Triadimefon Interactions with Organoclays and Organohydrotalcites

R. Celis, W. C. Koskinen, M. C. Hermosín, M. A. Ulibarri, and J. Cornejo

ABSTRACT

We determined the ability of several organoclays (octadecylammonium- and hexadecyltrimethylammonium-exchanged montmorillonite) and organohydrotalcites (dodecylsulfate- and dodecylbenzene-sulfonate-exchanged hydrotalcite) to sorb the uncharged pesticide triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-((1H,1,2,4-triazol-1-y1)-2-butanone] to test the potential use of these sorbents for decontamination purposes and as slow release formulations of the pesticide. Interlayered organoclays and organohydrotalcites were at least six times more sorptive than the untreated minerals. Triadimefon sorption was higher on paraffin-like sorbents (organohydrotalcites and organoclays prepared from high-charge Arizona montmorillonite) than on bilayered sorbents (organoclays prepared from low-charge Wyoming montmorillonite). The nature and amount of organic ion in the interlayer also influenced triadimefon desorption from the different sorbents. Desorption and spectroscopic studies suggested, in general, weak hydrophobic interactions between triadimefon and the interlayer organic phase of the organoclays and organohydrotalcites. However, hydrogen bonding between the carbonyl group of triadimefon and the monosubstituted amino group of octadecylammonium-exchanged organoclays reinforced the strength of the interaction and resulted in reduced desorption from these sorbents. Selecting the interlayer ion appeared, therefore, as a good strategy to control the sorptivity and desorption of the sorbed pesticide for organoclays and organohydrotalcites. The results showed that organoclays and organohydrotalcites may find application as sorbents of pesticides similar to triadimefon.

Contamination of soil and water environments with organic compounds, specifically pesticides, has become a national issue. The need to protect and restore contaminated soils and aquifers is stimulating research to look for suitable materials to be used as sorbents, containment barriers, and pollutant stabilizers (Jaynes and Vance, 1996; Xu et al., 1997). Different sorbent materials are also being proposed for controlled release formulations to minimize the impact of pesticides in the environment (Darvari and Hasiric, 1996; Fernández-Pérez et al., 1998).

Natural clays, particularly 2:1-type phyllosilicates, have very good sorbent properties because of their large specific surface areas. However, the strong hydration of the natural inorganic exchange cations produces a hydrophilic environment at the clay surface that considerably reduces the sorptive capacity of clays for hydrophobic organic compounds (Mortland, 1970; Jaynes and Vance, 1996). Replacement of natural inorganic exchange cations with large organic cations (i.e., alkylammonium cations) through ion-exchange reactions has been shown to yield organoclays with organophilic properties, and hence, this simple modification has been proposed for the improvement of the sorptive capacity of clays for hydrophobic organic compounds (Boyd et al., 1988b; Lee et al., 1989).

Although the theoretical and practical interest of organoclays was pointed out more than 40 years ago (Barrer and Ray, 1957; Cowan and White, 1963), there has been an increasing interest in the past decade in the use of these materials to remediate environmental contamination (Boyd et al., 1988c; Jaynes and Boyd, 1991; Hermosín and Cornejo, 1992, 1993; Zhao et al., 1996; Xu et al., 1997; Lemke et al., 1998). Even the treatment of soil with alkylammonium ions has been proposed to replace naturally occurring metal ions, thus promoting enhanced sorption and attenuated movement of organic pollutants in soil (Boyd et al., 1988a; Lee et al., 1989).

Hydrotalcites (HT) are synthetic layered double hydroxides that can be considered anti-types of 2:1 phyllosilicates. They consist of brucite layers with forsterite that is compensated with interlayer hydrated anions. These interlayer anions can be exchanged and, hence, HT has been shown to be a good sorbent for anionic organic contaminants (Hermosín et al., 1997). The inorganic hydrated anions of HT can also be exchanged with large organic anions rendering organohydrotalcites (Meyn et al., 1990; Clearfield et al., 1991; Zhao and Vance, 1997). Because of their similarity to clays, hydrotalcites exchanged with large organic anions or organohydrotalcites are also potential sorbents for hydrophobic organic compounds (Pavlovic et al., 1996; Zhao and Vance, 1998a,b).

Before organoclays and organohydrotalcites can be

Abbreviations: AEC, anion-exchange capacity; CEC, cation-exchange capacity; FT-IR, Fourier transform infrared; HDTMA, hexadecyltrimethylammonium; HT, hydrotalcites; ODA, octadecylammonium; SA, Arizona montmorillonite; SW, Wyoming montmorillonite.
used in the protection and restoration of soils and waters contaminated with organic pollutants, and as sorbents for controlled release formulations of pesticides, information is needed on specific sorbent–pesticide interactions, including information on desorption, on which there are very few published reports (Hermosin and Cornejo, 1992, 1993; Margulies et al., 1994; Celis et al., 1999a). In a previous paper (Celis et al., 1999a), we reported the sorption–desorption behavior of organoclays and organohydrotalcites for the anionic herbicide imazamox (2-[4,5-dihydro-4-methyl-(1-methyl-ethyl)-5-oxo-1H-imidazol-2-yl]-5-(methoxymethyl)-3-fwpuridine-carboxylic acid). Anionic contaminants are a concern because they are weakly retained by most soil and sediment components and many of them have been detected in ground waters (Hermosin and Cornejo, 1993). In the present work, we investigated the ability of several organoclays and organohydrotalcites as potential sorbents for the uncharged fungicide triadimefon (Fig. 1). Although the risk of ground water contamination for uncharged pesticides is usually lower than for anionic pesticides, the use of sorbents for pesticides such as triadimefon would be recommended not only for decontamination purposes, but also for controlled release formulations, since several processes, including photolysis and volatilization, may result in deactivation or decreased efficacy of this pesticide when directly applied to soil (Clark et al., 1978; Murphy et al., 1996; Nag and Dureja, 1997). The specific objectives of this work, therefore, were (i) to determine the capability of several montmorillonites and hydrotalcites exchanged with large organic ions to act as sorbents for triadimefon at different pH levels, (ii) to evaluate possible mechanisms involved in the sorption process, and (iii) to examine the reversibility of the sorption–desorption process for the different sorbents assayed. The sorption–desorption behavior of triadimefon in soil has been reported elsewhere (Celis et al., 1999b).

**MATERIALS AND METHODS**

**Chemical**

Triadimefon is a systemic fungicide with a water solubility of 70 mg L<sup>-1</sup>. Pure analytical triadimefon (chemical purity > 99%) was purchased from Chem Service (West Chester, PA).

**Fig. 1.** Chemical structure of triadimefon.

The [phenyl-U<sup>14</sup>C]triadimefon was donated by Mobay Chemical Corp. (now Bayer Corp., Stilwell, KS). It was purified by HPLC, and final radiochemical purity was > 98%.

**Sorbents**

Table 1 summarizes the characteristics of the different sorbents used in this study. The main differences between SW- and SA–montmorillonites, supplied by the Clay Mineral Repository of the Clay Minerals Society (Boulder, CO), is the density of layer charge in the octahedral layer resulting in cation-exchange capacities (CEC) of 76 cmol, kg<sup>-1</sup> for SW and 120 cmol, kg<sup>-1</sup> for SA. Two different organic cations, octadecylammonium (ODA) and hexadecyltrimethylammonium (HDTMA) and two different organic cation loadings (~50% and ~100% of the CEC of the clays) were used in the synthesis of the organoclays. For the synthesis of SW–organoclays, 10 g of SW–montmorillonite were treated with 50 or 100 mL of ethanol:water (50:50) solution containing 7.6 mmol of alkylammonium chloride. In the case of SA–organoclays, 10 g of SA–montmorillonite were treated with 50 or 100 mL of ethanol:water (50:50) solution containing 12.0 mmol of alkylammonium chloride. The suspensions were shaken at 20 ± 2°C for 24 h, centrifuged, washed with distilled water until Cl-free, then freeze-dried.

The hydrotalcite, HT [(Mg,Al(OH)<sub>3</sub>]<sub>r</sub>· CO<sub>r</sub>· (4H<sub>2</sub>O)], was prepared by the co-precipitation method by adding 250 mL of an aqueous solution containing 0.75 mol Mg(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O and 0.25 mol Al(NO<sub>3</sub>)<sub>3</sub>· 6H<sub>2</sub>O to a vigorously stirred solution (500 mL) containing 1.7 mol NaOH and 0.5 mol Na<sub>2</sub>CO<sub>3</sub>, then heating at 80°C for 24 h (Reichle, 1986). The anion-exchange capacity (ACE) of the hydrotalcite thus prepared was 580 cmol, kg<sup>-1</sup>. An aliquot of HT was calcined at 500°C for 24 h to obtain magnesium aluminum oxide, HT500. The organohydrotalcites were prepared by the reconstruction method, suspending 1 g of HT300 in 17 mM sodium dodecylsulfate (DDS) or sodium dodecylbenzenesulfonate (DBS). The suspensions were shaken for 24 h, thoroughly washed, then air dried (Celis et al., 1999a).

**Table 1. Characteristics of the sorbents†.**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Mineral phase</th>
<th>Interlamellar organic ion</th>
<th>OC</th>
<th>OIS</th>
<th>d&lt;sub&gt;002&lt;/sub&gt; at 25°C</th>
<th>d&lt;sub&gt;002&lt;/sub&gt; at 110°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>SWy2</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>1.26</td>
<td>0.98</td>
</tr>
<tr>
<td>SA</td>
<td>SAz1</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>1.52</td>
<td>1.49</td>
</tr>
<tr>
<td>HT</td>
<td>Hydrotalcite</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>HT500</td>
<td>Calcined-HT</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SW–ODA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SWy2</td>
<td>Octadecylammonium</td>
<td>9.9</td>
<td>60</td>
<td>1.73</td>
<td>1.60</td>
</tr>
<tr>
<td>SW–ODA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SWy2</td>
<td>Octadecylammonium</td>
<td>14.8</td>
<td>90</td>
<td>1.72</td>
<td>1.76</td>
</tr>
<tr>
<td>SW–HDTMA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SWy2</td>
<td>Hexadecyltrimethylammonium</td>
<td>9.8</td>
<td>85</td>
<td>1.68p</td>
<td>1.42p</td>
</tr>
<tr>
<td>SW–HDTMA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SWy2</td>
<td>Hexadecyltrimethylammonium</td>
<td>14.7</td>
<td>85</td>
<td>1.81</td>
<td>1.80</td>
</tr>
<tr>
<td>SA–ODA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SAz1</td>
<td>Octadecylammonium</td>
<td>17.3</td>
<td>67</td>
<td>3.20p</td>
<td>2.15p</td>
</tr>
<tr>
<td>SA–ODA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SAz1</td>
<td>Octadecylammonium</td>
<td>25.5</td>
<td>98</td>
<td>3.25</td>
<td>2.25</td>
</tr>
<tr>
<td>SA–HDTMA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SAz1</td>
<td>Hexadecyltrimethylammonium</td>
<td>14.8</td>
<td>54</td>
<td>2.20p</td>
<td>1.74</td>
</tr>
<tr>
<td>HDTMA&lt;sub&gt;50&lt;/sub&gt;</td>
<td>SAz1</td>
<td>Hexadecyltrimethylammonium</td>
<td>22.8</td>
<td>84</td>
<td>2.42</td>
<td>2.12</td>
</tr>
<tr>
<td>HTDDS</td>
<td>HT</td>
<td>Dodecylsulfate</td>
<td>26.0</td>
<td>91</td>
<td>2.67</td>
<td>2.67</td>
</tr>
<tr>
<td>HTDBS</td>
<td>HT</td>
<td>Dodecylbenzenesulfonate</td>
<td>28.0</td>
<td>73</td>
<td>3.12p</td>
<td>3.12p</td>
</tr>
</tbody>
</table>

† SW, Wyoming montmorillonite; SA, Arizona montmorillonite; HT, hydrotalcite; OC, organic carbon; OIS, percent of the ion-exchange capacity of the mineral saturated by organic ion; d<sub>002</sub>, basal spacing value; p, poorly defined.
Organic C content in the sorbents was determined in a
total elemental C analyzer (Perkin Elmer 240C; Perkin Elmer
Corp., Norwalk, CT). pH was measured with a combination
glass electrode. X-ray diffractograms were obtained on ori-
ented specimens with a Siemens D-5000 diffractometer (Si-
emens, Germany) using CuKα radiation.

Sorption–Desorption Experiments
Triadimefon sorption isotherms on the different sorbents
were obtained by the batch equilibration technique using
35-mL glass centrifuge tubes with Teflon-lined caps. Initial
triadimefon solutions were prepared in 0.01 M CaCl₂ at
concentrations ranging from 0.3 to 8.0 mg L⁻¹. Radiolabeled tria-
dimefon was added to nonradioactive solutions to give a
final solution radioactivity of ~70 Bq mL⁻¹. Duplicate 10 mg
sorbent samples were equilibrated with 10 mL of triadimefon
initial solution by shaking mechanically at 20 ± 2°C for 24 h.
Kinetic experiments showed that sorption equilibrium was
reached within 24 h. After equilibration, the suspensions were
centrifuged at 2500 × g for 30 min, and the radioactivity of the
supernatant determined by liquid scintillation counting
using a 1500 Packard Instrument liquid scintillation analyzer
(Packard Instruments Co., Downers Grove, IL). The amount of
triadimefon in solution was calculated from the specific
activity of the initial triadimefon solution. Previous work has
reported no significant degradation of triadimefon after 2 d
of equilibration with soil (Celis et al., 1999b).

Desorption was measured immediately after sorption from
the highest equilibrium concentration point of the sorption
isotherms. The 5 mL of supernatant removed for the sorption
analysis were replaced with 5 mL of 0.01 M CaCl₂. After
shaking at 20 ± 2°C for 24 h, the suspensions were centrifuged
and 5-mL supernatant removed for analysis. This desorption
cycle was repeated four times. Desorption experiments were
performed in triplicate.

Sorption and desorption isotherms were fit to the linearized
form of the Freundlich equation: \( \log C_s = \log K_f + \frac{1}{n} \log C_i \),
where \( C_s \) (mg kg⁻¹) is the amount of triadimefon sorbed
at the equilibrium concentration \( C_i \) (mg L⁻¹), and \( K_f \) and \( n \)
are the empirical Freundlich constants. Sorption coefficients
normalized to organic C, \( K_{oc} \), were calculated by dividing \( K_f \)
by the fraction of organic C in the sorbents. Hysteresis coeffi-
cients, \( H \), were calculated according to \( H = \frac{(1/n_1)}{(1/n_2)} \),
where \( 1/n_1 \) and \( 1/n_2 \) are the Freundlich slopes for the sorption
and desorption isotherms, respectively (O’Connor et al., 1980;Bar-
rioso et al., 1994).

pH Effect on Sorption
The effect of pH on sorption was determined at a single
triadimefon initial concentration of 3 mg L⁻¹ by adjusting the
pH of the initial pesticide solution between 1.5 and 4.5 with
HCl. A distribution coefficient, \( K_d = \frac{C_s}{C_i} \), was calculated.
Preliminary experiments showed that, because of the buffer
capacity of the sorbents, varying the pH of the initial triadime-
fon solution from 4.5 to 8 did not result in significant changes
in final pH (pH of the 24-h equilibrated suspensions). There-
fore, no significant changes in sorption were observed at
high pH.

Successive Saturation Experiments
SA–ODA₁₀₀ and SA–HDTMA₁₀₀ organoclays (10 mg) were
nested with 10 mL of 80 mg L⁻¹ triadimefon solution (1%
[v/v] methanol, 0.01 M CaCl₂). The suspensions were shaken at
20 ± 2°C for 24 h, centrifuged, and 7 mL of supernatant
removed, analyzed, and replaced with 7 mL of fresh triadime-
fon solution. This procedure was repeated four times. Control
and triadimefon-treated samples were washed twice with 10 mL
of distilled water, air-dried, and analyzed by x-ray diffraction
(Siemens D-5000 diffractometer, Siemens, Germany) and
Fourier transform infrared spectroscopy (FT-IR, Nicolet 5 PC
spectrometer, Nicolet Instruments Corp., Madison, WI). X-
ray diffractograms were obtained on oriented specimens and
FT-IR spectra on KBr disks.

RESULTS AND DISCUSSION
Characteristics of the Sorbents
The higher basal spacings of the alkylammonium ex-
changed montmorillonite compared with the pure clays, SW and SA, at both 25 and 110°C, indicated the
formation of interlayered complexes (Table 1). The
basal spacing values of the organoclays at 25°C sug-
gested that ODA and HDTMA cations formed bilayers
in SW–montmorillonite (\( d_{001} \approx 1.7–1.8 \) nm), whereas
paraffin-like complexes (\( d_{001} > 2.2 \) nm) were formed in the
case of SA–montmorillonite (Lagaly, 1982; Jaynes
and Boyd, 1991). Thus, the arrangement of the alky-
lation cations in the interlayer of the clays was deter-
mined more by the charge of the mineral than by the
size or amount of the exchanged organic cation: the
low-charge SW–montmorillonite favors horizontal ori-
entation of the alkyl chains of the organic cation in the
interlayer, which is stabilized by hydrophobic interac-
tions with non-charged regions of the clay surface; in
contrast, the proximity of two adjacent charges in SA–
montmorillonite promoted a vertical arrangement of the
alkyl chains that resulted in high basal spacings of the
resultant organoclays (Jaynes and Boyd, 1991; Brixie
and Boyd, 1994). Nevertheless, a better definition of the
basal diffractions and slightly higher basal spacing
values were observed for organoclays exchanged with
higher amounts of organic cation (Table 1), thus sug-
gesting a more uniform arrangement of the interlayer
cations in those organoclays. In the case of the organo-
hydrotalcites, HTDDS and HTDBS, the arrangement of the
alkylsulfate anions can be described in terms of
paraffin-like complexes, with basal diffractions > 2.2 nm
(Table 1). HTDBS basal diffractions were very well
defined, showing up to six orders of reflection, whereas
HTDDS showed only the first order reflection and it
was poorly defined. The organic C contents of HTDDS
and HTDBS, lower than those expected from the total
anion exchange capacity of HT, indicated that the layer
charge of HT should also be compensated with hydroxyl
interlayer ions. The existence of a diffraction peak in
HTDBS at 0.76 nm (not shown) was indicative of the
existence of some non-exchanged interlayers occupied
exclusively by inorganic anions, OH⁻ or CO₃²⁻.

Sorption–Desorption of Triadimefon
Kinetics
Triadimefon sorption kinetics on SW–ODA₁₀₀ organ-
clay and HTDBS–organoxydrotalcite indicated that
sorption equilibrium was nearly reached within 24 h of
shaking (not shown). The amounts of triadimefon
sorbed on SW–ODA₁₀₀ and HTDBS after 24 h were
>98% of the amounts sorbed after 48 h. Therefore, 24 h
was considered sufficient to reach sorption equilibrium
for triadimefon.
Sorption Isotherms

Triadimefon sorption isotherms on all sorbents studied fit the Freundlich equation with $r^2 > 0.995$ (Table 2, Fig. 2–4). Triadimefon did not sorb on the high-charge montmorillonite, SA, or the hydrotalcites, HT and HT500. Some measurable sorption on the low-charge montmorillonite, SW, can be attributed to hydrophobic, non-charged regions present on the surface of this clay, allowing the pesticide molecules to effectively compete with water molecules for those hydrophobic regions (Laird, 1995; Celis et al., 1999b). The high S-character ($1/n_t > 1$) of the sorption isotherm (Table 2) supported competition of triadimefon with water molecules for sorption sites on SW (Giles et al., 1960; Celis et al., 1999b).

Incorporation of large organic ions in the interlayers of montmorillonite and hydrotalcite resulted in organoclays and organohydrotalcites with great sorptive properties for triadimefon (Table 2). For instance, while no sorption of triadimefon was measured on pure SA, SA–HDTMA organoclays removed more than 90% of the triadimefon initially present in solution. Similarly, $K_f$ values for SW–organoclay were 6 to 16 times higher than the value obtained for pure SW (Table 2). The organic phase in the organoclay and organohydrotalcites changed the nature of the surfaces from hydrophilic to hydrophobic, increasing their affinity for the pesticide molecules (Mortland et al., 1986). The values of $1/n_t = 1$ obtained for SA–HDTMA organoclays and organohydrotalcites suggested minimum competition from water molecules for sorption sites on these sorbents, which is in agreement with partition of the chemical through hydrophobic-type interactions into the bulk state of the interlayer organic phase (Chiu et al., 1983). However, the values of $1/n_t < 1$ obtained for SW–organoclay and SA–ODA organoclays and the extremely high $K_{oc}$ values obtained for SA–HDTMA organoclays compared with the octanol–water partition coefficient reported for triadimefon, $K_{oc} = 1510$ (Worthing and Hance, 1991), suggest that partitioning alone may not be responsible for the observed isotherms.

An interesting feature in Table 2 is the higher triadimefon sorption ($K_f$ and $K_{oc}$) measured on SA–organoclays compared with similar SW–organoclay. These data indicate that the vertical arrangement of the alkylammonium cation in SA–organoclays provided a better medium for triadimefon sorption compared with

Table 2. Triadimefon sorption–desorption coefficients on the sorbents studied.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$K_f$</th>
<th>$1/n_t$</th>
<th>$K_{oc}$</th>
<th>$H$ ($\times$ 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>88 ± 7½</td>
<td>1.65 ± 0.07</td>
<td>–</td>
<td>50</td>
</tr>
<tr>
<td>SA</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HT</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HT500</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SW–ODA$_{10}$</td>
<td>630 ± 30</td>
<td>0.83 ± 0.03</td>
<td>6 400</td>
<td>66</td>
</tr>
<tr>
<td>SW–ODA$_{100}$</td>
<td>530 ± 20</td>
<td>0.85 ± 0.03</td>
<td>5 600</td>
<td>46</td>
</tr>
<tr>
<td>SW–HDTMA$_{10}$</td>
<td>540 ± 10</td>
<td>0.89 ± 0.01</td>
<td>5 500</td>
<td>94</td>
</tr>
<tr>
<td>SW–HDTMA$_{100}$</td>
<td>1 420 ± 30</td>
<td>0.88 ± 0.01</td>
<td>9 700</td>
<td>89</td>
</tr>
<tr>
<td>SA–ODA$_{10}$</td>
<td>1 590 ± 80</td>
<td>0.82 ± 0.04</td>
<td>9 200</td>
<td>38</td>
</tr>
<tr>
<td>SA–ODA$_{100}$</td>
<td>1 400 ± 50</td>
<td>0.78 ± 0.02</td>
<td>5 500</td>
<td>19</td>
</tr>
<tr>
<td>SA–HDTMA$_{10}$</td>
<td>10 790 ± 360</td>
<td>0.98 ± 0.01</td>
<td>73 000</td>
<td>–‡</td>
</tr>
<tr>
<td>HDTMA$_{10}$</td>
<td>17 340 ± 750</td>
<td>0.97 ± 0.02</td>
<td>76 000</td>
<td>–‡</td>
</tr>
<tr>
<td>HTDDS</td>
<td>2 450 ± 370</td>
<td>1.02 ± 0.05</td>
<td>16 000</td>
<td>74</td>
</tr>
<tr>
<td>HTDBS</td>
<td>1 630 ± 20</td>
<td>0.99 ± 0.01</td>
<td>5 800</td>
<td>119</td>
</tr>
</tbody>
</table>

† Value ± standard error.
‡ Ill defined desorption isotherms due to very high sorption on these sorbents.

Fig. 2. Triadimefon sorption–desorption isotherms on SW–organoclay: shaded circle, sorption; non shaded circle, desorption. Error bars for the plotted points are smaller than symbols.
the horizontal arrangement of the interlayer cations in SW–organoclays. These results are similar to those of previous work where the interlayer thickness was responsible for differences in the sorptivity of different organoclays (Jaynes and Boyd, 1991; Hermosin and Cornejo, 1992; Jaynes and Vance, 1996). However, the nature and amount of alkylammonium cation in the interlayer also influenced triadimefon sorption. For instance, for ODA-exchanged organoclays, there was a decrease in sorption ($K_r$ values) with increasing amounts of exchanged organic cation in both SW and SA, whereas the contrary was observed for HDTMA-exchanged organoclays (Table 2). The different hydration of the head group of ODA and HDTMA may have influenced the affinity of the interlayer organic cations for triadimefon. In addition, it is likely that the less voluminous ODA cation resulted in a more compact packing of the organic phase, thus reducing the free spaces for triadimefon sorption, especially in highly loaded ODA–organoclays. This was confirmed by the calculated $K_{oc}$ values, which indicated much higher efficiency in sorbing triadimefon of the organic C of highly loaded ODA–organoclays compared with similar ODA–organoclays, with SA–HDTMA samples displaying extremely high $K_{oc}$ values (Table 2). The nature of the interlayer organic anion also influenced triadimefon sorption by the organohydrotalcites, with HTDDS displaying three times higher sorptive capacity than HTDBS (Table 2). HTDDS had a higher organic anion density (91% of the AEC of HT) than did HTDBS (73% of the AEC of HT); however, the possible existence of some non-exchanged interlayers occupied by OH$^-$. 

![Fig. 3. Triadimefon sorption–desorption isotherms on SA–organoclays: shaded circle, sorption; non shaded circle, desorption. Error bars for the plotted points are smaller than symbols.](image)

![Fig. 4. Triadimefon sorption–desorption isotherms on organohydrontalcites: shaded circle, sorption; non shaded circle, desorption. Error bars for the plotted points are smaller than symbols.](image)
CO$_3^{2-}$ in HTDBS (see sorbents characteristics) may have resulted in decreased sorption on this sorbent.

**Desorption**

The similar triadimefon sorption and desorption Freundlich slopes found for HTDBS, HTDDS, and HDTMA–organoclays indicate reversible sorption and agreed with weak, hydrophobic-type interactions of the pesticide molecules within the interlayer organic phase of the sorbents (Fig. 2–4). These results are in contrast to the marked hysteretic behavior observed for ODA–organoclays, where Freundlich desorption slopes were significantly lower than the sorption slopes (Fig. 2–4). Significantly lower $H$ values (indicating higher irreversibility) were obtained for ODA-organoclay compared to HDTMA–organoclays and organohydrotalcites (Table 2). It can be speculated that hydrogen bonding between the C–O group of triadimefon and the monosubstituted amino group of ODA cations contributed to stabilize the binding of the pesticide in ODA–organoclays, resulting in reduced desorption. Spectroscopic results, which will be discussed later, further support this hypothesis. Lower $H$ values (higher irreversibility) were obtained for ODA–organoclays with higher amounts of organic cation. Selecting the interlayer ion and the degree of saturation appears, therefore, as a good strategy to control the desorption of the sorbed pesticide from organoclays and organohydrotalcites. Reversible behavior would be desirable in the use of sorbents for slow release formulations, whereas irreversible sorption would be advantageous for pollutant immobilization in the remediation of already contaminated soils.

**pH Effect on Sorption**

Changing the initial pH of hydrotalcite and its organo-derivatives suspensions between 7 and 2.5 resulted in minimum differences in the final pH (pH = 7) because of the buffer capacity of these sorbents and hence no differences in triadimefon sorption were observed (data not shown). In addition, previous research has shown that decreasing the final pH to levels <4 results in extensive dissolution of the hydroxide structure of hydrotalcite, which limits its use as sorbent in acidic conditions (Hermosin et al., 1997; Celis et al., 1999a).

The effect of pH on triadimefon sorption on SW, SA, and some of their organoclays is illustrated in Table 3. The increase in triadimefon sorption with decreasing pH observed for SW and SW–ODA organoclays is attributed to protonation of the triazol ring and sorption of the cationic species on cation–exchange sites on the clay (Celis et al., 1999b). The effect of pH on triadimefon sorption on SW–ODA organoclays was smaller than that observed on pure SW, most likely because many of the cation exchange sites on SW were blocked by the ODA cations in the interlayers, which are not easily displaced (Table 3). The small effect of pH on sorption observed for the high-charge SA–montmorillonite supports the hypothesis that some previous sorption of molecular species is a prerequisite before protonation can occur in the interlayers of montmorillonite (Celis et al., 1997). It is very interesting to note that interlayer ODA cations seem to provide SA–montmorillonite with some sorption capacity for triadimefon molecular species and, as a result, some increase in triadimefon sorption with decreasing pH (indicating further protonation) is observed for SA–ODA organoclays.

**Sorption Mechanisms**

The sorption estimated after four successive treatments of SA–ODA$_{10}$ and SA–HDTMA$_{10}$ with 80 mg L$^{-1}$ triadimefon solution were 80 and 180 mg g$^{-1}$, respectively, corroborating the extremely high sorption capacity of the organoclays for triadimefon. The $d_{10}$ values at 25 and 110°C indicated that the triadimefon-treated organoclays expanded upon sorption of the pesticide and that there was interlayer sorption of the pesticide in the organoclays. The basal spacing of SA–HDTMA$_{10}$ increased upon triadimefon treatment from 2.41 nm to 2.65 nm at 25°C and from 2.13 nm to 2.70 nm at 110°C. Fourier transform infrared spectra of SA–ODA$_{10}$, SA–HDTMA$_{10}$, and their complexes with triadimefon revealed the presence of bands corresponding to triadimefon in the complexes (Fig. 5). Bands corresponding to $\nu_{C=O}$ ketone (1727 cm$^{-1}$), $\nu_{C=O}$ azomethane (1491 cm$^{-1}$), and $\nu_{C-\cdot C}$ ethylidene (1278 or 1220 cm$^{-1}$) (Bellamy, 1980) can be clearly observed in the FT-IR spectra of the triadimefon-treated organoclays. It is interesting to note that very little shifting, if any, of these bands occurred when comparing their positions in the organoclay–triazidefon complexes with those for pure compound (Fig. 5). This reflects little change in bond strength and, therefore, weak interactions of triadimefon with the sorbents. However, the differences in the C–O stretching vibration band in pure triadimefon (1727 cm$^{-1}$), in triadimefon–SA–ODA$_{10}$ (1722 cm$^{-1}$), and in triadimefon–

| Table 3. Effect of pH on triadimefon sorption on pure clays and organoclays. |
|-------------|-------------|------------|-------------|
| Sorbent     | Initial pH† | Final pH‡  | $K_a$        | Sorption     |
|             | pH          | pH         |             | L kg$^{-1}$ | %          |
| SW          | 4.5         | 5.8        | 232 ± 4    | 19          |
|             | 3.0         | 3.5        | 1286 ± 31  | 56          |
|             | 2.5         | 2.8        | 5379 ± 460 | 84          |
|             | 1.5         | 1.7        | 60290 ± 1980 | 98         |
| SA          | 4.5         | 6.0        | 0          | 0           |
|             | 3.0         | 3.4        | 14 ± 5     | 1           |
|             | 2.5         | 2.7        | 29 ± 9     | 3           |
|             | 1.5         | 1.7        | 44 ± 21    | 4           |
| SW–ODA$_{10}$ | 4.5       | 5.3        | 526 ± 29   | 34          |
|             | 3.0         | 3.3        | 803 ± 11   | 45          |
|             | 2.5         | 2.5        | 969 ± 34   | 49          |
| SW–ODA$_{30}$ | 4.5       | 5.4        | 420 ± 14   | 30          |
|             | 3.0         | 3.4        | 1197 ± 101 | 54          |
|             | 2.5         | 2.5        | 1194 ± 16  | 54          |
| SA–ODA$_{10}$ | 4.5       | 5.6        | 1523 ± 43  | 60          |
|             | 3.0         | 3.4        | 7199 ± 226 | 88          |
|             | 2.5         | 2.5        | 6429 ± 186 | 87          |
| SA–ODA$_{30}$ | 4.5       | 5.6        | 1476 ± 95  | 60          |
|             | 3.0         | 4.1        | 7742 ± 257 | 89          |
|             | 2.5         | 2.6        | 7000 ± 81  | 88          |

† Initial pH: pH of the initial triadimefon solution.
‡ Final pH: pH of the 24 h-equilibrated clay–pesticide suspension.
§ Value ± standard error.
SA–HDTMA 100 (1729 cm⁻¹) should be noted. The shift of the position of the C=O stretching vibration to lower frequency observed for triadimefon–SA–ODA 100 has been attributed to participation of the carbonyl group in the binding of the molecule to the sorbent (Hermosin and Cornejo, 1993; Cox et al., 1995). Therefore, the C=O group of triadimefon seems to be involved in the binding of the pesticide to the ODA–organoclay, most likely through hydrogen bonding with the monosubstituted amino group of the interlayer organic cation (Hermosin and Cornejo, 1993). This could have contributed to reinforce the strength of the interactions in ODA–organoclay and may explain the desorption results indicating reduced desorption of the triadimefon sorbed on these systems compared with HDTMA–organoclay and organohydrotalcites.

CONCLUSIONS

Modification of montmorillonite and hydrotalcite with alkylammonium and alkylsulfate ions, respectively, resulted in interlayered organoclays and organohydrotalcites with very high sorptive properties for the uncharged pesticide triadimefon. Higher sorption of triadimefon took place on the paraffin-like sorbents, SA–organoclay and organohydrotalcites, than on the bilayered SW–organoclay. The nature and amount of organic ion in the interlayer influenced triadimefon sorption by the sorbents. Higher triadimefon sorption on the organoclay at lower pH was attributed to protonation of the triazol ring of triadimefon and sorption of cationic species on unblocked cation-exchange sites on the clay, whereas dissolution of the hydroxide structure of hydrotalcite at low pH (pH <4) limited their use as sorbents in acidic conditions. X-ray diffraction and FT-IR studies indicated interlayer sorption of triadimefon in the organoclay and, except for ODA–organoclay, weak interactions between the pesticide molecules and the sorbents, in agreement with the high reversibility observed in the sorption–desorption isotherms. For ODA–organoclay, hydrogen bonding between the carbonyl group of triadimefon and the monosubstituted amino group of the organic cation seemed to contribute to reinforce the strength of the interactions and resulted in decreased desorption. Selecting the interlayer ion and the degree of saturation, therefore, is a good strategy to control the sorptivity and desorbability of the sorbed pesticide for organoclay and organohydrotalcite. The results of this study show that organoclay and organohydrotalcite may find application as sorbents in soil and water decontamination and as supports for slow release formulation of pesticides similar to triadimefon.

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REFERENCES


