

PENTACHLOROPHENOL SORPTION BY ORGANO-CLAYS¹

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Abstract—Several clay organic complexes were prepared by placing organic cations on the exchange sites of smectite clays and studied as sorbents for pentachlorophenol (PCP). The organic cations used ranged from very hydrophobic in nature (e.g., dioctadecyldimethyl⁺ (DODMA⁺)- and hexadecyltrimethyl⁺ (HDTMA⁺)-ammonium) to those having minimal hydrophobic properties, such as tetramethylammonium⁺ (TMA⁺). In general, the more hydrophobic the cation on the smectite the greater the uptake of PCP from water. For the very hydrophobic clays (DODMA⁺- and HDTMA⁺-smectite) the uptake of PCP was via non-polar interactions between the alkyl (e.g., -C₁₈) groups on the organic cation and PCP. In a mechanistic sense, this interaction appeared to be similar to a partitioning process between water and the organic phase of the clay-organic complex. The organic phases of DODMA⁺-smectite were about 10 times more effective than the organic matter of natural sediments for removing PCP from water. For those organo-clays containing small organic cations (e.g., TMA⁺), the organic phase consisted of separate small organic moieties, such as the methyl group. This phase did not act as an effective partitioning medium despite a significant carbon content, and very little PCP was taken up. Results from this study suggest the possibility of treating soils and subsurface materials with large hydrophobic organic cations to enhance the sorptive properties of these natural materials.

Key Words—Adsorption, Hydrophobicity, Organo-clay, Pentachlorophenol, Smectite, Toxic wastes.

INTRODUCTION

The nature of clay-organic interactions has been extensively reviewed in the literature (Mortland, 1970; Theng, 1974; Solomon and Hawthorne, 1983; Mortland, 1986). Mechanisms of interaction include ion exchange, protonation coordination/ion dipole, hydrogen bonding, van der Waals forces, and entropy effects. If a clay mineral has metal cations occupying cation-exchange sites, its surface is hydrophilic because of the water molecules in the hydration shell solvating the cations. Such a surface is not a good adsorbent for removing hydrophobic, poorly water-soluble organic molecules from water. If certain organic cations are placed on the exchange complex by ion exchange, however, the surface becomes hydrophobic and, in turn, organophilic. Organic cations possessing long-chain alkyl groups are particularly able to impart the hydrophobic quality to the mineral surface (Pashley *et al.*, 1985). Such clay-organic complexes are able to sorb molecules which themselves are hydrophobic by what has been called hydrophobic bonding (McBride *et al.*, 1977; Garwood *et al.*, 1983; Wolf *et al.*, 1986; Boyd and Mortland, 1985, 1986; Mortland *et al.*, 1986). This process is essentially a non-polar interaction between the organic phase of the clay organic complex and the hydrophobic organic molecule. A partitioning process has been used to describe the sorption of nonionic

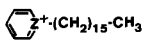


organic compounds by soil organic matter (Chiou *et al.*, 1979, 1983). This mechanism appears to account for many of the fundamental characteristics of non-polar interactions which have often been referred to as hydrophobic bonding.

Mortland *et al.* (1986) showed that phenol and its chlorinated congeners were sorbed by hexadecyltrimethylammonium (HDTMA⁺)-smectite and hexadecylpyridinium (HDPY⁺)-smectite in proportion to the number of chlorine atoms on the phenol structure. Thus, phenol itself was not sorbed significantly by these complexes, but trichlorophenol was strongly sorbed. In other words, as hydrophobicity of the molecule increased, sorption increased. The work reported here is an extension of that wherein pentachlorophenol (PCP), a widespread pollutant in water, was studied with respect to its sorption on a variety of laboratory-produced smectite-organic complexes. The hydrophobic nature of these complexes was varied by placing different organic cations on the clay. Wolf *et al.* (1986) obtained adsorption isotherms for several organic pollutants on several clay-organic complexes. The organic cations they used were primary amines, the cationic nature of which, and therefore, their adsorption as cations on the clay, was very much a function of pH. For that reason we have used quaternary ammonium ions whose cationic nature was not affected by pH and thus remained on the cation-exchange sites of the mineral by coulombic forces, regardless of pH. These clay-organic complexes may be useful sorbents for removing organic toxicants from contaminated waters over a wide range of pH.

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Table 1. Name and structural formula of organic cations on the exchange complex of smectite.

Name	Abbreviation	Structure	Carbon (%) ¹
Diocetyldecyltrimethylammonium	DODMA ⁺	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{N}^+-\text{(CH}_2\text{)}_{17}-\text{CH}_3 \\ \\ \text{(CH}_2\text{)}_{17}-\text{CH}_3 \end{array}$	29.47
Hexadecyltrimethylammonium	HDTMA ⁺	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{N}^+-\text{(CH}_2\text{)}_{15}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	17.32
Hexadecylpyridinium	HDPY ⁺		n.d. ²
Trimethylphenylammonium	TMPA ⁺		6.68
Tetramethylammonium	TMA ⁺	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{N}^+-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	4.01
4-mercaptopyridinium	4-MP ⁺		n.d.
Ammonium	NH ₄ ⁺	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}^+-\text{H} \\ \\ \text{H} \end{array}$	n.d.

¹ Percentage of carbon in the clay-organic complex.

² n.d. = not determined.

METHODS

The clay used was smectite from a Wyoming bentonite furnished by American Colloid Company. Ten grams of the sodium-saturated clay was dispersed in one liter of distilled water and allowed to stand several hours to allow settling of quartz sand and heavy minerals (5.1% of the whole). The suspension was decanted and treated with the bromide or chloride salt of the appropriate organic cation in an amount just equal to the cation-exchange capacity of the clay (90 meq/100 g for the dioctadecyldimethyl⁺ (DODMA⁺), HDTMA⁺, and HDPY⁺-smectites). For the rest of the clay preparations, excess salts were added to promote saturation. A summary of the names, abbreviations, and structural formulae of the organic cation used appear in Table 1. Inasmuch as these organic cations are strongly preferred by the exchange sites over the Na⁺ ions, most of the organic cation went on the exchange complex. Excess organic salt was not added for the DODMA⁺, HDTMA⁺, and HDPY⁺ systems because these organics may be retained by the clay in large excess of the exchange capacity. After the treated clay was washed on filter paper with distilled water, it was frozen, freeze-dried, and stored in bottles for use. Total carbon contents of the clay-organic complexes (Table 1) were determined by Huffman Laboratories (Golden, Colorado).

Sorption isotherms were obtained using the batch equilibration method. Fifty milligrams of clay or carbon was weighed into 125-ml Erlenmeyer flasks. One

hundred milliliters of a saturated solution of pentachlorophenol (7.5×10^{-5} mole/liter) was added to the flask and shaken overnight at 20°C on a rotary shaker. Other concentrations of PCP were also used in the amounts of 80, 60, 40, 20, and 10% of the saturated solution, all made up to 100-ml total volume with distilled water. At the end of the equilibration period, the solid and liquid phases were separated by filtration. PCP concentration in the aqueous phase were measured immediately by UV adsorption. In a competition study, 0.1, 0.2, and 0.5 mmoles of 3,4,5-trichlorophenol per gram of sorbent were added to the above systems; then sorption isotherms of PCP were obtained as above. Standard solutions of PCP (absorption at 318 nm) were made in various concentration levels of 3,4,5-trichlorophenol (absorption at 292 nm). Peak height of the PCP absorption above the shoulder of the trichlorophenol absorption was used to construct standard curves of PCP concentration. Isotherms of PCP on HDTMA⁺-smectite at pH 5.5 and 10.0 were obtained by using the ambient pH for the former and adding drops of NaOH for the latter. Analyses of the equilibrium solutions for PCP were obtained using a Perkin-Elmer 320 spectrophotometer set at 318.3 nm.

¹⁴C-labeled PCP (10 mCi/mole), uniformly ring labeled, was purchased from Pathfinder Laboratories, St. Louis, Missouri, and had a radiochemical purity of >98%. ¹⁴C-labeled PCP and non-labeled PCP were dissolved in methanol, and portions of this solution (10 to 100 μl) were added to flasks containing the clay or carbon (50 mg) and water (100 ml). The equilibra-

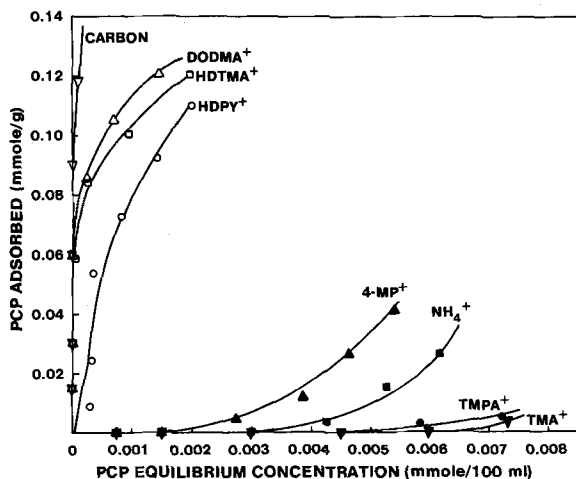


Figure 1. Sorption isotherms (20°C) for pentachlorophenol onto several smectite-organic complexes and carbon from water.

tion was conducted as described above. PCP concentrations in the aqueous phase were determined by assaying 1 ml in 10-ml scintillation cocktails using liquid scintillation counting.

RESULTS

Figure 1 shows sorption isotherms (20°C) of pentachlorophenol onto several modified smectite clays and carbon. Smectite containing DODMA⁺ and HDTMA⁺ as the exchange cations showed no measurable PCP in solution over the first three increments of PCP concentration. Sorption by HDPY⁺-smectite was nearly as effective. In contrast, smectite saturated with tetramethylammonium (TMA⁺) or trimethylphenylammonium (TMPA⁺) cations showed very weak sorption characteristics for PCP. The 4-mercaptopyridinium (4-MP⁺)- and ammonium (NH₄⁺)-clad smectites showed somewhat stronger affinities for PCP, but still gave type V isotherms (Gregg and Sing, 1982), which are typical for weak adsorbent-adsorbate interactions. The weakness of the adsorbent-adsorbate interactions causes the adsorption at low concentrations to be small; but once a molecule becomes adsorbed, it promotes the adsorption of more molecules in a cooperative fashion.

A closer examination of sorption on carbon, DODMA⁺- and HDMTA⁺-smectites at low PCP concentrations was made utilizing ¹⁴C-labeled PCP. These sorption isotherms (Figure 2) show carbon to be the strongest sorbent followed closely by DODMA⁺- and then HDTMA⁺-smectite. The adsorption of PCP by carbon reported here is nearly identical to that reported earlier (U.S.E.P.A., 1980). The isotherms over this concentration range were highly linear even though different sorptive mechanisms may have been operative. Clearly, uptake of PCP by carbon was via surface adsorption.

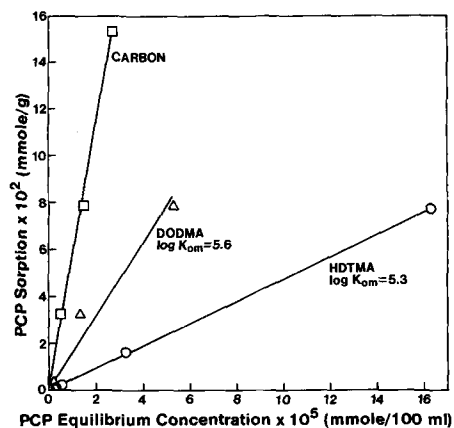


Figure 2. Sorption isotherms (20°C) for pentachlorophenol (PCP) onto carbon and two smectite-organic complexes at very low PCP concentrations utilizing ¹⁴C-labeled PCP.

For DODMA⁺- and HDTMA⁺-smectites uptake resulted from PCP interactions in and between alkyl groups projecting from the silicate surface. This type of organic phase can be viewed as a partitioning medium (Chiou *et al.*, 1979, 1983). Partition coefficients were calculated from the isotherms in Figure 2 to give a relative comparison of the degree of uptake. The partition coefficient *K* was calculated by dividing the amount of PCP sorbed (mmole/g) by the PCP equilibrium concentration (mmole/ml). Because the isotherms were linear, the value of *K* is constant over the concentration range used in Figure 2. The log *K* values for DODMA⁺- and HDTMA⁺-smectites were 5.2 and 4.7, respectively. Normalized on the basis of the organic matter (OM) content (Table 1) ($K_{om} = 100 K/\% OM$), log K_{om} values were 5.6 and 5.3.

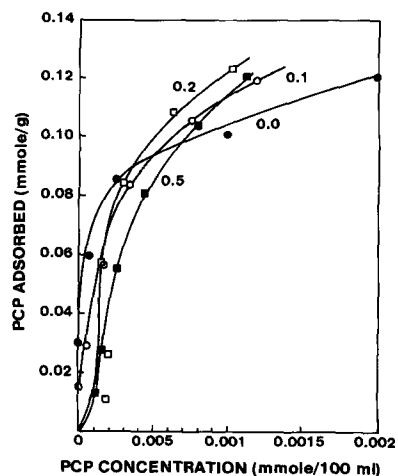


Figure 3. Sorption isotherms (20°C) for pentachlorophenol onto hexadecyltrimethylammonium-smectite in the presence of 0, 0.1, 0.2 and 0.5 mmole 3,4,5-trichlorophenol/g clay.

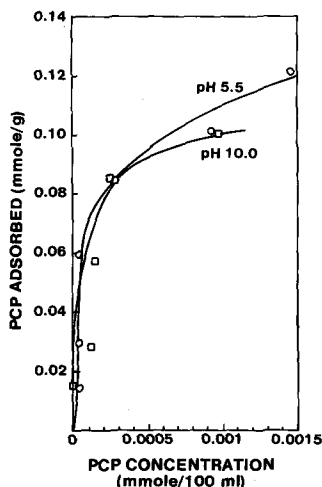


Figure 4. Sorption isotherms (20°C) for pentachlorophenol onto hexadecyltrimethylammonium-smectite at pH 5.5 and 10.0.

Figure 3 shows the sorption isotherms of PCP on HDTMA⁺-smectite in the presence of 0, 0.1, 0.2, and 0.5 mmoles of 3,4,5-trichlorophenol per gram of clay. Results of these studies suggest minimal competitive effects on PCP sorption by HDTMA-smectite. Earlier work has shown that 3,4,5-trichlorophenol is relatively strongly sorbed by HDTMA⁺-smectite, the isotherms being class I (Langmuir) in shape (Mortland *et al.*, 1986); however, its presence at these concentration levels did not greatly alter the sorption of PCP.

Figure 4 compares sorption isotherms of PCP on HDTMA⁺-smectite at pH 5.5 and 10. These data show that the isotherms were not affected by pH. Even though at pH 10, the phenol should have been completely anionic ($pK_a = 4.7$), it was still sorbed strongly by the clay-organic complex. This observation suggests that most of the sorption was non-coulombic and that hydrophobic or non-polar interactions between alkyl groups on the smectite with PCP were probably the chief mode of interaction. Schellenberg *et al.* (1984) observed a significant uptake of the pentachlorophenolate ion by the organic matter of natural sediments.

It was also of interest to find out if sorbed chlorophenols could be removed from the clay-organic complexes. Pentachlorophenol and 3,4,5-trichlorophenol were therefore sorbed from water onto HDTMA⁺-smectite, DODMA⁺-smectite, and carbon and were then extracted with three different solvents using a Soxhlet extractor. The resultant extraction data (Table 2) suggest: (1) at the levels of trichlorophenol (0.2 mmole/200 ml) and pentachlorophenol (0.015 mmole/200 ml) used, almost all was sorbed on the three matrices from water if 0.5 g of sorbent was present; (2) trichlorophenol was more easily extracted than was pentachlorophenol; and (3) the efficiency of extraction varied with solvent, methylene chloride being most efficient, hexane least,

and carbon tetrachloride intermediate. For the most part, it appeared to be easier to extract the chlorophenols from the two clay-organic complexes used, than from the carbon.

DISCUSSION

The data presented here demonstrate the wide diversity of clay-organic complexes for the sorption of PCP. Depending upon the nature of the organic cation placed on the exchange complex of the clay, very little if any sorption of PCP takes place as for TMA⁺-smectite, or extremely strong sorption takes place as for DODMA⁺-smectite. In general, the more hydrophobic the group(s) associated with the quaternary ammonium entity, the greater is the sorption of PCP. The sorbate (here) is also relatively hydrophobic, having a water solubility of less than 20 ppm (20°C).

The sorption process for the very hydrophobic (DODMA⁺- and HDTMA⁺-) clays can be represented as a partitioning of PCP between water and the hydrophobic environment provided by the alkyl groups; the organic phase formed by the alkyl groups bears some resemblance to a bulk organic solvent like hexane or octanol. For these complexes the mineral surface is obscured by the large organic cations. Thus, their sorption behavior is characteristic of an organic sorbent, such as soil organic matter. The $\log K_{om}$ values calculated for DODMA⁺- and HDTMA⁺-smectite compared favorably with the $\log K_{ow}$ (octanol/water partition coefficient) value (5.24) for PCP, and were significantly higher than the $\log K_{om}$ value (4.2) reported for the organic matter of natural sediments (Schellenberg, 1984). The similarity in K_{om} and K_{ow} values is expected for a partitioning-type interaction between PCP and the highly organophilic DODMA⁺- and HDTMA⁺-complexes. Another indication of a partitioning-type mechanism was the lack of a competitive effect on PCP uptake when 3,4,5-trichlorophenol was present. Even at levels (0.5 mmole/g 3,4,5-trichlorophenol) that exceeded the maximum uptake of PCP (Figure 3), a significant competitive effect was not observed. For an adsorptive (surface) process, a strong competitive effect would be expected because both penta- and trichlorophenol would be competing for the same binding sites. The lack of a competitive effect may be an attractive feature for a system in which it is necessary to remove a mixture of compounds from water.

The clay-organic complexes containing smaller organic cations (TMA⁺, TMPA⁺, 4-MP⁺) or an inorganic cation (NH₄⁺) behaved as conventional mineral sorbents. The organic 'phase' of these complexes is made up of separate small organic moieties, such as the -CH₃ group. This phase does not act as an effective partitioning medium despite a significant carbon content. The mineral surface in these complexes is exposed and

Table 2. Extraction of two chlorophenols from two clay-organic complexes and carbon by 24-hr Soxhlet extraction by three solvents.

Adsorbent	Trichlorophenol			Pentachlorophenol		
	Amt. added to H ₂ O (mmole/200 ml)	Amt. adsorbed (mmole/0.5 g)	Removed by extraction (%)	Amt. added to H ₂ O (mmole/200 ml)	Amt. adsorbed (mmole/0.5 g)	Removed by extraction (%)
Extracted with hexane						
HDTMA ⁺ -smectite	0.200	0.181	42.0	0.015	0.015	10.7
DODMA ⁺ -smectite	0.200	0.196	15.2	0.015	0.015	2.4
Carbon	0.200	0.200	14.0	0.015	0.0148	3.6
Extracted with CCl ₄						
HDTMA ⁺ -smectite	0.200	0.191	43	0.015	0.015	20.5
DODMA ⁺ -smectite	0.200	0.200	70	0.015	0.015	32.0
Carbon	0.200	0.200	35	0.015	0.015	10.0
Extracted with CH ₂ Cl ₂						
HDTMA ⁺ -smectite	0.200	0.180	100	0.015	0.015	71.0
DODMA ⁺ -smectite	0.200	0.200	100	0.015	0.015	60.0
Carbon	0.200	0.200	44	0.015	0.015	6.0

occupied largely by water. Pentachlorophenol is not capable of displacing the strongly held water on the mineral surface. Thus, no mechanism exists for the significant uptake of PCP by these complexes.

If the solvent was changed from water to a more organophilic material, most of the PCP was removed via Soxhlet extraction (i.e., methylene chloride extraction, Table 2). The DODMA⁺- and HDTMA⁺-smectites released PCP much more easily than did carbon in the extraction process. When methylene chloride was used as a solvent, the recovery of sorbed PCP was more than 10 times greater from DODMA⁺- and HDTMA⁺-smectite than from carbon. This property is important in any system in which it is desirable for a sorbent to be recycled.

The large partition coefficients observed for organo-clays, such as HDTMA- and DODMA-smectites, makes these materials attractive sorbents for removing organic toxicants from water. This simple ion-exchange reaction, in which hydrophobic organic cations such as HDTMA are exchanged for naturally occurring ions such as Ca²⁺ or Na⁺, very likely occurs in natural soils or related geologic materials, such as glacial tills. A practical application of this simple reaction may be the *in situ* formation of an organo-clay sorptive phase for the immobilization of organic toxicants present in leachate water. Perhaps one of the most useful applications would be in the construction of landfill liners that make use of subsurface materials such as glacial tills that have significant clay contents. By exposing a portion of the clay liner material to hydrophobic organic cations, during its installation, a sorptive phase could be created that would remove organic contaminants present in the landfill leachate. Such a procedure might be a simple, economical, and effective way to enhance the containment of organic toxicants in waste-disposal reservoirs.

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