

Research Article

TiO₂ Photocatalysis of the Organophosphorus Fenamiphos: Insight into the Degradation Mechanism

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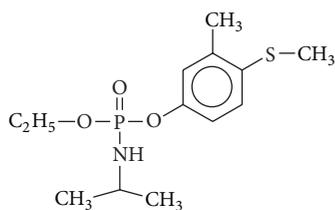
The photocatalytic degradation of the organophosphorus fenamiphos (FN) was studied using titanium dioxide as a photocatalyst and 365 nm as an excitation wavelength. Under our experimental conditions and in aerated solutions, the irradiation in the presence of TiO₂ P25 (1.0 g L⁻¹) permitted the evaluation of the half lifetime to 9.5 minutes. Laser flash photolysis experiments showed the formation of an initial species owing to the attack of the hydroxyl radical on FN. It was identified as the adduct [•]OH-FN. The second order rate constant for its formation was evaluated to 7.3 × 10⁹ mol⁻¹ L s⁻¹. All the products are formed via the formation of such transient intermediate. They were identified by means of HPLC/MS using electrospray in positive mode (ESI⁺). Two main processes are responsible for FN photocatalytic transformation: (i) hydroxylation on the aromatic structure and (ii) the scission of the C–O bond. A mechanistic scheme was proposed for the photocatalytic process of FN using titanium dioxide. An efficient mineralization was observed within 24 hours by using a suntest setup.

1. Introduction

Owing to the intensive agriculture within the last three decades, the varieties of employed pesticides have increased considerably. The presence of these chemicals in ground-water, streams, rivers lakes, and waste water effluents may present serious problems to the environment, human health, and the equilibrium of ecosystems. A considerable number of these pesticides in aqueous solutions may absorb in the actinic portion of the solar spectrum leading then to photochemical processes with solar light through direct as well as indirect photoreactions ($\lambda > 295$ nm) [1–5]. Within the former process, photochemical reactions such as dissociations, oxidation, and hydrolysis are observed and may lead to the generation of various byproducts that, in some cases, may be more harmful than the parent compound. In natural waters, indirect processes may be also observed via the excitation of substances such as Natural Organic Matters

(NOM) [6–8]. The solar light excitation of these substances leads to the formation of several reactive species such as triplet excited states or/and reactive oxygen species (ROS). Among these latter species, singlet oxygen ¹O₂, superoxide anion O₂^{•-}, and hydroxyl radical [•]OH represent the main reactive ones [6, 9].

When an efficient remediation of the contaminated environmental compartments is concerned, research activities toward the development of new treatment methods are undertaken. Various methods, the so-called advanced oxidation processes (AOPs), have been the subject of major interest in recent years [10]. Among them photochemical treatments that combine two inexhaustible sources, namely, solar light and molecular oxygen are very attractive. In this field of research, heterogeneous photocatalysis using semiconductors such as titanium dioxide has shown an efficient and complete degradation of several refractory pollutants [11–13].



SCHEME 1: Fenamiphos.

Absorption of light by semiconductors leads to the promotion of an electron from the valence band to the conduction band with the formation of a positive hole (h^+) in the valence band. The presence of molecular oxygen in the solution permits the increase of the efficiency by avoiding the hole-electron annihilation. Positive holes oxidize water molecules or ^-OH with the formation of hydroxyl radicals. The latter species have shown an efficient ability in the oxidation and degradation of a broad scale of organic pollutant [12]. The photocatalyst can be used as suspended material in the water effluent that has to be treated or immobilized on various types of supports [14–16].

Organophosphorus insecticides represent an important class of pest control chemicals that are moderate to highly toxic to fish and aquatic invertebrates [17]. They are used as systemic insecticides in a large number of plants. They are considered as good candidates to replace organochlorine compounds that show bioaccumulation process up the food chain [18].

The present work reports the results of the organophosphorus fenamiphos (ethyl 4-methylthio-m-tolyl isopropylphosphoramidate) (Scheme 1) degradation induced by heterogeneous photocatalysis using suspended titanium dioxide. Such organophosphorus and its main metabolites are believed to be toxic, for example, to birds and aquatic invertebrates [19]. The study was undertaken from both kinetic and analytical points of view leading us to propose a mechanistic scheme for fenamiphos photocatalysis by titanium dioxide.

2. Materials and Methods

2.1. Chemicals and Materials. Fenamiphos (99.9% purity) was from Riedel-de Haën. All solutions were prepared with deionised ultrapure water which was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity. All other reactants and solvents were of the highest grade available and were used as received. Iron(III) solutions were prepared from ferric perchlorate nonahydrate (Fluka, France). Titanium dioxide Degussa P25 was anatase/rutile (80/20) with a surface area of $55 \text{ m}^2 \text{ g}^{-1}$. Humic substances were provided by Aldrich (France). pH measurements were carried out with a JENWAY 3310 pH-meter to ± 0.01 pH unit. The deaeration of the solution was accomplished by constant bubbling of argon during the entire irradiation time. The saturation of the solution by molecular oxygen was obtained by replacing argon with pure oxygen.

2.2. Irradiations Apparatus. The irradiation device was equipped with one black light lamps emitting mainly at 365 nm (this line corresponds to roughly 94% of the radiant energy). The reactor was a Pyrex tube of 50 mL equipped with a water cooling system. It is located along one of the focal axes of a cylindrical mirror with an elliptic base. The distance between the lamp and the reactor was constant and equal to 13 cm. TiO_2 is maintained in suspension by magnetic stirring. The reaction mixture consists of 20 mL of fenamiphos and TiO_2 (1.0 g L^{-1}). It was stirred for about 30 minutes before starting the irradiation. Samples were taken at a given irradiation time and a centrifugation at 3500 rpm for 15 minutes prior to HPLC analysis was undertaken in order to remove titanium dioxide particles prior to HPLC analyses.

For total organic abatement, the samples were irradiated horizontally in Suntest CPS photoreactor (Atlas) equipped with a Xenon lamp and a filter that prevents the transmission of wavelength below 290 nm. The lamp was set at the intensity of 750 W/m^2 . The temperature of the sample was roughly maintained at 20°C by a continuous flow of cold water through the bottom of the photoreactor.

2.3. Analytical Equipment. The degradation of fenamiphos and the formation of the byproducts were followed by Waters Alliance 2695 (Waters SA, St-Quentin en Yvelines, France) photodiode array detector (DAD) chromatograph. A reversed-phase column distributed by Phenomenex (Kinetex MS C18, $2.6 \mu\text{m}$, $100 \text{ mm} \times 2.1 \text{ mm}$) was used at a flow rate of 0.2 mL min^{-1} and the injected volume was $20 \mu\text{L}$. The elution was accomplished, using an isocratic program, with water (0.1% formic acid) and acetonitrile at 60% and 40%, respectively. The HPLC-UV/MS analyses were performed using a Waters Alliance 2695 (Waters SA, St-Quentin en Yvelines, France) photodiode array detector (DAD) chromatograph. A reversed-phase column (Kinetex MS C18, 2.6 mm , $100 \text{ mm} \times 2.1 \text{ mm}$) distributed by Phenomenex (Le Pecq, France) was used at a flow rate of 0.2 mL/min . The mobile phase was composed of acetonitrile (solvent A) and acidified water (formic acid, 0.1% v/v; pH 2.6) (solvent B) at 60% of A and 40% of B. HPLC-ESI-MS analyses were performed using a Hewlett-Packard HP1100-MSD system working in positive and negative atmospheric pressure ionization. For the nebulization, a capillary potential of 4 kV was applied under nitrogen.

The UV-visible absorption spectra measurements were acquired on a Cary 3 double-beam UV-Vis (Varian) with a 1 cm quartz cuvette over the range 200–800 nm.

The progress of the mineralization of fenamiphos was monitored by measuring the total organic carbon (TOC) via a Shimadzu Model TOC-5050A equipped with an automatic sample injector. The calibration curve within the range $1\text{--}15 \text{ mg L}^{-1}$ was obtained by using potassium hydrogen phthalate and sodium hydrogen carbonate for organic and inorganic carbon, respectively.

2.4. Laser Flash Photolysis Equipment. Transient absorption experiments in the 20 ns to $400 \mu\text{s}$ time scale were carried out on a nanosecond laser flash photolysis spectrometer from

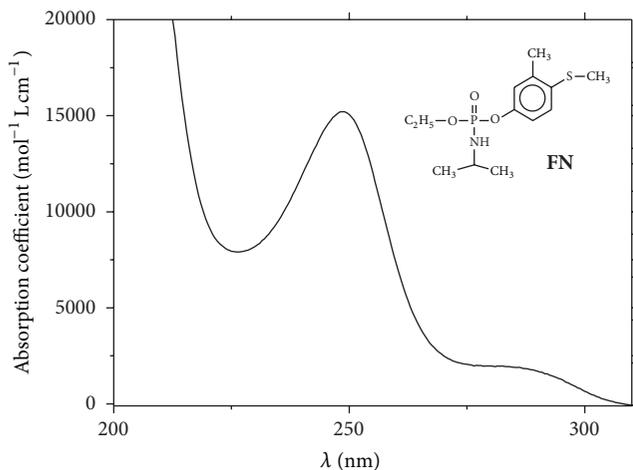


FIGURE 1: The UV absorption spectrum of fenamiphos in aqueous solution, $[FN] = 5.0 \times 10^{-5} \text{ mol L}^{-1}$, $\text{pH} = 5.3$.

Applied Photophysics (LKS.60). Excitation ($\lambda = 355 \text{ nm}$) was from the third harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width $\approx 5 \text{ ns}$) and was used in a right-angle geometry with respect to the monitoring light beam. A 3 cm^3 volume of an argon saturated solution was used in a quartz cell and was stirred after each flash irradiation. Individual cell samples were used for a maximum of 5 consecutive experiments. The transient absorbance at preselected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. A spectrometer control unit was used for synchronizing the pulsed light source and programmable shutters with the laser output. This also housed the high-voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitized signal.

3. Results and Discussion

The UV absorption spectrum of fenamiphos ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) in aqueous solution at $\text{pH} = 5.4$ is presented in Figure 1. It shows an absorption band with a maximum at 248 nm ($\epsilon_{248} = 15200 \text{ mol}^{-1} \text{ L cm}^{-1}$) and a shoulder at about 280 nm ($\epsilon_{280} = 1950 \text{ mol}^{-1} \text{ L cm}^{-1}$). No significant degradation of fenamiphos was observed within several days when the aqueous solution was kept in the dark and at room temperature, namely, 21°C . The absorption spectrum of fenamiphos shows a small overlap with that of the solar emission indicating that its degradation may be mainly owing to photoinduced process. This is the reason why its degradation was studied within the present work by excitation of titanium dioxide at 365 nm .

The photocatalytic degradation of fenamiphos (FN) ($3.4 \times 10^{-5} \text{ mol L}^{-1}$) was explored in the presence of titanium dioxide: Degussa P25 (Figure 2). The excitation at 365 nm of an aqueous suspension of the mixture TiO_2/FN ($1.0 \text{ g L}^{-1}/3.4$

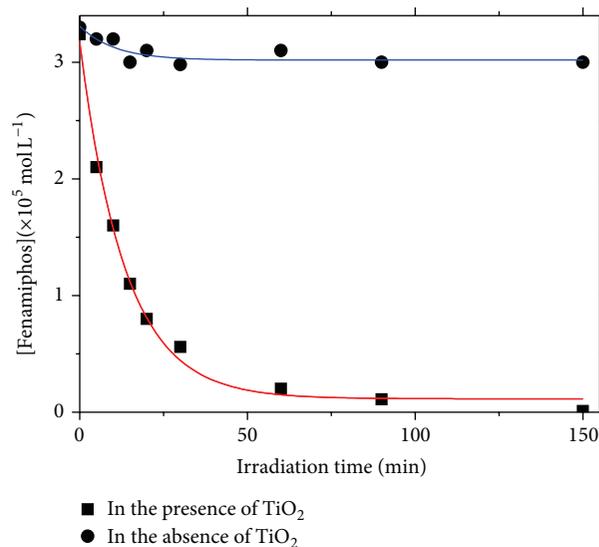


FIGURE 2: Disappearance of fenamiphos FN ($3.4 \times 10^{-5} \text{ mol L}^{-1}$) upon excitation of TiO_2 (P25) at 365 nm . $\text{TiO}_2: 1.0 \text{ g L}^{-1}$; aerated conditions; $\text{pH} = 5.2$. The plots were obtained using a monoexponential fitting function.

$\times 10^{-5} \text{ mol L}^{-1}$) at $\text{pH} = 5.2$ permitted the complete disappearance of FN within 100 minutes irradiation time. The kinetics of degradation followed a pseudo first kinetics with a rate constant of about $7.4 \times 10^{-2} \text{ min}^{-1}$ ($t_{1/2} = 9.5 \text{ minutes}$). It is worth noting that the photocatalytic efficiency was studied at variable amounts of TiO_2 and that 1.0 g L^{-1} corresponds to the appropriate amount to be suspended for high efficiency. No concentration changes were observed when the irradiation was performed in the absence of the photocatalyst and no significant adsorption was obtained when the mixture TiO_2/FN was left under stirring for more than 1 hour. Taking into account that no quantum yield can be estimated for this process owing to the solid suspension we evaluated the efficiency for the photocatalytic process by using phenol as a reference compound. Under the same experimental conditions, the rate constant for phenol disappearance was evaluated to $8.2 \times 10^{-2} \text{ min}^{-1}$ giving an efficiency of 90% for FN photocatalytic disappearance.

The effect of various experimental conditions such as oxygen concentration, presence of isopropanol, and the presence of humic substances was studied and the results are gathered in Table 1. As clearly shown, the disappearance of FN was totally inhibited in the presence of isopropanol, an efficient hydroxyl radical scavenger, indicating that the process mainly involves such highly reactive species. This aspect is consolidated by the fact that the efficiency of photocatalysis increased when the concentration of dissolved molecular oxygen increased. As largely demonstrated, oxygen plays a fundamental role by preventing the hole/electron annihilation and thus permitting an efficient formation of hydroxyl radicals [20]. The presence of humic substances (HS) at very low concentration slightly ($<0.5\%$) permitted an increase in the disappearance rate constant while at high

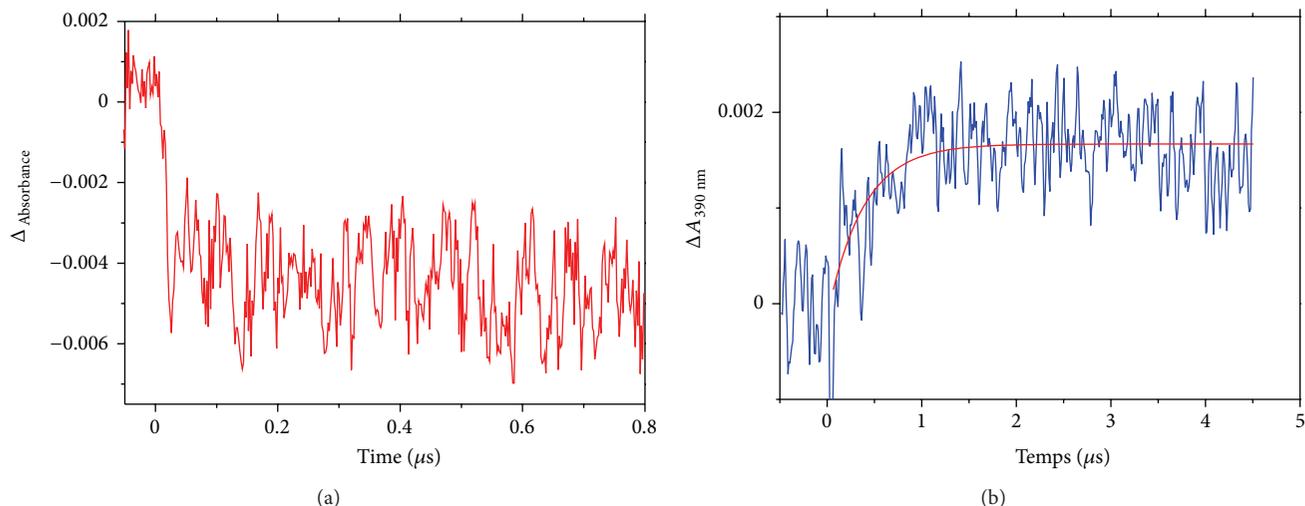


FIGURE 3: Laser flash photolysis at 355 nm in aerated aqueous solution at pH = 4.0 (a) $\text{Fe}(\text{OH})^{2+}$, alone at a concentration of $3 \times 10^{-4} \text{ mol L}^{-1}$; $\lambda_{\text{detection}} = 360 \text{ nm}$. (b) Mixture $\text{Fe}(\text{OH})^{2+}$ /fenamiphos ($3.0 \times 10^{-4} \text{ mol L}^{-1}/3.5 \times 10^{-4} \text{ mol L}^{-1}$); $\lambda_{\text{detection}} = 390 \text{ nm}$. The fitting was obtained using a monoexponential kinetic equation.

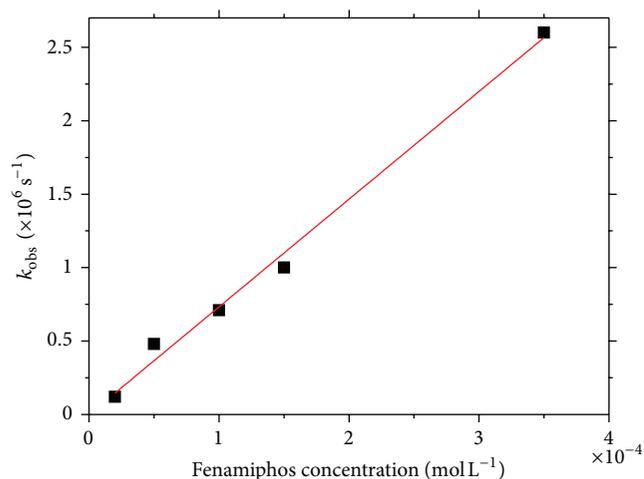


FIGURE 4: Observed rate constant, k_{obs} , for the formation of the adduct $\bullet\text{OH}$ -FN obtained from the laser flash photolysis traces at the detection wavelength 390 nm at various concentrations, X, of fenamiphos. Excitation at 355 nm; mixture $\text{Fe}(\text{OH})^{2+}$ /fenamiphos ($3.0 \times 10^{-4} \text{ mol L}^{-1}/X \text{ mol L}^{-1}$), pH = 4.2.

concentration it was mainly detrimental for FN disappearance. Two important factors are more likely involved in the presence of HS (i) they may partially absorb the excitation light by producing reactive species and thus participate in the degradation process of FN through the formation of oxygen reactive species (ROS) [6, 9] and (ii) they may also play the role of hydroxyl radical scavenger and thus reducing their stationary concentration during irradiation. These two factors are of course dominant at high concentrations of HS. It is worth noting that at high concentrations, the absorption of light by HS is also detrimental to photodegradation of FN due to screen effect phenomenon. All these results show

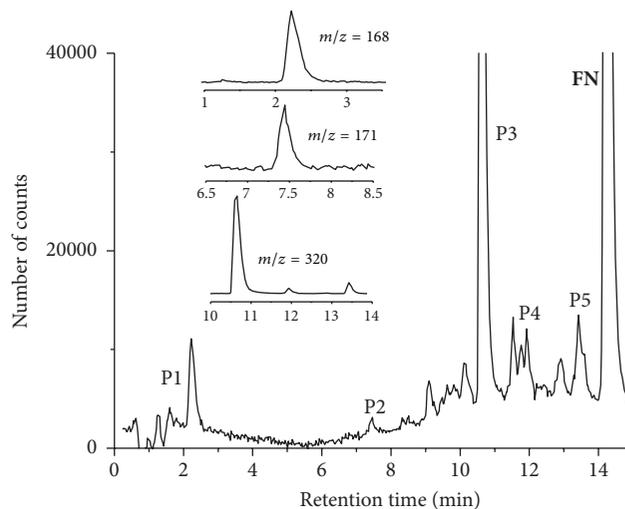


FIGURE 5: Total-ion chromatogram obtained with LC/ESI⁺ of an irradiated solution of FN ($1.0 \times 10^{-4} \text{ mol L}^{-1}$)/TiO₂ (1.0 g L^{-1}). Irradiation at 365 nm, pH = 5.2. The inset chromatograms correspond to the extracted spectra for a specific m/z value corresponding to $[\text{M}+\text{H}^+]$.

that hydroxyl radical is mainly involved in the photocatalytic process and is very reactive toward fenamiphos.

3.1. Laser Flash Photolysis Experiments. In order to evaluate the ability of hydroxyl radicals to oxidize fenamiphos we undertook laser flash photolysis experiments for the evaluation of the second order rate constant between $\bullet\text{OH}$ and FN. Within these experiments and with the aim of working with transparent media, the formation of hydroxyl radical was obtained from a selective excitation of iron(III) aqua complex, $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, as largely reported in the

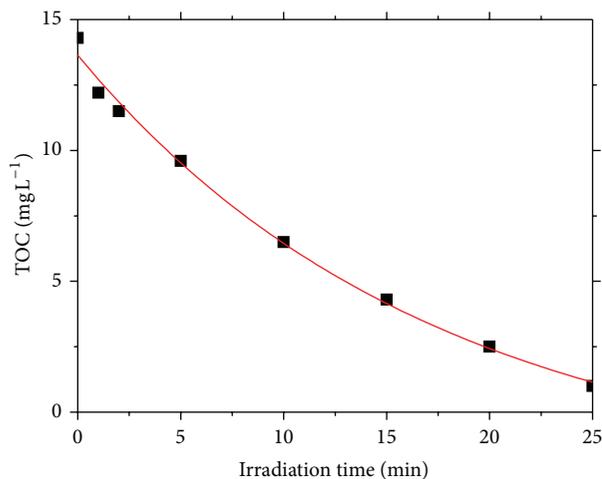
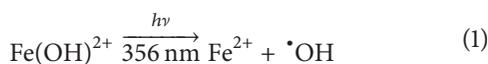


FIGURE 6: TOC evolution as a function of irradiation time. $[\text{FN}] = 1.0 \times 10^{-4} \text{ mol L}^{-1}$, TiO_2 at 1.0 g L^{-1} , $\lambda_{\text{excitation}} = 365 \text{ nm}$ aerated conditions.

literature [21–24]. The excitation of the iron(III) complex leads to an electron transfer process from the ligand ^-OH to the metal (MLCT) leading to the formation of iron(II) and $^{\bullet}\text{OH}$ with a quantum yield that was estimated to 0.075 at 360 nm [25]:



where $\text{Fe}(\text{OH})^{2+}$ refers to $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$.

It should be pointed out that, under our experimental conditions, the control experiments clearly showed that no thermal reaction or interaction was present when FN was mixed with the iron complex.

Upon laser excitation at 355 nm of an aerated aqueous solution of the iron(III) complex alone ($3.0 \times 10^{-4} \text{ mol L}^{-1}$), a bleaching was observed within the range at 320–400 nm (Figure 3(a)). This is owing to the photochemical disappearance of the iron complex in its ground state according to (1). However, in the presence of FN, an increase of the absorbance is clearly seen within the same wavelength region indicating the formation of a transient species **T** (Figure 3(b)). Such intermediate was not observed when isopropanol (0.1%) is present in the solution demonstrating the involvement of the hydroxyl radical in the process leading to its formation. The comparison with the laser flash photolysis results obtained for other aromatic compounds [26–28], **T**, may be assigned to the adduct $^{\bullet}\text{OH-FN}$ as shown in Scheme 2.

As clearly observed in Figure 3(b), the formation of $^{\bullet}\text{OH-FN}$ was perfectly fitted using a pseudo first order kinetics equation. Under our experimental conditions, namely, $[\text{FN}] = 3.5 \times 10^{-4} \text{ mol L}^{-1}$, the observed rate constant was estimated to $k_{\text{obs}} = 2.7 \times 10^6 \text{ s}^{-1}$. This observed rate constant varied linearly with the concentration of fenamiphos as shown in Figure 4. The second order rate constant for the reaction hydroxyl radical/FN (Scheme 2) was determined from the slope of the linear plot $k_{\text{obs}} = f([\text{FN}])$. It was

TABLE 1: The effect of oxygen concentration, isopropanol, and humic substance (HS) on the photocatalytic disappearance of fenamiphos, $[\text{FN}] = 3.0 \times 10^{-5} \text{ mol L}^{-1}$, TiO_2 : 1.0 g L^{-1} , $\lambda_{\text{excitation}} = 365 \text{ nm}$.

Conditions	$k, \text{ min}^{-1}$	Conditions	$k, \text{ min}^{-1}$
Aerated	7.4×10^{-2}	HS 0.2%	8.5×10^{-2}
Deaerated	0.02×10^{-2}	HS 1%	5.5×10^{-2}
Oxygenated	23.0×10^{-2}	HS 2%	2.5×10^{-2}
Isopropanol 0.1%	No disappearance		

estimated to $7.3 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$ indicating an efficient oxidation of FN by hydroxyl radicals species.

3.2. Photoproducts Analysis. The analysis of the products formed upon photocatalysis of FN by TiO_2 was performed using LC/MS experiments. The total-ion chromatogram was undertaken using electrospray ionisation source in positive mode (ESI^+). Figure 5 reports the TIC chromatogram for an irradiated mixture of FN ($1.0 \times 10^{-4} \text{ mol L}^{-1}$)/ TiO_2 (1.0 g L^{-1}) recorded after 25% conversion extent. It revealed the formation of several byproducts (P1 to P6) which present short retention times when compared to that of FN ($t_{\text{ret}} = 14.2 \text{ min}$) indicating the presence of small or more polar compounds. Their amounts increased with irradiation time and most of them are primary products since they were observed from the early stages of the photocatalytic process.

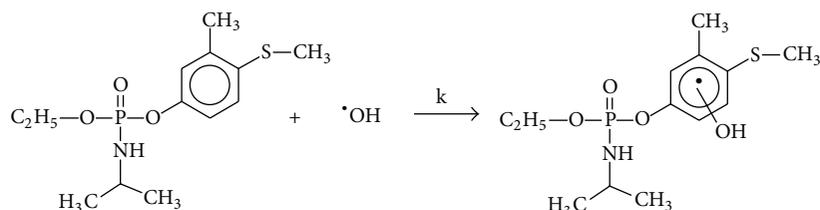
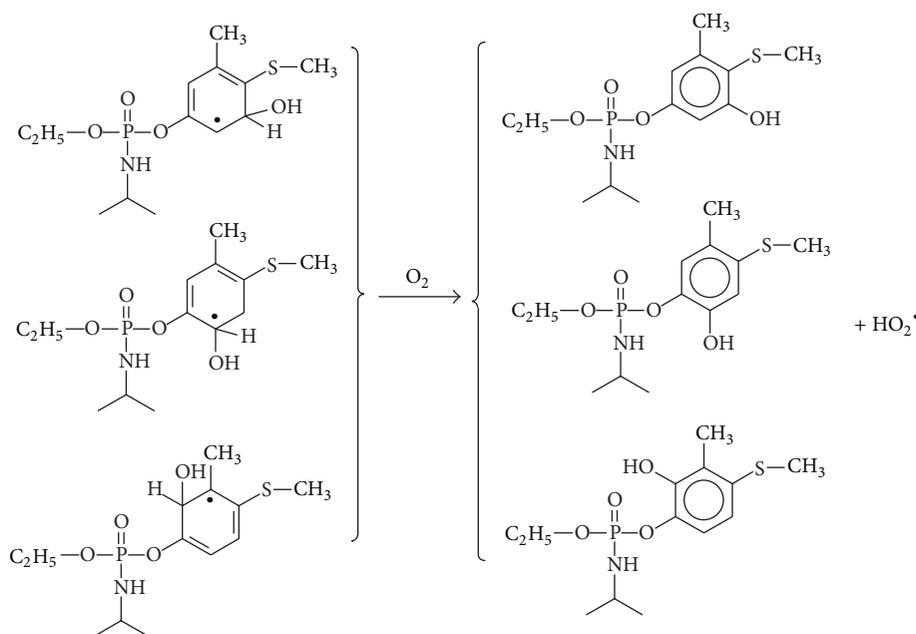
As clearly shown in the inset of Figure 5, indicating some extracted m/z value, the following data results were obtained: $m/z = 168$ at $t_{\text{ret}} = 2.2 \text{ minutes}$, $m/z = 171$ at $t_{\text{ret}} = 7.5 \text{ minutes}$, and $m/z = 320$ at three different retention times $t_{\text{ret}} = 10.7 \text{ min}$, 11.9 min and 13.4 min . This latter result clearly indicates the formation of three different isomers. One of them, namely, at $t_{\text{ret}} = 10.7 \text{ min}$, appears to be a dominant compound. The proposed structures for all detected products are presented in Table 2.

All the observed products are due to the reactivity of the hydroxyl radical with FN. Their formation was totally inhibited in the presence of isopropanol, used as hydroxyl radical trap. From the laser flash photolysis experiments as well as from the product analysis, it is clear that the adduct $^{\bullet}\text{OH-FN}$ is the precursor for the formation of all the detected products.

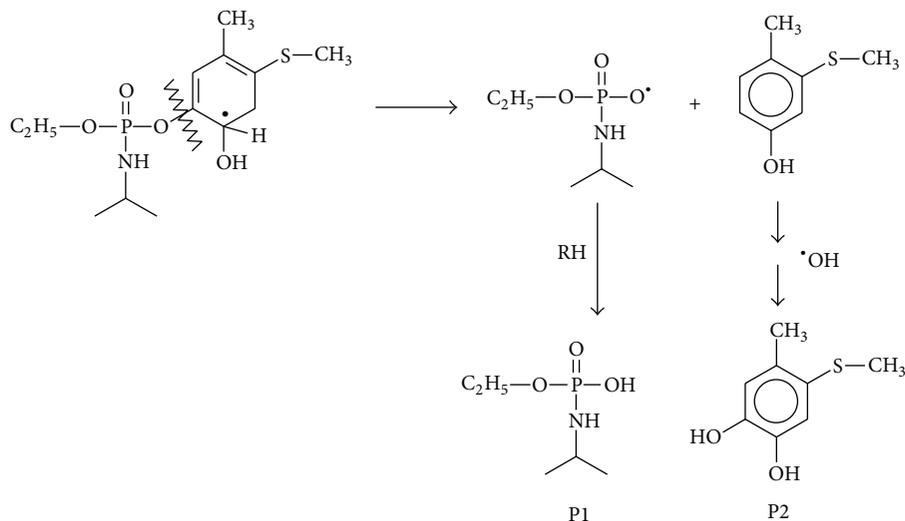
The addition of the hydroxyl radical on the aromatic moiety may occur on the three free positions leading to the formation of the hydroxylated compounds (P3, P4, and P5). This involves, in the presence of oxygen, the elimination of the hydroperoxide radical, HO_2^{\bullet} , as shown in the following scheme (Scheme 3).

The formation of the Products P1 and P2 involves the homolytic scission of the C–O bond from the adduct $^{\bullet}\text{OH-FN}$ as shown in Scheme 4. The intermediate product, X, was not observed under our experimental conditions more likely owing to its rapid oxidation by hydroxyl radical.

3.3. Mineralization. The mineralization of fenamiphos was studied by following the evolution of the total organic carbon (TOC) under illumination using a suntest setup ($\lambda > 295 \text{ nm}$)

SCHEME 2: Mechanistic scheme for the formation of the adduct $\bullet\text{OH-FN}$.

SCHEME 3: Formation of the hydroxylated compounds.

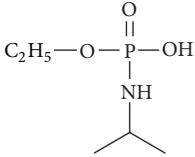
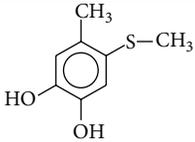
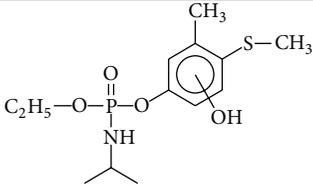
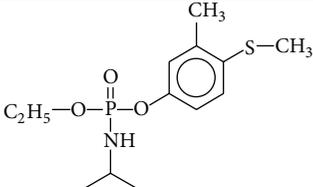


SCHEME 4: Formation of P1 and P2.

of the mixture FN ($1.0 \times 10^{-4} \text{ mol L}^{-1}$)/ TiO_2 (1.0 g L^{-1}). Owing to the high light intensity and the efficient photocatalytic process, as shown from the kinetic measurements, the decrease of TOC was observed from early stages of the irradiation and without any significant induction period. The

complete abatement was obtained within 25 hours irradiation time under our experimental conditions (Figure 6). This clearly demonstrates that fenamiphos together with its byproducts are efficiently oxidized by hydroxyl radical through the excitation of titanium dioxide.

TABLE 2: Proposed structures for the byproducts as obtained by LC/ESI⁺.

Product	Retention time, min	[M + H ⁺] m/z	Proposed molecular structure
P1	2.2	168	
P2	7.5	171	
P3, P4 and P5	10.7; 11.9; 13.4	320	 The three isomers may correspond to the three free positions on the aromatic ring
FN	14.2	304	

4. Conclusion

The photocatalytic degradation of fenamiphos (FN) has been examined using titanium dioxide P25 (DEGUSSA) and 365 nm as the excitation wavelength. This photocatalyst permitted a very efficient degradation and the total disappearance of fenamiphos was obtained within 100 minutes irradiation time. The primary step involves the formation of the adduct [•]OH-FN that leads to the formation of byproducts whose structures were proposed using LC/MS data. The transformation of fenamiphos involved C–O bond scission and hydroxylation of the aromatic moiety. TOC experiments show an efficient mineralisation by using a simulated solar light from a suntest setup.

Acknowledgments

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