were thermally desorbed at 270 °C in the GC injector port for 5 min.

A laboratory photoreactor model equipped with two low-pressure mercury lamps (8–10 W, 254 nm) was used. For on-fiber photodegradation experiments (photo-SPME), after SPME, the fiber with the analytes already absorbed was exposed to 254 nm irradiation for the required time (2–60 min). For aqueous photodegradation experiments 5–mL of an aqueous solution containing the pesticides were placed in synthetic quartz precision cells and submitted to UV radiation. After the required irradiation time (2–60 min), the photolized solution was placed in a 10 mL headspace vial and subjected to the SPME procedure.

For every set of experiments, a control extraction (same SPME procedure but without irradiation) was carried out.
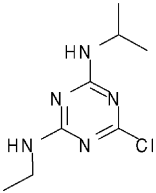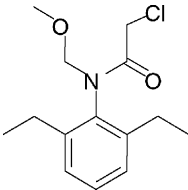
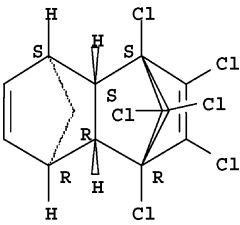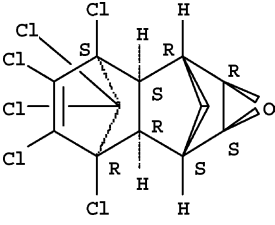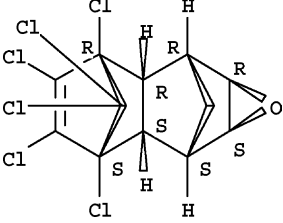### 2.3. Dark and thermal tests

Dark tests were carried out by placing the fiber inside a glass vial and covering the whole device with aluminium foil; the irradiation was kept as in the remainder of the experiments. For thermal tests, a laboratory heater kept at 50 °C was used, temperature high enough taking into account that inside the photoreactors the temperature never reaches more than ambient ±1 °C, due to the efficient cooling devices. The time of each test was 30 min.

In all the experiments the fiber is finally desorbed in the chromatographic system and GC–MS analysis is performed.

2.4. GC–MS analysis

Analyses were carried out on a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA), equipped with a 1079 split/splitless injector and an ion trap mass spectrometer Varian Saturn 2000. Experimental parameters were as follows: column: WCOT Fused Silica, 30 m × 0.25 mm i.d., coating CP-Sil 8 Low Bleed/MS 0.25 μm; temperature program: 55 °C, hold 2 min, rate 8 °C/min to 210 °C, hold 20 min, rate 10 °C/min to a final temperature of 280 °C. Helium was employed as carrier gas, with a constant flow of 1.3 mL/min. Injector was programmed to return to the split mode after 2 min from the beginning of a run. Split flow was set at 50 mL/min. Injector temperature was held constant at 270 °C. Trap, manifold and transfer line temperatures were 250, 120 and 280 °C, respectively. The mass spectrometer was used in the positive electron impact mode at 70 eV. The identification and quantification ions for each pesticide are listed in Table 1.

Table 1
Chemical structure, retention time (minutes), quantification and identification ions of the studied pesticides

Compound	Retention time (min)	Chemical structure	Quantification ion	Identification ions
Atrazine	19.52		216	216, 200, 215
Alachlor	21.48		188	188, 238, 160
Aldrin	22.79		293	293, 263, 291
Dieldrin	27.27		277	277, 279, 243
Endrin	28.54		281	281, 279, 245

3. Results and discussion

3.1. Preliminary experiments

Initially, different extraction conditions have been tested employing PDMS fibers. A spiked water solution with 20 ng/mL of each pesticide was prepared and 5 mL aliquots were extracted by direct SPME and headspace SPME, both at 25 and 100 °C. The samples were magnetically stirred. After extraction (30 min) the fiber was desorbed in the GC injector and the GC–MS analyses were performed. In these experiments, the highest responses were obtained in the following conditions: direct SPME and room temperature (25 °C). Therefore, these conditions were fixed for the rest of experiments.

Comparative experiments employing four commercial SPME fibers (see Section 2) have been carried out. The purpose of these studies was to establish the viability of performing on-fiber photodegradation studies of the target compounds. The concentration of each analyte in the working water solutions was 200 ng/mL. Aliquots of 5 mL were extracted by the different fibers using the selected extraction conditions indicated above. The fibers were then desorbed in the GC injector and GC–MS analyses were performed. In a second set of experiments, 5 mL aliquots of the same solution were extracted and each fiber was then exposed to UV radiation for 30 min. Table 2 summarizes the results obtained for both set of experiments. As can be seen, the most efficient fibers for the extraction of the different pesticides were: PDMS–DVB and PA for atrazine, PDMS–DVB for alachlor,

Table 2
Photodegradation experiments employing different commercial SPME fibers

Compound	Experiment	PDMS	PDMS–DVB	PA	CAR–PDMS
Atrazine	No irradiation	206829	776617	830768	149763
	UV irradiation	22751	716303	830150	163745
Alachlor	No irradiation	634206	1877537	607726	1345925
	UV irradiation	2663	1824413	510673	1310347
Aldrin	No irradiation	2315405	985046	856072	1805534
	UV irradiation	161384	683064	547182	1188007
Dieldrin	No irradiation	2123237	1884834	1815751	2590430
	UV irradiation	198522	1392290	1135131	2009411
Endrin	No irradiation	1839688	2042690	1690808	1871338
	UV irradiation	25019	1923035	1524669	1725744

Responses obtained without irradiation and after 30 min of irradiation.

and PDMS for aldrin. For dieldrin and endrin all the fibers gave approximately the same response.

In Table 2, the change in analytical response after UV irradiation (photo-SPME) is also shown. This change is clearly significant for PDMS fiber. For this coating, the responses after UV irradiation were between 0.5 and 12% of the initial responses. Dark and thermal tests performed with this fiber (see bellow in this section), as well as the detection of a large number of photoproducts in the fiber confirm the photodegradation of the five target analytes in PDMS coating. Photodegradation in the other coatings is also confirmed due to the generation of various photoproducts but it took place in a considerably minor extent. This different speed of degradation between PDMS and the other coatings could be due to the aggregation state of the coatings. PDMS is the only one exclusively constituted for a liquid phase, which could explain the major speed of photodegradation in this material. Consequently, photodegradation studies were carried out employing PDMS fiber.

Dark and thermal tests (see Section 2) were carried out to check if decreases in analytical response after UV irradiation of the PDMS coating were only due to the action of photons or, if in addition, some volatilization or thermal degradation losses have occurred as well. Table 3 shows the results obtained for both test (time: 30 min) compared with the ones ob-
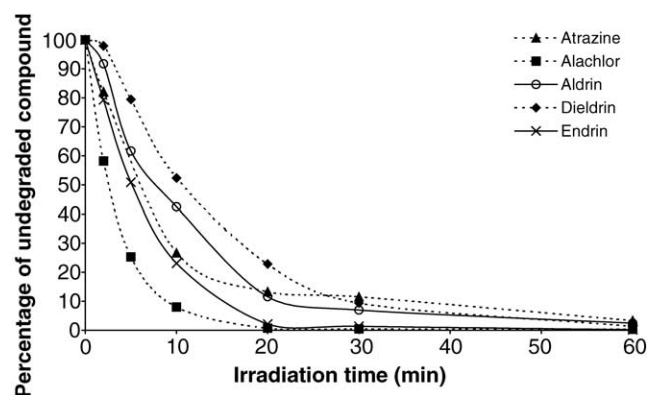
Table 3
Comparative responses obtained after dark test, thermal test and UV irradiation of the PDMS coating (30 min)

	Response (%)		
	Dark test	Thermal test	UV exposition
Atrazine	101	98	12
Alachlor	99	88	<1
Aldrin	72	76	7
Dieldrin	100	117	9
Endrin	101	119	2

tained after 30 min of UV irradiation of the fiber. Responses are expressed as percentage of the response obtained without any treatment. As can be seen, there are no losses of analytes through volatilization and/or thermal degradation with the exception of aldrin, which confirms the on-fiber photodegradation of atrazine, alachlor, dieldrin and endrin. Aldrin shows a decrease in the analytical response in dark and thermal tests of about 25% for both dark and thermal test. Considering that the reduction of response obtained in the irradiation experiments was greater than 92%, the photodegradation of this analyte is also confirmed. Furthermore, the formation of photoproducts in UV experiments confirm the photodegradation of aldrin, as well as of the rest of the pesticides studied (see Section 3.3).

Fig. 1. Kinetics of degradation obtained in photo-SPME experiments. Responses are expressed as percentage of undegradated compound.
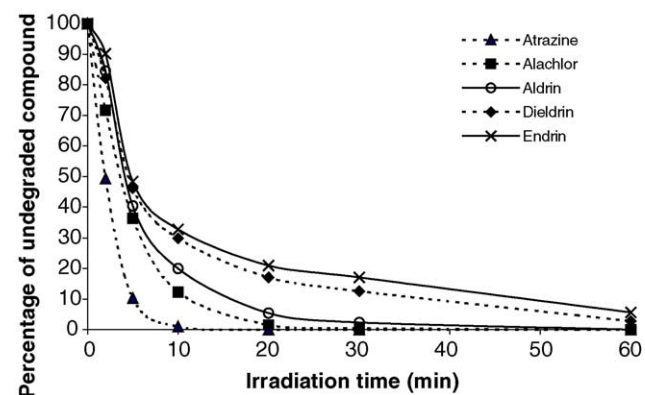

Fig. 2. Kinetics of degradation obtained in aqueous photodegradation experiments. Responses are expressed as percentage of undegradated compound.

Table 4
Photoproducts generated in the photo-SPME and aqueous photodegradation of atrazine

Key	Photoproduct	Quantification ion	Identification ions	Photo-SPME	Aqueous photodegradation
At1	N-(1-Methylethyl)-1,3,5-triazine-2,4-diamine	138	138, 153, 111	+	
At2	N-Ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine	181	181, 166, 138	+	
At3	6-Chloro-N-ethyl-1,3,5-triazine-2,4-diamine	145	145, 173, 158	+	
At4	6-Chloro-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine	172	172, 187, 145	+	
At5	4,6-Bis[(1-methylethyl)amino]-1,3,5-triazin-2(1H)-one	196	196, 211, 169	+	+

Table 5
Photoproducts generated in the photo-SPME and aqueous photodegradation of alachlor

Key	Photoproduct	Quantification ion	Identification ions	Photo-SPME	Aqueous photodegradation
Al1	N-(2,6-Diethylphenyl)methyleneamine	146	146, 118, 161	+	
Al2	Diethylbenzenamine	134	134, 149, 119	+	
Al3	8-Ethyl-3,4-dihydro-1-methyl-2(1H) quinolinone	121	121, 161, 136	+	+
Al4	7-Ethyl-2,3-dihydro-1H-indole	132	132, 147, 117	+	
Al5	7-Ethyl N-methylindoline	161	161, 133, 119	+	
Al6	8-Ethyl-1-methoxymethyl-1,2,3,4-tetrahydroquinolinone	160	160, 132, 191	+	+
Al7	N-(2,6-Diethylphenyl)-N-methylacetamide	161	161, 146, 178	+	+
Al8	Alachlor metabolite	219	219, 160, 174	+	
Al9	2-Oxo-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide	188	188, 217, 146	+	
Al10	2-Hydroxy-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide	188	188, 160, 219	+	+

3.2. Photo-SPME and aqueous photodegradation

To establish the photodegradation kinetics of these compounds, the influence of the UV irradiation time on analytical response has been studied. For these studies a water solution containing 200 ng/mL of each analyte was prepared (the concentration of atrazine was 2 µg/mL). The analytes were first extracted and then the fiber was exposed to UV light for different periods of time (0–60 min); subsequently, GC–MS analyses were carried out. Peak area changes were evaluated and Fig. 1 summarizes the results obtained expressed as percentage of undegraded compound. As can be seen, the "on fiber" photodegradation of the target pesticides is a quite fast process and after 30 min, the percentages of undegraded compounds ranged from 0.5% (alachlor) to 12% (atrazine). After 60 min of irradiation less than 4% of all the analytes remains in the fiber.

Another series of experiments was performed in order to compare photo-SPME and aqueous photodegradation of the target pesticides. In these experiments, aliquots of the water solution were exposed to UV irradiation for different periods of time (from 0 to 60 min) and then SPME–GC–MS analyses were performed. Fig. 2 shows the results obtained. The behaviour of the analytes in these experiments is quite similar to the one obtained in the photo-SPME experiments.

Table 6
Photoproducts generated in the photo-SPME and aqueous photodegradation of aldrin

Key	Photoproduct	Quantification ion	Identification ions	Photo-SPME	Aqueous photodegradation
P1	$C_{12}H_{11}Cl_3$	230	230, 195, 152	+	+
P2	$C_{12}H_{11}Cl_3$	195	195, 230, 152	+	+
P3	$C_{12}H_{10}Cl_4$	221	221, 187, 259	+	+
P4	$C_{12}H_{11}Cl_3$	193	193, 230, 259	+	+
P5	$C_{12}H_9Cl_5$	229	229, 187, 259	+	+
P6	$C_{12}H_{10}Cl_4$	229	229, 259, 187	+	+
P9	$C_{12}H_9Cl_5$	259	259, 222, 186	+	+
P25	$C_{12}H_9Cl_5O$	311	311, 229, 275	+	+
P27	$C_{12}H_9Cl_5$	259	259, 221, 187	+	+
P29	$C_{12}H_{10}Cl_4$	222	222, 187, 259	+	+
P32	$C_{12}H_8Cl_4O_2$	233	233, 197, 263	+	+
Dieldrin		277	277, 279, 243	+	+
P35	$C_{12}H_8Cl_5O_2$	268	268, 131, 196	+	
P37	$C_{12}H_8Cl_4$	259	259, 222, 187	+	+
P38	$C_{12}H_{10}Cl_6$	364	364, 195, 230	+	+
P40	$C_{12}H_9Cl_5$	293	293, 258, 221	+	+
P43	$C_{12}H_{12}Cl_6$	331	331, 295, 257	+	+

Table 7
Photoproducts generated in the photo-SPME and aqueous photodegradation of dieldrin

Key	Photoproduct	Quantification ion	Identification ions	Photo-SPME	Aqueous photodegradation
P7	$C_{12}H_{10}Cl_4O$	209	209, 175, 275	+	
P10	$C_{12}H_{10}Cl_4O$	275	275, 195, 175	+	
P16	$C_{12}H_{10}Cl_4O$	275	275, 187, 259	+	+
P18	$C_{12}H_{10}Cl_4O$	277	277, 209, 187	+	
P22	$C_{12}H_{10}Cl_4O$	195	195, 230, 277	+	
P24	$C_{12}H_9Cl_5O$	245	245, 209, 311	+	+
P25	$C_{12}H_9Cl_5O$	311	311, 229, 173	+	+
P26	$C_{12}H_9Cl_5O$	245	245, 283, 209	+	+
P28	$C_{12}H_{10}Cl_4O$	309	309, 275, 209	+	
P30	$C_{12}H_{10}Cl_4O$	245	245, 209, 311	+	+
P31	$C_{12}H_8Cl_6$	243	243, 325, 219	+	
P36	$C_{12}H_9Cl_5O$	209	209, 311, 273	+	+
P39	$C_{12}H_9Cl_5O$	283	283, 247, 311	+	+
P42	$C_{12}H_9Cl_5O$	209	209, 245, 311	+	+
P45	$C_{12}H_{10}Cl_6O$	281	281, 245, 345	+	+

Both studies (photo-SPME and aqueous photodegradation) were also performed using a water sample containing 20 ng/mL of each analyte (the concentration of atrazine was 200 ng/mL). Similar kinetics of degradation were obtained in spite of the different concentration level of the sample used (10-fold lower).

In addition, individual studies of all target pesticides have been carried out. No significant differences in the photodegradation kinetics were obtained. These individual studies permit to confirm the origin of each potential photoproduct generated. In these studies, dieldrin appears as a photoproduct of aldrin, which could explain the different kinetic behaviour observed in individual and mixture studies for this compound.

3.3. Identification of photoproducts

A large number of photoproducts were detected in these experiments and they were tentatively identified on the basis of their mass spectra and with the aid of literature [2,6,7,17–22]. Tables 4–8 summarize the generated photoproducts for each pesticide in individual studies for photo-SPME and aqueous photodegradation.

As can be seen in these Tables 4–8, all the photoproducts obtained in the aqueous photodegradation experiments were found in photo-SPME experiments. But some photoproducts identified in photo-SPME experiments do not appear when the water is exposed to UV irradiation. This fact can be explained taking into account that in "on-fiber" photodegradation, photoproducts are generated "in situ" on the fiber without additional steps of extraction. In aqueous photodegradation studies, photoproducts are generated in the solution and then, they must be extracted by SPME.

Proposed photodegradation pathways for atrazine are shown in Fig. 3. The main photoproduct is generated through the chlorine atom loss (At2). This photoproduct can loose the ethyl group (At1). The dechlorination of the molecule is a key step in the atrazine photodegradation since the dechlorinated product of atrazine loose the phytotoxicity of its parent

Table 8
Photoproducts generated in the photo-SPME and aqueous photodegradation of endrin

| Key	Photoproduct	Quantification ion	Identification ions	Photo-SPME	Aqueous photodegradation
P8	$C_{12}H_{14}Cl_4O$	283	283, 209, 247	+	+
P11	$C_{12}H_{10}Cl_4O$	211	211, 247, 175	+	
P12	$C_{12}H_{10}Cl_4O$	175	175, 211, 277	+	
P13	$C_{12}H_{11}Cl_3O$	211	211, 175, 277	+	
P14	$C_{12}H_{11}Cl_3O$	211	211, 247, 277	+	
P15	$C_{12}H_{10}Cl_4O$	277	277, 312, 247	+	+
P17	$C_{12}H_{13}Cl_5O$	315	315, 279, 243		+
P19	$C_{12}H_{10}Cl_4O$	247	247, 211, 275	+	+
P20	$C_{12}H_{10}Cl_4O$	211	211, 175, 275	+	
P21	$C_{12}H_{10}Cl_4O$	211	211, 277, 175	+	
P23	$C_{12}H_8Cl_4O_2$	298	298, 214, 143	+	
P26	$C_{12}H_9Cl_5O$	245	245, 283, 311	+	+
P30	$C_{12}H_{10}Cl_4O$	245	245, 209, 311	+	+
P33	$C_{12}H_9Cl_5O$	283	283, 311, 247	+	+
P34	$C_{12}H_9Cl_5O$	311	311, 245, 211	+	+
P39	$C_{12}H_9Cl_5O$	283	283, 311, 247	+	+
P41	$C_{12}H_{10}Cl_4O$	283	283, 245, 209	+	+
P44	$C_{12}H_{10}Cl_6O$	345	345, 281, 380	+	+
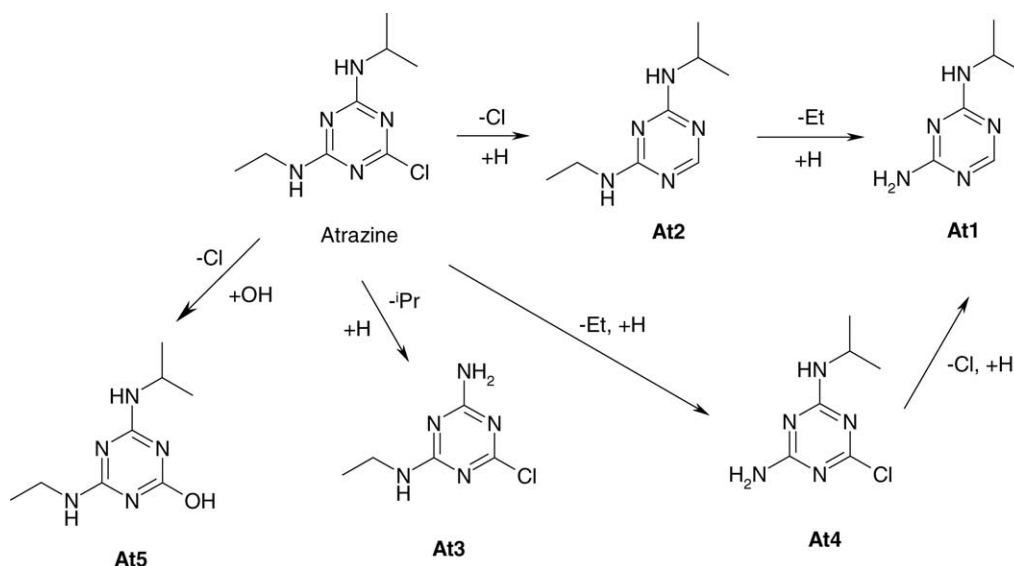
Fig. 3. Tentative photodegradation pathways of atrazine.

compound. This photoproduct have been also identified for Texier et al. [6]. Atrazine also undergo ethyl (At4) or iso-propyl group loss (At3). Other studies confirm the formation of desethylatrazine [5,6]. In addition a hydroxilated photo-product has been identified (At5). This photoproduct is gen-erated when a hydroxyl group substitutes the chlorine atom.

The postulated photoproduct generation mechanisms for alachlor are the following: reduction (e.g. A1, A2), cyclation (e.g. A3, A5, A6) and dechlorination (A7) (see Table 5). Most photoproducts have been identified in photo-SPME experi-ments whereas in aqueous photodegradation only A3, A6, A7 and A10 were found. Several authors studied photodegrada-tion of alachlor [17–22], and they have found some of the photoproducts identified in this study.

Photodegradation mechanisms of aldrin, dieldrin and en-drin, three chlorinated cyclodiene pesticides, are similar. They have similar structures, furthermore dieldrin and en-drin are structural isomers. The most important degradation mechanisms is successive dechlorination. Ivie and Casida [1] confirm dechlorination as the main photodegradation path-way for these chlorinated cyclodiene insecticides. Besides this reaction, photoproducts proceeding from reductions, ox-idations and isomerizations have been also identified. Fig. 4 show the quantification ion chromatograms of aldrin, diel-drin, endrin and some of their photoproducts, obtained for 0, 20 and 60 min in photo-SPME experiments. In this fig-ure, the degradation of the target analytes and the formation of some photoproducts can be observed. Individual stud-ies have permitted to know the origin of each photoprod-uct. The tentatively identified photoproducts are presented in Tables 6, 7 and 8. Most of the photoproducts found in photo-SPME appear in aqueous photodegradation experiments. P25 is obtained in the photodegradation of aldrin and in the pho-todegradation of dieldrin also. P26, P30 and P39 are gener-ated in the photodegradation of dieldrin and endrin.
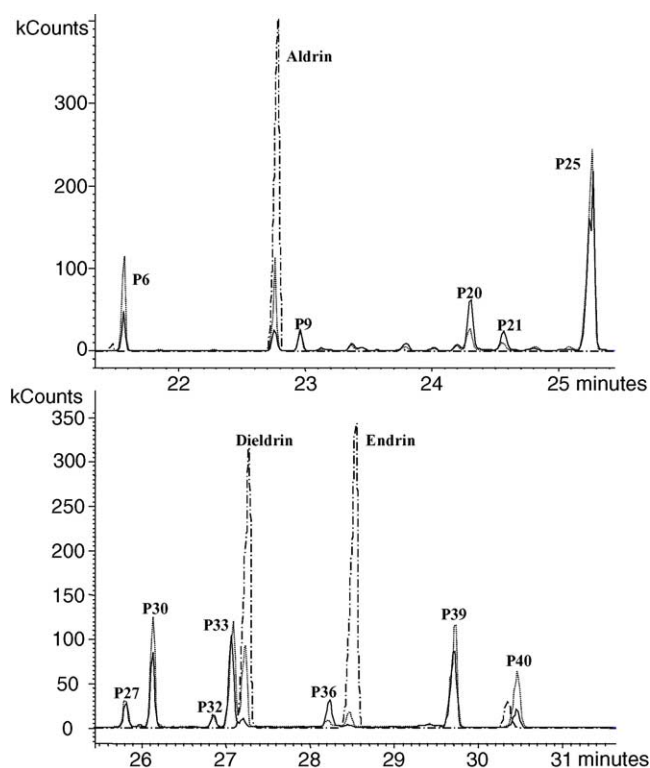

Fig. 4. Quantification ion chromatograms of aldrin, dieldrin, endrin and some of their photoproducts, obtained for 0 (–··–), 20 (···) and 60 min (—) in photo-SPME experiments.

3.4. Formation-photodegradation kinetics of the photoproducts

Formation-photodegradation kinetics of the photoprod-ucts can be establish by photo-SPME. Photoproducts are sus-ceptible to be photodegraded when the fiber is exposed to UV
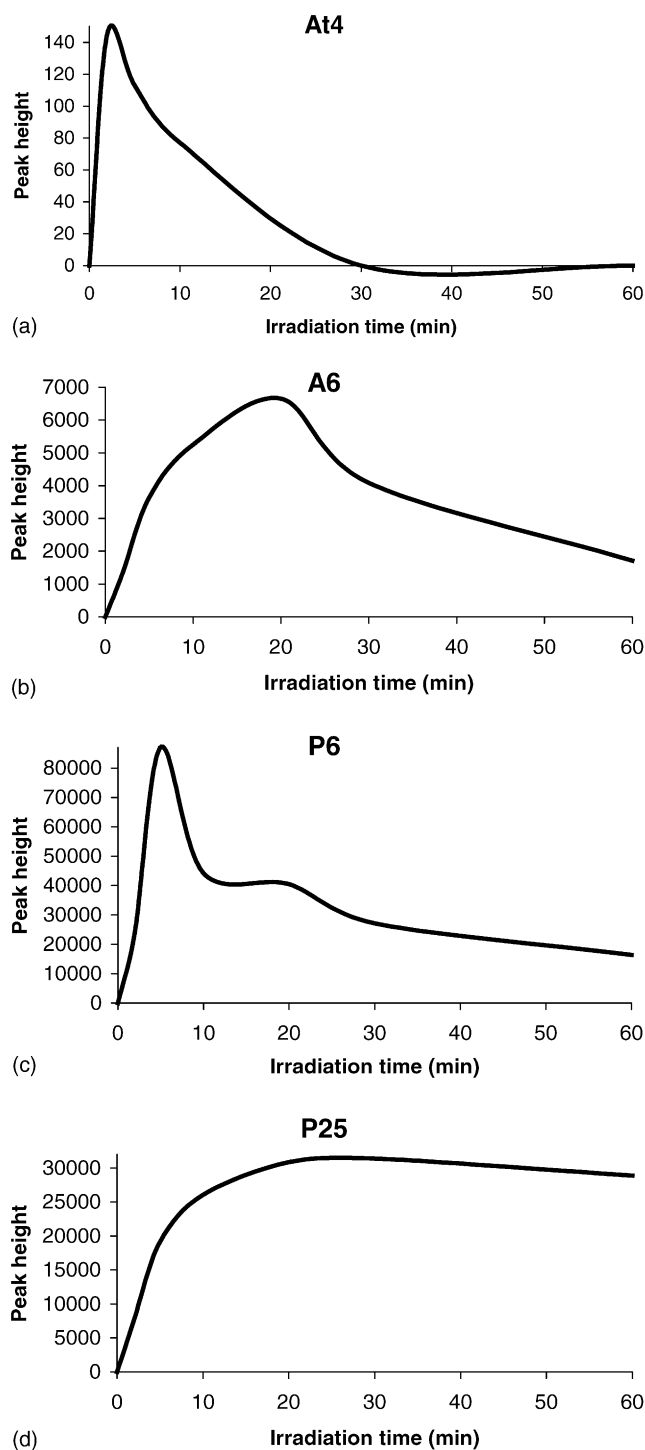
Fig. 5. Formation-photodegradation kinetics of some photoproducts in photo-SPME experiments: (a) Atrazine photoproduct (At4); (b) Alachlor photoproduct (A6); (c) Aldrin photoproduct (P6); (d) Dieldrin photoproduct (P25).

radiation. Thus, Fig. 5 shows the formation-photodegradation kinetics obtained for some photoproducts. Some photoproducts are detected after short irradiation times and afterwards their response decrease clearly; they can be considered easily photodegradable (e.g. At4). Other photoproducts are hardly photodegradable during the time interval evaluated (e.g. P25). And there is a group of photoproducts which shows an intermediate behaviour (e.g. A6). Similar behaviour has been observed in aqueous photodegradation experiments.

4. Conclusions

In this work, the photochemical behaviour of five priority pesticides has been studied employing a simple and powerful procedure, "photo-SPME". Comparative experiments with four commercial fibers showed that on-fiber photodegradation takes place in a considerably major extent using PDMS coating. The on-fiber photodegradation kinetics were determined by UV-irradiation of the PDMS fiber for different times. Aqueous photodegradation studies followed by SPME were performed and compared with photo-SPME. In both media (PDMS and water), all the analytes were degraded in a short period of time.

The use of SPME fibers as a support for photochemical degradation of organic pollutants allows the in situ generation of photoproducts, avoiding further manipulations of the samples before analysis. In this study, a large number of photoproducts were generated and tentatively identified by means of their mass spectra and with the aid of literature, and photodegradation pathways have been postulated. Formation-photodegradation kinetics of the photoproducts were also established. In summary, the use of photo-SPME constitutes a powerful tool that clearly simplifies monitoring of photo-transformation processes.

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