

Photocatalytic removal of the insecticide fenitrothion from water sensitized with TiO₂

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Abstract

The photocatalytic removal of the insecticide fenitrothion (IUPAC name: *O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate), C₉H₁₂NO₅PS, from water suspension of TiO₂, was investigated by following the disappearance of the original substance along with the formation and disappearance of intermediates via recording NMR (¹H and ³¹P) and UV spectra, as well as by pH measurements. Based on the obtained data, a possible reaction mechanism was proposed. It was found that ³¹P-NMR spectrometry can be successfully used to follow the kinetics of transforming organic into inorganic phosphorus in the course of the degradation ($k_a = 9.2 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}$, $r = 0.980$ for the illumination period after 15 h). The rate of fenitrothion aromatic ring decomposition was followed by UV spectrometry during the illumination ($k_a = 3.1 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$, $r = 0.989$). The complete mineralization was attained after about 66 h of irradiation.

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1. Introduction

It is known that pesticides have a significant role in modern agriculture because of their efficient action in plant protection [1]. Among them, organophosphorous insecticides have been widely used as an alternative to organochlorine compounds for pest control. However, most of them are highly toxic, can exhibit chemical stability and resistance to biodegradation [2–4] and, because of the probability of their being discharged into aquatic systems, great attention has to be paid to their degradation, to diminish their harmful effects on the environment. Of different innovative methods, heterogeneous photocatalysis with TiO₂ as semiconductor (which is non-toxic, stable to photocorrosion and cheap) appeared to be a very efficient procedure not only for destroying but also in majority of cases for complete mineralization of organic pollutants in water, including pesticides [5–9].

Recent literature data concerning photocatalytic degradation of some organophosphorous insecticides have been mainly related to the degradation kinetics and identification of byproducts [2,10–14]. All these studies were based on the use of liquid-liquid extraction or solid-phase extraction in combination with gas chromatography and solid-phase microextraction.

The present photocatalytic degradation study involves the application of NMR and UV spectrometries as analytical methods for the investigation of the photocatalytic activity of aqueous suspension of TiO₂ towards the decomposition of insecticide fenitrothion present in water at low concentration (higher than acute toxicity for fish—for example, LC₅₀ (48 h) for carp is 4.1 mg dm⁻³ [1]). Fenitrothion (*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate) was chosen as a model compound of a waste photodegradable substance in water in view of its wide use all over the world. Because of its partial solubility in water ($7 \times 10^{-5} \text{ mol dm}^{-3}$), it can penetrate to deep soil strata and reach the groundwater [15]. The harmful effect of this compound comes from the fact that when resorbed in the organism it irretrievably inhibits serine-dependent enzymes such as acetylcholinesterase [16]. Continuing on our previous investigation [17–19], the objective of this work was to study the reaction kinetics and the nature of intermediates involved and, consequently, to propose a probable mechanism of fenitrothion photodegradation.

2. Experimental

The insecticide fenitrothion (95% purity), dissolved in xylene, was obtained from the Chemical Factory “Župa”

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Kruševac (Yugoslavia). The commercial product was purified by evaporating xylene by vacuum distillation on a rotary evaporator (codistillation with chloroform) and its purity was controlled by measuring the index of refraction on an Abbe refractometer (Jena, Carl Zeiss) and confirmed by $^1\text{H-NMR}$ spectrometry (Bruker AC-250). On the basis of the refractive index of the purified fenitrothion (n_D at 20°C was 1.5480) and the literature value (n_D at 20°C 1.5528) the fenitrothion purity was estimated to be 99.7%.

All the experiments were carried out using 2 mg cm^{-3} suspensions of TiO_2 (Degussa P-25, predominantly anatase, specific area: $50\text{ m}^2\text{ g}^{-1}$, non-porous). Solutions were prepared in doubly distilled water or in D_2O for NMR experiments. Suspensions of TiO_2 containing the emulsion of fenitrothion ($\sim 7\text{ mmol dm}^{-3}$, lower initial concentrations were inadequate for NMR measurements) were sonicated for 15 min before illumination, to make the TiO_2 particles uniform. The photochemical cell (sample volume: 20 cm^3 , continuously flushed with O_2) was made of Pyrex glass with a plain window (on which the light beam was focused), equipped with a magnetic stirring bar, a water circulating jacket, and two openings: for O_2 stream and taking sample for NMR measurements. The process was carried out at a temperature of $40 \pm 1^\circ\text{C}$. A 125 W mercury lamp (Philips, HPL-N) was employed as the radiation source. During irradiation, the mixture was stirred at a constant speed.

For spectrophotometric measurements at different times of illumination, 0.18 cm^3 samples were taken and diluted to 10 cm^3 with doubly distilled water. After that, an inert electrolyte was added to the diluted sample to accelerate

TiO_2 precipitation and then centrifuged to remove the precipitated TiO_2 . UV spectra of the obtained clear solutions were recorded on a Specord UV-Vis (Jena, Carl Zeiss) spectrophotometer.

The change of pH values during the photodegradation was measured continuously with the aid of a combined glass electrode connected to a pH-meter ("Iskra" MA5706) and recorded by means of a chart recorder (Goerz-Electro Servogor Sb RE 647.9).

In the course of photodegradation, 0.5 cm^3 samples were taken for NMR analysis. The ^{31}P - and $^1\text{H-NMR}$ spectral profiles were monitored at different illumination times in the presence of TiO_2 particles.

3. Results and discussion

The photoexcitation of TiO_2 taking place under irradiation with the light of energy greater than its band gap, generates an electron-hole pair, creating the possibility for both reduction and oxidation processes to occur at the surface of the semiconductor. The valence band holes can be used to oxidize H_2O molecules and OH^- ions adsorbed on the photoexcited TiO_2 to hydroxyl radicals. Although a number of possible decomposition pathways can be envisioned, the formation and subsequent reactions of hydroxyl radicals, being a very strong oxidizing agent (standard redox potential: 2.8 V [20]), are generally accepted as the predominant degradation pathways of organic substrates in oxygenated aqueous solutions. Thus, it has been reported that in the

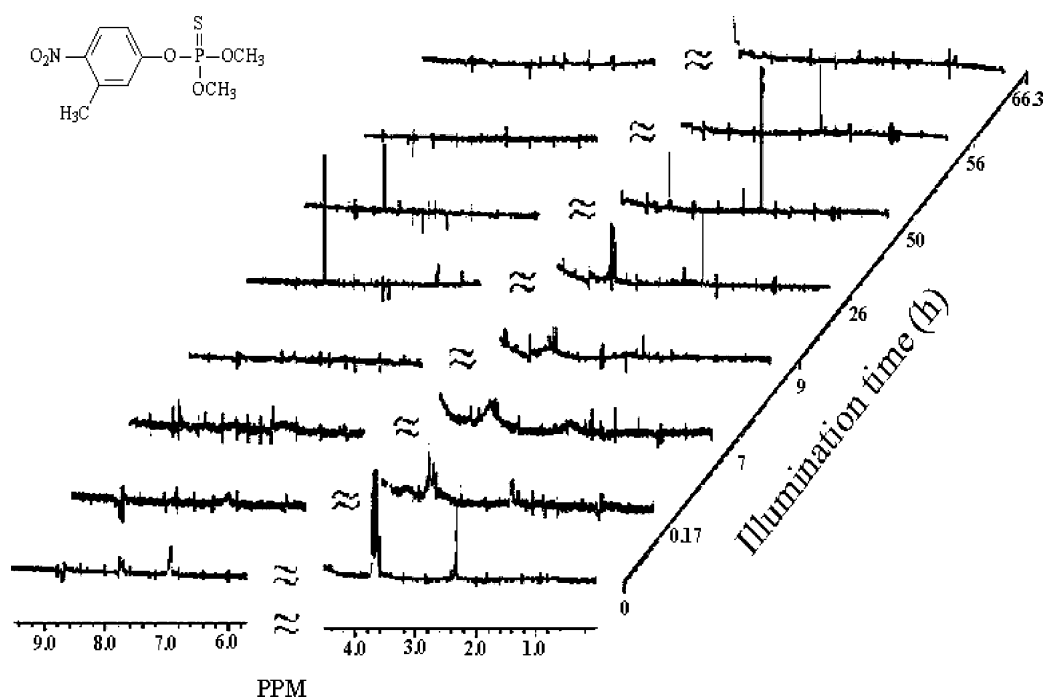


Fig. 1. Temporal $^1\text{H-NMR}$ spectral profiles recorded during the decomposition of fenitrothion ($\sim 7\text{ mmol dm}^{-3}$) in D_2O solution in the presence of TiO_2 (2 mg cm^{-3}).

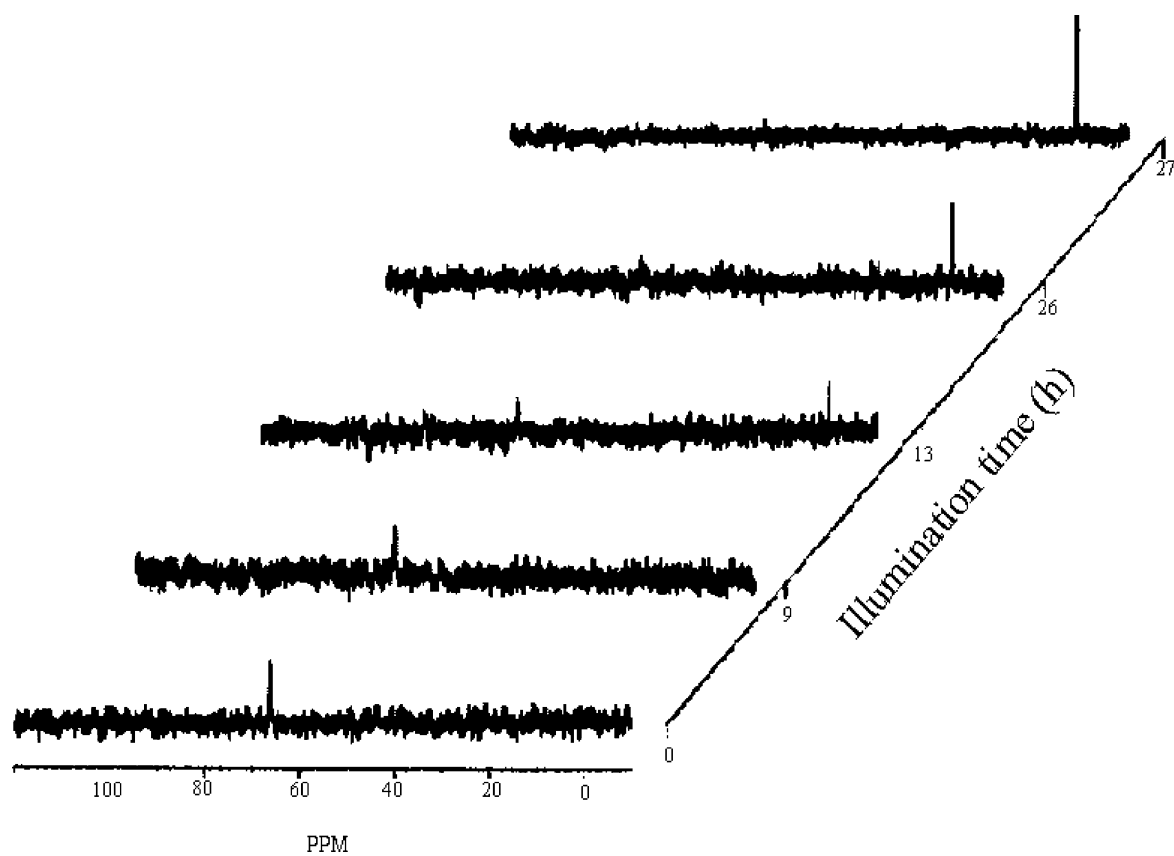


Fig. 2. Temporal ^{31}P -NMR spectral profiles recorded during the decomposition of fenitrothion ($\sim 7 \text{ mmol dm}^{-3}$) in D_2O solution in the presence of TiO_2 (2 mg cm^{-3}).

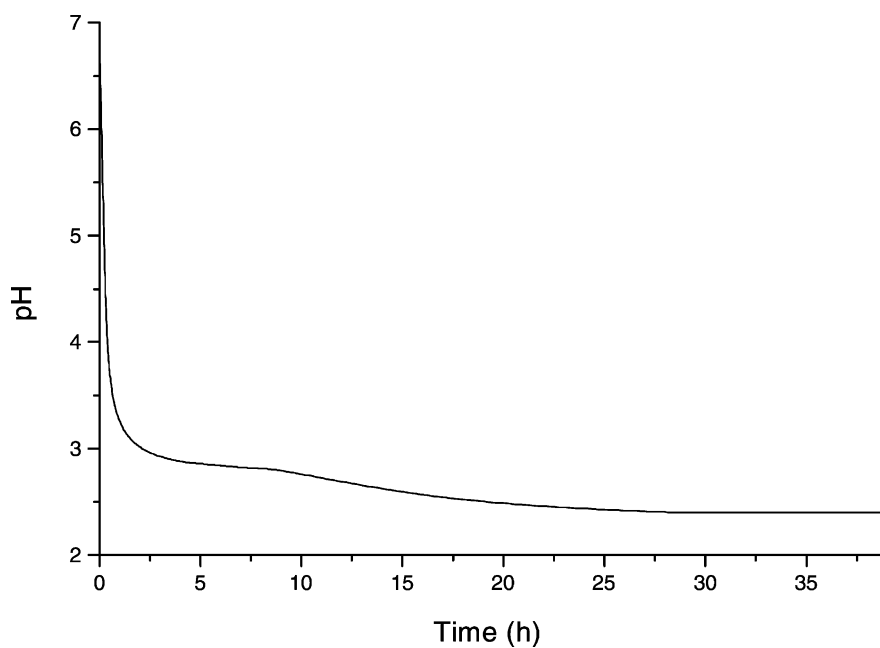


Fig. 3. Changes of pH during fenitrothion photodegradation.

majority of cases aromatic compounds with hetero atoms undergo complete mineralization to CO_2 , H_2O and corresponding inorganic species [21].

The photoassisted oxidative decomposition of fenitrothion in the presence of TiO_2 involves formation of a variety of intermediate species, whose temporal ^1H - and ^{31}P -NMR spectra are presented in Figs. 1 and 2. The ^1H -NMR signals (D_2O , δ (ppm)) of parent substance were: 2.31 (3H, s, $\text{CH}_3\text{-Ar}$); 3.66 (6H, d, $^3J_{\text{H,P}} = 14\text{ Hz}$, 2OCH_3); 6.80, 6.90 and 7.75 (3H, m, H-Ar), as well as the septet signal of the ^{31}P -NMR spectrum (66.04 ppm with $^3J_{\text{H,P}} = 14\text{ Hz}$). The signals of parent substance after 10 min of illumination showed a decrease, to disappear altogether after 27 h. After 7 h of illumination, two new signals of the degradation product appeared: singlet at 2.08 ppm that can be ascribed to the CH_3 group from acetic acid, and singlet at 8.23 ppm belonging to formic acid. These signals show a visible increase after 9 h of irradiation and reach a maximum for formic and acetic acid after 26 and 50 h, respectively. Formic acid, which is formed from OCH_3

groups, disappears after 56 h of illumination, and acetic acid (formed from the aromatic ring) disappears after 66 h (Fig. 1), which can be denoted as full photodegradation of the all intermediates. The septet signal in the ^{31}P -NMR spectrum (66.04 ppm, $^3J_{\text{H,P}} = 14\text{ Hz}$) belonging to organic phosphorus did not change significantly its intensity to 9 h of illumination. Only its multiplicity deformation and broadening were observed, which was a consequence of degradation of the original substance and appearance of new forms of organic phosphorus, which, being of very similar structure, exhibit approximately identical chemical shifts. This was also supported by the fact that significant increase in the intensity of the formic acid signal was also observed after 9 h of illumination, and this preceded the appearance of phosphate. Not until 9 h of illumination there appeared a new singlet signal at 0.78 ppm that could be ascribed to the phosphate ion. Taking into account that at this time of irradiation the pH value of the medium was 2.8 (Fig. 3) it can be concluded that about 80% of phosphate ions were in the form of H_2PO_4^- , the rest being in the form of H_3PO_4 .

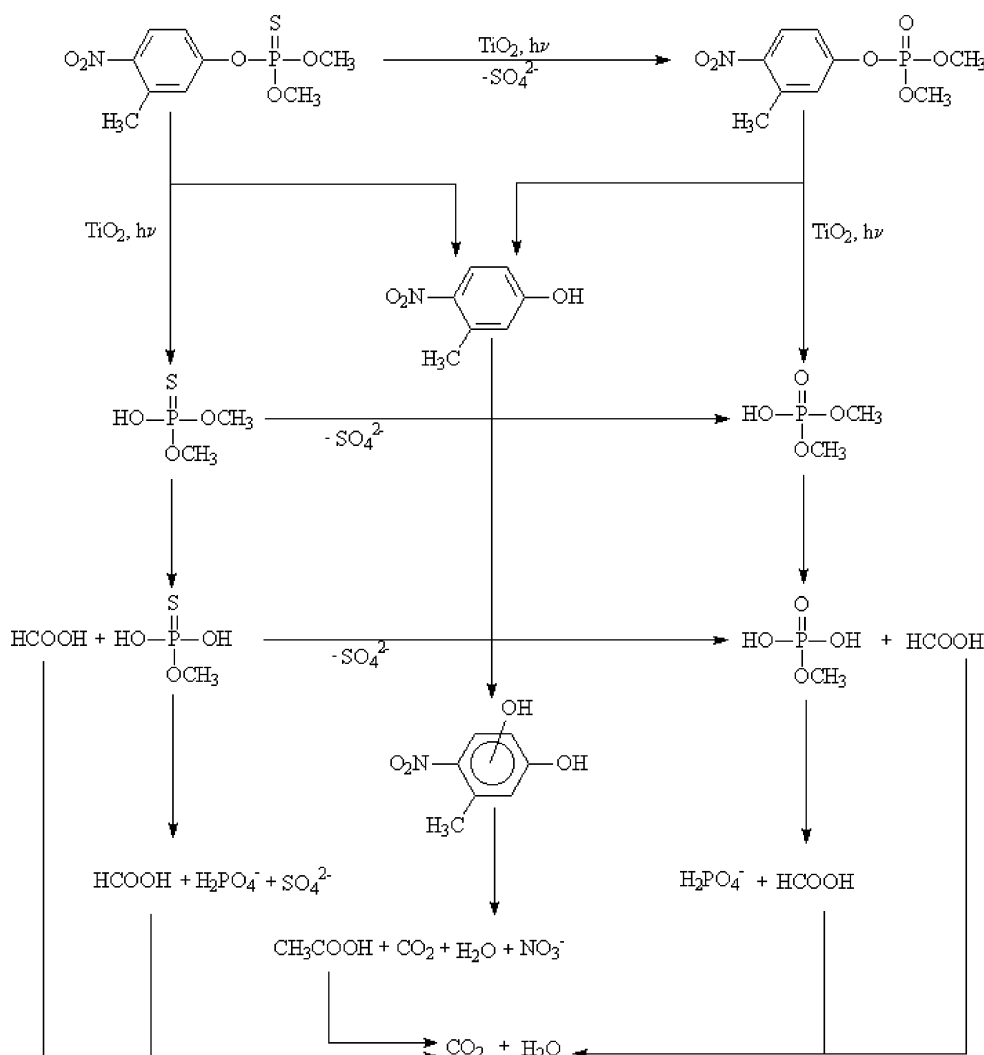


Fig. 4. Possible pathways of fenitrothion photodegradation in the presence of TiO_2 .

Taking into account the nature of some of the observed species and the rate of their disappearance, as well as the literature data [12,14], we proposed a probable scheme of fenitrothion degradation presented in Fig. 4. As can be seen, two possible degradation pathways are proposed: the first yields substitution of the S atom by O atom, whereas the second one proceeds in the direction of breaking the ester bond between the dimethyl ester of thiophosphoric acid and phenolic moiety of the molecule. After the S substitution, the first pathway becomes similar to in a the second one, i.e. the disruption takes place of the ester bond between phosphoric acid dimethyl ester and the phenolic part of the molecule. The phenolic moiety, by a successive substitution of H atoms from the ring by OH groups is transformed into a polyhydroxylic phenol that readily undergoes ring opening and further degradation to acetic acid, water, and nitrogen-involving inorganic ion (predominantly in the form of NO_3^- [12]). By a further action of OH radicals, acetic acid is decomposed into CO_2 and H_2O . On the other hand, the dimethyl ester of thiophosphoric acid can degrade in the direction of replacement of the S atom with O atom or in the direction of oxidation of one methoxy group to formic acid and methyl ester of thiophosphoric acid. The latter can undergo further substitution of S with O atom and oxidation of the other methoxy group to formic acid and dihydrogen phosphate. Similar degradation can also undergoes dimethyl ester (i.e. methyl ester) of phosphoric acid and the overall degradation yields dihydrogen phosphate and two molecules of formic acid. By a further oxidation, formic acid is decomposed into CO_2 and H_2O .

The kinetic curves of transforming organic phosphorus into the inorganic one (Fig. 5) and possible adsorption of the products formed (induction period) were obtained on the basis of ^{31}P -NMR spectral profiles. However, it should be pointed out that the species adsorbed on the semiconductor surface hinder photooxidation process [22,23]. On the basis of the linear segment of the curve for the degradation of organic phosphorus after 15 h of illumination, it was estimated that the mentioned transformation follows the zeroth-order kinetics, with a mean $k_a = 9.2 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}$ ($r = 0.980$).

In addition to ^1H - and ^{31}P -NMR spectrometry the degradation of fenitrothion molecule was also followed by potentiometric measurements of the solution pH during illumination. As is evident from Fig. 3, already after about first 30 min the medium attains a pH value of about 3.3. The abrupt decrease of the pH value can be probably ascribed to the oxidation of the hetero atoms (N and S) involved in the fenitrothion molecule and their transformation to nitrate and sulfate [12].

It was found that in the range from 200 to 300 nm, the UV spectra of the investigated compound have two distinct absorption maxima. The absorption maximum at the lower wavelength can be assigned to the nitro group of the original compound and the one at the higher wavelength to the aromatic ring. In the course of illumination, both absorption maxima show a decrease (Fig. 6), which indicates the destruction of the fenitrothion. The changes in concentration of aromatic ring during illumination are presented in Fig. 7. This curve was used to follow the

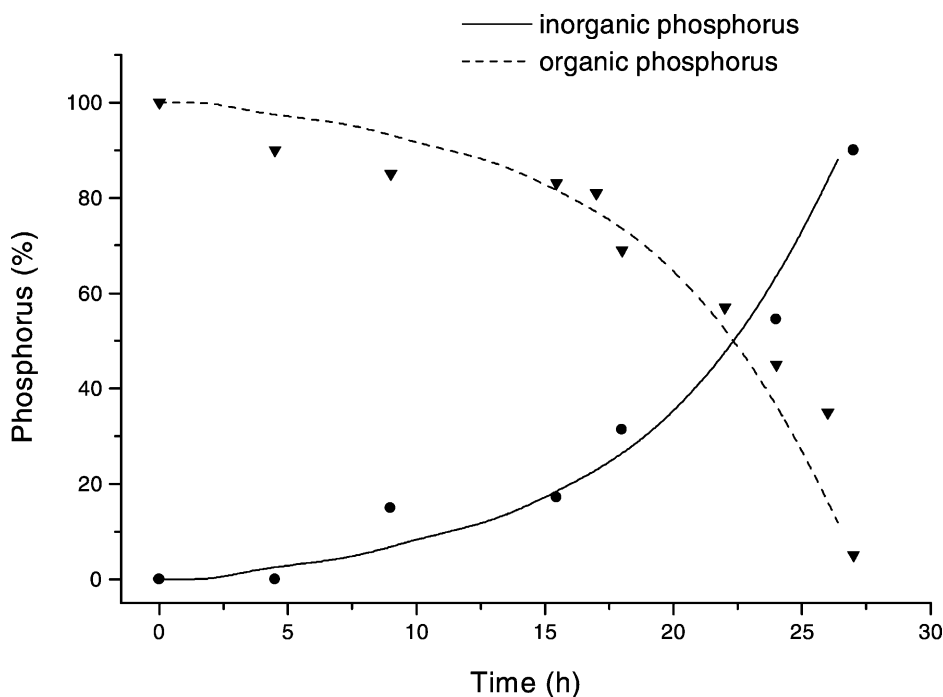


Fig. 5. Kinetics of transformation of the organic phosphorus from fenitrothion into inorganic form.

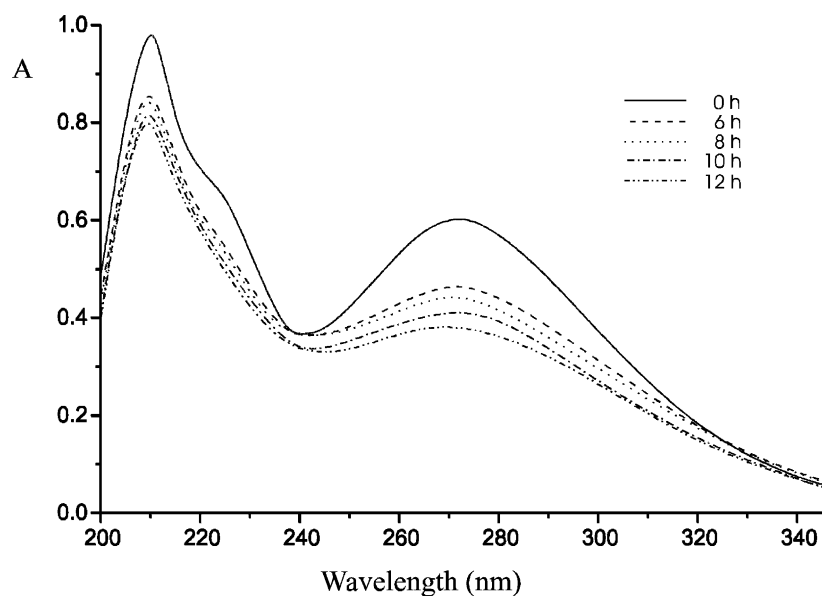


Fig. 6. Temporal UV spectral profiles recorded during fenitrothion photodegradation.

kinetics of the degradation of aromatic moiety during the photodegradation. It was found that the kinetics is characteristic of the zeroth-order reaction, which is in accordance with the Langmuir–Hinshelwood equation (the average value for the apparent reaction rate constant is $k_a = 3.1 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$, $r = 0.989$). The kinetic data thus obtained are complementary to those obtained by NMR spectrometry. The time needed for aromatic ring degradation calculated on the basis of this value of rate constant is in agreement with the time in which a maximum amount of acetic acid is obtained and which, as was

pointed out above, is obtained from the aromatic part of the molecule. The k_a values obtained in this work are in agreement with those reported for photodecomposition of herbicides mecoprop and MCPA [19,24].

Finally, it is evident that the photocatalytic degradation of fenitrothion in the presence of TiO_2 is an efficient method for its complete removal from water. The obtained results give good evidence that the rate of fenitrothion photodegradation can be successfully followed by ^1H - and ^{31}P -NMR spectrometric measurements in combination with monitoring pH and UV spectra.

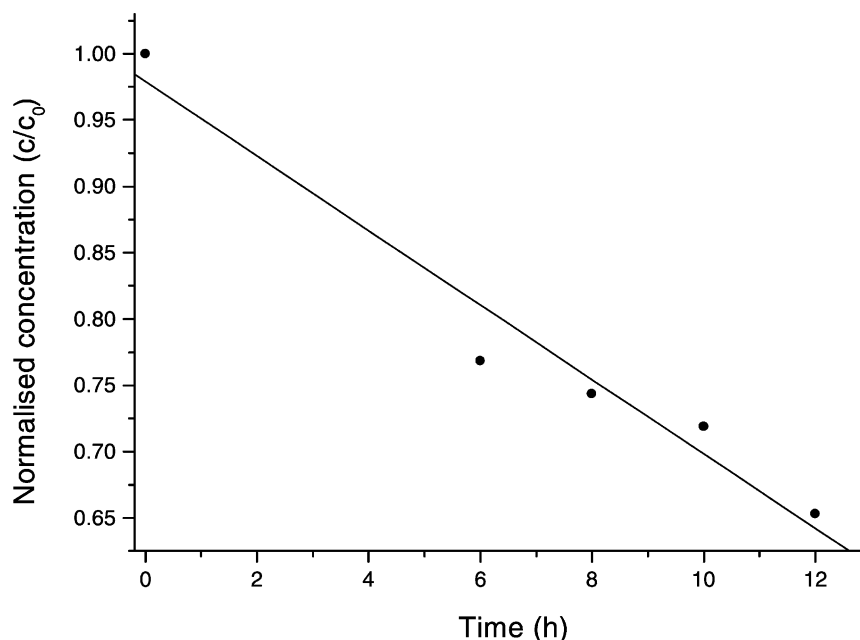


Fig. 7. Kinetics of decomposition of the aromatic moiety during fenitrothion photodegradation.

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