



Photodegradation of new herbicide HW-02 in organic solvents

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Abstract

HW-02 is a new organophosphates herbicide which is discovered and developed in China. The kinetics and mechanism of HW-02 photodegradation in the organic solvents were studied at 25°C under the irradiation of ultraviolet light. The results showed that photochemical reaction of HW-02 in organic solvents such as *n*-hexane, methanol, dimethyl benzene and acetone under UV light could be well described by the first kinetic equation, and the photodegradation efficiency decreased with a order of *n*-hexane > methanol > xylene > acetone. The photodegradation efficiency constant of HW-02 in *n*-hexane, methanol, xylene and acetone were 4.951×10^{-2} , 3.253×10^{-2} , 2.377×10^{-2} and $1.628 \times 10^{-2} \text{ min}^{-1}$, and the corresponding half-lives were 13.99, 21.20, 29.15 and 42.56 min, respectively. By separation and identification of photoproducts using GC-MS, it could be concluded that HW-02 was photolyzed through ester cleavage, photo-dechlorination and photoisomerization of the molecule itself.

Key words: HW-02; organic solvent; photodegradation kinetics; degradation mechanism

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Introduction

The degradation of pesticides is currently focused mainly on hydrolysis, photodegradation and microbial degradation (Pu et al., 2002; Tang et al., 2000; Yang et al., 1999; Zheng et al., 2001; Itoh et al., 2005; Abdennour et al., 2005; Li et al., 2008). Photodegradation of pesticides has a significant influence on pesticide residue, efficacy, toxicity and even the environment. The photochemical degradation properties of pesticides have become an important index in ecological environment safety evaluation of pesticide. It is required to provide information of photodegradation for pesticide registration in many countries. Photodegradation of pesticides in the environment as an important process of degradation plays a major role in residue and fate of pesticide in crop surface, atmospheric and water environment (Holmstead et al., 1978; Zheng et al., 2003). When the photochemical reaction of pesticides on the surface of crops is studied, by the reaction mediums of epidermal component of crop are usually *n*-hexane, methanol, acetone and other organic solvents (Pu et al., 2002; Tang et al., 2000; Yang et al., 1999).

HW-02 ($\text{C}_{12}\text{H}_{15}\text{O}_6\text{Cl}_2\text{P}$, O,O-dimethyl-1-(2,4-dichlorophenoxy-acetoxy)ethylphosphonate), as a new organophosphates herbicide, was found and developed by Huazhong Normal University of China. A large number

of laboratory and field tests proved that HW-02 has a good effect against dicotyledonous weeds, monocotyledonae weeds, cyperaceae weeds and fern, such as *Acalypha australis* L., and *Kummerowia striata* Thunb, *Mollugo pentaphylla* L., *Amaranthus retroflexus* L., *Eclipta prostrata* L., *Polygonum lapathifolium* L., *Conyza Canadensis* (L.) Cronq, *Cyperus iria* L., and *Kyllinga brevifolia* Rottb. Up to now, there has not been reported about the research on HW-02 and its analogues in environmental behavior. In order to understand the new pesticide HW-02 behavior of persistence, transference and transformation in the environments, and evaluate correctly environmental safety of the new pesticide HW-02, it is important to investigate the photodegradation of HW-02 in organic solvents.

In this article, the photoreaction kinetics and mechanism of HW-02 in *n*-hexane, methanol, xylene, and acetone were studied at room temperature (21°C), photoreactions were carried out using a medium pressure mercury lamp arc. The photolytic products of HW-02 in *n*-hexane, methanol, xylene, and acetone were determined using GC-MS. The photoreaction mechanism of HW-02 was preliminary discussed.

1 Materials and methods

All reagents and solvents (analytical grade) were obtained from Sinopharm Chemical Reagent Beijing Co.,

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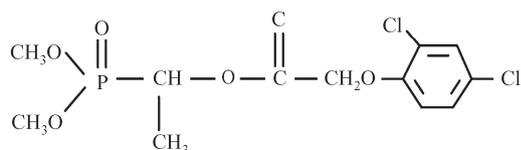


Fig. 1 Chemical structure of HW-02.

Ltd. Ultrapure water was obtained with a Milli-Q system (Millipore). HW-02 (Fig. 1) standard reference material (99% purity) was provided by Shandong Qiaochang Chemical Co., Ltd. Its molecular weight is 357.12 (calculated by the international atomic weight 1995). The pure product is yellow liquid, and the industrial product is slightly yellow liquid. The boiling point is 212–214°C (11 mmHg). It is soluble in most organic solvents such as acetone, ethanol and chloroform.

UV spectra were recorded using a XPA-7 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China). The reactor working conditions are as follows: UV light is medium pressure mercury lamp arc (500 W); the distance is 10 cm from lamp source to liquid level when irradiation; light intensity is 1.641×10^5 lux. The solution of HW-02 standard was prepared in *n*-hexane, methanol, xylene and acetone (20 mg/L), respectively. Ten milliliters of above solutions were irradiated at 1.641×10^5 lux with the medium pressure mercury lamp arc in quartz tubes at $(25 \pm 2)^\circ\text{C}$. The solutions of HW-02 standard were processed in the dark as control. Every treatment was repeated twice and the samples were analyzed at different time.

The samples were analysed using a Agilent 6890N-5973I MSD GC-MS equipped with a HP-5MS elastic quartz capillary column (30 m, i.d. 0.25 mm, 0.25 μm). GC operating conditions were: initial temperature, 100°C (hold 1 min), raised to 180°C (10 min) at 25°C/min, then to 260°C (hold 10 min) at 10°C/min. The injector and interface temperature was set at 280°C. Helium gas was used as carrier gas with a flow-rate of 1 mL/min. The injection mode was pulse nonbleeding and the injection volume was 1 μL . The MS analysis condition were: mass range was from 28 to 550 m/z with scanning interval of 0.50 sec and threshold of 150. The cutting time of solvents was 3 min. The quadrupole rod temperature was 150°C and ion source temperature was 230°C. The GC-MS was automatic tuned by PFTBA.

Quantitative analysis was done by standard curve method, with the detection mode of full scan, setting up standard curve of HW-02 at the concentrations of 5, 10, 20, 30, 40, 50, 100 mg/L (Fig. 2). Good linearity was achieved ($Y = 100072X + 3995.6$, $R^2 = 0.9998$) by peak area Y and injection concentration X .

Photodegradation efficiency (R_L) at different irradiation time was calculated as Eq. (1).

$$R_L = ((C_0 - C_t)/C_0) \times 100\% \quad (1)$$

All the statistical analysis of experimental data was conducted using DPS statistical software (Tang et al., 2002). Photodegradation data were fitted first-order kinetic equation using Marquardt method, and the photodegrada-

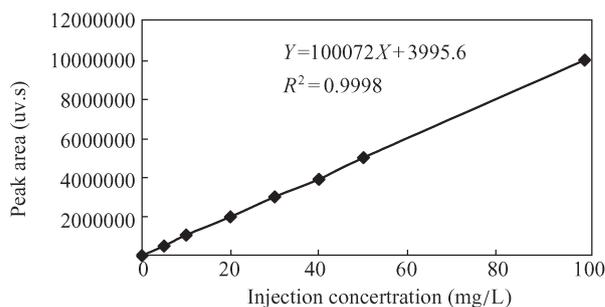


Fig. 2 Standard curve of HW-02.

tion efficiency constant k was obtained.

2 Results

2.1 Photodegradation kinetic of HW-02 in organic solvents

Residue and photodegradation curves of HW-02 in different organic solvents at different irradiation time are shown in Fig. 3. The results showed that HW-02 degradation was rapid in *n*-hexane, since the concentration of HW-02 was lower than the limit of detection (LOD) (0.01 mg/L) after 40 min under UV light; while it was slow in methanol, xylene, and acetone, the photodegradation efficiency was 72.72%, 54.39% and 42.87%, respectively, after 40 min.

The kinetic parameters of the HW-02 photodegradation reactions are listed in Table 1. All the photodegradation reactions fitted the first-order kinetic equation (Marquardt method). HW-02 degradation rate in a sequence as: *n*-hexane > methanol > xylene > acetone. The half-lives of photodegradation were 13.99, 21.30, 29.15 and 42.56 min in *n*-hexane, methanol, xylene and acetone, respectively.

2.2 Identification of photodegradation products of HW-02 in organic solvents

The color of photoreaction solution of HW-02 was from colorless to faint pink when the intensity of medium pressure mercury lamp was 1.641×10^5 lux, and the color gradual deepened with the extend of irradiation time,

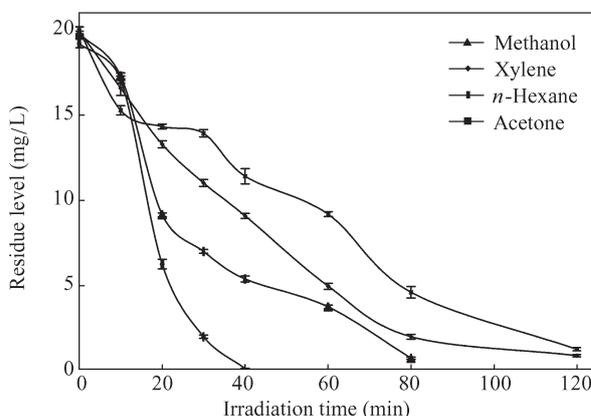


Fig. 3 Photodegradation dynamics curves of HW-02 in different solvents under UV light.

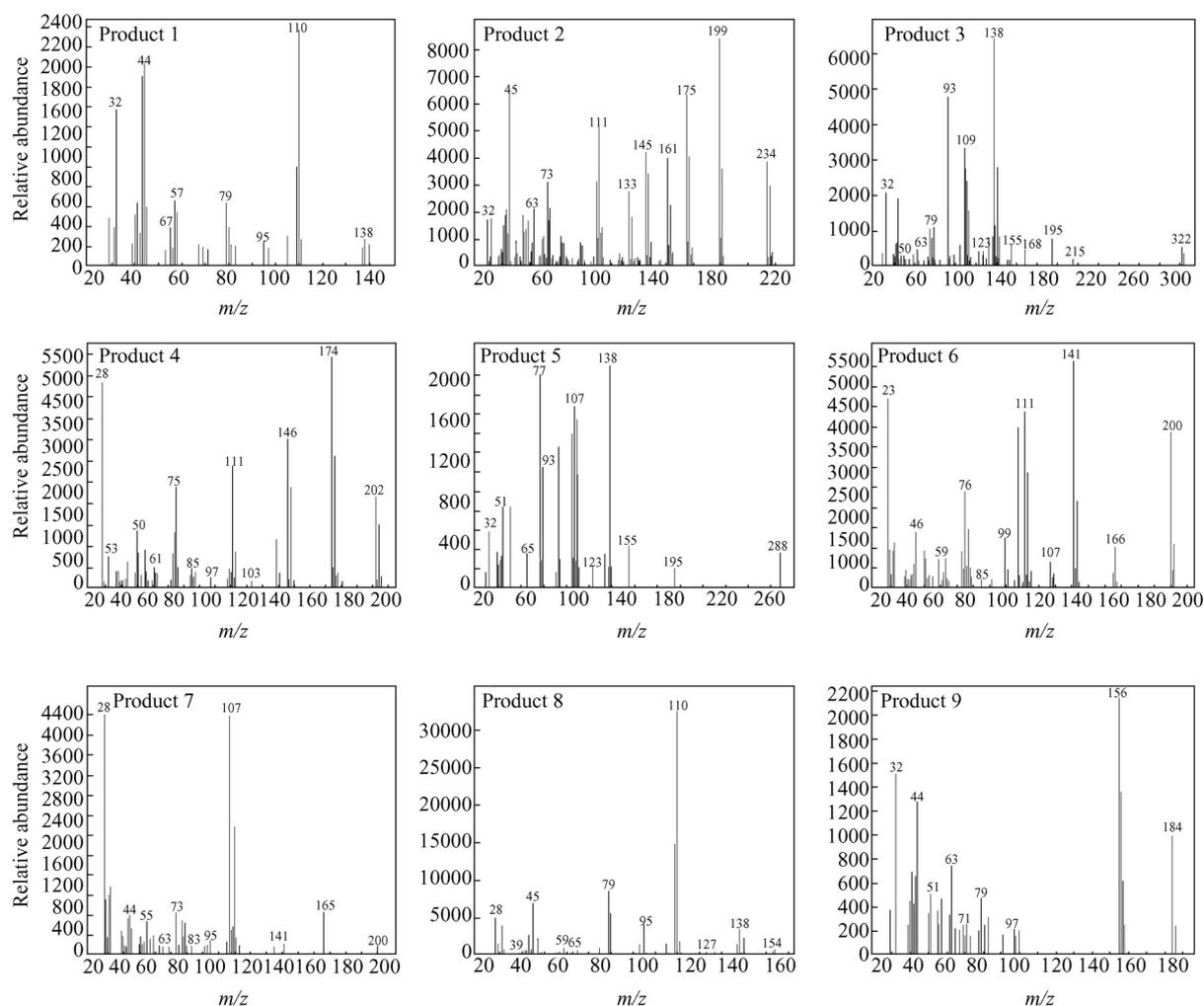


Fig. 4 Mass spectra of main photodegradation products of HW-02.

Table 1 Photodegradation of HW-02 in different organic solvents under UV light

Organic solvents	$T_{1/2}$ (min)	C_0 (mg/L)	K (min^{-1})	R	Fitness* (%)	F value	Significant level P
<i>n</i> -Hexane	13.99	19.17	4.951×10^{-2}	0.9311	97.97	13.47	6.6×10^{-2}
Methanol	21.30	19.74	3.253×10^{-2}	0.9820	95.21	108.19	4.8×10^{-4}
Acetone	42.56	19.94	1.628×10^{-2}	0.9863	98.87	215.19	1.0×10^{-5}
Xylene	29.15	19.89	2.377×10^{-2}	0.9866	97.59	146.05	2.7×10^{-4}

* Fitness means the identical degree between the observed data and kinetics equation.

turned pink and brown at last. Total ionic chromatograms of GC-MS (Fig. 4) in the four organic solvents during photodegradation showed that many peaks of photodegradation products were detected, and the concentration was increasing gradually with time. According to mass of fragment, relative abundance and structural characteristics of the parent compound and the molecular structure of photodegradation products were inferred after separation and detection by GC-MS. The identification of main photodegradation products are listed in Table 2 and the mass spectra of main products are shown in Fig. 4.

2.3 Photodegradation reaction mechanism of HW-02 in organic solvents

Possible mechanism of photodegradation can be inferred according to the identification of photodegradation products in the four solvents (Fig. 5). First, the ester cleavage of HW-02 induced three main photodegradation products O,O-dimethyl-1-hydroxyethyl phosphonate, 2,4-dichlorophenoxyacetic acid and O,O-dimethyl ethyl phosphonate. Second, two main photodegradation products, O,O dimethyl-1-(2-chlorophenoxy-acetoxy) ethyl phosphonate and 2,4-dihydroxyphenoxyacetic acid through

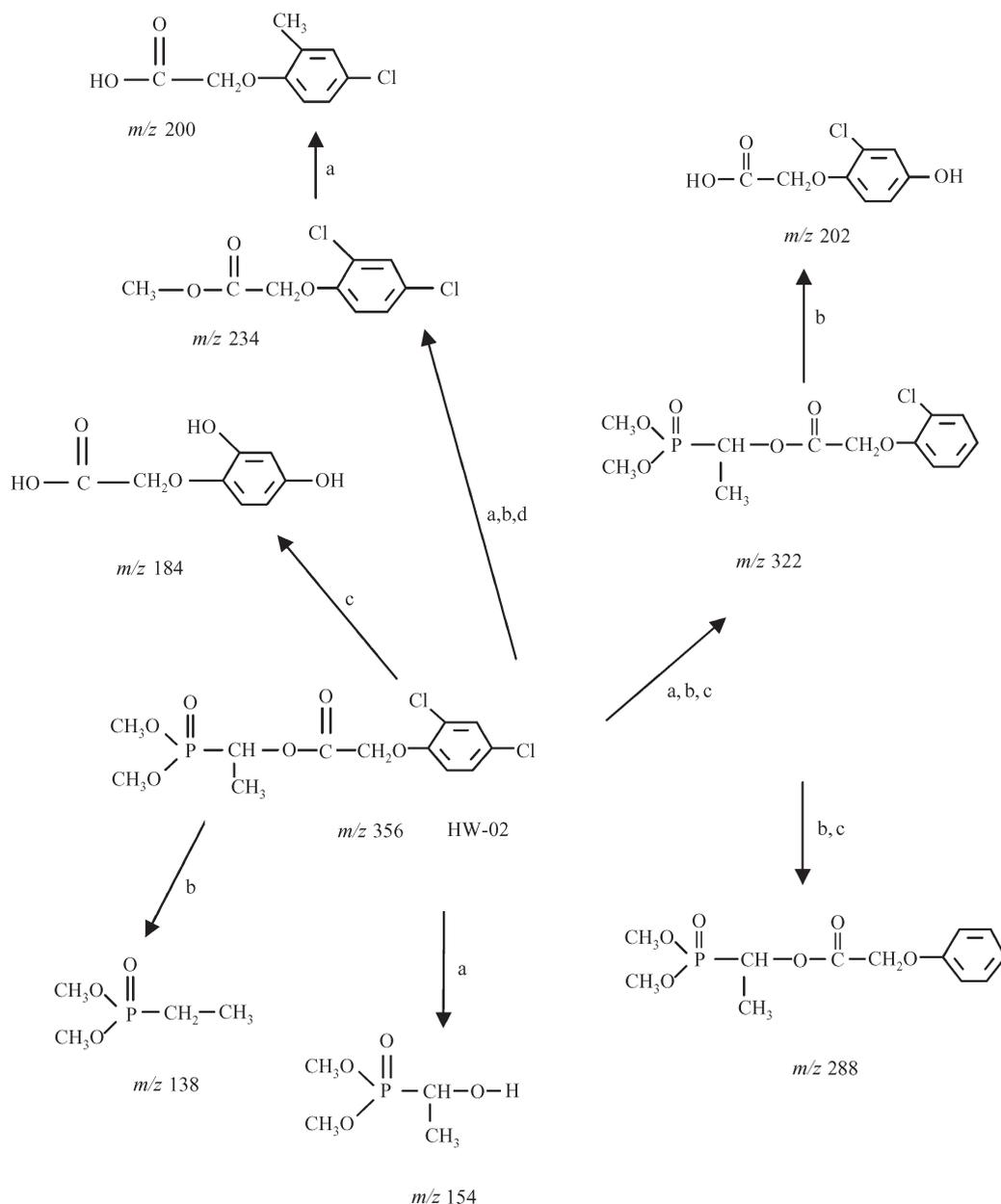


Fig. 5 Possible pathways of HW-02 photodegradation in methanol (a), acetone (b), *n*-hexane (c), and xylene (d) under the UV light.

HW-02 dechlorination reaction were observed. Third, by photoisomerization, only one photodegradation product, 2,4-dichlorophenoxyacetic methyl ester, was observed. The above mentioned photolysis intermediate are not

accumulated, and they can further photodegradation with irradiation time extending. The final mineralization products may be carbon dioxide, chloride ion, or phosphoric acid in accordance with the molecular structure of HW-02.

Table 2 Main photodegradation products of HW-02 in organic solvents under UV light

Products	Molecule weight	Main fragment ion peak (m/z)	Molecular formula	Organic solvents	Match extent
1	138	57 79 95 110 138	$C_4H_{11}PO_3$	Acetone	95
2	234	111 133 145 161 175 199 234	$C_9H_8O_3Cl_2$	Acetone, methanol, xylene	91
3	322	93 109 138 195 322	$C_{12}H_{16}O_6P$	Acetone, methanol, <i>n</i> -hexane	
4	202	75 111 145 174 202	$C_8H_7O_4Cl$	Acetone	83
5	288	73 93 107 138 195 288	$C_{12}H_{17}O_6P$	Acetone, <i>n</i> -hexane	
6	200	75 99 141 165 200	$C_9H_9O_3Cl$	Methanol	87
7	200	107 166 200	$C_9H_9O_3Cl$	Methanol	
8	154	79 95 110 138 154	$C_4H_{11}O_4P$	Methanol	89
9	184	51 63 77 112 140 155 168 184	$C_9H_9O_2Cl$	<i>n</i> -Hexane	94

3 Discussion

Photochemical degradation of pesticides in plant tissue was often simulated by certain functional groups of organic solvents, which is a commonly research method of photochemical degradation (Yang et al., 1999). In this study, the results showed that photodegradation efficiencies had an obvious difference in the four organic solvents under the UV light.

The polarity is 0 for *n*-hexane, 0.6 for methanol, 1.4 for xylene, and 6.2 for acetone (Awadh et al., 2002), indicating that UV photodegradation of HW-02 is independent of polarity of organic solvents, which is in accordance with the photodegradation of Imidacloprid, SV1 (Tang et al., 2000), Permethrin, HNPC-A9908 in organic solvents (Zheng et al., 2002).

The photodegradation activity of HW-02 decreased in a series of organic solvents with the order of *n*-hexane > methanol > xylene > acetone. This may be because the most UV wave was absorbed by acetone and caused the photochemical reaction of acetone, which reduced UV absorption and decreased the photodegradation activity of HW-02. This result is consistent to the photochemical degradation of hexaconazole in acetone (Ren et al., 2004). However, *n*-hexane has the weak UV absorption, which might cause the rapid photodegradation of HW-02. In short, the different photodegradation activity of HW-02 may be related to the different UV absorption in the four organic solvents. And further study should be performed for this mechanism. In this study, the photolysis site and the degradation products of pesticides were identified by isotope tracer technique. The main photodegradation products (Fig. 5) of HW-02 in the four solvents were separated and identified using GC-MS. However, it was difficult to identify the molecular structure of all unknown compounds only by GC-MS. The other unknown degradation products need further separate and identify through a variety of technologies, such as ¹H NMR, carbon NMR, IR and UV absorption spectra (Ning, 1989). Finally, the molecular structure of unknown compounds were identified after the comprehensive analysis of various spectra.

4 Conclusions

(1) Photodegradation of HW-02 in the organic solvents under UV light was described by the first-order kinetic equation, the degradation rate was in a sequence of: *n*-hexane > methanol > xylene > acetone. The half-lives of HW-02 photodegradation in the four organic solvents were 13.99, 21.20, 29.15, and 42.56 min, respectively.

(2) The pathways of HW-02 photodegradation in the organic solvents may be as the follows. First, the cleavage of carbon-oxygen ester bond of HW-02 induced the production of O,O-dimethyl-1-hydroxyethyl phosphonate, 2,4-dichlorophenoxyacetic acid and O, O-dimethyl ethyl

phosphonate; second, dechlorination, the carbon-chlorine bond scission, produce O,O-dimethyl-1-(phenoxy-acetoxy) ethyl phosphonate and 2,4-dihydroxy phenoxy acetic acid; third, 2,4-dichlorophenoxyacetic acid methyl ester formed by the photoisomerization of HW-02. The above intermediate products would continually undergo photodegradation, and final mineralize to the products of carbon dioxide, phosphoric acid and other non-toxic substances.

Acknowledgments

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References

- Abdenmour Z, Michel J, Bernadette L, Tahar S, 2005. Photodegradation of chlorinated pesticides dispersed on sand. *Chemosphere*, 58(3): 1431–1437.
- Awadh J A M, 2002. The photodegradation of chlorpyrifos. Ph.D Thesis, Zhejiang University, Hangzhou. 113–120.
- Holmstead R L, Casida J E, Ruzo L O, Fullmer D G, 1978. Pyrethroid photodecomposition: Permethrin. *Journal of Agricultural and Food Chemistry*, 26(3): 590–595.
- Itoh Y, Kaneko T, Akahane E, Shirai H, Kojima M, 2005. Photodegradation of 1,3,5-trichlorobenzene in aqueous surfactant solutions. *Bulletin of Environmental Contamination and Toxicology*. 74(2): 365–372.
- Li Q Y, Li Y, Zhu X K, Cai B L, 2008. Isolation and characterization of atrazine-degrading *Arthrobacter* sp. AD26 and use of this strain in bioremediation of contaminated soil. *Journal of Environmental Sciences*, 20(10): 1226–1230.
- Ning C Y, 1989. Structural Identification of Organic Compounds and Organic Spectroscopy. Tsinghua University Press, Beijing. 266–332.
- Pu Y, Yang X, Ding L, Wu G, Kong L R, 2002. Photolysis of pyridaben in methanol. *Journal of Nanjing University (Natural Science)*, 38(2): 211–215.
- Ren L P, Tian Q, Zhou Z Q, Jiang S R, Rao Z H, 2004. Photochemical degradation of hexaconazole. *Chinese Journal of Pesticide Science*, 6(4): 73–77.
- Tang F, Yue Y D, Hua R M, Chen J, 2000. Photodegradation of SV1 in various solvents. *Chinese Journal of Pesticide Science*, 2(2): 71–76.
- Tang Q Y, Feng M G, 2002. Practical Statistics Analysis and DPS Data Treatment System. Science Press, Beijing. 648.
- Yang X, Meng Q Y, Kong L R, Wang L S, 1999. Photolysis of methsulfuron-methyl in organic solvents. *Chinese Journal of Environmental Science*, 20(5): 66–68.
- Zheng H, Ye C, 2001. Photodegradation of acetochlor and butachlor in waters containing humic acid and inorganic ion. *Bulletin of Environmental Contamination and Toxicology*, 67(10): 601–608.
- Zheng H H, Ye C M, 2003. Photodegradation of acetochlor in water and UV photoproducts identified by mass spectrometry. *Journal of Environmental Sciences*, 15(6): 783–790.
- Zheng W, 2000. Physical chemistry and biochemistry behaviors of pesticide imidacloprid in environment. Ph.D Thesis, Zhejiang University, Hangzhou. 78–90.