



Photolysis and photodegradation of Fenamiphos insecticide by using slurry and supported TiO₂

A. El Yadini¹, B. Marouane¹, A. Ahmido¹, P. Dunlop², J. Anthony Byrne², M. EL Azzouzi¹, S. EL Hajjaji^{1*}

¹ *Equipe Physico-Chimie des Matériaux et Environnement, LS3ME, University Med V-Agdal, Faculty of Science, Av Ibn Battouta, BP 1014 Agdal, Rabat, Morocco.*

² *Nanotechnology and Integrated BioEngineering Centre, University of Ulster, United Kingdom.*

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*Corresponding author: S. El Hajjaji, e-mail: selhajjaji@hotmail.com, Tel: +212 6 61 30 31 02, Fax: +212 5 37 77 54 40

Abstract

Kinetics degradation of fenamiphos, an insecticide from organophosphorus class of pesticides, has been investigated in aqueous solution using UV light in absence and in presence of slurry titanium dioxide (TiO₂) or supported on borosilicate glass plates. Kinetic parameters were experimentally determined and an apparent first order kinetic was observed. For photolysis process of fenamiphos, 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. In presence of photocatalyst, Degussa P25 shows a good photocatalytic activity and a complete degradation was observed after 180 min.

Keywords: Titanium dioxide; photolysis; photocatalysis; Fenamiphos; kinetic; Degussa P25

1. Introduction

Organophosphorus compounds are the most widely used insecticides, accounting for an estimated 34% of world-wide insecticide sales [1]. Fenamiphos (ethyl 4-methylthiom-tolyl isopropylphosphoramidate), an organophosphorus pesticide is extensively used as a systemic and contact insecticide against soil nematodes in golf greens and horticultural crops all over the world. This pesticide is applied at various stages of plant growth such as pre-planting, at-planting, pre- and post-harvest on a variety of plants including tobacco, turf, bananas, pineapples, citrus and other fruit vines, vegetables, and grains [2]. Generally, under environmental conditions, fenamiphos can be oxidized primarily to fenamiphos sulfoxide (FSO) followed by further oxidation to fenamiphos sulfone (FSO₂) [3-5]. These oxidation products have nematicidal activity and toxicity similar to the parent compound. Due to the high solubility of fenamiphos in water (0.4 g/L) and moderate ability to adsorb onto soils [4; 6; 7], it can be readily leached from sites of application to surface and ground water bodies [8]. Hydrolysis of fenamiphos followed simple pseudo first order kinetics and depends on the pH and temperature [9]. 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 [8].

In recent years, novel methods for water and air purification have been developed including chemical, electrochemical and photochemical processes [10-13]. Indeed, photocatalytic degradation has been shown to be a promising technology for the treatment of water contaminated with organic and inorganic pollutants. Furthermore, photocatalysis has been reported to be effective for the degradation of persistent organic pollutants, such as pesticides, exhibiting chemical stability and resistance to natural biodegradation in water [14-20]. Heterogeneous photocatalysis involves the use of a semiconductor material which is excited by light with energy equal to or greater than the band gap. This leads to the formation of electron/hole pairs which react at the particle-water interface resulting in the degradation of chemical species by both oxidative and reductive pathways. Titanium dioxide (TiO₂) is the photocatalyst of choice for water decontamination treatment because it

is i) not soluble under normal pH ranges found in natural water, ii) photoactive, photostable, and relatively inexpensive. However, TiO₂ is a wide band gap semiconductor ($E_{bg}= 3.2$ eV for anatase) and can only be excited by UV light, meaning that only 5% of the solar spectrum can be utilised. The Degussa P25 TiO₂-type is a commercially available powder preparation and has emerged as the research standard in the field of photocatalysis. However, since the final filtration of titania powders in suspension for the release of cleaned water and the recovery of the catalysts is a tedious process, titania has been successfully deposited on different supports [21].

In this work, we used two forms of titanium dioxide P25- Degussa (TiO₂ powder and TiO₂ deposited on borosilicate glass) to determine and compare the rates of photolysis and photocatalytic of fenamiphos in water under UV light. High performance liquid chromatography / mass spectrometry (HPLC/MS) is used to characterise the main intermediate products.

2. Materials and Methods

2.1. Chemicals

Commercial fenamiphos with 99.5% purity was used. The absorbance spectrum of fenamiphos in aqueous solution is presented in Figure 1. All other chemicals were analytical grade and were used without further purification. Solutions were prepared with high purity water. Also all solvents used for HPLC analysis were of chromatography grade. A stock fenamiphos standard solution (1000 ppm in water and methanol) was prepared and an aliquot stock solution of 10 ppm was prepared.

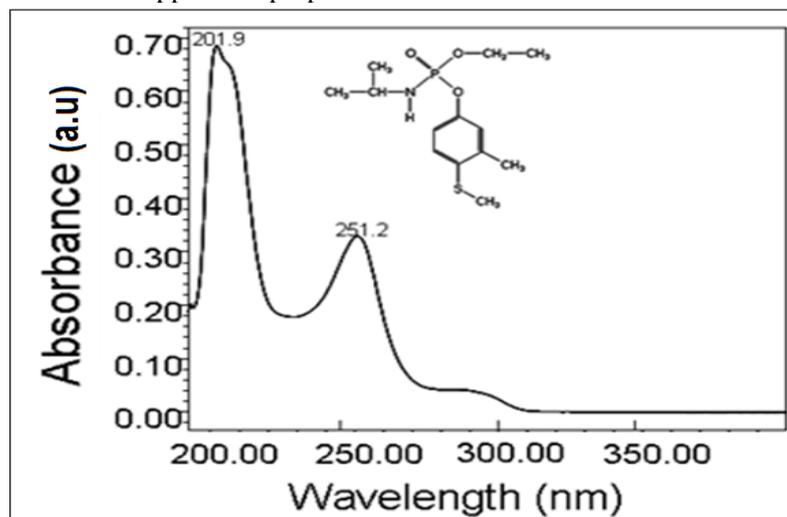


Figure 1 :Chemical structure and absorbance spectrum of fenamiphos

2.2. Immobilisation of TiO₂

TiO₂ Degussa P25 was immobilised on borosilicate glass using spray coating technique [21-22]. This is a simple and effective means to produce coatings on conducting and non-conducting supporting substrates. Borosilicate glass plates (110mm × 110mm) were cleaned by sonication in hot 5% Decon 90 / water solution, rinsed three times in distilled water, and then dried under a stream of nitrogen gas. The plates were then dried and weighed. TiO₂ was dipcoated from a 5% TiO₂ methanol suspension with a constant withdrawal rate 4.3 mm.s⁻¹. The spray gun reservoir was shaken between applications to ensure the catalyst powders remained in suspension. The plates were dried after each coat using an IR lamp. One side of the coated plate was cleaned to remove the TiO₂ and the plates were annealed in air at 673K for 1 h to improve particle adhesion to the glass and particle-particle cohesion. Gravimetric analysis of the plates was used to determine the TiO₂ loading. The amount of TiO₂ was deposited on the glass plates is about 1mg/cm². The borosilicate glass has a refractive index of 1.489 at $\lambda = 365$ nm, which gives a corresponding loss due to reflection of a perpendicular beam of 3.8%.

2.3. Irradiation experiment

The solutions were irradiated in a reactor using a low-pressure mercury vapour fluorescent lamp PL-S 9W/10 Phillips, to achieve a maximum intensity of UV light at $\lambda_{max} \geq 290$ nm under a continuous stirring using a magnetic stirrer. The samples were irradiated continuously for 2h. 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. The pH and temperature (25°C) remained constant during experiment.

2.4. Photocatalytic reactor

A custom built stirred tank photo-reactor (STR), previously reported [21 - 23], was used in this study. The closed system consisted of a water-jacketed walled vessel reservoir and a stainless steel propeller in order to create a turbulent flow. Thus, good mass transfer behaviour is obtained based on a turbulent flow inside the reactor. This principle transports the organic pollutant towards the coated TiO₂ plate and disperses oxygen from the headspace into the liquid. The TiO₂ coated glass plate was illuminated from below by PL-S 9W/10 UV-A fluorescent lamps (Philips) with a stable output between 350 and 400 nm (peak emission at 370 nm), positioned at a distance of 2.5 cm under the TiO₂ glass plate. The light intensity entering the reactor was determined by potassium ferrioxalate actinometry technique. Oxygen (99.5%) or air was added to the headspace of the reactor at a constant flow of 900 cm³ min⁻¹. A schematic representation of the STR is given in Figure 2.

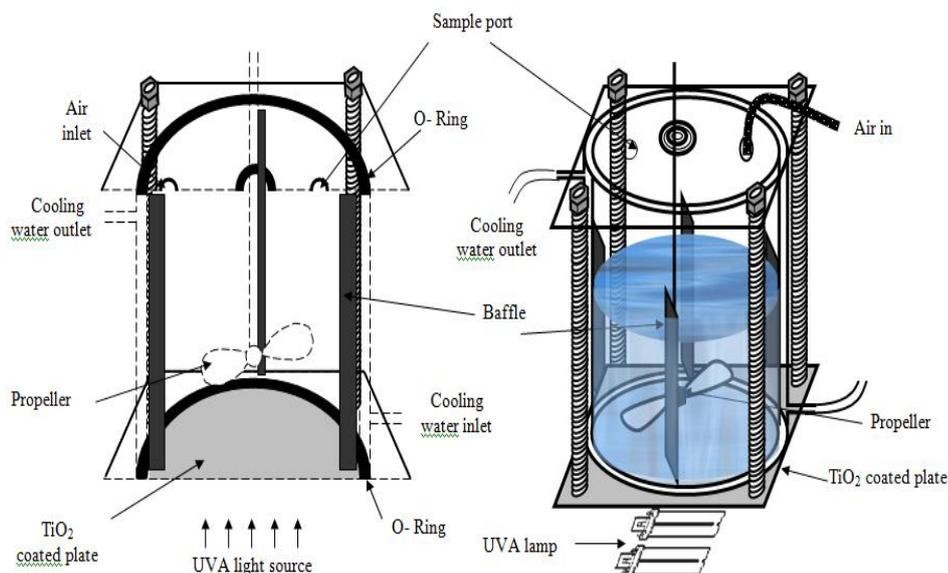


Figure 2: Schematic representation of a stirred tank reactor

2.4. Photocatalytic experiments and Kinetics

Prior to sample irradiation the UVA lamps were allowed to stabilize for a period of 10 min. An aqueous solution of fenamiphos was added to the reactor and equilibrated in the dark at the studied pH and temperature. For photolysis experiments (UVA only), a borosilicate glass plate was used without the TiO₂ coating. Dark control experiments were also carried out to investigate adsorption of the fenamiphos to the TiO₂ films. The kinetic experiments were performed by following the disappearance of fenamiphos by means of HPLC. All solutions were stirred and samples from considered solutions were taken at regular time intervals and then analyzed directly without preconcentration by HPLC. 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. All experiments were performed in duplicate. Hydrolysis experiments were also performed at the same time as the photolysis study and no hydrolysis effect was observed. The pH (5.8) and temperature (25°C) remained constant during experiment.

2.5. Analytical methods

2.5.1. High performance liquid chromatography (HPLC/MS)

The analysis was performed using an HPLC system. The instrument used for the photochemical study was a GBC equipped with a detector and a GBC LC 1150 pump. A column agilent zorbax SB-C18 (4.6*250mm) was used for analysis. The other HPLC conditions are the following i) mobile phase was a mixture of water (30%) and methanol (70%), ii) wave length: 249nm, iii) flow rate was 1 mL / min. 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 * 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 800 nm) and a detector mass spectrometer LCQ Advantage MAX ion trap type.

2.5.2. Total organic carbon analysis (TOC)

TOC analysis was carried out using a Shimadzu 5000A TOC analyser. This system uses a Pt furnace at 650°C with detection of carbon by IR-CO₂ analysis. Inorganic carbon (IC) is measured by CO₂ analysis following acidification. Total carbon (TC) – IC = TOC.

3. Results and discussion

3.1 Photolysis of fenamiphos

3.1.1 Photolysis of fenamiphos using UV light.

The direct excitation of a solution containing 10 ppm of fenamiphos was conducted over a period of 2 hours, 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 3). 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. When the concentration is reduced to 50 percent of its initial value, the half-life ($t_{1/2}$) can be calculated.

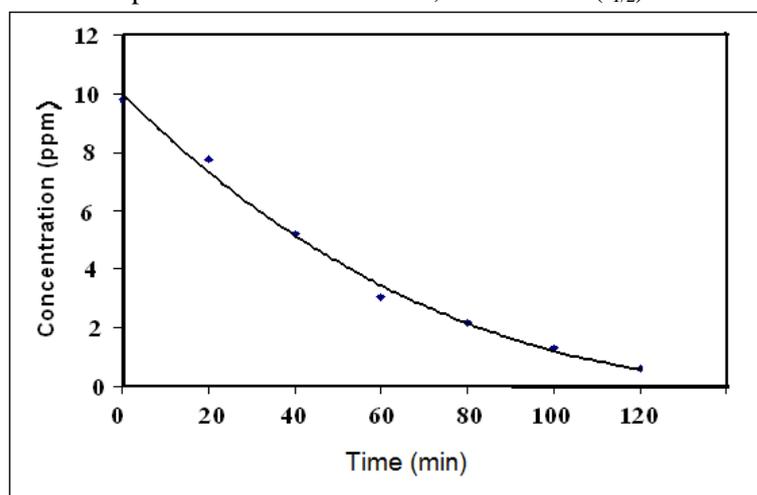


Figure 3: Variation of fenamiphos concentration in solution according to irradiation time

The evolution of $\ln(C/C_0)$ versus time is shown in Figure 4. The disappearance of fenamiphos follows first-order kinetics and the rate of photolysis is presented in table 1. The half-life value is estimated approximately to 35 minutes.

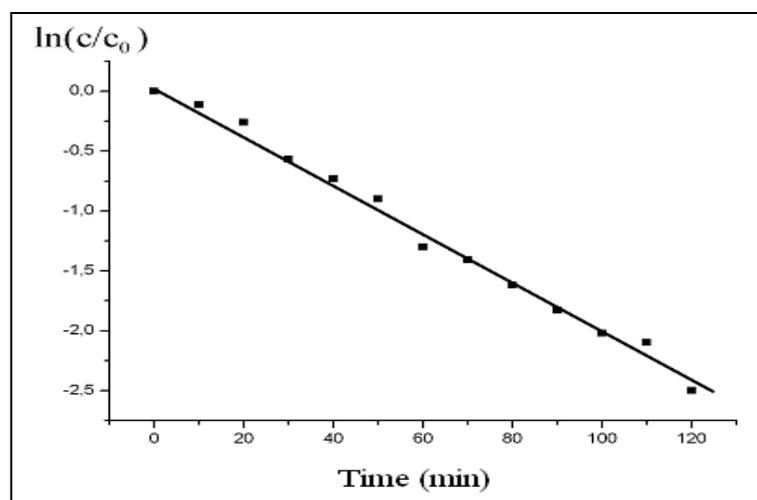


Figure 4: Semi-log plots of $\ln(C/C_0)$ over time was plotted for fenamiphos photolysis

Table 1: Rate constant (k) and half-life ($t_{1/2}$) of transformation of fenamiphos during photolysis process

kinetic constant k (min^{-1})	0.02
half-life $t_{1/2}$ (min)	34.6

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. The evolution of fenamiphos and its intermediate as a function of the irradiation time is shown in figure 5. We can clearly observe the appearance of two intermediates products, 10 and 20 minutes after the irradiation. 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 on 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 5.

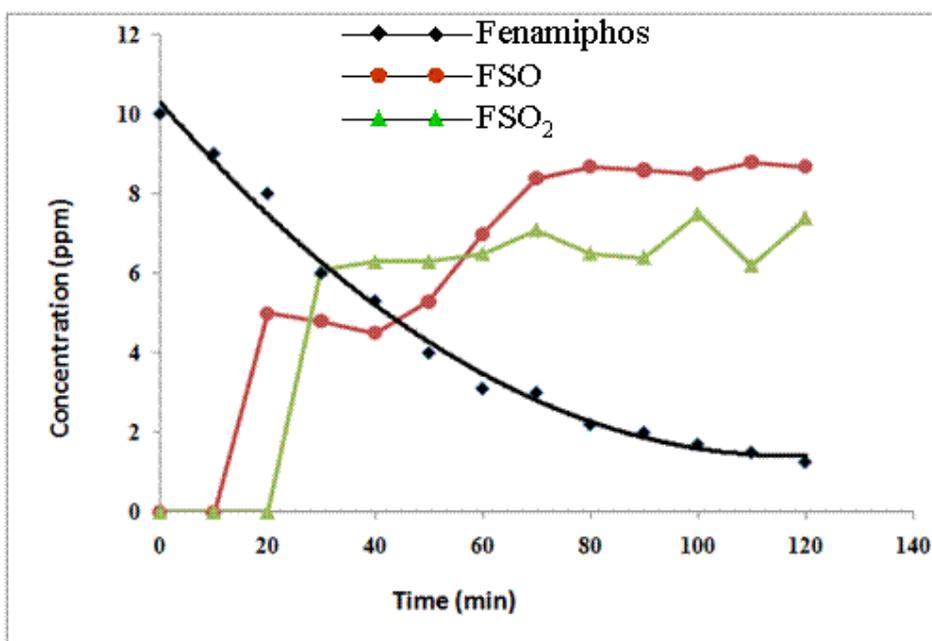


Figure 5: The evolution of fenamiphos and its intermediate as a function of the irradiation time

3.1.2. Photolysis of fenamiphos using sunlight.

Analysis by HPLC-UV of solutions shows a steady decrease in the concentration of fenamiphos versus time of irradiation and the photolysis of fenamiphos in water was modeled with a first order kinetic (Figure 6).

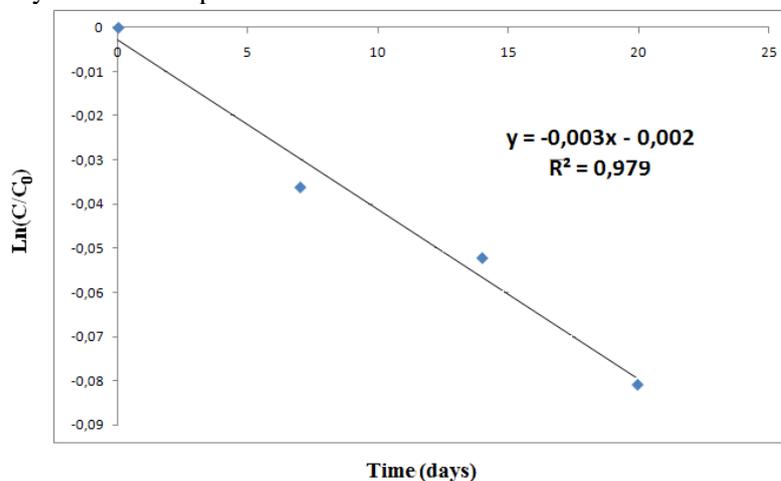


Figure 6: Semi-log plots of $\text{Ln}(C/C_0)$ over time was plotted for fenamiphos photolysis in presence of sun light

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 and 20 days respectively. The rate of photolysis by sunlight is presented in table 2

Table 2: Rate constant (k) and half-life ($t_{1/2}$) of transformation of fenamiphos during photolysis process using sunlight

kinetic constant k (10^{-3} days $^{-1}$)	0,0038
half-life $t_{1/2}$ (days)	180

3.2. Photocatalysis of fenamiphos

3.2.1 Using TiO_2 P25-degussa powder

In this part, we used the P25 TiO_2 powder as catalyst. Solutions of Fenamiphos (10 ppm) are introduced into a reactor with a capacity of 250 mL, in the presence of TiO_2 powder 1mg, and irradiated by HPK lamp. As presented in Figure 7, the indirect excitation of fenamiphos by the UV light in presence of TiO_2 powder shows that there is a steady decrease in the concentration of fenamiphos as a function of irradiation time (92% of the product that has been degraded in 2 hours).

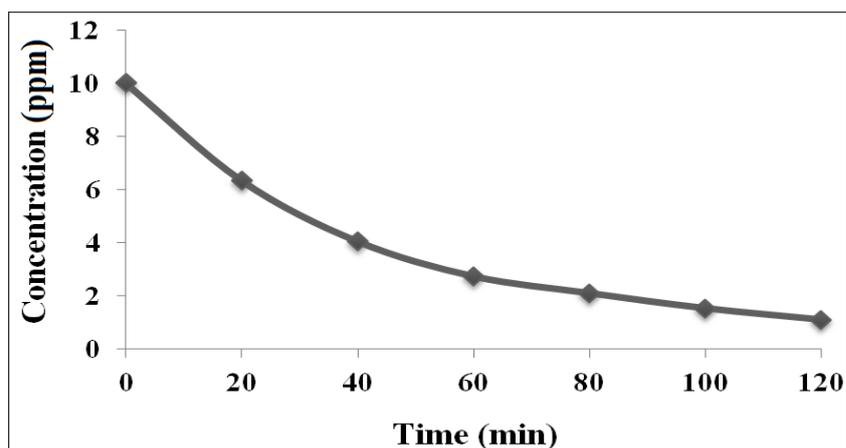


Figure 7: evolution of concentration of fenamiphos in function of the irradiation time in presence of 1g/L of TiO_2 P25 powder, pH = 5.8.

As shown in Figure 8, the photocatalytic degradation of fenamiphos follows a pseudo first order kinetic by a good linear correlation between concentrations and time. The data of the constant kinetic and the half life time are given in Table 3.

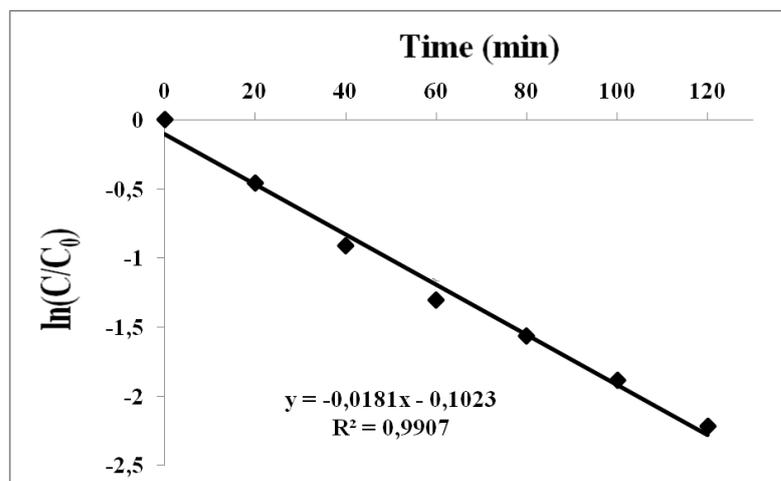


Figure 8: Semi-log plots of $\ln(C/C_0)$ over time was plotted for fenamiphos photocatalysis in presence of TiO_2 P25, powder (1mg, initial pH 5.8)

Table 3: Rate constant (k) and half-life ($t_{1/2}$) of degradation of fenamiphos during photocatalysis process

kinetic constant k (min^{-1})	0.01844
half-life $t_{1/2}$ (min)	37.58

3.2.2. Using TiO_2 P25-degussa supported on borosilicate glass

Solutions of Fenamiphos (10 ppm) are introduced into a reactor with a capacity of 250 mL, in the presence of 1mg/cm^2 TiO_2 supported on borosilicate glass. Also, the degradation follows pseudo first order kinetics (Figure 9). The data of the constant kinetic and the half life time are given in Table 4.

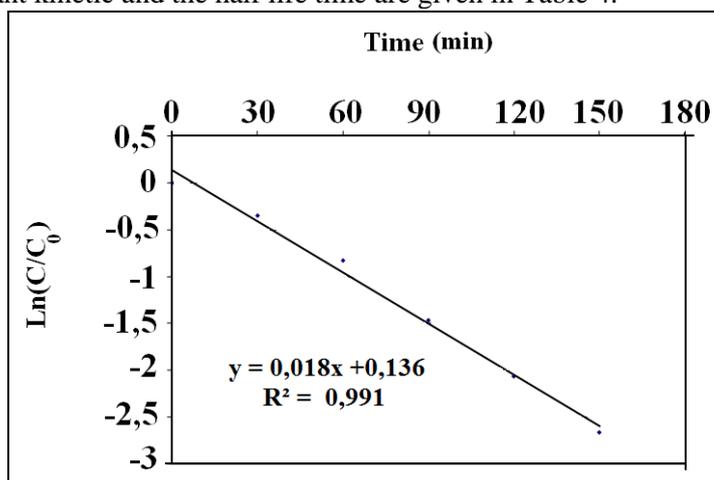


Figure 9: Semi-log plots of $\text{Ln}(C/C_0)$ over time was plotted for fenamiphos photocatalysis in presence of supported TiO_2 (1mg/cm^2 , initial pH 5.8)

Table 4: Rate constant (k) and half-life ($t_{1/2}$) of degradation of fenamiphos during photocatalysis process

kinetic constant k (min^{-1})	0.0183
half-life $t_{1/2}$ (min)	39

3.2.3. Evaluation of TOC

Finally, photocatalysis is a degradative process, the evaluation of the total organic carbon as a global measurement of the concentration of the organic intermediates produced during the degradation has been evaluated. Figure 10 shows the decrease of TOC vs time for the photocatalytic degradation of fenamiphos on P25. The TOC removal rate is much lower than the rate of degradation of the parent compound indicating that the first step is the oxidation process and the second step is mineralisation.

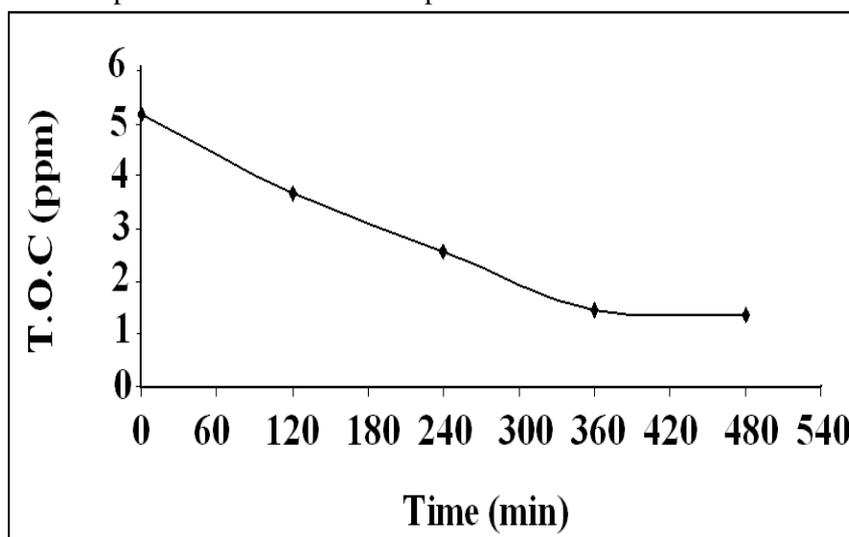


Figure 10: Total organic carbon versus time for the degradation of fenamiphos on P25.

Conclusion

This study focused on determining the kinetics of photolysis and photocatalysis of fenamiphos in aqueous medium and determination of photoproducts.

The photolysis kinetic study shows that fenamiphos oxidizes according to a first order reaction. Analysis of photoproducts by HPLC-MS showed that fenamiphos undergoes oxidation with formation of fenamiphos sulfoxide and fenamiphos sulfone.

The photocatalytic degradation of the pesticide fenamiphos was studied in a custom-built stirred tank photoreactor using TiO₂: Degussa P25 powder and TiO₂ supported on borosilicate glass. It was found that the degradation of fenamiphos followed pseudo first order kinetics in both cases TiO₂ (powder and supported on glass) studied. The removal of TOC was much slower than the degradation of the parent compound indicating that there is two step in the process, the first one is oxidation of fenamiphos like in photoysis and the second step is the mineralisation. These results show that the TiO₂ (powder or supported) used in this study are able to degrade the pesticide fenamiphos and may find application in the remediation of water contaminated with pesticide residues where efficient reactor design is employed.

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