

염화페놀류 화합물의 HDTMA-montmorillonite에 대한 수착 동력학에 미치는 pH의 영향

Effect of pH on the sorption kinetics of chlorophenols onto HDTMA-montmorillonite

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<요약문>

Sorption kinetics of 2-chlorophenol(2-ChP), 2,4-dichlorophenol(2,4-DChP) and 2,4,5-trichlorophenol (2,4,5-TChP), onto montmorillonite modified with hexadecyltrimethyl ammonium cations(HDTMA-mont) were investigated. One-site mass transfer model(OSMTM) and two compartment first-order kinetic model(TCFOKM) were used to analyze kinetics. 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. For all chlorophenols, the results of OSMTM analysis indicate that the predominant deprotonated speciation(at pH 9.15) exhibited higher mass transfer coefficient(k_s) than the protonated speciation(at pH 4.85). This is because the deprotonated speciation has stronger hydrophobic interaction than protonated speciation. Most sorption completes in three hours. The fraction of the fast sorption and the first-order sorption 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(f_1) and the sorption rate constants in the fast compartments(k_1) were in the order 2,4,5-TChP > 2,4-DChP > 2-ChP, which agrees with the magnitude of the K_{ow} . The first-order sorption rate constants in the fast compartment($10^{0.8} - 10^{1.22} \text{ hr}^{-1}$) were much larger than those in the slow compartment($10^{-1.74} - 10^{-2.622} \text{ hr}^{-1}$).

Key words : chlorophenol, organoclay, sorption, kinetics, OSMTM, TCFOKM.

1. Introduction

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.

The organically modified clays (“organoclays” for short) can provide a wide range of applications, such as wastewater treatment, permeable reactive barriers (PRBs), solidification and stabilization of waste effluents, and liners for hazardous waste landfills or gasoline storage tanks. Contaminant immobilization using organoclays coupled with *in situ* biodegradation would provide a comprehensive restoration technology to permanently eliminate target organic contaminants.

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 were focused on the sorption and/or desorption equilibrium aspects. Only a few studies have been reported on the sorption and/or desorption kinetics of sorbed contaminants on organoclays, despite its importance in evaluating the effectiveness of organoclays in wastewater treatment, clay liners, remediation, etc. Reliable estimation of the sorption and desorption processes is crucial to the design of organoclay barriers for the remediation of contaminated sites.

Chlorinated phenols are representative model compounds of ionizable organic compounds (IOCs), which have been encountered in many contaminated sites. In this work, montmorillonites modified with the HDTMA cations to the extent of 100% of the cation exchange capacity (CEC) of the clay (hereinafter, referred to as 100% 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 using one-site mass transfer model (OSMTM), two-compartment first-order kinetic model (TCFOKM) and a pseudo second-order model (SPOM). The objective of this study is to examine sorption kinetics of chlorophenols in 100% HDTMA-mont. The results of this study will provide a valuable insight into the development of remediation strategies for the groundwater polluted with IOCs using organoclays as a potential PRB.

2. Materials and Methods

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. 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. were prepared in an electrolyte solution containing 1 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.5 mM $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and buffer solutions. Acetate buffer (0.02M CH_3COOH and 0.03M CH_3COONa) and Borax buffer (0.01 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) solutions were used to control pH to be 4.85 and 9.15, respectively. After dissolving the ChPs in buffer solutions, the pH of the solution was adjusted by 0.1 M HCl and

NaOH. 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.

Preparation of HDTMA-Mont

HDTMA-mont was prepared by exchange adsorption of HDTMA onto the washed montmorillonite to the extent of 100% CEC. In order to prepare 100% HDTMA-mont, the exchange adsorption of HDTMA onto 20 grams of the washed montmorillonite was performed in a 2-L baffled beaker containing 1 L of 3,226 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.

Sorption Kinetic Studies

Sorption kinetic studies were conducted in batch mode using 40-mL glass vials with Teflon-faced silicone septa. The vials containing 0.5 g of HDTMA-mont each were filled with approximately 40-mL of stock chemical solutions minimizing headspace and then shaken at 150 rpm on an orbital shaker at 20°C. After predetermined time intervals(15 min to 24 hrs), the vials were centrifuged 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 result from sorption onto the solid phase. All experiments were run in duplicate.

3. Sorption model used.

One-Site Mass Transfer Model

In one-site mass transfer model(OSMTM) proposed by Nzengung et al.(1997), sorption rate was represented as a first order function of the concentration difference between the solution and sorbed phases under the assumption of the linear sorption equilibrium.

$$\frac{C(t)}{C_0} = \frac{C_e}{C_0} + \left(1 - \frac{C_e}{C_0}\right) \exp\left\{\left(-\frac{C_0}{C_e} k_s\right)t\right\} \quad (1)$$

where $C(t)$ = the solute concentrations in the solution(mg/L) at time t (hr), C_0 = initial concentration in the solution(mg/L), C_e = aqueous phase concentration at equilibrium(mg/L), and k_s = first-order sorption rate constant.

Two Compartment First-Order Kinetic Model

The overall sorption in two compartment first-order kinetic model(TCFOKM) was assumed to consist of the sum of the two first-order sorption rates in the fast and slow compartments(Opdyke and Loehr, 1999) :

$$\frac{C(t)}{C_0} = f_1 e^{-k_1 t} + (1 - f_1) e^{-k_2 t} \quad (2)$$

where f_1 and $f_2 (= 1 - f_1)$ are the fast and slow sorption fractions, respectively, and k_1 and k_2 are the sorption rate constants in the fast and slow compartments (hr^{-1}), respectively.

Values of the kinetic model parameters were determined by using a commercial software package, Table Curve 2D (Version 5.0, SPSS, Inc.).

4. Results and Discussion

Sorption Kinetics

Sorption of chlorophenols with time onto 100% HDTMA-mont was depicted in Figures 1-3. 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 interlamella spacing of the HDTMA-mont. Magnitude of the interaction is well reflected by the octanol-water partition coefficient, K_{ow} .

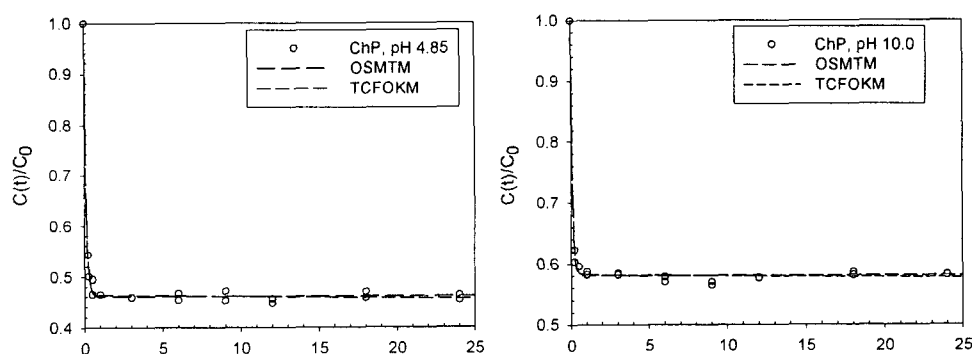


Figure 1. Sorption kinetics of ChP in 100% HDTMA-montmorillonite at different pHs.

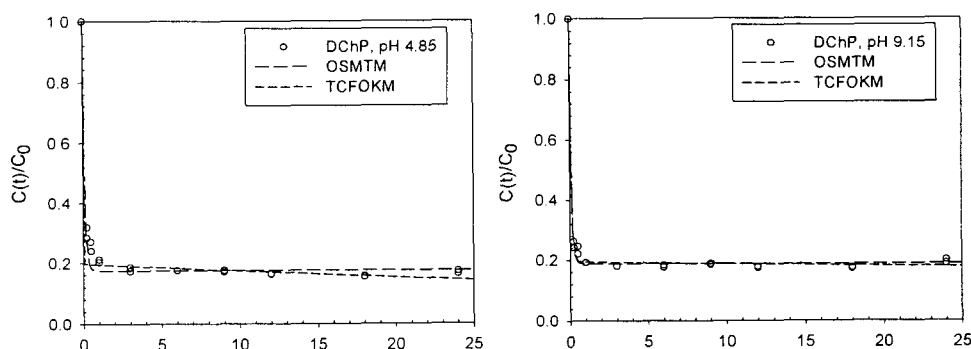


Figure 2. Sorption kinetics of DChP in 100% HDTMA-montmorillonite at different pHs.

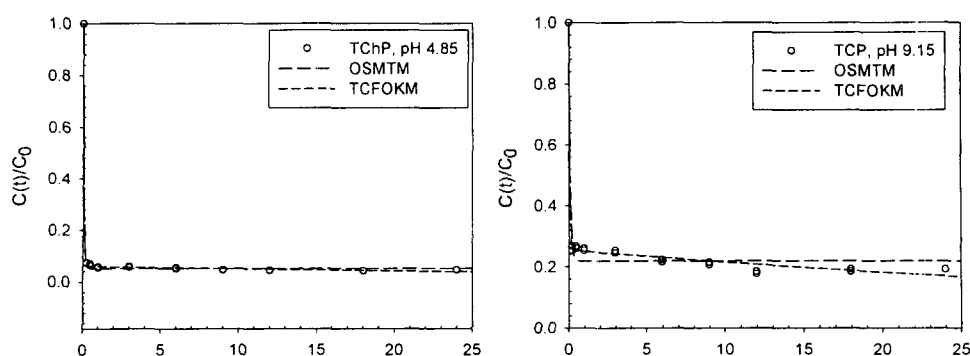


Figure 3. Sorption kinetics of TChP in 100% HDTMA-montmorillonite at different pHs.

All models were well fitted to the sorption kinetic data of each solute and fitted curves of the OSMTM and TCFOKM are shown together in Figures 1-3 for comparison. The model parameters of OSMTM and TCFOKM determined from the nonlinear curve fitting are listed in Tables 1-2, respectively.

In Figure 1-3, a substantial portion of the solute was sorbed within the first three hour, followed by a slow sorption over 24 hours of sorption period. Approximately 51% of 2-ChP, 83% of 2,4-DChP, and 95% of 2,4,5-TChP were sorbed at pH 4.85 and 66% of ChP, 63% of 2,4-DChP, and 78% of 2,4,5-TChP were sorbed at pH 9.15 in the first one hour, respectively 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.

Table 1. One-site mass transfer model parameters for sorption of chlorophenols in 100% HDTMA-montmorillonite(sorbent wt. = 0.5 g, C_0 = 100 mg/L). Numbers in parenthesis indicate the standard deviation.

Compound	pH	C_e (mg/L)	k_s (hr ⁻¹)	Equilibration time(hr)	R^2
2-ChP	4.85	45.73 (±0.723)	2.209 (±0.227)	2.80	0.953
	9.15	43.80 (±0.848)	2.964 (±0.419)	2.10	0.944
2,4-DChP	4.85	16.39 (±0.579)	1.600 (±0.179)	1.50	0.985
	9.15	32.01 (±1.165)	1.877 (±0.286)	2.30	0.929
2,4,5-TChP	4.85	5.121 (±0.204)	0.745 (±0.068)	1.00	0.999
	9.15	21.37 (±0.730)	2.475 (±0.457)	1.30	0.975

Table 2. Two compartment first-order kinetic model parameters for sorption of chlorophenols in 100% HDTMA-montmorillonite(sorbent wt. = 0.5 g, C0 = 100 mg/L). Numbers in parenthesis indicate the standard deviation.

Compound	Fast compartment			Slow compartment		
	pH	f_1	$k_1(\text{hr}^{-1})$	f_2	$k_2(\text{hr}^{-1})$	R^2
2-ChP	4.85	0.4822 (±0.0090)	5.6294 (±0.5249)	0.5178 (±0.0090)	0.0062 (±0.0014)	0.977
	9.15	0.5292 (±0.0098)	8.8820 (±1.3293)	0.4708 (±0.0098)	0.0076 (±0.0018)	0.973
2,4-DChP	4.85	0.7972 (±0.0090)	7.9658 (±0.6138)	0.0138 (±0.0041)	0.2028 (±0.0090)	0.990
	9.15	0.8074 (±0.0068)	10.188 (±0.8625)	0.0038 (±0.0030)	0.1926 (±0.0068)	0.993
2,4,5-TChP	4.85	0.9408 (±0.0020)	16.660 (±1.0924)	0.0591 (±0.0020)	0.0183 (±0.0034)	1.000
	9.15	0.7171 (±0.0061)	18.620 (±6.8201)	0.0167 (±0.0024)	0.2526 (±0.0061)	0.994

Comparison of R^2 values of OSMTM(Table 1) and TCFOKM(Table 2) 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) of pH 9.15 was higher than that of pH 4.15. However, k_s was not increasing as K_{ow} value was increasing. From Figures 1-3 and Table 2, the results of TCFOKM analysis indicate that 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 constant(k_1) at pH 9.15 was higher than that at pH 4.85. The first-order rate constants in the fast(k_1) and slow(k_2) compartments were found to $10^{0.8} - 10^{1.22} \text{ hr}^{-1}$ and $10^{-1.74} - 10^{-2.62} \text{ hr}^{-1}$, respectively.

The precision of estimated k_2 is only good when experiments were conducted to near the time of $1/k_2$ that corresponds to approximately 1,000 hours. 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 $10^{-1} \sim 10^{-2} \text{ hr}$ (i.e., $1/k_1$).

References

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