Sorption of Phenol and Alkylphenols from Aqueous Solution onto Organically Modified Montmorillonite and Applications of Dual-Mode Sorption Model

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ABSTRACT

Single- and multisolute competitive sorptions were carried out in a batch reactor to investigate the uptake of phenol, 4-methylphenol (MeP), 2,4-dimethylphenol (DMeP), and 4-ethylphenol (EtP) dissolved in water at 25°C onto organically modified montmorillonite. Hexadecyltrimethylammonium (HDTMA) cation was exchanged for metal cations on the montmorillonite to the extent of the cation-exchange capacity (CEC) of the montmorillonite to prepare HDTMA–montmorillonite, changing its surface property from hydrophilic to organophilic. It was observed from the experimental results that the adsorption affinity on HDTMA–montmorillonite was in the order 4-EtP ≈ 2,4-DMeP > 4-MeP > phenol. The Langmuir, dual-mode sorption (DS), and Redlich–Peterson (RP) models were used to analyze the single-solute sorption equilibria. The competitive Langmuir model (CLM), competitive dual-mode sorption model (CDSM), and ideal adsorbed solution theory (IAST), coupled with the single-solute models (i.e., Langmuir, DS, and RP models), were used to predict the multisolute competitive sorption equilibria. All the models considered in this work yielded favorable representations of both single- and multisolute sorption behaviors. DSM, CDSM, and IAST coupled with the DSM were found to be other satisfactory models to describe the single- and multisolute sorption of the phenolic compounds onto HDTMA–montmorillonite.

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INTRODUCTION

Various toxic chemicals have been discharged to the environment as industrial wastes, causing serious water and soil pollution. Removal of organic contaminants from wastewater has been extensively studied by using various physicochemical and biological techniques. Among these techniques, removal of organic contaminants using organically modified clays (hereafter referred to as organoclays) has drawn much attention. Natural clays, which are inherently hydrophilic due to hydration of the metal cations, become organophilic by ion exchanging a quaternary amine cation having short or long hydrocarbon chains for the metal cations on the clay.

Many investigators have studied sorption of organic contaminants from water using organoclays. Mortland et al. (1) and Boyd et al. (2) studied the uptake of phenol and chlorophenols from aqueous solution using smectites ion-exchanged with hexadecyltrimethylammonium (HDTMA) cation. To further reveal the influence of the exchanged organic cation on the sorption mechanism, Boyd et al. (3) studied the uptake of benzene and trichloroethylene from water onto HDTMA–smectite. They found that the solute uptake is mainly affected by the partitioning in the organic phase formed by the conglomeration of large C_{16} alkyl chains from the HDTMA cation.

Lee et al. (4) studied the sorption of aromatic compounds from water on tetramethylammonium (TMA)–smectite. Sorptive characteristics of TMA–smectite were notably different from those of HDTMA–smectite. Sorption isotherms of benzene, toluene, and o-xylene on TMA–smectite were nonlinear, indicating that sorption occurred by adsorption, not by partitioning like sorption on HDTMA–smectite.

Smith et al. (5) studied the sorption of tetrachloromethane from water on clay modified by each of 10 quaternary amine cations. They found that sorption of tetrachloromethane to organoclays modified with long-chain amine cations was characterized by linear isotherms and noncompetitive sorption behaviors with trichloroethene as a competing sorbate. This evidence indicates that sorption of a solute to long-chain cations occurs by a partition mechanism. However, uptake on organoclays with short-chain amine cations exhibits nonlinear isotherms and competitive sorption behaviors, characterizing an adsorption mechanism.

Our research group (6, 7) studied the single- and multisolute competitive sorption of 2-chloro-, 3-cyano-, and 4-nitrophenol from water either onto HDTMA (94% CEC)–montmorillonite (6) or onto the montmorillonite treated with both HDTMA and TMA cations, i.e., a dual TMA (40% CEC)/HDTMA (45% CEC)–montmorillonite (7). In both cases the single-solute isotherms were found to be nonlinear, and sorptive capabilities decreased when other solutes were present, exhibiting a typical adsorption mechanism. These facts re-

vealed that both partition in the organic medium formed by HDTMA cation, and adsorption on the surfaces of exchanged TMA/HDTMA cation(s) and bare clay minerals were actually in operation, resulting in the apparent nonlinearity in isotherms.

Recently, sorption of hydrophobic organic compounds to soil organic matter in *natural* soil or sediment was found to show nonlinear isotherms (8–11) and competitive effects in the presence of other solutes (10, 12, 13). To explain these results, Pignatello and coworkers (12, 13) utilized the dual-mode sorption model (DSM) which had been proposed earlier by Vieth and Sladek (14) to explain gas sorption behavior in glassy polymers. In the DSM it was assumed that some solute dissolves in the partition medium and the others adsorb in the adsorption sites. The linear isotherm was used for the partition mode, and the Langmuir model was employed to describe sorption by the adsorption mode. Weber and coworkers (9, 10, 15–17) introduced the distributed reactivity model (DRM) in a series of papers in which sorption processes in soils consist of multiple sorption reactions involving different reaction mechanisms. Later, they (16, 17) utilized the limiting form of the DRM, termed the dual reactive domain model, which is basically the same as the DSM.

In this context our research group (18) recently applied the DSM for the first time to describe sorption of phenolic compounds onto the HDTMA (/TMA)–montmorillonite reported previously (6, 7), regarding the resultant amount of sorption as a sum of partition and adsorption modes. In the paper we also proposed a competitive dual-mode sorption model (CDSM) to deal with the multisolute sorption, which was originally extended by Koros (19) to describe sorption of a binary gas mixture in glassy polymers. The empirical CDSM and the ideal adsorbed solution theory (IAST) (20) coupled with the DSM were used to examine the predictive power of the suggested models. However, any comparison with models well-known for the single- and multisolute competitive sorptions was not made.

Although organoclays find growing use in actual field applications, fundamental studies on single- and multisolute competitive sorption behaviors have not been fully achieved. In this work we chose phenol and a homologous series of alkylphenols (4-methylphenol, 2,4-dimethylphenol, and 4-ethylphenol) as solutes to further reveal the effect of the physical interaction between a solute and the long hydrocarbon chain of HDTMA cation and the shape/size of the solute on sorption affinity. Experimental isotherms and analyses that quantify the single- and multisolute competitive sorptions of phenol and three alkylphenols from water onto the HDTMA–montmorillonite will be presented. DSM, CDSM, and IAST coupled with the DSM will also be included in the analysis to compare with other well-known models and to reconfirm its applicability to sorption onto organoclays.

EXPERIMENTAL

Materials

Montmorillonite-KSF was purchased from Aldrich Chemical Co., and any impurities were removed by a digestion method using H_2O_2 (21). The digested montmorillonite particles were collected by gravity settling after washing with distilled water. According to Kim et al. (6), the CEC of this montmorillonite was 50.4 meq/100 g-clay by the Rhoades method (22), and the BET surface area of the washed montmorillonite was 97 m^2/g-clay by using Accusorb 2100E (Micromeritics Co., USA). The cation used as an organic modifier, hexadecyltrimethylammonium (HDTMA) chloride (25 wt%) solution in water, was obtained from Aldrich Chemical Co. and used as received. The four phenolic solutes used as sorbates were phenol, 4-methylphenol (MeP), 2,4-dimethylphenol (DMeP), and 4-ethylphenol (EtP) purchased from Aldrich Chemical Co. All reagents were of analytical grade and were used as received without further purification.

Preparation of HDTMA–Montmorillonite

HDTMA–montmorillonite was prepared following the procedures employed by Kim et al. (6): the exchange adsorption of HDTMA onto montmorillonite was performed in a 2-L batch reactor with a 5000 mg/L HDTMA solution. Thirty grams of washed montmorillonite were added to this reactor and then agitated with a mechanical stirrer at 500 rpm for 24 hours. After agitation, HDTMA–montmorillonite was collected and washed twice with 500 mL distilled water and dried in an oven at 60°C for 24 hours. The HDTMA–montmorillonite was kept in a brownish bottle until use. According to Kim et al. (6), the maximum uptake of HDTMA was about 152 mg/g-clay, which is tantamount to approximately 95% of the CEC of the montmorillonite used in this work.

Sorption onto HDTMA–Montmorillonite

Single-solute sorption isotherms on HDTMA–montmorillonite were obtained for the aqueous solutions of four phenolic compounds (phenol, 4-MeP, 2,4-DMeP, and 4-EtP) in a batch apparatus at 25°C. We prepared solutions of each phenolic compound at various mass concentrations of 100, 200, 300, 400, 600, 800, 1000, 1500, 2000, 2500, 3000, and 4000 mg/L. The initial pHs of the phenolic solutions ranged from about 5.6 to 6.9. Since the pK_a values of the phenolics (listed in Table 1) were always greater than the pH values, the dissociation of phenolics would not be significant. Each of the 20 mL solutions with different initial concentrations was poured into a capped 50 mL flask containing 0.500 g of HDTMA–montmorillonite, and then vigorously

TABLE 1
Physicochemical Properties of Phenolic Compounds Used

Solute[a]	MW	pK_a at 25°C	Total surface area[b] (Å^2)		UV wavelength (nm)
			By Yen	By Belfort	
Phenol	94.11	9.92	240	240	270
4-MeP	108.14	10.21	278	275	277
2,4-DMeP	122.17	10.60	316	310	278
4-EtP	122.17	10.20	297	302	276

[a] MeP = methylphenol, DMeP = dimethylphenol, EtP = ethylphenol.
[b] Data from Yen (26).

shaken on an orbit shaker for 24 hours at 25°C. Through a time study of the sorption of each phenolic compound, it was observed that sorption equilibrium was reached in about 2 hours on an orbit shaker revolving at 250 rpm. However, the sample batches were agitated for 24 hours throughout this study to ensure equilibrium. The solutions were then centrifuged at 2000 rpm for 20 minutes. The equilibrium concentrations of each solution were determined at the wavelengths of UV maxima using a UV-Visible spectrophotometer (Hewlett-Packard 8452A, USA). Since the reproducibility of the sorption onto the HDTMA–montmorillonite had been firmly demonstrated in the previous study (6), only sorption experiments of phenol were carried out in duplicate.

Three bisolute systems (phenol/4-MeP, phenol/2,4-DMeP, and 4-MeP/2,4-DMeP) and one trisolute system (phenol/4-MeP/2,4-DMeP) were prepared by mixing each phenolic solution of the same mass concentration in 1:1 and 1:1:1 volume ratios, respectively. Each 20 mL multisolute solution with several different initial mass concentrations was poured into a capped 50 mL flask containing 0.500 g of HDTMA–montmorillonite, and then vigorously shaken on an orbit shaker for 24 hours at 25°C. The solutions were then centrifuged at 2500 rpm for 30 minutes. Equilibrium concentrations in the mixtures were analyzed using an HPLC (Shimadzu LC-10AD, Japan) equipped with a UV-detector (Shimadzu SPD-10A, Japan).

SINGLE- AND MULTISOLUTE SORPTION MODELS USED

Single-Solute Sorption Models

The sorption isotherms frequently employed for single-solute systems are the 2-parameter Langmuir and the 3-parameter Redlich–Peterson (RP) (23) models that obey the correct thermodynamic boundary condition of Henry's

law over an infinitely dilute concentration range. The Langmuir and RP models for a solute in a single-solute system are written respectively as follows.

$$q = \frac{q_{LM}b_L C}{1 + b_L C} = \frac{a_L C}{1 + b_L C} \tag{1}$$

$$q = \frac{\alpha C}{1 + \beta C^\nu} \tag{2}$$

where C is the equilibrium concentration in the solution phase and q is the equilibrium sorbed concentration per unit weight of the sorbent. q_{LM} and b_L in the Langmuir model represent monolayer sorption capacity and a constant related to sorption equilibrium constant, respectively, and α, β, and ν in the RP model are empirical constants.

The dual-mode sorption model (DS model or DSM) assumes that some of a solute dissolves in the partition medium and the rest adsorbs in the adsorption sites. The linear isotherm and the Langmuir model were usually assigned to describe sorption by partition and adsorption modes, respectively. The Langmuir model was chosen due to its simplicity and satisfaction of Henry's law in the low concentration range. In this way, DSM itself also satisfies Henry's law in the limit of low concentrations. Thus, the 3-parameter DSM for a solute in a single-solute system is written as

$$q = KC + \frac{aC}{1 + bC} \tag{3}$$

The parameters K, a, and b are the partition coefficient in the partition medium and the Langmuir parameters on adsorption sites, respectively.

The DSM was fitted to the single-solute sorption data to estimate the three parameters using a nonlinear regression technique. However, many optimum sets of the three parameters could be obtained depending on the initial guesses used in the regression. To avoid this inconvenience and obtain parametric values having a physical meaning given in the original derivation, single-solute sorption data were first fitted to the classical Langmuir model, determining a_L and b_L. In the limit of zero concentrations, the Langmuir model (Eq. 1) and DSM (Eq. 3) lead to

$$\lim_{c \to 0} q = (K + a)C = a_L C \tag{4}$$

Hence, the partition coefficient K can be written as $(a_L - a)$ from the second equality. Therefore, DSM temporarily reduces to a 2-parameter model with known a_L:

$$q = (a_L - a)C + \frac{aC}{1 + bC} \tag{5}$$

By fitting Eq. (5) to the single-solute sorption data, we can estimate two parameters, a and b. Once a and b are determined, one remaining parameter K can be determined from $(a_L - a)$. Using these parameters as an initial starting point, we could consistently determine the three optimum parameters by curve-fitting the DSM to the single-solute sorption data.

Multisolute Competitive Sorption Models

To analyze multisolute competitive sorption behaviors, the competitive Langmuir model (CLM) (24), the competitive dual-mode sorption model (CDSM) (18, 19), and the ideal adsorbed solution theory (IAST) (20) were used in this study. The CLM is an extended form of the Langmuir model which allows predictions of the amount of a solute i sorbed per unit weight of sorbent, $q_{m,i}$, in the presence of other solutes:

$$q_{m,i} = \frac{q_{LM,i} b_{L,i} C_{m,i}}{1 + \sum_{j=1}^{N} b_{L,j} C_{m,j}} \qquad (6)$$

where $C_{m,i}$ is the equilibrium concentration of solute i in a mixture consisting of N solutes, and constants $b_{L,i}$ and $q_{LM,i}$ are parameters determined by fitting the Langmuir model to the single-solute sorption data of solute i alone.

Koros (19) extended the DSM for the first time to describe sorption of a binary gas mixture in glassy polymers. The DSM can be readily extended to multisolute competitive sorption (18). In a partition medium the partition coefficient of a solute is not affected by the presence of other solutes, not showing competitive sorption behavior until the sorbed quantity approaches the dissolving capacity of the medium. However, the adsorption term should be modified to consider the competition among the sorbing solutes for the limited adsorption sites. The single-solute Langmuir model was extended to consider the multisolute competitive adsorption, referred to as the CLM (24). Thus, by combining the invariant partition and multisolute adsorption terms, an extended form of the DSM, hereafter referred to as the CDSM, emerges as

$$q_{m,i} = K_i C_{m,i} + \frac{a_i C_{m,i}}{1 + \sum_{j=1}^{N} b_j C_{m,j}} \qquad (7)$$

where constants K_i, a_i, and b_i are parameters determined by fitting the DSM to the single-solute sorption data of solute i. Therefore, the CDSM can be readily utilized to predict multisolute competitive sorption using the model parameters determined from the single-solute sorption alone.

The IAST, originally proposed by Radke and Prausnitz (20), is of a descriptive nature and requires experimental equilibrium concentrations in the liquid phase to predict sorbed phase concentrations. To utilize the full predictive power and to simplify the calculation, we followed modifications made by Yen and Singer (25, 26). IAST is based on the equivalence of spreading pressure in a mixture under equilibrium. The equivalence of spreading pressure in a mixture containing N solutes leads to

$$\int_0^{q_1^*} \frac{d \log C_1}{d \log q_1} \, dq_1 = \int_0^{q_2^*} \frac{d \log C_2}{d \log q_2} \, dq_2 = \cdots = \int_0^{q_N^*} \frac{d \log C_N}{d \log q_N} \, dq_N \quad (8)$$

Other equations involved in IAST calculations are

$$C_{m,i} = z_i C_i^*, \qquad \sum_{i=1}^{N} z_i = 1, \qquad q_i^* = f(C_i^*),$$

$$\frac{1}{q_T} = \sum_{t=1}^{N} \frac{z_i}{q_i^*}, \qquad q_{m,i} = z_i q_T = \frac{V(C^0_{m,i} - C_{m,i})}{W}$$

(9)

In the above equations, z_i represents the mole fraction of solute i in the sorbed phase, and C_i^* and q_i^* refer to equilibrium concentrations in the liquid and solid phases of solute i that sorb singly from solution at the same temperature and spreading pressure as those of the mixture, respectively. The function f in $q_i^* = f(C_i^*)$ denotes a single-solute sorption model for solute i. $C^0_{m,i}$ is the initial concentration of solute i in a mixture, and q_T is the total sorbed concentration of all solutes in the mixture. V and W represent the solution volume and the adsorbent weight, respectively. Therefore, we can predict the multisolute sorption equilibria, $q_{m,i}$ vs $C_{m,i}$, by solving these equations simultaneously.

RESULTS AND DISCUSSION

Single-Solute Sorption onto HDTMA–Montmorillonite

The single-solute sorption of phenol, 4-MeP, 2,4-DMeP, and 4-EtP was performed using HDTMA–montmorillonite. Table 1 lists the physicochemical properties of the four phenolic compounds used in this work. Figure 1 shows the single-solute sorption isotherms of each phenolic compound. The order of the sorption affinity of the four phenolic compounds to HDTMA–montmorillonite was found to be 4-EtP ≈ 2,4-DMeP > 4-MeP > phenol.

The difference in sorption affinity can be explained mainly by the van der Waals interaction between a solute and the long hydrocarbon groups of the HDTMA cation, originating from the difference in molecular weights of the
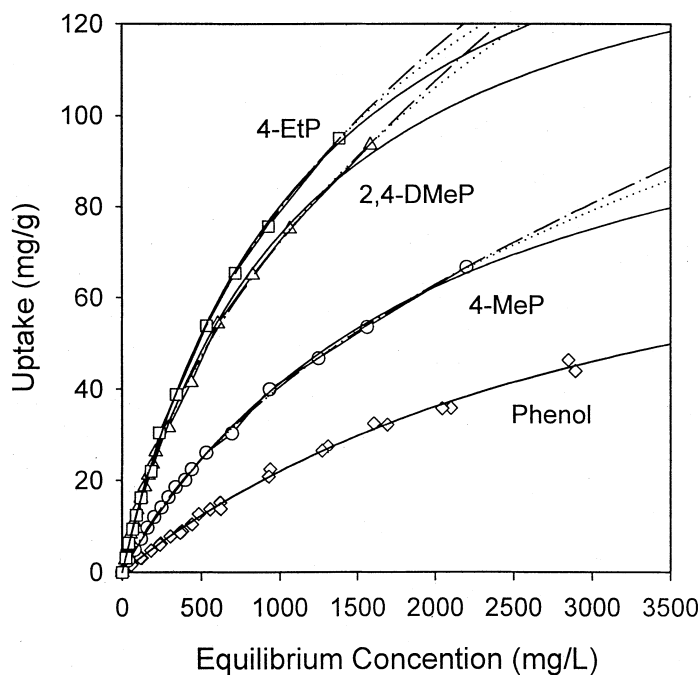
FIG. 1   Single-solute sorption isotherms of phenolic compounds on HDTMA–montmorillonite. Solid, dot-dashed, and dotted lines represent Langmuir, dual-mode sorption, and Redlich–Peterson models, respectively.

solute. In addition, steric hindrance due to the size and shape of the solute molecules was believed to cause the slightly different sorption affinities between 2,4-DMeP and 4-EtP, both of which have the same molecular weight. Since the total surface area of 4-EtP is smaller than that of 2,4-DMeP (see Table 1), 4-EtP exhibited slightly stronger sorption affinity than 2,4-DMeP. Kwon et al. (27) investigated the effect of steric hindrance in the sorption of 2-nitro-, 3-nitro, and 4-nitrophenol on HDTMA–montmorillonite. Among the three nitrophenol isomers, 2-nitrophenol exhibited the lowest affinity, and 3- and 4-nitrophenols nearly the same affinity. The sorption isotherm of phenol, which exhibited the lowest affinity, suggests that phenol in aqueous solution interacts more strongly with water by hydrogen bonding, and was not significantly attracted to the hydrophobic surfaces of the HDTMA–montmorillonite (1).

The 2-parameter Langmuir model and the 3-parameter DS and RP models were fitted to the experimental sorption data for each phenolic compound using the nonlinear regression method. Fitted curves of the Langmuir, DS, and RP models are shown together in Fig. 1 for comparison, and the parameters of each sorption model are tabulated in Tables 2 to 4, respectively. As a measure of the degree of fitness, the R^2 values for the single-solute sorption were com-

TABLE 2
Langmuir Parameters of Each Phenolic Compound on HDTMA–Montmorillonite

Solute	q_{LM} (mg/g)	b_L (L/mg)	a_L (L/g)	R^2
Phenol	101.4	2.76×10^{-4}	0.0280	0.9988
4-MeP	127.6	4.78×10^{-4}	0.0609	0.9994
2,4-DMeP	156.5	8.90×10^{-4}	0.139	0.9990
4-EtP	174.2	8.49×10^{-4}	0.148	0.9995

puted from the following equation (28):

$$R^2 = \frac{\sum q_i^2 - \sum (q_i - \hat{q}_i)^2}{\sum q_i^2} \tag{10}$$

In the above equations, q_i and $\hat{q}_i$ denote the experimental sorption data and the fitted results of each single-solute sorption model for the solute, respectively. In view of the R^2 values listed in Tables 2 to 4, the 3-parameter models exhibited a little better fit to the sorption data than the 2-parameter Langmuir model as expected from the number of parameters involved in the model. However, the three single-solute models seemed to agree well with the experimental data considering that all the R^2 values were greater than 0.99.

Multisolute Competitive Sorption onto HDTMA–Montmorillonite

Bisolute competitive sorptions were performed using the three binary systems of (a) phenol/4-MeP, (b) phenol/2,4-DMeP, and (c) 4-MeP/2,4-DMeP. Both the competitive sorption data and the predictions of the CLM, CDSM, and IAST for each bisolute system are shown together in Figs. 2(a) to (c) for comparison. Single-solute sorption models used in the multisolute predictive IAST were the Langmuir, DS, and RP models, the parameters of which were previously determined from the nonlinear curve-fitting to the single-solute sorption data (shown in Tables 2 to 4).

TABLE 3
Dual-Mode Sorption Parameters of Each Phenolic Compound on HDTMA–Montmorillonite

Solute	K (L/g)	a (L/g)	b (L/mg)	R^2
Phenol	1.31×10^{-11}	0.0280	2.76×10^{-4}	0.9988
4-MeP	0.0133	0.0539	9.87×10^{-4}	0.9997
2,4-DMeP	0.0258	0.133	18.7×10^{-4}	0.9996
4-EtP	0.0174	0.138	12.2×10^{-4}	0.9996

TABLE 4
Redlich–Peterson Parameters of Each Phenolic Compound on HDTMA–Montmorillonite

Solute	α (L/g)	$\beta \times 10^3$ (L/mg)$^{\nu}$	ν	R^2
Phenol	0.0280	0.276	1.00	0.9988
4-MeP	0.0746	6.62	0.702	0.9997
2,4-DMeP	0.187	14.9	0.675	0.9998
4-EtP	0.161	2.65	0.861	0.9996

The competitive sorption of the trisolute mixture of phenol/4-MeP/2,4-DMeP on HDTMA–montmorillonite was carried out in the same batch sorption apparatus at 25°C. The competitive sorption data for the three solutes are shown in Fig. 3, together with the predictions from the multisolute competitive sorption models.

To assess the predictive performances of the competitive sorption models considered in this study, both the R^2 values and the sum of the squares of the
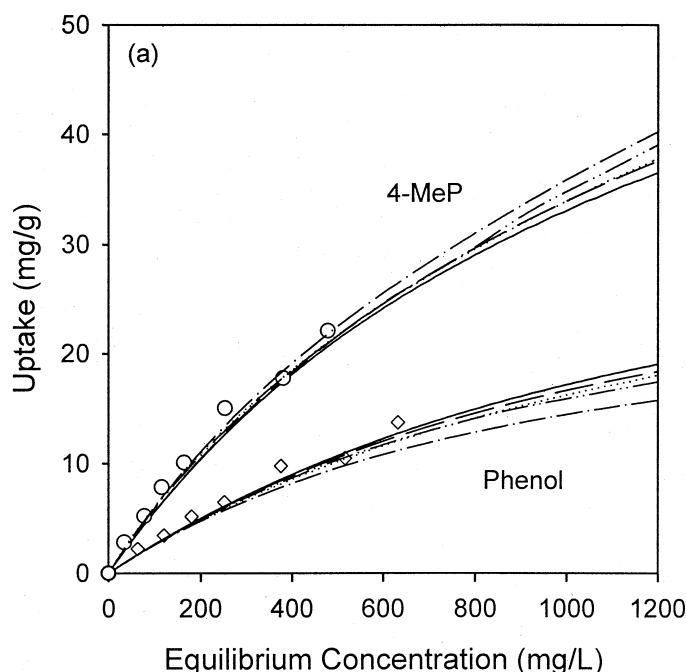
FIG. 2   Bisolute sorption isotherms of (a) phenol/4-MeP, (b) phenol/2,4-DMeP, and (c) 4-MeP/2,4-DMeP on HDTMA–montmorillonite. Solid and dot-dashed lines denote CLM and CDSM predictions, respectively, and dashed, dot-dot-dashed, and dotted lines represent IAST predictions based on Langmuir, dual-mode sorption, and Redlich–Peterson models, respectively.

FIG. 2   Continued

FIG. 3   Tri–solute sorption isotherm of phenol/4-MeP/2,4-DMeP on HDTMA–montmoril-lonite. Solid and dot-dashed lines denote CLM and CDSM predictions, respectively, and dashed, dot-dot-dashed, and dotted lines represent IAST predictions based on Langmuir, dual-mode sorption, and Redlich–Peterson models, respectively.
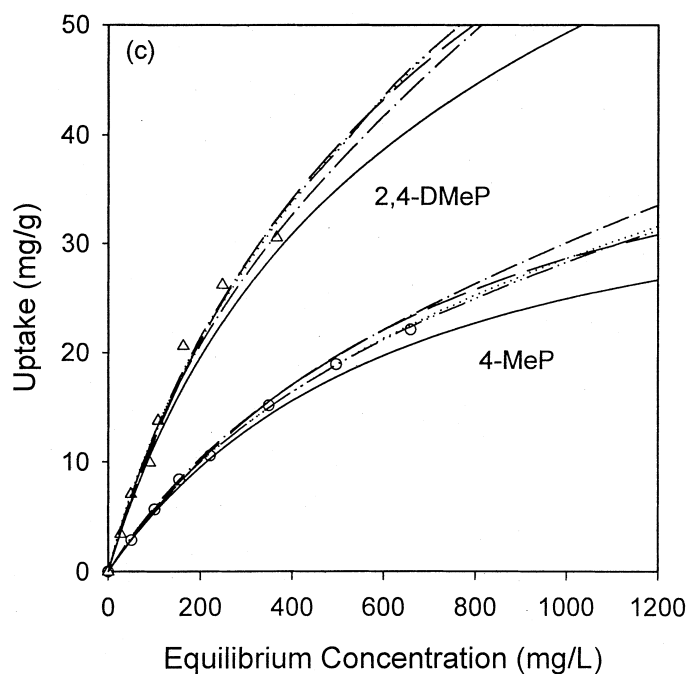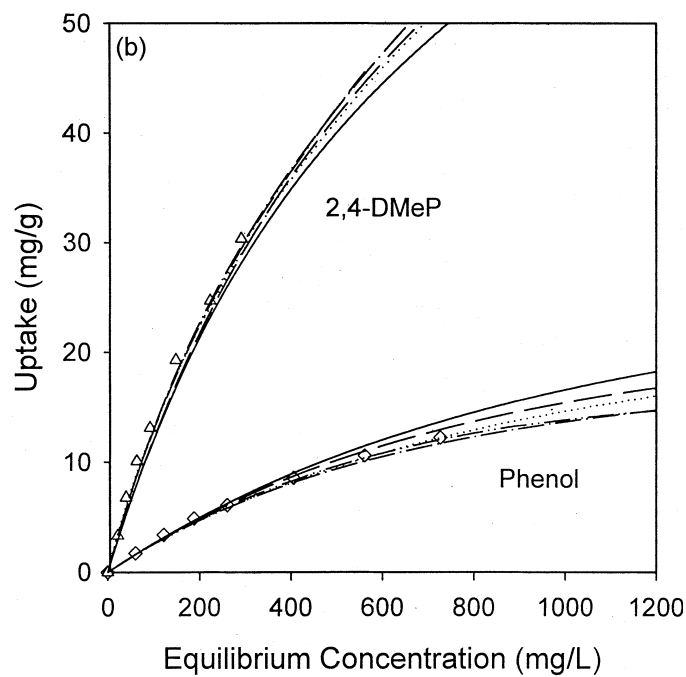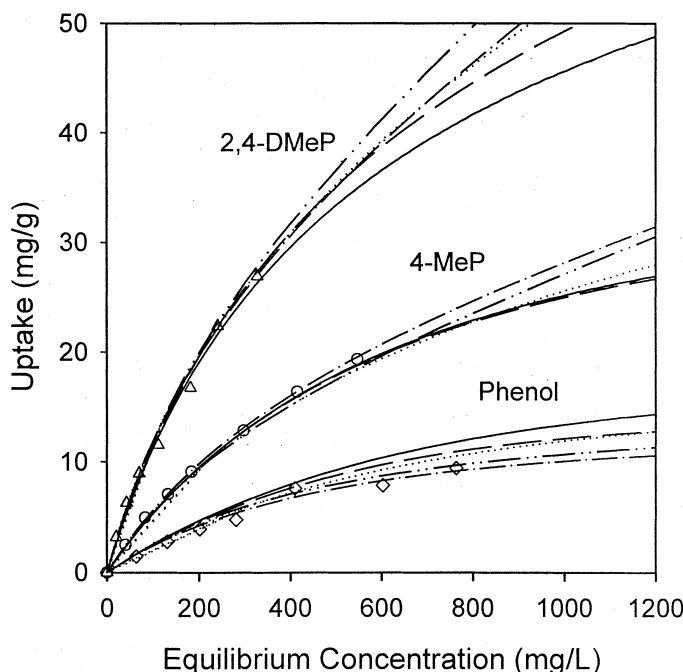
errors (SSE) for the multisolute sorption were utilized (28).

$$R^2 = \frac{\sum q_{\mathrm{m},i}^2 - \sum (q_{\mathrm{m},i} - \hat{q}_{\mathrm{m},i})^2}{\sum q_{\mathrm{m},i}^2} \tag{11}$$

$$\mathrm{SSE} = \sum (q_{\mathrm{m},i} - \hat{q}_{\mathrm{m},i})^2 \tag{12}$$

In the above equations, $q_{\mathrm{m},i}$ and $\hat{q}_{\mathrm{m},i}$ denote the experimental sorption data and the prediction of a competitive sorption model for the solute, respectively. The SSE and R^2 values of the multisolute competitive models for the binary and ternary systems are given in Tables 5 and 6, respectively. In view of these SSE

TABLE 5
SSE Values for Bi- and Trisolute Competitive Sorption Predictions from Multisolute Competitive Models

	CLM	CDSM	IAST coupled with		
			Langmuir	DS	RP
Phenol/4-MeP	3.65/12.7	12.0/4.75	4.43/11.0	6.48/8.74	6.16/6.48
Phenol/2,4-DMeP	3.06/23.0	0.531/5.16	0.698/16.5	0.432/6.43	0.697/5.96
4-MeP/2,4-DMeP	4.75/30.1	3.05/15.0	2.33/14.0	0.307/11.7	0.539/13.3
Phenol/4-MeP/2,4-DMeP	13.3/0.829/4.63	1.43/0.114/4.86	7.87/0.818/4.80	2.78/1.74/7.76	4.44/1.88/5.11

TABLE 6
R^2 Values for Bi- and Trisolute Competitive Sorption Predictions from Multisolute Competitive Models

	CLM	CDSM	IAST coupled with		
			Langmuir	DS	RP
Phenol/4-MeP	0.9924/0.9896	0.9750/0.9961	0.9907/0.9910	0.9865/0.9929	0.9872/0.9948
Phenol/2,4-DMeP	0.9926/0.9897	0.9987/0.9977	0.9983/0.9926	0.9989/0.9971	0.9983/0.9973
4-MeP/2,4-DMeP	0.9963/0.9874	0.9976/0.9937	0.9982/0.9942	0.9997/0.9951	0.9996/0.9944
Phenol/4-MeP/2,4-DMeP	0.9485/0.9991/ 0.9974	0.9944/0.9998/ 0.9973	0.9694/0.9992/ 0.9973	0.9892/0.9982/ 0.9956	0.9827/0.9981/ 0.9971

and R^2 values, the CLM, CDSM, and IAST coupled with the Langmuir, DS, and RP models provided favorable predictions for the multisolute competitive sorption of the phenolic compounds on HDTMA–montmorillonite.

As a typical case for competitive sorptions, Fig. 4 shows the sorption isotherms of phenol in single- and multisolute competitive sorptions. Sorption capacities of phenol obviously decrease when other solutes are present due to the competitive sorption among the solutes involved. In order to quantify the extent of reduction in sorption capacity, the Langmuir model was applied to
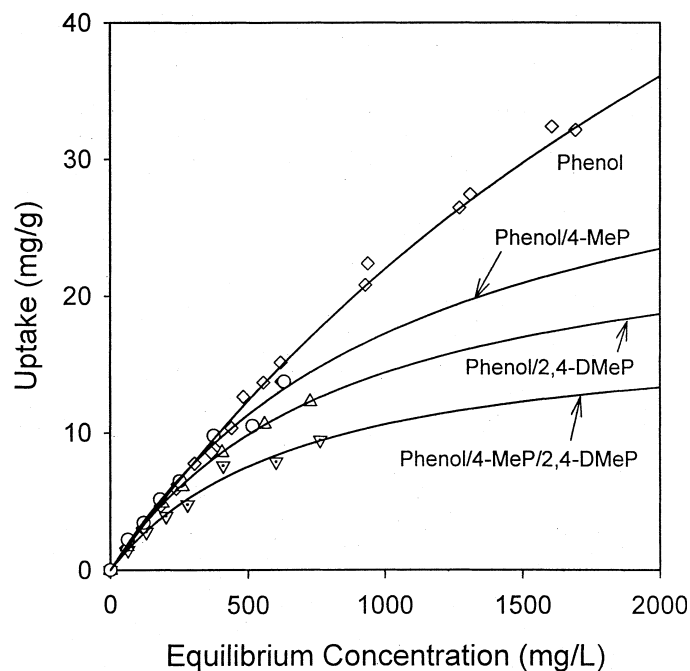

FIG. 4   Sorption isotherms of phenol on HDTMA–montmorillonite. Solid lines denote Langmuir models fitted to the single- and multisolute data.

TABLE 7

Langmuir Parameters and Percent Reductions in Monolayer Capacity of Each Phenolic Compound in Multisolute Systems Due to Competition

	System	q_{LM} (mg/g)	$b_L \times 10^4$ (L/mg)	% Reduction in q_{LM}	R^2
Phenol	Single	101.4	2.76	—	0.9970
	With 4-MeP	36.6	8.91	63.9	0.9876
	With 2,4-DMeP	26.7	11.6	73.6	0.9998
	Ternary	17.9	14.5	82.4	0.9836
4-MeP	Single	127.6	4.78	—	0.9984
	With phenol	49.9	15.9	60.9	0.9950
	With 2,4-DMeP	47.1	13.5	63.1	0.9996
	Ternary	42.8	14.9	66.5	0.9994
2,4-DMeP	Single	156.5	8.90	—	0.9978
	With phenol	70.0	25.5	55.3	0.9986
	With 4-MeP	67.9	23.7	56.6	0.9879
	Ternary	66.9	20.2	57.2	0.9934

the single- and multisolute sorption data of each phenolic compound, and it is listed in Table 7 along with the percentage reduction of the Langmuir monolayer capacity due to competition in binary and ternary systems. Phenol and 4-MeP in binary systems with 2,4-DMeP, which has the strongest sorption affinity, underwent about 74 and 63% reductions in q_{LM}, respectively, compared with the q_{LM}'s in single-solute sorption. However, 2,4-DMeP reduced only 55 and 57% in q_{LM} when competing with phenol and 4-MeP, respectively. Phenol, which shows the weakest sorption affinity, exhibited about 74% reduction of q_{LM} in the presence of 2,4-DMeP, while it reduced about 64% when paired with 4-MeP which has the medium-ranked sorption affinity among the three phenolic compounds studied. As for the trisolute system, the sorption capacities of 2,4-DMeP, 4-MeP, and phenol underwent about 57, 66, and 82% reductions in q_{LM} values in comparison with the single-solute sorption, respectively.

CONCLUSIONS

The sorptions of phenol, 4-MeP, 2,4-DMeP, and 4-EtP on montmorillonite organically modified with HDTMA cation have been studied using single- and multisolute systems in aqueous solution at 25°C. By means of the ion-exchange reaction with the HDTMA cation, the surface property of montmorillonite has been changed from hydrophilic to organophilic, thus enhancing the sorption capacity for organic contaminants. The sorption affinity of organic

phenols onto HDTMA–montmorillonite was in the order 4-EtP ≈ 2,4-DMeP > 4-MeP > phenol, and was possibly caused by the difference in the van der Waals attractive force due to molecular weight, and by a steric hindrance due to the molecular structure. The Langmuir, DS, and RP models were well fitted to single-solute sorption data, while all the predictive multisolute models examined in this work, CLM, CDSM and IAST coupled with the single-solute models (i.e., Langmuir, DS, and RP models), also showed good predictions for the multisolute competitive sorption of phenol and alkylphenols onto HDTMA–montmorillonite. We found from this work that DSM, CDSM, and IAST coupled with the DSM were other possible models to describe the single- and multisolute sorption behaviors of phenolic compounds onto HDTMA–montmorillonite.

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REFERENCES

1. M. M. Mortland, S. Shaobai, and S. A. Boyd, *Clays Clay Miner.*, *34*, 581 (1986).
2. S. A. Boyd, S. Shaobai, J. F. Lee, and M. M. Mortland, *Ibid.*, *36*, 125 (1988).
3. S. A. Boyd, M. M. Mortland, and C. T. Chiou, *Soil Sci. Soc. Am. J.*, *52*, 652 (1988).
4. J. F. Lee, M. M. Mortland, S. A. Boyd, and C. T. Chiou, *J. Chem. Soc.*, *Faraday Trans. 1*, 85, 2953 (1989).
5. J. A. Smith, P. R. Jaffe, and C. T. Chiou, *Environ. Sci. Technol.*, *24*, 1167 (1990).
6. Y. S. Kim, D. I. Song, Y. W. Jeon, and S. J. Choi, *Sep. Sci. Technol.*, *31*, 2815 (1996).
7. J. H. Lee, D. I. Song, and Y. W. Jeon, *Ibid.*, *32*, 1975 (1997).
8. W. P. Ball and P. V. Roberts, *Environ. Sci. Technol.*, *25*, 1223 (1991).
9. W. J. Weber Jr., P. M. McGinley, and L. E. Katz, *Ibid.*, *26*, 1955 (1992).
10. P. M. McGinley, L. E. Katz, and W. J. Weber Jr., *Ibid.*, *27*, 1524 (1993).
11. F. C. Spurlock and J. W. Biggar, *Ibid.*, *28*, 996 (1994).
12. B. Xing, J. J. Pignatello, and B. Gigliotti, *Ibid.*, *30*, 2432 (1996).
13. B. Xing and J. J. Pignatello, *Ibid.*, *31*, 792 (1997).
14. W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, *20*, 1014 (1965).
15. T. M. Young and W. J. Weber Jr., *Environ. Sci. Technol.*, *29*, 92 (1995).
16. E. J. Leboeuf and W. J. Weber Jr., *Ibid.*, *31*, 1697 (1997).
17. W. Huang, T. M. Young, M. A. Schlautman, H. Yu, and W. J. Weber Jr., *Ibid.*, *31*, 1703 (1997).
18. J. K. Huh, D. I. Song, and Y. W. Jeon, *Sep. Sci. Technol.*, *34*, 571 (1999).
19. W. J. Koros, *J. Polym. Sci.*, *Polym. Phys. Ed.*, *18*, 981 (1980).
20. C. J. Radke and J. M. Prausnitz, *AIChE J.*, *18*, 761 (1972).
21. H. van Olphen, "Note on the Preparation of Clay Suspension," in *Clay Colloid Chemistry*, 2nd ed., Wiley, New York, NY, 1977.
22. J. D. Rhoades, "Cation Exchange Capacity," in *Methods of Soil Analysis*, *Part II*, *Chemical and Microbiological Properties*, 2nd ed. (A. L. Page, R. H. Miller, and R. Keeney, Eds.), American Society of Agronomy, Madison, WI, 1982.
23. O. Redlich and D. L. Peterson, *J. Phys. Chem.*, *63*, 1024 (1959).

24. J. A. V. Butler and C. J. Ockrent, *Phys. Chem.*, *34*, 2841 (1930).
25. C. Y. Yen and P. C. Singer, *J. Environ. Eng.*, *110*, 976 (1984).
26. C. Y. Yen, "The Adsorption of Phenol and Substituted Phenols on Activated Carbon in Single- and Multi-Component Systems," Thesis Presented to the University of the North Carolina, Chapel Hill, NC, in 1983, in partial fulfillment of the requirements for the degree of Doctor of Philosopy.
27. S. C. Kwon, D. I. Song, and Y. W. Jeon, *Sep. Sci. Technol.*, *33*, 1981 (1998).
28. D. G. Kleibaum and L. L. Kupper, *Applied Regression Analysis and Other Multivariable Methods*, Duxbury Press, North Scituate, MA, 1978.

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