



SORPTION AND COSORPTION OF 1,2,4-TRICHLOROBENZENE AND TANNIC ACID BY ORGANO-CLAYS

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Abstract—Organo-clay sorbents were prepared by treating montmorillonite with four different quaternary ammonium compounds. The sorbents were then evaluated for the ability to remove a lower molecular weight hydrophobic organic, 1,2,4-trichlorobenzene (TCB), from water in the presence of larger, more hydrophilic organics such as tannic acid. Removal of each sorbate species was characterized separately, then the organo-clays' removal of TCB was assessed in the presence of the tannic acid. The quaternary ammonium compounds used were tetramethylammonium chloride (TMA), hexadecyltrimethylammonium bromide (HDTMA), hexadecylbenzyltrimethylammonium chloride (HDBDMA), and dioctadecyldimethylammonium bromide (DDDMA). The adsorption isotherms of tannic acid onto the organo-clays were all nonlinear; the TMA-modified clay led to unfavorable curvature, while the long-chain surfactants all produced favorable curvature. The ability of the organo-clays to remove tannic acid increased in the order TMA < HDBDMA, inconsistent with the organic carbon content of the clays. Adsorption, rather than partitioning, was the uptake mechanism. In contrast, sorption of TCB onto the organo-clays was by a partitioning mechanism, indicated by linear isotherms, uptake proportional to the percentage of the CEC exchanged by HDTMA, and a low heat of sorption. With two distinctive uptake mechanisms, the capacity of the modified clays for TCB was not affected by the presence of tannic acid, even with applied tannic acid concentrations of 50 mg/L. X-ray diffraction indicated that the tannic acid was excluded from internal sites, due to its size and polarity. Organo-clays thus may be usable to retain smaller, hydrophobic organic compounds such as TCB with no loss of capacity in the presence of tannic acid or similar natural organic matter present in surface and groundwaters. This was confirmed for TCB sorption in the presence of a humic acid sample. © 1998 Elsevier Science Ltd. All rights reserved

Key words: organo-clay, sorption, trichlorobenzene, montmorillonite, tannic acid.

INTRODUCTION

Naturally occurring clays are not efficient as adsorbents for the uptake of hydrophobic organics from water. This is due to the electrically charged and hydrophilic characteristics of their surfaces. However, clays such as montmorillonite may be modified in a manner that significantly improves their capability to remove hydrophobic contaminants from solution. These sorbent materials are termed organo-clays because the exchangeable inorganic cations are replaced by organic cations such as quaternary ammonium compounds (Barrer, 1978). The hydrophilic clay acquires organophilic properties due to the exposed alkyl groups (Boyd *et al.*, 1988a,b; Lee *et al.*, 1990). The larger organic cations may act as pillars, increasing the spacing between the tetrahedral sheets and creating an organophilic sorption zone between the layers of the clay (Barrer, 1978). Dimensions and structure of the organic cations, and the charge origins, cation exchange capacity (CEC),

and geometry of the base clay determine the resulting size and relative hydrophobicity of this adsorption zone.

These characteristics of the organo-clay may allow imbibition of some organics, but exclusion of others (Dentel *et al.*, 1995). Previous researchers (McBride *et al.*, 1977; Lee *et al.*, 1989; Cadena, 1989; Srinivasan and Fogler, 1989) have suggested that chemically modified clays may be synthesized with sorbate affinities sufficiently specific to enable their use in selective removal of organic contaminants from water. Such preferential sorption has been demonstrated using the binary solute systems trichlorophenol–pentachlorophenol (Boyd *et al.*, 1988b) and benzene–toluene (Lee *et al.*, 1990). In the systems TCE–CCl₄, and TCE–nitrobenzene, the latter component led to increased TCE uptake by cosolvency effects, rather than preferential uptake (Sheng *et al.*, 1996a).

Of more interest in environmental applications would be the ability to preferentially sorb low molecular weight, hydrophobic organic contaminants in

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the presence of larger, more hydrophilic organics. Such sorbents would allow drawbacks associated with the non-selectivity of activated carbon (Lalezary *et al.*, 1986; Summers *et al.*, 1989; Najm *et al.*, 1990) to be circumvented in a variety of applications. However, previous research has not characterized organo-clay performance in an appropriate binary system, or even organo-clay behavior in the presence of high molecular weight hydrophilic organics alone.

OBJECTIVES

The primary objective of this research was to evaluate the capabilities of organo-clays for selective removal of lower molecular weight, nonpolar organics from water in the presence of larger, more hydrophilic substances. The adsorption capacities of the organo-clays were then to be examined as a function of organic cation used and fraction of the exchange capacity substituted. Experimental conditions were selected such that, ultimately, results will assist in optimizing organo-clay use in environmental applications.

The organic compound 1,2,4-trichlorobenzene (TCB) was used as a representative organic contaminant in this research, and commercially obtained tannic acid was used as a larger, hydrophilic organic. Sorption of each of these onto the organo-clays was first characterized separately, and then the sorption of TCB was assessed in the presence of tannic acid.

MATERIALS AND METHODS

Sorbates

Tannic acid. Commercially available tannic acid (Sigma Chemical) was selected as a representative hydrophilic organic. It is reported by the supplier to have a mean molecular mass of 1700 with an empirical formula $C_{76}H_{53}O_{46}$, a water content of 5.8%, and an organic carbon content of about 50%. Tannic acid has been used in previous research (Lahoussine-Turcaud *et al.*, 1990; Cathalifaud *et al.*, 1997) as a reproducible surrogate for natural organic matter (NOM). The molecular mass appears to approximate mean values reported for surface waters (El-Rehaili and Weber, 1987; Summers *et al.*, 1989; Bruchet *et al.*, 1990; Newcombe *et al.*, 1997). Tannic acid also contains both saccharide and aromatic acid components that are significant in surface waters (Bruchet *et al.*, 1986; Gray *et al.*, 1992).

The tannins present in natural waters resemble humic substances in some of their properties such as adsorbability, color, and complex formation (Stumm and Morgan, 1981). However, tannic acid was used in preference to commercially available humic and fulvic fractions with the expectation that the higher molecular masses of the latter (3000–40,000) (El-Rehaili and Weber, 1987) would make them less likely to interfere with organo-clay uptake of the lower molecular weight organics. Tannins may be of additional concern due to their greater THM formation potential (Bruchet *et al.*, 1990).

1,2,4-trichlorobenzene (TCB). This is a synthetic organic compound and a U.S. EPA priority pollutant. The maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) were set at 0.07 mg/L for TCB in the fourth phase of the U.S. Safe Drinking Water Act regulations (Pontius, 1993). TCB is not known to occur as a natural product, but is released to the environment through its manufacture and use as a dye carrier, and its role as an intermediate in the manufacture of herbicides and higher chlorinated benzenes (Howard, 1989). TCB may also be considered as representative of halogenated organic water pollutants and disinfection by-products (Abrams *et al.*, 1975) that have been detected in groundwater (Howard, 1989) and in surface waters (Summers *et al.*, 1989). The value of its log octanol/water partition coefficient is approximately 4.1 (Montgomery and Welkom, 1990), indicating a definite potential for sorption by organic matter. It is also expected to significantly evaporate from water with reported half lives of 11–22 d (Howard, 1989).

Adsorbents

Montmorillonite clay. The clay used in this study was Wyoming montmorillonite which was obtained from the University of Missouri Source Clays Depository. Prior to use, the clay was purified by sedimentation to achieve a particle size of $<2\ \mu\text{m}$, saturated with sodium, washed and freeze-dried. The cation exchange capacity (CEC) of the clay was measured by MgCl_2 saturation and subsequent displacement by CaCl_2 (Rich, 1963; Okazaki *et al.*, 1963) and found to be 93.0 meq/100 g of the dry clay.

Organic cations. Four quaternary ammonium compounds were used as clay modifiers: tetramethylammonium chloride, hexadecyltrimethylammonium* bromide, hexadecylbenzyltrimethylammonium chloride, and dioctadecyl-dimethylammonium† bromide. The molecular structures and abbreviations used for them are shown in Table 1. Due to the quaternary ammonium serving as the source of positive charge, they are not affected by the solution pH (Rosen, 1989).

Batch isotherm tests

Isotherms were generated using a standard "bottle point" batch procedure, but including clay modification as the first of two procedural steps for each individual sample. Both steps were performed in the same 50 mL borosilicate glass centrifuge tubes, using Teflon-lined screw caps.

First, clay samples of 50 mg were weighed in each of the tubes, then the organic cation solutions were added in amounts sufficient to replace the desired percentage of the CEC. The longer-chain surfactants were added to the clay in the exact stoichiometric amounts of the desired % CEC, while TMA was added in five-fold excess of the desired % CEC. DDDMA was not soluble in water, so ethanol was used to enhance its solubility, with the stock solutions of DDDMA prepared using a mixture of ethanol and water in a ratio of 1:9. The tubes were then shaken on a rotary shaker (3 rpm) for a period of 16–24 h, although preliminary kinetic studies on HDTMA showed that the reaction was complete in 4–6 h. The clay suspension in the tubes was allowed to settle, and the separation of the phases was achieved by decantation and filtration. To provide organo-clays as might be commercially produced, samples were neither dialyzed nor freeze-dried. The uptake of organic cations by the clay were determined by analyses as described elsewhere (Jamrah, 1993).

Isotherms for the modified clays were then generated, adding tannic acid, 1,2,4-trichlorobenzene (TCB), or both to the glass centrifuge tubes containing the individual organo-clay preparations from the first step. Stock solutions of tannic acid and/or TCB were prepared, and

*Also may be termed cetyltrimethylammonium, or CTA.

†Also may be termed dimethyldistearylammonium.

Table 1. List of the cationic surfactants used in the study

Surfactant	Abbreviation	Molecular weight (g)	Structure
Tetramethylammonium chloride	TMA	109.6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
Hexadecyltrimethylammonium bromide	HDTMA	364.46	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - (\text{CH}_2)_{15} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
Hexadecylbenzyltrimethylammonium chloride	HDBDMA	396.0	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - (\text{CH}_2)_{15} \text{CH}_3 \\ \\ \text{CH}_2 - \text{C}_6\text{H}_5 \end{array}$
Dioctadecyldimethylammonium bromide	DDDMA	631.0	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_{17} \text{CH}_3 - \text{N}^+ - (\text{CH}_2)_{17} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$

added in the desired initial concentrations. A constant ionic strength of 0.001 M was maintained throughout the experiments using sodium nitrate. In the tannic acid experiments, the solution pH was adjusted to the desired final pH, and in the case of controlled pH experiments, the pH was periodically checked during the adsorption process and adjusted using either HCl or NaOH; a minimal headspace was allowed to insure good mixing throughout the adsorption experiment. In the TCB experiments, the tubes were completely filled to insure a zero-headspace procedure, and seven glass beads of 6 mm diameter were added to maintain complete mixing in the subsequent steps. The tubes were shaken on a rotary shaker (3 rpm), and covered during this time by a light shield box to prevent photochemical reactions, since tannic acid solutions have been reported as light-sensitive (Dentel *et al.*, 1995). A reaction period of 18–24 h was allowed, based on preliminary kinetic experiments showing that the tannic acid solution concentration had stabilized within this period. Following the reaction period, the tubes were allowed to settle and samples were taken for analysis of residual aqueous concentrations. Phase separation for tannic acid was achieved by filtration using 0.45 μm membrane filters, and a Hewlett-Packard 8542A UV-visible spectrophotometer was used for the analysis, at a wavelength of 276 nm. The effect of pH on the UV absorbance was also accounted for in the analysis. Control experiments included tannic acid alone; tannic acid with unmodified clay; TCB alone; TCB with unmodified clay; and TCB with surfactant. Control results all supported validity of the analytical techniques and data interpretation.

TCB analyses

Samples were analyzed for TCB using a Hewlett-Packard 5890 Gas Chromatograph with an HP1 capillary column and flame ionization detector. Prior to the analysis, a 20 mL sample from the supernatant liquid was transferred to a glass tube containing 10 mL of hexane and was vigorously shaken. A 7.5 mL sample was then taken and filtered through a 0.45 μm membrane filter into a glass vial containing 1.0 mL of 200 ppm-4-bromophenol internal standard. Control experiments showed complete recovery of the TCB.

X-ray diffraction analyses

The clays were prepared for X-ray analysis in series of one-liter beakers, where in each, two grams of the clay were dispersed. The surfactants were then added in

amounts to completely replace the CEC of the clay, and the suspension was mixed for 24 h. The mixture was centrifuged to separate the phases, and the treated clays were freeze-dried. The X-ray diffraction analyses for the organo-clays with tannic acid were prepared in a similar manner, but included the addition of tannic acid to the organo-clays. The X-ray analyses were obtained for the air-dried organo-clays using packed powder slides.

The X-ray diffraction unit was a Philips Electronics high angle goniometer model equipped with a copper target tube. Scanning rate was 1° (2 θ)/min for all diffractograms.

RESULTS

Uptake of surfactants by montmorillonite

Experiments were first performed to determine the percent of the added surfactants actually retained by the clay. The results, reported more completely elsewhere (Jamrah, 1993), are exemplified in Fig. 1. The isotherms allow surfactant amounts actually associated with the clay to be reported, as given in Table 2. These amounts were utilized in subsequent analyses; some previous researchers have assumed complete uptake of surfactants contrary to results in Table 2.

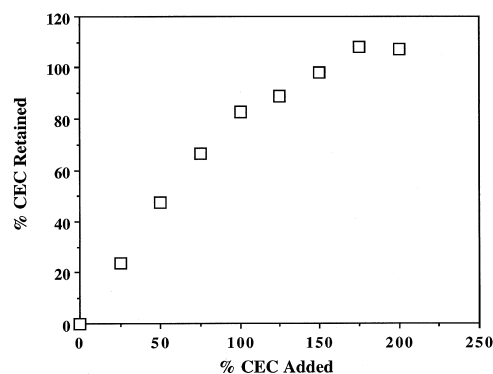


Fig. 1. HDTMA uptake on montmorillonite vs amount added, expressed as a percentage of the CEC. Surfactant concentrations determined as given in Jamrah (1993).

Table 2. Surfactant retention on montmorillonite, and surfactant effect on partition coefficient of 1,2,4-trichlorobenzene

Surfactant	% CEC added	% CEC exchanged	K_p (L/g) ^a	Intercept ^a (mg/g)	r^2 ($n = 6$)	K_p /CEC exchanged ^a
TMA	500	95.3	0.184 ± 0.077	-0.409 ± 1.013	0.884	0.193 ± 0.081
HDTMA	35	33.0	0.345 ± 0.069	0.048 ± 0.891	0.979	1.045 ± 0.209
HDTMA	70	59.0	0.715 ± 0.072	-0.165 ± 0.722	0.995	1.212 ± 0.122
HDTMA	100	82.7	1.318 ± 0.167	-0.329 ± 1.221	0.992	1.594 ± 0.202
HDBDMA	100	89.1	3.143 ± 0.586	-0.777 ± 2.537	0.982	3.527 ± 0.658
DDDMA	100	91.9	4.478 ± 0.955	0.094 ± 3.301	0.977	4.873 ± 1.039

^a95% confidence intervals given. For K_p /CEC values, uncertainty in CEC exchange values are not incorporated.

Tannic acid as sole sorbate

Influence of pH. The effect of pH was evaluated by conducting an adsorption experiment for tannic acid onto montmorillonite modified to 83% of the CEC with HDTMA at pH values between 5 and 8. The results, depicted in Fig. 2 as apparent partition coefficient ($K_p = q_e/C_e$) vs pH, show that the pH is not an important factor in determining tannic acid uptake. The values are indicated as *apparent* partition coefficients since neither linear isotherms nor a partitioning mechanism can be inferred from these results.

All subsequent experiments were performed in the pH range 5–6.5, including those using 1,2,4-TCB, which does not exhibit acid–base behavior.

Effect of surfactant used. The isotherms for tannic acid uptake by montmorillonite modified to 100% of the CEC with the four surfactants are shown in Fig. 3. Ordinate units are mass sorbed per mass of original clay content to facilitate comparison of the isotherms.

The isotherms in Fig. 3 are all nonlinear. The adsorption of tannic acid onto the clay modified with TMA is unfavorable and only slightly greater than with the original clay. These results also demonstrate quantitative recovery of the tannic acid added in these experiments.

In contrast, the long-chain organic surfactants increased the uptake of tannic acid considerably, exhibiting favorable isotherms. The HDBDMA-clay

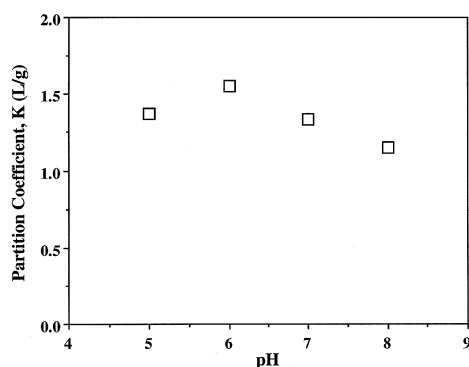


Fig. 2. The apparent partition coefficients of tannic acid onto 83% HDTMA-modified montmorillonite vs pH. ($C_o = 50$ mg/L, $I = 0.001$ M, $m = 50$ mg, and $V = 50$ mL).

and DDDMA-clay both possess particularly high capacities for tannic acid. The HDBDMA and the DDDMA both occupied *ca.* 90% of the CEC; due to the DDDMA's greater molecular mass, the amount of tannic acid removed per mass of organic carbon in the DDDMA-clay is substantially lower than for the HDBDMA-clay. In this case, the sorbent's organic carbon content clearly is not correlated to the extent of tannic acid uptake. Combined with the nonlinearity of the isotherms, this indicates that *adsorption* is the likely uptake mechanism for tannic acid by the modified clays. This is consistent with the findings of Dentel *et al.* (1995), who reported similar isotherms for the adsorption of tannic acid onto montmorillonite modified with DDDMA and partially exchanged with Na^+ or Ca^{+2} . These investigators also reported different adsorption capacities for the organo-clay exchanged with Na^+ and Ca^{+2} , which is consistent with, and supportive of, the secondary role played by the organic content of the clay.

Effect of surfactant on basal spacing. X-ray diffraction analyses were also performed following tannic acid adsorption to the organo-clays. A 6 mg/L addition of tannic acid was used to provide approximately 3 mg/L initial organic carbon (cf. Najm

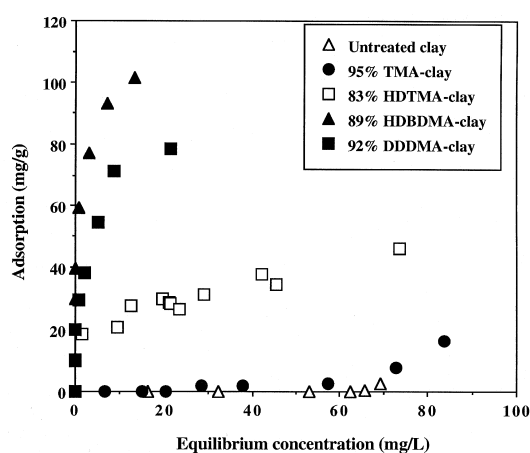


Fig. 3. Isotherms of tannic acid onto original and surfactant-modified montmorillonites. ($C_o = 10$ – 100 mg/L, $I = 0.001$ M, $\text{pH} = 5.0$ – 6.5 , $m = 50$ mg, $V = 50$ mL). Sorption quantities are given per unit mass of original clay, excluding the surfactant mass.

Table 3. Basal spacings of the montmorillonite and modified clays in the presence and absence of tannic acid

Clay or organo-clay	Basal spacing (Å)	
	No tannic acid	6 mg/L tannic acid
Montmorillonite (Mt)	12.150	
Mt-TMA	14.060	14.034
Mt-HDTMA	20.280	20.340
Mt-HDBDMA	19.290	18.990
Mt-DDDMA	20.210	20.230

et al., 1990). Individual diffractograms are presented in Jamrah (1993). The results, summarized in Table 3, show that there is no significant difference in the basal spacings of the modified clays in the presence and in the absence of tannic acid. This suggests that the tannic acid is being excluded from interstitial sorption sites because of its polarity and relatively high molecular mass (1700 g/mol). Nor is there evidence of organic cation extraction from the interlayers due to the tannic acid, which would lead to some decrease in the interlayer dimensions.

Scanning force microscopy results presented by Stapleton (1995) suggest that HDTMA added to montmorillonite locates itself not only interstitially, but also in external monolayers and, at 70% and 100% CEC additions, as external hemimicelles. Electrophoresis results of Jamrah (1993) support this hypothesis. These external structures would be likely sites for tannic acid uptake by electrostatic attraction. No increase in interstitial dimensions would accrue. Thus, though speculative, this hypothesis is consistent with the results presented in Table 3 and Figs 3 and 4.

Heats of adsorption for tannic acid uptake by an organo-clay. Added evidence of an adsorptive association between the tannic acid and organo-clays was provided by determination of the isosteric heats of adsorption for tannic acid uptake by HDTMA-montmorillonite. Isotherms were determined at

both 25°C and 37°C (Jamrah, 1993), fitted to Freundlich isotherms, and the Clausius–Clapeyron equation (Barrer, 1978; Smith and Jaffé, 1991) used to determine the heat of adsorption as a function of equilibrium concentration. The removal of tannic acid from solution increased significantly with increased temperature. The heats of adsorption, given in Fig. 4, show that the process is quite exothermic with values between –31 and –112 kcal/mol. Thus partitioning, which is largely entropic in nature, can be ruled out as an uptake mechanism for the tannic acid on HDTMA-montmorillonite.

1,2,4-trichlorobenzene as sole sorbate

The isotherms of 1,2,4-TCB onto surfactant-modified montmorillonite and onto the unmodified clay are shown in Fig. 5. The indicated % CEC replacement by surfactant was determined from analyses as exemplified in Fig. 1. Limits on the maximum final concentration attainable for each isotherm resulted from solubility restrictions on the initial TCB concentrations, degree of uptake, and use of constant clay concentration for all tests. Results shown for montmorillonite without any organocation treatment indicate no significant uptake of TCB, and thus demonstrate that the analytical recovery of added TCB was virtually complete.

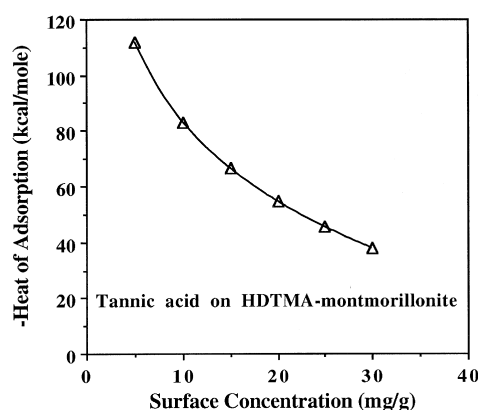


Fig. 4. Isosteric heats of adsorption for tannic acid onto HDTMA-montmorillonite. ($C_o = 10\text{--}100\text{ mg/L}$, $I = 0.001\text{ M}$, $\text{pH} = 5.0\text{--}6.5$, $m = 50\text{ mg}$, $V = 50\text{ mL}$, $T_1 = 25^\circ\text{C}$, $T_2 = 37^\circ\text{C}$).

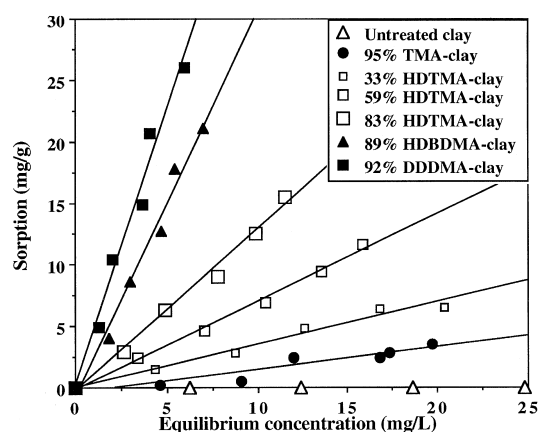


Fig. 5. Isotherms of 1,2,4-trichlorobenzene onto montmorillonite modified with different surfactants and indicated percent replacements of CEC. ($C_o = 5.0\text{--}30.0\text{ mg/L}$, $I = 0.001\text{ M}$, $\text{pH} = 5.0\text{--}6.0$, $m = 50\text{ mg}$, $V = 50\text{ mL}$).

All isotherms appear to be linear over a wide range of aqueous equilibrium concentrations, up to about 70% of the aqueous solubility of 1,2,4-TCB. This is consistent with previous reports (Boyd *et al.*, 1988a; Lee *et al.*, 1989; Smith *et al.*, 1990) on uptake of other hydrophobic organics by organo-clays. Linear regressions were thus performed for each isotherm, with results given in Table 2 and also depicted on Fig. 5. All regression lines pass through the origin within statistical (95%) confidence limits, and with the exception of the TMA-modified clay, all r^2 values exceeded 0.97. The non-linear isotherm characteristics reported by Sheng *et al.* (1996b) were not exhibited, because these only became apparent when the relative concentration exceeded 70%.

Of interest is a comparison to the 1,2,3-TCB used by Lee *et al.* (1989). Its partition coefficient with a TMA-smectite was approximately half that found herein for 1,2,4-TCB uptake by TMA-montmorillonite. Because the 1,2,3-TCB exhibits somewhat lesser solubility and a greater partitioning tendency (Mackay, 1992), the differences in results may be due to stereochemical effects.

Effect of varying CEC replacement for HDTMA. HDTMA was used to replace three differing percentages of the CEC (33, 59, and 83%). Three dissimilar isotherms resulted (Fig. 5), with more TCB uptake occurring when more surfactant was incorporated into the clay. Normalization for surfactant content was accomplished by reporting the sorbed TCB amount per mass of surfactant organic carbon present in the modified clay, based on the %CEC replacement and the surfactant molecular masses. Results of this conversion are shown in Fig. 6.

The normalized isotherms for HDTMA-modified clays are nearly superimposable, indicating that partitioning is the uptake mechanism. This result is consistent with earlier findings of Boyd *et al.* (1988a) for benzene and TCE uptake by HDTMA-modified smectites. The isotherm for the 83% HDTMA replacement is still somewhat higher,

suggesting that greater affinity is provided as interlamellar zones become more completely hydrophobic.

Comparisons of sorption using different surfactants. The TCB isotherms onto montmorillonite modified to 83–95% of the CEC using four different surfactants may also be compared in Figs 5 and 6. Sorption capacities of these clays increase in the order $DDDMA > HDBDMA > HDTMA > TMA$, which is the same order as their organic carbon content. Partition coefficients, K_p , for the isotherms were obtained as slopes from linear regression in Fig. 6 and are presented in Table 2. The values increase with alkyl chain length (or number of carbon atoms in the chain). This has been explained by Boyd *et al.* (1988a) and Lee *et al.* (1989) by considering the alkyl groups of the surfactants to be analogous to an organic solvent into which non-ionic organic compounds are solubilized.

The nature of the hydrophobic zone created in the spaces of the modified clay will vary with the surfactant added. Thus, the organophilic nature and the ability of this zone to solubilize organic compounds will also vary, as indicated by Fig. 6. The figure converts the isotherms of Fig. 5 to the amount of 1,2,4-TCB sorbed per gram organic carbon of the modified clay. Also shown is an isotherm of 1,2,4-TCB onto a sandy loam soil with an organic carbon content of 2% (DiVincenzo and Dentel, 1996).

The figure shows that the sorption capacity, expressed in mg TCB/g organic carbon, decreases in the order: $DDDMA = HDBDMA > HDTMA > TMA > \text{Soil}$. Evidently, both the amount and the nature of the organic carbon content are important factors in the partitioning removal of organic compounds. On the basis of their partition coefficients, the organic carbon fractions in TMA, HDTMA, HDBDMA, and DDDMA are, respectively, about 4, 9, 16, and 15 times more effective on a mass basis than is the soil's organic carbon in removing TCB from solution. This is consistent with the work of Garbarini and Lion (1986), who showed that the affinity of soil organic matter for nonionic organic compounds varies considerably and cannot be explained solely by organic carbon content. Lee *et al.* (1989) also reported the HDTMA cation to be much more effective than natural organic matter in removing non-ionic organic compounds from water.

This result can also be used to explain the differences in the partition coefficients of HDTMA-clay obtained in Figs 5 and 6. As shown in Table 2, the three K_p values are similar when normalized to the fraction of the CEC exchanged. The K values for the lower percent coverage are less than that at full coverage because, at 100% of the CEC, the K value is based on the total organic carbon of the sample: natural organic carbon (0.95%) plus the added carbon from the surfactant (7.1–17.3%) (DiVincenzo

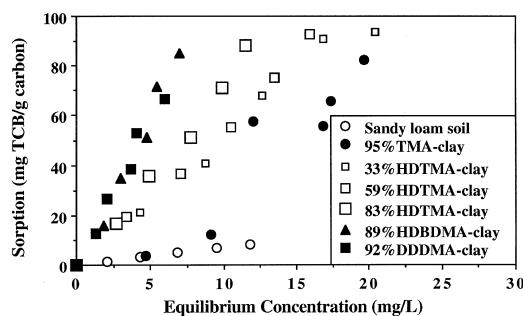


Fig. 6. Isotherms of 1,2,4-trichlorobenzene onto montmorillonite modified with different surfactants, and onto a sandy loam soil, as related to organic carbon content. ($C_0 = 5.0$ – 30.0 mg/L, $I = 0.001$ M, $pH = 5.0$ – 6.0 , $m = 50$ mg, $V = 50$ mL).

and Dentel, 1996). Since HDTMA is 9 times more effective than natural organic carbon, as the total organic carbon content decreases due to the decrease in the fraction CEC exchanged, the relative percentage of the natural organic carbon increases. This leads to a slight decrease in the K_p value.

The uptake mechanism of non-ionic organic compounds by TMA-modified montmorillonite is a subject of disagreement among researchers. While this work suggests that partitioning is the uptake mechanism for 1,2,4-TCB, Lee *et al.* (1989) have indicated an adsorptive mechanism for such uptake, although obtaining a linear isotherm for the sorption of 1,2,3-TCB onto TMA-smectite. Their conclusion was based on the following: (1) a nonlinear isotherm was observed for sorption of benzene by TMA-smectite, but a linear isotherm with HDTMA-smectite; (2) more soluble compounds such as benzene showed strong affinity for TMA-smectite, despite the fact that with a partitioning mechanism, the higher the water solubility, the lower the partitioning coefficient; and (3) the uptake of benzene from aqueous solution was higher for TMA-smectite than for HDTMA-smectite, although TMA-smectite has a much lower organic carbon content than that of HDTMA-smectite. Our results suggest that while this might be the case for benzene, it is not the case for 1,2,4-TCB. Supportive of our results is the work of McBride *et al.* (1977) who observed that partitioning onto TMA-montmorillonite was highly favored by small planar molecules such as benzene and phenol, but not large chlorinated benzenes. Furthermore, higher adsorption capacities for 1,2,4-TCB and *o*-dichlorobenzene were observed when HDTMA-montmorillonite was used. The results of McBride *et al.* (1977) led Cadena (1989) to suggest that chlorinated benzene molecules are too large to enter into the interlamellar regions of the TMA-montmorillonite. The results of this study on 1,2,4-TCB and those of Lee *et al.* (1989) on 1,2,3-TCB contradict this supposition.

Binary system: 1,2,4-trichlorobenzene and tannic acid

Sorption of 1,2,4-TCB onto organo-clays. Sorption of 1,2,4-TCB onto the modified clays in the presence of tannic acid is shown in Fig. 7. The uptake of TCB was unaffected by tannic acid, indicating that no site competition exists between TCB and tannic acid. An analysis of variance showed no correlation between initial concentrations of tannic acid and the extent of TCB uptake with a 99% confidence level. Thus, TCB is selectively removed with no significant interference from tannic acid. Similar results have been found for the removal of 2,4,6-trichlorophenol from water by HDTMA-montmorillonite in the presence of tannic acid (Jamrah, 1993).

Comparison with Fig. 2 suggests that tannic acid remains primarily in solution in the presence of the TMA-modified clay, but is mostly adsorbed in the presence of HDBDMA and DDDMA. Thus, tannic

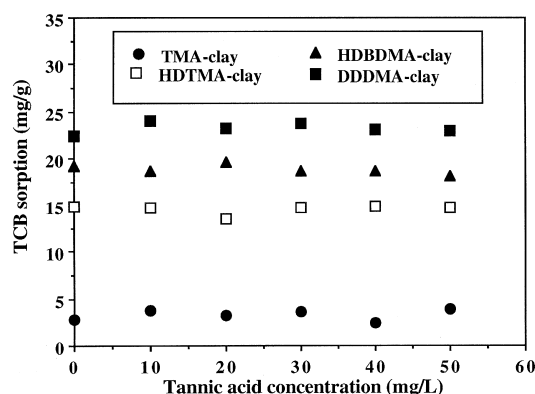


Fig. 7. Sorption of 1,2,4-trichlorobenzene onto montmorillonite modified with different surfactants in the presence of tannic acid. Initial TCB concentrations were 20.1, 25.2, 25.2, and 27.8 mg/L \pm 0.3 mg/L, for TMA, HDTMA, HDBDMA, and DDDMA respectively. Tannic acid C_0 = 10–50 mg/L, I = 0.001 M, pH = 5.0–6.0, m = 50 mg, V = 50 mL.

acid cannot be responsible for TCB removal, since this would lead to different TCB isotherms with varying tannic acid additions to each type of organo-clay. Because TCB uptake remains constant for all of these conditions, the uptake mechanisms are independent.

Effect of humic acid on TCB sorption. In order to confirm the cosorptive behavior of TCB with a high molecular weight, polar organic, the same experiment was repeated using humic acid, which is a higher molecular weight analog of NOM, obtained from Aldrich Chemical. Its properties have been summarized by El-Rehaili and Weber (1987). Inorganic components (0.07 mM Ca^{+2} , 0.42 mM Mg^{+2} , 0.07 mM CO_3^{-2}) were also added to insure that any possible effects of these ions were observed.

Figure 8 shows the effects of humic acid additions up to 50 mg/L on TCB sorption for the four organic cation-modified montmorillonites. Small increases in sorption are suggested, particularly for those organo-clays with the greater partitioning capability for TCB. Indeed, Chiou *et al.* (1987) have pointed out that commercial "humic acids", as used here, may have significantly greater affinity for nonpolar organics than do the more hydrophilic species actually comprising NOM. Nonetheless, statistical analysis of these and more extensive experimental data (Li, 1994) do not show a statistically significant decrease or increase in TCB sorption due to the Aldrich humic acid.

The results in Figs 7 and 8 suggest that the adverse effects of NOM on the adsorption capacity of activated carbon will not occur in the case of organo-clay sorbents. With carbon, these effects include NOM competition with the targeted compound for adsorption sites, as well as blockage of the adsorbent's micropores (Najm *et al.*, 1990; Carter *et al.*, 1992). In the case of activated carbon

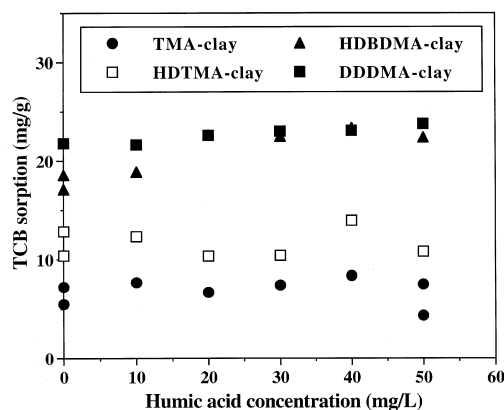


Fig. 8. Sorption of 1,2,4-trichlorobenzene onto montmorillonite modified with different surfactants in the presence of humic acid. Initial TCB concentrations were 26.2 ± 0.8 , 23.7 ± 0.4 , 26.1 ± 0.8 , and 24.7 ± 0.6 mg/L, for TMA, HDTMA, HDBDMA, and DDDMA respectively. Humic acid $C_0 = 10$ – 50 mg/L, pH = 5.0 – 6.0 , $m = 50$ mg, $V = 50$ mL.

columns, these interactions lead to the phenomenon known as preloading, which causes substantial reductions in capacity and breakthrough time (Summers *et al.*, 1989; Speth and Miltner, 1989; Carter *et al.*, 1992). It is apparent from Figs 7 and 8 that such drawbacks may not exist with organo-clays. Further results using continuous-flow column experiments have confirmed this hypothesis (Li, 1994). An additional advantage of the organo-clay sorbents is the ability for chemical rather than thermal regeneration, using either organic solvent or aqueous regenerant (Jamrah, 1993).

CONCLUSIONS

This study has evaluated the ability of organo-clay sorbents to selectively remove lower molecular weight hydrophobic organics from water in the presence of larger, more hydrophilic organics, using 1,2,4-trichlorobenzene (TCB) and tannic acid respectively as representative substances. The study has shown the following:

- The ability of the organo-clays to remove tannic acid increased in the order TMA < HDTMA < DDDMA < HDBDMA, inconsistent with the organic carbon content of the clays. The TMA-modified clay exhibited an unfavorable isotherm, while the other three were favorable. The organo-clays apparently retain tannic acid by an adsorption mechanism.

- Organo-clays remove the hydrophobic sorbate 1,2,4-trichlorobenzene from aqueous solution by a partitioning mechanism. The ability of the modified clays to remove trichlorobenzene increases in the order TMA < HDTMA < HDBDMA < DDDMA, which is compatible with the order of the organic carbon contents of these clays.

- The modified clays were able to sorb trichlorobenzene from water with no significant competition from tannic acid, which does not affect the organo-clays' basal spacings. Commercial humic acid also did not hinder the ability of an organo-clay to remove TCB from solution.

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