

Photochemistry of insecticide imidacloprid: direct and sensitized photolysis in aqueous medium

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Abstract: The direct and sensitized photodegradations of imidacloprid, 1-(6-chloro-3-pyridinylmethyl)-N-nitro-2-imidazolidinimine, were investigated in aqueous solution and with and without various photo-sensitizers. Results of the study revealed that the intensity of lamp-house and irradiation wavelength had significant effects on the photolysis of imidacloprid. Complete degradation of 20 mg/L imidacloprid in aqueous phase was observed in 40 min under ultraviolet (UV) irradiation system, suggesting the ultraviolet ray played significant role in direct photolysis of imidacloprid. The additions of various photo-sensitizers lead to improve the degradation efficiency of imidacloprid under the irradiation of black light fluorescent lamp. TiO_2 was the most efficient in the photo-catalytic degradation of imidacloprid among other photo-sensitizers in used this study. However, addition of acetone inhibited the photolysis of imidacloprid under the irradiation of UV, indicating the occurrence of competition between acetone and imidacloprid for photos. Mineralization of the imidacloprid was examined to clarify the final photochemical degradation products of the insecticide which were CO_2 , Cl^- and NO_3^- . Complete photo-oxidation of nitrogen to NO_3^- occurred very slowly via the intermediate formation of NH_4^+ and NO_2^- .

Keywords: imidacloprid; photolysis; photo-sensitizers; photo-oxidation; mineralization

Introduction

The use of pesticides has been an integral part of agricultural production in the world. However, many findings have confirmed that these anthropogenic chemicals became main sources to cause pollution in natural surface water via various routes such as leaching or runoff after application of pesticides (Capel, 1995; Koplin, 1996; Hatfield, 1999). Given the potential human and wildlife health risks associated with toxic pesticides in surface water, it is important to determine the fate of pesticides in nature water. Compared to various biotic and abiotic factors, photolysis generally plays critical role to affect on the final fate of pesticide in the natural water. Therefore, studies on the photochemistry of pesticides are necessary to develop its efficiency as well as low toxicity to aquatic organisms (Tsao, 1994).

In direct photolysis, pesticides absorb light energy in the ultraviolet (UV) spectra range which drive to undergo photochemical transformation. Whereas during sensitized photolysis, a species other than the substrates (pesticides) absorb the light energy and then the excited species transfer the energy directly to substrates or cause a series of reactions with the subsequent formation of oxidants such as singlet oxygen, hydroxy radical ($\text{OH}\cdot$) and alkylperoxy radicals (Hapeman, 1998). Therefore the photo-degradation of

pesticides may be strongly affected by the naturally occurring photo-sensitizers in the environment. Furthermore, the rate and route of photolysis of pesticides can be significantly different in natural waters containing humic substances and other photo-sensitizers (Mansour, 1997; Krieger, 2000).

Imidacloprid is a new systemic insecticide that has been used efficiently to control sucking pests such as aphids, white flies, plant bugs, planthoppers, thrips and other various harmful pest species including resistant strains (Elbert, 1990). Electrophysiological studies of the imidacloprid and its inhibition of α -bungarotoxin binding indicated that it has the same mode of action as the natural insecticide, nicotine, which acts as an agonist of nicotinic acetylcholine receptor (Bai, 1991). Owing to its high insecticide effectiveness and low mammalian toxicity, imidacloprid has been widely used in soil and foliar and seed treatment. Previous studies showed the degradation half-life of imidacloprid was 40 d in field experiment (Rouchaud, 1994) and its soil metabolism has also been reported in sugar beet field crops (Rouchaud, 1996). The studies on sorption and desorption of imidacloprid indicate that organic carbon in soil has the most significant effect and hysteresis was occurred in desorption process (Cox, 1998a; 1998b; Zheng, 2001). In additions, pesticide imidacloprid has been found to be stable in acidic and neutral waters, but readily hydrolyzed in alkaline water

with main hydrolysis product of [1-(6-chloro-3-pyridinylmethyl)-2-imidazolidone](Zheng, 1999).

Due to relatively high water solubility of imidacloprid (510 mg/L at 20°C), it has been regarded as a high potential contaminant to surface water. The objective of this study was to investigate direct and sensitized photolysis of imidacloprid in aqueous solution with and without various photo-sensitizers. In the course of this study, different systems regarding imidacloprid degradation were described and evaluated as follows: (1) direct photolysis under the different intensities of lamp-house, irradiation wavelengths as well as different photo-reactors. (2) photolysis of imidacloprid in the presence of various photo-sensitizers. In addition, the process of imidacloprid photolysis was carried out and the final mineralization products via photo-degradation pathway were determined.

1 Materials and methods

1.1 Chemicals

Imidacloprid containing 97.3% of purity was supplied from Linhua Co. (Zhejiang, China). Its solubility in water was 0.51 mg/L and much high in organic solvents. Double distilled water was passed through a 0.45 μm filter before use. Acetonitrile, methanol, chloroform were used as analytical grade solvents.

1.2 Photolysis experiments

All photochemical studies were conducted using a merry-go-round photo-reactor equipped with middle-pressure lamp (125 W), UV lamp (3 \times 8 W) and black light fluorescent lamp (3 \times 8 W). 200 ml of pesticide solution was irradiated in water tray quartz or special glass flasks that can tolerate at high temperatures occurred in photolysis procedure. The glass flask restricts the transmission of wavelengths below 290 nm. In all the experiments a steady stream of gas (300 ml/L) was bubbled into the solution so that irradiations were carried out under aerobic conditions and temperature was maintained at 25°C. Approximately 2 ml of each solution was removed at designated time intervals and analyzed by HPLC. In sensitized photolysis experiment photo-sensitizers were added and magnetically stirred before the mixed samples were irradiated.

1.3 Chemical analysis

The concentration of imidacloprid during the photolysis was determined by HPLC. A spectra physics liquid chromatography equipped with a 125 \times 4.6 mm i. d. RPC₁₈, a multi-wavelength spectra 100 UV-VIS detector operating at 267 nm and a workstation UPPER were used. The mobile phase (1 ml/min) was composed of acetonitrile + water (20:80 by volume) and phosphate was used to maintain pH = 4. The retention time for imidacloprid was 11.5 min. Calibration curve for quantification was performed using external standards and linear regression analysis.

Ions of chloride and nitrate were detected using a Water

Quanta 4000 capillary electrophoresis (CE) equipped with a 75 μm i. d \times 60 cm quartz capillary column. The evolution of ammonium ions in the irradiated solution was measured spectrophotometrically, using the Nessler reagent (Clesceri, 1989; Pramauro, 1993). UV-Visible (UV-Vis) spectra of photolysis process of imidacloprid were recorded on a PE-Lambda20 UV-Vis spectrophotometer.

2 Results and discussion

2.1 Direct photolysis

Aqueous solutions of insecticide imidacloprid contained in a quartz photo-reactor were irradiated by middle-pressure lamp (125 W) emitting a narrow band of radiation at 254 nm, UV lamp (24 W) at 254 nm and black light fluorescent lamp (24 W) at 365 nm, respectively. Samples for quantification of imidacloprid were collected at designated time intervals and measured by HPLC using a comparison of peak area to a standard curve. The linearity of plots demonstrating of the relationships between concentrations of imidacloprid ($\ln C$) versus irradiation time is illustrated in Table 1, indicating that photochemical degradation reaction was pseudo-first-order in imidacloprid aqueous. As clearly shown in Table 1, the intensity of lamp-house and irradiation wavelength had significant kinetic effects on the photolysis of imidacloprid. The higher of light intensity and short of wavelength of radiation lead to accelerate the photochemical reaction of insecticide imidacloprid in aqueous phase. Under a similar irradiation wavelength, the half-life of imidacloprid under middle-pressure lamp (125 W) decreased about 2 times of that of upon UV lamp (24 W). However, the half-life of imidacloprid under black light fluorescent lamp (365 nm) increased significantly by a factor of 120 compared to UV lamp (254 nm), even under the same light intensity. This finding drove us into conclusion that the wavelength of irradiation was a more critical factor in photolysis of imidacloprid than light intensity.

Table 1 Photolytic rate constant (k) and half-lives ($t_{1/2}$) for imidacloprid at different irradiation

Lamp	k, min^{-1}	$t_{1/2}, \text{min}$	R^2
Middle-pressure lamp (125 W)	0.128	5.4	0.987
UV lamp (24 W)	0.077	9.0	0.992
Black light fluorescent lamp (24 W)	6.4×10^{-4}	1089.9	0.989

Fig. 1 shows the degradation of imidacloprid in glass and quartz reactor under UV lamp irradiation. No significant disappearance of imidacloprid was observed in the dark (control experiment) and in glass reactor. Direct photolysis contributed only 4.1% to the degradation process of imidacloprid (20 mg/L) in 80 min irradiation in glass reactor and less than 0.5% of the initial imidacloprid was disappeared in the dark. However, complete degradation of 20 mg/L of imidacloprid solution was occurred in 40 min in quartz under the same irradiation condition. Due to materials

made of glass, the irradiation below 290 nm was excluded under glass reactor. Compared to quartz reactor, the irradiation energy or efficient photons that imidacloprid molecules were utilized were much less in glass reactor that resulted in very low photo-degradation process. The result also suggested that ultraviolet rays played an important role in photolysis of imidacloprid in aqueous solution.

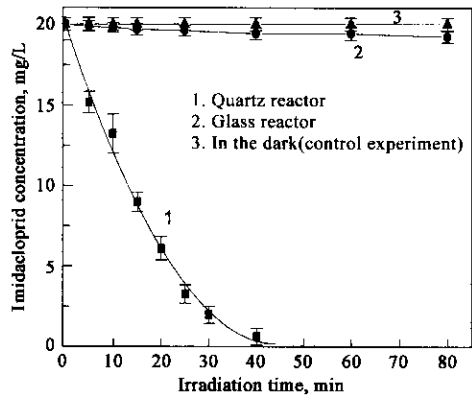


Fig.1 Plots for the photo-degradation of imidacloprid in glass and quartz reactor under UV lamp irradiation

2.2 Sensitized photolysis

With direct photolysis, the possibility of sensitized, or indirect photolysis must be taken into account whether it occurs as far as a light-absorbing photo-sensitizer exists by transferring energy, a hydrogen atom, a proton or an electron to another species(Larson, 1994). Natural photo-sensitizers such as dissolved organic carbon(DOC), hydrogen peroxide, nitrate, and bicarbonate were found to affect the mechanism and kinetics of pesticide photolysis(Wilson, 2000).

Control experiments showed that no significant degradation of imidacloprid was observed in 24 h in a dark reaction with the amendment of acetone, hydrogen peroxide or titanium dioxide, indicated that hydrolysis of imidacloprid could be neglected in the system. However, under the irradiation of black light fluorescent lamp, acetone, hydrogen peroxide and titanium dioxide could accelerate the photo-degradation of imidacloprid in aqueous solution. Fig. 2 displayed the photolysis of imidacloprid (20 mg/L) in presence of various photo-sensitizers. Among the photo-sensitizers used, TiO₂ was the most efficient since the formation of electron-hole pairs was promoted by the near UV light irradiation, which encompassed energies higher than corresponding band gap(Pramauro, 1993; Chen, 1998; Xu, 1999). Hydrogen peroxide was an effective oxidant only for limited compounds, such as phenol and cyanide. However, under the irradiation, hydrogen peroxide produced hydroxyl radicals that possess strong oxidation character. Thus, an enhancement on photo-degradation efficiency was demonstrated in imidacloprid solution containing H₂O₂ under the irradiation of fluorescent lamp. Acetone which has been widely distributed in natural water is triplet photo-sensitizer

and lead to the photo-degradation of organic compounds though electron energy. Even with small amounts of acetone exhibited the degradation process of imidacloprid.

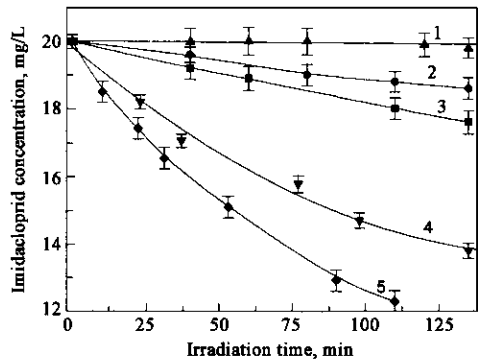


Fig. 2 Photo-degradation of imidacloprid under the irradiation of black light fluorescent lamp (BLFL) in presence of various photo-sensitizers
1. in the dark; 2. BLFL; 3. BLFL + 1% acetone;
4. BLFL + 0.1% H₂O₂; 5. BLFL + 0.1% TiO₂

Experiments were further conducted with UV lamp to investigate photolysis of imidacloprid in aqueous solution containing different concentrations photo-sensitizers, such as acetone and hydrogen peroxide. The results for photolysis in 10 min were obtained as shown in Table 2. As the hydrogen peroxide concentrations increased, the rate of imidacloprid photolysis was also increased accordingly. However, the presence of acetone caused the rate of imidacloprid photolysis decreased upon the irradiation of UV lamp. The magnitude of rate inhibition was increased while the acetone concentrations were increased. This result implied that the decrease in the rate of photolysis could be due to acetone competing with imidacloprid molecule and lead to few photons for imidacloprid direct photo-degradation. Compared to under the irradiation of black light fluorescent lamp(365 nm), the rate of direct photolysis of imidacloprid was far lower upon UV lamp irradiation (254 nm) and the photosensitization of acetone played an important role in the situation.

Table 2 Influence of photo-sensitizers in imidacloprid photolysis upon UV lamp irradiation Unit: mg/L

Photo-sensitizer concentration, mg/L	0.02	0.1	1.0
Control		7.99	
H ₂ O ₂	6.67	2.95	2.36
Acetone	9.63	10.69	13.70

2.3 Analysis of imidacloprid photo-degradation

2.3.1 UV-Vis spectra in the process of imidacloprid photolysis

The variation of UV spectra in the process of imidacloprid photolysis under UV lamp irradiation is shown in Fig. 3. The UV spectrum of imidacloprid displayed two intense absorptions at 287 nm and 211 nm respectively. As time of photolysis increased, the intensity of absorption at 287 nm decreased, indicating the molecule weight of

intermediate products was less than that of imidacloprid and molecule structure was simple as well. According to the findings of intermediates of imidacloprid, we proposed a possible photolytic pathway in this experimental condition (Zheng, 2001).

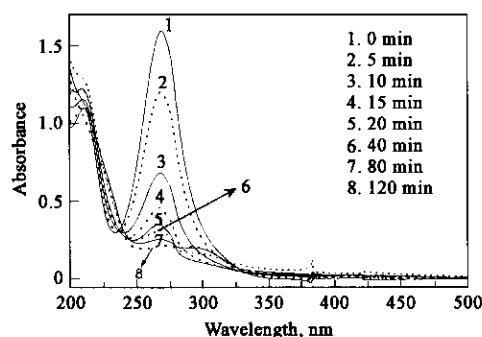


Fig. 3 UV absorbance spectra of photolysis aqueous solution of imidacloprid

2.3.2 Process of mineralization

The organic compounds would be degraded gradually under irradiation and finally lead to the formation of inorganic ions or molecules that are no harmful for environment (Pramauro, 1993). According to the molecular structure of imidacloprid and experimental analysis, the final photochemical degradation products of imidacloprid were CO_2 , Cl^- and NO_3^- . Chloride ion formation in this study is observed in Fig. 4. Imidacloprid in quartz reactor was completely disappeared under UV lamp irradiation in 40 min (Fig. 1). However, the mass balance of chlorine in process of imidacloprid photolysis under the same irradiation condition was slow and required 250 min to reach the expected amounts of Cl^- calculated stoichiometrically, implying that the dechlorination of imidacloprid took place after breakage of ring structure in pesticide molecule. Moreover, the intermediate products via photo-degradation did not contain chlorine even after treating irradiation for 250 min. The formation of nitrate is also shown in Fig. 4. Meanwhile, the NH_4^+ and NO_2^- were detected and the changes of their concentrations were significantly complicated during irradiation due to imidacloprid molecular structure containing five nitrogen atoms. However, the photoreaction

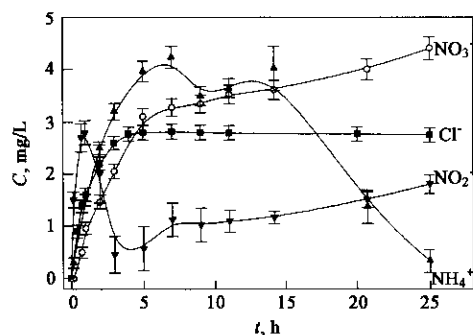
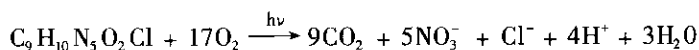


Fig. 4 The formation and evolution of mineralization ions in the process of imidacloprid photolysis

mineralization of N took place as $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ in accordance with the findings in Low *et al.* (Low, 1991) and transformation of N was also demonstrated (Fig. 4). This process was very slow and nitrate was final product of N conversion in imidacloprid photolysis.

With long irradiation process in the presence of oxygen, the overall equation of imidacloprid photo-degradation reaction was proposed as follows:



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