

Photocatalytic Degradation of the Insecticide Acetamiprid on TiO₂ Catalyst

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O trabalho está relacionado com a degradação fotocatalítica da acetamipride, uma base piridínica amplamente utilizada em inseticida neonicotinóides, em suspensões aquosas de O₂/TiO₂ irradiada por UV. A taxa de degradação foi estudada por HPLC/DAD e espectrofotometria UV. Verificou-se que a reação é de pseudo-primeira ordem, no intervalo de concentração de (0,5-2,0 mg cm⁻³). A análise de RMN de ¹H indicou que além do acetaldeído, ácido fórmico e acético, foram formados intermediários contendo piridina (por exemplo, o ácido 6-chloronicotínico). Medidas por CLAE/EM revelaram também a presença da degradação de aromáticos intermediários. Durante o processo fotocatalítico o pH sofreu alteração de três unidades, de 5 a 2. Em contraste com os resultados obtidos nas condições experimentais na degradação fotocatalítica, a acetamipride mostrou-se estável. Para ter uma visão específica do complexo processo fotocatalítico da acetamipride, a degradação fotocatalítica do ácido 6-chloronicotínico, também foi investigada o produto detectado da degradação da base piridínica.

The work is concerned with the photocatalytic degradation of acetamiprid, a widely used pyridine-based neonicotinoid insecticide, in UV-irradiated aqueous suspensions of O₂/TiO₂. The rate of degradation was studied by HPLC/DAD and UV spectrophotometry. It was found that the reaction in the investigated concentration range (0.5-2.0 mg cm⁻³) is of a pseudo-first order. The ¹H NMR analysis indicated that beside acetaldehyde, formic and acetic acid, pyridine-containing intermediates (e.g. 6-chloronicotinic acid) formed during the process. The HPLC/MS measurements also proved the presence of aromatic degradation intermediates. During the photocatalytic process the pH changed by even three units, from 5 to 2. In contrast to the photocatalytic results in the photolytic experimental conditions, acetamiprid appeared to be stable. To get a deeper insight into the complex photocatalytic process of acetamiprid, the photocatalytic degradation of 6-chloronicotinic acid, the detected pyridine-based degradation product, was also investigated.

Keywords: acetamiprid, 6-chloronicotinic acid, degradation, TiO₂ photocatalysis, water treatment

Introduction

The removal or mineralization of different persistent organic contaminants, such as industrial chemicals (textile dyes, surfactants), pharmaceuticals (antibiotics, steroids), antifouling compounds, and crop protection agents, is an area that has received extensive attention.¹⁻⁸ Apart from the frequently used biodegradation processes for wastewater treatment, aiming at the total mineralization of organic pollutants, advanced oxidation processes (AOPs) are of special importance. AOPs such as Fenton and photo-Fenton catalytic reactions,⁹⁻¹¹ the H₂O₂/UV process,¹² and TiO₂-mediated photocatalysis,¹³⁻¹⁸ have been studied under

a range of experimental conditions in order to reduce the toxicity of a variety of pollutants.

Neonicotinoids are one of the newer classes of synthetic systemic insecticides with worldwide use in the last three decades, accounting for 11-15% of the insecticide market. Thanks to their specific action on the postsynaptic nicotinic acetylcholine receptors of the insect's central nervous system, they are recommended as substitutes for some organophosphate and carbamate agents.¹⁹ Because of their widespread use, these compounds are increasingly present in the environment. Numerous literature reports have been published concerning the oxidation and hydrolysis of some pyridine-based members of this group, the majority of them being devoted to imidacloprid. As observed by Zheng and Liu,²⁰ the persistence of imidacloprid is primarily

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determined by the pH and temperature. Moza *et al.*²¹ investigated the photolytic degradation of imidacloprid and found that the irradiation at 290 nm resulted in 90% substrate transformation in 4 h. A progressive photocatalytic oxidation of imidacloprid in aqueous solution over TiO₂ was reported by Malato *et al.*²² These authors have designed a pilot plant for photocatalytic degradation of different pesticides, including imidacloprid.^{23–25} Krohn reported that thiacloprid was stable in water between pH 5.0–9.0 for a relatively long period of time.²⁶ Černigoj *et al.*²⁷ studied the photocatalytic degradation of thiacloprid and imidacloprid in the presence of O₂, O₃ and TiO₂.

Although acetamiprid, known also by its commercial formulations as “Volley”, “Mospilan”, “Assail”, “Pristine”, “Rescate” and “Saurus”, is one of the most widely used neonicotinoids, its photocatalytic degradation has been less frequently investigated.^{28,29} As a continuation of our investigations in the area of the stability of selected neonicotinoids,³⁰ in this work we elaborated the photocatalytic degradation of acetamiprid (E-*N*¹-[(6-chloro-3-pyridyl)methyl]-*N*²-cyano-*N*¹-methylacetamide, Figure 1(a) on a widely used TiO₂ (Degussa P-25) catalyst in the presence of O₂, including the reaction kinetics and the detection of some intermediates. To get a deeper insight into the understanding of the degradation of this insecticide, we have also studied the photocatalytic degradation of 6-chloronicotinic acid, 6-CNA (6-chloropyridine-3-carboxylic acid, Figure 1(b), a compound with an aromatic structure similar to the investigated one, and which is known from the literature as the last stable product in the degradation chain of imidacloprid.²⁴

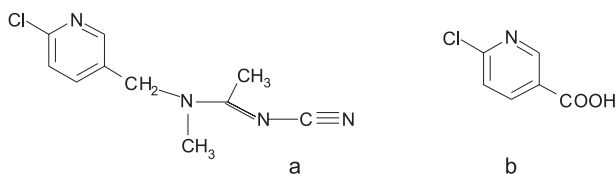


Figure 1. Acetamiprid and 6-CNA.

Experimental

Chemicals and solutions

All chemicals used were of analytical reagent grade. The investigated compounds were acetamiprid (Dr Ehrenstorfer GmbH, Germany, purity 99.0%) and 6-CNA (Fluka, Germany, purity > 95.0%). For the identification of intermediates, apart from, 6-CNA, formic acid (Zorka, Serbia, *p.a.*), acetic acid (Zorka, Serbia, *p.a.*) and acetaldehyde (Centrohém, Serbia, *p.a.*) were used.

Acetamiprid solutions for photocatalytic/photolytic investigations were prepared in D₂O for ¹H NMR and double-

distilled water in all other investigations and the applied concentrations covered a relatively high concentration range from 0.5 to 2.0 mg cm⁻³, suitable for direct ¹H NMR measurements without an additional preparation of the samples. For the photocatalytic investigations the aqueous suspension contained, also 2.0 mg cm⁻³ of the TiO₂ (Degussa P-25) catalyst.

HPLC-grade acetonitrile was purchased from J. T. Baker (Mailinckrodt Baker B. V., Neerland) and phosphoric acid (85%) from Centrohém (Serbia). LC-grade water was produced using a Milli-Q water purification system (Millipore Corporation, USA).

Apparatus

The photochemical cell (sample volume 30.0 cm³) was made of Pyrex glass with a plain window (on which the light beam was focused), magnetic stirring bar, water circulating jacket, and openings for O₂ stream and sampling. The samples were irradiated with a 125 W mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335 and 366 nm, maximum emission at 366 nm), using an appropriate concave mirror.

The NMR spectrometric measurements were performed on a Bruker AC-250 instrument (Bruker, Germany) with standard Bruker software. All measurements were carried out using regular 5 mm NMR tubes. Standard pulse sequences were used in the NMR experiments. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. The D₂O was used for lock and reference to sodium salts of 3-trimethylsilyl-1-propane sulfonic acid (DSS, $\delta_{\text{H}} = 0.00$ ppm). For recording ¹³C NMR spectra, CDCl₃ (Merck, Germany, purity 99.8%) was used. In this case samples were prepared in distilled water, which was followed by the pre-concentration reconstitution step (see Analytical procedures).

Spectrophotometric measurements were performed on an ANTHELIE Data UV-Vis (SECOMAM, France) single-beam spectrophotometer with a fixed slit width (2 nm), quartz cuvette of 1 cm, and furnished with computer-loaded ANTHELIE Data software.

Chromatograms were recorded on an Agilent 1100 series liquid chromatograph (Agilent Technologies Inc., USA) with the use of an Agilent ODS-C18 column (4.6 mm × 150 mm, 5 μ m) and Agilent 1100 diode-array detector (DAD) and on an Agilent 1200 series liquid chromatograph with Zorbax-C18 rapid resolution cartridge column (2.1 mm × 30 mm, 3.5 μ m) and 6410 Triple Quad LC/MS detector.

The pH measurements were made using a combined glass-calomel electrode (Iskra, Slovenia) on a previously calibrated pH-meter (Radiometer, Netherlands).

Photodegradation

Aqueous suspensions of TiO₂ were sonicated before irradiation. The process of photocatalytic/photolytic degradation was conducted under controlled conditions at 43 °C with constant stirring and O₂ bubbling through the solution. Samples for analysis were taken at 10, 15 or 30 min. intervals. All experiments were carried out in triplicate.

Analytical procedures

Optimal experimental conditions for ¹H NMR: temperature of NMR samples 23 °C, relaxation delay 0.5 s, data points 32 K, time domain 32 K, receiver gain 4, number of dummy scans 2, pulse width 2.0 μs, acquisition time 3.28 s, spectral width 5000 Hz (with digital resolution (HZ/PT) 0.318 Hz/number of points), line broadening 0.2. The number of scans was 256. The dynamics of the photocatalytic degradation of the investigated compounds was monitored by determining the rate of decrease of the characteristic ¹H NMR signals. For the ¹³C NMR identification of the quaternary carbon atoms the J-modulated spin echo technique (APT) was used. For these measurements (initial acetamiprid concentration 4 mg cm⁻³) aliquots of 5.00 cm³ were taken periodically, filtered through Hewlett Packard 0.22 μm syringe filters, and evaporated to remove solvents. The residues were reconstituted into 0.50 cm³ deuterio-chloroform.

For spectrophotometric measurements, aliquots of 0.30 cm³ of the reaction mixture, taken at regular time intervals, were diluted to 25.0 cm³. The solutions containing TiO₂ were filtered through Hewlett Packard 0.22 μm syringe filters and their spectra were recorded in the wavelength range from 200 to 360 nm. The kinetics of the degradation was monitored at 245 nm with baseline correction.

For the HPLC/DAD analysis, sample aliquots of 0.30 cm³ were taken periodically and diluted to 25.0 cm³. These solutions were filtered through Hewlett Packard 0.22 μm syringe filters. The mobile phase was a mixture of water (containing 0.2% phosphoric acid) and acetonitrile (85:15, v/v). The separation was performed at isocratic regime, with the eluent flow rate of 1.0 cm³ min⁻¹ and stabilized column temperature of 25 °C. Aliquots of 20.0 μL were manually injected through an injection loop and the acetamiprid signal was detected at 245 nm. Concentrations of acetamiprid were determined from the area of the peak at t_r = 11.44 min. In the case of model solutions of 6-CNA, this compound had the peak at t_r = 7.89 min, and was measured at 224 nm. For the HPLC/MS measurements the mobile phase was a mixture of water (containing 1% formic acid)

and acetonitrile (85:15, v/v). The fragmentor (extraction voltage) of the MS detector was optimized at 80 V. The nitrogen drying gas flow rate and nitrogen nebulizer gas pressure were 9 dm³ min⁻¹ and 40 psi, respectively. The scan range 40 to 400 m/z, scan speed 2.85 s/cycle.

Changes in the pH during the degradation were monitored at defined time intervals, without sample filtering, using a combined electrode connected to a pH-meter.

Results and Discussion

The photo-assisted oxidative degradation of acetamiprid in the presence of TiO₂ involves the formation of a variety of intermediate species. The time-dependent ¹H NMR spectral profiles of the reaction mixture are presented in Figure 2.

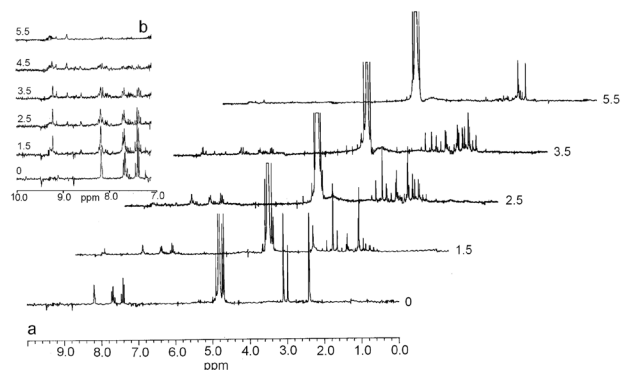


Figure 2. Time-dependent ¹H NMR spectral profiles of the photo-oxidative decomposition of acetamiprid (2.0 mg cm⁻³) in D₂O solution in the presence of TiO₂ (a). The inset shows aromatic proton signals (b). The numbers on each line represent the irradiation time in h.

As can be seen, the degradation is moderately fast: approximately 95% of the parent substance signals [δ_{H} (ppm): 2.37 (s, 3H, CCH₃) 3.07 (s, 3H, NCH₃), 7.38 (d, 1H, ³J 7.5 Hz, H-5), 7.65 (dd, 1H, ³J₁ 8.2 Hz, ³J₂ 2.5 Hz, H-4), 8.18 (d, 1H, ³J 2.5 Hz, H-2)] reduced substantially after 4.5 h, to disappear altogether after 7 h of irradiation. The signals of methylene protons (NCH₂) overlapped with the HOD signals from D₂O, which hindered their monitoring during the degradation process. In accordance with previous observations, two configurational isomers were present in the initial solution, and one of them was thermodynamically more stable.³⁰ Therefore, the signals at 2.43 ppm and 2.98 ppm also belong to the parent compound. Three proton signals from the aromatic ring (δ_{H} range 7.38-8.18 ppm), belonging to the same isomer, are overlapped by the signals of the main component.

After 45 min of irradiation, the first signals of the degradation products appeared: new signals appeared as singlets between 1.90-3.40 ppm and in the range of aromatic protons as shown in the inset (Figure 2b). The

first new signals probably belonged to a new methyl singlet at 2.70 ppm, and another one that appeared at 3.24 ppm could be ascribed to the alicyclic part of the aromatic degradation products. After 2 h of irradiation, some other new signals appeared in the range of alicyclic protons. At 2.10 ppm, there appeared a doublet (d, 3J 3.0 Hz) belonging to acetaldehyde, which by the addition of the OH $^\bullet$ radical produced acetic acid (1.97 ppm).^{31,32} The signals of aromatic protons of the parent compound (7.38–8.18 ppm) showed a gradual decrease. At the same time, there appeared signals belonging to some aromatic intermediates. For example, the singlets at 8.15 ppm and 9.20 ppm attained a maximum intensity between 2.5 and 4.5 h, then showed a decrease and disappeared almost completely after 7.5 h. The ^1H NMR spectra obtained after about 9.0 h of irradiation showed that at the end of photodegradation there was no signal at 1.97 ppm, which indicated that all acetic acid was transformed into CO_2 and H_2O .

The potential degradation products—acetaldehyde, acetic and formic acids were identified by the standard addition method. To this end, a defined amount of these compounds was subsequently added to an aliquot of irradiated acetamiprid solution. As can be seen from Figure 3, the increased degradation product signals: singlet at 1.97 ppm (2a), doublet at 2.10 ppm (d, 3J 3.0 Hz) (2a) and singlet at 8.15 ppm (3b) after the addition of the above compounds, confirmed the presence of acetic acid (3a), acetaldehyde (4a), and formic acid (4b) as intermediates in the irradiated sample. Furthermore, the addition of 6-CNA (3b) showed that one of the aromatic degradation products had signals with the same chemical shifts, and this confirmed the presence of 6-chloronicotinic acid. In addition, there appeared very similar signals at 7.49 (d, 3J 7.5 Hz), 8.02 (dd, 3J_1 8.2 Hz, 3J_2 2.5 Hz) and 8.75 (d, 3J 2.5 Hz), which could be ascribed to another aromatic degradation product with a higher electronic shield than 6-CNA. It can also be seen that the amount of aromatic degradation products was low.

The ^1H NMR spectroscopic measurements enabled the monitoring of the photo-oxidative decomposition of selected fragments of acetamiprid molecule, as was the case with the alicyclic signal at 3.07. Based on this method, the half-life for the photocatalytic degradation of the alicyclic part was 75.9 min. It can also be observed that the formic acid concentration reached its maximum around 4 h, and after that the signal intensity decayed, which can be explained by the mineralization of the degradation products.

The APT ^{13}C NMR spectra of acetamiprid, recorded in CDCl_3 (Figure 4 a) prior to irradiation, showed the basic ^{13}C NMR signals with the following chemical shifts [ppm]: 19.28; 37.31, 50.31(q); 117.30 (q); 124.53; 129.42 (q);

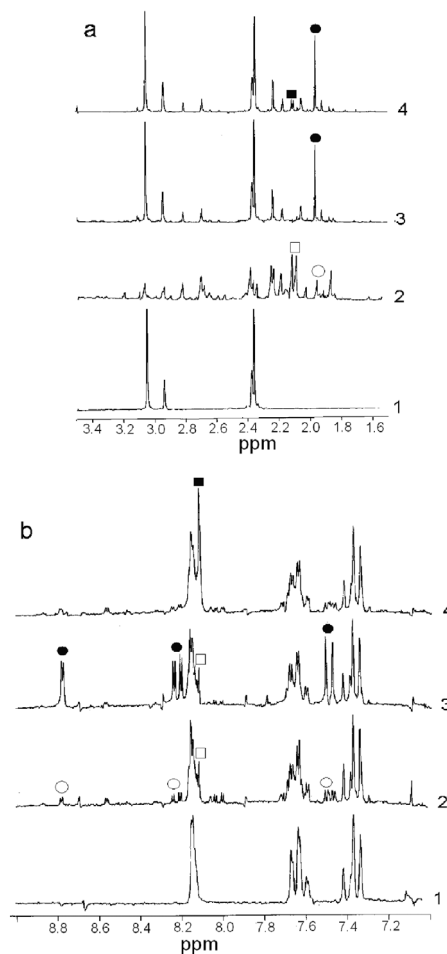


Figure 3. Section plots of ^1H NMR spectra of the non-irradiated acetamiprid (2.0 mg cm^{-3}) solution (1a, b), irradiated acetamiprid sample (2a, b) and the irradiated acetamiprid sample with the standard addition of different compounds: acetic acid (3a, ●), acetaldehyde (4a, ■), 6-CNA (3b, ○) and formic acid (4b, ■). In all cases the solutions contained TiO_2 catalyst.

136.95; 149.13; 151.15 and 172.06 (q). After 8 h of irradiation of the solution, water evaporation and reconstitution of the dry residue in CDCl_3 (see Experiment section), it was still possible to identify the following signals (Figure 4b) [ppm]: 19.28; 37.31, 50.31(q); 124.53; 129.42 (q); 136.95; 149.13; 151.15 and 172.06 (q). Some new signals were observed between 20 and 40 ppm, and the quaternary carbon at 117 ppm (the signal from the cyano functional group marked in Figure 4) was no longer visible. This means that the most pronounced changes occurred in the alicyclic part of the molecule in the given time interval.

In the case of the degradation of 6-CNA (not shown) in D_2O solution in the presence of TiO_2 , using the test system of the mentioned purity, complete mineralization of the sample occurred after 6 h. During this photocatalytic process only one degradation product, observed as a singlet at 8.15 ppm, belonged to formic acid, which was proved by standard addition of that acid to the analyte.

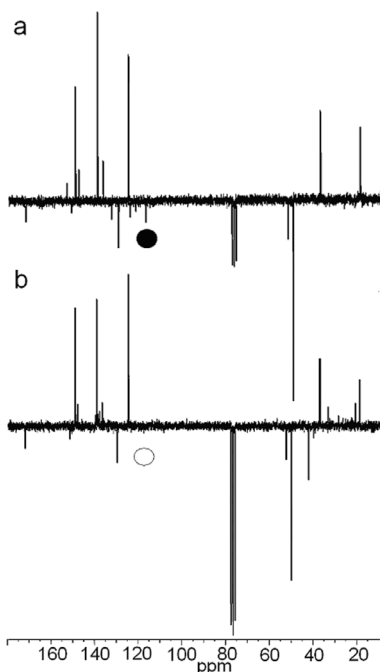


Figure 4. APT ¹³C spectra of acetamiprid before irradiation (a) and after 8 h of irradiation (b). The presence and absence of the quaternary signal from the cyano functional group is marked in the figure at 117 ppm. The spectra were obtained after sample concentration step in CDCl₃ (see Experiment section).

Triple quad HPLC/MS measurements were carried out to identify the acetamiprid degradation intermediates. For the MS evaluations the positive molecular ion mode (M+H)⁺ was applied. In the case of acetamiprid several main degradation products (*m/z*) with typical 1Cl isotope clusters were observed, (e.g. 185, 209 and 257) of the parent compound (223) and the presence of the 6-CNA (158) was also detected. The value of 257 can perhaps be ascribed to the emergence of hydroxo- derivatives through the binding of two OH[•] radicals to the acetamiprid molecule.

The proposed pathway of hydroxylation of the aromatic ring is probably in accordance with the observations of Mylonas and Papaconstantinou,³³ Mylonas *et al.*,³⁴ and Theurich *et al.*,³⁵ who mentioned that OH[•] radicals, as the main oxidant attacking the substrate, yielded hydroxylation products and quinonidal structures and opening of the ring. However, in the case of 6-CNA, after the initial OD[•] radical attack, all of these processes were very fast, so that the only measurable degradation product was formic acid.

The observed evolution of the UV spectra of acetamiprid (2.0 mg cm⁻³) under irradiation in the presence (a) and absence (b) of the catalyst is shown in Figure 5. The spectra of acetamiprid show two merged absorption bands with the absorption maxima at 218 and 245 nm, of which the latter is more intensive. During the irradiation, the change in absorbance was

the most significant at 245 nm and, therefore, this wavelength was used to monitor the complex process of photocatalysis. As the preliminary examinations of the pH effect on the acetamiprid spectrum showed no significant shifts of the absorption bands in the range pH 2.0-7.0, the changes in the spectrum during the irradiation could also be ascribed to pyridine-based intermediates. After 7 h of irradiation, the spectrum was completely different: a broader band with a maximum at 210 nm only could be seen. On the other hand, in the case of photolytic process (Figure 5 d) no significant changes of the parent spectrum occurred. Similar to imidacloprid^{27,28} and thiacloprid,²⁷ the absorbance maximum of acetamiprid is in the UVC (280-200 nm) range, but the absorption spectra of these molecules extend far into the UVB (320-280 nm) range. The applied UVA (400-320 nm) light source emits radiation down to *ca.* 300 nm and, as can be seen in Figure 5 d, acetamiprid signals decreased insignificantly in the O₂/UV process. Since the photons emitted from the source were not efficiently absorbed by acetamiprid, very slow changes were observed. Hence, in the irradiation time period, the main cause of acetamiprid degradation was photocatalysis. The same explanation holds, for 6-CNA (Figure 5 c, d), but it should be noted that the model compound was prone to photolysis and photocatalysis, which was probably evidenced as a decrease of the band with a maximum at 270 nm.

Based on the UV spectra of acetamiprid the HPLC/DAD determinations were carried out at 245 nm (Figure 6). It was found that the peak with a retention time of 11.48 min corresponds to acetamiprid (2.0 mg cm⁻³). After 30 min of irradiation, a peak with a retention time of 7.87 min appeared, which increased up to 240 min and then decreased, which is in agreement with the results obtained by the ¹H NMR spectrometry. After adding 6-CNA to the irradiated sample this signal increased (Figure 6b). The UV spectrum of 6-CNA corresponds to that of the degradation intermediate obtained by DAD detector. Thus, 6-CNA could be identified as the degradation intermediate, as was also concluded on the basis of the ¹H NMR investigations. Another three peaks of very low intensity are observed at 4.12, 5.76 and 6.13 min; the intensities of these peaks, apart from those of acetamiprid and 6-CNA, indicate that the pyridine-containing intermediates that absorb in the near UV range were present only in low concentrations.

The effect of the initial acetamiprid concentration on the reaction kinetics was investigated at four concentration levels (0.5, 1.0 1.5 and 2.0 mg cm⁻³) and the results are summarized in Table 1. Assuming that the reaction

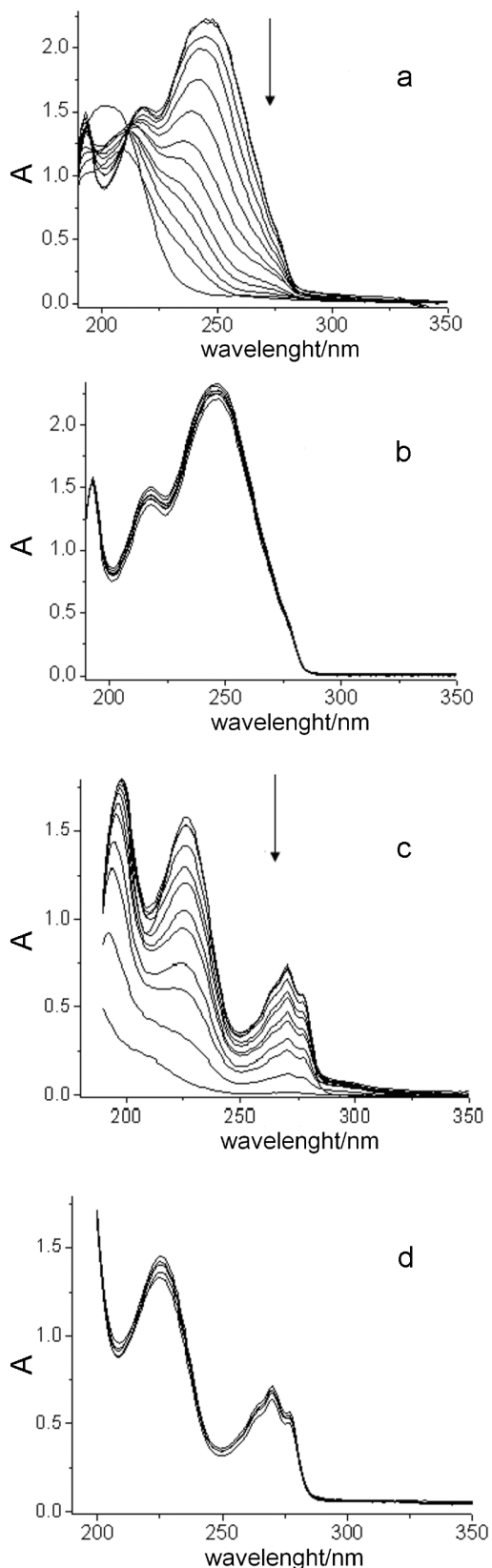


Figure 5. Time dependence UV spectral profiles of the photocatalytic (a, c) and photolytic (b, d) degradation of acetamidrid (2 mg cm^{-3}) and 6-CNA (1.5 mg cm^{-3}) during the irradiation periods of 0-7 and 0-6 h, respectively.

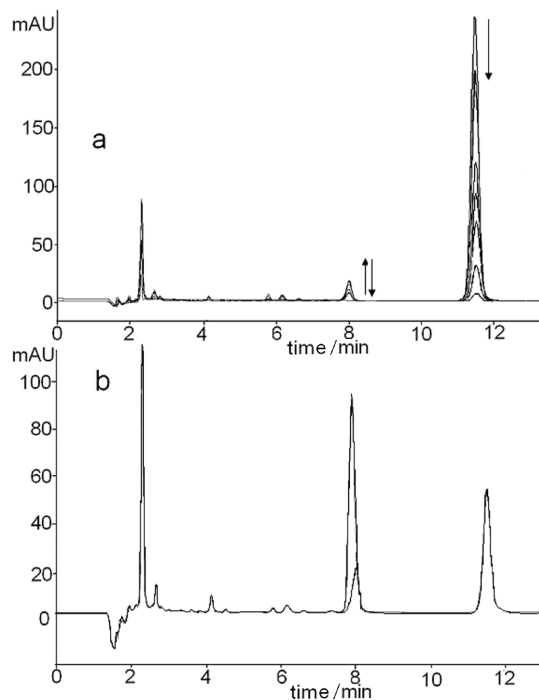


Figure 6. Time-dependent chromatograms of the photo-oxidative decomposition of (a) acetamidrid (initial concentration 2.0 mg cm^{-3}) between 0 and 8 h and (b) the sample taken after 4 h of irradiation from the reaction mixture with and without addition of 6-CNA standard.

between the OH^\bullet radicals and insecticide molecule is the rate-determining step, the rate equation can be written as:

$$r = k_{\text{OH}}^\bullet [\text{OH}^\bullet] C^n = k_{\text{ap}} C^n$$

where C and $[\text{OH}^\bullet]$ are the insecticide and OH^\bullet concentrations in the initial stage of the degradation; n is the reaction order; k_{OH}^\bullet is the reaction rate constant, while k_{ap} is the apparent rate constant.

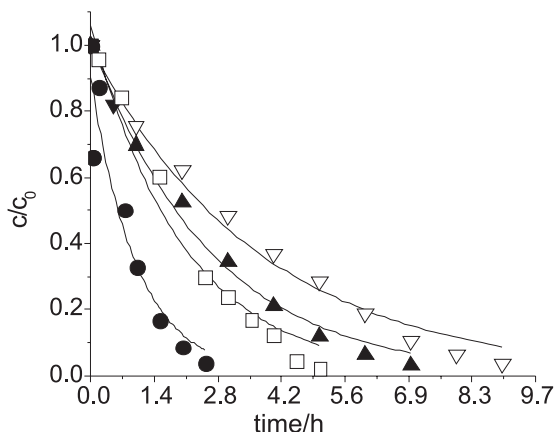
Since the concentration of OH^\bullet radicals is constant during the reaction, the rate of photodegradation in the beginning of the process depends on the acetamidrid concentration, indicating that the reaction is of pseudo-first order,^{32,33} which is in agreement with the above Langmuir–Hinshelwood kinetic model. On the basis of these results, a linear regression fit (by the least squares method with simple weighting) to the $\ln C_A/C_0$ (C_0 initial and C_A actual insecticide concentrations) *versus* t (irrad.) plots was obtained with the slope k_{ap} for all the four initial acetamidrid concentrations (Table 1), indicating thus that the reduced form of the Langmuir–Hinshelwood equation can be used as a good approximation over the range of the initial degradation process (Figure 7).

As the literature data show, in the case of some simple molecules such as chloroform, tetrachloromethane or dichloromethane, where practically no intermediates

Table 1. Effect of initial concentration of acetamiprid on the photocatalytic degradation rate

$c/\text{mg cm}^{-3}$	$k_{\text{ap}}/\text{min}^{-1}$	r	$t_{1/2}/\text{min}$
0.50	-0.0203	0.998	34.65
1.0	-0.0098	0.993	70.87
1.5	-0.0070	0.992	99.02
2.0	-0.0040	0.998	173.0

k_{ap} : Pseudo-first order rate constant; $t_{1/2}$: Half-life; r : Linear regression coefficient

**Figure 7.** Effect of different initial concentrations of acetamiprid (mg cm^{-3}) on the photocatalytic degradation rate: 1) 0.5; 2) 1.0; 3) 1.5 and 4) 2.0. All measurements were prepared in triplicates.

are formed, the formation of hydronium ions directly corresponds to the kinetics of degradation of the initial compound. However, this is not always the case with more complex compounds, where the pH changes cannot be used for kinetic analysis. Even so, the pH monitoring during a photocatalytic process can give a valuable insight into the net changes in the investigated system. In our case the decrease of the pH from 5.0 to 2.0 can be explained by the presence of the acidic intermediates like formic, acetic and hydrochloric acids. The pH increase can be ascribed to the beginning of ammonia production. Further investigations are in progress to elucidate the fate of the nitrogen and chlorine containing parts of the investigated compound molecule.

On the basis of all the above, it can be supposed that the centers that are most susceptible to the attack of OH[•] radicals are those on the alicyclic part of the acetamiprid molecule in the close neighborhood of the amino and imino nitrogens.

Conclusions

The photo-assisted oxidative degradation of acetamiprid in the presence of TiO₂ involves the formation of a variety of intermediate species. The ¹H NMR spectroscopy allows

the monitoring of the degradation of the different parts of the molecule. The signals of the parent substance showed an abrupt decrease, and after 5 h of irradiation they disappeared. After 45 min, new signals appeared as singlets between 1.90-3.40 ppm and in the range of aromatic protons. They attained a maximum intensity between 2.5 and 4.5 h, then showed a decrease and disappeared almost completely after 8.0 h. In the case of the degradation of 6-CNA, complete mineralization of the sample was observed after 6 h. By the standard addition method it was proved that in the different phases of the process intermediates were formed, such as acetaldehyde, formic, acetic acid, and traces of only a few pyridine-containing intermediates (e.g. 6-CNA). The HPLC/DAD measurements confirmed the presence of 6-CNA and also of some other aromatic intermediates at very low concentrations. The quantitative analysis showed that the reaction is of a pseudo-first order. Thus, the advanced oxidation process based on O₂/TiO₂ and UV light appeared to be a simple and rapid procedure for the removal of acetamiprid, probably without significant detrimental effects to the environment.

Acknowledgements

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