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Phototransformation of organophosphorus pesticide in aqueous solution under irradiation light

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ABSTRACT

Fenamiphos is a widely used organophosphate insecticide/nematocide in vegetables and bananas to control pathogenic nematodes. This work reports the phototransformation of Fenamiphos under different intensity of UV light in distilled water. The rate of photolysis of Fenamiphos followed apparent first order kinetics ($C_t = C_0 e^{-kt}$). The rate constants calculated at 25°C and pH 6.9 were $14.47 \cdot 10^{-3} \text{ min}^{-1}$ (HPK 125W), $4.11 \cdot 10^{-3} \text{ min}^{-1}$ (PL-S 9W/10) and 3.1 days^{-1} (sunlight). Apparent rate constant was proportional to $I^{0.5}$ (Intensity of light). Half-life ($t_{1/2}$) values calculated were 48min (HPK 125W), 168.6min (PL-S 9W/10) and 223 days (sunlight). From this study, two photoproducts were identified and characterized using High Performance Liquid Chromatography/mass spectrometry (HPLC/MS). The plausible mechanism of photolysis involved is oxidation of sulphonamide group.

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KEYWORDS

Photolysis;
UV light;
By-products;
Pesticides;
Organophosphorus.

INTRODUCTION

The large amount of industrial waste and excessive use of pesticides necessary in intensive agriculture represent the main cause of contamination of soils, ground waters and surface waters. Most of these products are persistent and may cause important damage to the environment and human health^[7,23,25]. An important success has been obtained in the development of methods for characterisation and detection of the pesticides dispersed in the environment^[2,8,16,20,22]. Their removal from contaminated waters appears now to be a pressing ecological problem which needs to be solved.

Organophosphorus pesticides (OPPs) are generally seen as safe chemicals for use on crops and animals due to their relatively fast degradation rates. However, they are also the most toxic to humans of all pesticides^[13]. OPPs have relatively high solubility in water, thus they are transported readily through soils and into groundwater or surface waters. Many of these pollutants which are present in soil or in water can undergo photochemical transformation with solar light via direct as well as indirect photoreactions^[1,6,9,15,17]. Therefore, information about their toxicity, stability to natural decomposition (i.e. abiotic or biotic degradation) and their persistence in the environment is of great interest

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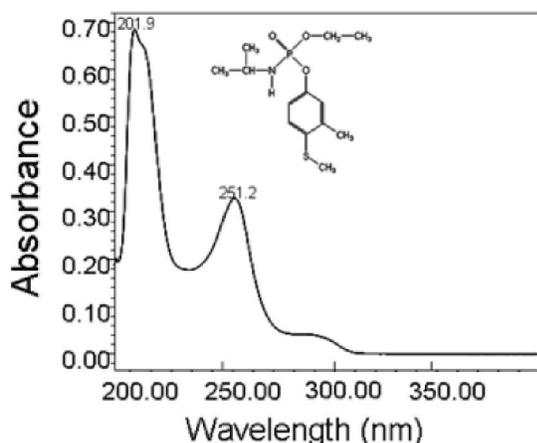


Figure 1 : Chemical structure and absorbance spectrum of fenamiphos

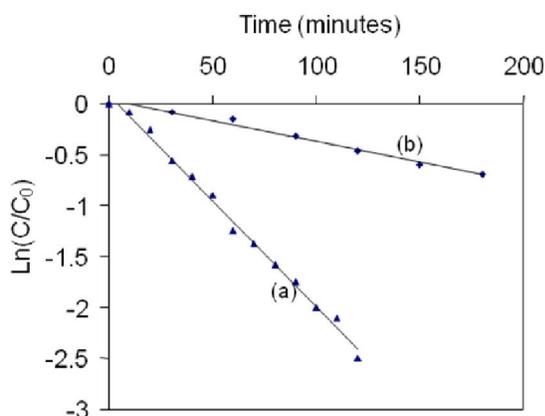


Figure 3 : First order linear transforms $\ln(C/C_0) = f(\text{time})$ of fenamiphos photolysis, using HPLK 125W Phillips lamp (a) and PL-S 9W/10 Phillips lamp (b)

to understand their environmental fate in the environment.

Fenamiphos (ethyl 4-methylthio-m-tolyl isopropylphosphoramidate), an organophosphorus group of insecticide and nematicide, is used to control soil nematodes in turf and horticultural crops^[3,5,14]. Generally, in soil, fenamiphos oxidize rapidly to fenamiphos sulfoxide which is then oxidized more slowly into fenamiphos sulfone^[11,12,27]. Fenamiphos sulfone and fenamiphos sulfone have pesticidal activity and toxicity similar to that of fenamiphos^[26], but they are much more mobile and persistent. The photodegradation of fenamiphos has been studied in various clay matrices^[11]. The process depends on the amount of humic substances and iron (III). The degradation rate increased in the presence of water, due to the photohydrolysis process.

Hydrolysis has a major role in the breakdown and degradation of pesticides. Hydrolysis of fenamiphos followed simple pseudo first order kinetics and depends

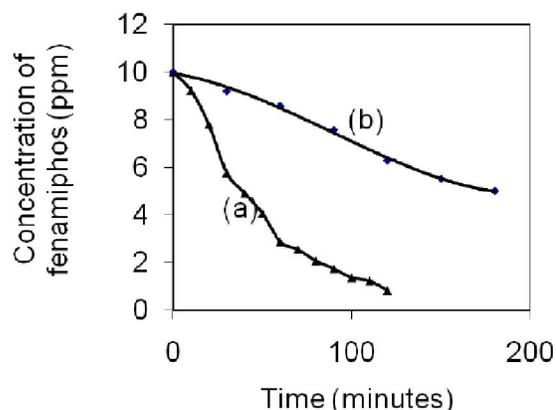


Figure 2 : Photochemical degradation of fenamiphos at varying intensity. (a) HPLK 125W Phillips lamp; (b) PL-S 9W/10 Phillips lamp

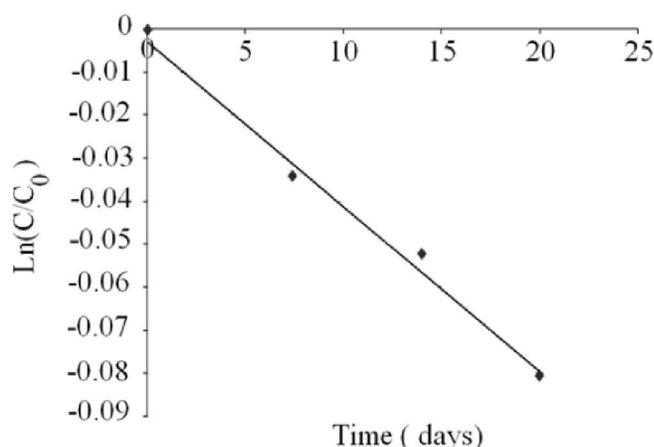


Figure 4 : First order linear transforms $\ln(C/C_0) = f(\text{time})$ of fenamiphos photolysis, using sunlight

on the pH and temperature^[4]. The reaction is very slow at low temperature and in neutral water, but complete hydrolysis of the product is observed in basic water at 50°C. So, the more alkaline soil, the faster the hydrolysis. However, the soils of a neutral nature favour the accumulation of residues of this pesticide for a longer time which may contribute to groundwater pollution^[19]. Therefore, determination of the rate and route of photolysis transformation in water is important to determinate the impact of fenamiphos use.

Exposition of the aqueous solution of fenamiphos to UV light is a useful method for determining the rate and the reaction pathways of fenamiphos photolysis. In the present work, we determinate and compared the rate of photolysis of fenamiphos in water under UV light using two type of lamps with different light intensity and wave length. High performance liquid chromatography / mass spectrometry (HPLC/MS) is

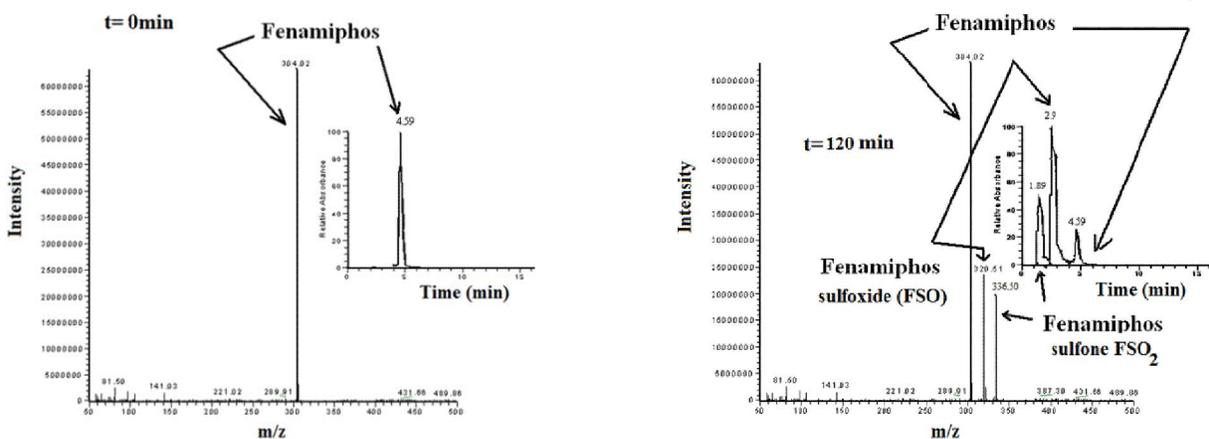


Figure 5 : Identification of the by-products by HPLC-MS after 120minutes of irradiation time of fenamiphos solution

used to characterise the main intermediate products.

EXPERIMENTAL

Reagents

Fenamiphos with 99.5% purity is used as received without further purification. All other chemicals were analytical grade and were used without further purification. Solutions were prepared with high purity water. Samples from considered solution were taken at regular time intervals and analysed directly by HPLC coupled to Diode Array UV detector. All the experiments were run in duplicate. All solvents used for HPLC analysis were of chromatography grade. A stock solution of fenamiphos (3.29mM) was prepared in methanol. From stock solution, a 0,0329mM working standard solution in water was prepared. The absorbance spectrum of fenamiphos in aqueous solution is presented in figure 1. The concentrations were determined from the calibration curve (concentration vs absorbance) produced from known concentrations.

Irradiation experiment

The solutions were irradiated in a reactor using two types of lamps: High-pressure mercury lamp HPLK 125W-Phillips (high level of UV radiation, provide maximum energy at 365 nm, with substantial radiation also at 435, 313, 253 and 404 nm) and a low-pressure mercury vapour fluorescent lamp PL-S 9W/10 Phillips (Emit long-wave UV-A radiation, range of wave length is 350-400 nm), to achieve a maximum intensity of UV light at $I_{\max} \geq 290$ nm under a continuous stirring using a magnetic stirrer. A cylindrical Pyrex glass vessel of 250 mL was used as a batch reactor. Other tests were made

on the degradation kinetics using natural sunlight. The samples were irradiated continuously for 2h under the effect of light lamps and for 20 days under the effect of sunlight. Test controls were incubated in the dark to ensure that the transformation of fenamiphos was only due to light absorption. The progress of reaction was followed by successive sampling at regular time intervals and was analysed directly by HPLC coupled to Diode Array UV detector. Hydrolysis experiments were also performed at the same time as the photolysis study and no hydrolysis effect was observed. The pH (6.9) and temperature (25°C) remained constant during experiment.

Instrumental analysis

HPLC was performed using a GBC equipped with a UV diode array detector set at 249 nm. The column was a 250mm \times 4.6 mm agilent Zorbax SB C18 column. The mobile phase was a mixture of water and methanol (30/70, v/v). The flow rate of isocratic elution was 1 mL/min and the injection volume was 20mL.

The HPLC coupled to mass spectrometer (HPLC/MS) used in this study is equipped with HPLC LC type Surveyor brand Thermo-Electron, C18 column (4.6 \times 150 mm), quaternary gradient pump with integrated degasser, oven included in the ferryman, stable between 5 and 95°C, UV detector diode array SURVEYOR (spectral range from 190 to 800nm) and a detector mass spectrometer LCQ Advantage MAX ion trap type.

RESULTS AND DISCUSSION

Photolysis of fenamiphos

The direct irradiation of a solution containing

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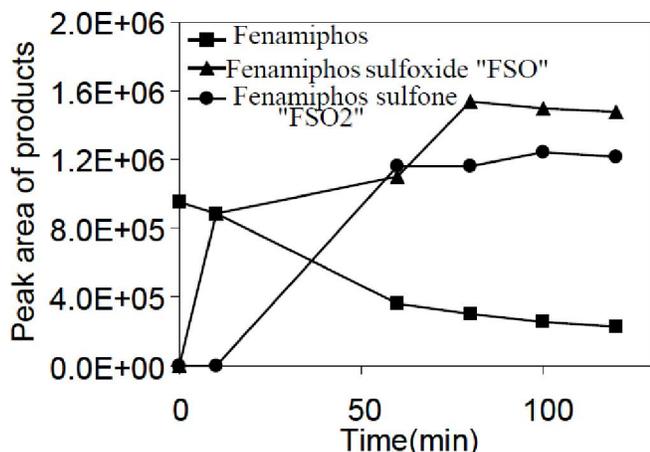


Figure 6 : The evolution of fenamiphos and its intermediate as a function of the irradiation time

0,0329mM (10ppm) of fenamiphos was conducted over a period of 2 hours or 3 hours using UV light, with regular sampling every 10 minutes. Analysis by HPLC-UV of solutions shows a steady decrease in the concentration of fenamiphos versus time of irradiation (Figure 2). The photolysis of fenamiphos in water was modeled with a first order kinetic. The first order rate constant 'k' is determined from the slope of the linear plot of the logarithm of fenamiphos concentration at various sampling intervals against the irradiation time. The half life values were calculated by using the regression analysis and the rate constant k was calculated from the first order rate equation.

$$C_t = C_0 e^{-kt}$$

where C_t is the concentration of pesticide at time t, C_0 represents the initial concentration and K is the rate constant. When the concentration is reduced to 50 percent of its initial value, the half-life ($t_{1/2}$) can be calculated.

The evolution of $\ln(C/C_0)$ versus time is shown in figure 3 and 4. The disappearance of fenamiphos follows apparent first-order kinetics and the rate constant is presented in TABLE 1.

The rate of photolysis and the half-life varied with respect to the intensity of light, being more rapid with HPLK lamp than with PL-S 9W/10 or sunlight. The kinetics of transformation of fenamiphos depends on the intensity of the light used for irradiation. Apparent rate constant is proportional to $I^{0.5}$ (Intensity of light). The dependence between light intensity and the decomposition of different pesticides has been widely

studied^[1,10,21,24].

HPLC/MS analysis was carried out to follow the main intermediates resulted from the photolytic process of fenamiphos.

Identification of photoproducts

As presented in figure 5, HPLC chromatograms showed the presence of three peaks corresponding to fenamiphos and two intermediates products at retention times 4.59, 2.9 and 1.89 minutes, respectively (TABLE 2).

Eighty percent of the initial concentration of fenamiphos was degraded after 2 hours. Analysis by HPLC-MS allowed us to identify the by-products of photolysis with $m/z = 320.68$ and $m/z = 336.50$, which can be assigned respectively to the fenamiphos sulfoxide (FSO) and fenamiphos sulfone FSO₂ (Figure 5).

The evolution of fenamiphos and its intermediate as a function of the irradiation time is shown in figure 6. We can clearly observe the appearance of two intermediates products, 10 and 20 minutes after the irradiation by UV Lamps. The transformation of fenamiphos follows two steps. The first step corresponds to the transformation of fenamiphos to fenamiphos sulfoxide (FSO) which occurs rapidly and continues during the irradiation (2 hours). After 20 minutes, fenamiphos sulfoxide (FSO) oxidizes to fenamiphos sulfone (FSO₂) and the concentration of FSO decreases during the first 30 minutes, but the rate of fenamiphos transformation on FSO is more important than the oxidation of FSO on FSO₂ as shown in figure 6 and TABLE 2.

Using sunlight, only 10% of the product has been transformed for a period of 20 days of irradiation. Fenamiphos sulfoxide FSO and fenamiphos sulfone are observed after 7 days 20 days respectively.

On the basis of the identified photoproducts and the sequence of their formation during the experiment, we would suggest that the photolysis of fenamiphos in water proceeds via oxidation pathway^[18]. The fenamiphos oxidizes to fenamiphos Sulfoxide (FSO) by the effect of light and it oxidizes to fenamiphos sulfone (FSO₂). No other products were observed like the phenol derivative which corresponds to the photohydrolysis of fenamiphos as generally observed for the photodegradation of fenamiphos in soil^[11].

TABLE 1 : Rate constant (K) and half-life ($t_{1/2}$) of transformation of fenamiphos during photolysis process using HPLK 125W Phillips lamp (a), PL-S 9W/10 Phillips lamp (b) and sunlight

Lamp	Kinetics parameters	R ²
HPLK 125W	kinetic constant k (10^{-3} min^{-1})	14.47 0.9941
HPLK 125W	half-life $t_{1/2}$ (min)	48
PL-S 9W/10	kinetic constant k (10^{-3} min^{-1})	4.11 0.9893
PL-S 9W/10	half-life $t_{1/2}$ (min)	168.6
Sunlight	kinetic constant k ($10^{-3} \text{ days}^{-1}$)	3,1
Sunlight	half-life $t_{1/2}$ (days)	223 0,979

TABLE 2 : Retention time and m/z values of phototransformation products of fenamiphos after 120minutes of irradiation time

	Fenamiphos	Fenamiphos sulfoxide (FSO)	Fenamiphos Sulfone (FSO ₂)
Masse (m/z)	304.02	320.51	336.50
Retention time (min)	4.59	2.9	1.89

CONCLUSION

This study focused on determining the kinetics of photolysis of fenamiphos in aqueous medium and determination of effect of intensity light.

The kinetic study by different lamps shows that fenamiphos oxidizes according to a pseudo first order reaction. The kinetic depends on the intensity of lamp. Analysis of photoproducts by HPLC-MS showed that fenamiphos undergoes oxidation with formation of fenamiphos sulfoxide and fenamiphos sulfone.

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