

# Adsorption of phenthoate and acetochlor from water by clays and organoclays

LIAO Min, XIE Xiao-mei

(College of Environmental and Resource Sciences, Department of Resources Science, Zhejiang University, Hangzhou 310029, China. E-mail: liaomin@zju.edu.cn)

**Abstract:** Adsorption of phenthoate and acetochlor onto kaolin, montmorillonite, bentonite clays and respective organoclays prepared by the exchange of quaternary ammonium as tetradecyltrimethyl ammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB), and cetylpyridinium chloride (CPC) were studied. The adsorption equilibrium data points were fitted to Freundlich isotherm equations. The adsorption of phenthoate and acetochlor were significantly enhanced by surfactant treatment of the clays. The amount of both pesticides adsorbed per unit mass of organoclay followed the order of TTA-kaolin < TTA-montmorillonite < TTA-bentonite, which is inconsistent with the organic carbon content of the clays. The removal efficiency of organomontmorillonite to treat acetochlor is in the order of CP(C<sub>16</sub>)-montmorillonite > TTA(C<sub>14</sub>)-montmorillonite > DTA(C<sub>12</sub>)-montmorillonite. Phenthoate is adsorbed to greater extent than acetochlor by each adsorbent, which may be due to the higher hydrophobicity of phenthoate, indicating considerable hydrophobic interaction between adsorbent/adsorbate systems.

**Keywords:** adsorption; clays; organoclays; phenthoate; acetochlor

## Introduction

Immobilization or separation of contaminants contained in polluted water is an objective of increasing importance in a variety of environmental settings. The extent of pesticide contamination of the water environment has recently raised much concern because of the potential health hazards associated with the entry of these compounds into the food chain of humans and animals (Pimentel, 1993; Jin, 2001). The pollution of the water environment with pesticides is affected through their use in the control of weeds and insects, leaching run-off from agricultural and forest lands, deposition from aerial applications and discharge of industrial wastewater (Thompson, 1992; Huang, 2002).

The wide range of pesticides used makes it extremely difficult to produce a single method for pesticide disposal that applies widely. Therefore, several methods for removal and disposal of these chemicals may be required to solve this problem. Adsorption on solid substrates, such as clay or activated carbon, is one of the methods, which have been used for removing organic pollutants from water (Weissmahr, 1997; Martin, 1997; Jaynes, 1991).

In an attempt to design new adsorbents to remove non-ionic organic contaminants from waste water, several researchers have replaced the inorganic cations of clays by large alkyl ammonium cations in order to change the hydrophilic surface of clay into hydrophobic (Sheng, 1996; Zhu, 1997; Boyd, 1988a). The resulting organoclay surface sorbs effectively a wide variety of organic compounds from water and air. This is due to lesser tendency of organic

cations to hydrate and to their inherent organophilic nature (Sheng, 1996). These organoclays have generally been considered as good adsorbents of non-ionic organic contaminants from industrial wastes, such as  $\alpha$ -naphthylamine (Zhu, 1997) or pentachlorophenols (Boyd, 1988c). However, very few works have been reported on adsorption of agricultural chemicals by organoclay (Zhu, 1997; Sanchez-Martin, 1991; 1984).

The objective of the present study is to evaluate the effectiveness of organoclays in removing the pesticides from water and how the alkyl chain length of quaternary ammonium cation exchanged onto clays affect the magnitude of solute sorption. We investigated the adsorption of phenthoate [*o*, *o*-dimethyl-*s*-( $\alpha$ -ethoxycarbonylbenzyl) phosphorodithioate] and acetochlor [2'-ethyl-6'-methyl-N-(ethoxymethyl)-2-chloro-acetanilide] from water by kaolin, tetradecyltrimethylammonium (TTA)-kaolin, montmorillonite, TTA-montmorillonite, bentonite and TTA-bentonite. While adsorption of acetochlor was also made on dodecyltrimethylammonium (DTA)-montmorillonite and cetylpyridinium (CP)-montmorillonite to study the effect of alkyl chain length of surfactant exchanged.

## 1 Experimental procedure

### 1.1 Materials

#### 1.1.1 Adsorbents

Three clays namely kaolin, montmorillonite and bentonite were used in this study. Kaolin was procured from Zhejiang Songyang Kaolin Limited Company (China). Montmorillonite and bentonite were obtained from Zhejiang

Yuhong Clay Chemical Limited Company (China). Bentonite is composed of montmorillonite. The three clays have different cation exchange capacity (CEC) and CEC was determined by 0.1 mol/L NH<sub>4</sub>AC exchanging method (Bao, 2000). The CEC of kaolin, montmorillonite and bentonite are 10.0, 44.0, and 102.0 meq 100 g<sup>-1</sup>, respectively.

### 1.1.2 Organic cation

The quaternary ammonium cations (surfactants) used for preparing organoclays were 95% tetradecyltrimethyl ammonium bromide (TTAB), 99% dodecyltrimethyl ammonium bromide (DTAB) and 98% cetylpyridinium chloride (CPC). All of them were procured from Sigma Chemical Company.

### 1.1.3 Adsorbates

The adsorbates used in this study are technical grade (99%) phenthoate and acetochlor and were supplied by Bayer Chemical Company.

### 1.2 Preparation of organoclay

The organoclays were prepared by the similar way as described by G. Sheng *et al.* (Sheng, 1996). The organoclays have relatively high surface area compared with clay. The surface area of clays and organoclays are listed in Table 1 as determined by BET N<sub>2</sub> adsorption method.

Table 1 Surface area of clays and organoclays

Material	Surface area, m <sup>2</sup> /g
Kaolin	13.10
TTA-kaolin	23.45
Montmorillonite	83.00
TTA-montmorillonite	103.30
Bentonite	148.50
TTA-bentonite	191.04

### 1.3 Adsorption equilibrium experiment

In adsorption experiments fixed amount (50 mg) of adsorbent and 50 ml of an aqueous solution of pesticide of varied concentration were placed in 250 ml Erlenmeyer flask and shaken on shaker bath at constant temperature (25 ± 1 °C) for 24 h to ensure the equilibrium. All the adsorption experiments of pesticides were carried out at their natural pH (6.0–6.5). After equilibrium the suspension was centrifuged and concentration of solutes determined by a high-pressure liquid chromatograph (HPLC) equipped with UV detector and C<sub>18</sub> reversed-phase column. Separation of phenthoate was performed by a mixed solution as mobile phase (mixed with (v/v) 100% *n*-hexane, 0.1% 2-propanol) and detected at 230 nm. While separation of acetochlor was performed by a mixed solution as mobile phase (mixed with (v/v) 75% methyl alcohol, 25% water) and detected at 220 nm. The flow rate was 1 ml/min and injection volume was 10 μl.

## 2 Results and discussion

### 2.1 Equilibrium isotherms study

Adsorption isotherms of phenthoate and acetochlor on

kaolin, TTA-kaolin, montmorillonite and TTA-montmorillonite, bentonite and TTA-bentonite were fitted to Freundlich equation with  $r > 0.98$ . The Freundlich isotherms for adsorption of pesticides are shown in Figs. 1–3. The Freundlich models for liquid phase adsorption can be written as follows:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e,$$

where,  $C_e$  is the equilibrium concentration,  $q_e$  is the amount adsorbed at equilibrium (mg/g) and  $n$ ,  $K_f$  constants for a given adsorbate-adsorbent system.

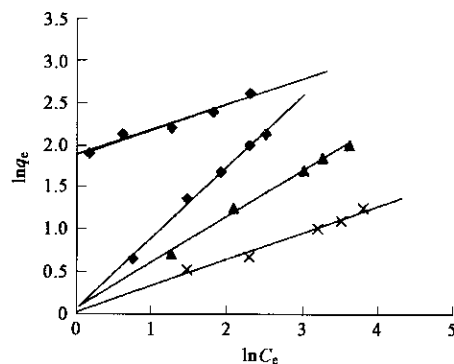


Fig. 1 Freundlich plot for adsorption of pesticides on kaolin and TTA-kaolin  
◆ phenthoate on TTA-kaolin; ■ phenthoate on kaolin; ▲ acetochlor on TTA-kaolin; × acetochlor on kaolin

Both  $K_f$  and  $n$  are constant being indicative of the extent of adsorption and degree of non-linearity between solution concentration and adsorption, respectively. The different parameters of Freundlich model are shown in Table 2.

Table 2 Freundlich parameters for adsorption of pesticides on clays and organoclays

Adsorbate	Adsorbent	$K_f$	$N$	Correlation coefficient, $r$
Acetochlor	Kaolin	1.02	3.21	0.9870
	TTA-K	1.07	1.84	0.9975
	Montmorillonite	0.49	1.01	0.9946
	TTA-M	1.34	1.18	0.9927
	Bentonite	0.38	1.10	0.9999
Phenthoate	TTA-B	2.53	0.826	0.9901
	Kaolin	1.06	1.19	0.9974
	TTA-kaolin	6.53	3.35	0.9805
	Montmorillonite	2.38	1.72	0.9993
	TTA-M	5.57	1.22	0.9893
Bentonite		1.15	1.350	0.9988
	TTA-B	3.25	0.769	0.9996

The calculated  $K_f$  value indicated the high adsorption affinity of organoclay for pesticides than their respective clay. This is attributed to alkyl organic phase on organoclays prepared by exchanging with longer alkyl chain quaternary ammonium cation having higher hydrophobicity. Non-ionic organic compounds are easy to be adsorbed on alkyl organic phase, in which adsorption mechanism is governed by one partitioning process (Boyd, 1988b; Lee, 1989; Jaynes,

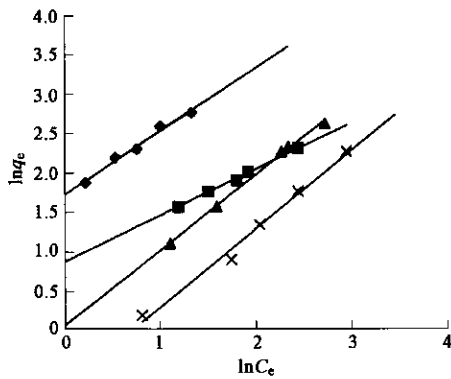


Fig.2 Freundlich plot for adsorption of pesticides on montmorillonite and TTA-montmorillonite

◆ phenthoate on TTA-montmorillonite; ■ phenthoate on montmorillonite; ▲ acetochlor on TTA-montmorillonite; × acetochlor on montmorillonite

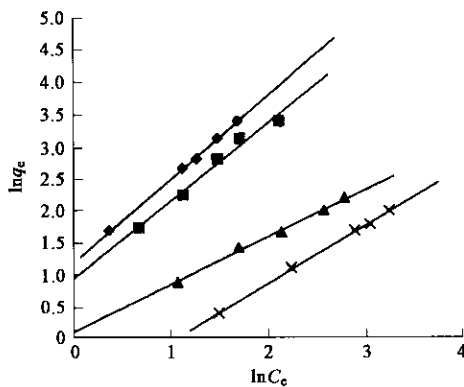


Fig.3 Freundlich plot for adsorption of pesticides on bentonite and TTA-bentonite

◆ phenthoate on TTA-bentonite; ■ phenthoate on bentonite; ▲ acetochlor on TTA-bentonite; × acetochlor on bentonite

1991; Wang, 1997). This fact suggested that adsorption of non-ionic pesticides phenthoate and acetochlor by organoclay is governed mainly by hydrophobic interaction between pesticide molecules and hydrophobic surface of clay.

## 2.2 Comparison of adsorbates

The hydrophobic sorption characteristics of organic compounds from water on organoclays are closely related to their solute properties such as water solubility and octanol-water partition coefficient (Zhu, 1997). To compare adsorptive capacity of organoclay removal efficiency ( $R$ ) is calculated by using the following equation:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100.$$

Where,  $C_0$  is the initial concentration of pesticide and  $C_e$  is the equilibrium solution concentration.  $R$  is expressed in terms of percentage.

As can be seen from Table 3, adsorption of phenthoate is greater than acetochlor. The higher adsorption of phenthoate by clay and organoclay compared with that of acetochlor is probably due to the low water solubility (greater hydrophobicity) of phenthoate. Phenthoate is less water soluble, more hydrophobic (solubility = 10 mg/L) compared

with acetochlor (solubility = 235 mg/L), and hence has higher adsorption affinity due to hydrophobic interactions (Sheng, 1996).

Table 3 Adsorption efficiency of clay and organoclay for pesticides<sup>a</sup>

Adsorbate	Adsorbent	Removal, %	Amount adsorbed, mg/g	
Acetochlor	Kaolin	13.21	1.321	
	TTA-K	27.32	2.732	
	Montmorillonite	37.23	3.723	
	DTA-M	52.33	5.233	
	TTA-M	63.14	6.314	
	CP-M	78.81	7.881	
Bentonite	Bentonite	33.50	3.350	
	TTA-B	89.15	8.915	
	Phenthoate	Kaolin	46.36	4.636
		TTA-K	72.50	7.250
		Montmorillonite	48.31	4.831
		TTA-M	90.57	9.057
Bentonite	Bentonite	53.60	5.360	
	TTA-B	99.35	9.935	

Notes: <sup>a</sup>Acetochlor  $C_0 = 10$  mg/L; phenthoate  $C_0 = 10$  mg/L; weight of adsorbent = 50 mg

## 2.3 Comparison of sorption using different organoclays

The adsorption of organic, non-ionic and sparingly soluble contaminants by soils in aqueous media is essentially governed by the organic matter content in the soil. The positive correlation between the organic matter content and the adsorption of non-ionic organic contaminants, such as pesticides, is well documented in the literature (Sanchez-Camazano, 1994). The removal percentage of organoclays (TTA-kaolin, TTA-montmorillonite and TTA-bentonite) to remove phenthoate and acetochlor was positive relative to the amount of cationic surfactant exchanged. As move from kaolin to bentonite, the cation exchange capacity increases in the order of bentonite > montmorillonite > kaolin. The higher the cation exchange capacity of clay the more will be the exchange of surfactant and resulting clay surface will be more hydrophobic. Adsorption capacities of organoclays increased in the order of TT-Abentonite > TTA-montmorillonite > TTA-kaolin. To assess hydrophobicity of organoclay surface  $P_{oc}$  (organic carbon content) is an important parameter.  $P_{oc}$  can be obtained from the following equation:

$$P_{oc}(\%) = f_{oc} \times 100,$$

where,  $f_{oc}$  is the organic carbon mass fraction (carbon amount in TTA-bromide adsorbed on clay)/weight of clays (mg). The magnitude of  $P_{oc}$  for different organoclays namely TTA-kaolin, TTA-montmorillonite and TTA-bentonite are 1.87, 8.14 and 19.86, respectively. From  $P_{oc}$  data it is clear that higher adsorption of pesticides on TTA-bentonite is due to its higher  $P_{oc}$  value.

## 2.4 Effect of chain length of surfactants

Effect of chain length of exchanged surfactant on adsorption of pesticides on montmorillonite system is shown in Fig.4, Table 3 and Table 4, respectively. It can be seen from Fig. 4, Table 3 and Table 4 that as the chain length of

cationic surfactant increases from dodecyltrimethyl ammonium ( $C_{12}$ ) exchanged montmorillonite to cetyl pyridinium ( $C_{16}$ ) exchanged montmorillonite adsorption of acetochlor increases. The calculated  $K_F$  value also increased with the chain length of cationic surfactant increasing, which is attributed to longer chain alkyl having higher hydrophobicity (Wang, 1997). This also indicated that hydrophobic interactions are playing an important role in adsorption.

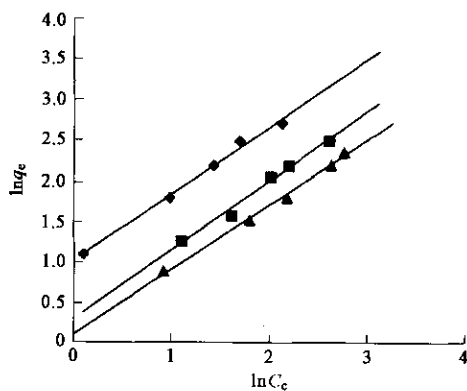


Fig.4 Freundlich plot for adsorption of acetochlor on DTA-montmorillonite, TTA-montmorillonite and CP-montmorillonite

◆ CP-montmorillonite; ■ TTA-montmorillonite; ▲ DTA-montmorillonite

Table 4 Freundlich parameters for adsorption of acetochlor on organoclays

Adsorbate	Adsorbent	$K_F$	$n$	Correlation coefficient, $r$
Acetochlor	CP-montmorillonite	2.78	1.23	0.9971
	TTA-montmorillonite	1.34	1.18	0.9927
	DTA-montmorillonite	1.12	1.26	0.9977

### 3 Conclusions

The adsorption of phenthoate and acetochlor on clays and organoclays has been studied. The cationic surfactants were exchanged onto the clay surface by ion-exchange, whereby the hydrophilic surface of clay was rendered hydrophobic and enhanced the adsorption capacity of organoclays for pesticides compared with clays. Freundlich equation gives the best fit to adsorption of phenthoate and acetochlor by clays and their organoclays over the entire concentration range studied. Higher adsorption of phenthoate by clay and organoclay may be attributed to its low water solubility compared with acetochlor. Among all the organoclay studied TTA-bentonite has high adsorption capacity due to its higher  $P_{oc}$  value. As the chain length of exchanged quaternary ammonium cations increases, adsorption increases indicating that adsorption of pesticides by organoclay is predominantly governed by hydrophobicity of clay.

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