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Sorption of methyl-parathion and carbaryl by an organo-bentonite

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Abstract The modification of bentonite clays by cetyltrimethylammonium bromide (CTMAB) surfactant via cation-exchange produces materials (“organo-clays”) with an increased capacity for sorbing organic compounds such as pesticides. The sorption from solutions of two nonionic pesticides, methyl-parathion and carbaryl, by an organo-bentonite has been investigated. The pesticides are partitioned into the surfactant. The distribution coefficients, K_{ss} , show a strong dependence on surfactant loading of the bentonite. The surfactant configuration at the clay surface has a marked influence on the effective volume and density of the bound surfactant. At low surfactant loadings, the K_{ss} values increased, reached a maximum, and then decreased as the extent of loading increased. At low loading levels, the surfactant appears to form a monolayer (organic film) that effectively adsorbs the pesticides, resulting in very high K_{ss} values. At high loadings, the sorbed surfactant appears to form a bulk-like medium that behaves essentially as a distribution phase. As a result, the K_{ss} values decreased appreciably, and became less dependent on the CTMAB loading. Moreover, when the surfactant concentration in water was greater than the critical micelle concentration, the surfactant uptake on the clay reaches a plateau and an increasing fraction of the micelles remain in solution, together with the pesticides which bound to them. The competition for the pesticides between the aqueous micelles and the sorbed surfactant leads to a decrease in distribution coefficients.

Keywords Organo-clay · Pesticides · Sorption

Introduction

The contamination of soils, groundwater, and surface waters by hydrophobic organic compounds (HOCs) is currently a significant concern throughout the world because many of these compounds are detrimental to both human health and the environment. The cleaning up of water contaminated with HOCs is one of the most difficult and expensive goals in environmental engineering. Diverse approaches to removing HOCs from contaminated waters have been devised and developed (Brixie and Boyd 1994; Hayworth and Burris 1997; Boving and Brusseau 2000; Rebhun et al. 1998; Carrizosa et al. 2003; Hanna and Brauer 2004) based on two principles. The first involves the partitioning of HOCs into a mobile phase, increasing the compounds’ mobility. The second principle is the in situ immobilization or fixation of HOCs. Adsorption of HOCs by organo-clays or organo-oxides is an economically and technically feasible remediation approach (Holsen et al. 1991; Nayyar et al. 1994; Sun and Jaffe 1996). According to Boyd and coworkers (Boyd et al. 1991; Xu et al. 1997), surfactants are 10–30 times more effective on a unit-weight basis than natural soil organic matter for sorbing nonpolar or weakly polar organic contaminants. Moreover, soils may be modified in situ by injecting surfactant solutions. The treated soils can intercept and immobilize leached pollutants, preventing further groundwater and aquifer contamination. Cetyltrimethylammonium bromide (CTMAB) has been widely studied for HOC immobilization because it is strongly adsorbed by clays and has little degradability (Yang et al. 2003).

The partitioning of HOCs into surfactant sorbed on soil and mineral surfaces has been well documented. Ko et al. (1998) have examined the partitioning of HOCs into aqueous surfactant micelles and kaolinite-sorbed surfactants. The distribution coefficients (K_{ss}) for sorbed surfactants were highest at low surfactant loadings, decreasing sharply as loading levels increased. Li and

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Bowman (1998) found that the sorption of perchloroethylene by a surfactant-modified zeolite was dependent on the configuration of the bound surfactant molecules, as well as on the fractional organic carbon content. Likewise, Sun and Jaffe (1996) found that the partitioning of phenanthrene into an adsorbed dianionic surfactant phase is generally 5–7 times more effective than into the same surfactant in water. Zhu et al. (2003) attributed the change in HOCs' distribution coefficients on the surfactant-modified solids to the different structures between the sorbed surfactant thin film and bulk-like medium. Laboratory and in situ studies have been carried out to assess the usefulness of surfactants in remediating soils and aquifers that have been polluted by HOCs; mainly monocyclic and polycyclic aromatic hydrocarbons, chlorinated hydrocarbons (West and Harwell 1992; Sahoo and Smith 1997; Pascoe et al. 1998). Similar investigations have been conducted with organic pesticides (Brixie and Boyd 1994; Hermosin et al. 1998; Nir et al. 2000; Carrizosa et al. 2000). Many pesticides are hydrophobic or moderately hydrophobic. Their complex structure and the presence of polar groups in their molecules differentiate them from hydrocarbons and their chlorinated derivatives.

Here, we investigate the sorption of two model hydrophobic organic pesticides, methyl-parathion and carbaryl, by a surfactant-modified bentonite. The main objective is to assess the effect of bound surfactant (CTMAB) concentration on sorption capacity, with particular emphasis on the variation of K_{ss} with surfactant loading. The results may contribute to a better understanding of the impact of a surfactant on the distribution of pesticides between soils/sediments and water.

Materials and methods

Materials

The pesticides methyl-parathion (>99% purity), and carbaryl (>99% purity) were obtained from the Chinese Institute of Pesticide Science, Department of Agriculture, China. Both are solid forms and moderately hydrophobic compounds. CTMAB was of analytical grade and purchased from Shanghai Chemical (China). Methanol was of spectroscopic grade. The natural bentonite used was primarily Na^+ -montmorillonite, collected from Guangdong Province in China. The raw clay was ground to less than 100 mesh. The Brunauer–Emmett–Teller N_2 surface area of the ground sample was $30.8 \text{ m}^2/\text{g}$, the organic carbon content (f_{oc}) was 0.049% w/w, and the cation exchange capacity (CEC) was 74.64 cmol/kg .

Solubility enhancement of organic pesticides by CTMAB

Batch experiments were conducted to quantify the change in pesticide aqueous solubility as a function of the aqueous concentrations of CTMAB. Solutions of varied CTMAB

concentrations were placed in 50-mL Erlenmeyer flasks with glass caps, and methyl-parathion and carbaryl were added to each flask in amounts slightly more than required to saturate the solution. The CTMAB concentrations covered a wide range of values below and above the nominal critical micelle concentration (CMC). Duplicate samples were prepared for each surfactant concentration; these samples were then equilibrated. The flasks were rotated at 150 rpm on a gyratory shaker for 24 h at 25°C , and then centrifuged at 4,000 rpm for 20 min to completely separate the undissolved pesticide. The methyl-parathion and carbaryl in the aqueous phase was analyzed by UV spectrophotometry.

Sorption of CTMAB by bentonite

The sorption capacity of the bentonite for CTMAB was determined by weighing 0.1 g of the clay into 50-mL Erlenmeyer flasks with glass caps and adding 25 mL of 0.005 mol/L CaCl_2 solution containing different amounts of CTMAB. The flasks were placed on a reciprocating shaker for 48 h at 25°C . The solution was separated from the bentonite by centrifugation at 4,000 rpm for 20 min. An appropriate aliquot of the supernatant was removed and analyzed for CTMAB by spectrophotometry. The amount of CTMAB sorbed was estimated from the difference in concentration between the initial and equilibrium solutions.

Sorption of organic pesticides to bentonite

The sorption of methyl-parathion and carbaryl by bentonite from water in the presence or absence of CTMAB was measured as follows: Varied quantities of the pesticides were added to 50-mL Erlenmeyer flasks with glass caps, containing 0.1 g of ground clay in 25 mL of 0.005 mol/L CaCl_2 and a range of CTMAB solutions (0–2,500 $\mu\text{g/mL}$). The suspensions were shaken for 24 h at 25°C on a gyratory shaker at 150 rpm. We had previously ascertained that this time was sufficient for equilibrium to be reached. The suspensions were then centrifuged at 4,000 rpm for 20 min. Aliquots of the supernatant solution were removed and analyzed for both of the pesticides by UV and for CTMAB by colorimetric method. No major changes in the UV spectral pattern of the pesticides were observed over the range of CTMAB concentrations used. The equilibrium concentrations of methyl-parathion and carbaryl were calculated from the final UV readings, while the sorbed amounts were computed simply from the difference between the initial and final pesticide concentrations. All determinations were carried out in duplicate. To eliminate the effect of CTMAB on the analysis of methyl-parathion, blanks with the same CTMAB concentrations, but without organic pesticide, were also analyzed.

Analytical methods

UV spectrophotometry (Shanghai Instrument, China) was used to quantify the pesticides in aqueous solution. The wavelengths used for UV detection were 260 nm for carbaryl and 276 nm for methyl-parathion. The effects of surfactant on the UV spectra of the pesticides were negligible within the range of experimental concentrations. The colorimetric method described by Few and Ottwell (1956) was adapted to quantify aqueous CTMAB concentrations. All analyses used standard external calibration curves over their linear responses and produced results well above the instrumental and method detection limits.

Results and discussion

Solubility enhancement of pesticides by CTMAB in aqueous solution

The change in apparent aqueous solubility of methyl-parathion and carbaryl as a function of the CTMAB concentrations in solution is shown in Fig. 1a,b. The results prove that the data are bilinear; the marked increase in slope indicating the presence of a micellar pseudophase. The value corresponding to the break in the curves approximates the CMC. Previous studies have demonstrated that the sub-CMC slope (s_1) is related to the HOC partitioning coefficient between the surfactant monomer pseudophase and the bulk aqueous phase, while the supra-CMC slope (s_2) is related to the HOC partitioning coefficient between the surfactant micellar pseudophase and the bulk aqueous phase (Kile and Chiou 1989; Edwards et al. 1994). There is not much change in the amount of aqueous phase pesticide at concentrations below the critical micelle level when no micellar phase exists. The apparent water solubility of a solute in a micelle-forming surfactant solution may be mathematically described by (Kile and Chiou 1989):

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc} \quad (1)$$

where S_w^* is the apparent solute solubility at a total stoichiometric surfactant concentration of X ; S_w is the intrinsic solute solubility in pure water; X_{mn} is the concentration of the surfactant as monomer in water ($X_{mn}=X$, if $X \leq \text{CMC}$; $X_{mn}=\text{CMC}$, if $X > \text{CMC}$); X_{mc} is the concentration of the surfactant as micelles in water ($X_{mc}=X-\text{CMC}$); K_{mn} and K_{mc} are the partition coefficients of the solutes between

Fig. 1 Apparent enhancement of **a** methyl-parathion and **b** carbaryl by CTMAB solutions

surfactant monomers and water and micelles and water, respectively. The use of X_{mn} and X_{mc} in volumetric concentrations results in dimensional K_{mn} and K_{mc} values and an advantageous representation when modeling contaminant transport (Hayworth and Burris 1997).

Water solubility enhancement of methyl-parathion and carbaryl by CTMAB at concentrations ranging from below to above the normal CMC was assessed. As defined in Eq. (1), these relationships can be written as $K_{mn}=s_1/S_w$ and $K_{mc}=s_2/S_w$, where S_w is equal to the aqueous solubility of the pesticide in surfactant-free water; s_1 and s_2 are the sub-CMC slope and supra-CMC slope, respectively. The results indicate that water solubility of methyl-parathion and

Table 1 Solubility enhancement data of methyl-parathion and carbaryl with CTMAB and associated K_{mn} , K_{mc} , CMC, and S_w values

Pesticides	Concentration	Equation of solubility enhancement	Corresponding coefficient	K_{mn} (mL/g)	K_{mc} (mL/g)	CMC ($\mu\text{g/mL}$)	S_w ($\mu\text{g/mL}$)
Methyl-parathion	$\leq \text{CMC}$	$Y=0.0533X+56.60$	0.987	941.7	2,332.16	257	56.6
	$\geq \text{CMC}$	$Y=0.132X+35.56$	0.999				
Carbaryl	$\leq \text{CMC}$	$Y=0.012X+40.87$	0.896	292.7	2,780.5	252	41.0
	$\geq \text{CMC}$	$Y=0.114X+15.12$	0.999				

carbaryl was significantly enhanced by CTMAB above the CMC. The data of K_{mn} , K_{mc} , and S_w for pesticides and CMC for surfactant are calculated from the solubility enhancement data and presented in Table 1.

Sorption of CTMAB on bentonite

The batch sorption isotherm in Fig. 2 describes the equilibrium distribution of surfactant between water and the solid. At amounts added less than the CEC, nearly 100% of surfactant molecules are adsorbed onto the solid particles, indicating a very large affinity of the cation to the clay mineral (Boyd et al. 1988). The adsorbed mass increases with surfactant concentrations and eventually reaches a plateau when the CTMAB equilibrium concentration in water is approximately equal to the CMC (about 250 $\mu\text{g/mL}$). The isotherm is distinctly nonlinear and exhibits the characteristics of an L-type curve as previously reported (Lee et al. 2000; Rosen and Li 2001; Mishael et al. 2002; Zhu et al. 2003). The sharpest curvature on the isotherm occurs at an aqueous concentration close to the CMC. This behavior is consistent with those reported by Edwards et al. (1994) and Zhu et al. (2003). Surfactant sorption would be expected to reach a limiting maximum value at the CMC if the sorbing species are monomers because the concentration of monomers is constant above the CMC. On progressing toward this limiting value, the sorbed surfactant (CTMAB) undergoes presumably a structural change from submonolayer to bilayer or multilayer on the solid (Lee and Kim 2002a,b; Li and Ishida 2002, 2003; He et al. 2004a,b). The plateau adsorption, calculated by the Langmuir model, is about 620 mg/g for CTMAB. Surfactant sorption by the bentonite tested was comparatively high based on previous studies with some soils (Zhu et al. 2003). According to our calculation, the plateau value in Fig. 2 corresponds to about 2.3 times the CEC; that is, the CEC corresponds to 273 mg/g. Also, adsorption above the CEC would be accompanied by that of bromide (Lee and Kim 2002b). The saturated capacity of CTMAB is much more than that of the estimated capacity in which the CTMAB sorption to bentonite occurs exclusively by cation exchange. The sharp rise in sorption, up to CEC, can be interpreted as being a change from surfactant monomer sorption to surface coverage by surfactant aggregates that form such bilayer, pseudo-trilayer, and paraffin-like structures, depending on the concentration used, and layer charge of the clay mineral (Lee and Kim 2002a,b; Li and Ishida 2002, 2003; He et al. 2004a,b).

Solid-water distribution of methyl-parathion and carbaryl with CTMAB

The adsorption of methyl-parathion and carbaryl by natural bentonite in the presence of different CTMAB concentrations is shown in Fig. 3a,b. It is noteworthy that the sorption of methyl-parathion and carbaryl from water by a

Fig. 2 Sorption of CTMAB onto bentonite

natural bentonite increased to a maximum and then decreased as the CTMAB concentration increased. In the presence of a surfactant in a solid–water system, two competitive processes affect the distribution of organics between the aqueous phase and the solid phase: (1) partitioning of organics into aqueous phase surfactant micelles and (2) sorption of organics by the sorbed surfactant (Edwards et al. 1994; Sun et al. 1995). Depending on the net effect of these two processes, the apparent solute solid–water distribution coefficient (K_d^*) in a mixture containing surfactant may increase or decrease relative to the intrinsic distribution coefficient (K_d) of the same solute without surfactant. At low CTMAB concentrations, CTMAB is sorbed preferentially by cation exchange onto the solid surface to form an “adsorbed film,” and then further sorption at high CTMAB concentrations creates a partition-like medium, which may be viewed as a surface-micelle phase (Mishael et al. 2002; Polubesova et al. 2005). The alternate explanation for our results is that some enhancement of pesticide sorption on bentonite is due to the formation of such thin film by adsorption of CTMAB, whereas there is also enhancement due to binding of the pesticides to the surface-micelle phase. When CTMAB concentration is further increased, the surfactant uptake on the clay reaches a plateau and an increasing fraction of the micelles remain in solution, together with the pesticides which bound to them. This explains the observed maximum in Figs. 3, 4, and 5.

The relationship between K_d^* and K_d for a subsaturated contaminant in a soil/solid–water mixture with or without a surfactant as a function of the contaminant level in solid and solution phase has been established (Sun et al. 1995; Lee et al. 2000),

$$K_d^* = K_d(1 + f_{\text{SOC}}K_{\text{SS}}/K_d)/(1 + K_{\text{mn}}X_{\text{mn}} + K_{\text{mc}}X_{\text{mc}}) \quad (2)$$

where K_d^* is the ratio of bound solutes to mobile ones in the presence of surfactant. $K_d = f_{\text{oc}}K_{\text{oc}}$ is the solute distribution coefficient with the solid without the addition of surfactant, in which case $K_{\text{mn}}X_{\text{mn}} + K_{\text{mc}}X_{\text{mc}} = 0$. f_{oc} and f_{soc} are the mass fractions of natural organic-carbon and the sorbed surfac-

Fig. 3 The sorption of **a** methyl-parathion and **b** carbaryl as a function of CTMAB concentration. The data in the *small box* in the upper right corner are the concentrations of pesticides in the system

tant organic-carbon in the solid, respectively, and K_{oc} and K_{ss} are the carbon-normalized solute distribution coefficients with the natural organic matter and the sorbed surfactant in solid, respectively. However, it is noteworthy that Eq. (2) does not differentiate the pesticide distribution coefficients that resulted from the structural change between “adsorbed film” and the surface-micelle phase.

The K_d^* values for methyl-parathion and carbaryl on bentonite with CTMAB are calculated and the relationships between K_d^* values of pesticides and CTMAB concentrations are presented in Fig. 4. In the absence of CTMAB, K_d^* is equal to K_d . The K_d values for pesticides are proportional to f_{oc} values. Distribution coefficients of methyl-parathion

Fig. 4 The apparent distribution coefficients of pesticides in relation to CTMAB concentration

Fig. 5 The K_{ss} values of **a** methyl-parathion and **b** carbaryl in relation to the CTMAB concentration

and carbaryl to bentonites in water without CTMAB are 290.16 and 197.32 mL/g, respectively. At low aqueous CTMAB concentrations, K_d values increase with increasing surfactant concentration because the amount of CTMAB adsorbed to bentonite increases rapidly in this region, and because the sorbed CTMAB is very effective for solute partitioning. As shown, the K_d^* values are higher than the K_d values, which indicates that the level of CTMAB applied decreases the pesticide mobility, a trend noted for other contaminants at low-to-moderate surfactant levels when the solid has a low f_{oc} value (Lee et al. 2000). When the concentration of CTMAB in the solution reaches its CMC, surfactant sorption to bentonite levels off to a plateau and the micelles that form in solution compete for pesticide molecules, causing a decrease in K_d^* .

From previously determined K_d^* and K_d values, the solute solubility enhancement factor with CTMAB [i.e., $(1+K_{mn}X_{mn}+K_{mc}X_{mc})$], and solid f_{soc} values, K_{ss} values can be calculated for each distribution data point using Eq. (2). Figure 5a,b shows the dependence of the K_{ss} values for pesticides on CTMAB equilibrium concentration. Both the K_{ss} and X values are very high; the logarithms are simply used to show the relationship between them. As the amount of sorbed surfactant on the bentonite increases, the respective K_{ss} values increase sharply to a maximum at low surfactant concentration and then decrease with increasing surfactant concentration. K_{ss} values for CTMAB calculated directly from each pesticide distribution data point are always larger than the corresponding micellar K_{mc} and solid K_{oc} values. The results are consistent

with those reported by Ko et al. (1998), who found that sorbed surfactant [sodium dodecyl sulfate (SDS), Tween 80] distribution coefficients were generally larger than the micellar partition coefficients. Nayyar et al. (1994) reported a similar finding for the polar compound naphthol in SDS-alumina systems. This observation has been attributed to differences in structure between sorbed and dissolved surfactant aggregates. Li and Bowman (1998) demonstrated that the perchloroethylene distribution coefficient on surfactant-modified zeolite is a function of CTMAB loading and resultant organic phase density. Perchloroethylene is most efficiently sorbed by surfactant-modified zeolite when the surfactant is present at or below full monolayer coverage. At higher surfactant loading levels, perchloroethylene sorption is apparently limited by a reduced effective volume and an increased density of the hydrophobic core of the sorbed surfactant bilayer. Zhu et al. (2003) reported very high K_{ss} values at low surfactant concentrations and a subsequent decrease of K_{ss} . This observation can be explained on the basis of a change in the structure of the sorbed surfactant. The very high K_{ss} values at low surfactant levels suggest that the sorbed surfactant acts as a surface film on which the contaminant adsorbs, rather than as a partition phase. These results from different investigators are in agreement with our present observation that pesticide sorption is partly dependent on the surfactant configuration at mineral surfaces (Holsen et al. 1991; Ko et al. 1998). Our results reinforce the notion that the structure of natural organic matter, as well as quantity, controls the sorption of nonpolar organics to soils and solids.

In summary, a CTMAB-modified bentonite is an effective sorbent for the removal of methyl-parathion and carbaryl pesticides from water. The distribution coefficient for these pesticides is influenced by the surfactant loading and the resultant organic phase density. The pesticides are most efficiently sorbed when CTMAB is present at or below full monolayer coverage, which functions as an adsorptive surface rather than a partition phase; the reverse is true at high surfactant loadings. The greater hydrophobicity of the monolayer as compared to the bulk-like medium may also contribute to the greater sorption efficiency of the monolayer system. This is reflected by the very large K_{ss} values at low CTMAB levels and the subsequent large reduction to values comparable with the solution micellar K_{mc} values. Our results indicate that organo-bentonites containing up to a monolayer of CTMAB can effectively remove nonionic pesticides from water.

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