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Kinetics of Acetamiprid Photolysis in Solution

**Xie Guohong · Liu Guoguang · Sun Dezhi ·
Zheng Liqing**

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Abstract Photolysis of acetamiprid was investigated in detail under different reaction conditions. The photolysis of acetamiprid in solution followed pseudo-first-order kinetics under the experimental conditions. Acetamiprid kept stable under irradiation of high-pressure xenon lamp but degraded relatively fast when exposure to medium-pressure mercury lamp irradiation. The experimental results indicated that the degradation rate of acetamiprid in acetone was the largest among the used media and acetamiprid was more stable in basic media. The addition of oxygen, increase of light intensity and temperature will enhance the photolysis.

Keywords Acetamiprid · Photolysis · Kinetics

Pesticides enter into natural water bodies by direct application and by leaching from soil and vegetation. Many of these chemicals present in aqueous media may undergo photochemical transformation under the irradiation of light by direct or indirect photoreaction. Information of the photoreaction over a wide range of environmental conditions is indispensable for an ecotoxicological evaluation of these chemicals in the environment (Leifer 1988).

Acetamiprid, (E)-N^1-[(6-chloro-3-pyridyl)methyl]-N^2-cyano-N^1-methylacetamidine, with CAS number of 135410-20-7 (Fig. 1), belongs to a relatively new class of insecticide known as neonicotinoids, which act on the insect nicotinic (acetylcholine) receptor (nAChR). It has being used to control Hemiptera, mainly aphids, Thyasnoptera and Lepidoptera on a wide range of crops, especially vegetables, fruits and tea (Roberts and Hutson 1999; Mateu-Sanchez et al. 2003). Due to its special acting mechanism, high efficacy, and relatively low toxicity, and no evidence of carcinogenicity, neurotoxicity, mutagenicity or endocrine disruption, acetamiprid is being more competitive and has been considered as a favorable alternative to the organophosphate insecticides, which have caused severe environmental pollution and been banned in many countries (U.S. Environmental Protection Agency 2002). Based on the normal agricultural practice the recommended dose of acetamiprid is 25–75 g a. i. ha^{-1} in China and 0.3–0.6 Ib a. i. per acre in USA.

Owing to its insecticidal effectiveness and environmental safety, acetamiprid is extensively used in agricultural areas (Cao et al. 2005). To our knowledge, no reports have been found to investigate the environmental fate of acetamiprid up to now. The goal of this study is to determine the degradation kinetics under different conditions.

Materials and Methods

Acetamiprid (analytical standard, 99.9% purity) is purchased from Riedel-de Häen (Germany). Methanol (Aldrich), acetonitrile (Merck), isopropyl alcohol (Merck)

X. Guohong · L. Guoguang (✉) · S. Dezhi
School of Municipal and Environmental Engineering,
Harbin Institute of Technology, Harbin 150090,
People's Republic of China
e-mail: liuguoguange303@163.com

X. Guohong
College of Resources and Environment,
Henan Institute of Science and Technology,
Xinxiang 453003, People's Republic of China

L. Guoguang · Z. Liqing
Henan Key Laboratory for Environmental Pollution Control,
College of Chemistry and Environmental Science,
Henan Normal University, Xinxiang 453007,
People's Republic of China

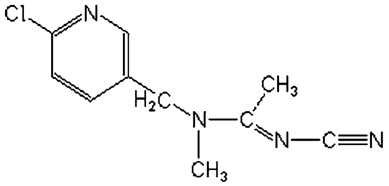

Fig. 1 Molecular structure of acetamiprid

and acetone (Merck) were of HPLC-grade and used as received. Sodium hydroxide, potassium hydrogen phthalate, potassium dihydrogen phosphate, boric acid, which was all analytical grade and used to prepare buffer solution. Deionized water was distilled with potassium permanganate. Buffer solutions were prepared according to literature (Yang and Mo 1994).

Stock solutions of acetamiprid were prepared with concentration of 5 mg/L in water, organic solvents or buffer solutions. 100 mL samples of these stock solutions were taken and placed in quartz tubes(30 cm × 2.5 cm ID) for irradiating for a period of 20–180 min. Reasonable volume of sample was taken at different interval for analysis.

A 125 W medium-pressure mercury lamp or a 500 W high-pressure xenon lamp was utilized as light source. The lamp was placed inside a double-walled quartz well in which cooling water was flowed through to maintain the reaction temperature during photoreaction.

The effect of light intensity on the photolysis of acetamiprid was investigated by changing the distance between the quartz tube and the lamp. The effect of temperature was studied at three different temperatures (288, 298 and 308 K). A quartz tubular oven connected to a temperature controller located around the bottom of the quartz tube was used for heating the solutions. The effect of oxygen was investigated by bubbling O_2 or N_2 in the experimental solution.

The taken samples were treated and analyzed with an HP1100 high performance liquid chromatography equipped with diode array detector, Zorbax-C18 column (250 mm × 4.6 mm ID). Injection volume was 20 μL, column temperature was controlled at 25°C, mobile phase was 0.1% phosphoric acid/acetonitrile (70/30) and flow rate was 1 mL/min. The wavelength was set at 245 nm. Control samples were also analyzed for a set interval which were kept in the dark during irradiation. All experiments were performed in triplicate and the results were averaged.

Results and Discussion

The result showed that, acetamiprid was stable when protected from light and had no no sign of photodegradation. However, it undergone photochemical transformation to a certain extent when exposed to the irradiation of light.

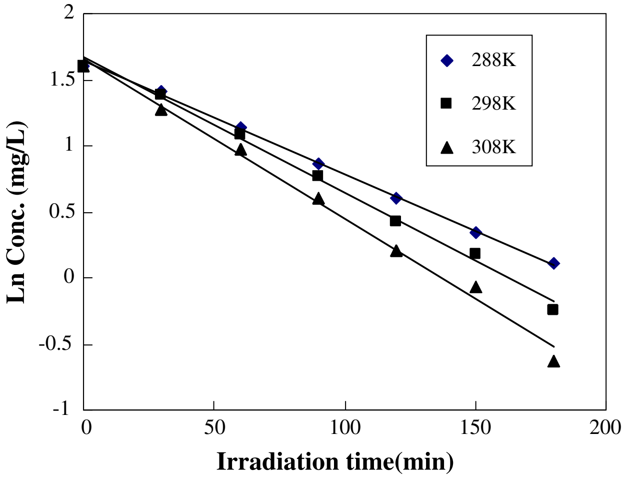

Fig. 2 Plots of ln concentration versus irradiation time at different temperatures during acetamiprid photolysis

The relationship between natural logarithm of acetamiprid concentration and irradiation time was shown on Fig. 2. From the figure, it was found that the photodegradation process follows a pseudo-first-order kinetic equation. This result was in agreement with that of most pesticide photolysis (Da Silva et al. 2003). The rate constants of acetamiprid photolysis under different conditions were determined, and listed in Table 1.

From Table 1, we can see that, the photolysis rate of acetamiprid was dependent on the solvents used, pH value of the solution, light source and intensity, temperature, and the presence of oxygen. The half-life values in different conditions were calculated and they were in the range of 9.183–2,785 min (Table 1).

In this experiment, water, methanol, acetonitrile, isopropyl alcohol and acetone were chosen as the media. The photolysis of acetamiprid in these media was investigated in detail, respectively. The experimental data exhibited that the rate constant followed the sequence: acetone > water > methanol > acetonitrile > isopropyl alcohol. That is to say, in acetone medium, photolysis rate of acetamiprid was the largest, and the difference of photolysis rates in methanol, acetonitrile and isopropyl alcohol were very small and the photolysis rate of acetamiprid in water was very near to that in acetone medium. The effect of solvent on photolysis of pesticides has been reported by other investigators (Zhu et al. 2005).

A series of experiments were designed for investigating the effect of pH values. pH value changed in the range of 4–10. From Table 1, it was obviously that the degradation rate was very close to each other when pH was in the range of 5–10, and acetamiprid was degraded very rapidly at pH

Table 1 Kinetic parameters of Acetamiprid photolysis under different reaction conditions

Factor	Value (type)	Rate constant (min^{-1})	$t_{1/2}$ (min)	R
Solvent	Water	1.028×10^{-2}	67.43	0.9976
	Methanol	9.710×10^{-3}	71.38	0.9981
	Acetonitrile	8.269×10^{-3}	83.82	0.9996
	Isopropyl alcohol	5.472×10^{-3}	126.7	0.9977
	Acetone	1.410×10^{-2}	49.16	0.9969
Buffer	pH = 4	1.187×10^{-2}	58.39	0.9991
	pH = 5	8.600×10^{-3}	80.60	0.9995
	pH = 6	8.117×10^{-3}	85.39	0.9993
	pH = 7	7.027×10^{-3}	98.64	0.9989
	pH = 8	6.303×10^{-3}	110.0	0.9992
	pH = 9	6.152×10^{-3}	112.7	0.9989
	pH = 10	6.645×10^{-3}	104.3	0.9998
Xenon lamp	>200,000 lux	2.489×10^{-4}	2.785	0.9936
Mercury lamp	>200,000 lux	7.548×10^{-2}	9.183	0.9962
	47,000 lux	1.873×10^{-2}	37.01	0.9964
	28,000 lux	1.028×10^{-2}	67.43	0.9976
Gas present	O_2	1.097×10^{-2}	63.19	0.9996
	N_2	6.965×10^{-3}	99.52	0.9986
Temperature	288 K	8.549×10^{-3}	81.08	0.9992
	298 K	1.028×10^{-2}	67.43	0.9976
	308 K	1.208×10^{-2}	57.39	0.9964

If not specially noted, the experiment was carried out in water, with 28,000 lux irradiation of medium-pressure mercury lamp at 298 K, and no gas bubbled in

4. Minero et al. (2006) have studied the effect of pH on the photolysis of pollutants.

Table 1 showed the effect of light source and intensity on the photolysis of acetamiprid. Acetamiprid kept stable when high-pressure xenon lamp was served as light source, the half-life of acetamiprid was 2,785 min even when the light intensity was over 200,000 lux, however, when exposed to the irradiation of medium-pressure mercury lamp, it degraded quickly, and the rate constant increased significantly with the increase of light intensity. The rate constant has increased by a factor of 7.34 when the light intensity increased from 28,000 to >200,000 lux. Acetamiprid strongly absorbs UV radiation in the wavelength range of 200–282 nm (Fig. 3). Its absorption spectrum focused on UV region and gave two maxima at 216 and 245 nm, and two minima at 201 and 223 nm. Clearly, only those UV sources with good output below approximately 280 nm could be useful for the photolysis of acetamiprid. The irradiation spectra of high-pressure xenon lamp and medium-pressure mercury lamp have great difference. The irradiation spectrum of high-pressure xenon lamp was mainly in the range from 290 to 1,000 nm, while the medium-pressure mercury lamp has various outputs in the range from 205 to 500 nm, so medium-pressure mercury lamp is more effective in photolyzing acetamiprid than high-pressure xenon lamp.

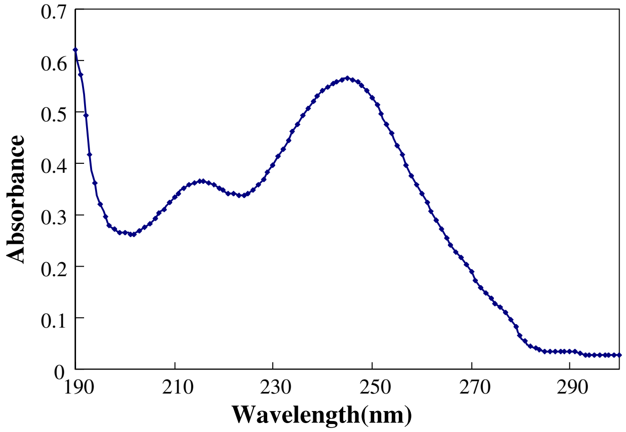

Fig. 3 The absorbance spectrum of acetamiprid in water

Bubbling oxygen into acetamiprid solutions has a slight effect on its photolysis, and it led to a slight increase of the rate constant. On the other hand, bubbling nitrogen has led to a relatively large decline of the rate constant (Table 1). This result perhaps indicated that acetamiprid photolysis did not go through a triplet excited state since O_2 was an excellent quencher of triplets and it could absorb the energy from triplet excited state to ground state, and inhibit the photolysis of pesticide. Many papers reported the effect of dissolved oxygen on pesticide photolysis (Hirahara et al. 2003; Shirayama and Tohezo 2000).

The effect of temperature on the photolysis of acetamiprid was shown in Fig. 2 and Table 1. When the temperature raised even up to 308 K in the control solution, no obvious disappearance of acetamiprid was found. However, when exposed to the irradiation of medium-pressure mercury lamp, the rate constant increased with the increases of temperature. For example, when the temperature was increased from 288 to 308 K, an increase by almost 41.3% in the rate constant was observed. The approximate activation energy, E_a, obtained from Arrhenius equation, was 12.75 kJ/mol.

In conclusion, acetamiprid was more stable in methanol, acetonitrile and isopropyl alcohol, and easy to undergo photolysis in water and acetone. The photodegradation rate of acetamiprid in acetone was larger than that in water media. The raise of pH values prolonged the photolysis of acetamiprid. The irradiation of high-pressure xenon lamp almost could not activize the photolysis of acetamiprid, but the irradiation of medium-pressure mercury lamp made it degraded quickly. The presence of oxygen and increase of the temperature could enhance the photolysis of acetamiprid significantly.

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