Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Young S. Kim[a]; Dong I. Song[a]; Young W. Jeon[b]; Sang J. Choi[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, KYUNGPOOK NATIONAL UNIVERSITY, TAEGU, KOREA [b] DEPARTMENT OF ENVIRONMENTAL ENGINEERING, KYUNGPOOK NATIONAL UNIVERSITY, TAEGU, KOREA

To cite this Article Kim, Young S. , Song, Dong I. , Jeon, Young W. and Choi, Sang J.(1996) 'Adsorption of Organic Phenols onto Hexadecyltrimethylammonium-Treated Montmorillonite', Separation Science and Technology, 31: 20, 2815 — 2830
To link to this Article: DOI: 10.1080/01496399608000829
URL: http://dx.doi.org/10.1080/01496399608000829

SEPARATION SCIENCE AND TECHNOLOGY, **31**(20), pp. 2815–2830, 1996

Adsorption of Organic Phenols onto Hexadecyltrimethylammonium-Treated Montmorillonite

YOUNG S. KIM and DONG I. SONG
DEPARTMENT OF CHEMICAL ENGINEERING

YOUNG W. JEON* and SANG J. CHOI
DEPARTMENT OF ENVIRONMENTAL ENGINEERING

KYUNGPOOK NATIONAL UNIVERSITY
TAEGU, 702-701, KOREA

ABSTRACT

Montmorillonite used as an adsorbent was organically modified by using a cationic surfactant, hexadecyltrimethylammonium (HDTMA), to enhance the removal capacity of organic phenol contaminants dissolved in an aqueous solution. This modification produces a change of the surface property of montmorillonite from hydrophilic to organophilic. The single- and multicomponent competitive adsorptions were performed in a batch reactor to investigate the removal of three toxic organic phenols, 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol, on the modified HDTMA–montmorillonite. It was observed from the experimental results that the adsorption affinity for HDTMA–montmorillonite was 2-chlorophenol, 4-nitrophenol, 3-cyanophenol in decreasing order. Langmuir and the Redlich–Peterson models were used to analyze the single-component adsorption results, while the IAST and the LCM models predicted the multicomponent adsorption equilibria. These models yielded favorable representations of both individual and competitive adsorption behaviors.

INTRODUCTION

Various chemical materials and energy sources have been discharged unreasonably to the environment as industrial wastes. This unsuitable dischargement plays a large part in water and soil pollution. Rapidly in-

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* To whom correspondence should be addressed.

creasing industrial wastewater and growth in the usage of organic detergents and agricultural chemicals are especially accelerating water pollution. Therefore, the removal of organic contaminants from wastewater has been extensively researched by using various physicochemical and biological techniques. Among these researches, the removal of organic contaminants by means of adsorption using organically modified clays has drawn much attention (1–3). This modification of natural clay is achieved by fixing a quaternary amine cation such as hexadecyltrimethylammonium (HDTMA) on the inorganic clay surface through an ion-exchange reaction. The quaternary amine cation used in this modification is a cationic surfactant which has carbon chains comprised of over 10 carbon atoms. Smectitic clays like montmorillonite and bentonite, which have a large specific surface area and a cation-exchange capacity (CEC), are the usual choices as a support medium. The major interactions between the surfactant and the support are adsorption, intercalation, and ion exchange.

Brownawell et al. (4) performed the adsorption of dodecylpyridinium, an amphilic organic cation, on the montmorillonite surface. They found that dodecylpyridinium was strongly adsorbed on montmorillonite, and that the amount of adsorption was governed by the CEC of montmorillonite. They also observed that pH had little effect on the adsorption reaction. Zhang and his colleagues (5) studied on a laboratory scale and confirmed that an amine cation is adsorbed by ion exchange in the CEC range and that this adsorption is irreversible in the presence of other ions. Therefore, it appears feasible to use organomontmorillonite as an adsorbent for removing organic contaminants from an aqueous solution.

Many investigators have studied the adsorption of organic contaminants by using organoclays (6–10). Liquid- and gas-phase adsorptions of aromatic compounds such as benzene, toluene, *p*-xylene, ethylbenzene, *o*-xylene, *o*-dichlorobenzene, 1,2,3-trichlorobenzene, and lindane by smectite exchanged with tetramethyl-ammonium (TMA) were studied by Lee et al. (6, 7). They observed that the adsorption capacity of aromatic compounds on TMA–smectite was considerably enhanced, and the adsorption affinity of relatively large molecules such as *o*-xylene and 1,2,3-trichlorobenzene was less than other solutes due to the molecular sieve effect caused by water molecules. Lee also studied the adsorption of benzene, toluene, and ethylbenzene on A-horizon and B_t-horizon soils treated with nonyltrimethylammonium (C_9), dodecyltrimethylammonium (C_{12}), and hexadecyltrimethylammonium (C_{16}) which have different alkyl chain lengths. In this study he emphasized that organic cations act as partition media, and hence adsorbents with more organic carbon content should have a larger partition coefficient. Cadena (8) experimented with the adsorption of benzene, toluene, and *o*-xylene on TMA–bentonite in variable pH conditions. According to his results, pH did not affect the adsorption of the organics on TMA–bentonite while benzene was sorbed selectively in the interlamellar space.

Smith et al. (9, 10) studied the adsorption of tetrachloromethane on clay that was modified by 10 quaternary amine cations. They found that the adsorption isotherms of trichloromethane on organoclays modified with long-carbon-chain amine cations such as dodecyltrimethylammonium (C_{12}), tetradecyltrimethylammonium (C_{14}), and hexadecyltrimethylammonium (C_{16}) showed linear isotherms and noncompetitive adsorption behaviors. So, sorption of a solute to a long-carbon-chain cation is characterized by a partition mechanism. However, the adsorption isotherms of trichloromethane on organoclays modified with short-carbon-chain amine cations such as tetramethylammonium (C_1), tetraethylammonium (C_2), benzyltrimethylammonium (C_1), and benzyltriethylammonium (C_2) show nonlinear isotherms and competitive adsorption behaviors. They reconfirmed these phenomena through the adsorption of a solute on organoclay modified with dual long- and short-chain cations. Therefore, they suggested the use of this dual organoclay for the removal of organic contaminants from water of either low or high solute concentration. Typical applications of organoclays in environmental fields are a filter system for separating organic contaminants from wastewater, solidification of organic wastes and contaminated soil, fuel spill control, and a liner system for fuel storage tanks (3).

Although these organoclays find growing usage in environmental applications, studies of the sorption mechanism of toxic organics and competitive adsorption behaviors have not been fully achieved. This paper presents the experimental results and analyses of single- and multicomponent adsorption equilibria of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol on HDTMA-treated montmorillonite.

EXPERIMENTAL

Preparation of HDTMA–Montmorillonite

Montmorillonite–KSF was obtained from Aldrich Chemical Company, and impurities were removed by a digestion method using H_2O_2, introduced by Olphen (11). The digested montmorillonite particles, ranging from 15 to 35 μm, were collected by settling during washing with distilled water. An average particle size was about 15 μm. The CEC of this montmorillonite was 50.4 meq/100 g-clay, measured by a Rhoades method (12). Accusorb 2100E (Micromeritics Co., USA) was used to determine the BET surface area of the washed montmorillonite to be 97 m^2/g-clay. X-ray fluorescence (XRF, PW 1404/10, Philips Company) analysis was carried out at 40 kV and 30 mA to specify the exchangeable cation species. The most exchangeable cations were Ca, K, and Na, and their contents in oxide form were 0.27, 2.07, and 0.94%, respectively. Hexadecyltrimethylammonium chloride (Aldrich Chemical Company, Inc., 25 wt%), a cationic surfactant, was used as an organic modifier, and its critical micelle concentration (CMC) was 1.4 mmol or 448 mg/L (13).

The adsorption of HDTMA onto montmorillonite was performed in a 2-L batch reactor with 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 before use. A colorimetric method developed by Few and Ottewill (14) was used to quantify the equilibrium concentration of HDTMA.

Adsorption of Phenolic Compounds

Adsorption isotherms were determined for aqueous solutions of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol with HDTMA–montmorillonite in a batch apparatus at 25°C. The phenolic compounds used as adsorbates were of analytical reagent grade (99+%) and purchased from Aldrich Chemical Company. Table 1 shows the physicochemical properties of the phenolic compounds. All reagents were used as received. Solutions of each phenolic compound were prepared at concentrations of 100, 200, 300, 500, 750, 1000, 1500, 2000, 2500, and 3000 mg/L. The pHs of these solutions ranged from 4.6 to 6.8. It was revealed in a previous study that the adsorption capacity of phenols on activated carbon is reduced drastically when the pH value is larger than the pK_a values of phenols in an aqueous solution (15). In this study the pK_a values of the phenols used

TABLE 1
Physicochemical Properties of the Phenolic Compounds Used

Compound[a]	Molecular weight	pK_a	Surface area[b] (Å^2)	UV maximum wave length (nm)
2-ChP	128.56	8.45	267	274
3-CyP	119.12	8.51	275	292
4-NiP	139.11	7.08	299	318

[a] 2-ChP: 2-chlorophenol. 3-CyP: 3-cyanophenol. 4-NiP: 4-nitrophenol.
[b] Data from Yen (22).

were always greater than the pH values, so the dissociation of phenolic compounds might not be significant. Each 20 mL solution was placed into a capped 50 mL flask containing 0.5 g 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 concentration of each solution was determined at the wavelengths of UV maxima using a 8452A diode array UV-visible spectrophotometer (Hewlett-Packard).

Bi- and tri-solute systems were prepared by incorporating two and three phenolic compounds into a solution, respectively. Three bi-solute systems of 2-chlorophenol/3-cyanophenol, 3-cyanophenol/4-nitrophenol, and 2-chlorophenol/4-nitrophenol and one tri-solute 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. The equilibrium concentrations of multicomponent solutions were also determined using an UV analysis which correlated the absorbances at different wavelengths to the concentrations of the phenolic compounds involved.

SINGLE AND MULTICOMPONENT ADSORPTION MODELS USED

The adsorption isotherms frequently employed for single-solute systems are the 2-parameter Langmuir (16) and the 3-parameter Redlich–Peterson (17) models that obey the correct thermodynamic boundary conditions of Henry's law in the range of infinitely dilute concentrations.

The Langmuir and the Redlich–Peterson models for liquid-phase adsorption are written

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad \text{(Langmuir model)} \qquad (1)$$

$$q_e = \frac{\alpha C_e}{1 + \left(\frac{\alpha}{\beta}\right) C_e^{(1-\gamma)}} \qquad \text{(Redlich–Peterson model)} \qquad (2)$$

In these equations, C_e is the equilibrium concentration and q_e is the adsorbed solute concentration on the adsorbent surface per unit weight of adsorbent. In the Langmuir model, q_m and b represent monolayer adsorption capacity and a constant related to an equilibrium constant, respectively, while α, β, and γ are empirical constants for the Redlich–Peterson model.

The ideal adsorbed solution theory (IAST) model (18–20) and Langmuir competitive model (LCM) (18, 20) were used to analyze multicomponent competitive adsorption behaviors in this study. The IAST model is based on the equivalence of spreading pressure in a mixture under equilibrium. The spreading pressure can be evaluated by using the Gibbs' isotherm as in

$$\pi(q_{e,i}) = \frac{RT}{A}\int_0^{q^*_{e,i}} \frac{d\log C_{e,i}}{d\log q_{e,i}}\,dq_{e,i} \tag{3}$$

The equivalence of spreading pressure in a mixture is

$$\pi_1 = \pi_2 = \pi_3 = \cdots = \pi_n \tag{4}$$

Other equations for the IAST calculation are

$$C_{m,i} = z_i C^*_{e,i} \tag{5}$$

$$\sum_{i=1}^{n} z_i = 1 \tag{6}$$

$$q_{e,i} = f(C_{e,i}) \tag{7}$$

$$\frac{1}{q_{e,t}} = \sum_{i=1}^{n} \frac{z_i}{q^*_{e,i}} \tag{8}$$

$$q_{m,i} = z_i q_{e,t} \tag{9}$$

$$q_{m,i} = \frac{C^0_{m,i} - C_{m,i}}{M} \tag{10}$$

Here $C_{m,i}$ and $q_{m,i}$ denote equilibrium concentrations in the liquid phase and in the adsorbed phase of a solute i in a mixture, respectively. z_i is a mole fraction of a solute i, while $C^*_{e,i}$ is the liquid-phase concentration corresponding to $q^*_{e,i}$ in single-solute systems. $q_{e,t}$ is the total amount adsorbed from the mixture. $C^0_{m,i}$ is the initial concentration of solute i, and M is an adsorbent amount per unit volume. Equation (7) is used to represent the functional relationship between $q_{e,i}$ and $C_{e,i}$ in the single-solute systems (e.g., Langmuir or Redlich–Peterson model). There are $5n + 1$ equations in total, while $C_{m,i}$, $q_{m,i}$, $C^*_{e,i}$, $q^*_{e,i}$, z_i, and $q_{e,t}$ comprise a set of $5n + 1$ unknowns. Therefore, we can predict multicomponent adsorption equilibria by solving these simultaneous equations.

The LCM is an extended form of the Langmuir model and was used as another competitive adsorption model. This adsorption model permits calculation of $q_{e,i}$, the amount of solute i adsorbed per unit weight of adsorbent in the presence of other solutes.

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{j=1}^{n} b_j C_{e,j}} \tag{11}$$

Here, $C_{e,i}$ is an equilibrium concentration of solute i in a mixture, while $C_{e,j}$ are the equilibrium concentrations of all the adsorbing solutes in the mixture. The constants b_i, b_j, $\cdots$ and $q_{m,i}$, $q_{m,j}$, $\cdots$ are those determined from single-solute systems, as given in Eq. (1).

RESULTS AND DISCUSSION

Preparation of HDTMA–Montmorillonite

The impurities in montmorillonite, which showed high UV absorbances, were removed nearly completely through the pretreatment process of digestion and washing. Although a very minute amount of impurities still remained, it was not believed to influence the subsequent adsorption of phenolic compounds. Figure 1 shows the adsorption of HDTMA onto the washed montmorillonite with time. Equilibrium was reached in 24 hours. The adsorption isotherm of HDTMA on the montmorillonite is presented in Fig. 2. An adsorption amount was about 152 mg-HDTMA/g-clay, and this amount is equivalent to 94% of the CEC of montmorillonite used in this study. The observation is in good agreement with Stapleton's (21)

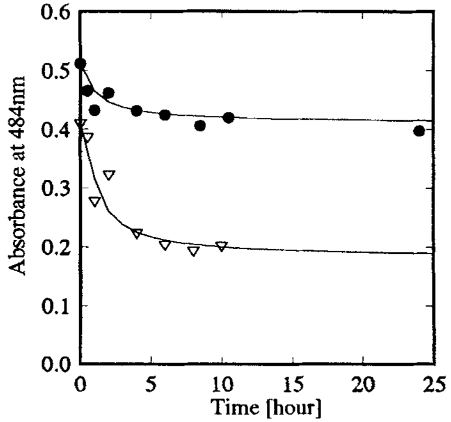

FIG. 1 Adsorption of HDTMA on montmorillonite vs time elapsed. (●) 0.3 g clay in 400 mL solution with initial concentration of 500 mg/L; dilution factor: 40. (▽) 0.2 g clay in 400 mL solution with initial concentration of 200 mg/L; dilution factor: 40.

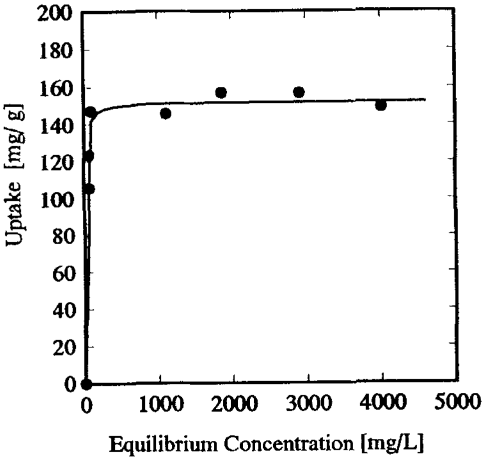

FIG. 2 Adsorption isotherm of HDTMA on montmorillonite.

result that HDTMA was adsorbed to over 98% of the CEC of montmorillonite. The monolayer adsorption of HDTMA on montmorillonite was achieved by ion-exchange reaction in the CEC range. This adsorption produces a very strong bond which has been proved to be stable through not only short-term desorption in 4–7 days but also long-term desorption over 180 days (5). This stable immobilization of HDTMA permits organo-montmorillonite to be applicable for environmental pollution control.

Adsorption of Phenols

Single-Component Adsorption

The adsorptions of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol were performed using HDTMA–montmorillonite. Prior to an experiment for adsorption equilibrium, a time study of adsorption of each phenolic compound was made to determine an equilibrium 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 guarantee equilibrium. Adsorption isotherms for three phenolic compounds are presented in Fig. 3. The single-component adsorption results show that the adsorption affinity of 2-chlorophenol is the largest, followed by 4-nitrophenol and 3-cyanophenol. The 2-parameter Langmuir model and 3-parameter Redlich–Peterson (RP) model were used to analyze the adsorption behaviors of each phenolic compound as shown in Fig. 3. Tables 2

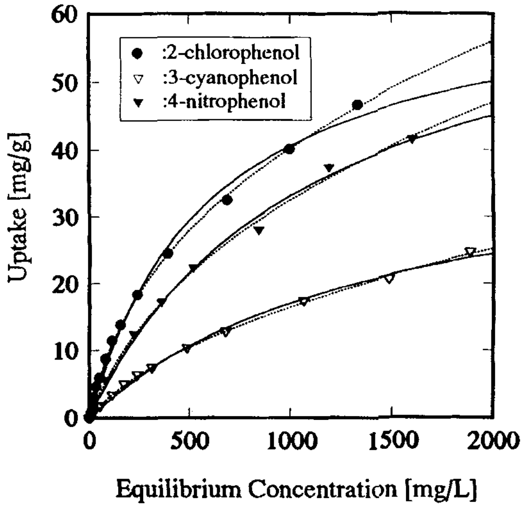

FIG. 3 Single-solute adsorption isotherms of phenols on HDTMA–montmorillonite. The lines represent Langmuir (——) and RP (···) adsorption isotherms.

and 3 show the adsorption parameters of both models as obtained by a nonlinear optimization method. Although the 3-parameter Redlich–Peterson model shows a little better fit to adsorption data than the 2-parameter Langmuir model, both models were in good agreement with the actual data as indicated by correlation coefficient values over 0.99. To determine the correlation coefficient, SSE $= \sum C_i^2$ and SSY $= \sum (C_i - C_p)^2$ were calculated. Then the correlation coefficient was subsequently obtained by (SSY − SSE)/SSY. Here, C_i and C_p represent an experimental measurement and a predicted value, respectively. Considering the parameters *a*

TABLE 2
Langmuir Parameters for the Adsorption of Phenolic Compounds on HDTMA–Montmorillonite

Compound[a]	q_m	*b*	*a*	Correlation coefficient
2-ChP	65.32	0.001644	0.1087	0.995
3-CyP	42.95	0.000661	0.0284	0.998
4-NiP	70.34	0.000891	0.0627	0.998

[a] 2-ChP: 2-chlorophenol. 3-CyP: 3-cyanophenol. 4-NiP: 4-nitrophenol.

TABLE 3
Redlich–Peterson Parameters for the Adsorption of Phenolic Compounds on HDTMA–Montmorillonite

Compound[a]	α	β	γ	Correlation coefficient
2-ChP	0.1830	4.370	0.3547	1.000
3-CyP	0.0522	0.9704	0.4653	1.000
4-NiP	0.0898	5.668	0.3182	0.999

[a] 2-ChP: 2-chlorophenol. 3-CyP: 3-cyanophenol. 4-NiP: 4-nitrophenol.

and *b* in the Langmuir model, the adsorption affinities of the phenols used are sequenced 2-chlorophenol, 4-nitrophenol, 3-cyanophenol in decreasing order.

The different affinities of the phenols for HDTMA–montmorillonite can be explained by the physical adsorptive interaction between organic solutes and organically modified HDTMA–montmorillonite. A major attraction force comes from the van der Waals interaction between a HDTMA tail group and a solute, originated from different molecular weights of the phenolic compounds. In addition, a steric hindrance effect related to the shape and size of the phenol molecules was thought to produce the different adsorption affinities. It has been shown that steric hindrance is affected in the adsorption of chlorophenol isomers such as 2-chlorophenol, 3-chlorophenol, and 4-chlorophenol on activated carbon (22). 2-Chlorophenol, which has a functional group in the ortho-position, has the smallest molecular surface area, and this is an advantage for it to diffuse into the pores of activated carbon particles. Yen's results also indicated that the adsorption capacity of each phenolic compound on activated carbon decreased in the order 4-nitrophenol, 2-chlorophenol, 3-cyanophenol according to their decrease in molecular weight. In this study, however, their adsorption capacities decreased in the order 2-chlorophenol, 4-nitrophenol, 3-cyanophenol, which might be caused by a compromise of the van der Waals force and a steric hindrance effect.

Multicomponent Adsorption

Binary competitive adsorption experiments were performed using the three binary systems 2-chlorophenol/3-cyanophenol, 3-cyanophenol/4-nitrophenol, and 2-chlorophenol/4-nitrophenol. Figures 4, 5, and 6 show the competitive adsorption behaviors of each binary system along with the graphical predictions of the IAST and LCM models. The correlation coef-

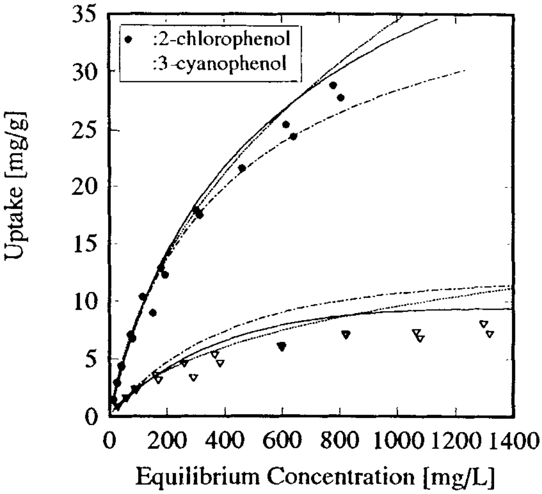

FIG. 4 Bi-solute adsorption of 2-chlorophenol and 3-cyanophenol on HDTMA-montmorillonite. LCM prediction (-·-) and IAST predictions based on Langmuir (——) and RP (···) adsorption models.

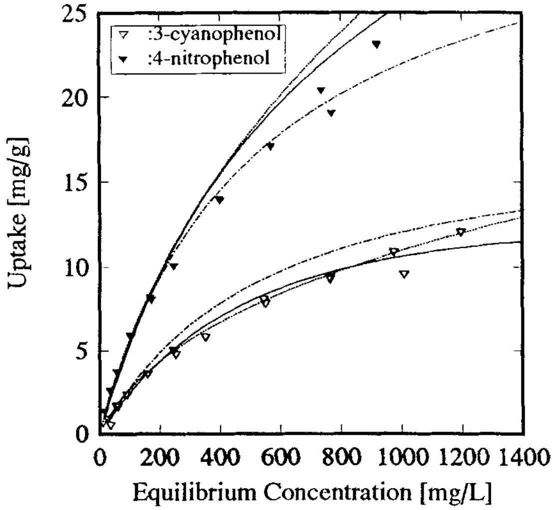

FIG. 5 Bi-solute adsorption of 3-cyanophenol and 4-nitrophenol on HDTMA-montmorillonite. LCM prediction (-·-) and IAST predictions based on Langmuir (——) and RP (···) adsorption models.

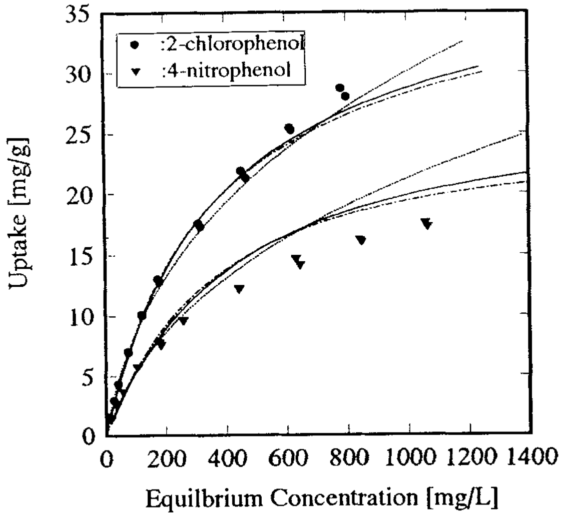

FIG. 6 Bi-solute adsorption of 2-chlorophenol and 4-nitrophenol on HDTMA–montmorillonite. LCM prediction (-·-) and IAST predictions based on Langmuir (——) and RP (···) adsorption models.

ficients of both models for binary and ternary systems are given in Table 4. The correlation coefficient for the 2-chlorophenol/3-cyanophenol system was 0.95, while the other systems showed values greater than 0.98. In view of these high correlation coefficient values, both the IAST and LCM models provided favorable predictions for the binary competitive adsorption of phenols on HDTMA–montmorillonite.

In order to determine the extent of reduction in monolayer capacity, the Langmuir model was applied to the adsorption data of each phenolic

TABLE 4
Correlation Coefficients for Adsorption Model Predictions in Binary and Ternary Systems

Compounds combination[a]	IAST–Langmuir	IAST–RP	LCM
2-ChP/3-CyP	0.988	0.986	0.949
3-CyP/4-NiP	0.991	0.988	0.995
2-ChP/4-NiP	0.992	0.988	0.993
2-ChP/3-CyP/4-NiP	0.990	0.987	0.987

[a] 2-ChP: 2-chlorophenol. 3-CyP: 3-cyanophenol. 4-NiP: 4-nitrophenol.

TABLE 5
Langmuir Parameters of Each Phenolic Compound in Multicomponent Adsorption[a]

Compounds combination	Compound	q_m	b	a
2-ChP/3-CyP	2-ChP	43.1	0.00226	0.0974
	3-CyP	9.37	0.00325	0.0305
3-CyP/4-NiP	3-CyP	18.2	0.00145	0.0263
	4-NiP	37.4	0.00155	0.0578
2-ChP/4-NiP	2-ChP	41.8	0.00249	0.104
	4-NiP	22.4	0.00302	0.0674
2-ChP/3-CyP/4-NiP	2-ChP	34.7	0.00313	0.109
	3-CyP	8.75	0.00336	0.0294
	4-NiP	17.8	0.00377	0.0672

[a] 2-ChP: 2-chlorophenol. 3-CyP: 3-cyanophenol. 4-NiP: 4-nitrophenol.

compound in the binary and ternary systems. The Langmuir parameters of each phenolic component in multisolute systems are shown in Table 5. The percentage reduction of the Langmuir monolayer capacity due to competition in binary and ternary systems is listed in Table 6. As these results indicate, 3-cyanophenol and 4-nitrophenol paired with 2-chlorophenol show about 78 and 68% reductions of q_m compared with their

TABLE 6
Percent Decrease in the Langmuir Adsorption Capacity of Each Phenolic Compound in Multicomponent Systems Due to Competition[a]

Compound	Adsorbate mixture	Langmuir constant, q_m	Decrease in q_m (%)	Correlation coefficient
2-ChP	Alone	65.3	—	0.995
	2-ChP/3-CyP	43.1	34.0	0.997
	2-ChP/4-NiP	41.8	36.0	0.999
	2-ChP/3-CyP/4-NiP	34.7	46.9	0.999
3-CyP	Alone	43.0	—	0.998
	2-ChP/3-CyP	9.37	78.2	0.995
	3-CyP/4-NiP	18.2	57.7	0.997
	2-ChP/3-CyP/4-NiP	8.75	79.7	0.997
4-NiP	Alone	70.3	—	0.998
	2-ChP/4-NiP	22.4	68.1	0.999
	3-CyP/4-NiP	37.4	47.0	0.997
	2-ChP/3-CyP/4-NiP	17.8	74.7	0.999

[a] 2-ChP: 2-chlorophenol. 3-CyP: 3-cyanophenol. 4-NiP: 4-nitrophenol.

single-component adsorption isotherms, respectively. However, 2-chlorophenol yielded only 35% reduction of q_m in these systems. 3-Cyanophenol exhibited about 78% reduction of q_m in the 2-chlorophenol/3-cyanophenol system, while it showed about 47% reduction when paired with 4-nitrophenol. 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. Here, we may speculate that competition between adsorbates drives out the weakly adsorbed fractions from the adsorbed phase, thereby forming a stronger adsorbed phase on HDTMA–montmorillonite. It is observed that the species which showed a stronger affinity for HDTMA–montmorillonite in single-component adsorption occupied larger adsorption sites than other components in competitive adsorptions.

The competitive adsorption of the tri-solute mixture 2-chlorophenol/3-cyanophenol/4-nitrophenol on HDTMA–montmorillonite was carried out in the same batch adsorption apparatus at 25°C. The competitive adsorption behaviors of the three solutes are shown in Fig. 7. Comparing the adsorption capacity with the case for single-component adsorption, 2-chlorophenol, 4-nitrophenol, and 3-cyanophenol underwent 47, 75, and 80% reduction of q_m values in the tri-solute adsorption, respectively, as seen in Table 6. It is also observed that the species which showed a stronger affinity for the HDTMA–montmorillonite in single-component

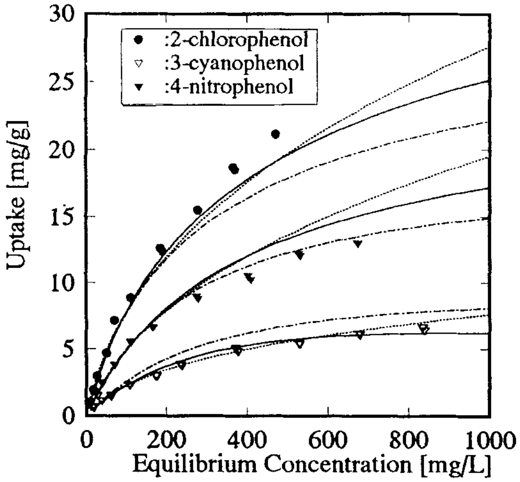

FIG. 7 Tri-solute adsorption of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol on HDTMA–montmorillonite. LCM prediction (-·-) and IAST predictions based on Langmuir (——) and RP (···) adsorption models.

adsorption occupied larger adsorption sites in tri-solute adsorption. The correlation coefficients of this tri-solute system with the IAST and LCM predictions were determined to be over 0.98, as listed in Table 4. Overall, the IAST and the LCM were good predictive models for this ternary competitive adsorption. Considering all of the experimental measurements and the predictions of adsorption models used, it is concluded that the adsorption affinity for HDTMA–montmorillonite is in the order 2-chlorophenol > 4-nitrophenol > 3-cyanophenol.

CONCLUSION

The adsorption of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol on montmorillonite modified with HDTMA, a cationic surfactant, has been studied using single- and multicomponent systems in aqueous solution at 25°C. HDTMA was ion-exchanged irreversibly in the range of CEC of montmorillonite. By means of fixing a HDTMA on montmorillonite, the hydrophilic surface property of montmorillonite is changed into organophilic, enhancing the sorption capacity for organic contaminants. Adsorption affinities of organic phenols for HDTMA–montmorillonite were differently determined, possibly because of compromised physical adsorption factors: attraction by the van der Waals force due to molecular weight, and retardation by a steric hindrance effect due to molecular structure. Both the Langmuir and Redlich–Peterson models fit well to single component adsorption data, while the IAST and LCM models showed favorable predictions for the competitive adsorption behaviors of phenols on HDTMA–montmorillonite. From the experimental results for both individual and competitive adsorption behaviors, it was observed that the adsorption affinity of the phenols for HDTMA–montmorillonite was sequenced in the decreasing order 2-chlorophenol, 4-nitrophenol, and 3-cyanophenol.

ACKNOWLEDGMENT

Grateful acknowledgment is extended to the YeonKang Foundation, Korea, for its financial support of this work under YeonKang Contract 05-380-5.

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Received by editor January 11, 1996