Comparative degradation kinetics of alachlor in water by photocatalysis with $FeCl_3$, TiO_2 and photolysis, studied by solid-phase disk extraction followed by gas chromatographic techniques

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Abstract

A comparative degradation study of alachlor spiked at 30–60 $\mu g/l$ in water using photocatalysis with $FeCl_3$, TiO_2 and photolysis using a xenon arc photoreactor was performed. After irradiation the water samples were preconcentrated using solid-phase disk extraction with C_{18} and analyzed by gas chromatography–electron capture and mass spectrometric detection (GC–ECD and GC–MS, respectively). Three photoproducts were unequivocally identified corresponding to 2-hydroxy-2,6'-diethyl-N-methylacetanilide, 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetraquionoline and hydroxyalachlor. Two photoproducts were identified by GC–MS although their chemical structure is unknown and corresponded to two compounds with base peaks at m/z values of 146 and 218 and molecular masses of 221 and 233, respectively. Although alachlor showed high stability in water when exposed to natural sunlight irradiation for a period of more than 120 h, by the use of photocatalysis with of $FeCl_3$ or TiO_2 the degradation was very fast with half lives varying from 10–17 min. The degradation kinetics followed a first order reaction and the relative derivation, for $n=4$, varied from 2–16 or 27–33% under photocatalysis or photolysis.

Keywords: Kinetic studies; Environmental analysis; Water analysis; Alachlor; Pesticides

1. Introduction

The degradation of pesticides and other contaminants in water is an area of research interest and sunlight photoalteration processes are known to play an important role. In this respect, we reported [1,2] the degradation of various organophosphorus pesticides in water under natural sunlight conditions and of alachlor and bentazone [3] using xenon arc lamp irradiation. Natural sunlight photodegradation processes are usually compared with those obtained under controlled conditions, generally using xenon arc lamp [3,4]. These studies permit to model pesticide behavior after application, to obtain information about the kinetic of degradation and so pesticide half-lives and to increase the knowledge about the degradation products that can be formed under natural conditions. However, in the critical range of 280–300 nm there are some discrepancies between solar irradiation and artificial light and care should be taken in assigning equivalents to solar illumination [5].

Photocatalytic oxidation by semiconductor oxides such as TiO_2 or the Fenton reagent is another area of environmental interest but in this case for the treatment of contaminated waste-waters. In the pres-

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ence of oxygen and near-UV light, many organic pollutants can be rapidly transformed to less toxic compounds. Photocatalytic reactions have been reported to exhibit appreciable rate increase by adding H_2O_2. Hydrogen peroxide is a better electron acceptor than molecular oxygen and it may split photolytically to produce OH directly thus increasing the rate toward it would have been had an adequate oxygen supply [5]. The most commonly used photocatalytic oxidation reaction reported in the literature involved TiO_2 in water and it was used for a variety of chemical pollutants such as bentazone [6], dichlorophenols [7], secondary alcohol ethoxylate [8], 2,4-D [9] and alachlor [10]. Other processes included ozonization in combination or not with photolysis for alachlor [11].

Fenton's reagent (Fe^{2+} and H_2O_2) has been a technology scarcely used for elimination of contaminants. The main advantage of Fenton's reagent over other OH systems is that it is cheaper than TiO_2 particles or ozone generators. Little information is available on the degradation of different contaminants and recently results were reported for atrazine [12] and 2,4-D [9]. It was found that the degradation of atrazine by the Fenton's reagent was similar to the treatment described with TiO_2 and UV light in terms of chlorinated and dechlorinated compounds detected. To our knowledge no previous study using this reagent was reported for alahclor.

In this respect there is a lack of comparative degradation studies in water. In addition, many of the studies conducted up till now employed pesticide concentration in water at mg/l levels, such as for alachlor with TiO_2 that used 100 ppm in water–methanol mixtures [10]. We reported previously on photolysis at μg/l level [3] so in this way the behavior of the chemicals reflects more closely what happens in the real environment situations. By doing this an additional enrichment step is required before the irradiated solution can be analyzed. In this respect we have combined solid-phase extraction (SPE), after irradiation, and irradiated solutions were enriched being the extracts injected into gas chromatography or liquid chromatographic systems. This was also carried out under natural sunlight conditions [1,2].

In addition to that, the use of SPE disks, mainly with C_{18} material, was reported to be an adequate methodology for preconcentrating pesticides from water samples [1–3]. The SPE disks permit concentration of the analytes and consequently it can be used to follow the degradation of pesticides under current environmental concentration (at μg/l level). By combining photodegradation with SPE followed by GC–ECD and GC–MS it is possible to perform laboratory experiments that closely approach environmental situations.

The objectives of this study were: (i) to compare the degradation kinetics of alachlor in water by using natural photolysis, xenon arc irradiation, photocatalysis with TiO_2 particles and $FeCl_3$, (ii) to determine the different products formed by means of GC–ECD and GC–MS and (iii) to establish a degradation pathway of the various degradation processes and to give recommendation about the degradation of alachlor in water.

2. Experimental section

2.1. Chemicals

Alachlor (99%) was purchased from Promochem (Wesel, Germany), Iron III chloride 6-hydrate (98–102%) from Panreac (Barcelona, Spain) and Titandioxid P25 from Degussa (Japan). Ethyl acetate was obtained from Panreac, methanol and acetone were purchased from Merck (Darmstadt, Germany). Hydrogen peroxide (30% solution) was from Foret (Barcelona). Organic-free water (pH 8.0) was prepared with a Milli-Q system from Millipore-Waters. Ground water (pH=8.0, 75 mg/l nitrate, 387 mg/l sulfate, 254 mg/l Ca, 88 mg/l Mg, conductivity 2020 μS/cm) was used in some of the experiments.

2.2. Chromatographic conditions

The kinetic of photodegradation was determined by gas chromatography using a Hewlett–Packard 5890 equipped with an electron-capture detector). A DB-5 column (30 m×0.23 mm I.D.) was programmed from 60–280°C at 6°C/min; 60°C was held for 1 min and 280°C was held for 20 min. Injector and detector temperatures were held at 270°C and 310°C, respectively. Helium was used as the carrier

gas at 2.8 ml/min and nitrogen was used as the make-up gas at 70.0 ml/min.

2.3. Mass spectrometric analysis

A Fisons MD 800 mass spectrometer coupled to a Fisons GC 8000 apparatus was used for GC–MS in the electron impact (EI) mode. EI spectra was obtained at 70 eV, in full scan mode from m/z 40 to 300. A HP-5 column (30 m×0.25 mm I.D.) was programmed from 60 to 280°C at 6°C/min; 60°C was held for 1 min and 280°C for 20 min. Injector temperature was 270°C, ion source temperature 280°C. Helium was used as the carrier gas with a pressure of column head of 12 psi. (1 p.s.i.=6894.76 Pa).

2.4. Photodegradation experiments

Irradiations were carried out using a Suntest apparatus from Heraus (Hanau, Germany) equipped with a xenon arc lamp, as reported previously [3]. Few experiments were carried out using natural sunlight irradiation, with quartz reservoirs placed capped on a terrace roof at our institute in Barcelona, during September 95. Water samples were spiked with alachlor by adding the standard pesticide in methanol using quartz reaction reservoirs of 500 or 1000 ml, before starting the photodegradation experiments. The mixture was homogenized for 15 min by careful agitation. Alachlor concentration in water varied between 30–60 μg/l, and this was enough for carrying out the kinetic studies performed by GC–ECD. For the unequivocal identification of the degradation products GG–MS at higher alachlor concentration, 60–100 μg/l, was used. At different periods of time, water samples were removed from reactor and stored in refrigerator. The preconcentrated volume of water after each irradiation time was dependent on the period of the degradations study. In this respect, generally at the beginning of the photodegradation experiment, water volumes of 25 ml were preconcentrated whereas 300 ml of water were used in some of the photocatalysis studies at the end of the irradiation period. This is not a problem for the recovery of alachlor since water volumes higher than one litre can be used for

alachlor preconcentration in C_{18} SPE disks without any breakthrough loss.

2.5. Photocatalysis

In the experiments of photocatalysis either $FeCl_3$ or TiO_2, were used. TiO_2 was used at 25 mg/l and 150 mg/l (as TiO_2) whereas $FeCl_3$ was used at 15 mg/l and 50 mg/l (as Fe^{3+}). In all the experiments of photocatalysis, H_2O_2 at 0.05% (v/v) was added, as reported [12]. The experiments began with the addition of either TiO_2 or $FeCl_3$ to the water, afterwards the mixture was homogenized for 15 min by careful agitation followed by the addition of alachlor standard solution, more agitation and finally the H_2O_2 was added.

2.6. Sample preparation

The procedure used followed previous methods used in our laboratory [1,2]. C_{18} Empore disks were placed on a sintered glass filter funnel apparatus attached to a vacuum source. 10 ml of ethyl acetate was added to the filter funnel and the disks were dried for 2 min. Subsequently, 10 ml of acetone was added and the disks were dried for 5 min. Afterwards, 15 ml of methanol was added and when film of methanol was very thin, 10+10 ml of deionized water was added. 25–300 ml of water sample (the amount of sample was dependent on the reaction time and type of photodegradation experiment) were preconcentrated in the Empore disks. The solvents and sample were drawn through the disk at a rate of approximately 0.5 ml/s. After the sample was drawn through, the vacuum was left on for 30 min to allow the disk to dry. The filtration system was put in a reservoir to receive the extract of alachlor and degrade compounds. The extraction was done with three 20 ml portions of ethyl acetate. When the first portion was added, the vacuum was left on for 5 min and when the second and third portions were added, the vacuum was left on for 3 min. The reservoir with the extract was placed in a rotaevaporator system and the extract was carried to a volume between 0.1–1.0 ml. The concentrated extract was analyzed by GC–ECD and/or GC–MS. The samples were quantified by external standard using automated injection. Calibration graphs in GC–ECD were performed by

plotting area (y) versus amount injected (x), with the calibration equation constructed at absolute amounts of alachlor injected of 25, 60, 120, 1500 and 2000 pg. The calibration equation was: $y = 14\,986\,x + 111$, being $R^2 = 0.994$.

2.7. Calculation of half-lives

The calculation of half-lives [13] was performed using the first-order rate equation:

$$C_t = C_0 e^{-kt} \qquad (1)$$

where C_t represents the concentration at time t; C_o represents the initial concentration; and k is the rate constant. When the concentration is reduced to 50% of its initial amount, half-life ($t_{1/2}$) can be determined by:

$$t_{1/2} = 0.693/k \qquad (2)$$

where k is the degradation constant.

3. Results and discussion

3.1. Qualitative information

Five photodegradation products were identified after photolysis irradiation using the Suntest apparatus. Only one of these compounds (compound 1) was detected after photocatalysis experiments. Typical GC–MS chromatogram of the experiments performed under photolysis (Fig. 1B) and photocatalysis with TiO$_2$ (Fig. 1C) and with FeCl$_3$ (Fig. 1 D) are reported Fig. 1. The mass spectra of compounds 1–6 are shown in Fig. 2.

Some of the compounds identified corresponded mainly to dechlorination processes of alahclor, as reported in other studies [3,11]. In previous paper from us using photolysis [3] we identified compounds 2 and 5 corresponding to base peak values at m/z 146 and 218, respectively and 8-ethyl-1-methoxy-methyl-4-methyl-2-oxo-1,2,3,4-tetraquionoline (compound 3), hydroxyalachlor (compound 4). Compound 6 corresponds to alachlor itself. Compound 1, with a base peak at m/z 177, corresponding to 2-hydroxy-2,6'-diethyl-N-methylacetanilide was not identified in our previous work of photolysis irradia-
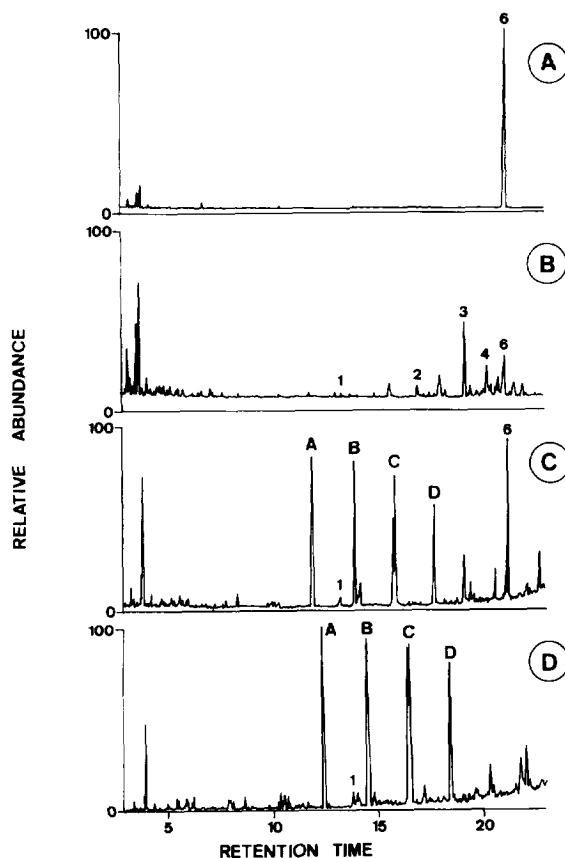

Fig. 1. GC–MS traces obtained under full scan conditions of (A) alachlor standard, (B) after SPE extract of alachlor exposed to photolysis with the Suntest apparatus after 210 min, (C) after SPE extraction of alachlor photocatalysis using TiO$_2$ particles exposed for 30 min and (D) after SPE extraction of alachlor exposed to photocatalysis using FeCl$_3$ for 30 min. Compounds 1 to 6 correspond to: 2-hydroxy-2,6'-diethyl-N-methylacetanilide (1), unknown of molecular mass 221 (2) 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetraquionoline (3), hydroxyalachlor (4), unknown of molecular mass 233 (5) and alachlor (6). A, B, C and D peaks in (C) and (D) correspond to a series of compounds of base peaks at m/z 57 and secondary ions at m/z 71 and 85. Concentration levels of alachlor used and chromatographic conditions used, see Section 2

tion of alachlor, but it was reported in two previous studies of alachlor treatment with UV light and ozone [11] and it was also recently detected when monitoring well water samples that contained alachlor [14].

The various compounds unequivocally identified usually exhibited loses of 31, 32, 44, 45, 76 and 90 corresponding to OCH$_3$,HOCH$_3$ CH$_2$OCH$_2$,
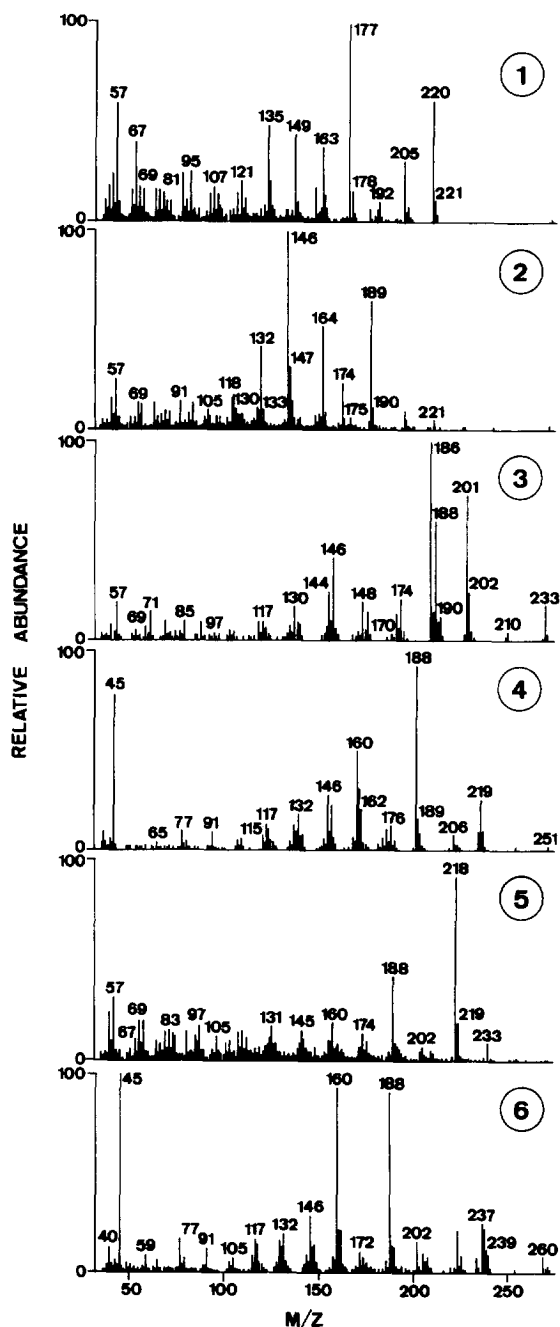
Fig. 2. MS spectra of compounds of Fig. 1B. Compound number, see Fig. 1.

of the studied compounds match with previous spectra from the literature [3,11,14], there is not agreement on the base peaks in many cases when different GC–MS instruments were used, e.g., compound 1. This is because the GC–MS system used can change the relative abundance of the peaks, and although m/z 177 is the base peak (for compound1) in another article [14] this ion was a secondary ion and not the base peak. Similarly with alachlor itself (compound 6, Fig. 2) that give as base peaks m/z 45, 160 and 180, whereas standard GC–MS spectra give usually m/z 45 as base peak and then other two ions exhibit an abundance below 50% [14,15]. This is probably caused by the fact that GC–MS from Fisons, used in our experiments, gives generally much more molecular base peak information than other commercially available GC–MS instruments. The chemical structures of the different metabolites of alachlor and the photolysis degradation pathway are shown in Fig. 3.

The most relevant fact is that compound 1 was found in all the experiments performed, including photolysis and photocatalysis. There is only one previous report using photocatalysis with TiO_2 particles [10] and this compound was not identified and to our knowledge no previous paper using Fenton's reagent was reported. Secondly, as is noticed from the GC–MS trace of the various extracts analyzed,
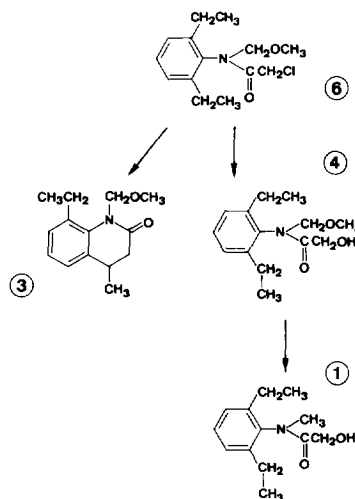

Fig. 3. Photolysis scheme of alachlor. The MS spectra of the transformation products of alachlor and alachlor itself (compound 6) are shown in Fig. 2. Compound number, see Fig. 2.

CH_2OCH_3, $COCH_2OCH_3$ and $NCOCH_2OCH_3$, respectively.

First comment to be made, although the fragments

Table 1

Photolysis and photocatalysis (using $FeCl_3$) of alachlor exposed to natural sunlight irradiation in deionized water

Time (h)	Without FeCl$_3$ concentration (μg/L)	With FeCl$_3$ concentration (μg/L)
0	48.77	54.42
1	48.77	1.04
2.5		0.94
6		0.74
24	48.22	0.00
120	49.85	0.00

Mean concentration of alachlor.

the photolysis experiments are cleaner as regards interferences than the photocatalysis experiments which showed compounds A, B, C and D (Fig. 1C and D) which corresponded to interferences coming from TiO_2 or $FeCl_3$ particles. These interferences corresponded to compounds of the same series with base peaks at m/z 57 and secondary ions at m/z 71, 85, giving the structure of tritetracontane, heptadecane, 2,6,10,15-tetramethyl or hexadecane, 7-methyl, when matched with library search. These peaks are interferences from the photocatalysis experiments and do not correspond to intermediates or photoproducts obtained during the experiments performed.

3.2. Natural sunlight irradiation and photolysis

It is known that alachlor is quite stable compound in waters with a reported half-life of 15 days [3]. Table 1 indicates that alachlor was not degraded at the end of five days of exposure under natural sunlight irradiation in deionized water but it was degraded very fast in water that contained $FeCl_3$. This gave an indication to us of the destruction power of $FeCl_3$ for this compound.

The photolysis of the alachlor with the Suntest apparatus is slow and its total degradation in deionized water takes less than 7 h. The photolysis rate constant of alachlor determined in this work ($1.70 \cdot 10^{-2}$) Table 2 is very similar to that calculated in a previous work [3] ($1.79 \cdot 10^{-2}$). This gave us an indication of the reproducibility of the system used. In this work, the kinetic was determined by GC–ECD and in the previous work it was determined by liquid chromatographic (LC) techniques.

Photolysis in ground water is also of first-order and the rate constant of 0.014 min^{-1} is smaller than in deionized water. This ground water did not contain suspended solids and its composition is reported in Section 2.1. The difference in the rate constants between the two waters used is attributed mainly to the difference in the pH of the two water samples. Kochany and Maguire [4] reported that the
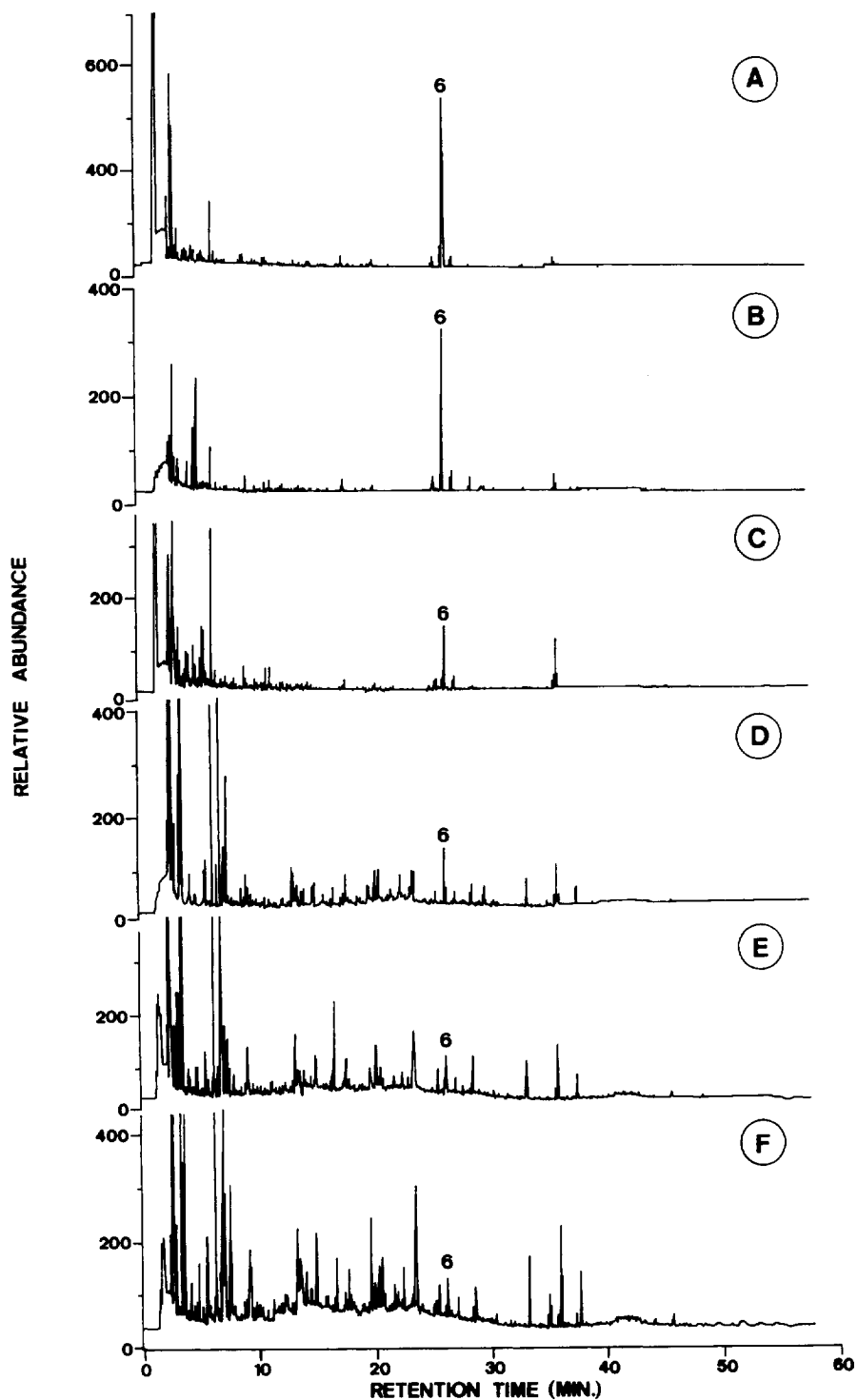
Table 2

Reaction-order, rate constant and half-life of alachlor in water under photolysis and photocatalysis

Photodegradation	Reaction order	Rate constant (min^{-1})	Half-life (min)
Photolysis in deionized water	1	0.017	40.8 (RSD = 27.%)
Photolysis in ground water	1	0.014	49.5 (RSD = 33.%)
Photocatalysis with 25 mg/L of TiO$_2$	1	0.040	17.3 (RSD = 3%)
Photocatalysis with 150 mg/L of TiO$_2$	1	0.053	13.1 (RSD = 16%)
Photocatalysis with 15 mg/L of FeCl$_3$	1	0.065	10.7 (RSD = 2%)
Photocatalysis with 50 mg/L of FeCl$_3$	1	0.069	10.0 (RSD = 9.9%)

Number of experiments, for each sample, $n = 4$. RSD = Relative standard deviation.

Fig. 4. GC–ECD traces of (A) alachlor standard, (B) after SPE of alachlor irradiated under photolysis experiments for 90 min and (C) 210 min, (D) after SPE of alachlor irradiated under photocatalysis using 150 mg of TiO$_2$ for 30 min, (E) using 15 mg/L of FeCl$_3$ for 8 min and (F) 15 mg/L of FeCl$_3$ for 30 min.

photolysis rate constant of metolachlor, very similar compound to alachlor, was increasing slowly when pH was increased, as we observe for alachlor. The GC–ECD traces of the photolysis experiments performed are shown in Fig. 4B and C and the reaction kinetic experiments are shown in Fig. 5A and B.

3.3. Photocatalysis

GC–ECD traces of the photocatalysis experiments using TiO_2 and $FeCl_3$ are shown in Fig. 4D–F. Fig. 5C and D show the percentage of degradation of alachlor under these two photocatalysis experiments.

From the various experiments performed, first we notice that when using photocatalysis, the coefficient of variation of the experiments is smaller (2–16%) as compared to photolysis (27–34%) (see Table 2). This can be attributed to a better performance of kinetic experiments under photocatalysis. The second point is good agreement with all the experiments performed and reproducibility for these experiments.

This a key issue, since we should not forget that all the experiments were performed at relatively low concentration levels of alachlor in water, ppb, in contrast with the literature that usually are performed at ppm level. By introducing another step in the analytical protocol —SPE— another variation is added. However, even with this step, the results are acceptable. To our knowledge no data on the precision of the photocatalysis and/or photolysis experiments at this low level of irradiation was previously reported.

An important question is that from the data reported in Table 2, it can be observed that the concentration of $FeCl_3$ necessary for degradation of alachlor is relatively small (15 mg/l is enough), giving a shorter half-life as compared to 150 mg/l of TiO_2. This is a very relevant and economical factor, since when applied to water-treatment processes $FeCl_3$ is cheaper and more effective than TiO_2. In addition, it is always more favourable also to destroy contaminants in waste-water treatment plants under
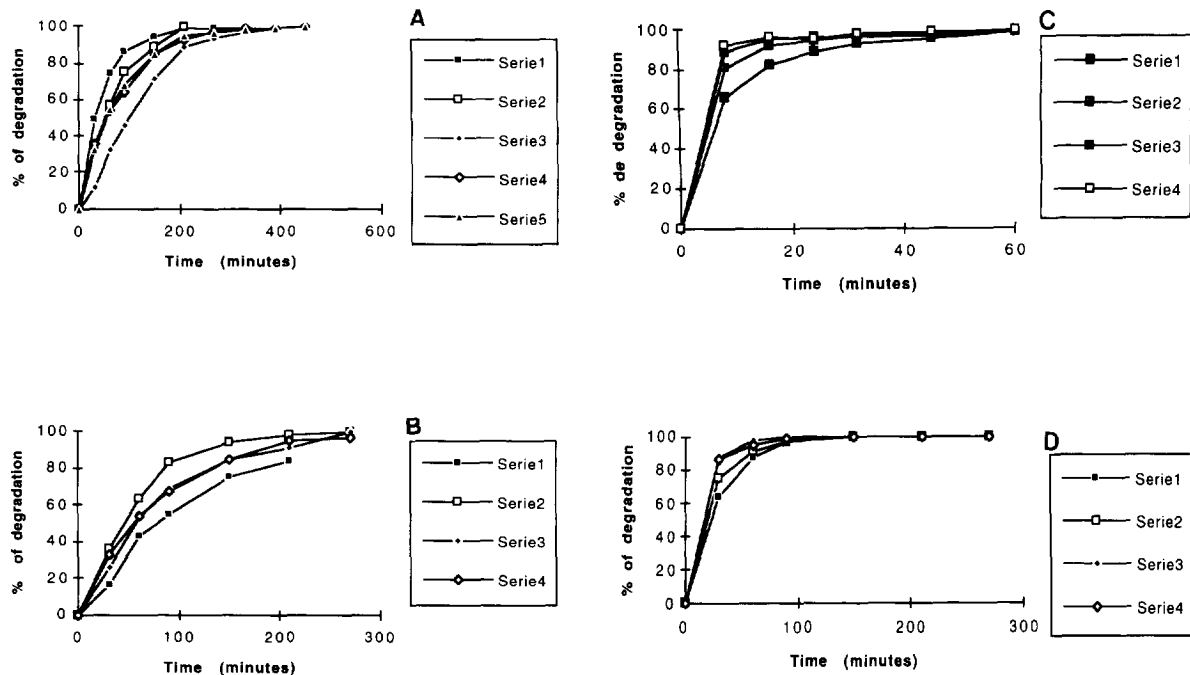

Fig. 5. (A) Photolysis of alachlor in deionized water using the Suntest apparatus. (B) same as (A) but in ground water (C) Photocatalysis of alachlor in deionized water $FeCl_3$ irradiated using the Suntest apparatus at 15 mg/L of $FeCl_3$ (series 1 and 2) or with 50 mg/L of $FeCl_3$ (series 3 and 4) (D) Photocatalysis of alachlor in deionized water using TiO_2 and the Suntest apparatus. Series 1 and 2 correspond to experiments with 25 mg/L of TiO_2; series 3 and 4 with 150 mg/L of TiO_2. The different series in all the experiments are replicate samples.

homogeneous phase catalysis (with $FeCl_3$) than with heterogeneous phase catalysis (with TiO_2).

Finally, the effect of H_2O_2 that produces HO was the same for all photocatalysis work and so a possible effect of this chemical is discarded. The differences observed are attributed to either $FeCl_3$ or TiO_2.

4. Conclusions

Five major transformation products of alachlor were identified after photolysis with the Suntest apparatus or photocatalysis with TiO_2 or $FeCl_3$. The final compound reported in all the experiments corresponded to 2-hydroxy-2,6'-diethyl-N-methyl-acetanilide.

It was shown that using only 15 mg/l of $FeCl_3$ is a very effective method for the destruction of alachlor, better than the use of 150 mg/l of TiO_2. Certainly $FeCl_3$ can be more appropriate than TiO_2 since it is cheaper and offers shorter reaction half-live for alachlor.

The approach presented here can be used for controlling alachlor residues in waste treatment processes since the concentration of alachlor used for the experiments reflect current environmental levels of this compound.

Acknowledgments

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