Evaluation of photocatalytic degradation of imidacloprid in industrial water by GC-MS and LC-MS

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Abstract. The insecticide Imidacloprid was oxidized in water at 50 mg/L under photocatalytic TiO_2 in presence of formulating agents. Analysis of oxidized solutions was performed with both GC-Ion Trap-MS using either EI and CI as ionization modes and LC-Atmospheric Pressure Chemical Ionization (APCI)-MS in order to confirm and evaluate the decay of Imidacloprid and the presence of degradation products (DPs). LC-APCI-MS techniques allowed the monitoring of Imidacloprid and 6-chloronicotinic acid along the degradation process. GC-MS techniques allowed the detection of five DPs, three of which were unequivocally identified. Other complementary techniques such as Total Organic Carbon (TOC) and Ion Chromatography (IC) allowed the evaluation of the mineralization degree achieved. A tentative degradation pathway of Imidacloprid under photocatalysis is proposed. After 450 minutes of irradiation, none of the DPs or Imidacloprid were detected. Nearly total mineralization was achieved after 700 minutes of irradiation.

Introduction

The use of "advanced oxidation processes" (AOPs), as photochemical or ozonation treatments, has arisen as a clean, fast and effective degradation process for polluted water detoxification, containing pesticides and other organic compounds. Numerous literature has been published in this area [1-5]. Important causes of pesticide water pollution are effluents from agricultural industries and from formulating or manufacturing pesticide plants which may generate water pollution at concentrations of up to 500 mg/L.

Nitrogen containing pesticides, organophosphorous, organochlorine insecticides and herbicides in water have been extensively investigated under photocatalytic treatments and total or partial mineralization of some of these compounds have been reported [6-8]. Nevertheless, in most of the cases no attention was paid to the possible formation of intermediates or degradation products (DPs), which allow a better understanding and evaluation of the degradation processes and so enables the researcher to make comparisons between degradation pathways of different classes of compounds, functional groups, chemical oxidation parameters etc. On the other hand some of the DPs obtained are of interest, because they may be more toxic and persistent than the parent compound. In some cases of photocatalytic TiO_2 treatments, only traces of these metabolites are detectable, because they are degraded faster than the parent compounds and practically total mineralization is achieved in a short period of time [3]. However in other cases such as s-triazine herbicides, the overall conversion to the final degradation products takes longer, and several DPs are isolated, identified and quantified [6].

In order to analyze a reaction mixture containing pesticides and their DPs, it is necessary to have analytical screening methods available that permit separation and identification of compounds with very different hydrophilic-hydrophobic characteristics and spanning very different concentration ranges. The use of gas chromatography with classical detectors, like ECD, NPD or FPD is obviously insufficient. So, the application of gas or liquid chromatographic systems coupled to mass spectrometry (GC-MS and LC-MS) represents a good and fast alternative to obtain very useful structural information of the compounds generated during such processes. Important advantages of the GC-MS based methods are the high structural information yielded and the possibility of using commercial libraries which make the identification of the DPs feasible, but they have an important drawback as a consequence of the low capacity to analyze very polar and low volatile compounds. In order to increase the range of DPs covered by GC-MS methods, derivatization procedures represent an interesting alternative, but their use can imply the generation of artificial new compounds and tedious, time-consuming procedures [1,9]. Therefore, there is a clear tendency to use LC-MS techniques [10], but in this case the structural information achieved is low and makes the DPs structure elucidation difficult [11]. As a consequence of the complexity of the DPs obtained, MS based techniques do not provide enough structural information for the unequivocal structure elucidation of the DPs in the majority of the cases. This has to be carried out by means of more complex and time-consuming techniques such as LC-MS-MS [12] or NMR [13]. But the combination of both GC-MS and LC-MS allows obtaining very useful and in many cases enough structural information in a fast way to evaluate the degradation process [9]. In addition, other analytical measures such as Total Organic Carbon (TOC) or Ion Chromatography (IC) can be of great help in order to assess the success of the degradation process by evaluating the mineralization rate achieved or by making a mass balance of the whole process [14].

Imidacloprid is a new insecticide from the chloronicotinyl group, which is not amenable for GC analysis [15]. This insecticide has a high water solubility (0.58 g/L) and a water stability of >30 days (at pH 5-7). Previous reports concerning oxidation and hydrolysis studies of this insecticide

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and formulated product detected 6-chloronicotinic acid as the last product in the degradation chain before total mineralization [16,17].

In this study, we have applied gas chromatography with ion trap analyzer (GC-MS) in combination with liquid chromatography with atmospheric pressure chemical ionization interface (LC-APCI-MS) to evaluate the decay of Imidacloprid; as well as to determine possible DPs arising from photocatalytic-TiO$_2$ degradation of water solutions of this insecticide as standard and commercial product at concentration levels of 50 mg/L. MS analyzers exceed the possibilities of quadrupole instrumentation in the field of degradation studies, because full scan electron impact (EI), chemical ionization (CI) and MS-MS modes can be easily performed, yielding complementary and useful information for DP identification purposes [18,19]. LC-MS with atmospheric pressure chemical ionization (APCI) provide important advantages in this study as a consequence of its ability to analyze a large range of polar compounds, such as 6-chloronicotinic acid that we can expect in these degradation processes and the ability to analyze non-volatile GC compounds, such as Imidacloprid [10,11,20,21].

The objectives of this study were: (i) application of the GC-MS technique in EI and CI modes for the evaluation of the degradation products generated by the photocatalytic degradation with TiO$_2$ of Imidacloprid in water; (ii) application of LC-APCI-MS to the monitoring of Imidacloprid and 6-chloronicotinic acid; (iii) to propose a degradation pathway of formulated Imidacloprid under photocatalysis at high concentration levels in water; and (iv) to evaluate the mineralization degree of Imidacloprid achieved.

Experimental section

Chemicals

Commercial formulation (Confidor LS, 20% weight/volume of Imidacloprid) and technical grade Imidacloprid (97.9%) were supplied by Bayer AG (Leverkusen, Germany). Imidacloprid analytical standard (99.7%) was purchased from Dr. Ehrenstorfer (Augsburg, Germany), 6-Chloronicotinic acid from Sigma Chemical Company (St. Louis, USA) and 3-Pyrinecarboxaldehyde from Fluka Chemie AG (Buchs, Switzerland).

Pesticide-grade ethyl acetate, cyclohexane and anhydrous sodium sulphate were supplied by Scharlau (Barcelona, Spain). LC-grade water and methanol were purchased from Merck (Darmstadt, Germany). Ammonium formiate and formic acid were purchased from Fluka (Buchs, Switzerland). Ammonium chloride P.A., anhydrous sodium tartrate P.A and Nessler reagent R.E. used in the ammonium ion determination were obtained from Panreac (Barcelona, Spain).

All photocatalytic degradation assays were carried out by using titanium dioxide P25 grade from Degussa (Frankfurt, Germany), with a surface area of 51 – 55 m^2 g^{-1}, as photocatalyst. The water used in the experiments was obtained from the PSA Desalination Plant (evaporation by a multi-effect system using solar energy, conductivity < 10 µS cm^{-1}, organic carbon < 0.5 mg dm^{-3}).

Standard solutions

For LC-APCI-MS analysis, stock standard solutions of Imidacloprid and 6-chloronicotinic acid (100 µg/mL) were prepared in methanol. Diluted solutions containing from 0.05 to 10 µg/mL were prepared in methanol and analyzed, in duplicate, to calculate the linear range of the detector. The resulting calibration curves were used for quantitative analysis.

For GC-MS analysis, a 6-chloronicotinic acid and 3-pyrinecarboxaldehyde stock standard solutions were prepared in acetone at an initial concentration of 1 mg/mL. Diluted solutions of 5 – 0.5 µg/mL were prepared in cyclohexane:ethyl acetate (9:1) and analyzed by GC-MS for identification and quantitation purposes.

Analytical determinations

LC-MS. A Hewlett Packard Model G1946A (Palo Alto, CA) LC-API-MS quadrupole mass spectrometer and a Hewlett Packard Model G2710AA instrument for data acquisition and processing were used. The eluent was delivered by a gradient HP1100 serie pumping system (Palo Alto, CA). A Hewlett Packard analytical column 100 ¥ 4 mm i.d. Hypersil ODS packed with 3 µm particle size was used. A gradient elution was performed with an eluent A (containing methanol/5% water with 1% formic acid) and an eluent B (containing water with 1% formic acid). The LC eluent conditions varied from 98% of B (5 min isocratic conditions) to 100% of A in 35 min at 0.3 mL/min. Back to initial conditions in 5 min.

APCI LC-MS interface conditions were: a) APCI. Source and probe temperatures were set at 200 °C and 300 °C, respectively. Corona discharge emission current was set at 6 mA. Fragmentor (extraction voltage) was optimized at 100 V. Nitrogen drying gas flow rate and nitrogen nebulizer gas pressure were 4 L/min and 40 psi, respectively. Scan range 50 to 500 *m/z*, scan speed 2.85 s/cycle.

GC-MS. Saturn 3 system (Varian, Harbor City, CA), consisting of a Varian 3400 gas chromatograph, a Model 1093 septum-programmable injector (SPI) and a 8200 autosampler were used for the identification of metabolites. Data acquisition and processing, and instrument control were performed by Saturn GC-MS workstation version 5.2 software loaded into a 486 DX, 66 MHz computer. A DB-5MS (J&W Scientific, Folsom, USA) capillary column, 30 m × 0.25 µm i.d., 0.25 mm film thickness was connected to the system. Operating GC conditions were: 1.0 µL injection volume; solvent plug 0.1 µL; 0.1 s needle hold time in port before injection; 60 °C injection port for 0.5 s followed by ramping to 280 °C at 150 °C/min; 9 psi He column head pressure, column flow rate 1.1 L/min; oven temp programme: 1.0 min at 60 °C, 25 °C/min to 180 °C, 5 °C/min to 280 °C (4 min). Transfer line temperature, 280 °C; detector manifold temperature, 230 °C. GC-MS-EI mode operating conditions were as follows: 35 µA filament current; 1350V electron multiplier tube and automatic gain control at 40 000. The mass spectra were acquired from 50 to 300 *m/z*.

For GC-MS in CI mode, the same conditions already described for EI mode were used. Acetonitrile was selected as reagent gas. The CI parameters were optimized as follows: maximum ionization time 2.5 msec, maximum reaction time 50 msec, ionization storage level 12.5 *m/z*,

reagent ion eject amplitude 8V and reaction storage level *m/z* 20.

Ion determinations. The formation of chloride and nitrate ions was followed by ion chromatography (IC), using a Dionex apparatus equipped with 100 mm long × 4 mm i.d. BT1AN column (Biotronik). The eluent was a mixture of Na^2CO^3 (1 mM) and $NaHCO^3$ (2 nM), at a flow rate of 1.5 mL min⁻¹. The presence of ammonium ions in the samples was detected spectrophotometrically, using a Shimadzu V-160 spectrophotometer (Kyoto, Japan). The absorbance of the reaction product was measured at 400 nm.

TOC. The Total Organic Carbon determinations were carried out using direct injection of the samples into an Heraeus-Foss Electric TOC-2001 (Hanau, Germany) (UV-Peroxydisulphate method, EPA 415.1), in order to follow the mineralization rate in the contaminated water.

Photocatalysis experiments

All the experiments carried out in this work were done in Almería (latitude 37 ºN, longitude 2.4 ºW), using natural sunlight irradiation. A compound parabolic collector field (CPC), designed by PSA (Plataforma Solar de Almeria), was used for the photocatalytic degradation assays. The pilot plant has been described in detail in previous works [22,23] and consists of 6 modules connected in series containing 8 parallel reflectors (polished aluminium) with UV transparent tubular receivers. The contaminated water flows directly from one to the other and finally to the reservoir tank. A centrifugal pump then returns the water to the collectors in a closed circuit.

Photocatalysis assays with commercial formulation were performed in the following way. At the beginning of the experiment, with collectors covered, 62 mL of Confidor and 49 g of TiO_2 were added to 247 L of distilled water resulting in a 50 mg/L Imidacloprid solution and 210 mg/L TiO_2 slurry. After a time of agitation to let the suspension stabilize, the cover was removed and the experiment started. The daily exposure was from 9 am to 6 pm and the experiment was carried out, in duplicate, in December and February. Experiments using Imidacloprid technical grade were performed in the way already described, but in this case 12.6 g of the technical product was used to obtain the same Imidacloprid concentration.

Sampling

To estimate the degradation kinetic of Imidacloprid and time evolution of the metabolites formed, a series of samples were collected, at different periods of time, and pH and TOC measures and IC, LC-APCI-MS and GC-MS analyses were carried out. In the experiments with commercial formulation, samples were collected every thirty minutes during the first part of the experiment (the first three hours), because it is in this period when we expected a more rapid appearance of the metabolites. After this time, the periodicity of the sampling was one per hour. When Imidacloprid technical grade was used, samples were collected more often, one every ten minutes during the first two hours, one every twenty minutes the next three hours and then one per hour until the end of the experiment.

Sample handling

For the LC and IC analysis, samples were directly injected after filtration through 0.45 µm Millipore filters. TOC and pH measures were also carried out directly on samples, but no filtration was done in this case.

For the GC analysis, an extraction and preconcentration of the samples was necessary previous to the injection. An ethyl acetate/sodium sulphate liquid-liquid extraction was applied in the following way: volumes of 100 mL of water samples were acidified at pH 2.5 with sulfuric acid. After the addition of 50 g of anhydrous sodium sulphate, the samples were extracted at high speed for three minutes with 75 × 50 mL of ethyl acetate. The combined organic extracts were filtered through a thin layer of anhydrous sodium sulphate and concentrated in a rotatory evaporator down to 2 – 3 mL. The extracts so obtained were again evaporated to dryness with a gentle N^2 stream and redissolved with sonication in 1 mL of cyclohexane:ethyl acetate (9:1) for GC.

6-chloronicotinic acid recovery studies were performed at 1.0 µg/mL fortification level with the extraction method proposed. With this aim, 1 L volumes of distilled water were spiked with aliquots of the stock standard solutions above described, and extracted three times.

The presence of ammonium ions was detected spectrophotometrically, using Nessler reagent. The calibration curve, prepared using NH^4Cl, was linear in the NH^{4+} concentration range of 0.3 - 10 mg/L. The absorbance of the reaction product was measured at 400 nm against a blank.

Evaluation of Imidacloprid and chloronicotinic acid

Imidacloprid and chloronicotinic acid evaluation was performed by LC-MS in single ion mode using in both cases the molecular (M+H)+ ions at *m/z* 256 and *m/z* 158 as quantitation masses for Imidacloprid and 6-chloronicotinic acid respectively.

Results and discussion

Kinetic and mineralization of imidacloprid

Imidacloprid is stable in water and no loss via chemical hydrolysis was observed after 12 hours in solution kept in the dark. Figure 1 shows the kinetics of disappearance of Imidacloprid (50 mg/L) in commercial formulation solution of Confidor and technical product with the evolution of the concentration of Imidacloprid as a function of the irradiation time. The use of commercial formulation permitted a better approach to real decontamination conditions where the presence of inert ingredients affect the pesticide degradation rate. A rapid initial decrease in the pesticide concentration is observed with irradiation time between 0 and 120 min in the case of Confidor solution. The half-life time obtained at an initial Imidacloprid concentration $C_0 = 50$ mg/L was about 1 h and the complete disappearance took place after 270 min. When technical Imidacloprid was used, at the same initial concentration (50 mg/L), a faster degradation rate was observed achieving total disappearance of imidacloprid after only 140 minutes with a half-life time of about 12 min. This fact is probably a consequence of the competition existing

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between the pesticide and the formulation components for the reaction with hydroxyl radicals, principal responsible for the initial attack on organic solutes during the photocatalytic process over semiconductor metal oxides [24].

Mineralization of the photocatalytic processes were followed by the evolution of the total organic carbon content (TOC) and the evaluation of inorganic species (Cl^-, NO_3^- and NH_4^+) in the water solution.

Initial TOC measurements higher than 120 mg/L in the Confidor solution confirmed the presence of a high concentration of additional ingredients corresponding to the commercial formulation. These compounds produce a high decrease in the mineralization rate. 90% abatement of the initial concentration of Imidacloprid took place after 700 min. Initial TOC concentration in the case of technical grade was 20 mg/L and 200 min were necessary to achieve similar results in the case of technical Imidacloprid (Fig. 1).

The chloride, nitrate and ammonia ion formation is shown in figure 2. A stoichiometric recovery of Cl^- (7 mg/L) was achieved after about 5 hours of irradiation when Imidacloprid and all the chloride containing detected metabolites had disappeared or were present at negligible concentrations. From this moment, the molar ratio of Cl^- ions produced per degraded Imidacloprid molecule was stable and around 114% of the expected value. It is reasonable to suppose that this little excess is due to analytical errors in the determination method of Cl^- and to the design of the experiment where a water volume of 247 L is treated.

The nitrogen mass balance of Imidacloprid is a more complex process. Both ammonia and nitrate have been detected in different relative concentrations. After 400 min of irradiation time, the nitrogen mass balance of imidacloprid is almost constant (11 mg/L) and slightly lower than stoichiometric (13.7 mg/L). The incomplete nitrogen mass balance of Imidacloprid indicates that other nitrogen-containing compounds must be present in the solution as a consequence of the formation of reaction intermediates [25,6].

Degradation products

Quantitative analysis

Following the LC-MS procedure described in the Experimental Part, linear relationships between the peak heights of imidacloprid and 6-chloronicotinic and their concentration were obtained in the range 0.01 – 5 and 0.08 – 4 mg/L, showing linear correlation coefficients of 0.9999 for Imidacloprid and 0.9994 for 6-chloronicotinic acid. The detection limits calculated with a S/N of 3, were 0.005 and 0.03 µg/L respectively. Figure 3 shows LC-APCI-MS (positive mode) chromatograms of a standard solution of these compounds and a water sample after 112 minutes of photocatalytic treatment of formulated Imidacloprid.

The average of 6-chloronicotinic acid recovery obtained by the application of the proposed LLE method followed by GC-MS method was 82% with a coefficient of variation of 23%. In the case of other DPs evaluated such as 6-chloronicotinic aldehyde by GC-MS, due to the impossibility of obtaining analytical standards, quantitation was carried out by using 3-pyridinecarboxaldehyde as external standard, to which a similar response factor can be assigned as a conse-
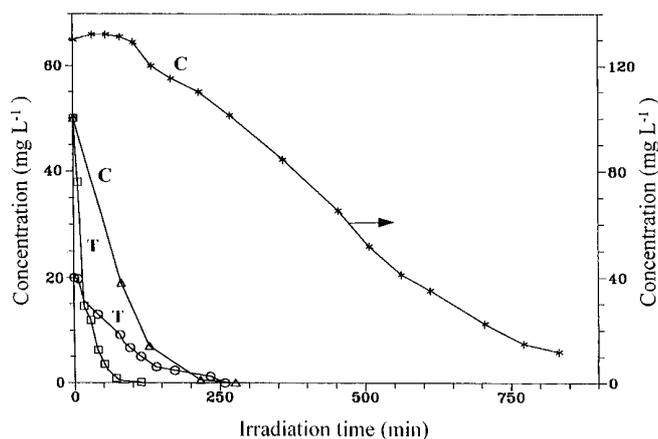

Fig. 1. Kinetics of disappearance of Imidacloprid (▲ and ❏) and evolution of Total Organic Carbon (✳ and ◯) as a function of illumination time in commercial formulation (C) (50 mg/L) and technical product (T) (50 mg/L).
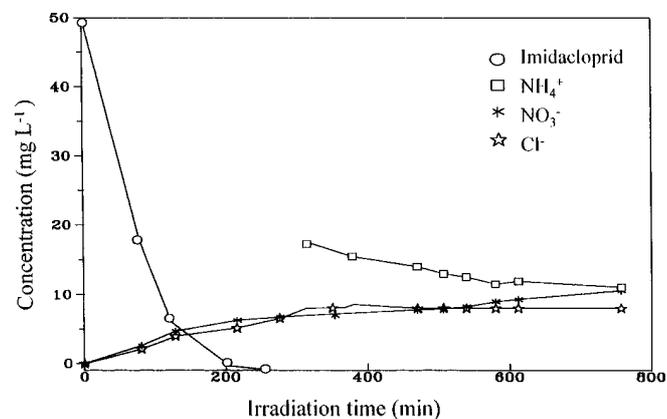

Fig. 2. Formation of NH_4^+, NO_3^- and Cl^- as a function of irradiation time in the photomineralization of Imidacloprid (commercial formulation). The degradation of imidacloprid is included as a reference.

quence of its very similar chemical structure. In such conditions we can expect significant errors of about 30%.

Identification of DPs

Compounds were regarded as DPs provided that their concentration increased and decreased as a function of the reaction time. During the photocatalytic process, Imidacloprid yielded at least five possible intermediates. Three of them were unequivocally identified by GC-MS analysis using EI and CI ionization modes. The retention time and the fragments' tentative assignation is shown in table I. Other peaks present in the chromatograms showed stable profiles versus time or showed a continuous decrease. They were identified as phthalates exhibiting typical *m/z* 149 ions, linear alkyl compounds exhibiting typical losses of 14 amu or other compounds. They originated from the extraction procedure, or compounds present in the formulated product as can be noted in the liquid-liquid extracts of Imidacloprid commercial formulation solution before sunlight exposure (Fig. 4).
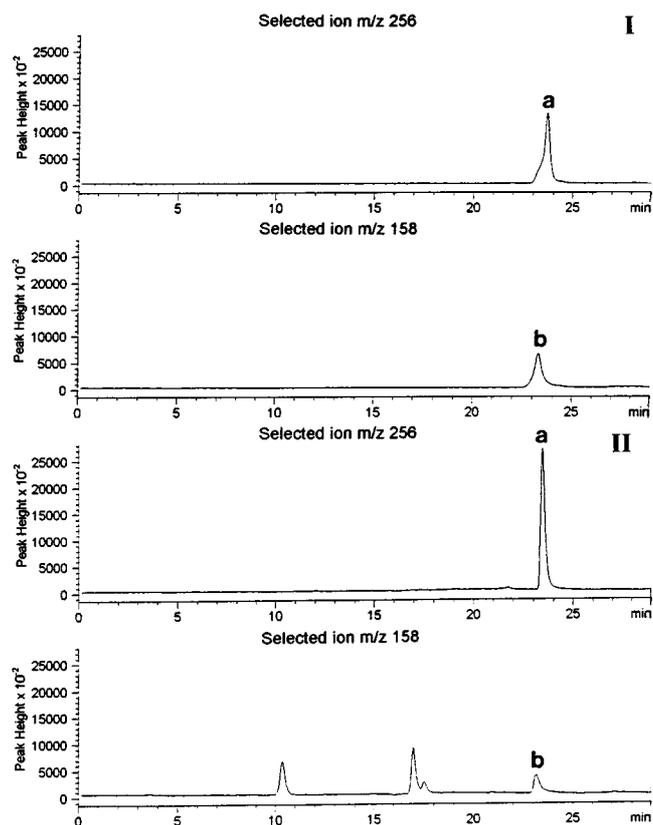
Fig. 3. LC-APCI-MS (positive mode) chromatograms obtained in SIM mode for: (I) a standard mixture of a) Imidacloprid (4.2 mg/L) and b) 6-chloronicotinic acid (11.0 mg/L) and (II) a sample analysis of a) Imidacloprid and b) 6-chloronicotinic acid in a 50 mg/L Imidacloprid commercial formulation solution after 112 minutes of irradiation time.
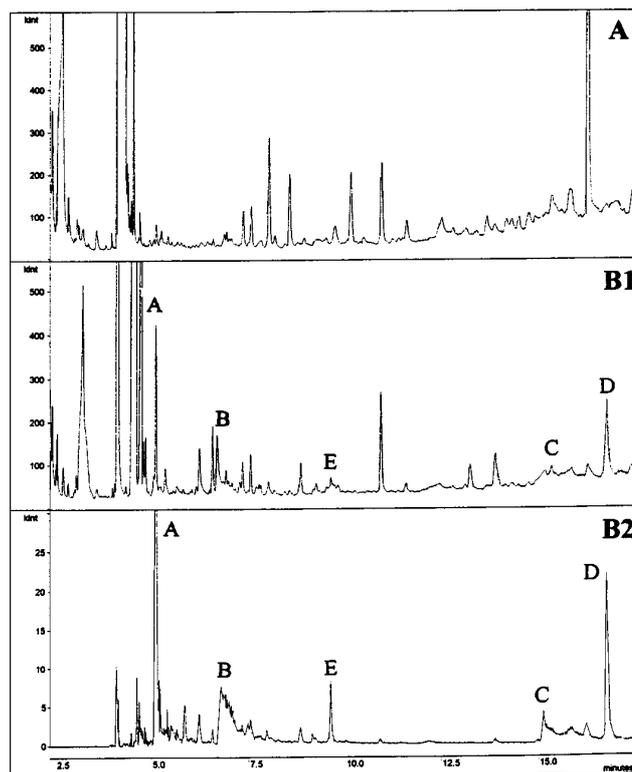

Fig. 4. GC-MS chromatograms corresponding to: A) liquid-liquid extracts of Imidacloprid commercial formulation solution before sunlight exposition (EI mode, total ion) and B) sample analysis of the same solution after 112 minutes of irradiation in (B1) EI mode, total ion and (B2) CI mode, selected ions: 142 (A), 158 (B), 212 (C), 226 (D) and 199 (E).

Compound B (Fig. 4) was identified by GC-MS analysis as 6-chloro nicotinic acid by comparing the retention time and EI mass spectrum of the standard under the same GC conditions. The identification of this compound by a spectrum library search, using the available commercial Nist library, showed a concordance or fit value of 87%. But the relative abundances of the different ions present in the sample and library spectra had different distributions. Similar discrepancies have been pointed out in other works about pesticide analysis by GC-MS [18]. In addition, in LC-APCI-MS analysis this compound showed the ion 158 as base peak, corresponding to the molecular weight ion $(M^+H)^+$.

The identification of the compounds A and C (Fig. 4) was done based on the EI and CI spectra. Compound A gave a base peak that is characteristic of aldehydes of M – 1 by loss of aldehyde hydrogen and an important secondary fragmentation by loss of 38 amu corresponding to a CO group. Compound C presented a more complex spectrum. The base peak was 235 m/z ion which can be assigned to the molecular ion. Losses at m/z 99 to 126 were assigned to the break of the linkages corresponding to the methyl group. Peaks at m/z 182 and 168 can be tentatively assigned to the opening of the imidazolidine ring by the fission of the contiguous linkages to the carbonyl group. The fragments at m/z 176 (M – Cl)+ y m/z 195 (M – O)+ were less abundant.

Confirmation of the molecular weight of these compounds was obtained by the positive CI analysis using acetonitrile as reagent gas. Base peaks corresponding to the protonated molecular ions $(M^+H)^+$ of 142, 158 and 211 were obtained for the compounds A, B and C respectively (Tab. I).

The compounds D and E were not identified, but the one arising from photodecomposition of Imidacloprid is suspected by the presence of one chlorine atom in their molecule and the occurrence of common ions (m/z = 78, 126) to correspond to the Imidacloprid moiety (Tab. I).

The proposed degradation pathway is shown in figure 5. As we can see, these compounds result from losses of the nitro group and oxidation at the imidazolidine ring, hydrolysis to 6-chloronicotinic acid and mineralization.

The kinetics of formation and decomposition of the DPs as a function of the irradiation time is depicted in figure 6. Typical bell-shaped profiles were obtained. From these charts it can be observed that all the intermediates detected persist after total disappearance of Imidacloprid. Although the formation of all DPs detected start at the initial time, the sequential formation can be assigned following the times when their maxim arise. Therefore 6-chloronicotinic aldehyde and 6-chloronicotinic acid are the last stages in the process. The sum of both compounds can be estimated at 250 min in 35 mg/L, when Imidacloprid has been
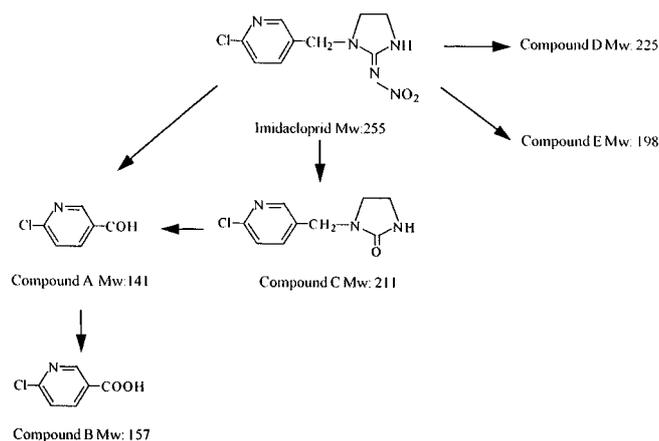
Fig. 5. Scheme of the proposed degradation pathway for formulated Imidacloprid under photocatalytic TiO_2 treatment in water.
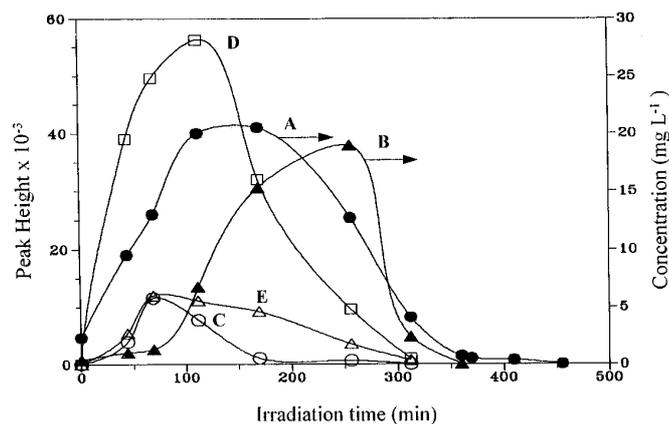

Fig. 6. Formation and degradation kinetics of Imidacloprid degradation products (see Fig. 5) *versus* irradiation time. Compound A was evaluated by LC-MS and compounds B, C, D and E by GC-MS.

Table I. Imidacloprid degradation products (DPs) molecular weight (Mw), retention time (RT), main ions and their relative abundance (RA) and tentative assignation using GC-ITMS in EI and CI modes.

Mw	DPs	RT (min)	Main ions (RA %)		Tentative assignation
			EI	CI	
141	Compoud A (Chloronicotinic aldehide)	5.12	140 (100)		$[M–1]^+$
			112 (36)		$[M – COH]^+$
			76 (20)		$[M – Cl\ COH]^+$
				142 (100)	$[M + 1]^+$
157	Compound B (Chloronicotinic acid)	6.42	139 (100)		$[M – H_2O]^+$
			157 (59)		$[M]^+$
			112 (37)		$[M – COOH]^+$
			76 (31)		$[M – Cl\ COOH]^+$
				158 (100)	$[M + 1]^+$
211	Compound C (1-(6-chloro-3pyridilmethyl)-imidazolidin-2-ona)	15.19	211 (100)		$[M]^+$
			126 (47)		
			99 (22)		
			78 (15)		$[C_5H_4N]^+$
				212 (100)	$[M+1]^+$
225	Compound D (Unkown)	16.80	225 (100)		$[M]^+$
			168 (38)		
			153 (32)		
			196 (17)		
			126 (11)		
			78 (10)		
				226 (100)	$[M+1]^+$
198	Compound E (Unkown)	9.61	169 (100)		
			141 (89)		
			78 (36)		
			198 (21)		$[M]^+$
			114 (20)		
			126 (12)		
				199 (100)	$[M+1]^+$
				171 (36)	

completely depleted and the presence of the other DPs is practically negligible. This fact indicates that at least 70% of the total amount of Imidacloprid initially present yield these compounds before the total mineralization.

Conclusions

GC-MS using EI and CI ionization modes yielded enough structural information to identify three DPs of Imidacloprid

under photocatalytic treatment, but failed in the correct identification of two DPs which had more complex structures. LC-APCI-MS represented a good and complementary alternative for the monitoring of very polar compounds such as 6-chloronicotinic acid or non-volatile compounds such as Imidacloprid. But this technique did not provide enough structural information for structure elucidation. The combination of both GC-MS and LC-APCI-MS techniques provided enough structural characterization in order to evaluate the results of the phocatalytic treatment in a fast way. Complementary techniques such as TOC and IC provideed very useful information in order to evaluate the achieved mineralization degree correctly. It was stated that oxidation of Imidacloprid by photocatalysis mainly occurs through the formation of 6-chloronicotinic aldehyde and acid. After 450 min of oxidative reaction both the DP and Imidacloprid concentrations are practically negligible.

Acknowledgement

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