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Adsorption of Organic Phenols onto Dual Organic Cation Montmorillonite from Water

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ABSTRACT

Single- and multicomponent competitive adsorptions were carried out in a batch reactor to investigate the removal of three toxic organic phenols, 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol, using organically modified montmorillonite. To study the removal capacity of phenolic contaminants dissolved in aqueous solution, two organic cations, tetramethylammonium (TMA) and hexadecyltrimethylammonium (HDTMA), were exchanged for the metal cations on the montmorillonite to the extent of about 40 and 45% of the cation-exchange capacity (CEC) of the montmorillonite, respectively, resulting in a surface property change from hydrophilic to organophilic. From the experimental results it was observed that adsorption affinity on TMA/HDTMA–montmorillonite is in the order 2-chlorophenol > 4-nitrophenol > 3-cyanophenol. The Langmuir and the Redlich–Peterson models were used to analyze the single component adsorption equilibria. On the other hand, the IAST and LCM models were used to predict the multicomponent competitive adsorption equilibria. These models yielded favorable representations of both individual and competitive adsorption behaviors.

INTRODUCTION

Various toxic chemicals have been discharged to the environment as industrial wastes, causing serious water and soil pollution. Removal of

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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 clay has drawn much attention; natural clays are organically modified by exchanging a quaternary amine cation having either short- or long-chain hydrocarbons for the metal cations on the clay through an ion-exchange reaction. Montmorillonite, the main component in bentonite (in general, up to 80% by weight), is the usual choice as a model support medium due to its large internal surface area and its high cation-exchange capacity (CEC), even though the use of pure montmorillonite as an adsorbent is highly limited in practical environmental applications because of the difficulties associated with separation and purification of montmorillonite from natural clays.

Many investigators have studied sorption of organic contaminants from water using organo-clays. 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 effected by the partitioning in the organic phase formed by the conglomeration of large C_{16} alkyl chains from HDTMA cation. Sorption enhancement of low organic matter soils was also achieved by ion exchange with HDTMA (4).

Lee et al. (5) 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. They also reported that the uptake of benzene from aqueous solution was larger on TMA–smectite than on HDTMA–smectite, despite the fact that TMA–smectite has a much lower organic carbon content (4%) than HDTMA–smectite (17%). Lee et al. found that TMA–smectite exhibited a high degree of selectivity based on the size and shape of an adsorbate in the presence of water, as evidenced by a progressive reduction in uptake with the increase in molecular size from benzene to larger aromatic compounds. This unique selectivity in an aqueous system was attributed to the molecular size/shape of adsorbates as well as of water molecules which may weakly hydrate TMA cations and solvate mineral sites of TMA-smectite, thereby resulting in insufficient interlamellar space to accommodate relatively larger molecules. Cadena (6) studied the adsorption of benzene, toluene, and *o*-xylene on TMA–bentonite in various pH conditions. According to his results, pH did not affect the adsorption of the nonionizing organics on TMA–bentonite, while benzene was selectively sorbed in the interlamellar space.

Smith et al. (7) 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 partition mechanism. However, uptake on organoclays with short-chain amine cations exhibits nonlinear isotherms and competitive sorption behaviors, characterizing adsorption mechanism.

Recently, Smith and Galan (8) modified Wyoming bentonite by exchanging two classes of quaternary amine cations, both the short-chain alkyl or aryl functional groups and long-chain alkyl groups (more than 10 carbons), for the metal cations on bentonite. Sorption isotherms for tetrachloromethane, trichloroethene, and benzene from aqueous solution to the dual organic cation bentonite were studied. Removal by an adsorption mechanism is appropriate for environmental applications involving a small number of contaminants at low concentrations compared with their solubility in water, while removal by a partition mechanism is suitable for application when multiple contaminants are present at higher concentrations. The objective of a dual organic cation bentonite is to share the advantages of both adsorption and partition mechanisms associated with short- and long-chain hydrocarbon cations, respectively.

Although these organoclays find growing usage in environmental applications such as contaminant fixation and fuel spill control (9), studies on the sorption mechanism of toxic organics and competitive adsorption behaviors have not been fully achieved. In this work, experimental isotherms and analyses that quantify the single- and multicomponent competitive adsorptions of three phenolic compounds, 2-chlorophenol (2-ChP), 3-cyanophenol (3-CyP), and 4-nitrophenol (4-NiP), from water to the dual cation TMA/HDTMA–montmorillonite will be presented.

EXPERIMENTAL

Preparation of TMA/HDTMA–Montmorillonite

Montmorillonite was purchased from Aldrich Chemical Co., and any impurities were removed by a digestion method using H_2O_2 (10). The digested montmorillonite particles, which ranged from 15 to 35 μm in diameter, were collected by settling during washing with distilled water.

The CEC of this montmorillonite was found to be 50.4 meq/100 g clay by the Rhoades method (11). The internal surface area of the washed montmorillonite was found to be 97 m^2/g clay by using Accusorb 2100E (Micromeritics Co., USA). X-ray fluorescence (XRF, PW 1404/10, Philips Co.) analysis was done at 40 kV and 30 mA to identify the exchangeable cation species. Most exchangeable cations were Ca^{2+}, K^+, and Na^+, and their contents in oxide form were 0.27, 2.07 and 0.94%, respectively. Two cations used as organic modifiers, hexadecyltrimethylammonium (HDTMA) chloride (25 wt%) solution in water and tetramethylammonium (TMA) bromide (98 wt%), were obtained from Aldrich Chemical Co. and used as received.

In order to prepare a dual organic cation montmorillonite (hereinafter referred to as TMA/HDTMA–montmorillonite), TMA cations were first exchanged for the metal cations of the montmorillonite, followed by the HDTMA cations. Adsorption of TMA onto montmorillonite was carried out in a 2-L batch reactor with 1 L TMA solution containing four times the CEC of montmorillonite. Thirty grams of washed montmorillonite were added to this reactor and agitated with a mechanical stirrer at 300 rpm for 24 hours. Then TMA–montmorillonite was allowed to settle by gravity for 1 hour. The collected TMA–montmorillonite was washed with 1 L distilled water under mechanical stirring three times until a negligible amount of TMA was found in the washed solution. Supernatant solutions from each washing step were analyzed for TMA concentration by using a total organic carbon analyzer, TOC-5000 (Shimadzu, Japan). After that, TMA–montmorillonite was collected and dried in an oven at 60°C for 24 hours. Subsequently, adsorption of HDTMA onto the TMA–montmorillonite was performed in a 2-L batch reactor with 1 L HDTMA solution, the concentration of which corresponded to the remaining CEC of the TMA–montmorillonite. Thirty grams of dried TMA–montmorillonite were added to the reactor and agitated mechanically at 300 rpm for 24 hours. After agitation, TMA/HDTMA–montmorillonite was collected by settling for 1 hour. The collected TMA/HDTMA–montmorillonite was washed twice, using 1 L of distilled water each time while stirring mechanically, until little HDTMA was found in the washed solution. All the supernatant solutions were analyzed for the desorbed HDTMA using a TOC analyzer. The TMA/HDTMA–montmorillonite thus prepared was preserved in a brown bottle until use.

Adsorption of Phenolic Compounds

Adsorption isotherms on TMA/HDTMA–montmorillonite were obtained for the aqueous solutions of three phenolic compounds in a batch

TABLE 1
Physicochemical Properties of Phenolic Compounds Used

Compound[a]	MW	Surface area[b] (Å^2)	UV maximum wavelength (nm)
2-ChP	128.56	267	274
3-CyP	119.12	275	292
4-NiP	139.11	299	318

[a] 2-ChP: 2-chlorophenol; 3-CyP: 3-cyanophenol; 4-NiP: 4-nitrophenol.
[b] Data from Yen (12).

apparatus at 25°C. The three phenolic compounds used as adsorbates were 2-chlorophenol (99+%), 3-cyanophenol (99%), and 4-nitrophenol (99+%) purchased from Aldrich Chemical Co. All reagents were of analytical grade and were used as received without further purification. Table 1 lists the physicochemical properties of the three phenolic compounds used in this work.

Solutions of each phenolic compound were prepared at concentrations of 50, 100, 200, 400, 500, 750, 1000, 1500, 2000, and 2500 mg/L. Each 20 mL solution was placed into a capped 50 mL flask containing 0.5 g of TMA/HDTMA–montmorillonite and then vigorously shaken on an orbit shaker for 24 hours at 25°C. After shaking, the solutions were centrifuged for 20 minutes at 2000 rpm. The equilibrium concentrations of each solution were determined at the wavelengths of UV maxima using a 8452A diode array UV-visible spectrophotometer (Hewlett-Packard, USA).

Bi- and trisolute systems were prepared by incorporating two and three phenolic compounds into a solution, respectively. Three bisolute systems of 2-chlorophenol/3-cyanophenol, 3-cyanophenol/4-nitrophenol, and 2-chlorophenol/4-nitrophenol, and one trisolute system of 2-chlorophenol/3-cyanophenol/4-nitrophenol were prepared. Multicomponent adsorption experiments were carried out by following the same procedures as described for single-component adsorption experiments. Equilibrium concentrations were also determined using a UV analysis which correlated absorbances at different wavelengths to the concentrations of the multiple phenolic compounds involved.

SINGLE- AND MULTICOMPONENT COMPETITIVE ADSORPTION MODELS USED

The adsorption isotherms frequently employed for single-component systems are the 2-parameter Langmuir and the 3-parameter Redlich–Peterson (RP) (13) models that obey the correct thermodynamic boundary condition of Henry's law over an infinitely dilute concentration range. The Langmuir and the RP models for liquid phase adsorption are written respectively as follows.

$$q_e = \frac{q_m b C_e}{1 + bC_e} = \frac{aC_e}{1 + bC_e} \tag{1}$$

$$q_e = \frac{\alpha C_e}{1 + \frac{\alpha}{\beta} C_e^{1-\gamma}} \tag{2}$$

In these equations, C_e is the equilibrium solute concentration in the solution phase and q_e is the equilibrium adsorbed concentration of solute per unit weight of adsorbent. q_m and b in the Langmuir model represent monolayer adsorption capacity and a constant related to the adsorption equilibrium constant, respectively, and α, β, and γ in the RP model are empirical constants.

To analyze multicomponent competitive adsorption behaviors, the Langmuir Competitive Model(LCM) (14–16) and Ideal Adsorbed Solution Theory(IAST) model (15–17) were used in this study. The LCM is an extended form of the Langmuir model and allows calculation of $q_{e,i}$, the amount of solute i adsorbed per unit weight of adsorbent in the presence of other solutes.

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{j=1}^{n} b_j C_{e,j}} \tag{3}$$

Here, $C_{e,i}$ is an equilibrium concentration of solute i in a mixture, while $C_{e,i}$ are the equilibrium concentrations of all the adsorbing solutes in the mixture. The constants b_i, b_j, ..., and $q_{m,i}$, $q_{m,j}$, ..., are those parameters determined by fitting the Langmuir model, i.e., Eq. (1), to the single component adsorption data of solute i, j, ..., alone, respectively.

The IAST model, selected as another competitive adsorption model, is based on the equivalence of spreading pressure in a mixture under equilibrium. The spreading pressure can be evaluated using the Gibbs isotherm as follows:

$$\pi(q^*_{e,i}) = \frac{RT}{A} \int_0^{q^*_{e,i}} \frac{d \log C_{e,i}}{d \log q_{e,i}} \, dq_{e,i} \tag{4}$$

The equivalence of spreading pressure in a mixture is

$$\pi_1 = \pi_2 = \pi_3 = \cdots = \pi_n \tag{5}$$

Other equations for the IAST calculation are:

$$C_{\mathrm{m},i} = z_i \cdot C^*_{\mathrm{e},i}, \qquad \sum_{i=1}^{n} z_i = 1, \qquad q_{\mathrm{e},i} = f(C_{\mathrm{e},i}) \tag{6a}$$

$$\frac{1}{q_{\mathrm{e,t}}} = \sum_{i=1}^{n} \frac{z_i}{q^*_{\mathrm{e},i}}, \qquad q_{\mathrm{m},i} = z_i \cdot q_{\mathrm{e,t}}, \qquad q_{\mathrm{m},i} = \frac{C^0_{\mathrm{m},i} - C_{\mathrm{m},i}}{M} \tag{6b}$$

Here, $C_{\mathrm{m},i}$ and $q_{\mathrm{m},i}$ denote equilibrium concentrations in the liquid and adsorbed phases of a solute i in a mixture, respectively. z_i is a mole fraction of a solute i in the adsorbed phase, and $C^*_{\mathrm{e},i}$ and $q^*_{\mathrm{e},i}$ refer to equilibrium concentrations in the liquid and solid phases of a solute i in a single component system at the same temperature and spreading pressure as that of the mixture, respectively. The function f in $q_{\mathrm{e},i} = f(C_{\mathrm{e},i})$ denotes the solute adsorption model for the solute i alone. $q_{\mathrm{e},t}$ is the total adsorbed concentration of all solutes in the mixture. $C^0_{\mathrm{m},i}$ is the initial concentration of solute i, and M is an adsorbent weight per volume of the solution. There are $5n + 1$ equations in total, while $C_{\mathrm{m},i}$, $q_{\mathrm{m},i}$, $C^*_{\mathrm{e},i}$, $q^*_{\mathrm{e},i}$, z_i and $q_{\mathrm{e,t}}$ comprise a set of $5n + 1$ unknowns. Therefore, we can predict multicomponent adsorption equilibria by simultaneously solving these equations.

RESULTS AND DISCUSSION

Preparation of TMA/HDTMA–Montmorillonite

The impurities in montmorillonite, which showed relatively high UV absorbance, were removed nearly completely through the pretreatment process of digestion and washing. Although a very minute amount of impurities still remained, it was considered not to affect the subsequent adsorption of phenolic compounds. Through time studies of TMA and HDTMA uptake onto the washed montmorillonite, it has been revealed that TMA adsorption reaches equilibrium in about an hour while HDTMA takes about 10 hours, possibly due to the much larger size of HDTMA compared to TMA. This reasoning is in line with the report that the interlamellar distance of montmorillonite plates expands to about 8 Å to accommodate bulky HDTMA cation and becomes about 4 Å for the compact TMA adsorption (18).

The single cation adsorption isotherms of TMA and HDTMA on montmorillonite are shown together in Fig. 1 for comparison. Maximum amounts of uptake for TMA and HDTMA are found to be about 32 and 152 mg/g clay, respectively. These are tantamount to approximately 40 and 95% of the CEC of the montmorillonite used in this study. The observation is in good agreement with the result of Stapleton et al. (19) that

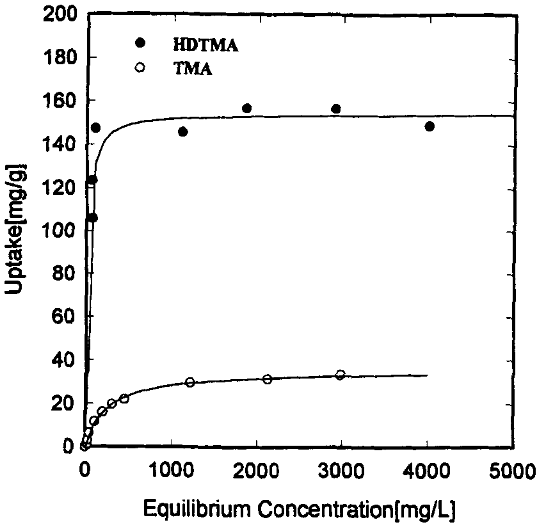

FIG. 1 Adsorption isotherms of TMA and HDTMA on montmorillonite.

HDTMA was adsorbed to over 98% of the CEC of montmorillonite. q_m and b values of the Langmuir model for the single cation adsorption equilibrium were 35.8 mg/g, 3.96×10^{-3} L/mg and 154.3 mg/g, 5.57×10^{-2} L/mg for the TMA and HDTMA cations, respectively. In view of the b values, it was revealed that adsorption affinity of HDTMA is much higher than that of TMA.

Table 2 shows variations of the solution concentration of both unadsorbed TMA during adsorption and desorbed TMA during washing under mechanical stirring. The final uptake amount of TMA was calculated from the mass balance, being equivalent to about 40% CEC on average. In the second stage, HDTMA cation was sequentially adsorbed to the TMA–montmorillonite prepared in the previous step. The initial concentration of the HDTMA solution was adjusted to make it equal to about the remaining 60% CEC of the TMA–montmorillonite. Solution concentrations of both unadsorbed HDTMA during adsorption and desorbed HDTMA during the washing step are listed in Table 3. The average uptake of HDTMA onto the TMA–montmorillonite was computed to be about 45% of the CEC from the mass balance. In this way a dual organic cation adsorbent, 40% TMA/45% HDTMA—montmorillonite, was prepared and used in the subsequent adsorption experiments of the three phenolic compounds.

TABLE 2

Variations of TMA Concentration in Supernatant and Washed Solutions

Repeated run	1	2	3
Initial solution, 1 L	9292 ppm	9290 ppm	9178 ppm
Supernatant solution, 1 L	8026 ppm	7965 ppm	7777 ppm
Solution after first washing, 1 L	344 ppm	332 ppm	333 ppm
Solution after second washing, 1 L	28 ppm	0 ppm	11 ppm
Solution after third washing, 1 L	0 ppm	0 ppm	0 ppm
Total TMA freed, mg	8398	8297	8121
TMA uptake on 30 g montmorillonite, mg	894	993	1057
Specific uptake, mg/g	29.8	33.1	35.2
% CEC	38.4	42.6	45.3

Adsorption of Phenols

Single Component Adsorption

The single solute adsorption of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol was performed using TMA/HDTMA–montmorillonite. Prior to an experiment for adsorption equilibrium, the time study of adsorption of each phenolic compound was carried out to determine an equilibration time. It was observed that equilibrium was reached in 2 hours on an orbit shaker set at 250 rpm. However, the sample batches were agitated for 24 hours to ensure equilibrium.

Figure 2 shows single solute adsorption isotherms on 40% TMA– and 95% HDTMA–montmorillonite for each phenolic compound. The adsorption isotherm of 3-cyanophenol on 40% TMA–montmorillonite suggests that 3-cyanophenol was not significantly intercalated by the TMA–mon-

TABLE 3

Variations of HDTMA Concentration in Supernatant and Washed Solutions

Repeated run	1	2	3
Initial solution, 1 L	2608 ppm	2613 ppm	2664 ppm
Supernatant solution, 1 L	392 ppm	419 ppm	615 ppm
Solution after first washing, 1 L	44 ppm	0 ppm	0 ppm
Solution after second washing, 1 L	0 ppm	0 ppm	0 ppm
Total HDTMA freed, mg	436	419	615
HDTMA uptake on 30 g TMA–montmorillonite, mg	2172	2194	2049
Specific uptake, mg/g	72.4	73	72
% CEC	45	45	44

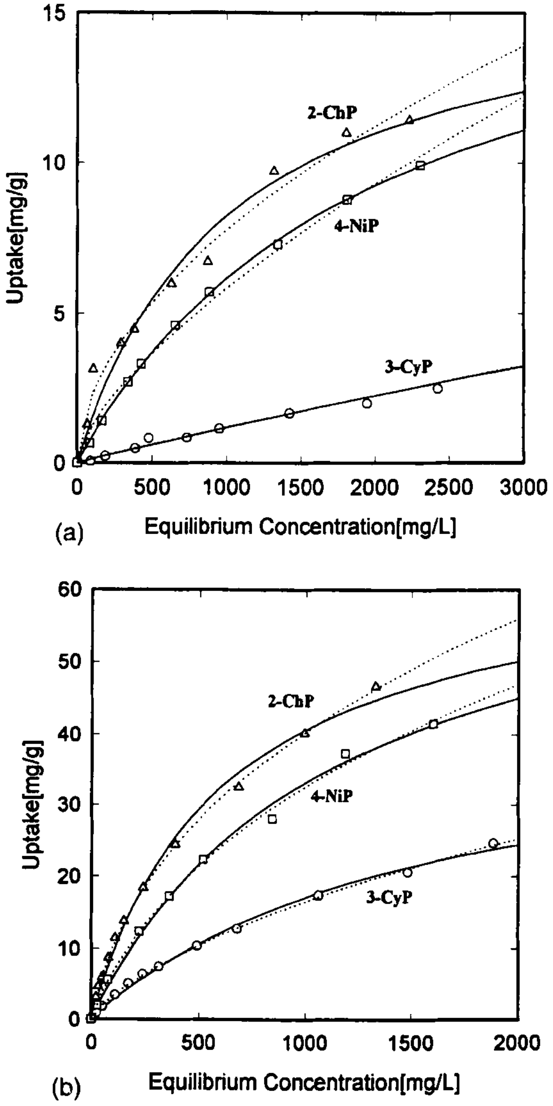

FIG. 2 Single solute adsorption isotherms of phenolic compounds on (a) 40% TMA-montmorillonite, and (b) 95% HDTMA-montmorillonite. Solid and dotted lines represent Langmuir and Redlich–Peterson isotherms, respectively.

tmorillonite. It can be seen from Fig. 2 that the order of the adsorption affinity of the three phenolic compounds, i.e., 2-chlorophenol > 4-nitrophenol > 3-cyanophenol, is the same regardless of the type of organic cations exchanged, though the maximum amount of uptake has changed appreciably.

Adsorption isotherms on 40% TMA/45% HDTMA–montmorillonite are shown in Fig. 3. In terms of the adsorption affinity for the TMA/HDTMA–montmorillonite, 2-chlorophenol has the largest affinity followed by 4-nitrophenol and 3-cyanophenol. The 2-parameter Langmuir and the 3-parameter RP models were fitted to the experimental adsorption data for each phenolic compound using the nonlinear regression method. Fitted curves of the Langmuir and the RP models are shown in Fig. 3 for comparison, and the parameters of both adsorption models are tabulated in Tables 4 and 5, respectively. As a measure of the degree of fitness, correlation coefficients were computed following Yen (12, 15). In view of the values of correlation coefficient in the tables, the 3-parameter RP model exhibited a little better fit to the adsorption data than the 2-parameter Langmuir model as expected from the number of parameters involved in the model. However, both models seemed to agree well with the experimental data considering that both correlation coefficients are greater than

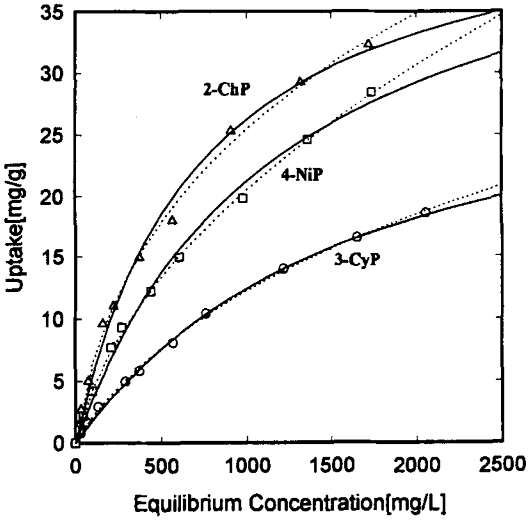

FIG. 3 Single solute adsorption isotherms of phenolic compounds on 40% TMA/45% HDTMA–montmorillonite. Solid and dotted lines represent Langmuir and Redlich–Peterson isotherms, respectively.

TABLE 4
Langmuir Parameters of Each Phenolic Compound on 40% TMA/45% HDTMA–Montmorillonite

Compound	q_m (mg/g)	*b* (L/mg)	*a* (L/g)	Correlation coefficient
2-ChP	45.1	0.00138	0.0624	0.9989
3-CyP	34.4	0.00057	0.0194	0.9997
4-NiP	46.8	0.00082	0.0386	0.9991

0.99. The values of the parameters *a* and *b* appearing in the Langmuir model reconfirm the order of adsorption affinity of the phenolic compound used, i.e., 2-chlorophenol > 4-nitrophenol > 3-cyanophenol.

The difference in affinity of the phenols on the TMA/HDTMA–montmorillonite can be explained by the physical adsorptive interaction between organic solutes and organically modified montmorillonite. The major attractive force comes from the van der Waals interaction between tail groups of two organic cations and a solute, originating from the difference in molecular weights of the phenolic compounds. In addition, steric hindrance due to the shape and size of the phenol molecules was believed to cause the different adsorption affinities. Yen (12) investigated the effect of steric hindrance in the adsorption of chlorophenol isomers such as 2-chlorophenol, 3-chlorophenol, and 4-chlorophenol on activated carbon. Among the three chlorophenol isomers, 2-chlorophenol has the smallest molecular surface area and is of advantage to diffuse into the micropores of activated carbon. According to Yen, the adsorption capacity on activated carbon decreased in the order 4-nitrophenol > 2-chlorophenol > 3-cyanophenol, which is actually the decreasing order of the molecular weight.

TABLE 5
Redlich–Peterson Parameters of Each Phenolic Compound on 40% TMA/45% HDTMA–Montmorillonite

Compound	α	β	γ	Correlation coefficient
2-ChP	0.1070	3.682	0.319	0.9995
3-CyP	0.0257	2.597	0.316	0.9998
4-NiP	0.0823	1.082	0.467	0.9999

In this study, however, the adsorption capacity on the dual organic cation, TMA/HDTMA-montmorillonite, decreased in the order 2-chlorophenol > 4-nitrophenol > 3-cyanophenol, which might be caused by the compromise between the van der Waals force and the steric hindrance effect.

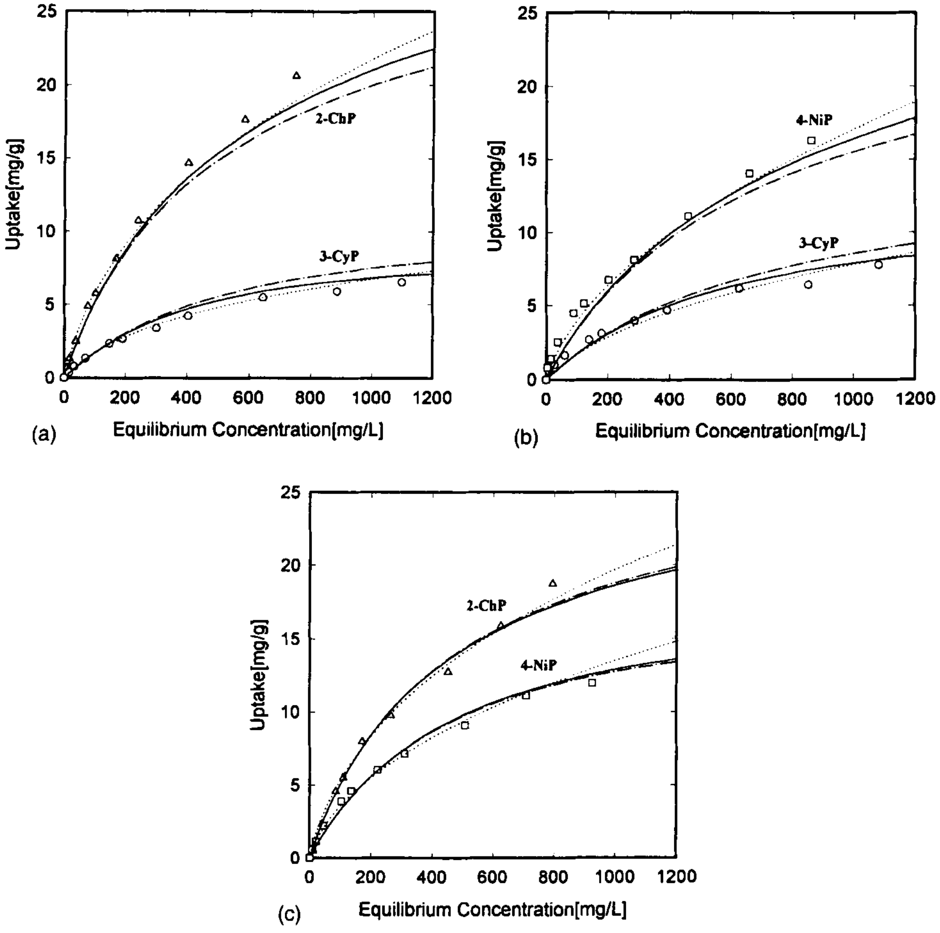

FIG. 4 Bisolute adsorption isotherms of (a) 2-chlorophenol/3-cyanophenol, (b) 3-cyanophenol/4-nitrophenol, and (c) 2-chlorophenol/4-nitrophenol on 40% TMA/45% HDTMA-montmorillonite. Solid and dotted lines denote IAST predictions based on Langmuir and Redlich–Peterson models, respectively, and dot-dashed lines, LCM predictions.

Multicomponent Adsorption

Binary competitive adsorptions were performed using the three binary systems of 2-chlorophenol/3-cyanophenol, 3-cyanophenol/4-nitrophenol, and 2-chlorophenol/4-nitrophenol. Both the competitive adsorption data and the predictions of the IAST and LCM models for each binary system are shown in Fig. 4. Single component adsorption models used in the multicomponent predictive IAST model were Langmuir and RP models, the parameters of which were determined from the nonlinear curve fitting to the single component adsorption data as listed in Tables 4 and 5. The correlation coefficients of both models for binary and ternary systems are given in Table 6. In view of these high correlation coefficients, both the IAST and LCM models provided favorable predictions for the binary competitive adsorption of the phenols on TMA/HDTMA–montmorillonite.

One of the main features of adsorption is that adsorption capacity of a single component is reduced when multiple solutes are present, due to the finite adsorption sites available. Figure 5 shows the adsorption isotherms of each phenolic compound for the single- and multi-component competitive adsorptions. Adsorption capacities of each phenolic compound decrease when other solutes are present due to the competitive adsorption for the available sites. In order to quantify the extent of reduction in adsorption capacity, the Langmuir model was applied to the adsorption data of each phenolic compound in binary and ternary systems. The Langmuir parameters of each phenolic compound in multisolute systems are shown in Table 7, along with the percentage reduction of the Langmuir monolayer capacity due to competition in binary and ternary systems. Either 3-cyanophenol or 4-nitrophenol forming a binary system with 2-chlorophenol, which has the strongest adsorption affinity, underwent about 73 and 65% reductions in q_m, respectively, compared with q_m's in single component adsorption. However, 2-chlorophenol reduced only 24 and 34% in q_m in competition with 3-cyanophenol and 4-nitrophenol, respectively. 3-Cyanophenol, which shows the weakest adsorption affinity,

TABLE 6
Correlation Coefficients of Each Phenolic Compound in Binary and Ternary Systems

System	IAST (Langmuir)	IAST (RP)	LCM
2-ChP/3-CyP	0.9968/0.9946	0.9977/0.9981	0.9941/0.9835
3-CyP/4-NiP	0.9942/0.9948	0.9952/0.9981	0.9869/0.9921
4-NiP/2-ChP	0.9978/0.9983	0.9986/0.9987	0.9981/0.9984
2-ChP/3-CyP/4-NiP	0.9962/0.9943/0.9978	0.9977/0.9948/0.9991	0.9959/0.9774/0.9973

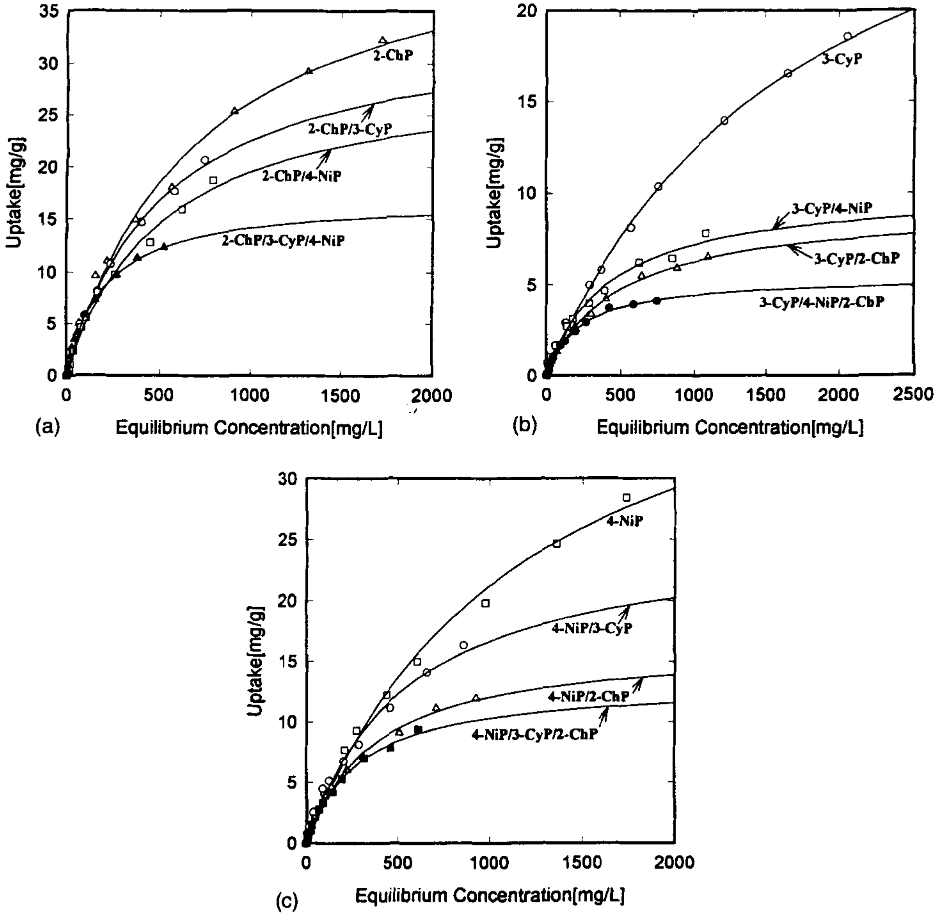

FIG. 5 Adsorption isotherms of (a) 2-chlorophenol, (b) 3-cyanophenol, and (c) 4-nitrophenol on 40% TMA/45% HDTMA–montmorillonite. Solid lines represent Langmuir isotherms fitted to the data.

exhibited about 73% reduction of q_m in the 2-chlorophenol/3-cyanophenol system, while it reduced about 71% when paired with 4-nitrophenol, having the medium ranked adsorption affinity among the three compounds studied.

On the contrary, the values of b, the parameter related to adsorption strength in the Langmuir model, were greater than those for single component adsorptions. We may speculate that competition between adsorbates

TABLE 7
Langmuir Parameters and Percent Reductions in Monolayer Capacity of Each Phenolic Compound in Multicomponent Systems Due to Competition

	System	q_m	b	Reduction in q_m (%)	Correlation coefficient	Remarks
2-ChP	Single	45.1	0.00138	—	0.9989	Fig. 5(a)
	2-ChP/3-CyP	34.4	0.00189	23.7	0.9997	
	2-ChP/4-NiP	29.7	0.00192	34.2	0.9987	
	Ternary	17.0	0.00498	62.4	0.9997	
3-CyP	Single	34.4	0.00057	—	0.9997	Fig. 5(b)
	3-CyP/2-ChP	9.21	0.00213	73.2	0.9995	
	3-CyP/4-NiP	10.1	0.00243	70.5	0.9978	
	Ternary	5.44	0.00438	84.2	0.9996	
4-NiP	Single	46.8	0.00082	—	0.9991	Fig. 5(c)
	4-NiP/2-ChP	16.4	0.00272	64.9	0.9992	
	4-NiP/3-CyP	25.8	0.00183	45.0	0.9974	
	Ternary	13.1	0.00362	72.0	0.9991	

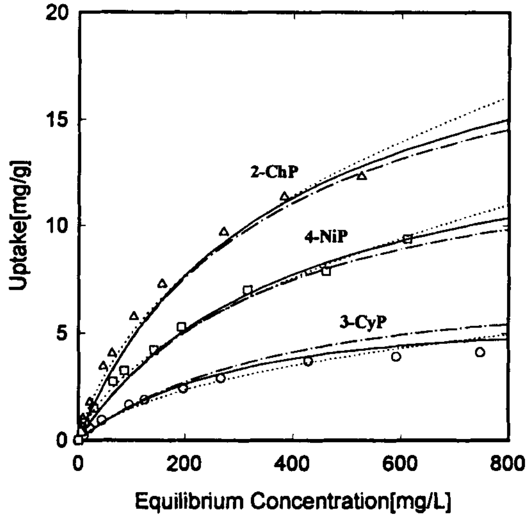

FIG. 6 Trisolute adsorption of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol on 40% TMA/45% HDTMA-montmorillonite. Solid and dotted lines denote IAST predictions based on Langmuir and Redlich–Peterson models, respectively, and dot-dashed lines, LCM predictions.

drives out the weakly adsorbed fractions from the adsorbed phase, thereby forming a stronger adsorbed phase on TMA/HDTMA–montmorillonite. It is observed that the species which showed stronger affinity for the TMA/HDTMA–montmorillonite in single component adsorption have occupied larger adsorption sites than other components in competitive adsorptions.

The competitive adsorption of the trisolute mixture of 2-chlorophenol/3-cyanophenol/4-nitrophenol on TMA/HDTMA–montmorillonite was carried out in the same batch adsorption apparatus at 25°C. The competitive adsorption behaviors for the three solutes are shown in Fig. 6. As can be seen in Table 7, the adsorption capacities of 2-chlorophenol, 4-nitrophenol, and 3-cyanophenol underwent 62, 72, and 84% reduction of q_m values in comparison to single component adsorption, respectively. It is also observed that the species which showed stronger affinity for the TMA/HDTMA–montmorillonite in single component adsorption occupied larger adsorption sites in multisolute competitive adsorption. The correlation coefficient of this trisolute system with the IAST and LCM models was found to be over 0.98 as listed in Table 6. After all, the IAST and the LCM models were still good predictive models for this ternary competitive adsorption system.

CONCLUSIONS

The adsorptions of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol on montmorillonite organically modified with both TMA and HDTMA cations have been studied using single and multicomponent systems in aqueous solution at 25°C. By means of the ion-exchange reaction with the TMA and HDTMA cations, the surface property of montmorillonite has been changed from hydrophilic to organophilic, thus enhancing the sorption capacity for organic contaminants. Adsorption affinities of organic phenols for the TMA/HDTMA–montmorillonite were possibly influenced by the two physical adsorption factors: attraction by the van der Waals force due to a molecular weight effect and exclusion by a steric hindrance effect due to a molecular structure. Both the Langmuir and the RP models were well fitted to single-component adsorption data, while the IAST and the LCM models also showed good prediction in the competitive adsorption of phenols on TMA/HDTMA–montmorillonite. From the experimental results for both single and competitive adsorption behaviors, it was observed that the adsorption affinity of phenols to TMA/HDTMA–montmorillonite was sequenced in the order 2-chlorophenol > 4-nitrophenol > 3-cyanophenol. In the effect of an amine type on the adsorption behavior, it appears that HDTMA plays a much larger part in enhancing the sorption capacity for the phenols than TMA. In addition, the experimental results reveal that the adsorption levels of the phenols are approximately proportional to the total amount of organic carbon loaded on the montmorillonite.

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