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Dong-Geun Kim[a]; Dong-Ik Song[a]; Young-Woong Jeon[b]
[a] Department of Chemical Engineering, Kyungpook National University, Taegu, Korea [b] Department of Environmental Engineering, Kyungpook National University, Taegu, Korea

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pH-DEPENDENT SORPTIONS OF PHENOLIC COMPOUNDS ONTO MONTMORILLONITE MODIFIED WITH HEXADECYLTRIMETHYLAMMONIUM CATION

Dong-Geun Kim, Dong-Ik Song,[1],*
and Young-Woong Jeon[2]

[1]Department of Chemical Engineering and
[2]Department of Environmental Engineering,
Kyungpook National University, Taegu 702-701, Korea

ABSTRACT

Single-solute sorptions onto the organically modified montmorillonite were completed at 2 different pH conditions, 7 and 11.5, in a batch reactor to investigate the pH-dependent uptake of 2-chlorophenol (ChP), 3-cyanophenol (CyP), and 4-nitrophenol (NiP) dissolved in water at 25°C. During the preparation of HDTMA-clay, hexadecyltrimethylammonium (HDTMA) cation was exchanged for metal cations on the montmorillonite at the cation exchange capacity of the montmorillonite. During the process, the montmorillonite changed from having a hydrophilic to an organophilic surface. Experimental results show that the sorption affinity on HDTMA-clay was in the order of 2-ChP $>$ 4-NiP $>$ 3-CyP for the 2 pH conditions. The Langmuir and the Redlich-Peterson (RP) models were used to fit the single-solute sorption equilibria data graphically. The ideal adsorbed solution theory

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*Corresponding author. Fax: 82-53-950-6615; E-mail: disong@knu.ac.kr

(IAST) coupled with a single-solute model (i.e., either Langmuir or RP model) was used to predict the multisolute competitive-sorption equilibria. Predictions from the IAST at each pH condition yielded favorable representations of multisolute competitive sorption of the phenolic compounds onto HDTMA-clay.

INTRODUCTION

Various toxic chemicals have been discharged into the environment as industrial wastes, causing serious water and soil pollution. Removal of organic contaminants from wastewater has been extensively studied through the use of 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 the hydration of the metal cations, become organophilic by ion-exchanging a quaternary amine cation with short or long hydrocarbon chains for the metal cations on the clay. Among many quaternary amine cations, the hexadecyltrimethylammonium (HDTMA) cation is widely used. The organic compounds dissolve in the nonpolar organic medium formed by conglomeration of the long hydrocarbon tail group of the HDTMA cation.

Many investigators have studied sorption of organic compounds from water through the use of organoclays (1–7). However, studies on sorption behaviors of ionizable organic compounds in solutions of controlled pH are very rare. Boyd et al. (2) reported the sorption of pentachlorophenol (PCP) in aqueous solution, at pH 5.5 and 10, onto smectite modified with HDTMA cation. The 2 isotherms were found to be nearly identical, even though the phenol ($pK_a = 4.75$) should have completely dissociated to the phenolate anion at pH 10. The maximum equilibrium concentration used in obtaining isotherms was only about 4 mg/L. This concentration range was too narrow to discern pH-dependent sorption. Stapleton, Sparks, and Dentel (8) studied the sorption of PCP between pH 4 and 8.5 onto montmorillonite modified with HDTMA cation (HDTMA-clay). They observed that the sorption of the deprotonated species at higher pH was represented by a Langmuir-type adsorption isotherm due to the two-dimensional sorption of the exposed HDTMA surface on the organoclays. They found that the sorption of the protonated species at lower pH was represented by a linear partition-type isotherm due to the dissolution in the three-dimensional lipophilic organic medium formed by conglomeration of the long hydrocarbon chains of the HDTMA. Dentel et al. (9) studied the effect of pH on sorption of phenol and 2,4,5-trichlorophenol to montmorillonite modified with dimethyldistearylammonium cation. They reported that single-solute uptake onto the organoclays increased in the order of increasing solute hydrophobicity and that the role played by solute hydrophobicity was also maintained at several different pH values. Their results show that sorption was more favorable when the uncharged (protonated) species was predominant.

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Although organoclays are used with increasing frequency in field applications, such as landfill liners and for fuel spill control, fundamental studies on single- and multisolute competitive sorption behaviors as a function of pH have not been fully achieved. In this work we chose 2-chlorophenol (ChP), 3-cyanophenol (CyP), and 4-nitrophenol (NiP) as solutes dissolved in water at pH 7.0 and 11.5 over wide concentration ranges. Experimental isotherms and analyses that quantify the single- and multisolute competitive sorptions of ionizable phenolic compounds from water onto the HDTMA-clay will be presented to elucidate the influence of pH on sorption behavior of each solute.

EXPERIMENTAL

Materials

Montmorillonite-KSF was purchased from Aldrich Chemical Co (Sheboygan, WI, USA). The cation exchange capacity of this montmorillonite measured by the Rhoades method (10) was 50.4 mEq/100 g clay (6). This value was equivalent to about 160 mg HDTMA/g clay. The cation used as an organic modifier, a 25% (wt) HDTMA chloride solution, was obtained from Aldrich Chemical Co and used as received. Three phenolic solutes used as sorbates, ChP, CyP, and NiP, were purchased from Aldrich Chemical Co. All reagents were of analytical grade and were used as received without further purification.

Preparation of HDTMA-Clay

The impurities in montmorillonite were removed by washing it 4 times with distilled water at 60°C. The washed montmorillonite samples collected after filtering were dried for 24 hours and stored in a brown bottle until use. To prepare HDTMA-clay, the exchange adsorption of HDTMA onto washed montmorillonite was first performed in a 2-L beaker with 1 L HDTMA solution at a concentration of 5000 mg/L. Thirty grams of montmorillonite were added to this beaker and then agitated with a mechanical stirrer at 250 rpm for 24 hours. After agitation, HDTMA-clay was collected, washed with distilled water, and filtered through a membrane filter. This washing and filtering procedure was repeated 3 times. The collected HDTMA-clay was dried in an oven at 60°C for 24 hours and kept in a brown bottle until use.

Sorption onto HDTMA-Clay

Single-solute sorption isotherms on HDTMA-clay were obtained for the aqueous solutions of each phenolic compound in a batch apparatus at 25°C. We prepared solutions of each phenolic compound at mass concentrations of 100, 200, 300, 500, 750, 1000, 1500, 2000, 2500, and 3000 mg/L. The pH values of the phenolic solutions were controlled at 7 and 11.5 using buffer solutions. A buffered stock solution of pH 7 (11.5) was prepared as follows; first, 0.2 mol of K_2HPO_4 (K_3PO_4) was dissolved in 800 mL of distilled water. Second, a small amount of 1 mol/L HCl solution was added until the solution pH reached 7 (11.5). Finally, distilled water was added to the solution to make a total volume of 1 L. The pH was measured at the beginning and end of each sorption. Variation in pH was less than 0.15 unit.

Each 20 mL solution with different initial concentrations was poured into a capped 50-mL flask containing 0.5 g of HDTMA-clay and then shaken at 160 rpm on an orbit shaker for 24 hours at 25°C. The sorption equilibrium of each phenolic solution was reached in approximately 4 hours. However, the sample batches were agitated for 24 hours throughout this study to ensure equilibrium. The solutions were then centrifuged at 1500 rpm for 20 minutes. The equilibrium concentration of each solution was determined at maxima UV wavelengths through the use of a UV-Visible spectrophotometer (Hewlett-Packard 8453, U.S.A.). Because the reproducibility of the sorption onto the HDTMA-clay was firmly demonstrated in a previous study (6), all sorption experiments were not duplicated.

Three bisolute systems (2-ChP and 3-CyP, 3-CyP and 4-NiP, and 4-NiP and 2-ChP) were prepared by mixing each phenolic solution of the same mass concentration in a 1:1 volume ratio. Initial phenolic concentrations were 100, 200, 300, 500, 750, 1000, 1200, and 1500 mg/L for each solute. One trisolute system (2-ChP, 3-CyP, 4-NiP) was similarly prepared by mixing each phenolic solution of the same mass concentration in a 1:1:1 volume ratio. The resulting concentrations of 100, 200, 300, 500, 600, 800, and 1000 mg/L of each solute were used in the experiments. Multisolute sorption experiments were carried out through the same procedures as described for single-solute sorption experiments. The equilibrium concentrations in the mixtures were determined using the UV-Visible spectrophotometer.

SINGLE- AND MULTISOLUTE SORPTION MODELS USED

The sorption isotherms frequently employed for single-solute systems are the 2-parameter Langmuir and the 3-parameter Redlich-Peterson (RP) (11) models that obey the thermodynamic boundary condition of Henry's law over an infinitely dilute concentration range. The Langmuir and the RP models for a solute in a single-solute system are written respectively as follows:

$$q = \frac{q_{max}bC}{1 + bC} = \frac{aC}{1 + bC} \tag{1}$$

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

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

The ideal adsorbed solution theory (IAST) originally proposed by Radke and Prausnitz (12) 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 (13,14). 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

$$\int_0^{q_1^*} \frac{d\log C_1}{d\log q_1}\,dq_1 = \int_0^{q_2^*} \frac{d\log C_2}{d\log q_2}\,dq_2 = \cdots = \int_0^{q_N^*} \frac{d\log C_N}{d\log q_N}\,dq_N \tag{3}$$

Other equations involved in the IAST calculation are

$$C_{\mathrm{m},i} = z_i C_i^*; \qquad \sum_{\mathrm{i}=1}^{N} z_i = 1;\ q_i^* = f(C_i^*); \qquad \frac{1}{q_{\mathrm{T}}} = \sum_{\mathrm{i}=1}^{N} \frac{z_i}{q_i^*};$$
$$q_{\mathrm{m},i} = z_i q_{\mathrm{T}} = \frac{V(C_{\mathrm{m},i}^0 - C_{\mathrm{m},i})}{W} \tag{4}$$

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, which sorbs singly from solution at the same temperature and spreading pressure as does the mixture. The function f in $q_i^* = f(C_i^*)$ denotes a single-solute sorption model for solute i. $C_{\mathrm{m},i}^0$ 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, one can predict the multisolute sorption equilibria, $q_{\mathrm{m},i}$ vs. $C_{\mathrm{m},i}$, by solving these equations simultaneously.

RESULTS AND DISCUSSION

Single-Solute Sorption onto HDTMA-Clay

The single-solute sorptions of 2-ChP, 3-CyP, and 4-NiP at 2 different pH conditions were performed using HDTMA-clay. Table 1 lists the physicochemical properties of the 3 phenolic compounds used in this work. UV calibration curves were prepared for total species (neutral and anionic) at the isosbestic point at pH 7.0 and for anions at pH 11.5. Figure 1a shows the single-solute sorption

Table 1. Physicochemical Properties of Phenolic Compounds Used

					UV Wavelength (nm)	
Solute	M.W.	Solubility (mg/L)	Log K_{ow}*	pK_a at 25°C	Isosbestic Point	Phenolate Anion
2-ChP	128.56	1.13×10^4	2.15	8.45	277.0	293.0
3-CyP	119.12	0.7349×10^4	1.70	8.51	300.8	319.0
4-NiP	139.11	1.16×10^4	1.91	7.08	347.2	399.0

* Octanol-water partition coefficient.

isotherms of each phenolic compound at pH 7, where most of 2-ChP and 3-CyP remain as neutral species, dissociating only about 3%. However, 4-NiP dissociates into 4-nitrophenolate anion by approximately 45% throughout the sorption because pH ≈ pK_a. Total concentrations of both neutral species and phenolate anions were measured at the isosbestic point of each phenol. Hence, the abscissa and ordinate of Fig. 1a should be understood as total equilibrium concentration and total uptake, respectively. Sorption affinity of the 3 phenolic compounds to HDTMA-clay was found in the order of 2-ChP > 4-NiP > 3-CyP. The order of the initial slope of each isotherm ("a" values in Table 2) at pH 7 agrees with the order of the K_{ow} values of each compound listed in Table 1; this result was found even though as much as 45% of the 4-NiP dissociates at pH 7. Most neutral species are believed to dissolve in the pseudo-organic medium formed by the conglomeration of the long hydrocarbon chains of the HDTMA cation exchange-adsorbed in the interlamellar spacing of the clay (8). Figure 1b shows the single-solute sorption isotherms of each phenolic compound at pH 11.5, where all solutes are present as the corresponding phenolate anions because pH >> pK_a for each solute. Sorption affinity of the anionic species was also in the order 2-ChP > 4-NiP > 3-CyP, though the affinity difference between 2-ChP and 4-NiP was greatly reduced when present as anionic species. Phenolate anions are difficult to sorb in the

Table 2. Langmuir Parameters of Each Phenolic Compound on HDTMA-Clay

Solute	pH	q_{max} (mg/g)	b (L/mg) × 10^4	a (L/g) ×10^2	R^2
2-ChP	7	103.7	16.3	16.9	0.9989
	11.5	23.3	21.2	4.94	0.9961
3-CyP	7	67.6	6.63	4.48	0.9974
	11.5	15.4	20.8	3.21	0.9758
4-NiP	7	72.1	12.8	9.26	0.9956
	11.5	19.7	29.2	5.74	0.9896

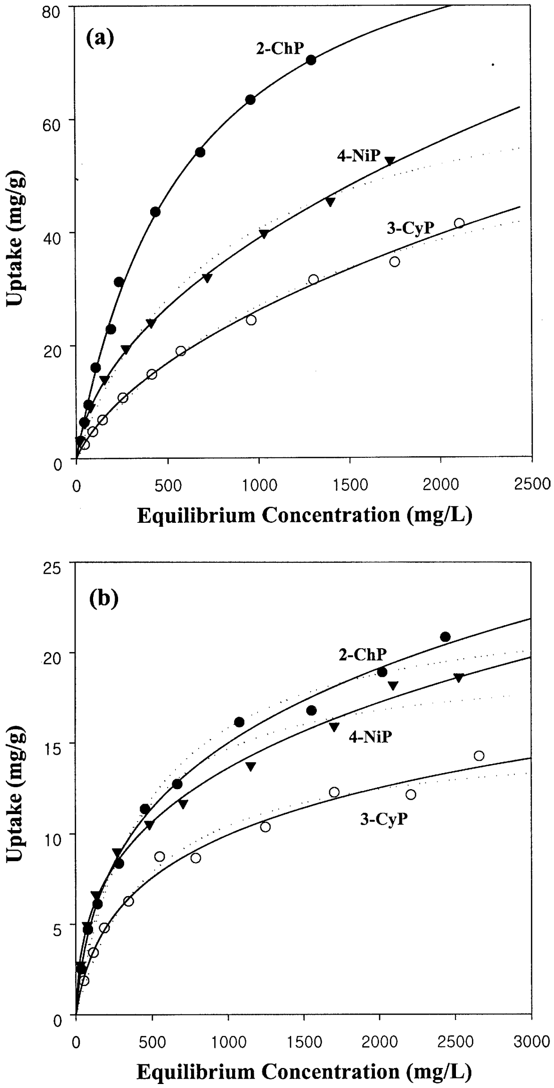

Figure 1. Single-solute sorption isotherms of phenolic compounds on HDTMA-montmorillonite. Dotted and solid lines represent Langmuir and Redlich-Peterson models, respectively. (a) pH 7.0 and (b) pH 11.5.

core of the pseudo-organic medium due to the hydration of the hydrophilic moiety of the ionic center. Hence, they are believed to sorb on the two-dimensional surface of the pseudo-organic medium with the hydrophobic part of the anion sorbing on the surface and the hydrophilic moiety protruding into the aqueous solution phase (8).

Sorption affinity of the 3 phenolic compounds to HDTMA-clay was in the order 2-ChP $>$ 4-NiP $>$ 3-CyP at pH 7.0 and 11.5. The difference in sorption affinity can be explained mainly by the hydrophobic interaction between a solute and the pseudo-organic medium formed by the hydrocarbon chains of HDTMA. Steric hindrance due to the size and shape of the solute molecules was also believed to cause affinity differences as well.

The 2-parameter Langmuir and the 3-parameter RP models were fitted to the single-solute sorption data for each phenolic compound using the nonlinear regression method. Fitted curves of the Langmuir and the RP models are shown together in Fig. 1 for comparison, and the parameters of each sorption model at 2 pH values were tabulated in Tables 2 and 3, respectively. As a measure of the degree of fitness, the R^2 values for the single-solute sorption were computed from the following equation (15):

$$R^2 = \frac{\sum q_i^2 - \sum (q_i - \hat{q}_i)^2}{\sum q_i^2} \tag{5}$$

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, respectively. According to the R^2 values listed in the Tables 2 and 3, the 3-parameter RP model exhibited a slightly better fit to the sorption data than did the 2-parameter Langmuir model as had been expected from the number of parameters involved in the model. However, the 2 single-solute models seemed to agree well with the experimental data; nearly all the R^2 values were greater than 0.99.

To further clarify the influence of pH on sorption behavior of each solute, we showed single-solute sorption isotherms for 2-ChP, 3-CyP, and 4-NiP in Figs. 2a, 2b, and 2c by using pH as a parameter after regrouping sorption data in Fig. 1.

Table 3. Redlich-Peterson Parameters of Each Phenolic Compound on HDTMA-Clay

Solute	pH	α (L/g) $\times 10^2$	β (L/mg)^{v} $\times 10^2$	v	R^2
2-ChP	7	16.9	0.163	1.00	0.9989
	11.5	11.5	4.52	0.723	0.9987
3-CyP	7	8.78	5.31	0.549	0.9982
	11.5	5.84	2.36	0.771	0.9969
4-NiP	7	37.9	23.9	0.521	0.9997
	11.5	30.6	19.2	0.683	0.9988

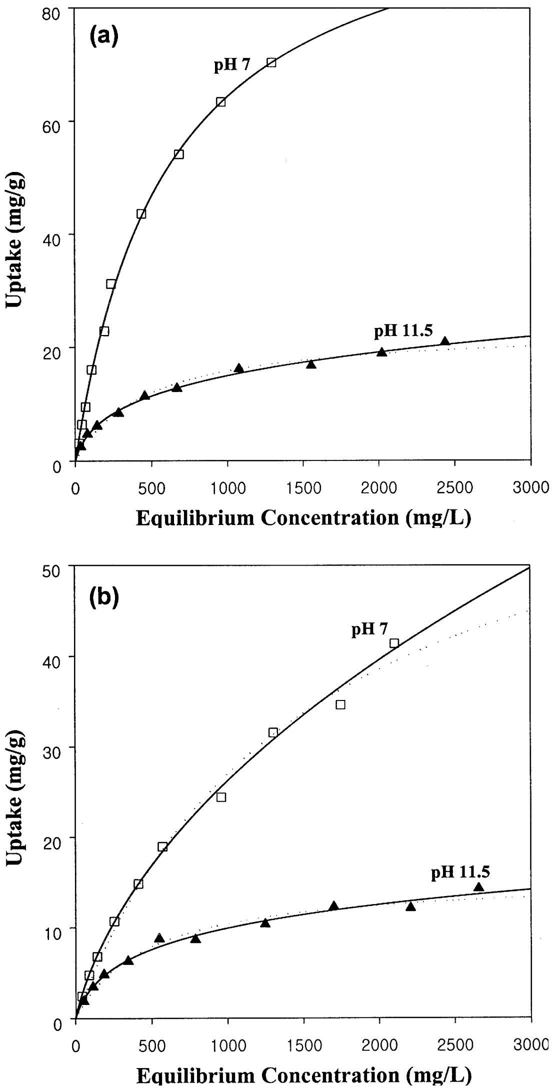

Figure 2. Single-solute sorption isotherms of each phenolic compound on HDTMA-clay as a function of pH. Dotted and solid lines represent Langmuir and Redlich-Peterson models, respectively. (a) 2-ChP, (b) 3-CyP, and (c) 4-NiP.

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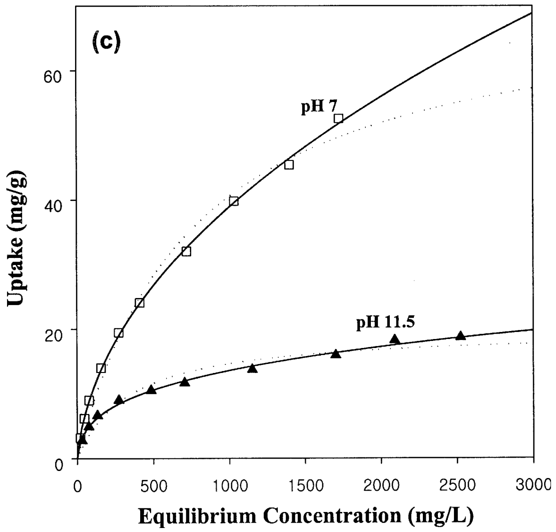

Figure 2. Continued.

As can be seen in Fig. 2, uptake was quite low at pH 11.5 where all solutes were present as anions, compared with uptake at pH 7.0. We believe that this reduction in sorption affinity was caused by low solubility of anions in the organic-medium core due to the unfavorable hydrophobic interaction between hydrated anions and the nonpolar pseudo-organic medium.

Dissociation equilibrium in the solution breaks when neutral and anionic species do not have the same sorption affinity to the organoclays. As neutral species with higher sorption affinity disappear from the solution due to sorption, anionic species with lower sorption affinity either sorb onto the organoclays as well or turn into neutral species to maintain the dissociation equilibrium in solution. Thus, phenolate anions for 2-ChP, 3-CyP, and 4-NiP are always present at approximately the 3, 3, and 45% level, respectively, in the solution of pH 7. In this respect, sorptions at pH 7 are essentially binary competitive sorptions between better-sorbing neutral and less-sorbing anionic species. However, their competitiveness is rather weak due to the different sorption sites involved: the dominant two-dimensional surface versus the three-dimensional core of the nonpolar pseudo-organic medium as sorption sites for the anionic and neutral species, respectively. We believe that total uptake at pH 7 for the solutes consists of both partition of neutral species in the core of the organic medium and surface sorption of anionic species on the two-dimensional surface of the organic medium.

Multisolute Competitive Sorption onto HDTMA-Clay

Bisolute competitive sorptions were performed using the 3 binary systems of 2-ChP and 3-CyP, 3-CyP and 4-NiP, and 4-NiP and 2-ChP at 2 different pH values. Bisolute competitive sorption data at pH 7 were selected as a typical data set and shown in Fig. 3. As expected, when 2 solutes compete for sorption in a bisolute system, the sorption amount of each solute is less than that of each solute in a single-solute system. The solute with a lower sorption affinity in the single-solute system showed a greater reduction of sorption amount in bisolute system. This tendency was the same for the bisolute sorption data at pH 11.5 (figures not shown). Predictions made through the IAST for each bisolute system are shown together in Fig. 3 for comparison. Langmuir and RP models were used to describe the single-solute sorption in the multisolute predictive IAST. The parameters of the models were previously determined from the nonlinear curve fitting to the single-solute sorption data (shown in Tables 2 and 3). To compare both predictions, we computed R^2 and SSE from the following equations (15) and listed them in Tables 4 and 5:

$$R^2 = \frac{\sum q_i^2 - \mathrm{SSE}}{\sum q_i^2} \tag{6}$$

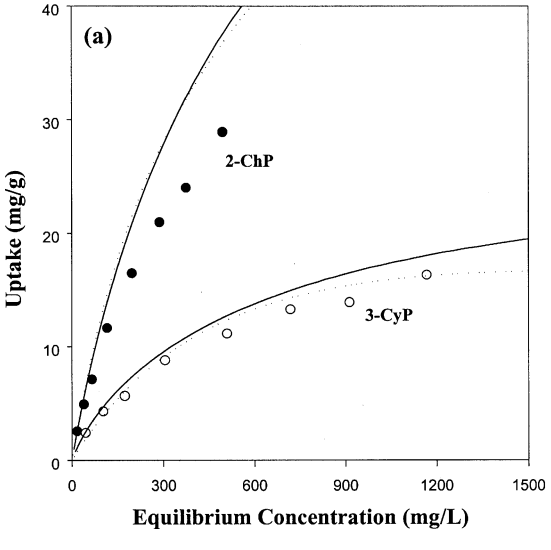

Figure 3. Bisolute sorption isotherms of (a) 2-ChP and 3-CyP, (b) 3-CyP and 4-NiP, and (c) 4-NiP and 2-ChP at pH 7.0 on HDTMA-clay. Dotted and solid lines denote IAST predictions based on Langmuir and Redlich-Peterson models, respectively.

(continued)

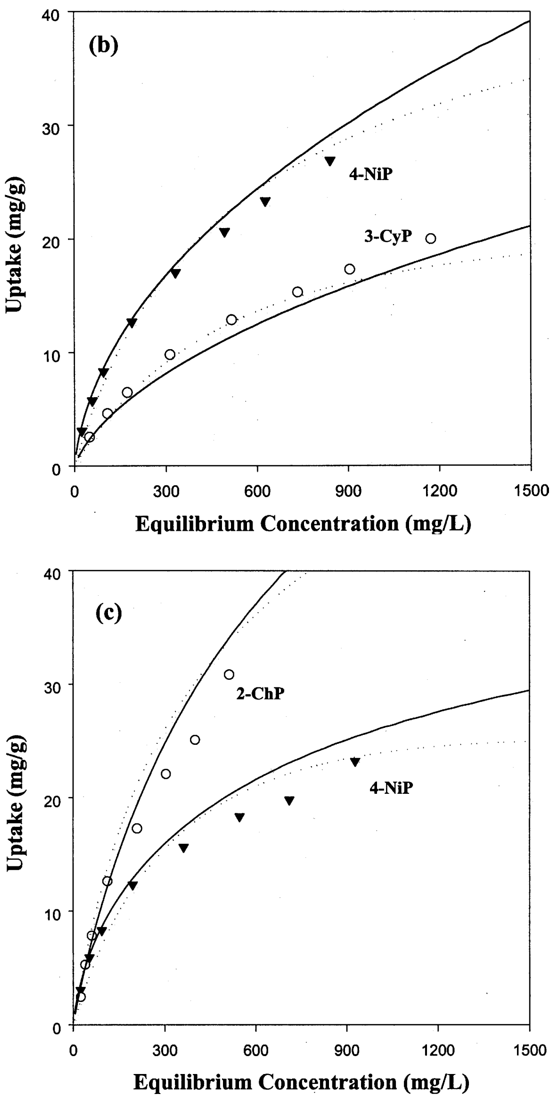

Figure 3. Continued.

Table 4. SSE and R^2 for the Bisolute and Trisolute Competitive Sorption Predictions from IAST Coupled with Langmuir Model

	pH	SSE	R^2
2-ChP/3-CyP	7	206/5.58	0.9118/0.9937
	11.5	10.6/10.8	0.9836/0.9494
3-CyP/4-NiP	7	4.74/7.60	0.9962/0.9966
	11.5	12.0/7.10	0.9412/0.9878
4-NiP/2-ChP	7	17.2/11.0	0.9903/0.9729
	11.5	1.80/1.74	0.9952/0.9958
2-ChP/3-CyP/4-NiP	7	162/2.14/8.46	0.8896/0.9961/0.9921
	11.5	2.62/2.02/1.28	0.9887/0.9685/0.9937

where

$$\mathrm{SSE} = \sum (q_i - \tilde{q}_i)^2 \tag{7}$$

In the above equation, $\tilde{q}_i$ denotes the predicted uptake of a solute. From the R^2 and sum of the square of the errors (SSE) values shown in Tables 4 and 5, predictions for all solutes, except for the 2-ChP in the 2-ChP and 3-CyP bisolute system, at pH 7 were found to be in good agreement with data.

The competitive sorption data for the 3 solutes are shown in Figs. 4a to 4b at each pH condition together with the predictions from the multisolute competitive IAST. As in a bisolute system, the sorption amount of each solute involved in a trisolute system was relatively low. The solute with a higher affinity tended to be reduced less than the lower affinity solutes. To compare the performance of the IAST predictions, the R^2 and SSE values were also computed and listed in the last row of Tables 4 and 5. Except for the IAST predictions coupled with the single-

Table 5. SSE and R^2 for the Bisolute and Trisolute Competitive Sorption Predictions from IAST Coupled with Redlich-Peterson Model

	pH	SSE	R^2
2-ChP/3-CyP	7	198/17.2	0.9125/0.9807
	11.5	5.27/13.0	0.9918/0.9394
3-CyP/4-NiP	7	14.5/7.08	0.9885/0.9969
	11.5	17.0/2.81	0.9169/0.9952
4-NiP/2-ChP	7	25.4/45.4	0.9857/0.9827
	11.5	0.186/0.984	0.9995/0.9976
2-ChP/3-CyP / 4-NiP	7	12.7/5.43/0.598	0.9914/0.9901/0.9994
	11.5	1.94/2.52/0.517	0.9916/0.9607/0.9975

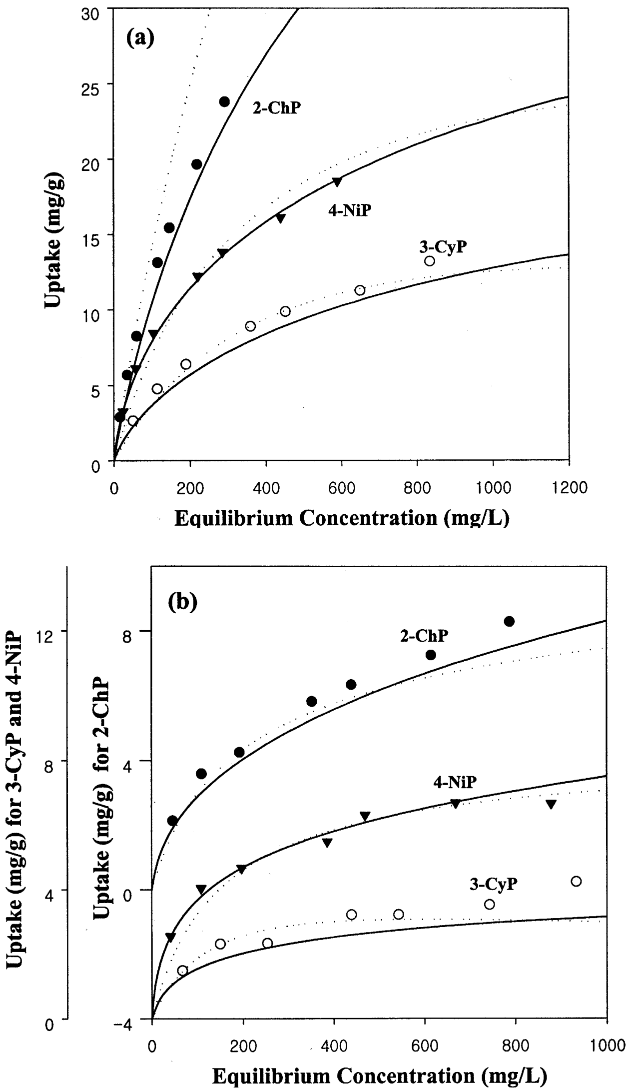

Figure 4. Trisolute sorption isotherm of 2-ChP, 3-CyP, 4-NiP on HDTMA-clay. Dotted and solid lines denote IAST predictions based on Langmuir and Redlich-Peterson models, respectively. (a) pH 7.0 and (b) pH 11.5.

solute Langmuir model for the 2-ChP in the trisolute system, all the predictions were found to be in close agreement with the trisolute sorption data.

CONCLUSIONS

The sorptions of 2-ChP, 3-CyP, and 4-NiP on montmorillonite organically modified with HDTMA cation were studied with 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 changed from hydrophilic to organophilic, thus enhancing the sorption capacity for organic contaminants. The sorption affinity of phenolic compounds onto the HDTMA-clay was in the order 2-ChP $>$ 4-NiP $>$ 3-CyP regardless of the solution pH. The affinity differences were possibly caused by the difference in the hydrophobic interactions between the solute and the pseudo-organic medium formed by conglomeration of the long hydrocarbon chains of the exchange-adsorbed HDTMA cation and by a steric hindrance due to molecular structure. The Langmuir and the RP models were well fitted to single-solute sorption data. The predictions from IAST coupled with the single-solute models (i.e., either Langmuir or RP model) for multisolute competitive sorptions also showed good agreement with the sorption data. We found that IAST data coupled with the well-known single-solute models were capable of describing the multisolute competitive sorption behaviors of the phenolic compounds onto HDTMA-clay regardless of the degree of dissociation of each solute, i.e., neutral and anionic species at pH 7.0 and anionic species at pH 11.5.

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REFERENCES

1. Mortland, M.M.; Shaobai, S.; Boyd, S.A. Clay-organic Complexes as Adsorbent for Phenol and Chorophenols. Clay, Clay Miner. **1986,** *34* (5)*,* 581.
2. Boyd, S.A.; Shaobai, S.; Lee, J.F.; Mortland, M.M. Pentachlorophenol Sorption by Organoclays. Clay. Clay, Miner. **1988,** *36* (2)*,* 125.
3. Boyd, S.A.; Mortland, M.M.; Chiou, C.T. Soil Sci. Soc. Am. Boyd, S.A. Sorption Characteristics of Organic Compunds on Hexadecyltrimethylammonium-smectite. J. **1988,** *52* (3), 652.

4. Lee, J.F.; Mortland, M.M.; Boyd, S.A.; Chiou, C.T. Shape-selective Adsorption of Aromatic Molecules from Water by Tetramethylammonium-smectite. J. Chem. Soc., Faraday Trans. I **1989,** *85* (9), 2953.
5. Smith, J.A.; Jaffe, P.R.; Chiou, C.T. Effect of Ten Quarternary Ammonium Cations on Tetrachloromethane Sorption to Clay from Water. Environ. Sci. Technol. **1990,** *24* (8), 1167.
6. Kim, Y.S.; Song, D.I.; Jeon, Y.W.; Choi, S.J. Adsorption of Organic Phenols onto Hexadecyltrimethylammonium-treated Montmorillonite. Sep. Sci. Technol. **1996,** *31* (20), 2815.
7. Lee, J.H.; Song, D.I.; Jeon, Y.W. Adsorption of Organic Phenols onto Dual Organic Cation Montmorillonite from Water. Sep. Sci. Technol. **1997,** *32* (12), 1975.
8. Stapleton, M.G.; Sparks, D.L.; Dentel, S.K. Sorption of PCP to HDTMA-clay as a Function of Ionic Strength and pH. Environ. Sci. Technol. **1994,** *28* (13), 2330.
9. Dentel, S.K.; Bottero, J.Y.; Khatib, K.; Demougeot, H.; Duguet, J.P.; Anselme, C. Sorption of Tannic Acid, Phenol, and 2,4,5-Trichlorophenol on Organoclays. Wat. Res. **1995,** *29* (5), 1273.
10. Rhoades, J.D. Cation Exchange Capacity. In *Methods of Soil Analysis, Part II, Chemical and Microbiological Properties*, 2nd Ed.; Page, A.L., Miller, R.H., Keeney, R., Eds.; American Society of Agronomy: Madison, Wis, 1982;149–157.
11. Redlich, O.; Peterson, D.L. A Useful Adsorption Isotherm. J. Phys. Chem. **1959,** *63,* 1024.
12. Radke, C.J.; Prausnitz, J.M. Thermodynamics of Multi-solute Adsorption from Dilute Liquid Solutions. AIChE J. **1972,** *18* (4), 761.
13. Yen, C.Y.; Singer, P.C. Competitive Adsorption of Phenols on Activated Carbon. J. Environ. Eng. **1984,** *110* (5), 976.
14. Yen, C.Y. The Adsorption of Phenol and Substituted Phenols on Activated Carbon in Single- and Multi-Component Systems. Ph.D. diss., University of North Carolina, Chapel Hill, NC, 1983.
15. Kleibaum, D.G.; Kupper, L.L. *Applied Regression Analysis and Other Multivariable Methods*; Duxbury Press: North Scituate, Mass., 1978;71–77.

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