Use of Cetyltrimethylammonium Bromide-Bentonite To Remove Organic Contaminants of Varying Polar Character from Water

L I Z H O N G Z H U ,* X I A O G A N G R E N , A N D
S H A O B I N Y U

Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang, China 310028

Cetyltrimethylammonium bromide (CTMAB)-bentonite was produced by the exchange of cetyltrimethylammonium (CTMA) cations for inorganic ions on the internal and external surfaces of bentonite. CTMAB-bentonite was used to remove organic contaminants of varying polar character from water. The properties and mechanisms for CTMAB-bentonite to sorb benzene, toluene, ethylbenzene, nitrobenzene, aniline, phenol, and *p*-nitrophenol in water were investigated in some detail. Benzene, toluene, and ethylbenzene sorption to CTMAB-bentonite was characterized by linear isotherms, indicating solute partition between water and the organic phase composed of the large alkyl functional groups of the CTMA cations. Phenol and *p*-nitrophenol sorption to CTMAB-bentonite was caused primarily by adsorption with relatively strong solute uptake. Their isotherms were nonlinear. Nitrobenzene and aniline sorption to CTMAB-bentonite was weak, and the isotherms were approximately linear. Their sorption was caused by both partition and solute uptake. The sorption data were also evaluated in terms of the octanol−water partition coefficients of the organic compounds.

Introduction

Bentonite is primarily a Na-montmorillonite, which is a 2:1 layered silicate that swells when contacted by water. The inner layer is composed of an octahedral sheet of the general form $M_{2-3}(OH)_6$ (where M is typically Al^{3+}), which is situated between two SiO_4 tetrahedral sheets. The substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer result in a net negative surface charge on the clay. The charge imbalance is offset by exchangeable cations such as H^+, Na^+, or Ca^{2+} on layer surfaces. In aqueous systems, water is intercalated into the interlamellar space of the montmorillonite, resulting in expansion of the mineral. Adsorption of nonionic organic solutes from water to bentonite is relatively weak because of the preferential attraction of polar water molecules to the polar mineral surfaces. Bentonite typically has a low organic carbon content; therefore, nonionic solute sorption by partition into the bentonite organic matter is also relatively weak (*1*, *2*). Thus, bentonite is not a strong sorbent for uptake of nonionic organic pollutants from water.

Organobentonites are produced by the exchange of organic cations (typically having a quaternary ammonium and aliphatic structure) for inorganic ions (e.g., H^+, Na^+, Ca^{2+}) on the layer surfaces of bentonite (*3*). The sorption properties of modified bentonite surfaces may be significantly altered by this exchange reaction. The modified mineral surfaces of the resulting organobentonite may become organophilic because the organic functional groups of the quaternary ammonium cations are not strongly hydrated by water. As a result, organobentonites are powerful sorbents for nonionic organic pollutants relative to natural bentonite and other clays (*1*, *2*, *4*−*6*).

Jordon and co-workers (*7*, *8*) developed a series of organobentonite complexes which he called "bentones". Barrier and co-workers (*9*−*11*) made the first studies describing the reaction and the effects of loading and chemical character on the sorption. Because of their unique sorption capabilities, organobentonites have been investigated for a wide variety of environmental applications. Harper and Purnell (*12*) have studied the use of organobentonites as a selective sorbent for sampling airborne organic contaminants. Other researchers in laboratory and field studies have investigated the feasibility of using bentonite exchanged with dodecylpyridinium and hexadecyltrimethylammonium cations to retard the transport of nonionic organic contaminants in groundwater (*13*). Some organobentonites were found to effectively remove organic pollutants from solution and were suggested for use in wastewater treatments (*14*, *15*). Boyd, Mortland, and co-workers have applied organo-clay synthesized with various quaternary ammonium cations to remove trace organic pollutants from wastewater (*16*−*21*).

It is important to understand the mechanism of nonionic solute sorption to organobentonites. Recent research indicates that the magnitude and mechanism of sorption are functions of the molecular structure of the exchanged organic cation, the extent of cation exchange, the solution chemistry, the molecular structure of the solute, and the cation-exchange capacity of the bentonite.

The sorption properties of organobentonites depends greatly on the characteristics of the exchanged organic cations. Smith et al. (*2*, *22*) demonstrated that tetrachloromethane sorption to bentonite modified by exchanged small organic cations was characterized by nonlinear isotherms, strong solute uptake, and competitive sorption. In contrast, tetrachloromethane sorption to bentonites modified by relatively large organic cations (C > 10) was characterized by essentially linear isotherms, lower solute uptake, and noncompetitive sorption. The authors concluded that the differences between the two groups of organo-clay sorbents were attributable to different sorption mechanisms: adsorption for bentonite modified with organic cations of small functional groups and partition for bentonite modified with organic cations of relatively large functional groups. The small organic cations (e.g., benzyltriethylammonium) create a relatively rigid, nonpolar surface amenable to nonionic solute uptake by adsorption. The larger organic cations (e.g., cetyltrimethylammonium bromide) create an organic partition medium through the conglomeration of their flexible alkyl chains. Smith et al. (*23*) compared tetrachloromethane sorption to an alkylammonium- and an alkyldiammonium-bentonite. For bentonite with decyltrimethylammonium (DTMA) cation, only one end of the 10-carbon alkyl chain is attached to the silica surface of the bentonite, and tetrachloromethane sorption is characterized by isotherm linearity, noncompetitive sorption, weak solute uptake, and a relatively low heat of sorption. For bentonite with decyltrimethyldiammonium (DTMDA) cation, both ends of the 10-carbon chain are attached to the silica surface of the

* Corresponding author fax: 86-571-8273802.

TABLE 1. Interlayer Spacings and Organic Carbon Contents of Natural Bentonite and CTMAB-Bentonite

		CTMAB concentration used in synthesizing CTMAB-bentonite						
	natural bentonite	1%	2%	3%	4%	5%	6%	7%
interlayer spacing (nm)	1.295	1.376	1.434	1.544	1.644	1.834	1.928	1.902
organic carbon (%)	0.057	6.630	12.00	15.90	20.00			

bentonite, and tetrachloromethane sorption to DTMDA-bentonite is characterized by nonlinear isotherms, competitive sorption, strong solute uptake, and a relatively high, exothermic heat of sorption.

Besides the molecular structure, the length of alkyl chain, and the concentration of organic cation in modified bentonite, the sorption characteristics of organic pollutants to organobentonites from water are related to the properties of organic compounds (24−26). Usually, nonionic (polar and nonpolar) organic pollutants and ionic organic pollutants coexist in water and wastewater. Most recent research in sorption to organobentonites was concerned mainly with nonionic (especially nonpolar) organic compounds from water. There is relatively little published information on the sorption of relatively polar organic pollutants to organobentonites. Moreover, recent research has concentrated mainly on the effects of organic cations on sorption capacities and mechanisms (e.g., partition and adsorption) of organobentonites. There is limited information on the effects of organic compound properties on organobentonite sorption characteristics and mechanisms.

In this paper, cetyltrimethylammonium bromide (CTMAB)−bentonite was synthesized by the exchange of cetyltrimethylammonium (CTMA) cations for inorganic ions on the surfaces of bentonite. The capacity of the CTMAB-bentonite to remove low molecular weight organic contaminants of varying polar character and the effects of CTMAB loading on the selectivity and efficiency of contaminant removal from water were investigated. A comparison was made on the characteristics and mechanisms of polar and nonpolar organic solute sorption from water to CTMAB-bentonite. The sorption data was also evaluated in terms of the octanol−water partition coefficients of the solutes. This research also gives considerations for the optimal concentrations of organic cations for organobentonite synthesis for wastewater treatment.

Materials and Methods

Materials. Bentonite used was primarily Na⁺-montmorillonite from Linan, Zhejiang. Its cation-exchange capacity (CEC) is 74.64 mequiv/100 g. CTMAB and other reagents used were of analytical grade.

Analytical Methods. Aniline and nitrobenzene concentrations in water were analyzed by ultraviolet spectrophotometry, the detection limits being 0.12 μg/mL. Phenol and p-nitrophenol in water were analyzed by ultraviolet spectrophotometry, the detection limits being 0.1 and 0.05 μg/mL, respectively. Benzene, toluene, and ethylbenzene were analyzed by gas chromatography, the detection limits being 0.9, 2.9, and 1.6 μg/mL, respectively.

Preparation of Organobentonite. CTMAB-bentonite was synthesized by exchanging cetyltrimethylammonium cations for inorganic ions on the bentonite. A total of 20 g of previously dried bentonite was mixed with 200 mL of various CTMAB solutions. The mixtures were subjected to mechanical stirring for 2 h in a 60−70 °C water bath. The treated bentonites were separated from water by vacuum filtration and washed twice by distilled water. The bentonites were dried at 80−90 °C, activated for 1 h at 105 °C, and mechanically ground to less than 100 mesh. A series of CTMAB-bentonites

were made by the exchange of CTMA cations for inorganic ions on the bentonite.

CTMAB-bentonite is identified by a prefix that states the percentage concentration of CTMAB cations used in modifying the bentonite. For example, 4% CTMAB-bentonite refers to the CTMAB-bentonite that was synthesized by adding 200 mL of 4% CTMAB solution to 20 g of previously dried bentonite.

Procedures for Water Treatment. A combination of 0.500 g of CTMAB-bentonite and 50 mL of solution with an appropriate concentration of the organic contaminant was combined in 125 mL Erlenmeyer flasks with glass caps. The flasks were shaken for 1 h at 25 °C on a gyratory shaker at 120 rpm. After being centrifuged, the organic compound in the aqueous phase was determined by ultraviolet spectrophotometry or gas chromatography. The removal percentages for CTMAB-bentonite to treat the organic compounds in water were calculated. The losses of the compounds by both photochemical degradation and sorption to the Erlenmeyer flask in water treatment were found to be negligible. The volatilization losses of organic compounds were analyzed by contrasting to the blank with no shaking and centrifugation. The results showed insignificant losses of phenol, p-nitrophenol, aniline, and nitrobenzene by shaking and centrifuging. The volatilization losses of benzene, toluene, and ethylbenzene were 14.8%, 8.7%, and 6.03%, respectively. The experiments were duplicated.

Results and Discussion

X-ray Powder Diffraction Analysis. The properties of natural bentonite and a series of CTMAB-bentonites were investigated by X-ray powder diffraction (XRD) analyses. The XRD analyses showed that the interlayer spacing of natural bentonite is 1.295 nm with 75% relative humidity in the laboratory. The interlayer spacing of CTMAB-bentonite increased gradually with increasing amount of cetyltrimethylammonium cation used in synthesizing the clays (Table 1). When the concentration of CTMAB used in synthesis was over 6% (where the amount of CTMAB was equal to 82.4 mmol/100 g bentonite, more than the CEC of the natural bentonite), the interlayer spacing of CTMAB-bentonite did not increase further.

Optimal Conditions for CTMAB−Bentonite To Remove Organic Compounds from Water. The removal rates for CTMAB-bentonite to treat the nonionic compounds aniline, nitrobenzene, benzene, toluene, and ethylbenzene were not much different over the pH range 2−12. The pK_a values of phenol and p-nitrophenol were 9.96 and 7.16, respectively. At pH < pK_a, the removal rates for CTMAB-bentonite to treat phenol and p-nitrophenol remained unchanged. At pH > pK_a, the removal rates greatly increased (Table 2). The solutions containing organic compounds were adjusted to pH 8−9 in consideration of their application for wastewater treatments.

The percentages of removal of organic compounds by CTMAB-bentonite varied with time at pH 8−9 and 120 rpm of shaking. After the flasks were shaken for 45 min, the removal rates of organic compounds from water were, however, not much different. Thus, the shaking time was set to be 1 h in the following experiments. In addition, the amounts of CTMAB-bentonite used in water treatment

TABLE 2. Effects of pH on Removal Percentages of Organic Compounds from Water

	benzene	toluene	ethylbenzene	nitrobenzene	aniline	phenol	p-nitrophenol
removal rate(%)	51−58	60−68	73−78	33−37	38−42	72−78[a] 86−100[b]	91−95[a] 98−100[b]

[a] pH < pK_a. [b] pH > pK_a.
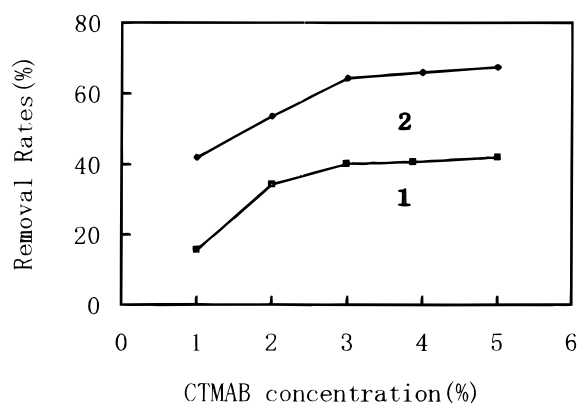
FIGURE 1. Effects of CTMAB concentrations on the removal rates of aniline (1) and toluene (2) from water by CTMAB-bentonite: concentration, 50 μg/mL; pH 8.
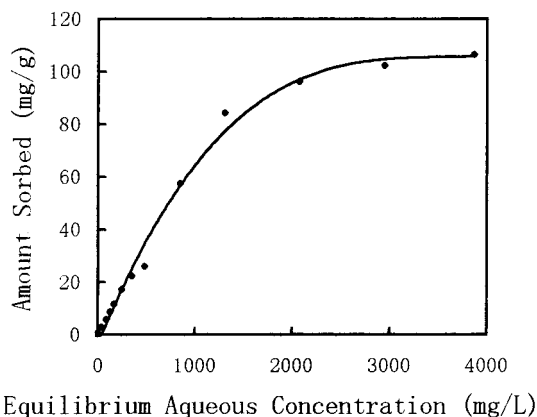
FIGURE 2. Isothermal sorption curve of phenol.

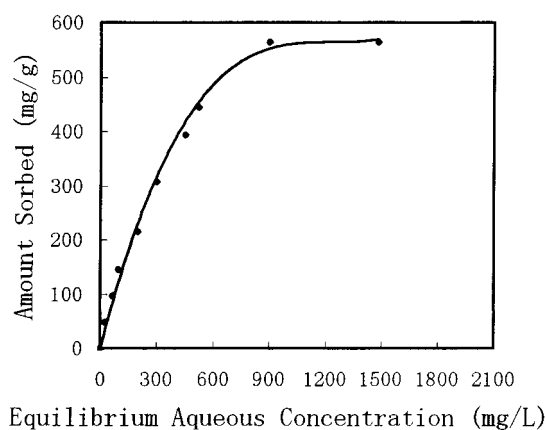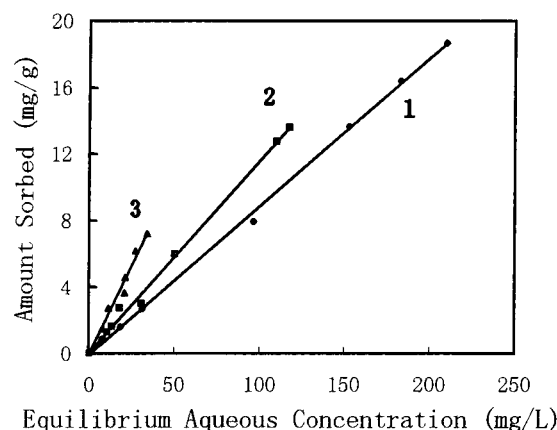FIGURE 3. Isothermal sorption curve of p-nitrophenol.

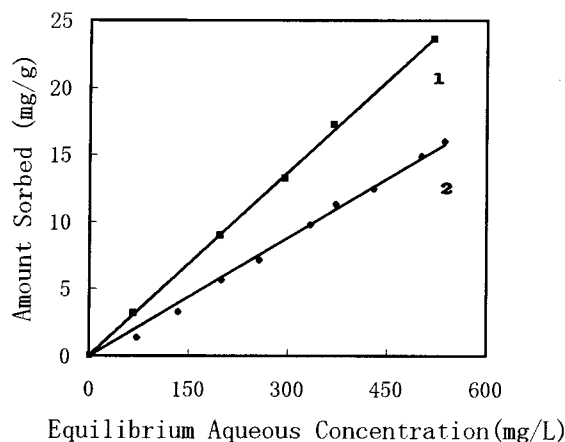FIGURE 4. Benzene (1), toluene (2), and ethylbenzene (3) sorption to 4% CTMAB-bentonite from water.

FIGURE 5. Aniline (1) and nitrobenzene (2) sorption to 4% CTMAB-bentonite from water.

affected the removal rates of the organic compounds; the removal rates increased gradually with increasing amounts of CTMAB-bentonite used in water treatment. The amounts of CTMAB-bentonite was selected as 0.25 g/25 mL solution in the following experiments in consideration of both the removal rate and the treatment cost.

Effects of CTMAB Concentrations on Sorption Properties of CTMAB−Bentonite. The effects of CTMAB concentrations used in modifying the bentonite (1−5%) on the removal rates of organic compounds (aniline, toluene) from water by CTMAB-bentonite were investigated. Figure 1 indicates that the removal rates of organic compounds from water by CTMAB-bentonite were increased with increasing the CTMAB concentrations (<3%) for modifying the bentonite. When the CTMAB concentration was over 3%, the removal rates of organic compounds reached nearly a constant level. A 4% CTMAB-bentonite clay was used to remove organic compounds from water in further studies.

Mechanism for CTMAB-Bentonite To Remove Organic Compounds from Water. Isothermal Sorption Curves. Isothermal sorption curves for 4% CTMAB-bentonite to sorb seven organic compounds at pH 8 are shown in Figures 2−5. Different initial concentration ranges of organic compounds were chosen because of their different solubilities. The initial concentrations of phenol and p-nitrophenol were less than

6000 and 14 000 mg/L, respectively. Figures 2 and 3 show that sorption of phenol and p-nitrophenol to 4% CTMAB-bentonite is characterized by relatively strong solute uptake and isotherm nonlinearity of a concave-downward shape. The sorption of phenol and p-nitrophenol to CTMAB-
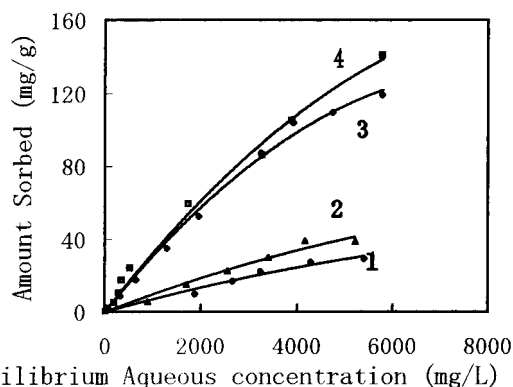
FIGURE 6. Isothermal sorption curves of aniline by (1) natural bentonite and a series of CTMAB-bentonites: (2) 1% CTMAB-bentonite, (3) 2% CTMAB-bentonite, (4) 4% CTMAB-bentonite.
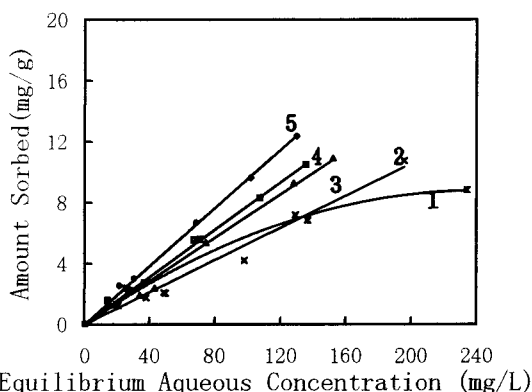

FIGURE 7. Isothermal sorption curves of toluene by (1) natural bentonite and a series of CTMAB-bentonites: (2) 1% CTMAB-bentonite, (3) 2% CTMAB-bentonite, (4) 3% CTMAB-bentonite, (5) 4% CTMAB-bentonite.

TABLE 3. Linear Regression Data for Sorption Isotherms

organic compounds	regression equation	correlation coefficient
benzene	$Y = 0.088X - 0.104$	0.995
toluene	$Y = 0.117X + 0.147$	0.994
ethylbenzene	$Y = 0.228X - 0.084$	0.962
aniline	$Y = 0.046X + 0.133$	0.999
nitrobenzene	$Y = 0.031X - 0.537$	0.999

bentonite can be fit to a Freundlich equation by a least-squares regression; the Freundlich equations of phenol and *p*-nitrophenol were $Y = 0.133C^{0.869}$ and $Y = 17.14C^{0.494}$, respectively. Therefore, the sorption of phenol and *p*-nitrophenol at low concentrations to CTMAB-bentonite from water appeared to result significantly from adsorption or other specific interaction in addition to partition, as evidenced by the nonlinear and relatively strong solute uptake. The presumed low partition may be attributed to the large disparity in polarity of the (polar) phenols and the (nonpolar) CTMAB medium.

Figure 4 shows isotherm data for benzene, toluene, and ethylbenzene sorption to 4% CTMAB-bentonite from water at 25. Benzene, toluene, and ethylbenzene sorption to CTMAB-bentonite was measured at aqueous concentrations

less than 700, 450, and 180 mg/L, respectively. Sorption of all three solutes to 4% CTMAB-bentonite is characterized by relatively low solute uptake and isotherm linearity. These characteristics suggest that benzene, toluene, and ethylbenzene sorption occur primarily by partition to the CTMAB phase, as may be expected from the similarity of the compound and CTMAB polarities (*27, 28*). Nitrobenzene and aniline sorption to CTMAB-bentonite was weak, and the isortherms were linear at low concentrations (Figure 5, Table 3). Moreover, their isotherms (such as aniline, Figure 6) were approximately linear at high concentrations. The linear regression equations and correlation coefficients for these compounds with CTMAB-bentonites are listed in Table 3.

The sorption characteristics of organic compounds from water on organobentonites are closely related to solute properties, such as the water solubility and octanol−water partition coefficient (K_{ow}). The solubilities and octanol−water partition coefficients of seven organic compounds are listed in Table 4. For weakly polar organic compounds, the larger the K_{ow} is, the stronger is the partition of the solute in the organic phase composed of the large CTMA alkyl groups on organobentonites. For relatively polar organic compounds, the larger the K_{ow} is, the stronger is the solute adsorption by organobentonites. Thus, the removal rates for organobentonites to treat organic pollutants from water are improved.

Effects of CTMAB Concentrations on Sorption Properties of Organobentonites. Effects of CTMAB concentrations on the sorption of organobentonites are shown in Figures 6 and 7. Figure 6 shows that the removal rates and sorption capacities of CTMAB-bentonite for aniline are proportional to CTMAB concentrations used in modifying the bentonite. Figure 7 shows that toluene sorption to natural bentonite was characterized by nonlinearity. However, toluene sorption to CTMAB-bentonite was characterized by relatively weak solute uptake and linearity. The linear slopes are increased with increasing CTMAB concentrations used in modifying the bentonite. Therefore, toluene sorption from water to CTMAB-bentonite was caused mainly by partitioning. Organic carbon contents of organobentonites are proportional to CTMAB concentrations (1−4%) exchanged on the bentonite (Table 1). The partition of solutes in organobentonite was improved because of increasing the organic carbon content. Thus, removal rates for organobentonites to treat organic pollutants increased with increasing amounts of quaternary ammonium cations (<CEC) used in modifying the bentonite.

Because quaternary ammonium organic cations were exchanged into the interlamellar space of the bentonite and the interlayer spacings were increased, some micropores of the bentonite were occupied by quaternary ammonium cations. Thus, the specific surface areas of the organobentonites were reduced with increasing concentrations of quaternary ammonium cations incorporated into the bentonite. Therefore, as the concentrations of quaternary ammonium cations increased, the removal rates of organic compounds from water by organobentonite were enhanced, due mainly to increased partition rather than adsorption.

The removal rates of organobentonites for organic compounds from water were higher than that of natural bentonite. Nonionic organic compound sorption to CTMAB-bentonite from water was related to polarity. Polar organic

TABLE 4. Solubility and Octanol−Water Partition Coefficient of Organics (*29*)

	benzene	toluene	ethylbenzene	phenol	*p*-nitrophenol	aniline	nitrobenzene
K_{ow}	140	540	1400	29	81	7.9	71
solubility (g/100 mL)	0.072	0.045	0.015	8.2	1.6	3.6	0.2

compound sorption to CTMAB-bentonite from water was influenced more by adsorption or other specific interaction than by partition, which resulted in relatively strong solute uptake. The associated isotherms were nonlinear. Nonpolar organic compound (benzene, toluene, ethylbenzene) sorption to CTMAB-bentonite from water was caused primarily by partitioning as indicated by relatively low solute uptake and linear isotherms. Sorption of weakly polar organic compounds to CTMAB-bentonite was weaker than that of nonpolar compounds, and the isotherms were approximately linear. The sorption was caused essentially by a weaker partition to the CTMAB medium, with possibly a weak adsorption effect. The removal efficiencies and sorption capacities of organobentonites for organic compounds in water increased with increasing amounts of associated quaternary ammonium cations in the bentonite.

Acknowledgments

Literature Cited

(1) Boyd, S. A.; Mortland, M. M.; Chiou, C. T. *Soil Sci. Soc. Am. J.* **1988**, *52*, 652.
(2) Smith, J. A.; Jaffe, P. R.; Chiou, C. T. *Environ. Sci. Technol.* **1990**, *24*, 1167.
(3) Smith, J. A.; Tuck, D. M.; Jaffe, P. R.; Mueller, R. T. In *Organic substance and sediments in water*; Backer, R., Ed.; Lewis: Chelsea, MI, 1991; p 201.
(4) Zhu, L.; Zhang, C.; Zhou, L.; Ren, J.; Chai J. *China Environ. Sci.* **1994**, *14* (5), 346.
(5) Zhu, L.; Hu, J.; Shen, X.; Chai, J. *Acta Sci. Circumstantiae* **1995**, *15* (3), 316.
(6) Zhu, L.; Zhang, J.; Li, Y.; Shen, X.; Qi, W. *J. Environ. Sci.* **1996**, *8* (3), 378.
(7) Jordon, J. W. *J. Phys. Chem.* **1949**, *53*, 294.
(8) Jordon, J. W.; Hook, B. J.; Finlayson, C. M. *J. Phys. Chem.* **1950**, *54*, 1196.
(9) Barrer, R. M.; Macleod, D. M. *Trans. Faraday Soc.* **1955**, *51*, 1290.
(10) Barrer, R. M.; Reay, J. S. S. *Trans. Faraday Soc.* **1957**, *53*, 1253.
(11) Barrer, R. M.; Kelsey, K. E. *Trans. Faraday Soc.* **1961**, *57*, 452.
(12) Harper, M.; Purnell, C. *Environ. Sci. Technol.* **1990**, *24*, 55.
(13) Smith, J. A.; Jaffe, P. R. *J. Environ. Eng.* **1994**, *120*, 1559.
(14) Park, -J.-W.; Jaffe, P. R. *Environ. Sci. Technol.* **1993**, *27*, 2559.
(15) Holsen, T. M.; Taylor, E. R.; Seo, Y.-C.; Anderson, P. R. *Environ. Sci. Technol.* **1991**, *25*, 1585.
(16) Boyd, S. A.; Mortland, M. M. *Soil Sci. Soc. Am. J.* **1985**, *49*, 619.
(17) Mortland, M. M.; Shaobai, S.; Boyd, S. A. *Clays Clay Miner.* **1986**, *34*, 581.
(18) Boyd, S. A.; Shaobai, S.; Lee, J.-F.; Mortland, M. M. *Clays Clay Miner.* **1988**, *36*, 125.
(19) Jaynes, W. F.; Boyd, S. A. *J. Air Waste Manage. Assoc.* **1990**, *40*, 1649.
(20) Jaynes, W. F.; Boyd, S. A. *Soil Sci. Am. J.* **1991**, *55*, 43.
(21) Sheng, G.; Xu, S.; Boyd, S. A. *Environ. Sci. Technol.* **1996**, *30*, 1553.
(22) Smith, J. A.; Galan, A. *Environ. Sci. Technol.* **1995**, *29*, 685.
(23) Smith, J. A.; Jaffe, P. R. *Environ. Sci. Technol.* **1991**, *25*, 2054.
(24) Zhu, L.; Li, Y.; Zhang, J. *Environ. Sci. Technol.* **1997**, *31*, 1407.
(25) Li, Y.; Zhu, L.; Wang, J.; Zhang, J. *Chem. J. Chin. Univ.* **1997**, *18*, 723.
(26) Zhu, L.; Li, Y.; Chen, S.; Liu, W.; Bao, L. *Environ. Chem.* **1997**, *16* (3), 233.
(27) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227.
(28) Daniel, E. K.; Chiou, C. T.; Zhou, H.; Li, H.; Xu, O. *Environ. Sci. Technol.* **1995**, *29*, 1401.
(29) James, R. C. *Environ. Sci. Technol.* **1985**, *19*, 980.