CHEMICAL ENGINEERING TRANSACTIONS
VOL. 59, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216
DOI: 10.3303/CET1759162

The Anoxic Degradation of Deltamethrin in Bohai Coastal Sediment

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At present, the qualities of the coastal aquatic ecosystems and sediments have seriously deteriorated as a result of excessive using the pyrethroid insecticides in the tidal farms. Deltamethrin is one of the most frequently detected pyrethroid in the coastal sediment. In this paper, the anoxic degradation behavior and mechanism of deltamethrin in bohai coastal sediment was studied. The results showed that deltamethrin could be degraded in natural coastal sedimentary environment at a relatively slow rate. The degradation kinetics followed the first-order kinetic with the rate constant 0.0055 h^{-1}.The m-phenoxyphenyl-acetonitril was the main metabolic product, and the possible degradation pathway was that deltamethrin was hydrolyzed at ester bond firstly, and then was reduced to be m-phenoxyphenyl-acetonitril. Adequate addition of carbon sources could significantly promote the microbial degradation of deltamethrin, but oversupplying carbon source inhibited it.

1. Introduction

Pyrethroids are synthetic derivatives of pyrethrins, which are natural insecticides that are produced by certain chrysanthemum (Chrysanthemum cinera-riaefolium) (Sankowska and Gajek, 2016). Pyrethroid insecticides have been used since the 1970s, and its application increased rapidly after the ban on some organophosphorus insecticides for their high insecticidal activity, low mammalian toxicity, and adequate stability in air and light (Xie et al., 2008). In China, pyrethroids are not only used as agricultural insecticides, but also extensively used in tidal farms of the coastal cities. But pyrethroids are high toxic to aquatic organisms, including fish such as bluegill and lake trout, with LC50 values less than 1.0 part per billion (Weston et al., 2005). For example, deltamethrin and cypermethrin have 96 h LC50s of about 0.01 ng/mL in lobster (Homarus americanus) and shrimp (Crangon septemspinosa).

Pyrethroids are lipophilic insecticides. They are adsorbed easily by particulate matter or oil drop once they enter into the water environment, and then subside onto the sediments, which will reduce their degradability (Laskowski, 2002). Presently, the qualities of the coastal aquatic ecosystems and sediments have seriously deteriorated as a result of excessive using the pyrethroid insecticides in the tidal farms (Amweg et al., 2006). In China, deltamethrin is one of the most frequently detected pyrethroid in the coastal sediment, whose content in bohai coastal sediment even beyond 100 μg/kg according to our study result. Now the photolysis (Liu et al., 2010) and aerobic biodegradation (Zhang et al., 2016) behavior of pyrethroids in the soil and water have been reported. But the coastal sedimentary environment is very different from the soil and water environment for it is always under anoxic conditions and lack of sunlight. The coastal sediment is mainly reducing environment and the microorganism existing in sediment are mainly facultative anaerobic and anaerobic microorganisms. Therefore in coastal sediment, the possibility of photolysis and aerobic biodegradation is very small. Some studies have found that some insecticides in the sediment, such DDT (Dichlorodiphenyltrichloroethane) (Zhao et al., 2002), HCB (Hexachlorobenzene) (Wang et al., 2002) could be degraded by micro-organism under the anoxic condition. So anoxic biodegradation may be important metabolic way of pyrethroids in coastal sediment. However, to the best of our knowledge, there were few reports on the anoxic degradation of pyrethroids in sediment.

In this paper, we studied anoxic degradation behavior and approach of deltamethrin as a representative pyrethroid insecticide in coastal sediment. Because pyrethroid insecticides have similar degradation pathways

Please cite this article as: Shuaijie Wang, Nannan Di, Yao Guan, Laizhou Song, Jun He, 2017, The anoxic degradation of deltamethrin in bohai coastal sediment, Chemical Engineering Transactions, 59, 967-972 DOI:10.3303/CET1759162

usually, the result would provide a basis of assessing the general fate of pyrethroids in sediment. Meanwhile, the effect of carbon source on the anoxic degradation of deltamethrin in coastal sediment was also studied. Result from it will provide scientific basis of artificial restoration of coastal sediment.

2. Materials and methods

2.1 Chemicals

Deltamethrin standard, which has the purity of 99.5 %, were supplied by Shanghai Troody Analytical Instrument Co.Ltd. A portion of deltamethrin standard was dissolved into petroleum ether to give a concentration of 0.71 mg/ml. Petroleum ether and acetone were of analytical grade and obtained from Tianjin Chemical Company. Glucose and sodium acetate were of analytical grade and obtained from Qinhuangdao Chemical Company.

2.2 Coastal water and sediment used

The samples of coastal water and sediments were collected at Bohai coastal zone near Heibei Street in Qinhuangdao City. Sediment samples were collected from a layer which was 10-20 cm depth under the surface sediment, and then were reserved at 4 ˚C in the refrigerator in 24 h after collection. The pH of the coastal water sample was 8.37. The basic properties of coastal sediment were analyzed before experiments (Table 1).The content of organic matter in sediment was determined with the potassium dichromate volumetric method. The content of Total P in sediment was determined with Mo-Sb anti spectrophotometric method. The content of Total N in sediment was determined with ultraviolet spectrophotometry method after digestion. The content of Hg, Cu and Cd in sediment were determined by atomic absorption spectrophotometry after digestion.

Table 1: Some basic properties of the sediment studied

Organic Matter (%)	Total P (mg/g)	Total N (mg/g)	Hg (μg/g)	Cu (μg/g)	Cd (μg/g)
0.10	0.17	0.08	23	140	8.4

2.3 Deltamethrin degradation

Fresh coastal sediments, each equivalent to 10 g of dry sediment, were placed in a series of 125 ml tapered bottle containing 10 ml sea water. Appropriate amount of deltamethrin solutions were added into the sediment to obtain a concentration of 1775 μg/kg (deltamethrin/sediment). The bottles were then placed on an oscillator for 2 h at 200 rpm, and then were incubated at 25 ˚C after injecting nitrogen gas for 10 min and sealing. The residues of deltamethrin in the sediments were determined at different intervals.
At the same time, enhanced degradation at the presence of supplementary glucose or sodium acetate were observed to study the effect of easily degradable carbon source on the anoxic degradation of deltamethrin in the coastal sediment.

2.4 Determination of extractable residues

Deltamethrin was extracted from the sediment using 20 ml of petroleum ether and acetone (1:1, v/v) in an ultrasonic bath. After partition, clean-up, and concentration, residues dissolved in petroleum ether were taken for GC analysis. Recoveries of deltamethrin residues in the sediment samples at 375 μg/kg, 1065 μg/kg and 1775 μg/kg were from 97.9 % to 106.4 %, with a relative standard deviation (RSD) ranging from 1.15 % to 1.93 %.
Deltamethrin was determined using GC-ECD HP7890 SeriesII gas chromatography (Palo Alto, CA, USA) with a Hewlett-Packard HP-5 capillary column (30 m×0.32 mm×0.25 μm), equipped with an electron capture detector(ECD-63Ni). Metabolic product was analyzed by GC-MS Agilent 7890 Series Plus gas chromatography linked to a quadrupole mass spectrometer (Agilent 5975C) with a HP-5 MS capillary column (30 m×0.25 mm×0.25 μm).

3. Results and discussion

3.1 Anoxic degradation of deltamethrin

Figure 1 shows the degradation curve of deltamethrin in Bohai coastal sediment. As indicated, 43.15 % applied dose of deltamethrin was removed from the fresh coastal sediment after 110 h. The degradation rate was relatively slow within the beginning 14 h, which had some connection with metabolism of microorganisms. The enzymatic reaction is the essence of microbial degradation of pesticides. After deltamethrin was added into the sediment, the microorganisms in coastal sediment needed time to create new degrading enzymes by

the recombination or transform of genes, which resulted in the lag phase during the biodegradation process. After 14 h of incubation, the anoxic degradation rate increased rapidly, which implied new degrading enzymes had been created and microorganism in the sediment had adapted to the new environment.
The model of pseudo-first-order kinetics is used usually to describe the biodegradation process of pollutants in sediment/soil.

$$\ln C_t = -k \cdot t + \ln C_0 \quad (1)$$

Where C_0 is the initial concentration, C_t is the instantaneous concentration, k is the degradation rate constant determined by linear regression of the data $\ln C_t$ versus the incubation time (t). The fitting result was shown in Figure 2.

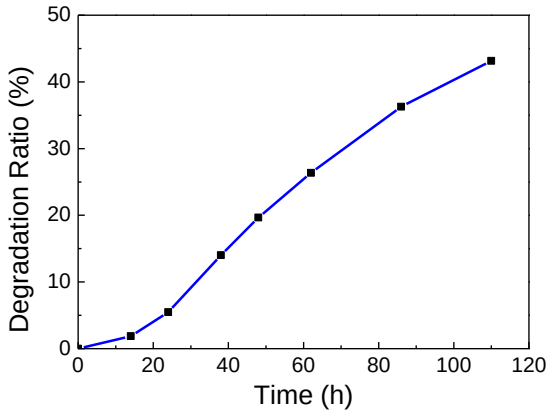

Figure 1: The degradation curve of deltamethrin in Bohai coastal sediment.

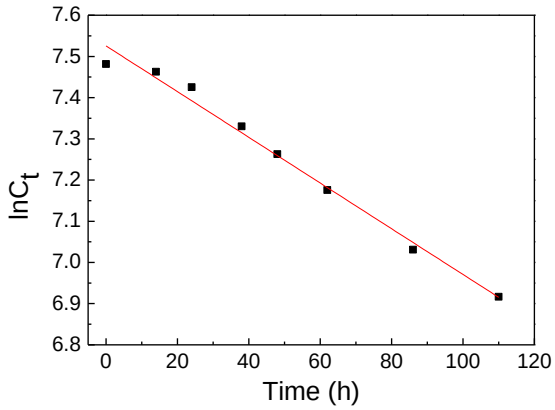

Figure 2: The degradation kinetics of deltamethrin in Bohai coastal sediment.

From the Figure 2, we could see that the degradation process followed the pseudo first-order kinetics with the reaction rate constant k=0.0055 h^{-1}. An almost good linear relationship with the correlation coefficient R^2=0.985 was achieved. The result indicated that the degradation rate was proportional to the concentration of deltamethrin.

3.2 Metabolism of deltamethrin

In order to investigate the anoxic degradation approach of deltamethrin in the coastal environment and estimate the secondary pollution in the degradation process of deltamethrin according to the toxicity of its metabolite. The metabolic products of deltamethrin was qualitatively analyzed with GC-MS. The result showed that the m-phenoxyphenyl-acetonitril was the main metabolic product. Simultaneously, pH and the oxidation-reduction potential (ORP) in the degradation process were also determined and the change curve of ORP and pH was shown in the Figure 4. During the degradation process, the ORP fluctuated from -44.0 mV to -58.6 mV, which belonged to anoxic condition. As ORP is 0 mV to -100 mV, cytochrome b and flavoenzyme mainly

exist in the reductive system of the organism and they are reductase and dehydrogenation body. Therefore it was suggested that deltamethrin in the coastal sediment was degraded by reduction reaction and the degradation pathway might be as follows. The possible metabolic pathway is that deltamethrin is hydrolyzed at ester bond firstly, and then is reduced to be m-phenoxyphenyl-acetonitril.

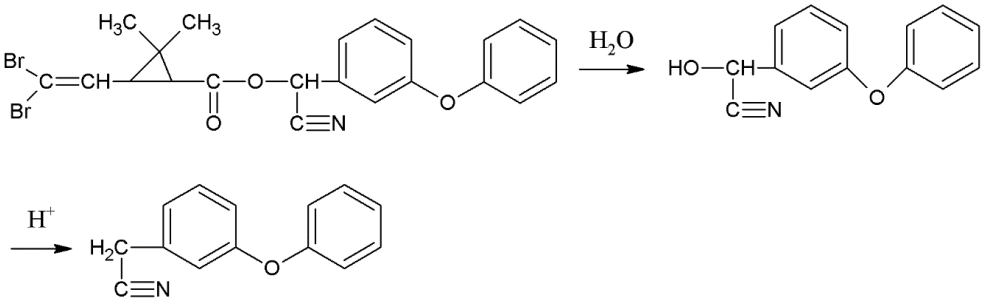

Figure 3: The degradation pathway of deltamethrin in Bohai coastal sediment.

From the Figure 4, we could see that the tendency of ORP was negatively correlated with the pH. During the degradation process of deltemethrin, pH decreased firstly, followed by increasing, and then decreased again. Obviously, the degradation experienced the acidogenic stage and alcaligenic stage. This might because organic matter in the sediment was used by microogranism to generate fatty acid, hydrogen and carbon dioxide, etc., making pH of system declined rapidly. Then fatty acid, hydrogen and carbon dioxide were used by methanogens to generate methane, making pH of system increasing (Carotenuto et al., 2016). Nextly, acetogenic bateria turned hydrogen and carbon dioxide into acetic acid, the pH decreased again.

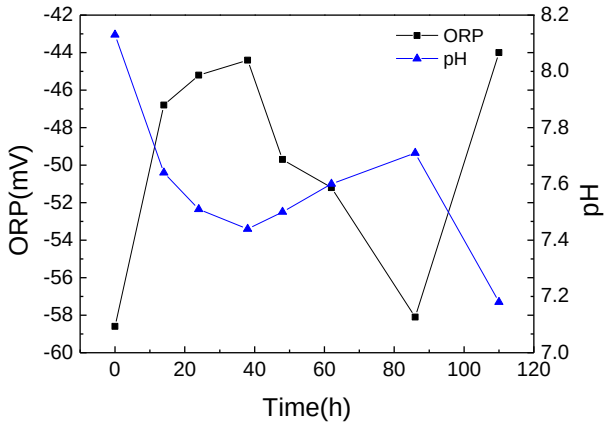

Figure 4: The change curve of ORP and pH in the degradation process of deltamethrin.

3.3 Effect of carbon source on deltamethrin degradation

Some studies showed that the presence of easily degradable carbon sources could enhance the biodegradation of more persistent chemicals (Zhao et al., 2002). Figure 5 and Figure 6 show the anoxic degradation curves of deltamethrin in Bohai coastal sediment with the addition of glucose and sodium acetate respectively.

The model of pseudo-first-order kinetics was still used to describe the anoxic degradation process of deltamethrin in Bohai coastal sediment with the addition of carbon source. The degradation rate constants and the correlation coefficients of the degradation kinetics equations were shown in Table 2.

From Table 2, we could see that with the addition of carbon source, the degradation kinetics still followed the pseudo-first-order kinetic with the value of correlation coefficient R^2 ranged from 0.973 to 0.983. Adequate addition of small molecule carbon sources could significantly improve the microbial degradation of deltamethrin in the sediment, but oversupplying carbon source inhibited it. When the addition amount of glucose was 0.5, 2.1 g/kg sediment, the degradation rate constant increased from 0.0055 h^{-1} to 0.0099 h^{-1}, 0.0093 h^{-1}. When the addition amount of sodium acetate was 0.2, 1.0 g/kg sediment, the anoxic degradation

rate constant increased from 0.0055 h^{-1} to 0.0107 h^{-1}, 0.0113 h^{-1}. Moreover, no lag phase was observed throughout the experiment. So it was speculated that cometabolism happened during the degradation process. But when the addition amount of glucose was 45 g/kg sediment, the addition amount of sodium acetate was 12.4 g/kg sediment, the degradation rate decreased from to 0.0055h^{-1} to 0.0048 h^{-1}, 0.0033 h^{-1}. According to Speece's findings (1983), co-metabolic process requires proper concentration ratio of primary substrate to secondary substrate. Microbial enzymes maintaining co-metabolism are mainly produced by the usage of primary substrate, so there is competition between primary substrate and secondary substrate (Zhang et al., 2007). During the degradation process, oversupplying primary substrate carbon source inhibited the induced generation of deltamethrin degradation enzyme, making the degradation rate decreased. Compared with glucose and sodium acetate, the promoting effect of sodium acetate was slightly better than glucose.

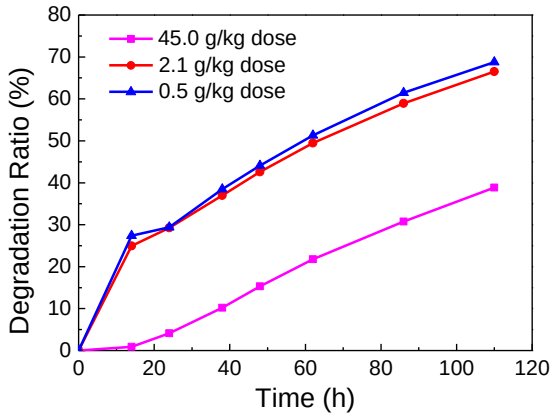

Figure 5: The degradation curves of deltamethrin in the sediment with the addition of glucose.

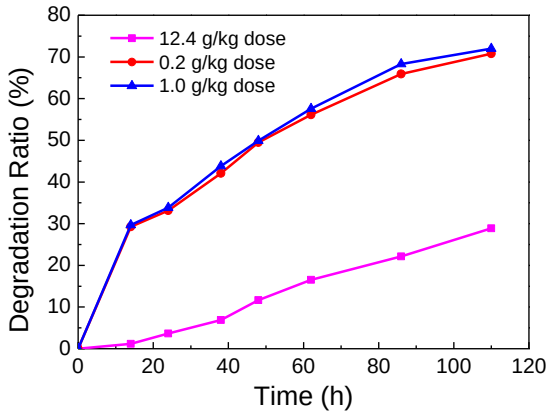

Figure 6: The degradation curves of deltamethrin in the sediment with the addition of sodium acetate.

Table 2: The degradation rate constants and the correlation coefficients of the degradation kinetics equations of deltamethrin with the addition of carbon source

Carbon source	Degradation rate constant(h^{-1})	Correlation coefficient R^2
0.5 g (2.78 mmol) glucose /kg sediment	0.0099	0.982
2.1 g (11.65 mmol) glucose /kg sediment	0.0093	0.983
45.0 g (0.25 mol) glucose /kg sediment	0.0048	0.981
0.2 g (2.44 mmol) sodium acetate /kg sediment	0.0107	0.973
1.0 g (12.20 mmol) sodium acetate /kg sediment	0.0113	0.973
12.4g (0.15 mol) sodium acetate /kg sediment	0.0033	0.983

4. Conclusions

Deltamethrin could be degraded in natural coastal sedimentary environment at a relatively slow rate. 43.15 % of deltamethrin in Bohai coastal sediment was degraded after 110 h. The anoxic degradation of deltamethrin in the sediment followed the first-order kinetic with the degradation rate constant 0.0055 h^{-1}.

The metabolic product of deltamethrin in Bohai coastal sediment was mainly m-phenoxyphenyl-acetonitril. The possible metabolic pathway is that deltamethrin is hydrolyzed at ester bond firstly, and then is reduced to be m-phenoxyphenyl-acetonitril.

Adequate addition of small molecule carbon sources such as glucose or sodium acetate could significantly promote the microbial degradation of deltamethrin. Cometabolism might happen during the degradation process because no lag phase was observed throughout the experiment. So adding small molecule carbon sources to promote the bioremediation of pyrethroid polluted sedimentary environment is very promising.

Acknowledgments

The authors gratefully acknowledge the support from the Hebei provincial science and technology support program (Grant No. 15273613) and the Hebei provincial higher education teaching reform research and practice project (Grant No. 2016GJJG042).

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