Application of solid-phase microextraction (spme) for photocatalytic studies of fenitrothion and methyl parathion in aqueous TiO$_2$ suspensions

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APPLICATION OF SOLID-PHASE MICROEXTRACTION (SPME) FOR PHOTOCATALYTIC STUDIES OF FENITROTHION AND METHYL PARATHION IN AQUEOUS TiO₂ SUSPENSIONS

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The photocatalytic degradation of the organophosphorus insecticides fenitrothion and methyl parathion has been studied in aqueous titanium dioxide TiO₂ suspensions under simulated solar irradiation. The degradation kinetics followed a pseudo-first-order reaction and has been monitored by headspace solid-phase microextraction (HS-SPME) and gas chromatographic techniques (GC-FTD). Degradation of both insecticides has been a rapid process with half-lives varied between 3.7 and 12.9 min depending on the TiO₂ concentration as well as on the structure of the compound. The generated transformation by-products formed during the process were extracted by SPME used in two approaches: (a) by direct immersion in the filtered sample and (b) by exposing the fiber in the sample headspace. The intermediates were formed predominately via oxidation processes and were identified by gas chromatography and mass spectroscopy techniques.

Keywords: Photocatalytic studies; TiO₂; Solid-phase microextraction; Fenitrothion; Methyl parathion

INTRODUCTION

Organophosphorus insecticides are some of the most useful and diverse in use for almost five decades. They are widely used in agriculture for crop protection and tree treatment in place of the prohibited organochlorines, which are persistent in the environment and bioaccumulate along the food chain. Although they are widely used, organophosphorus insecticides are extremely toxic compounds, acting on acetyl-cholinesterase activity [1], and their presence as contaminants in aquatic environments may cause serious problems to human beings and other organisms [2]. Consequently, it is necessary to remove the residues of these toxic compounds from matrices such as water by devising an efficient and economic purification method.

Among the new oxidation methods the so-called ''advanced oxidation processes'' (AOPs) have become a promising method of aquatic detoxification [3,4]. Of these,

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heterogeneous photocatalysis, which involves electron–hole pair formation initiated by gap excitation of semiconductor particles, appears as an emerging destructive technology leading to the total mineralization of most of the organic pollutants [5,6].

Suspended TiO_2 particles have been widely used as efficient catalysts, in particular for the decomposition of a variety of organic contaminants present in water and aqueous wastes [7,8]. It has been reported that in the charge separation event that occurs on irradiation of the semiconductor particles by light quanta with energy $\geq$ the band gap energy, the valence band holes (h^+) can be used to oxidize H_2O molecules and OH^- ions adsorbed at the particle surface to hydroxyl $OH^\bullet$ radicals. The hydroxyl radical is a short-lived, extremely potent oxidizing agent, capable of oxidizing organic compounds.

The photocatalytic degradation of some organophosphorus insecticides has been discussed previously, mostly in terms of degradation kinetics [9,10] and identification of by-products [11–13]. In all these studies the degradation kinetics as well as the identification of photocatalytic products was performed using LLE (liquid–liquid extraction) or SPE (solid-phase extraction) in combination with gas chromatography.

However, these methods involve multiple extraction steps and the use of complicated sampling equipment such as pumps, filters, and sorbent cartridges. The liquid–liquid extraction procedure is time consuming and uses large amounts of organic solvents which are expensive with respect to waste disposal. Furthermore, it is limited in the presence of transformation by-products, which are not always efficiently extracted. SPE methods eliminate most of the disadvantages of LLE, but can be quite lengthy, with a series of stages including drying and conditioning, and the presence of particulate matter in the samples can frequently cause plugging of the cartridges or disks, which are usually disposed off after one to four extractions [14]. The use of the solid-phase microextraction (SPME) technique, which has been developed by Pawliszyn and co-workers, provides a solution to these problems [15]. The technique exploits the affinity of analytes for a fiber coated with an adsorbent polymer to extract them from an aqueous solution either by direct immersion or by exposing the fiber in the sample headspace. The wide range of commercially available fibers of different thickness and polarity makes this technique attractive for the screening of analytes with different physicochemical properties in water [16,17] and other kinds of samples [18,19]. Furthermore, this solvent-free technique is simple, rapid, relatively inexpensive, and compatible with analytical separation systems such as gas and liquid chromatography.

The present photocatalytic degradation study of fenitrothion and methyl parathion, two of the most widely used organophosphorus insecticides, involves the application of the solid-phase microextraction method as an analytical tool for the determination of both kinetics and the identification of the transformation products formed. For this purpose both headspace and immersion modes of SPME were applied and compared with the well-established SPE.

EXPERIMENTAL

Chemicals

Fenitrothion and methyl parathion analytical grade standards (99.5% purity) were purchased from Riedel-de Häen (Germany) and used without further purification.

Pesticide grade dichloromethane and ethyl acetate were purchased from Labscan Ltd (Dublin, Ireland). Titanium dioxide (Degussa P25), a known mixture of 80% anatase and 20% rutile form with an average particle size of 30 nm, non-porous with a reactive surface area of $50 \pm 10 \, m^2 \, g^{-1}$ was used as received for all degradation experiments. Doubly distilled water, filtered through 0.45-μm HA cellulose acetate membranes (Millipore), was used throughout the work. SPME holder and fiber coatings, polyacrylate (PA 85 μm), polydimethylsiloxane (PDMS 100 μm), carbowax-divinylbenzene (CW-DVB 65 μm) and polydimethylsiloxane-divinylbenzene (PDMS-DVB 65 μm) were supplied from Supelco (Bellefonte, PA). Sodium sulfate and sodium chloride were supplied from Merck (Darmstadt, Germany).

Irradiation Procedure

Degradations were performed on 50 mL of stirred aqueous solutions containing the desired concentration of insecticides (~10 μg/L) and three different amounts of TiO_2 (100, 250 and 500 mg/L) at natural pH. The suspensions were allowed to stay in the dark for 60 min with stirring to reach adsorption equilibrium on the semiconductor surface. For the identification of photoproducts, 100 mL of pesticide solution (1 mg/L) was irradiated separately in a 100-mL UV-reactor under the same experimental conditions in order to provide an adequate concentration factor for our applications.

The irradiation was carried out in a 100-mL cylindrical duran glass UV-reactor using a Suntest CPS+ apparatus from Heraeus (Hanau, Germany) equipped with a xenon arc lamp (1500 W) and special glass filters restricting the transmission of wavelengths below 290 nm. Chamber and black panel temperature were regulated by a pressurized air cooling circuit and monitored using thermocouples supplied by the manufacturer. The temperature of samples did not exceed 25°C using a tap-water cooling circuit for the UV-reactor.

Kinetic Studies

At specific time intervals samples of 5 mL were withdrawn from the reactor and were placed in 10-mL crimp-top headspace vials and mixed with 1.5 g anhydrous Na_2SO_4. The vial was heated and after 10 min the fiber was exposed for 15 min to the headspace above the water sample which was kept at (75°C ± 1°C) and stirred by a small bar (960 rpm). Finally the compounds were thermally desorbed from the fiber in the GC injector for 5 min.

The analysis of fenitrothion and methyl parathion was performed using a Shimadzu 14A gas chromatograph equipped with a flame thermionic detector (FTD). The DB-1 capillary column, 30 m × 0.32 mm i.d. used, contained methylsilicone (J&W Scientific, Folsom, CA) followed a temperature program: 150°C for 2 min, from 150 to 210°C with a rate of 5°C/min, at 210°C for 10 min, 210 to 270°C with a rate of 10°C/min, and at 270°C for 3 min. The detector gases were air and hydrogen, and their flow rates were regulated at 120 mL/min and 4.0 mL/min respectively. The ion source was an alkali metal salt (Rb_2SO_4) bonded to a 0.2-mm spiral of platinum wire. The temperatures were set at 220°C for the injector and 250°C for the detector. Helium was used as the carrier and make-up gases.

By-products Evaluation

A relatively low amount of TiO_2 (100 mg/L) was used in the experiments for the identification of organic intermediates, which enables us to obtain slower kinetics and provides favorable conditions for the determination of by-products.

Both headspace and immersion modes of SPME technique have been applied using the PDMS-DVB coating. 20 mL of irradiated sample were filtered with 0.45 μm HVLP filters and extracted for 45 min after the addition of NaCl 25 (w/v) for the determination of by-products by direct mode. In the headspace mode the unfiltered water sample (20 mL) was extracted by the optimum extraction conditions described previously.

These techniques were also compared with the solid-phase extraction (SPE) technique that has been demonstrated to be more efficient than traditional liquid–liquid extraction (LLE) in the analysis of water samples containing very polar intermediates resulting from photocatalytic degradation process [20,21].

The analytical procedure for SPE extraction followed by GC-MS analysis in EI mode has been described by our group in previous work [12].

The GC-MS instrument was equipped with a DB-5-MS capillary column, 30 m × 0.25 mm i.d. coated with methylphenylsiloxane (5% phenyl) (J&W Scientific, Folsom, CA) used under the following chromatographic conditions: Injector temperature 220°C, column program of temperatures 55°C, 55–200°C (5°C/min), 200–210°C (1°C/min) 210°C (2 min), 210–270°C (20°C/min), 270°C (3 min). Helium was used as the carrier gas at a rate of 1.0 mL/min. The interface was kept at 270°C. Qualitative analyses were performed in the electron impact (EI) mode, at 70 eV potential using full scan mode.

RESULTS AND DISCUSSION

Development of the HS-SPME Procedure

In previous studies it was demonstrated that SPME fibers are very good supports for photocatalytic [22] and photodegradation studies [23,24]. Those preliminary studies were considered extremely successful, not only because the SPME fiber was shown to work as a photoreaction support, but also because of the possibility of the photoproducts formed in such experiments being detected.

Two types of sampling can be considered for the SPME procedure: direct aqueous sampling and headspace sampling. The latter is mainly used for complex matrices which contain solid materials, for example TiO_2, which can alter the fiber by direct contact. To eliminate the need for filtration of solid particles in heterogeneous processes, as in photocatalytic degradations (risk of analyte volatilization and interferences due to the solid coating on the fiber if direct adsorption was used), headspace sampling has been performed on an aqueous solution containing solid.

Thermodynamic equilibrium for the partitioning of fenitrothion and methyl parathion between the SPME sorbent and the aqueous phase was achieved in roughly 60 min. Eventually, a relative short extraction time of 20 min has been selected for the kinetics of both insecticides since the sensitivity and precision of the method are acceptable under these conditions. A temperature of 75°C and 30% (w/v) Na_2SO_4 was selected for the analysis of both insecticides. Heating a sample provides energy

for molecules to overcome energy barriers that tie them to the matrix; however, high temperature can adversely affect the uptake of analytes by the coating as a result of both a decrease in the partition coefficient and enhanced hydrolysis of the organo-phosphorus compounds [25].

In headspace SPME the rate-limiting step is considered to be diffusion of the analytes from the aqueous phase to the headspace. However, in these complex samples (slurry with TiO_2), the matrix itself might cause the rate-limiting step to be transport of the analytes through the sample. Because of this it has been necessary to investigate whether the matrix of the samples has affected the performance of the HS-SPME procedure. For this purpose, the relative recovery of both insecticides was obtained by triplicate analysis of spiked water solutions contained 100, 250 and 500 mg/L of TiO_2 (Fig. 1). Because SPME is a non-exhaustive extraction procedure the relative recovery, which is determined as the peak area ratio of the treated sample and an ultrapure water sample spiked with analytes at the same level was employed instead of absolute recovery as used in exhaustive extraction procedures.

The results obtained indicated that at the highest concentration level of TiO_2 (500 mg/L) recoveries were satisfactory with values over 80% for both insecticides. Thus, HS-SPME could be successfully applied as a sampling method in the present matrix samples, for the determination of degradation kinetics.

In order to normalize the influence of the TiO_2 concentration between the spiked water samples used for calibration curves and the samples used for kinetic study, the same TiO_2 content was added in all samples.

The linearity of the method was investigated by determining the calibration curve over the concentration range of interest (0.5 to 50 µg/L) using three different concentrations of TiO_2 (100, 250 and 500 mg/L). The line of best fit for the relationship between the average peak area and the concentration of analyte in the sample was determined by linear regression. The results are presented in Table I, together with the results obtained for precision.

Five replicate measurements were performed by extracting insecticide standards at a spiking level of 10 µg/L in three concentrations of 100, 250 and 500 mg/L TiO_2. The precision was evaluated by calculating the relative standard deviation (%RSD) of the
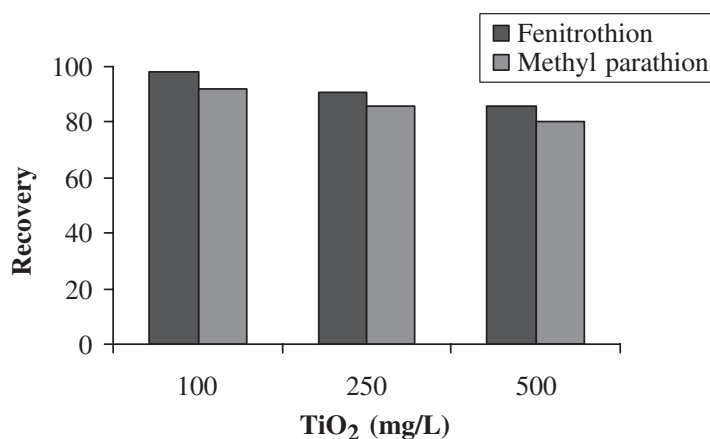
FIGURE 1 Effect of TiO_2 on extraction efficiency of fenitrothion and methyl parathion at four concentration levels (50, 100, 250 and 500 mg/L).

observed values. The RSD values obtained were higher at the highest concentration level (500 mg/L) of TiO$_2$ for both insecticides but always within the established tolerances.

Kinetics of Disappearance

Both insecticides were degraded at a relatively low rate by illumination with UV light in the absence of TiO$_2$, (Figs. 2 and 3 curves A) contributing about 20% and less than 4% to the degradation of fenitrothion and methyl parathion, respectively. The photolysis kinetic parameters of both insecticides are shown in Table II.

The kinetics of disappearance for both compounds follows an apparent pseudo-first-order (Figs. 2 and 3 curves C and D), in agreement with the generally observed Langmuir–Hinshelwood mechanism, with the rate r being proportional to the coverage θ which becomes proportional to C at low concentrations

$$r = k\theta = \frac{kKC}{1 + KC} = kKC = k_{\text{obs}}C \tag{1}$$

TABLE I   Linearity and precision studies performed at three concentration levels of TiO$_2$

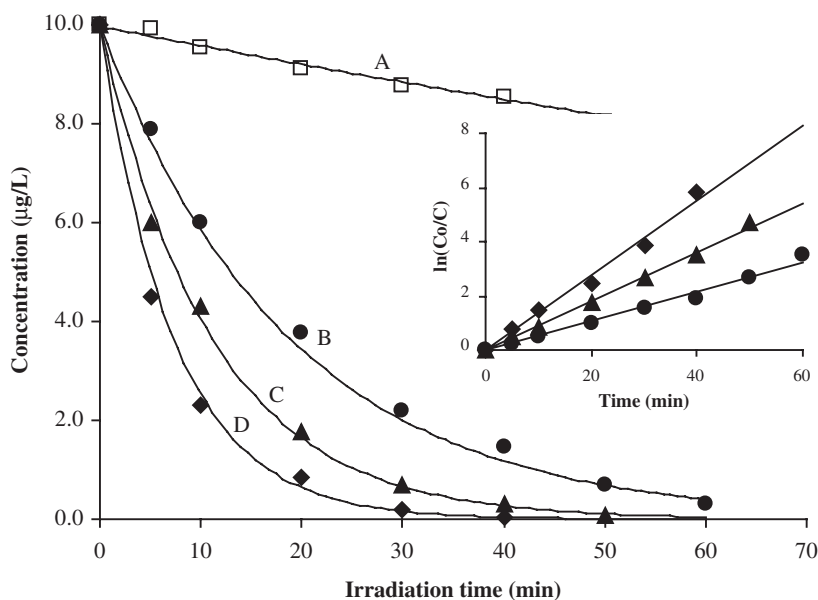| | Linearity (R^2) | | | Precision RSD (%) | | |
	TiO$_2$ Concentration (mg/L)			TiO$_2$ Concentration (mg/L)		
	100	250	500	100	250	500
Fenitrothion	0.999	0.997	0.992	7	10	12
Methyl Parathion	0.998	0.997	0.990	8	14	19

FIGURE 2   Disappearance of fenitrothion: curve A: UV-irradiation ($\lambda > 290$ nm); curve B: UV-light with TiO$_2$ (100 mg/L); curve C: UV-light with TiO$_2$ (250 mg/L); curve D: UV-light with TiO$_2$ (500 mg/L). The inset represents the semi-logarithmic plots of curves B, C and D.
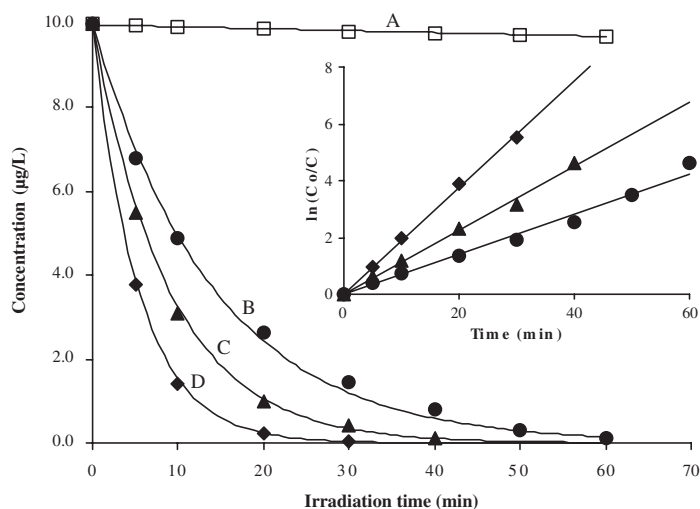
FIGURE 3   Disappearance of methyl parathion: curve A: UV-irradiation ($\lambda \geq 90\,\text{nm}$); curve B: UV-light with TiO$_2$ (100 mg/L); curve C: UV-light with TiO$_2$ (250 mg/L); curve D: UV-light with TiO$_2$ (500 mg/L). The inset represents the semi-logarithmic plots of curves B, C and D.

TABLE II   Kinetic parameters of fenitrothion and methyl parathion photocatalytic degradation in distilled water and in TiO$_2$ suspensions in distilled water under simulated solar irradiation

Irradiation medium	Fenitrothion			Methyl parathion		
	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
Distilled water	0.0041	169.0	0.982	0.0005	1386.0	0.964
TiO$_2$ 100 (mg/L)	0.0536	12.9	0.986	0.0708	9.8	0.985
TiO$_2$ 250 (mg/L)	0.0906	7.6	0.996	0.1125	6.2	0.996
TiO$_2$ 500 (mg/L)	0.1377	5.0	0.989	0.1875	3.7	0.998

where $r =$ the oxidation rate of the reactant [mg/(L min)], $C =$ the concentration of the reactant (mg/L), $t =$ the illumination time, $k =$ the reaction rate constant [mg/(L min)], and $K =$ the adsorption coefficient of the reactant (L/g) and k_{obs} is the apparent photodegradation rate.

The linearity of the plots of ln C_o/C versus time (Figs. 2 and 3 inset) allowed the calculation of the rate constants k_{obs}. Table II lists the values of k_{obs} and the linear regression coefficients for pseudo-first-order kinetics of fenitrothion and methyl parathion photocatalytic degradation. According to these values the appropriate first-order relationship appears to fit well. The effect of the semiconductor concentration on the degradation rate is increasing as the concentration increases. The k_{obs} values in the presence of 100, 250 and 500 mg/L of TiO$_2$ were 0.0536, 0.0906 and 0.1377 min^{-1} for fenitrothion and 0.0708, 0.1125 and 0.1875 min^{-1} for methyl parathion respectively, confirming the positive influence of the increased number of TiO$_2$ active sites on the process kinetics. However, this beneficial effect tends to level off and then to decrease for TiO$_2$ concentrations higher than 1–2 g/L depending on the reactor, owing to scattering of the incident light [26,27]. In addition higher TiO$_2$ concentrations caused a decrease in the detector response for both insecticides due to the matrix effect as described previously.

Direct SPME Procedure

Identification of intermediate products with the direct SPME mode was carried out using the more polar coating fibers such as PA, PDMS-DVB and CW-DVB. A sampling time of 120 min and a volume sample of 20 mL were chosen as optimum extraction parameters based on our previous reports [22,28,29]. These conditions were considered sufficient for the analysis of both insecticides as well as their degradation products, since all compounds have almost reached equilibrium with all fibers at this selected time with acceptable extracted amounts even for the intermediates with lower transformation rates.

Water samples treated with TiO_2 were analyzed after filtration with 0.45-μm HVLP filters and addition of 25% (w/v) NaCl (optimum conditions for both insecticides). A time of 10 min was selected for thermal desorption of the compounds. It was noticed that a greater diversity of intermediate products were detected with the PDMS-DVB fiber-making it more favorable than other tested polar coatings such as PA and CW-DVB for the subsequent analysis.

Fenitrothion and Methyl Parathion Photocatalytic Degradation Pathway

It is generally accepted that conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy (3.2 eV). Two oxidative agents can be considered: photo-produced holes h^+ and hydroxyl radicals $OH^\bullet$, which are known to be strongly active non-selective agents responsible for the heterogeneous TiO_2 photodecomposition of organic substrates. $OH^\bullet$ can be produced either by oxidation of water by holes or by transient formation of hydrogen peroxide radicals [30].
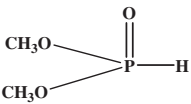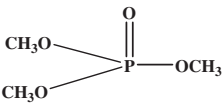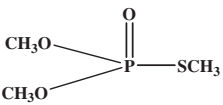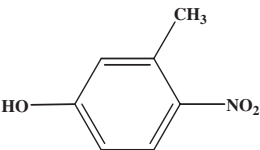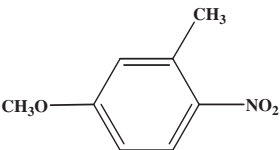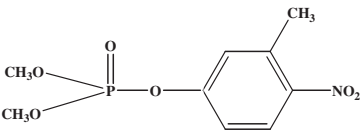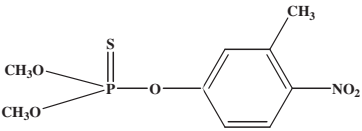
The present study has focused more on the identification of the major aromatic intermediates rather than byproducts derived from cleavage of the aromatic ring. For this purpose sample extracts were analyzed after 60 min of irradiation, just before the complete disappearance of the parent compounds.

The transformation products generated during the photodegradation process were analyzed by GC-MS and identified using an identification program of the NIST library, with a fit value higher than 70% in all cases. Tables III and IV list the structures, the retention times and the basic ions of the major degradation products formed during the photocatalytic treatment of fenitrothion and methyl parathion, identified by the SPE procedure.

The oxon analogs (methyl paraoxon, fenitrooxon) of both insecticides were found to be among the primary products derived from the oxidizing attack of $OH^\bullet$ and the substitution of sulfur by oxygen on the P=S bond. In both cases formation of the respective phenols of each insecticide (4-nitrophenol for methyl parathion and 3-methyl-4-nitrophenol for fenitrothion) was observed as a consequence of splitting of the phosphorus–phenoxy bond. Measurable amounts of different alkyl phosphorothioate esters and substituted benzenes (3-methyl-4-nitroanisole) were also formed, consistent with other photocatalytic degradation studies [10].

Figure 4 shows the total ion chromatogram obtained from SPE and DI-SPME extracts of methyl parathion solution after 60 min of irradiation. The distribution pattern of the intermediates detected by SPE, HS-SPME and DI-SPME techniques is shown in Table V. Both SPME techniques have demonstrated very similar results.
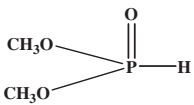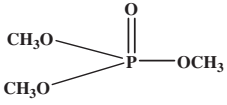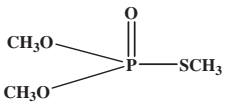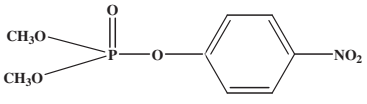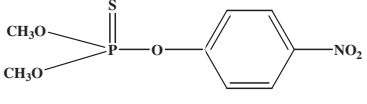
TABLE III   GC-MS-EI retention times (t_R) and mass spectral characteristics of fenitrothion photoproducts identified by SPE

Structure	t_R	Characteristic ions (m/z)
	6.1	$[M]^+ = 110, 109, 95, 80, 79$ (1) dimethyl phosphite
	10.2	$[M]^+ = 140, 110, 109, 95, 79$ (2) trimethyl phosphate
	13.4	$[M]^+ = 156, 126, 125, 110, 109, 95, 80, 79$ (3) O,O,S trimethyl phosphorothioate
	23.8	$[M]^+ = 153, 136, 108, 77$ (4) 3-methyl-4-nitrophenol
	24.3	$[M]^+ = 167, 150, 137, 122, 106, 91, 77$ (5) 3-methyl-4-nitroanisole
	31.4	$[M]^+ = 261, 244, 150, 127, 109, 79$ (6) fenitrooxon
	32.34	$[M]^+ = 277, 260, 214, 125, 109, 93, 79$ (7) fenitrothion

In some cases the headspace approach seems to be less favorable than the direct mode because, at the elevated temperatures used (e.g., 75°C), some by-products may be degraded, presumably due to hydrolysis, or they demonstrate a low Henry coefficient and are never available for adsorption onto the fiber. Small differences were observed in the product profile detection, with the DI-SPME technique (PDMS-DVB fiber) displaying fewer by-products than the SPE method.

Evaluation of these results should take into account that the extracted masses are different for the insecticides and their by-products, indicating that the variation in concentration of analytes in the sample generate a non-equivalent variation in the extraction performance of the fiber. In this case the extraction performance of the

TABLE IV   GC-MS-EI retention times (t_R) and spectral characteristics of methyl parathion photoproducts identified by SPE

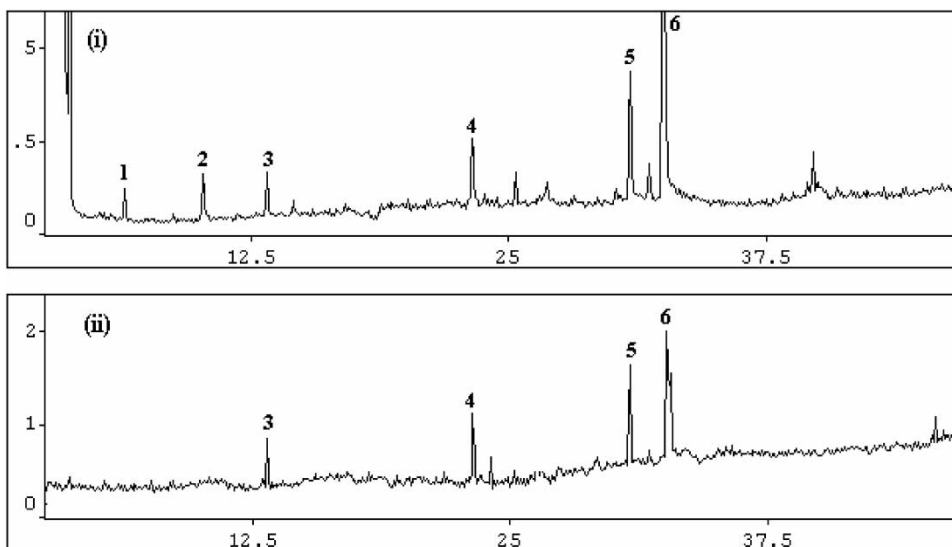| Structure	t_R	Characteristic ions (m/z)
CH₃O, CH₃O—P(=O)—H	6.1	$[M]^+ = 110, 109, 95, 80, 79$ (1) dimethyl phosphite
CH₃O, CH₃O—P(=O)—OCH₃	10.2	$[M]^+ = 140, 110, 109, 95, 79$ (2) trimethyl phosphate
CH₃O, CH₃O—P(=O)—SCH₃	13.4	$[M]^+ = 156, 126, 125, 110, 109, 95, 80, 79$ (3) O,O,S trimethyl phosphorothioate
HO—⟨ring⟩—NO₂	23.3	$[M]^+ = 139, 123, 109, 93, 81$ (4) 4-nitrophenol
CH₃O, CH₃O—P(=O)—O—⟨ring⟩—NO₂	30.7	$[M]^+ = 247, 230, 200, 139, 109, 96, 79$ (5) methyl paraoxon
CH₃O, CH₃O—P(=S)—O—⟨ring⟩—NO₂	31.8	$[M]^+ = 263, 125, 109, 93, 79$ (6) methyl parathion

FIGURE 4   GC-MS/EI total ion chromatogram obtained for (i) SPE and (ii) DI-SPME extracts of methyl parathion aqueous solution, irradiated in the presence of TiO₂ (100 mg/L) under simulated solar irradiation. Peaks labeled with numbers correspond to the identified degradation intermediates (Tables III and IV).

TABLE V   Product profile of intermediates identified by SPE, DI-SPME and HS-SPME techniques

Fenitrothion	SPE	DI-SPME	HS-SPME
(1)[a]	+	−	−
(2)	+	−	+
(3)	+	+	−
(4)	+	+	+
(5)	+	+	+
(6)	+	+	+
(7)	+	+	+
Methyl parathion			
(1)[b]	+	−	−
(2)	+	−	+
(3)	+	+	−
(4)	+	+	+
(5)	+	+	+
(6)	+	+	+

+, Product identified; −, product not identified.
[a]Numbers correspond to degradation intermediates in Table III; [b]numbers correspond to degradation intermediates in Table IV.

fiber coating is concentration dependent, and this indicates that mass transfer for the extraction of insecticides is higher than for by-products, covering mainly the fiber surface. In agreement with our observation, Semenov *et al.* [31] reported that molecules of analytes with smaller affinity to the coating can be displaced from the surface of the coating by strongly absorbable substances before having the opportunity to migrate to the interior of the porous fiber.

Furthermore, it should be kept in mind that the type of interaction between solid porous polymer-coated fibers such as PDMS-DVB and samples containing mixtures of analytes may vary.

CONCLUSIONS

The results of this study demonstrate that heterogeneous titanium dioxide photocatalyzed decomposition is a feasible and rapid treatment for the removal of the selected insecticides present in polluted surface waters. Degradation of the insecticides follows pseudo-first-order kinetics and complete disappearance is observed in a few minutes, working with moderate amounts of TiO_2, under simulated solar light. Headspace SPME was tested and validated for determination of the kinetics, while both direct and headspace extraction modes seem to be a promising new analytical tool for the identification of transformation products formed during the photocatalytic treatment of polluted waters.

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