Sorption of 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT) by clays and organoclays

Rong-Ling Dai · Gang-Ya Zhang · Xiao-Zhi Gu · Ming Kuang Wang

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Abstract This study focused on the sorption isotherms of 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-DDT) and 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene (p,p'-DDE) on different original clays (i.e., zeolite, montmorillonite and attapulgite) and organoclay complexes. Sorption of organic pollutants was determined using gas chromatographic (GC) techniques to investigate the sorption behavior, and characterize the effect of, different organic cations. The original clays only sorbed low amounts of p,p'-DDT and p,p'-DDE, and the sorptive curves can be classified as L-shaped. Organoclays exhibited higher amounts of p,p'-DDT and p,p'-DDE sorption. The p,p'-DDT and p,p'-DDE sorption increased with increasing total organic carbon (OC) content of the organoclays. For hexadecyltrimethylammonium (HDTMA)-modified organoclays, the dominant adsorptive medium showed the partitioning sorption of hydrophobic–hydrophobic interaction, indicating no competitive sorption. The sorptive curves can be classified as C-shaped of constant partition (CP). However, benzyltrimethylammonium (BTMA)-modified organoclays exhibited competitive sorption. The sorption isotherm curves can be classified as S-shaped. The sorptive capacity of the HDTMA-modified organoclays for p,p'-DDT were higher than those for p,p'-DDE, but the BTMA-modified organoclays showed a reverse trend. This can be attributed to the different structures and shapes of organic cations, giving different sorptive mechanisms. The p,p'-DDT and p,p'-DDE sorption onto HDTMA-modified organoclays were caused by chemical interaction, with the BTMA modified organoclays occuring due to physical sorption.

Keywords p,p'-DDT · p,p'-DDE · Adsorption · Clays · Organoclays

Introduction

1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-DDT), which is an organochlorine pesticide (OCP), is a typical persistent organic pollutant (POP). Because of its persistence, low volatility, bioaccumulation potential and high toxicity, it is a major environmental
issue, drawing much scientific and public attention. The $p,p'$-DDT can transferred throughout the food chain and pollute the entire ecological environment, also posing problems to human health. Under aerobic and anaerobic conditions, $p,p'$-DDT can decompose, and commonly its metabolites are 1,1-dichloro-2,2-bis($p$-chlorophenyl) ethylene ($p,p'$-DDE) and 1,1-dichloro-2,2-bis($p$-chlorophenyl) ethane ($p,p'$-DDD). Both of them are dangerous and toxic compounds. In spite of the ban on the use of DDT for many years, DDT and its metabolites of $p,p'$-DDE (DDE) and $p,p'$-DDD (DDD) have been reported recently in different environmental media, including soils, waters, air, plants and animals (Andrade et al. 2005; Binelli et al. 2003; Giesy et al. 2001; Kosubova et al. 2005; Tao et al. 2005; Shen et al. 2005; Zhang et al. 2005; Zhao et al. 2005). It has been over 20 years since China banned the use of $p,p'$-DDT, but the ratio of DDT/DDE in soils indicates that new inputs could be present in the soils (Chen et al. 2005; Gao et al. 2005; Shi et al. 2005). Removal of DDT, DDE and DDD from contaminated soils and wastewaters is critical in order to ensure the safety of farm produce for human and animal consumption.

For soils that are contaminated by organic pollutants, there are usually two kinds of remediation technologies available, namely in situ and ex situ remediations. Ex situ remediation may gradually be replaced by in situ remediation (Sui et al. 2003). Among the many in situ remediation technologies, remediation of contaminated soils and groundwaters by organoclays has been a topic under development (Wang et al. 1997; Pernyeszi et al. 2006; Nzungung et al. 1996; Özcan et al. 2006; Zhou et al. 2006; Oyanedel-Craver et al. 2006; Hermosín et al. 2006). Organoclays are synthesized by exchanging the naturally occurring inorganic cations with organic cations. By exchanging organic cations on the surface of clay minerals, a material with radically different physical and chemical properties is produced (Seki et al. 2005; Jaynes et al. 1991). Modification of clay minerals by ion exchange with organic cations has been shown to have a significant impact on their sorptivity (Richard et al. 2001; Wiles et al. 2005; Klumpp et al. 2004).

In this study, zeolite, Na-montmorillonite and attapulgite were used as original clays. Synthesized organoclays are organophilic rather than hydrophilic, and able to sorb nonpolar organic contaminants, unlike unmodified clays, which are poor sorbents for these compounds (Seki et al. 2005; Redding et al. 2002; Yasser et al. 2004). Because the naturally occurring inorganic cations in the interlamellar spaces and on the surface of clays are not part of the inter-clay structure, they can easily be replaced by organic cations (Smith et al. 1995). Sorption of hydrophobic organic contaminants (HOCs) by organoclays can occur via different mechanisms and to different degrees depending on the type of organic cations used, the type of original clay and its cation exchange capacity (CEC), the proportion of CEC satisfied by organic cations, and characteristics of sorbate, such as size, shape, solubility and hydrophobicity (Richard et al. 2001; Redding et al. 2002; Yasser et al. 2004).

This study aimed to evaluate the sorption isotherms of $p,p'$-DDT and $p,p'$-DDE by organoclays and original clays, to characterize the influence of the original clay type and sorbate characteristics on the adsorption behaviour of $p,p'$-DDT and $p,p'$-DDE on organoclays, and to further elucidate the impact of total organic carbon (OC) contents and cation exchange structure on the sorptive properties of two types of organoclays, including HDTMA and BTMA organoclays.

### Materials and methods

The clays used in this study were zeolite (zeo, clinoptilolite), from the mining resources of Quanhu County, Zhejiang Province, China, Na-montmorillonite (mont) purchased from Laiyang County, Shandong Province, China, and attapulgite (atta) supplied by the attapulgite mine at Liuhe County, Jiangsu Province, China. The clays were ground and passed through a <50-μm mesh and kept in plastic bottles at 25°C. Cation exchange capacity and total OC contents of these original clays are listed in Table 1.

Hexane, H2SO4, Na2SO4, Na2SO4 ⋅ 10H2O and methanol were purchased from Nanjing Chemical, China. Hexane, H2SO4, methanol, Na2SO4 and Na2SO4 ⋅ 10H2O are analytical grade reagents, and hexane was re-distilled by means of glass evaporators. Na2SO4 was heated at 650°C in an oven for 4 h, cooled down to 25°C, and stored in a closed glass chamber for further use.
Hexadecyltrimethylammonium (HDTMA) and benzyltrimethylammonium (BTMA) were purchased as bromide salts from Chemical Academe of Changzhou. They had a chemical purity of 99% and were used without further purification. Sorbates of \( p,p'\)-DDT and \( p,p'\)-DDE were powdered compounds. The \( p,p'\)-DDT and \( p,p'\)-DDE were compounds of analytical grade obtained from the Institute of Standard Materials, National Standard of China. These standard compounds were dissolved in hexane to make stock solutions and subsequently diluted to the desired concentrations between 0.1 and 10 mg l\(^{-1}\), which were used for quantitative analysis of samples by gas chromatographic (GC) analysis. The chemical structure and chemical properties of \( p,p'\)-DDT and \( p,p'\)-DDE are shown in Fig. 1 and Table 2, respectively.

Sorbents used in this study were zeolite, montmorillonite and attapulgite clays modified with organic cations, such as HDTMA and BTMA and denoted as zeo-H, zeo-B, mont-H, mont-B, atta-H and atta-B, respectively. HDTMA has an aliphatic group of the trimethylammonium with a long 16-carbon aliphatic hydrocarbon chain attached, and BTMA have an aromatic benzylammonium group without a long hydrocarbon chain attached. Organoclays were prepared by adding 0.1 g of natural clays to 30 ml HDTMA or BTMA solvent (the cation surfactants load on the clays according to 100% CEC of the clays are 0.50, 0.28, 0.08 g HDTMA per gram clay for zeo-H, mont-H, atta-H and atta-B, respectively. Organoclays were equilibrated for 8 h. The suspension was equilibrated at 60°C with continuous stirring for approximate 6 h. Organoclays were then separated by gravity sedimentation followed by being washed five times with 50% (v/v) ethanol–water solution and distilled water until free of Br\(^{-}\) ions (Seki et al. 2005; Richard et al. 2001). The sample was then freeze-dried and ground to less than 50 μm, and stored in plastic bottles at 25°C.

Total OC content can be determined by potassium dichromate capacity under conditions of 25°C and 50% relative humidity. These organoclays were investigated by scanning electron microscope (Jeol, JSM 5310 SEM). For FT-IR spectroscopic analysis, the HDTMA- and BTMA-clays were also freeze-dried and prepared as KBr disks (Nicolet 380 FT-IR) and scanned at 4,000–500 cm\(^{-1}\).

Stock solutions of \( p,p'\)-DDT and \( p,p'\)-DDE were prepared by dissolving the pure chemical into methanol, and working solutions were prepared by dilution of the stock solutions with distilled water. Concentration of methanol in the sorption experiment was less than 5%; thus, its effect on the sorption process is neglected (Richard et al. 2001; Yasser et al. 2004; Nkedi et al. 1985). Fresh working solutions were prepared every time.

The concentrations of DDT and DDE were determined by an HP5890 GC equipped with a \( ^{63}\)Ni electron-capture detector (GC-ECD). The column used was an HP1 quartz capillary with an inner diameter of 0.32 mm, a film thickness of 0.25 μm, and a length of 30 m. The carrier gas used was pure

### Table 1: Selected chemical properties of original clays and organoclays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeo</th>
<th>Zeo-H</th>
<th>Zeo-B</th>
<th>Mont</th>
<th>Mont-H</th>
<th>Mont-B</th>
<th>Atta</th>
<th>Atta-H</th>
<th>Atta-B</th>
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<tr>
<td>CEC (cmol kg(^{-1}))</td>
<td>135</td>
<td>–</td>
<td>–</td>
<td>76</td>
<td>–</td>
<td>–</td>
<td>23</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total OC content (%)</td>
<td>0.03</td>
<td>15.84</td>
<td>12.28</td>
<td>0.08</td>
<td>11.13</td>
<td>8.56</td>
<td>0.05</td>
<td>5.26</td>
<td>4.69</td>
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</table>

### Table 2: Selected chemical properties of sorbates

<table>
<thead>
<tr>
<th>Properties</th>
<th>( p,p')-DDT</th>
<th>( p,p')-DDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass (g mol(^{-1}))</td>
<td>354.5</td>
<td>318.0</td>
</tr>
<tr>
<td>Aqueous solubility at 20°C (mg l(^{-1}))</td>
<td>0.25</td>
<td>1.2</td>
</tr>
<tr>
<td>Log ( K_{ow} )</td>
<td>4.89–6.914</td>
<td>5.69–6.96</td>
</tr>
<tr>
<td>Henry’s constant (( K_H )) (l atm mol(^{-1}))</td>
<td>( 1.29 \times 10^{-5} )</td>
<td>( 0.21 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Fig. 1 Chemical structure of the DDT and DDE compounds
N\textsubscript{2} and the flow rate was 1 ml min\textsuperscript{-1}, and a 2-ml sample was injected in the splitless mode. The oven temperature program started at 140 °C; it was increased to 280 °C at 10 °C min\textsuperscript{-1} with a final hold time of 2 min. Injector and detector interface temperatures were kept constant at 240 and 290 °C, respectively. The peak height of speciation was used for quantification. Typical gas chromatograms of \( p,p' \)-DDE and \( p,p' \)-DDT can be seen from Fig. 2.

Sorption isotherms

Batch sorption of DDT and DDE on original clays and organoclays were conducted at room temperature (25 ± 1 °C). Sorption isotherms of DDT and DDE by original clays and organoclays were conducted in aqueous and organic solvent systems, respectively. Solutions of varying initial concentrations \((C_0)\) were placed into a 30-ml centrifuge tubes containing a known weight of sorbent, and the volume of solution was 20 ml. When adding the solute, took care to avoid volatilization loss of the solvents. A blank tube containing only sorbate and distilled water was utilized to monitor volatilization loss of solutes, glass, and/or Teflon-lined septa for calibration for calculation of sorption. Each treatment was tested in triplicate. After assembly, the batch reactors were rotated at 150 rpm for 24 h to allow for equilibration to take place. A period of 24 h was allowed for the reaction to take place, the tubes were centrifuged at 4,500 rpm (i.e., about 10,000g) for 10 min. The supernatant was extracted with 10 ml hexane and purified using concentrated H\textsubscript{2}SO\textsubscript{4}, and neutralized using 2% of Na\textsubscript{2}SO\textsubscript{4} \cdot 10H\textsubscript{2}O aqueous solution. After drying over anhydrous Na\textsubscript{2}SO\textsubscript{4}, the recovery ranged between 85.7 and 110.1%. DDT and DDE concentrations were then determined by GC and qualified by retention time. The concentrations of DDT and DDE in the supernatant were calculated from the standard curve. Equilibrium solid-phase concentrations \((q_e, \mu g \text{ g}^{-1})\) were determined for each experiment using a mass balance between the initial and equilibrium solution-phase concentrations (i.e., \( C_0 \) and \( C_e, \mu g \text{ ml}^{-1} \)), calibrating the solution volumes \((V, \text{ml})\) and sorbent doses \((D_0, \text{g})\).

\[
q_e = \frac{C_0 - \left( C_e \times \frac{100}{100 - \% \text{system loss}} \right) 	imes 100}{D_0} \cdot V
\]

Statistical analysis

Curves were fitted by means of Microsoft Excel analysis. The means were compared using the least significant difference (LSD) with a probability less than 0.05 \((P < 0.05)\). Correlations were analyzed by calculating the relationship equations and the simple linear correlation coefficients.

Results and discussion

Characterization of organoclays

Total OC content

Total organic carbon (OC) content of organoclay is the most important characteristic that can influence
sorption of organic pollutants. Table 1 shows that total OC content of HDTMA-clay is greater than that of BTMA-clay because the molecular weight of HDTMA is greater than that of BTMA. Total OC content of organoclay increased with increasing original clay CEC, owing to greater amount of organic cationic surfactant sorbed by original clays.

Scanning electron micrographs (SEM)

In general, the surface texture of unmodified clays appears to be irregular in shape, showing the hemstitching phenomenon, while that of modified clays is smoother, showing that a high degree of stretching is a characteristic of the crystals. These indicate that the modifier, after entering the layer of clays, enlarges the spacing of the layer. The specific surface area of modified organoclays is then reduced because the surface of clays are aggregated with the modifier groups and bases. Generally speaking, the response mechanism is ionic exchange when the amount of cationic organic quaternary ammonium compounds added is small. The N-functional group (i.e., positive-charge end or hydrophilic end) of the cationic organic quaternary ammonium compounds which enter the layer of clay through ionic exchange, is sorbed in the clay surface that has a negative charge. The alkyl chain end (i.e., neutral end or hydrophobic end) is outside and far from the surface of the clays. Thus, it causes the organoclay particle to flocculate through hydrophobic bonding between the alkyl chain end members with the organoclay pellets forming aggregates.

Fourier-transform infrared (FT-IR) measurements

Infrared spectra of original clays, cation surfactants and organoclays are shown in Fig. 3a, b and c, respectively. The particular absorbtion peaks are shown in Tables 3, 4 and 5. For original clays, the hydroxide (–OH) that is adsorbed on the surface of the clay showed stretching at 3,430 cm\(^{-1}\), and when the clay is dried, this peak will weaken evidently. Hydroxide (–OH) stretching at 3,697–3,615 cm\(^{-1}\) is in interlayer spacing of clay. From Fig. 3, in addition to the characteristic peaks of clays on infrared spectra of HDTMA-clays and BTMA-clays, there are characteristic peaks of HDTMA and BTMA. And the HDTMA- and BTMA-clay complexes shifted the C–H stretching to a higher wave number. Infrared spectra of HDTMA-clays and BTMA-clays also showed –OH stretching at 3,685–3,615 cm\(^{-1}\), and the stretching intensity is much weaker than that of original clays, which indicate that hydrophilic properties of HDTMA- and BTMA-clay weaken markedly. All of these indicate that HDTMA and BTMA have entered the interlayer spacing of clay (Hsu et al. 2000; Liao et al. 2006).

Sorption isotherms of original clays

The sorption isotherms of DDT and DDE onto the original clays were found by plotting the amount of DDT and DDE adsobed by clays \( (q_e, \mu g \text{ g}^{-1}) \) versus DDT and DDE concentration at equilibrium \( (C_e, \mu g \text{ ml}^{-1}) \). The sorption curves of DDT and DDE on the original clays are shown in Figs. 4 and 5.

In terms of the slope of the initial sorption of the curves, the shapes of the isotherms corresponding to zeo, mont and atta, classified as L-type in the Giles classification (Giles et al. 1960, 1974). This type of isothem implies that zeo, mont and atta have a medium affinity for the DDT and DDE molecules and that no strong competition from the solvent for adsorption sites occurred. The curves tend to a constant value of \( q_e \), indicating the formation of a complete monolayer of DDT and DDE molecules covering the surface of sorbents (Seki et al. 2005).

In order to determine the sorption capacities of original clays, the logarithmic forms of the Langmuir and Freundlich equations were used and showed as following Eqs. 2 and 3, respectively:

\[
\frac{1}{q_e} = \frac{1}{q_m K_a C_e} + \frac{1}{q_m}
\]

\[
\log q_e = \log K_f + n_f \log C_e
\]

where \( q_m \) = the sorption capacity (maximum amount that can be adsorbed by adsorbent as a monolayer \( (\mu g \text{ g}^{-1}) \), and \( K_a \) = binding coefficient. \( K_f \) can be considered as a relative measure of the adsorption capacity, because its value coincides with \( q_m \) when \( C_e = 1 \) in the above equation 3, and thus it can be given in the same units as \( q_m \). It can also be considered as the sorption strength. The \( n_f \) parameter can be determined from the linearity of the
Freundlich sorption isotherm equation 3 (Socias-Viciana et al. 1998).

The DDT and DDE sorptions by original clays were fitted well by both the Langmuir equation 2 and Freundlich equation 3. The correlation coefficients \((R)\) were in three cases greater than 0.95 (Table 6).

The sorption parameters of DDT and DDE on original clays and organoclays corresponding to the Langmuir equation are given in Table 4. As can be seen, \(q_m\) values were 81.3, 292.3 and 227.3 \(\mu g \, g^{-1}\) for DDT on zeo, mont, atta, respectively, and \(q_m\) values were 67.1, 108.7 and 87.7 \(\mu g \, g^{-1}\) for DDE on zeo, mont, atta, respectively. \(K_l\) values were 40.13,
53.74 and 49.93 for DDT in the order of zeo, mont, atta, respectively, and 
K_f values were 11.61, 19.95 and 16.03 for DDE in the order of zeo, mont, atta, respectively (Table 6). In addition, q_m values of DDT on the original clays were greater than those of DDE sorption isotherms.

Sorption isotherms on HDTMA organoclays

The sorption isotherms of DDT and DDE onto organoclays zeo-H, mont-H and atta-H are presented in Figs. 4 and 5, showing a linear relationship between the constant partition sorption of hydrophobic–hydrophobic interaction and the degree of DDT and DDE sorbed by HDTMA organoclays, which increases with increasing CEC of original clays. The trend as seen is of zeo-H > mont-H > atta-H clays.

The linearity of the data supports the conclusion that constant partitioning (CP) is the dominant mechanism of sorption for the HDTMA organoclays, which are composed of long 16-carbon aliphatic hydrocarbon chain cations (Redding et al. 2002; Zhu et al. 2000; Shu et al. 2005; Smith et al. 1990). The linear type of sorption isotherms showed a constant partitioning to the HDTMA organoclays, due to its log K_ow values (i.e., p,p'-DDT of 4.89–6.914 and p,p'-DDE of 5.69–6.96) and hydrophobic–hydrophobic interaction (Table 2, Figs. 4 and 5).

The data were well fitted by the Freundlich equation 3, showing a linear relationship of sorption isotherms of equation 4.

q_e = K_d C_e + b

(4)

where b = linear isotherm parameter, and K_d = distribution coefficient.

The K_d and R values of linear sorption isotherm coefficients are shown in Table 6. The n_I values are close to those reported by Giles et al. (1960, 1974); isotherms of S, L and C-shaped (Beck et al. 1993): n_I > 1 correspond to the S-shaped, n_I = 1 to C-shaped and n_I < 1 to L-shaped. The n_I values of DDT and DDE sorption isotherms on original clays presented as the L-shaped isotherms fitted well for zeo-, mont- and atta-(Figs. 4, 5, and Table 6). In contrast to those of the original clays, the n_I values of the HDTMA organoclays were approximately 1, and the shape of isotherms of organoclays were thus close to C-shaped. The linear equation gave a good fit for HDTMA clays. The correlation coefficients of the three cases are greater than 0.9750. For HDTMA clays, it was anticipated that increasing the total OC content in the clay sample would increase p,p'-DDT and p,p'-DDE sorption, as well as distribution coefficient K_d is also increased. As shown in Table 6, K_d values were 1,292.6, 663.8 and 235.0 l kg^-1 for p,p'-DDT on zeo-H, mont-H, atta-H, respectively, and 971.8, 332.2 and 97.5 l kg^-1 for p,p'-DDE on zeo-H, mont-H and atta-H, respectively. Moreover, K_d values of p,p'-DDT on HDTMA clays were greater than p,p'-DDE sorption.

Sorption isotherms on BTMA organoclays

Sorption isotherms of DDT and DDE on zeo-B, mont-B and atta-B are shown in Figs. 4 and 5. The application of the logarithmic form of the Freundlich equation to the isotherms data gave sorption parameters summarized in Table 6.
Figures 4 and 5, and \( n_f \) parameters in Table 6 showed that the DDT and DDE isotherms of the BTMA clays were all of S-shape (\( n_f > 1 \)). The S-shaped isotherms probably appeared due to the following reasons (Yasser et al. 2004; Giles et al. 1960): (1) the fairly large hydrophobic moiety, the unmarked localization of the forces of attraction for the organoclay complexes over a short section of its periphery, and DDT and DDE sorption as a single unit and not in the form of a micelle; (2) a relatively moderate intermolecular interaction between sorbates and BTMA organoclays, causing DDT and DDE molecules to pack vertically in a regular array in the adsorbed layer; and there was a fixed site of sorption between sorbents and sorbates; and (3) strong competition from solvent molecules, and competition between molecules of adsorbate.

The S-shape signified that BTMA organoclay complexes have a low affinity for DDT and DDE at low concentrations, but that the sorption becomes easier as the concentration of DDT and DDE increases in the liquid phase. Figures 4 and 5 showed that when the concentration exceeded a certain threshold, a drastic increase took place in the sorption observed with the BTMA organoclay complexes. Curvatures of isotherms indicated that DDT and DDE sorption onto zeo-B, mont-B and atta-B were not caused by partitioning, and these results suggested that interaction occurs via physical forces (Yasser et al. 2004). According to the results shown in Table 6, \( K_f \) values of the BTMA organoclay complexes increased in the order of atta-B < mont-B < zeo-B. These values are lower than those of HDTMA organoclay complexes.

The original clays have a low concentration of DDT and DDE sorption. This was due to hydrated mineral surfaces of the original clays and the hydrophobic nature of DDT and DDE molecules. In contrast, the sorption of DDT and DDE onto the organoclay complexes increased dramatically due to hydrophobic–hydrophobic interaction. The degree of DDT and DDE sorbed by organoclay complexes increased in proportion to the increase in the CEC of the original clays. On the other hand, the OC content of organoclays was also proportional to the sorptive capacity of organoclay complexes and enhances their sorption (Allred et al. 1994; Upson et al. 2006).

The total OC contents for HDTMA organoclays are in the order of zeo-H > mont-H > atta-H, while those for BTMA organoclays also showed a similar

### Table 6 Sorption isotherm coefficients for DDT and DDE to original clays and organoclays

<table>
<thead>
<tr>
<th>Adsorbate Adsorbent</th>
<th>Adsorbate Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Linear</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( K_a )</td>
<td>( q_m )</td>
<td>( R )</td>
<td>( K_f )</td>
</tr>
<tr>
<td>( p,p' )-DDT</td>
<td>Zeo</td>
<td>0.23</td>
<td>81.3</td>
<td>0.9870</td>
</tr>
<tr>
<td></td>
<td>Mont</td>
<td>0.26</td>
<td>292.3</td>
<td>0.9503</td>
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<tr>
<td></td>
<td>Atta</td>
<td>0.22</td>
<td>227.3</td>
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<tr>
<td>( p,p' )-DDE</td>
<td>Zeo</td>
<td>0.17</td>
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<td>Mont</td>
<td>0.19</td>
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<td>Atta</td>
<td>0.18</td>
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trend of zeo-B > mont-B > atta-B. It was anticipated that increasing total OC contents in the organoclays would lead to an increase in p,p'-DDT and p,p'-DDE sorptions. For HDTMA organoclays, the order of the adsorptive capacity for p,p'-DDT and p,p'-DDE was: zeo-H > mont-H > atta-H, and BTMA clays also showed a similar trend.

The $K_t$ values indicated that the sorptive capacity of the original clays and HDTMA organoclays for DDT was higher than that of DDE sorption. This could be due to different chemical characteristics of DDT and DDE. On the other hand, the solubility of DDE being larger than that of DDT could also account for the phenomena (Table 2). The extent of sorption of DDT and DDE by original clays and organoclays were observed to be inversely related to the solubility of the organic solvent (i.e., $p_{p'-DDT} > p_{p'-DDE}$). In contrast to HDTMA organoclays, BTMA organoclays demonstrated the opposite trend. The $K_t$ values of BTMA organoclays for DDT were lower than those of DDE. This could be due to different organic cation structures, giving different sorptive mechanisms (Fig. 1). For HDTMA organoclays, it was anticipated that the isotherms would show a linear relationship, because of the long chain of aliphatic hydrocarbons. Cations can induce extractive action (partitioning action) for HOCs from aqueous solution (Redding et al. 2002), but the isotherms of DDT and DDE sorption on BTMA organoclays showed nonlinear relationships presented as the S-shaped sorption isotherms. Compared with the sorption onto HDTMA organoclays, DDT and DDE sorption onto BTMA organoclays are not caused by chemical binding forces, but favors physical sorption. The possible sorption mechanisms involve the interactions between the phenyl rings of the aromatic cation (BTMA) and the polycyclic aromatic ring of DDT and DDE molecules, possibly by $\pi-\pi$ interactions and hydrogen bonding (Yasser et al. 2004).

Conclusions

Comparison of the sorptive behaviour between original clays and organoclays demonstrates several distinct trends. It is clear that the addition of organic cations to the clay surface enhances the sorptive capacity of natural clays. For in situ soil applications such as sorptive barriers, the organoclays perform well due to their ability to swell in the presence of nonpolar liquids, which results in a lower permeability and decreased advective transport. In addition, organoclays like HDTMA-clays do not exhibit competitive sorption behavior, unlike BTMA organoclays. HDTMA-clays may perform better in the presence of a complex mixture of solutes. HDTMA-zeolite showed the best performance in sorption of p,p'-DDT and p,p'-DDE, and has no competitive sorption behavior. In general, the results of this study could be employed to prevent p,p'-DDT and p,p'-DDE from transporting through HDTMA-zeolite, montmorillonite and attapulgite to groundwater.

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References


