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Sorption of 2,4-Dichlorophenoxyacetic Acid by Model Particles Simulating Naturally Occurring Soil Colloids

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Binary and ternary model particles containing montmorillonite, ferrihydrite, and humic acid (HA) were used to determine the changes in the sorption behavior of the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) upon the interassociation of these three major soil constituents. On single sorbents, 2,4-D sorption was high with S-type isotherms on ferrihydrite, moderate with L-type isotherms on HA, and zero on montmorillonite. In binary sorbents, ferrihydrite and humic acid coatings on montmorillonite provided sorption sites for 2,4-D, although the exclusion of the anionic form from highly charged clay surfaces partially obscured the role of Fe and HA as sorbents of 2,4-D. Sorption of 2,4-D on ferrihydrite-HA binary particles was not very different from that on pure ferrihydrite because most of the ferrihydrite surface area was from micropores being not accessible to large humic macromolecules and hence remained available for herbicide sorption. In ternary sorbents HA coatings reduced the sorption of 2,4-D by the montmorillonite−ferrihydrite binary complex, indicating that HA blocked many of the sorption sites provided by the Fe coatings. This work shows that the amount and nature of the surface that remains available after the interassociation of single soil constituents is a critical parameter in determining the sorptive behavior of the resultant aggregate for ionizable contaminants such as 2,4-D. Thus, the use of calculated sorption parameters such as K_{oc}, K_{ow}, $K_{mineral}$, or K_{Fe}, for modeling contaminant behavior in aquatic or soil environments may result in serious deviation from the reality.

Introduction

Pesticide sorption by soil colloids is often governed by organic matter content (*1−3*). A rather good correlation has been observed between the soil organic C content and the sorption of many pesticides. However, the contribution of the mineral soil constituents to sorption may be significant for ionic or highly polar pesticides or when the organic C content of the soil is low relative to the clay mineral content (*4−6*). For these cases, little is known about the relative contribution of the various soil components (i.e., clay minerals, metal oxides, humic substances) to pesticide sorption and even less about how association processes between the different soil constituents influence pesticide sorption on soil colloids.

Naturally occurring soil colloids are multicomponent associations of minerals and organic matter (*7−9*). Clay mineral surfaces are usually coated with metal oxides and oxyhydroxides. Organic matter modifies the hydrophilic/hydrophobic character of the mineral surfaces making them more hydrophobic and, therefore, more reactive to hydrophobic organic compounds. The consequences of interactions between soil components on pesticide sorption are not fully understood and depend on the interaction mechanisms between soil constituents and on the nature of the pesticide. Some authors have reported that the interassociation processes may block sorptive functional groups on mineral and organic surfaces (*10−12*); however, the different soil constituents may also complement one another in the role of pesticide sorption leading to enhanced sorption on the resultant aggregate (*13, 14*).

In a series of previous papers, we have used different types of model associations of the three main active soil constituents, montmorillonite, Fe oxide, and humic acid, to show important modifications of the sorptive properties of the individual constituents upon their interassociation (*15−17*). Pesticides used in these studies were polar or weakly basic herbicides (thiazafluron, metamitron, atrazine, and simazine), and the consequences of interassociation were found to depend on soil constituent interactions and on the chemical characteristics of the pesticide. For instance, Fe coatings on montmorillonite surfaces decreased sorption of the polar uncharged herbicide thiazafluron but promoted sorption of more basic herbicides metamitron, atrazine, and simazine on the clay surfaces (*15−17*). Many pesticides have weakly acidic character and may exist as anions which are weakly retained by most soil or sediment components, and, hence, many of them have been detected in surface waters and groundwaters (*18*). In the present paper, 2,4-D, 2,4-dichlorophenoxyacetic acid ($pK_a = 2.6$), is used as a test compound to determine the sorption of a weak acid herbicide by the three main active soil colloids, montmorillonite, Fe oxide, and humic acid, and the changes in the sorption behavior produced by their interassociation in binary and ternary colloidal aggregates.

Materials and Methods

1. Herbicide and Single Sorbents. Analytical grade 2,4-D (chemical purity >98%) was purchased from Sigma. The two montmorillonites used were the <2 μm fraction of calcium-saturated Wyoming montmorillonite (CaSWy) and the <2 μm fraction of calcium-saturated Arizona montmorillonite (CaSAz), supplied by the Clay Mineral Repository of the Clay Minerals Society. The main difference between CaSWy and CaSAz is the density of layer charge in the octahedral layer, resulting in cation exchange capacities of 76.4 and 120 $cmol_c\ kg^{-1}$, respectively (*19*). Two Fe oxides were prepared in the laboratory and characterized by X-ray diffraction and specific surface area (SSA) measurements. Poorly crystallized ferrihydrite ($Ferrih_{pc}$) was prepared by neutralizing a 0.5 M $Fe(NO_3)_3$ solution with NH_4OH to a pH of 7.5. The precipitate was washed with deionized water until NO_3^- free and then freeze-dried. The X-ray diffractogram of $Ferrih_{pc}$ showed only two very broad bands at about 0.254 and 0.150 nm, respectively, and its nitrogen SSA was 315 $m^2\ g^{-1}$. These data indicated the poor crystallinity of the Fe oxide obtained (*20, 21*). Well crystallized ferrihydrite, $Ferrih_{wc}$, was prepared by boiling for 8 min a 0.5 M $Fe(NO_3)_3$ solution (*22*). The suspension was dialyzed against deionized water until NO_3^- free and then freeze-dried. The X-ray diffractogram of $Ferrih_{wc}$ showed the six diffraction lines corresponding to a well

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crystallized ferrihydrite (*21*), and its nitrogen SSA was 152 m^2 g^{-1}. The humic substances (HA) used were a commercial humic acid (Fluka Chem. Corp., Ronkonkoma) used as received and a soil humic acid extracted from a Typic Xerochrept soil on a shale parent rock. The soil was extracted with cold 1:1 solution of 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH under N_2, the extract centrifuged and acidified to pH 2 with HCl, and the precipitated humic acid removed by centrifugation (*23*).

2. Synthesis of Binary and Ternary Model Sorbents. Montmorillonite−Fe Oxide Associations. Two types of montmorillonite−Fe oxide associations were prepared resembling two extreme types of interaction: Fe precipitation on the montmorillonite particles (at high pH) and Fe specific adsorption on the clay (at low pH) (*16, 24, 25*).

(a) Montmorillonite-Precipitated Fe Associations. Aqueous solutions with two different concentrations of $Fe(NO_3)_3$ (7.5 and 15.0 mM) were stirred for 10 min in the presence of 2 g clay/100 mL solution. A blank sample was also prepared by treating the clays (CaSWy or CaSAz) with a HNO_3 solution at the same pH as the Fe(III) solutions but without $Fe(NO_3)_3$. The importance of using blank samples should be emphasized as the blanks help distinguish the effects of the different treatments from changes in the clay produced during the synthesis of the associations. All these suspensions (Fe-coated clays and blank clays) were neutralized with NH_4OH to a pH of 7.5 and shaken overnight. *Precipitated Fe*-coated clays and blanks were washed, centrifuged, freeze-dried, and stored at room temperature until used.

(b) Montmorillonite-Adsorbed Fe Associations. A poly[Fe-(III)-OH] cation suspension (pH = 2.6) was prepared following the method of Rengasamy and Oades (*24*) by dialyzing fresh 0.1 M $Fe(NO_3)_3$ solution against distilled water for 24 h. According to these authors, the assumed molecular weight (MW) of the polymer was >100 000. The montmorillonite−polycation associations were obtained by adsorbing on CaSWy and CaSAz, the amount of poly[Fe(III)-OH] (MW > 100 000) corresponding to the plateau of the adsorption isotherm, as described elsewhere (*16*). We obtained *adsorbed Fe*-coated clays with a maximum sorption of 48 mg Fe g^{-1} CaSWy and of 25 mg Fe g^{-1} CaSAz. Blank clays for this second type of polymer were also prepared (without Fe species, but otherwise handled identically).

Montmorillonite−Humic Acid Associations. CaSWy−soil HA and CaSWy−Fluka HA associations were obtained by adding 2.5 g of CaSWy to a solution (pH 6.5) of 500 mL of 500 mg L^{-1} humic acid previously dissolved using 0.5 mL of 1 M NaOH. To minimize ionic strength changes, 0.01 M NaCl was used as background electrolyte. The corresponding blank clay was prepared by treating 2.5 g of CaSWy with the same NaOH and NaCl solution (but without the presence of HA), which will account for the possible Ca^{2+}/Na^+ exchange on clay. After shaking for 24 h, clay−humic acid associations and blank clay were dialyzed (MW cutoff: 10 000 Da), freeze-dried, and stored at room temperature until used.

Ferrihydrite−Humic Acid Associations. Ferrihydrite−humic acid associations were prepared by mixing 2.5 g of poorly crystallized ferrihydrite ($Ferrih_{pc}$) with 500 mL of 500 mg L^{-1} humic acid (0.01 M NaCl, pH = 6.5) following the same procedure used for the synthesis of clay−humic acid associations and their corresponding blanks.

Montmorillonite−Fe Oxide-Humic Acid Ternary Associations. The ternary associations of model sorbents were obtained by adding 2.5 g of the CaSWy-precipitated Fe binary complex prepared from the 15 mM Fe(III) solution to a solution of 500 mL of 500 mg L^{-1} humic acid (0.01M NaCl, pH 6.5). After shaking for 24 h, CaSWy-precipitated Fe−humic acid associations and the blank sample were dialyzed, freeze-dried, and stored at room temperature until used.

TABLE 1. Some Physicochemical Properties of the Model Particles

				SSA[a]	d_{001} (nm)	
	Fe (%)	C (%)	pH	(m^2/g)	25 °C	K-300 °C[b]
Single Sorbents						
CaSWy			7.9	24	1.52	0.99
CaSAz			7.6	85	1.52	1.01
$Ferrih_{wc}$			6.3	152		
$Ferrih_{pc}$	52.3		5.4	316		
Soil HA		42.5	2.9	0		
Fluka HA		41.0	4.6	0		
Montmorillonite−Fe Oxide Binary Associations						
CaSWy precip Fe	0 (blank)		6.3	18	1.49	0.99
	1.88		5.8	45		
	3.43		5.7	56	1.37	0.99
CaSAz-precip Fe	0 (blank)		6.5	102	1.50	1.01
	1.91		6.3	120		
	3.82		6.2	136	1.30	1.01
CaSWy-adsorbed Fe	0 (blank)		3.8	25	1.51	0.99
	5.01		3.8	63	1.49	0.99
CaSAz-adsorbed Fe	0 (blank)		4.0	69	1.50	1.01
	2.10		4.0	80	1.49	1.01
Montmorillonite−HA Binary Associations						
CaSWy (blank)		0	7.1	24	1.53	
CaSWy−soil HA		2.4	5.0	5	1.54	
CaSWy−Fluka HA		2.8	5.2	9	1.56	
Ferrihydrite−HA Binary Associations						
$Ferrih_{pc}$ (blank)		0	5.9	317		
$Ferrih_{pc}$−soil HA		3.6	5.2	293		
$Ferrih_{pc}$−Fluka HA		3.4	5.6	298		
Ternary Associations						
CaSWy-precip Fe (blank)	3.40	0	4.9	55	1.45	
CaSWy-precip Fe−soil HA	3.23	3.5	5.1	13	1.46	
CaSWy−precip Fe−Fluka HA	3.10	4.3	4.9	10	1.47	

[a] Specific surface area measured by N_2 adsorption. [b] After saturation with K^+ and heating at 300 °C.

3. Sorbents Characterization. Fe content in the associations was determined by 0.2 M ammonium oxalate/0.2 M oxalic acid extraction following the procedure of McKeague and Day (*26*), and the total C was determined in a total elemental C analyzer (Perkin-Elmer 240 C). The pH of the samples was measured in 1:100 solid to 0.01 M $CaCl_2$ ratio (the same as used in the sorption experiments). Specific surface areas were obtained by N_2 adsorption at 77 K using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan). Samples were outgassed at 80 °C and equilibrated under vacuum for 15 h before measuring the N_2 adsorption isotherm. X-ray diffraction studies were performed with a Siemens D-500 diffractometer (Siemens, Stuttgart) using Cu $K\alpha$ radiation.

4. 2,4-D Sorption−Desorption Experiments. Sorption−desorption isotherms for 2,4-D on the different sorbents were obtained using the batch equilibration procedure: 100 mg of sorbent were treated with 10 mL of 2,4-D solutions (0.01−1 m*M*) with 0.01 M $CaCl_2$ as background electrolyte. The pH of these experiments were not specifically controlled because buffers could interfere with sorption of 2,4-D species. However, the pH in 0.01 M $CaCl_2$ suspension for the diverse sorbents are given in Table 1, and the low 2,4-D concentrations used did not significantly alter those pHs (*27*). Suspensions were shaken at 20 ± 2 °C for 24 h and centrifuged, and equilibrium concentration of the supernatants were determined by HPLC. The following HPLC conditions were used: Nova-Pack column of 150 mm length × 3.9 mm i.d.; column packing C18; flow rate, 1 mL min^{-1}; eluent system, 45:55 (v:v) methanol:diluted phosphoric acid (pH 2.0); UV detection, 230 nm. Differences between initial (C_{ini}) and equilibrium (C_e) concentrations were assumed to be sorbed (C_s). Desorption was measured after sorption from the highest equilibrium point of the sorption isotherms. The 5 mL of supernatant removed for the sorption analysis were replaced with 5 mL of 0.01 M $CaCl_2$. After shaking at 20 ± 2 °C for 24 h, the suspensions were centrifuged, and concentration of the herbicide determined in the supernatant. This desorption procedure was repeated three times. All sorption and desorption studies were conducted in duplicate.

Saturation of the Iron Oxides with 2,4-D. Fifty milligrams of $Ferrih_{pc}$ and $Ferrih_{wc}$ were saturated with 2,4-D by successive treatments with 1 mM herbicide solution in 0.01 M $CaCl_2$. Control and 2,4-D saturated samples were washed twice with deionized water, air-dried, and analyzed by Fourier transform infrared spectroscopy (FT-IR) as KBr disks using a Nicolet 5 PC spectrometer (Nicolet Instr. Corp., WI).

Results and Discussion

Physicochemical Properties of the Sorbents. Table 1 summarizes the most relevant properties of the untreated individual model sorbents, the binary and ternary model associations, and the different blank samples that affect sorption processes. It should first be pointed out in Table 1 that the blank-treated individual sorbents primarily differed from the corresponding untreated samples in the pH of the suspension and, to a lesser extent, in specific surface area (SSA). The suspension pHs after blank treatment of the clays decreased from 0.8 units for CaSWy−HA association blank up to 4.1 units for CaSWy-adsorbed Fe blank. This pH decrease should be due to some exchange of the original saturating cation (Ca^{2+}) by protons on external positions, since the unaltered d_{001} values (Table 1) suggest the interlayer remained unchanged (*27, 28*). $Ferrih_{pc}$ showed a pH increase upon blank treatment for HA association from 5.4 to 5.9 because NaOH probably neutralized some surface protons. In contrast, the binary system CaSWy-precipitated Fe (Table 1: CaSWy-precip Fe with 3.40% Fe) decreased pH from 5.7 to 4.9 upon blank treatment for HA association. These pH changes are very important from the point of view of 2,4-D sorption, which has been shown to be dramatically pH-dependent (*29, 30*). Comparison of the sorptive behavior and physicochemical properties of the associations were done with their corresponding blank samples instead of the untreated individual sorbents, thus allowing direct evaluation of the effects of component interassociation without including the side effects (i.e., pH effects, NH_4^+, H^+, Na^+/Ca^{2+} exchange) produced during synthesis of those associations.

The binary and ternary organomineral associations prepared were highly stable in aqueous solution (1:100 solid to 0.01 M $CaCl_2$ suspensions). No solubilization of Fe(III) was measured at pH > 3, and the amounts of HA solubilized (measured by UV absorption at 285 nm using an external standard curve for quantification) were, in general, <10% of the total HA in the complexes. Amounts of soluble HA measured for the sorbents containing Fe were even lower (<3%), indicating that Fe stabilizes the bonding of the HA to the mineral constituents in the associations (*17*).

Data in Table 1 show that Fe precipitation on montmorillonite increased the SSA of the blank clay and slightly decreased pH. Basal spacing values, d_{001}, for the montmorillonite−Fe oxide binary associations showed a collapse to 1.0 nm after heating the K-saturated sample to 300 °C, which indicates the absence of pillars of Fe hydroxy-polymers (*31*). However, the lower basal spacings of the air-dried montmorillonite-precipitated Fe associations than those for clays without Fe (corresponding blank samples) suggest partial substitution of the original Ca^{2+} ions and their water molecules by less hydrated Fe species (small Fe-polymers or even monomers). This phenomenon was not observed in the montmorillonite-adsorbed Fe complexes because the large size of the Fe polycations (MW > 100 000) used in the synthesis of these complexes limited their access to the internal spaces of montmorillonite (*24, 25, 27*).

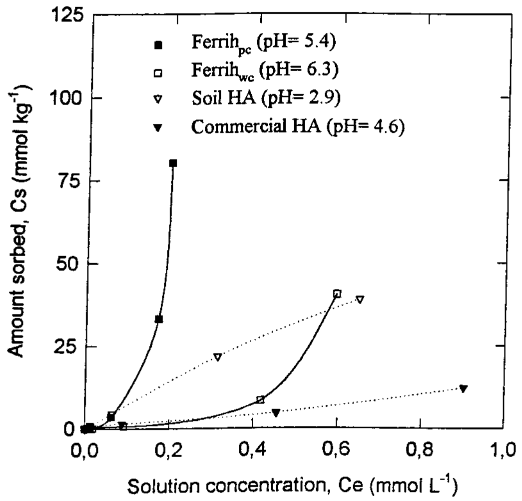

FIGURE 1. Sorption isotherms of 2,4-D on single sorbents.

Association of HA with CaSWy and $Ferrih_{pc}$ led to a decrease in pH and in SSA measured by N_2 adsorption. The greater decrease in SSA observed in the case of CaSWy compared to $Ferrih_{pc}$ may be related to HA macromolecules acting as bridges between packets of montmorillonite producing aggregation (*32*). SSA also decreased in ternary systems and will be discussed later. No evidence was found for the presence of interlayer HA in any of the associations prepared (no significant differences in d_{001} values in Table 1), which is in agreement with the large size of the HA macromolecules and their anionic character at the pH (pH 6.5) of the synthesis of the associations (*33, 34*).

Sorption of 2,4-D on Single Model Sorbents. Montmorillonites, CaSWy and CaSAz, did not sorb 2,4-D. In fact, equilibrium herbicide concentrations were found to be slightly greater than the respective initial concentrations. Apparently, the dried clays adsorbed water in preference to 2,4-D leading to an increase in the concentration of 2,4-D in the bulk of the solution resulting in a net effect of *negative* sorption. This phenomenon is reasonable because at the pH of the clay suspensions (pH > 7, Table 1), 2,4-D is predominantly in the anionic form and would be repelled by the negatively charged clay particles (*35, 36*).

Sorption isotherms for 2,4-D on $Ferrih_{pc}$ and $Ferrih_{wc}$ (Figure 1) were of S-type according to the Giles et al. (*37*) classification. Sorption isotherms on $Ferrih_{pc}$ and $Ferrih_{wc}$ are identical in shape to those obtained by Madrid and Diaz-Barrientos (*29*) on lepidocrocite. Such isotherms may indicate that water or ionic species in solution compete strongly with the organic compound or that there is a strong intermolecular attraction within the sorbed layer of organic compound (*37, 38*). At the pH of the sorption experiment (Table 1) 2,4-D species exist as anionic form which may be sorbed with their $-COO^-$ groups oriented toward the positively charged Fe oxide surface and their large aromatic rings directed toward the solution. In such a situation, strong competition between the organic compound and −Cl, −OH, or even H_2O at the ferrihydrite surface is expected as well as favorable van der Waals interactions between the aromatic rings of the sorbed anions (*30, 39, 40*). The greater sorption of 2,4-D on $Ferrih_{pc}$ compared to $Ferrih_{wc}$ agrees with the high SSA of $Ferrih_{pc}$ (315 $m^2\ g^{-1}$) compared to $Ferrih_{wc}$ (152 $m^2\ g^{-1}$). The lower pH of $Ferrih_{pc}$ (Table 1) would also contribute to greater sorption on this Fe oxide since at lower pH values the oxide surface becomes more positively charged, thus increasing the attraction for the 2,4-D anionic species (*30, 41*).

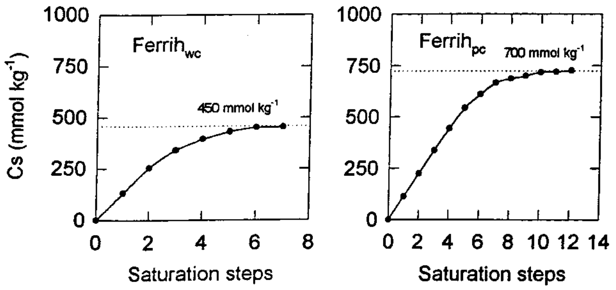

FIGURE 2. Successive saturation of Ferrih$_{wc}$ and Ferrih$_{pc}$ with 2,4-D.

The L-type isotherms (*37*) found for soil and commercial HA (Figure 1) suggest minimum competition from water molecules for sorption sites on the humic acids (*37, 42*). Soil HA sorbed much more 2,4-D than commercial HA (Figure 1), probably due to the lower pH of the soil HA suspension (Table 1), very close to the pK_a of the herbicide which increases the amount of molecular form. This likely reduces unfavorable repulsions between the COO$^-$ group of 2,4-D and deprotonated carboxylic groups on humic acid (*43*) and favors hydrophobic and polar interactions between the molecular form of the herbicide and HA.

Because the shape of the sorption isotherms were markedly different depending on the sorbent, no comparisons were done in this work in terms of Freundlich coefficients, which are frequently used to quantitatively compare sorption capacities for different sorbents (*44, 45*). However, sorption isotherms in Figure 1 show the importance of the Fe oxides in sorbing 2,4-D at high herbicide concentrations compared to HAs, whereas the relative importance of the HAs increases at low 2,4-D concentrations.

Saturation of the Fe Oxides with 2,4-D and IR Spectroscopy Study. The maximum sorption estimated from successive treatments of Ferrih$_{pc}$ and Ferrih$_{wc}$ with 1 mM 2,4-D solution were 450 mmol kg^{-1} for Ferrih$_{wc}$ and 700 mmol kg^{-1} for Ferrih$_{pc}$ (Figure 2). This is equivalent to one 2,4-D species sorbed per 56 Å^2 of surface of Ferrih$_{wc}$ and to one 2,4-D species sorbed per 75 Å^2 of surface of Ferrih$_{pc}$. A similar result was found by Watson et al. (*30*) for the sorption of 2,4-D on goethite, where one species was sorbed per 70 Å^2 of surface. The low value obtained in the present work in the case of Ferrih$_{wc}$ (56 Å^2/species) may indicate a high accessibility of the surface of this Fe oxide for the 2,4-D species, as a result of lower microporosity (*27, 28*).

FT-IR spectra of Ferrih$_{wc}$, Ferrih$_{pc}$, and their complexes with 2,4-D revealed the presence of bands corresponding to 2,4-D in the complexes, thus demonstrating the presence of 2,4-D sorbed on the Fe oxides (Figure 3). Notably absent in the spectra were bands corresponding to the protonated $-$COOH group of the acid (*46*) in the complexes saturated with 2,4-D (especially the band at 1735 cm^{-1}) and the appearance of bands corresponding to the carboxylate anion, at 1559 and 1339 cm^{-1} (Figure 3). These results confirmed that 2,4-D sorption on Ferrih$_{pc}$ and Ferrih$_{wc}$ occurred essentially through the carboxylate anion of 2,4-D with negligible participation of the molecular form. Thus, as reported by Kavanagh et al. (*39*), it seems that sorption occurred primarily in response to a favorable Coulombic interaction between the sorbing anion and the positively charged surface of the Fe oxides. Coulombic forces, as opposed to strong bonding mechanisms such as ligand exchange, have previously been proposed to govern the sorption of 2,4-D on Fe oxides (*30, 39*).

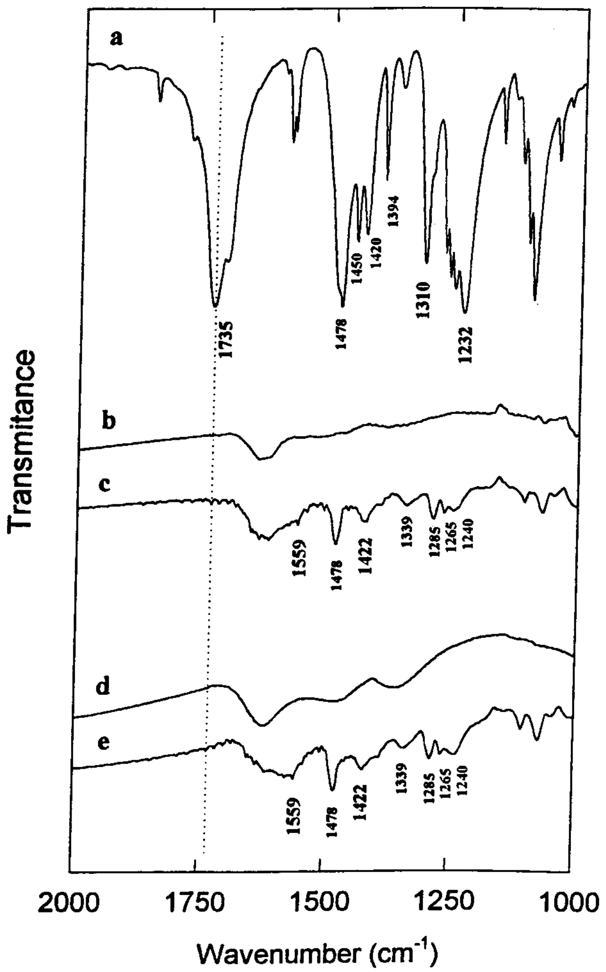

FIGURE 3. FT-IR spectra of (a) 2,4-D acid, (b) Ferrih$_{wc}$, (c) Ferrih$_{wc}$ + 2,4-D (d) Ferrih$_{pc}$, and (e) Ferrih$_{pc}$ + 2,4-D.

2,4-D Sorption on Binary Model Sorbents. The blank treatments "*per se*" slightly increased 2,4-D sorption on CaSWy due to partial H_3O^+ saturation on external exchange positions and the subsequent decrease in pH of the suspension (Table 1). In fact, 2,4-D sorption on the diverse CaSWy and CaSAz blanks illustrates the pH effect on 2,4-D sorption by smectites, with increased sorption at lower pH. Sorption increased from the untreated CaSWy (pH 7.9, negative sorption not shown) to the respective blanks for HA association (pH 7.1), Fe precipitation (pH 6.3), and Fe adsorption (pH 3.8) (Figures 4 and 5). The same tendency was observed for CaSAz. The pH decrease favors the proportion of the herbicide in molecular form, which can be sorbed either by polar interactions or even by hydrophobic interaction with smectite surface (*17*). The increase in sorption with decreasing pH is evidenced by the K_d values obtained at single 2,4-D concentration 1 mM ($K_{d-1mM} = C_s/C_e$) for the untreated and blank-treated clays, included in Table 2. A similar behavior was observed for Ferrih$_{pc}$ whose blank corresponding to HA-treatment gave higher pH and lower 2,4-D sorption than the untreated sample (Table 2).

Both Fe precipitation and Fe adsorption on CaSWy led to a significant increase in 2,4-D sorption compared to sorption on blank clay without Fe, indicating that Fe coatings on CaSWy provided sorption sites for 2,4-D probably as anionic species (Figure 4). The sorption of 2,4-D on blank CaSAz kept rendering a net *negative* sorption because its high number of exchangeable Ca^{2+} adsorbed more water than in the case of the low charge SWy montmorillonite. Hence, Fe coatings were less effective (Figure 4) in reducing the exclusion of the 2,4-D anionic species from the highly charged surface of CaSAz. Thus, the associations containing CaSWy (low layer charge) were more sorptive than those containing CaSAz (high layer charge). Also, the associations containing

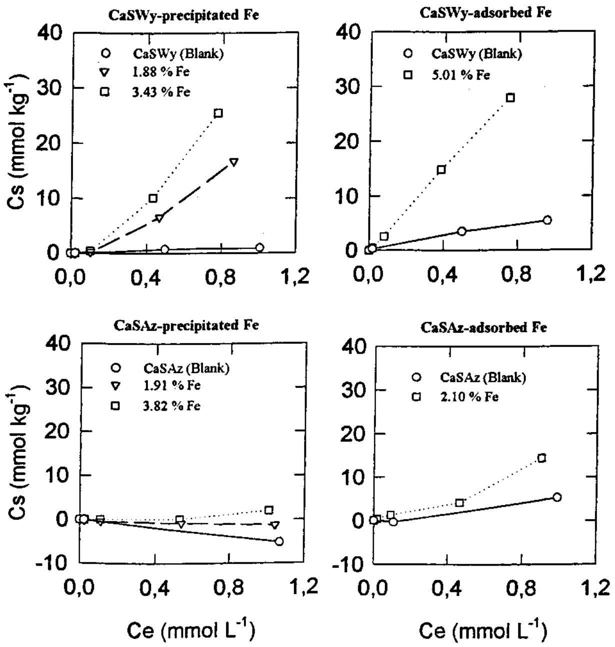

FIGURE 4. 2,4-D sorption isotherms on montmorillonite-Fe oxide binary associations.

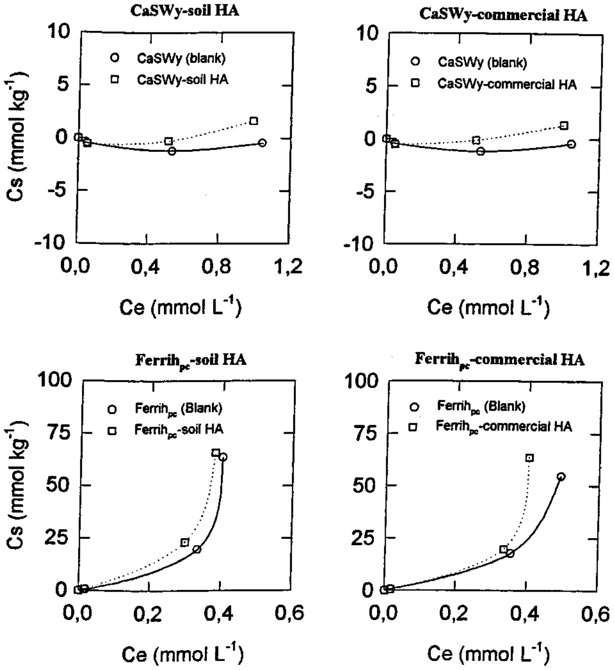

FIGURE 5. 2,4-D sorption isotherms on CaSWy-HA and Ferrih$_{pc}$-HA binary associations.

adsorbed Fe were more sorptive than those containing precipitated Fe (Figure 4), which could be related to the lower pH of the montmorillonite-adsorbed Fe associations (pH $\approx$ 4, Table 1). At such low pH values, a high positive charge on Fe coating surface is expected, increasing the attraction for the 2,4-D anionic species

TABLE 2. Distribution Coefficients, K_{d-1mM}, Obtained at Single 2,4-D Concentration of 1 mM for Single and Binary Model Sorbents and Corresponding Values Normalized to the Fe Content (K_{Fe}) and Organic C Content (K_{oc}) of the Samples

sorbent	pH	Fe (%)	C (%)	K_{d-1mM} (L kg^{-1})	K_{Fe}	K_{oc}
CaSWy	7.9			<0		
Ferrih$_{pc}$	5.4	52.3		409	783	
Soil HA	2.9		42.5	60		141
Fluka HA	4.6		41.0	14		34
CaSWy (blank)	6.3	0		1		
CaSWy-precip Fe	5.8	1.88		20	1064	
CaSWy-precip Fe	5.7	3.43		33	962	
CaSWy (blank)	3.8	0		6		
CaSWy-adsorbed Fe	3.8	5.01		37	740	
CaSWy (blank)	7.1		0	0		
CaSWy−soil HA	5.0		2.4	1.6		67
CaSWy−Fluka HA	5.2		2.8	1.3		46
Ferrih$_{pc}$ (blank)	5.9	52.3	0	158	302	
Ferrih$_{pc}$−soil HA	5.2	48.6	3.6	172	354	4800
Ferrih$_{pc}$−Fluka HA	5.6	48.6	3.4	111	229	3300

An estimation of the effectiveness of the Fe associated with CaSWy compared to that of the pure Fe oxide was made by normalizing the distribution coefficients measured at single herbicide concentration of 1 mM (K_{d-1mM}) to the Fe content of the different sorbents (Table 2). The Fe-normalized distribution coefficient, K_{Fe}, for the CaSWy-adsorbed Fe association was very similar to the value obtained for pure Ferrih$_{pc}$, whereas the K_{Fe} values for the CaSWy-precipitated Fe associations were significantly higher. Because the high pH of the CaSWy-precipitated Fe associations do not contribute to increase the positive charge of the Fe coatings (Table 1), the high effectiveness of this Fe in sorbing 2,4-D has to be attributed to a great surface area exposed when associated with the clay. These results illustrate how the interassociation of a sorbing soil component (Fe oxide) with other nonsorbing constituents (clay) may result in enhanced or similar sorption for a given organic compound, depending on the way in which interassociation occurs (i.e., precipitation or specific adsorption of Fe species).

Sorption isotherms for 2,4-D on CaSWy-HA binary associations, for both HAs (Figure 5), were very similar to that reported above for the CaSAz-adsorbed Fe complex (Figure 4). Sorption increased at higher herbicide concentrations for both HAs. In contrast to Fe coatings, HA was not expected to reduce the negative charge of the surface of montmorillonite, but some 2,4-D sorption on the HA coatings through weak hydrophobic interactions may have compensated for the exclusion of the organic anion from the clay surfaces. The result was no measurable sorption at low herbicide concentrations and some sorption at high herbicide concentrations (Figure 5). The observed increase in K_{d-1mM} value upon HA association (Table 2) should be attributed to 2,4-D sorption on HA associated with the external surface of the clay. The C-normalized K_{d-1mM} values (K_{oc}) for the CaSWy−Fluka HA association did not appreciably change compared to the pure Fluka HA, whereas that of the CaSWy−soil HA association dramatically decreased. The low effectiveness (K_{oc}) of the organic C of CaSWy−soil HA association in sorbing 2,4-D was likely due to the high pH of this association compared to pure soil HA as well as high intimate association with the clay surface. The latter is supported by the lower SSA of CaSWy−soil HA compared to CaSWy−Fluka HA (Table 1) and agrees with the behavior previously observed for the sorption of weakly basic herbicides by similar binary associations (*17*).

Sorption isotherms on Ferrih$_{pc}$−HA associations showed that 2,4-D sorption on Ferrih$_{pc}$ was just slightly influenced by soil HA and Fluka HA associations (Figure 5). Accordingly, based on the individual isotherms (Figure 1), both HAs should have reduced 2,4-D sorption on Ferrih$_{pc}$, Fluka HA more so than soil HA. However, the observed effect of soil HA was to slightly increase 2,4-D sorption, whereas the contrary was observed for commercial HA (Figure 5). The same tendency was observed after normalizing the sorption distribution coefficients K_{d-1mM} to the Fe content of the samples (K_{Fe}) (Table 2). On the other hand, the extremely high K_{oc} values

TABLE 3. Specific Surface Areas (SSA), pH Values, and 2,4-D Sorption Parameters on Ternary Model Particles

sorbent	pH	SSA (m^2 g^{-1})	% sorption	K_{d-1mM} (L kg^{-1})	K_{Fe}	K_{oc}
CaSWy-precip Fe (blank)	4.9	55	28	39.1	1150	
CaSWy-precip Fe−soil HA	5.1	13	7	7.9	245	205
CaSWy-precip Fe−Fluka HA	4.9	10	8	8.8	284	226

for these associations compared to the pure HAs indicated that most of the sorption took place on the Fe oxide (Table 2). These results are surprising because the association of HA with ferrihydrite has been widely reported to block much of the surface of the Fe oxide available for herbicide sorption and greatly reduces its positive surface charge (*8, 47, 48*). It seems that the low size porosity of Ferrih$_{pc}$ (*27*), responsible for its high SSA, was not accessible for the large humic macromolecules, although it remained accessible for the small 2,4-D species. This is supported by the fact that the SSAs of the Ferrih$_{pc}$−HA complexes were nearly the same as that of pure Ferrih$_{pc}$ (Table 1), indicating that most of the surface of the Fe oxide remained uncovered by HA and, therefore, was still available for the sorption of 2,4-D. The different behavior observed for the Ferrih$_{pc}$−soil HA and Ferrih$_{pc}$−Fluka HA could be due to different pH of their suspensions (Table 1), which has been shown to be a critical parameter in the sorption of 2,4-D by Fe oxides (*29, 30*). In these ferrihydrite−HA binary associations, suspension pH more than humic acid coatings seems to determine the sorption of 2,4-D.

2,4-D Sorption on Ternary Model Sorbents. Associations of soil HA and commercial HA with the CaSWy-precipitated Fe complex greatly reduced the 2,4-D sorption capacity provided by the Fe coatings on CaSWy (Table 3). The decrease in the effectiveness of the Fe in the ternary associations to sorb 2,4-D, compared to the binary system, is evident from the decrease in both K_{d-1mM} and K_{Fe} values. All ternary systems had nearly the same pH (pH 5), so differences in sorption could not be attributed to pH effects. In contrast, SSAs indicated that much of the mineral surfaces was blocked after HA association (Table 3).

The different effect of HAs observed in ternary systems (high decrease in K_d and K_{Fe} and slight increase in K_{oc}) compared to Ferrih−HA binary systems (small changes in K_d and K_{Fe} and large increase in K_{oc}) could be explained as follows: Fe coatings on CaSWy have exposed a higher flat or open surface accessible to the large humic macromolecules leading to greater and more efficient binding of the HA to those Fe coatings than that to the pure ferrihydrite particles (*27, 28*). This is supported by the higher SSA decrease of CaSWy−Ferrih$_{pc}$ upon HA association compared to that for pure Ferrih$_{pc}$ (Table 1). It is likely that the binding of the HA to CaSWy-precip Fe took place preferentially through the Fe coatings on CaSWy (*9, 49*) reducing the positive charge of the surface (*8*) and, therefore, reducing the number of sorption sites for the 2,4-D anionic species. Sorption could have been limited to some unblocked ferric centers through Coulombic forces (anionic species) and to the external coatings of HA through weak hydrophobic interactions (molecular species). Some 2,4-D sorption on Fe is suggested by the relatively high K_{oc} values obtained for the associations compared to the pure HAs, especially in the case of Fluka HA (Table 2).

Desorption Studies. Desorption of 2,4-D was highly reversible for soil and commercial HA, in agreement with sorption through weak hydrophobic interactions (Figure 6).

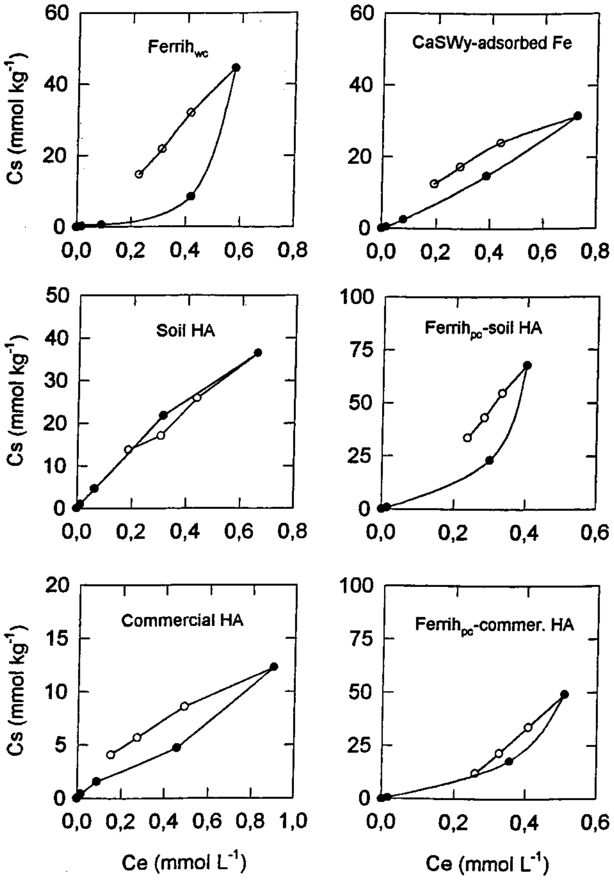

FIGURE 6. Sorption (●) and desorption (○) isotherms of 2,4-D on selected model particles.

Desorption of 2,4-D from pure ferrihydrite and from the binary sorbents containing Fe oxide was hysteretic, but hysteresis loops tended to close down with increasing number of desorption steps. This could be due to slow desorption rate as a result of steric hindrance inside the Fe oxide micropores as well as to intermolecular attraction of the sorbed 2,4-D, which should increase the activation energy for desorption, especially at high surface coverages. The shape of the hysteresis loops suggests that most of the sorbed 2,4-D can be desorbed with additional desorption steps, supporting a sorption mechanism through relatively weak forces (i.e., van der Waals forces in the case of HA and Coulombic interactions in the case of iron oxides).

Environmental Implications. Sorption and desorption in natural particles is a key process dealing with the fate and transport of contaminants and even with remediation techniques. The results of this study show how the complexity of the surface of a natural particle is far from the sum of its individual components (i.e., clay mineral, iron oxide, and humic acid), with respect to the sorption of an organic weak acid contaminant such as 2,4-D. The use of calculated sorption parameters, such as K_{oc}, K_{ow}, $K_{mineral}$, or K_{Fe}, for modeling may result in serious deviation from the reality, because the sorption capacity of a natural particle is highly dependent on the nature and amount of surface ultimately exposed which, in turn, is determined by the degree of interassociation of the individual constituents.

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