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HYDROLYSIS OF CHLORPYRIFOS IN AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES AND pH

(Hidrolisis Klorpirifos dalam Larutan Akueus pada Suhu dan pH Berbeza)

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Abstrak

Hidrolisis klorpirifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothionate) telah dikaji dalam media akues pada suhu dan keadaan pH yang berbeza. Pemalar kadar dan jangka hayat separa yang diperolehi menunjukkan bahawa klorpirifos lebih stabil dalam keadaan berasid. Kadar degradasi meningkat apabila nilai pH bertambah. Suhu juga mempengaruhi kadar hidrolisis. Hidrolisis klorpirifos dalam air mematuhi tindak balas tertib pertama. Jangka hayat separa klorpirifos dalam larutan akues adalah pendek (di antara 4.57 hingga 14.0 hari), dan ianya bergantung pada kepekatan asal klorpirifos dan jenis larutan akues. Kadar degradasi adalah perlahan dalam larutan 0.02M $CaCl_2$ dengan kepekatan asal klorpirifos yang tinggi. Perbandingan antara kadar hidrolisis dalam laruatan air steril dan tidak steril tidak menunjukkan peranan biodegradasi yang ketara dalam air tidak disteril. Keputusan ini menunjukkan bahawa parameter pH sahaja tidak mencukupi untuk menjangkakan kadar hidrolisis klorpirifos.

Katakunci: Klorpirifos, hidrolisis, pestisid organofosforus

Abstract

The hydrolysis of chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothionate) was investigated in buffered aqueous media at different temperature and pH conditions. Rate constants and half-life studies revealed that chlorpyrifos was relatively stable in acidic medium. The rate of degradation increased as the pH increased. Temperature showed a significant effect on the rate of hydrolysis. The hydrolysis of chlorpyrifos in water follows first-order kinetics. The half-life of chlorpyrifos in aqueous solutions was short (half-lives ranged from 4.57 to 14.0 days), depending on the initial concentration of chlorpyrifos and the type of the aqueous solutions. The rate of degradation was slower in the 0.02M $CaCl_2$ solution containing higher initial concentration of chlorpyrifos. Comparison between hydrolysis rate of chlorpyrifos in sterilized and non-sterilized water did not showed significant contribution of biodegradation component. These results indicate that pH alone cannot be used as a single parameter to predict hydrolysis of chlorpyrifos.

Keywords: Chlorpyrifos, hydrolysis, organophosphorus pesticide

Introduction

Chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothionate) (Figure 1) is a broad-spectrum insecticide whose mode of activity is as a cholinesterase inhibitor. It is used to kill a wide variety of insects including cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice by disrupting their nervous system. It is also used as a soil treatment (pre-plant and at planting), as a seed treatment and as a foliar spray, directed spray and dormant spray. Chlorpyrifos degradation is governed by both abiotic (e.g.: hydrolysis, photolysis) and biotic factors (e.g.: microbial degradation). After release in the aquatic compartment, degradation via hydrolysis is among the main transformation pathways for chlorpyrifos. Hydrolysis may occur at several reactive centres in the pesticide molecule, in the presence of OH^- or H_2O acting as nucleophilic reagents [1].

The degradation pathway of chlorpyrifos in aquatic environments involves the breakdown of the thiophosphoric esters, forming 3,5,6-trichloropyridinol (TCP) and desethyl chlorpyrifos (DEC) as main metabolites.

The hydrolysis rate of chlorpyrifos in aquatic environments is influenced by environmental factors such as pH, temperature and other solution constituents. Reported hydrolysis half-lives (ranged from 18.9 to 120d) showed more rapid hydrolysis under alkaline conditions compared to neutral or acidic conditions [2]. The rate of hydrolysis was reported to increase an average of 3.5-fold and 5-fold for each 10°C rise in temperature by Meikle and Youngson in 1978 [3] and Noblet [4], respectively. The aqueous hydrolysis of chlorpyrifos may be catalyzed by dissolved copper ions [5] and free chlorine [3,6].

Surface water and groundwater quality may be affected by the widespread use of pesticides in the agricultural areas. As a widely used organophosphorus insecticide in Malaysia, there is a need to evaluate the fate of chlorpyrifos in the environment to which it may be applied. Most of the hydrolysis study of chlorpyrifos has been carried out in temperate zone, but there is still limited information on the fate and behaviour of chlorpyrifos in the tropical environment. The objective of this study was to investigate the hydrolysis of chlorpyrifos in aqueous media at different pH and temperatures.

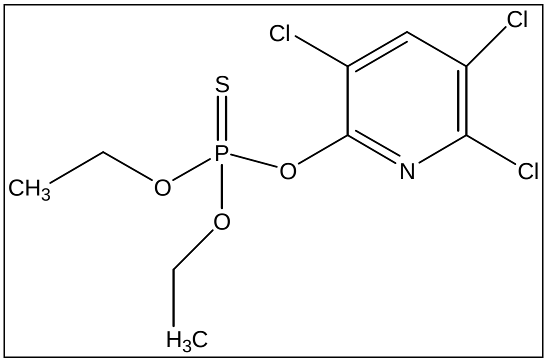

Figure 1: Structure of chlorpyrifos

Experimental

Chlorpyrifos standard (>99.5% purity) were purchased from Sigma-Aldrich (Brand Riedel-de Haën). Stock solution was prepared by dissolving chlorpyrifos in acetonitrile. The effect of pH on the hydrolysis of chlorpyrifos was investigated using three triplicate sets of distilled water (50mL) fortified with 1.45mgL^{-1} chlorpyrifos in tightly stoppered flasks. The pH of the samples was buffered at 4.0, 7.0 and 10.0. The initial concentration (C_o) was measured immediately after sample preparation was completed. The samples were kept in constant temperature bath at 29±1°C. 5mL of samples were drawn, extracted three times with n-Hexane (10mL, 5mL and 5mL, respectively) and analyzed daily by using ThermoFinnigan GC fitted with AT^{TM}-1 Capillary Column (0.25µm x 0.25mm x 30m Alltech) and a Nitrogen Phosphorus Detector (NPD). The column temperature was programmed from 125 to 230°C at rate of 30°C/min, held at 230°C for 6 min, the detector and injector temperatures were 300 and 200°C, respectively. The effect of temperature on hydrolysis of chlorpyrifos was also investigated using another set of samples (1.45mgL^{-1} chlorpyrifos) buffered at pH 7.0 and incubated in thermostated water baths maintained at 20, 30 and 40±1°C. The concentrations of chlorpyrifos in the aqueous solution were then monitored daily as above. Hydrolysis of chlorpyrifos (initial concentration = 0.50, 1.00 and 1.80 mgL^{-1}) in 0.02M $CaCl_2$ was also investigated at room temperature (29±1°C).

Results and discussion

Chemical hydrolysis of chlorpyrifos at 29±1°C was investigated using buffered solutions at pH values 4, 7 and 10. All plots of the logarithm of the normalized concentration as a function of the reaction time (Figure 2) gives straight lines, indicating the reaction tends to be a pseudo-first-order reaction. The rate constants and half-lives (Table 1) indicate the relative fast degradation of chlorpyrifos in aqueous solution. The stability of chlorpyrifos decreased as the pH increased. The effect of temperature on rates of hydrolysis was also significant (Table 1, Figure 3). The half-life of chlorpyrifos in distilled water at pH 7.0 was 12.3 and 8.12 days at 16 and 40°C, respectively.

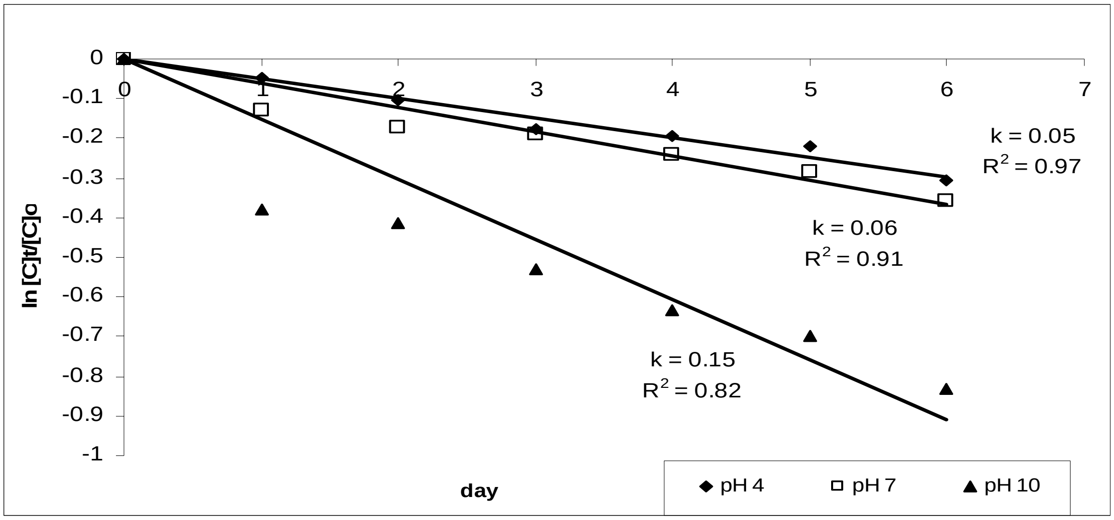

Figure 2: Hydrolysis kinetics of chlorpyrifos at various pH values at room temperature (29°C).

Table 1: Kinetic data for the hydrolysis of chlorpyrifos at various pH values and temperature.

	pH	Temperature (°C)	k (d^{-1})	$t_{1/2}$ (d)	R^2
This study	Buffer pH 4	29±1	0.05	14.0	0.97
	Buffer pH 7	16±1	0.06	12.3	0.92
		29±1	0.06	11.3	0.91
		40±1	0.09	8.12	0.92
	Buffer pH 10	29±1	0.15	4.57	0.82
	Buffer pH 7 (RO water)	29±1	0.06	11.9	0.94
Wu [3]	Milli-Q water (Ci = 0.257µmolL^{-1}) pH 6.50	23±2	0.01	56.8	-
	Milli-Q water (Ci = 1.283µmolL^{-1}) pH 6.50	23±2	$4.4x10^{-3}$	158	-
Noblet [4]	Buffer pH 8 (sterilized)	40	0.06	11.2	-
Dow AgroSciences LLC [7]	Buffer pH 4.7	25	-	63	-
	Buffer pH 6.9	25	-	35	-
	Buffer pH 8.1	25	-	23	-
Liu *et al.* [8]	De-ionized water pH 5.72	-	0.02	45.9	-
Deerasamee and Tiensing [9]	De-ionized water pH 5.5	Outdoor condition	-	2.72	-

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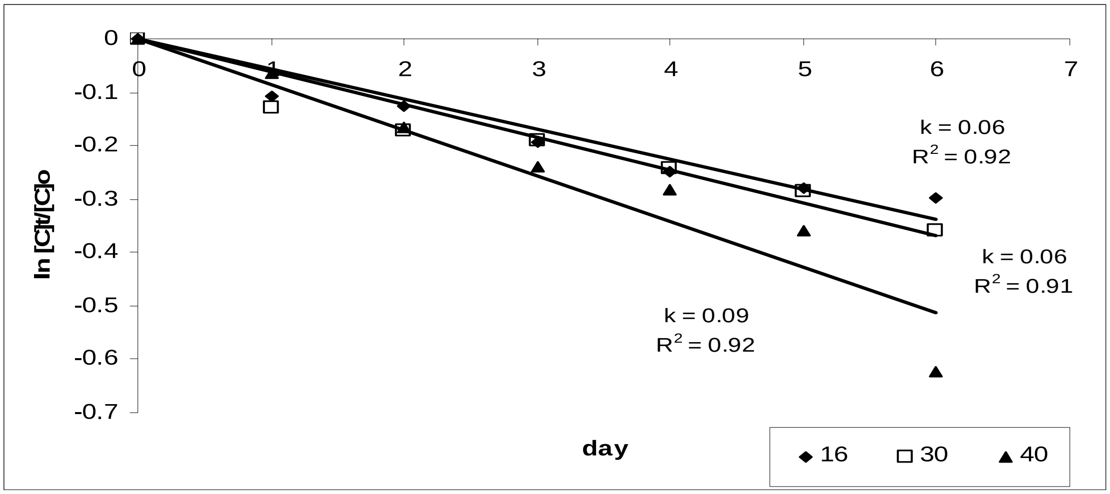

Figure 3: Hydrolysis of chlorpyrifos in pH 7 buffer at various temperatures.

For hydrolysis in 0.02M $CaCl_2$, the results showed that degradation of chlorpyrifos still occurred very fast when the initial concentration of chlorpyrifos was low (0.5 mgL^{-1}). However at higher initial concentration (1.8 and 1.0 mgL^{-1}), the half-life for chlorpyrifos was 1.5-2 times longer (Table 2, Figure 4). Although the hydrolysis rates obtained in this study is relatively faster as higher concentration of $CaCl_2$ solution and higher experimental temperature had been chosen, but the trend is in agreement with previous study [3].

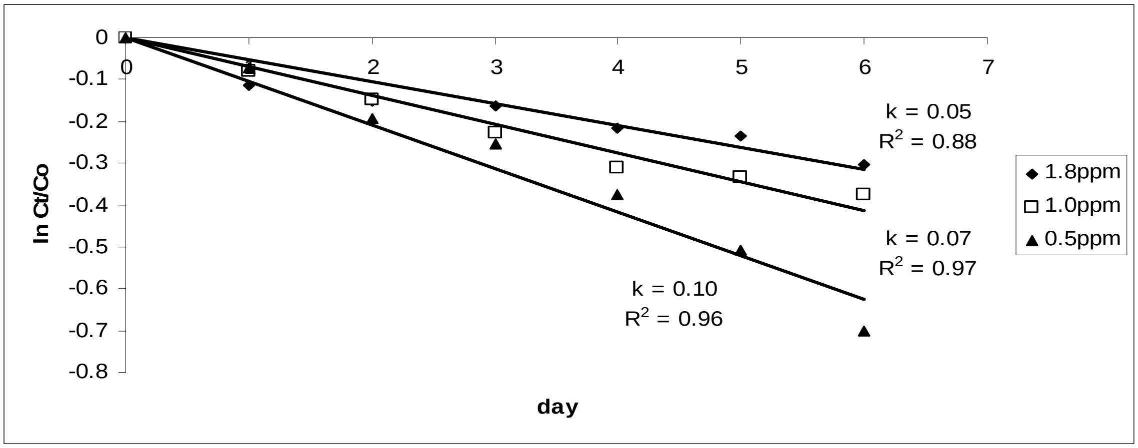

Figure 4: Hydrolysis of chlorpyrifos in 0.02M $CaCl_2$.

Table 2: Kinetic data for the hydrolysis of chlorpyrifos in 0.02M $CaCl_2$.

	This study (0.02M $CaCl_2$)			Wu (0.01M $CaCl_2$)	
Initial concentration	1.80 mgL^{-1}	1.00 mgL^{-1}	0.50 mgL^{-1}	1.283$\mu molL^{-1} \approx$ 0.45 mgL^{-1}	0.257$\mu molL^{-1} \approx$ 0.09 mgL^{-1}
Temperature (°C)	29±1	29±1	29±1	23±2	23±2
k (d^{-1})	0.05	0.07	0.10	0.01	0.01
$t_{1/2}$ (d)	13.2	10.1	6.66	60.3	52.9
R^2	0.88	0.97	0.96	-	-

- : not stated

The results obtained in this study showed faster hydrolysis rate for a comparable pH value and temperature condition compared to previous studies [3-4,7-8] (Table 1 and Table 2). In this study, only preliminary screening experiments were carried out to determine roughly the rates of hydrolysis at various pHs and temperatures, meanwhile majority of the reported data was derived from experiments that followed well-established hydrolysis test protocols which consist of a multi-level approach as described by Noblet [4]. As a comparison, hydrolysis test was performed with reverse osmosis water buffered at pH 7, however the half-life obtained was not significantly longer compared to non-sterile water (Table 1). On the other hand, a half-life of 2.72 days in deionized water (outdoor condition) has been observed in Thailand by Deerasamee and Tiensing [9], showing that the hydrolysis of chlorpyrifos is relatively faster in tropical environment. Besides, the chlorine, metals and other cations residue in distilled water may also responsible for the rapid hydrolysis of chlorpyrifos observed in this study [3,6]. Other experimental errors such as losses due to volatilization, adsorption onto glass surface [10] and pH changes might also resulted in higher hydrolysis rates.

Conclusions

The hydrolysis of chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothionate) is greatly influenced by pH and temperature. Hydrolysis is slower in acidic condition and lower temperature. The hydrolysis of chlorpyrifos in different aqueous media follows first-order kinetics, with half-lives ranged from 4.57 to 14.0 days. Hydrolysis rate is slower in the 0.02M $CaCl_2$ solution containing higher initial concentration of chlorpyrifos. Comparison between sterilized and non-sterilized water suggested the contribution of biodegradation component. These results indicate that pH alone cannot be used as a single parameter to predict the hydrolysis of chlorpyrifos, other parameter such as temperature, metal content and water quality also showed significant effect on the hydrolysis rate.

Acknowledgements

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