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Sorption and Desorption Kinetics of Chlorophenols in Hexadecyltrimethyl Ammonium-Montmorillonites and Their Model Analysis

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Abstract−Sorption and desorption kinetics of chlorophenols, 2-chlorophenol (2-ChP), 2,4-dichlorophenol (2,4-DChP) and 2,4,5-trichlorophenol (2,4,5-TChP), in montmorillonite modified with hexadecyltrimethyl ammonium cations (HDTMA-mont) were investigated by using laboratory batch adsorbers. To investigate the effect of chemical concentration and sorbent weight on the sorption or desorption rate constants, the initial chemical concentration and sorbent weight were varied from 50 to 150 mg/L and from 0.2 to 1.0 g, respectively. A one-site mass transfer model (OSMTM) and two compartment first-order kinetic model (TCFOKM) were used to analyze kinetics. The OSMTM applicable to desorption rate analysis was newly derived. As expected from the number of model parameters involved, the three-parameter TCFOKM was better than the two-parameter OSMTM in describing sorption and desorption kinetics of chlorophenols in HDTMA-mont. The mass transfer coefficient for sorption (k_s) in OSMTM generally increased as K_{ow} value increases, except for 2,4,5-TChP, while the mass transfer coefficient for desorption (k_d) consistently increases as K_{ow} value decreases, due to the weaker hydrophobic interaction between the solute and the organoclay. Since most sorption and desorption complete in an hour and half an hour, respectively, k_d values were found to be greater than k_s values for all three solutes studied. The fraction of the fast sorption (or desorption) and the first-order sorption (or desorption) rate constants for the fast and slow compartments in TCFOKM were determined by fitting experimental data to the TCFOKM. The results of kinetics reveal that the fraction of the fast sorption or desorption and the sorption rate constants in the fast and slow compartments were in the order 2,4,5-TChP>2,4-DChP>2-ChP, which agrees with the magnitude of the octanol-water partition coefficient, K_{ow}. The first-order sorption rate constants in the fast and slow compartments were found to vary 10^1-10^2 hr^{-1} and 10^{-3}-10^{-2} hr^{-1}, respectively. However, the desorption rate constants in the fast and slow compartments were not correlated well with K_{ow}. The first-order desorption rate constants in the fast compartment (10^1-10^2 hr^{-1}) were found to be much larger than those in the slow compartment (10^{-3}-10^{-4} hr^{-1}). Sorption affinity and desorption resistance of each chlorophenol in 50% HDTMA-mont were found to show the same tendency: the weakly-sorbed chlorophenol (i.e., 2-ChP) was easily desorbed, while the strongly-sorbed chlorophenol (i.e., 2,4,5-TChP) was rather resistant to desorption.

Key words: HDTMA, Organoclay, Sorption, Desorption, Kinetics

INTRODUCTION

Montmorillonite clays are inherently hydrophilic due to the hydration of inorganic cations existing in the interlamellar spacing of the clay. As a result, montmorillonites are not effective in removing the neutral organic compounds (NOCs) in an aqueous system. Montmorillonites can be modified by ion-exchanging the inorganic cations on the surface of clay with the quaternary ammonium cations having long hydrocarbon chains, thus changing the surface property from hydrophilic to organophilic. The intercalated organic cations such as hexadecyltrimethylammonium (HDTMA) cation may expand the interlamellar spacing of the clay and form pseudo-organic phase that increases the sorption capacity for NOCs from water.

Clays modified with quaternary ammonium cations were known to exhibit increased sorption capabilities for aqueous phase organic contaminants. Some studies demonstrated that HDTMA-derived organic matter in clays is 10-30 times more effective than natural soil organic matter for sorbing toxic organic contaminants from water, and that soil modification greatly attenuates the mobility of organic contaminants in soils [Burris and Antworth, 1992; Boyd et al., 1988; Lee et al., 1989].

The organically modified clays ("organoclays" for short) can provide a wide range of applications, such as wastewater treatment [Srinivasan and Fogler, 1990; Zhu and Zhang, 1997], permeable reactive barriers (PRBs) [Scherer et al., 2000; Gullick and Weber, 2001], solidification and stabilization of waste effluents [Boyd, 1993; Lo, 1996], and liners for hazardous waste landfills or gasoline storage tanks [Li et al., 1996; Smith and Jaffe, 1994; Lo and Lijestrand, 1996; Lo, 1997, 2001; Lo and Yang, 2001a, b]. Contaminant immobilization using organoclays coupled with *in situ* biodegradation would provide a comprehensive restoration technology to permanently eliminate target organic contaminants [Scherer et al., 2000; Nye et al., 1994]. Sorption and desorption characteristics determine the feasibility of organoclays as a potential medium for the application mentioned above. Most of the recent studies on organoclays have focused on the sorption and/or desorption equilibrium aspects, though [Carrizosa et al., 2001; Boyd et al., 1988; Dentel et al., 1995; Kim et al.,

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Table 1. Physicochemical properties of chlorophenols used

Compound	M.W.	Solubility (mg/L)	log K_{ow}*	pK_a at 25 °C	Isosbestic point (nm)
2-ChP	128.6	2.13×10^4	2.15	8.56	278
2,4-DChP	163.0	4.5×10^3	3.06	7.89	290
2,4,5-TChP	197.4	1.2×10^3	3.72	7.00	296

*Octanol-water partition coefficient

1996; Huh et al., 2000]. Only a few studies have been reported on the sorption and/or desorption kinetics of sorbed contaminants on organoclays [Zhang and Sparks, 1993; Nzegung et al., 1997; Deitsch et al., 1998], despite its importance in evaluating the effectiveness of organoclays in wastewater treatment, clay liners, remediation, etc. Especially, desorption of sorbed contaminants from organoclays is very important because determination of further treatments or risk assessment of the treated sites is highly dependent on desorption phenomena. Desorbed contaminants from the organoclays can be further treated with other remedial skills like biodegradation. Desorption rate can directly affect the efficiency of the biodegradation and is also a concern of risk assessment in the remediation using organoclays. Therefore, reliable estimation of the sorption and desorption processes is crucial to the design of organoclay barriers for the remediation of contaminated sites.

Phenol and chlorinated phenols are representative model compounds of ionizable organic compounds (IOCs), which have been encountered in many contaminated sites [Verschueren, 1977; Wu et al., 2002]. In this work, montmorillonites modified with the HDTMA cations to the extent of 50% of the cation exchange capacity (CEC) of the clay (hereinafter referred to as 50% HDTMA-mont) were used as sorbent. 2-chlorophenol (2-ChP), 2,4-dichlorophenol (2,4-DChP) and 2,4,5-trichlorophenol (2,4,5-TChP) were used as sorbates. Sorption and desorption kinetic experiments were carried out in a batch-type adsorber and were analyzed by using a one-site mass transfer model (OSMTM) and two-compartment first-order kinetic model (TCFOKM). The objective of this study was to examine sorption and desorption kinetics of chlorophenols in 50% HDTMA-mont. The results of this study provide valuable insight into the development of remediation strategies for the groundwater polluted with IOCs using organoclays as a potential PRB.

MATERIALS AND METHODS

1. Materials

The impurities of the montmorillonite-KSF (purchased from Aldrich Chemical Co.) were removed by washing it several times with distilled water at 60 °C. The washed montmorillonite was collected by settling, dried for 24 hours, and stored in a brownish bottle. The cation exchange capacity (CEC) of montmorillonite was measured to be 50.4 meq/100 g clay [Kim et al., 1996]. This value was equivalent to about 161.3 mg HDTMA/g montmorillonite. The cationic surfactant used as an organic modifier, HDTMA chloride solution (25 wt%), was obtained from Aldrich Chemical Co. and used as received.

Aqueous solution of 2-ChP, 2,4-DChP, and 2,4,5-TChP purchased from Aldrich Chemical Co. was prepared in an electrolyte solution containing 1 mM $CaCl_2 \cdot 2H_2O$, 0.5 mM $MgCl_2$, and 0.01 M $Na_2B_4O_7 \cdot 10H_2O$. 200 mg/L of NaN_3 was added to the electrolyte solution as a bacterial inhibitor. All reagents were of analytical grade and were used without further purification. Table 1 lists the physicochemical properties of the chlorinated phenols used in this study.

2. Preparation of HDTMA-Mont

HDTMA-mont was prepared by exchange adsorption of HDTMA onto the washed montmorillonite to the extent of 50% CEC following the procedures previously reported by Kim et al. [1996]. To prepare 50% HDTMA-mont, the exchange adsorption of HDTMA onto 31 grams of the washed montmorillonite was performed in a 2-L baffled beaker containing 1 L of 2,500 mg/L HDTMA solution. The slurry was agitated with a mechanical stirrer at 250 rpm for 24 hours. After agitation, HDTMA-mont was collected and washed twice with distilled water. The collected HDTMA-mont was dried in an oven at 60 °C for 24 hours, sieved with #200 mesh, and kept in an amber bottle until use.

3. Sorption and Desorption Kinetic Studies

Sorption kinetic studies were conducted in batch mode using 20-mL glass vials with Teflon-faced silicone septa. Vials containing 0.5 g of HDTMA-mont each were filled with approximately 20-mL of stock chemical solutions minimizing headspace and then shaken at 150 rpm on an orbital shaker at 20 °C.

After predetermined time intervals (1 min to 24 hrs), the vials were centrifuged at 1,500 rpm for 30 minutes. To investigate the effect of chemical concentration and sorbent weight, the initial chemical concentration and sorbent weight were varied from 50 to 150 mg/L and from 0.2 to 1.0 g, respectively.

A desorption kinetic experiment was conducted using the solute-loaded HDTMA-mont obtained from the preceding sorption experiment (i.e., sorption equilibration time of 24 hrs). After centrifugation, approximately 95% of the supernatant was replaced with about 19 mL of the electrolyte solution. The exact amount of the supernatant removed was gravimetrically determined and nonzero initial concentration of the aqueous solution in desorption stage was computed from the mass balance accordingly. The vials were placed on an orbital shaker at 20 °C and shaken at 150 rpm. After predetermined time intervals (1 min to 24 hrs), the HDTMA-mont was separated from the solution by centrifuging at 1,500 rpm for 30 minutes.

The aqueous phase equilibrium concentration of each solution was determined by using a diode array UV-Visible spectrophotometer (Hewlett-Packard, 8453) at the isosbestic point of each chlorophenol. The solid phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase resulted from sorption onto the solid phase. All experiments were run in duplicate.

SORPTION AND DESORPTION RATE MODELS USED

1. One-Site Mass Transfer Model

The One-site mass transfer model (OSMTM) for *sorption rate* was first proposed by Nzengung et al. [1997]. In OSMTM, the sorption rate is represented as a first order function of the concentration difference between the solution and sorbed phases under the assumption of a linear sorption equilibrium. Substituting for q from the integral mass balance equation in the batch adsorber, $W(q-q_0)=V(C_0-C)$, we get the following differential equation on C.

$$\frac{V}{W}\frac{dC}{dt} = k_s(q - K_{p,s}C) = k_s\left(q_0 + \frac{V}{W}(C_0 - C) - K_{p,s}C\right)$$
$$\text{with } C=C_0 \text{ at } t=0 \qquad (1)$$

where V and W are the volume of the solution phase (L) and the sorbent weight (g), respectively, $K_{p,s}$ represents the partition coefficient for sorption (L/g), C and q denote the solute concentrations in the solution (mg/L) and solid phases (mg/g) at time t (hr), respectively, and k_s is the mass transfer coefficient (hr^{-1}) for sorption between the solution and solid phase; the subscript 0 denotes initial concentration in each phase. Eq. (1) leads to $q_e=K_{p,s}C_e$ at sorption equilibrium, where the subscript e denotes equilibrium concentration in each phase. Assuming fresh sorbent (i.e., $q_0=0$), integration of Eq. (1) yields:

$$\frac{C(t)}{C_0} = \frac{C_e}{C_0} + \left(1 - \frac{C_e}{C_0}\right)\exp\left[\left(-\frac{C_0}{C_e}k_s\right)t\right] \qquad (2)$$

Values of C_e and k_s were estimated by fitting Eq. (2) to the sorption kinetic data by using a nonlinear curve fitting technique.

We derived OSMTM for *desorption rate*, taking the same concept as Nzengung et al. [1997] did in their original derivation for sorption rate. Substituting for dC and C from the differential ($Wdq=-VdC$) and integral mass balance equations for the batch adsorber, respectively, we obtain the following differential equation on q with the assumption of linear desorption isotherm like in derivation of OSMTM for sorption rate.

$$\frac{V}{W}\frac{dC}{dt} = k_d(q - K_{p,d}C) \text{ or } -\frac{dq}{dt} = k_d\left(q - K_{p,d}\left\{C_0 - \frac{W}{V}(q - q_0)\right\}\right)$$
$$\text{with } q=q_0 \text{ at } t=0 \qquad (3)$$

where k_d and $K_{p,d}$ are the mass transfer coefficient (hr^{-1}) and partition coefficient for desorption (L/g), respectively. Similarly, Eq. (3) is reduced to $q_e=K_{p,d}C_e$ at desorption equilibrium. We assumed different partition coefficients ($K_{p,s}$ vs. $K_{p,d}$) and mass transfer coefficients (k_s vs. k_d) in sorption and desorption kinetic analysis, due to the possible hysteresis between sorption and desorption isotherms.

Since the initial concentration of the solution, C_0 is, in general, not exactly zero in a desorption experiment, the solution of OSMTM for desorption can be written as the following:

$$\frac{q(t)}{q_0} = \frac{q_e}{q_0} + \left(1 - \frac{q_e}{q_0}\right)\exp\left[\left(-\frac{q_0}{q_e}k_d'\right)t\right] \text{ where } k_d' \equiv k_d K_{p,d}\left(\frac{C_0}{q_0} + \frac{W}{V}\right) \qquad (4)$$

The main structure of Eq. (4) is very similar to Eq. (2) for sorption, except for the variable q in desorption instead of C in sorption. Furthermore, the desorption mass transfer coefficient, k_d should be determined from the apparent mass transfer coefficient for desorption (k_d') to compare with the sorption mass transfer coefficient k_s. Values of q_e and k_d' were estimated by fitting Eq. (4) to desorption kinetic data.

2. Two Compartment First-Order Kinetic Model

The overall sorption (or desorption) in the two compartment first-order kinetic model (TCFOKM) was assumed to consist of the sum of the two first-order sorption (or desorption) rates in the fast and slow compartments [Brusseau and Rao, 1991; Schrap et al., 1994; Cornelissen et al., 1997; Opdyke and Loehr, 1999]:

$$\frac{C(t)}{C_0}\left(\text{or } \frac{q(t)}{q_0}\right) = f_1 e^{-k_1 t} + (1 - f_1)e^{-k_2 t} \qquad (5)$$

where f_1 and f_2 ($=1-f_1$) are the fast and slow sorption (or desorption) fractions, respectively, and k_1 and k_2, the sorption (or desorption) rate constants in the fast and slow compartments (hr^{-1}), respectively. Values of the three model parameters, f_1, k_1 and k_2, were determined by using a commercial software package, Table Curve 2D® (Version 5.0, SPSS, Inc.).

RESULTS AND DISCUSSION

1. Sorption Kinetics

Since the pH values of each chlorophenol solution were not con-

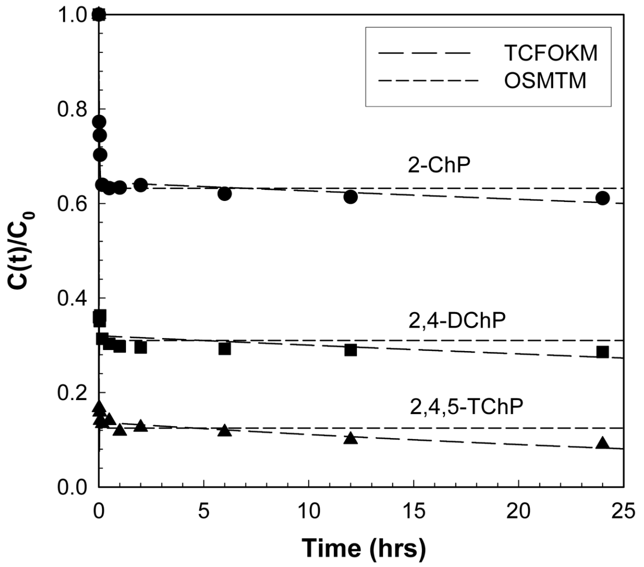

Fig. 1. Sorption kinetics of chlorophenols in 50% HDTMA-montmorillonite.

Table 2. One-site mass transfer model parameters for sorption of chlorophenols in 50% HDTMA-montmorillonite (soil wt.=0.5 g, C_0= 100 mg/L). Numbers in parenthesis indicate the standard deviation

Compound	C_e (mg/L)	k_s (hr^{-1})	Equilibration time (hr)	R^2
2-ChP	63.2 (±1.17)	21.60 (±4.18)	0.68	0.935
2,4-DChP	31.0 (±0.88)	48.82 (±10.74)	0.17	0.986
2,4,5-TChP	12.5 (±0.67)	22.58 (±4.20)	0.13	0.995

Table 3. Two compartment first-order kinetic model parameters for sorption of chlorophenols in 50% HDTMA-montmorillonite (soil wt.=0.5 g, C_0=100 mg/L). Numbers in parenthesis indicate the standard deviation

Compound	Fast compartment		Slow compartment		R^2
	f_1	k_1 (hr^{-1})	$f_2 = 1 - f_1$	k_2 (hr^{-1})	
2-ChP	0.3549 (±0.0143)	39.05 (±8.03)	0.6451 (±0.0143)	2.88×10^{-3} (±0.0023)	0.945
2,4-DChP	0.6800 (±0.0095)	170.23 (±37.70)	0.3200 (±0.0095)	6.36×10^{-3} (±0.0036)	0.990
2,4,5-TChP	0.8626 (±0.0036)	200.73 (±22.69)	0.1374 (±0.0036)	2.12×10^{-2} (±0.0049)	0.999

trolled throughout the kinetic experiments, we used the isosbestic point of each compound to obtain the *total* phenolic concentration (i.e., both the protonated and the deprotonated chlorophenols) when analyzing the equilibrium concentration of the solution. Sorption of chlorophenols with time onto 50% HDTMA-mont is depicted in Fig. 1. As indicated by a greater reduction in the remaining fraction, $C(t)/C_0$, sorption affinity was in the order 2,4,5-TChP>2,4-DChP>2-ChP, mainly due to the stronger hydrophobic interaction between the solute and the pseudo-organic medium formed by the conglomeration of the long hydrocarbon chains of HDTMA in the interlamellar spacing of the HDTMA-mont. Magnitude of the interaction is well reflected by the octanol-water partition coefficient, K_{ow} (see Table 1). Both OSMTM and TCFOKM were well fitted to the sorption kinetic data of each solute and fitted curves of the OSMTM and TCFOKM are shown together in Fig. 1 for comparison. The model parameters of OSMTM and TCFOKM determined from the nonlinear curve fitting are listed in Tables 2 and 3, respectively.

In Fig. 1, a substantial portion of the solute was sorbed within the first one hour, followed by a slow sorption over 24 hours of sorption period. Approximately 37% of 2-ChP, 69% of 2,4-DChP, and 88% of 2,4,5-TChP were sorbed in the first one hour and very little was sorbed in the subsequent period of sorption. The uptake fraction was increasing as K_{ow} value of the chlorophenols was increasing. This is attributed to the fact that a solute with higher hydrophobicity (as indicated by K_{ow} value) has stronger interaction with the pseudo-organic medium formed by the long chain hydrocarbons of HDTMA.

Comparison of R^2 values of OSMTM (Table 2) and TCFOKM (Table 3) shows that TCFOKM fitted the data better than OSMTM for sorption of chlorophenols in HDTMA-mont as expected from the number of fitting parameters involved in each model (i.e., two *vs.* three). The mass transfer coefficient for sorption (k_s) generally increases as K_{ow} value increases, except for 2,4,5-TChP. From Fig. 2 and Table 3, the fast fraction (f_1) and the first-order rate constant (k_1) in the fast sorption compartment increased in the order, 2-ChP< 2,4-DChP<2,4,5-TChP, which agrees with the order of K_{ow} values. The first-order rate constants in the fast (k_1) and slow (k_2) compartments were found to be in the range of 10^1-10^2 hr^{-1} and 10^{-3}-10^{-2} hr^{-1}, respectively.

The precision of estimated k_2 is only good when experiments are conducted to near the time of $1/k_2$ (approximately 1,000 hours) [Opdyke and Loehr, 1999]; the sorption in the slow (or fast) fraction occurs most significantly at $1/k_2$ (or $1/k_1$) hrs. However, an extension of time frame to 1,000 hrs would be unrealistic for the sorption of chlorophenols in HDTMA-mont because most of the fast sorption fraction is sorbed within one hour. Therefore, the precision of k_2 values obtained in this study may be unsatisfactory, and only an order of magnitude estimate is useful in interpreting the time frame for the sorption in the slow sorption compartment. However, precision of k_1 in this study would be useful since the time frame in the fast compartment is 10^{-1}-10^{-2} hr (i.e., $1/k_1$).

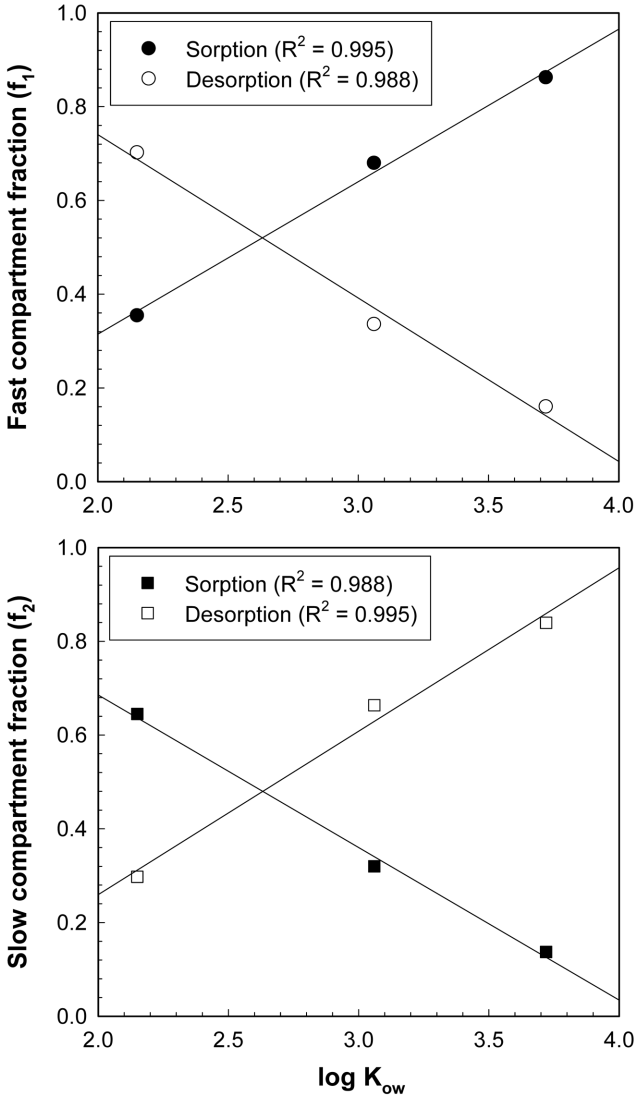

Fig. 2. Relationship between the fast (f_1) and slow (f_2) compartments versus log K_{ow}.

2. Effect of Initial Concentration

The effect of initial aqueous phase concentration of 2-ChP on the sorption kinetics is presented in Fig. 3. About 30%, 39% and 35% of 2-ChP were sorbed in one hour for the three different initial

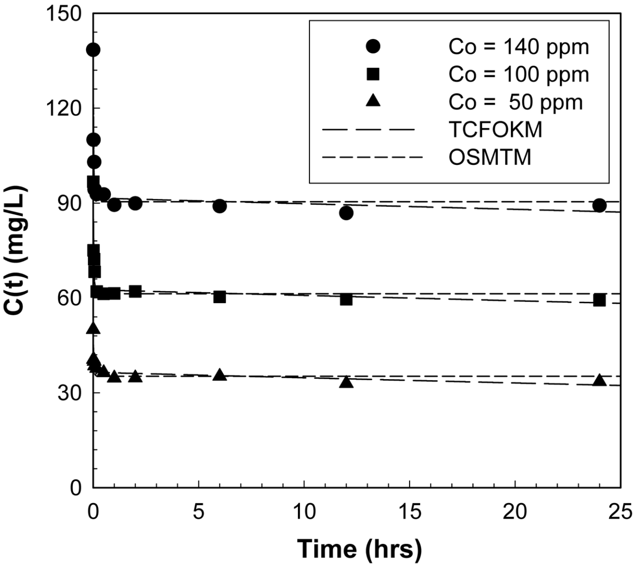

Fig. 3. Effect of initial solute concentration on sorption kinetics of 2-ChP.

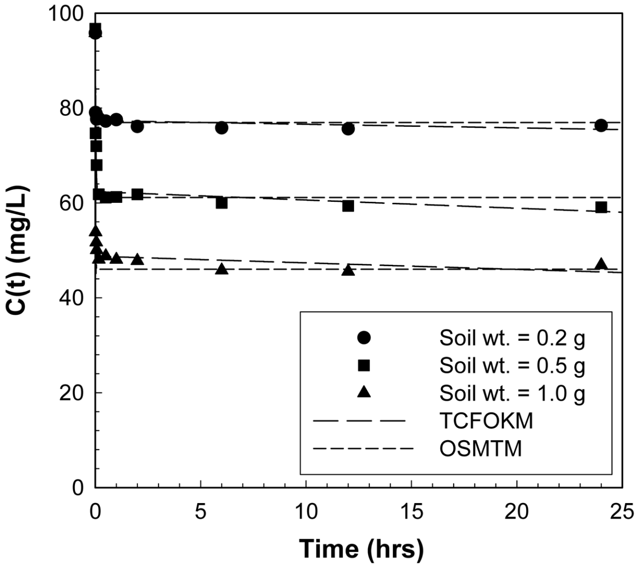

Fig. 4. Effect of sorbent weight on sorption kinetics of 2-ChP.

Table 4. Effect of initial concentration on sorption kinetics of 2-ChP. One-site mass transfer model parameters for 2-ChP in 50% HDTMA-montmorillonite (soil wt.=0.5 g). Numbers in parenthesis indicate the standard deviation

C_0 (mg/L)	C_e (mg/L)	k_s (hr^{-1})	R^2
50	35.2 (±0.71)	22.70 (±6.43)	0.860
100	61.3 (±1.12)	21.13 (±4.04)	0.936
140	90.4 (±1.17)	26.08 (±4.14)	0.960

Table 6. Effect of sorbent weight on sorption kinetics of 2-ChP. One-site mass transfer model parameters for 2-ChP in 50% HDTMA-montmorillonite (C_0=100 mg/L). Numbers in parenthesis indicate the standard deviation

Soil wt.	C_e (mg/L)	k_s (hr^{-1})	R^2
0.2 g	76.96 (±0.33)	104.57 (±23.25)	0.973
0.5 g	61.14 (±1.13)	21.60 (±4.18)	0.935
1.0 g	48.05 (±0.61)	62.59 (±9.90)	0.986

concentrations of 50, 100 and 140 mg/L, respectively. Again, very little was sorbed for the rest sorption period. The result of OSMTM analysis summarized in Table 4 shows that the first-order mass transfer coefficient (k) is nearly independent of the initial chemical concentration (C_0). Similarly, the initial concentration did not significantly affect the model parameters (f_1, k_1 and k_2) of the TCFOKM, either (see Table 5). Apparently, initial chemical concentration seemed to have no influence on sorption kinetics.

3. Effect of Sorbent Weight

Fig. 4 depicts the effect of sorbent weight on the sorption kinetics of 2-ChP. The results of OSMTM and TCFOKM are shown together for comparison. The uptake fraction increased as larger amount of sorbent was used. As listed in Table 6, the results of OSMTM indicate that equilibrium concentration in the aqueous solution decreased from 77 mg/L to 48 mg/L as sorbent weight increased from 0.2 g to 1.0 g. However, there was no consistent increase or decrease in the mass transfer coefficient as the sorbent weight was varied. Comparison of OSMTM (Table 6) and TCFOKM (Table 7) indicates that the three-parameter TCFKM is better than the two-parameter OSMTM in fitting sorption kinetic data. The fast fraction was increasing as sorbent weight increases simply due to the increased availability of the fast sorption compartment. However, the first-order rate constants of the fast and slow compartments were not increasing accordingly. Therefore, it is concluded that sorbent weight has no effect on sorption rate constants in the fast and slow compartments.

In Fig. 5, the 2-ChP sorption equilibrium data from different kinds of experiments (i.e., sorption equilibrium data estimated from the kinetic studies with different initial solute concentration and sorbent weight, and separate sorption equilibrium data) are shown together to examine the consistency of equilibrium data. All the equilibrium

Table 5. Effect of initial concentration on sorption kinetics of 2-ChP. Two compartment first-order kinetic model parameters for 2-ChP in 50% HDTMA-montmorillonite (soil wt.=0.5 g). Numbers in parenthesis indicate the standard deviation

C_0 (mg/L)	Fast compartment		Slow compartment		R^2
	f_1	k_1 (hr^{-1})	$f_2=1-f_1$	k_2 (hr^{-1})	
50	0.2704 (±0.0147)	48.87 (±15.19)	0.7296 (±0.0147)	4.83×10^{-3} ($\pm2.18\times10^{-3}$)	0.910
100	0.3532 (±0.0142)	37.87 (±7.69)	0.6468 (±0.0142)	3.28×10^{-3} ($\pm2.57\times10^{-3}$)	0.946
140	0.3385 (±0.0103)	43.41 (±7.15)	0.6615 (±0.0103)	1.99×10^{-3} ($\pm1.59\times10^{-3}$)	0.967

Table 7. Effect of sorbent weight on sorption kinetics of 2-ChP. Two compartment first-order kinetic model parameters for 2-ChP in 50% HDTMA-montmorillonite (C_0=100 mg/L). Numbers in parenthesis indicate the standard deviation

Soil wt.	Fast compartment		Slow compartment		R^2
	f_1	k_1 (hr^{-1})	$f_2=1-f_1$	k_2 (hr^{-1})	
0.2 g	0.1926 (±0.0036)	142.13 (±31.45)	0.8074 (±0.0036)	9.92×10^{-4} ($\pm4.86\times10^{-4}$)	0.982
0.5 g	0.3549 (±0.0143)	39.05 (±8.03)	0.6451 (±0.0143)	2.88×10^{-3} ($\pm2.26\times10^{-3}$)	0.945
1.0 g	0.4909 (±0.0067)	132.39 (±19.65)	0.5091s (±0.0067)	2.93×10^{-3} ($\pm1.49\times10^{-3}$)	0.990

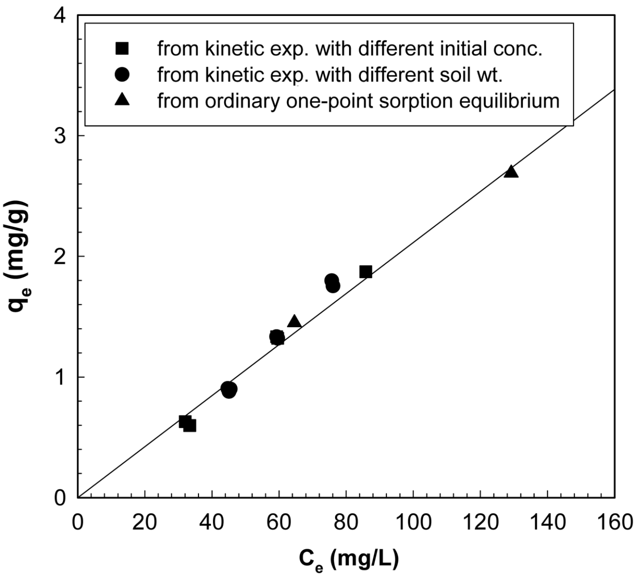

Fig. 5. Consistency check for sorption equilibrium data of 2-ChP from various kinds of experiments.

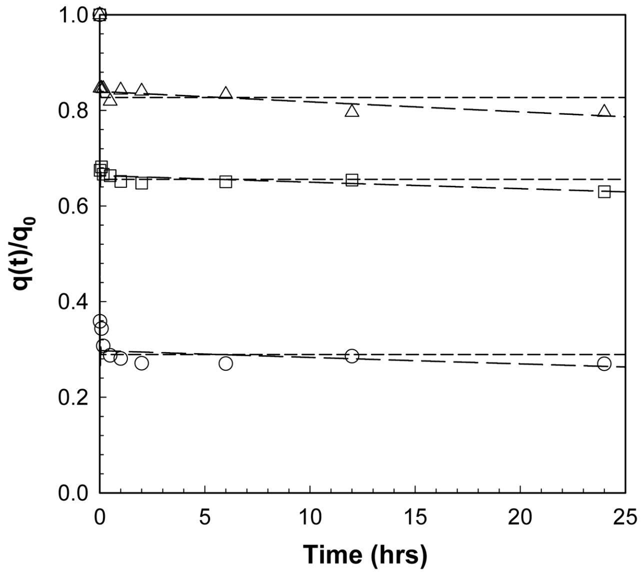

Fig. 6. Desorption kinetics of chlorophenols from 50% HDTMA-montmorillonite.

points were found to be quite consistent, resulting in a well-correlated linear equation, q_e=0.022C_e, with R^2=0.971.

4. Desorption Kinetics

Desorption kinetic studies were conducted by using the 50% HDTMA-mont preloaded with equal amount of solute. Duplicate vials were sacrificed at predetermined time interval. The fraction of chlorophenols released as a function of time is plotted in Fig. 6, together with the fitted curves of OSMTM and TCFOKM for comparison. The two-parameter OSMTM and three-parameter TCFOKM were fitted to desorption kinetic data using the nonlinear regression method. Sorption affinity in desorption was the same as that in sorption (2,4,5-TChP>2,4-DChP>2-ChP). The OSMTM and TCFOKM parameters are summarized in Tables 8 and 9, respectively. In Fig. 6, a substantial portion of the chemical was released within 30 minutes,

Table 8. One-site mass transfer model parameters for desorption of chlorinated phenols from 50% HDTMA-montmorillonite (soil wt.= 0.5 g). Numbers in parenthesis indicate the standard deviation

Compound	q_0 (mg/g)	q_e (mg/g)	k_d'(hr^{-1})	k_d (hr^{-1})	Equilibration time (hr)	R^2
2-ChP	1.39	0.40 (±0.01)	40.45 (±6.657)	100.8 (±16.58)	0.18	0.990
2,4-DChP	1.35	0.89 (±0.01)	113.8 (±31.25)	60.91 (±16.73)	0.14	0.985
2,4,5-TChP	1.34	1.11 (±0.01)	108.8 (±53.90)	23.14 (±11.47)	0.18	0.893

Table 9. Two compartment first-order kinetic model parameters for desorption of chlorinated phenols from 50% HDTMA-montmorillonite. Numbers in parenthesis indicate the standard deviation

Compound	q_0 (mg/g)	Fast compartment		Slow compartment		R^2
		f_1	k_1 (hr^{-1})	$f_2=1-f_1$	k_2 (hr^{-1})	
2-ChP	1.39	0.7025 (±0.0099)	146.4 (±23.67)	0.2975 (±0.0099)	4.89×10^{-3} (±0.0037)	0.992
2,4-DChP	1.35	0.3364 (±0.0044)	203.7 (±57.72)	0.6636 (±0.0044)	2.10×10^{-3} (±0.0007)	0.993
2,4,5-TChP	1.34	0.1605 (±0.0050)	187.2 (±105.4)	0.8395 (±0.0050)	2.60×10^{-3} (±0.0006)	0.969

followed by a slow release over 24 hours of desorption time. This pattern was similar to that observed in sorption (see Fig. 1). Approximately 71% of 2-ChP, 34% of 2,4-DChP, and 17% of 2,4,5-TChP was desorbed within 30 minutes. The desorbed fraction from the HDTMA-mont was decreasing as K_{ow} value of the chlorophenols was increasing. This is attributed to stronger interaction between chlorophenol with higher K_{ow} and the pseudo-organic medium formed by the HDTMA cation.

Comparison of R^2 values of OSMTM (Table 8) and TCFOKM (Table 9) shows that TCFOKM is better fitted than OSMTM to desorption kinetic data of chlorophenols. The mass transfer coefficient for desorption (k_d) increases due to the weaker interaction between the solute and the organoclay, as K_{ow} value decreases. As mentioned earlier, since most sorption and desorption complete in an hour and half an hour, respectively, k_d values were found to be greater than k_s values for all three solutes studied. Contrary to the sorption kinetics, the fast fraction in desorption was increasing in the order 2-ChP >2,4-DChP>2,4,5-TChP, being in the reverse order of their K_{ow} values. A less hydrophobic solute (i.e., a solute with a lower K_{ow}) will be weakly sorbed and thus more easily desorbed from the HDTMA-mont. In contrast to the observations in sorption, however, the rate constants in the fast and slow desorption compartment are not increasing as the K_{ow} of the chlorophenol increases. The desorption rate constants in the fast compartment were approximately 10^2 hr^{-1}, while the desorption rate constants in the slow compartment were about 10^{-3} hr^{-1}; i.e., a significant desorption in the fast (or slow) compartment occurs at about 10^{-2} (or 1,000) hrs.

As discussed in the sorption kinetics, the precision of k_2 is good only when many samples are taken near the time corresponding to $1/k_2$. This means that desorption kinetic data should be obtained over 1,000 hrs to have a reliable estimate of k_2. However, for desorption of chlorophenols from HDTMA-mont, an extension of desorption time to 1,000 hrs is not practical, since fast desorption fraction reached desorption equilibrium within an hour. As a result, the precision of k_2 values obtained in this study may be unsatisfactory and only an order of magnitude estimate is useful considering the timescale needed for the desorption in the slow desorption compartment. However, precision of k_1 in this study would be useful since the time frame for the fast fraction is only 10^{-2} hr ($=1/k_1$). The fast desorbing fraction of the sorbent is directly associated with the amount of organic contaminants that is available for immediate transport or biodegradation.

The results of this study are consistent with a previous study on the sorption and desorption of phenol in HDTMA-mont [Zhang and Sparks, 1993]. They reported that sorption equilibrium was obtained in 40 minutes and desorption in 20 minutes, respectively. In our study, approximately 37% of 2-ChP, 69% of 2,4-DChP and 88% of 2,4,5-TChP were sorbed within one hour showing little sorption afterwards, while about 71% of 2-ChP, 34% of 2,4-DChP and 17% of 2,4,5-TChP was desorbed within 30 minutes exhibiting apparent desorption equilibrium. A weakly-sorbed chlorophenol (i.e., 2-ChP) was easily desorbed, while a strongly-sorbed chlorophenol (i.e., 2,4,5-TChP) was rather resistant to desorption.

CONCLUSIONS

A One-site mass transfer model (OSMTM) and two compartment first-order kinetic model (TCFOKM) were used to analyze the sorption and desorption kinetics of three chlorophenols (2-ChP, 2,4-DChP and 2,4,5-TChP) in 50% HDTMA-mont. The OSMTM applicable to *desorption* was derived in this work. As expected, the three-parameter TCFOKM was better than the two-parameter OSMTM in describing sorption and desorption kinetics due to the presence of one more parameter in TCFOKM.

Sorption affinity was in the order 2,4,5-TChP>2,4-DChP>2-ChP, mainly due to stronger hydrophobic interaction between the solute and the pseudo-organic medium formed by the conglomeration of the long hydrocarbon chains of HDTMA in the interlamellar spacing of the HDTMA-mont, which is well reflected in the octanol-water partition coefficient, K_{ow} of each solute. Sorption kinetics was found to be independent of initial solute concentration and the sorbent to solution ratio, at least in the experimental ranges covered in this work. The sorption equilibrium data estimated by fitting the sorption kinetic data to OSMTM were found to be in good agreement with those from batch-sorption equilibrium data.

Analysis of OSMTM and TCFOKM indicates that apparent sorption and desorption equilibria were obtained within 1 hour and 30 minutes, respectively: approximately 37% of 2-ChP, 69% of 2,4-DChP, and 88% of 2,4,5-TChP were sorbed within an hour and very little was sorbed in the subsequent period of sorption, while about 71% of 2-ChP, 34% of 2,4-DChP, and 17% of 2,4,5-TChP was desorbed in the first 30 minutes showing little desorption afterwards. The mass transfer coefficient for sorption in OSMTM (k_s) generally increases as K_{ow} value increases, except for 2,4,5-TChP, while the mass transfer coefficient for desorption (k_d) consistently increases as K_{ow} value decreases, due to the weaker hydrophobic interaction between the solute and the organoclay. Since most sorption and desorption complete in an hour and half an hour, respectively, k_d values were found to be greater than k_s values for all three solutes studied.

From the analysis of TCFOKM for the sorption and desorption kinetic data, the fraction of the fast sorption (or desorption), f_1 and the sorption rate constants in the fast (k_1) and slow (k_2) compartments were found to be in the order 2,4,5-TChP>2,4-DChP>2-ChP, which agrees with the order in K_{ow}: i.e., the higher the K_{ow} value is, the larger f_1, k_1 and k_2 values are. The first-order sorption rate constants in the fast and slow compartments were found to vary 10^1-10^2 hr^{-1} and 10^{-3}-10^{-2} hr^{-1}, respectively.

Other than the tendencies in the sorption kinetics, the desorption rate constant in the fast (k_1) and slow (k_2) compartments were not correlated well with the K_{ow} in a consistent manner. The first-order desorption rate constants in the fast compartment were much larger (10^1-10^2 hr^{-1}) than those in the slow compartment (10^{-3}-10^{-4} hr^{-1}).

Sorption affinity and desorption resistance of each chlorophenol in 50% HDTMA-mont were found to exhibit the same tendency: a weakly-sorbed chlorophenol (i.e., 2-ChP) was easily desorbed, while a strongly-sorbed chlorophenol (i.e., 2,4,5-TChP) was rather resistant to desorption.

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