

Sorption-Desorption of Lead (II) and Mercury (II) by Model Associations of Soil Colloids

M. Cruz-Guzmán, R. Celis, M. C. Hermosín, P. Leone, M. Nègre, and J. Cornejo*

ABSTRACT

Sorption by soil colloids largely determines the bioavailability of heavy metals and their movement in soil and aquatic environments. Due to soil constituents' interactions, the sorption behavior of natural soil colloids may not correspond to the simple sum of their individual constituents. In this work, sorption of Pb(II) and Hg(II) ions by binary and ternary model particles containing Wyoming montmorillonite (SW), poorly crystallized ferrihydrite (Ferrih), and soil humic acid (HA) was investigated and the results obtained were compared with the sorption behavior of the individual constituents. For single sorbents, Pb(II) sorption was high on HA, moderate on SW and zero on Ferrih, whereas Hg(II) sorption decreased in the order: HA \gg Ferrih $>$ SW. Ferrihydrite coatings on SW had little effect on Pb(II) and Hg(II) sorption by the clay. Humic acid coatings on SW significantly enhanced sorption of both heavy metals, whereas, unexpectedly, HA coatings on Ferrih did not enhance heavy metal sorption. This last result was attributed to blockage of the functional groups of HA responsible for heavy metal sorption (such as carboxylic groups) as a result of their interaction with the Ferrih surface. A similar behavior was observed for Pb(II) in ternary particles containing HA. Sorption by the model associations was highly reversible. The results of this study confirmed that the sorptive behavior of colloidal particles for heavy metals is not the simple sum of the contributions of the single constituents, indicating the usefulness of considering polyphasic model sorbents to achieve a more realistic interpretation of the sorption process in soil.

NATURAL SOIL COLLOIDS are organomineral associations of various soil constituents, which are the main contributors to sorption and transport processes affecting contaminants in soil and aquatic environments. Because interactions between soil constituents can significantly alter the amount and nature of the surface exposed by soil colloids for contaminant sorption, predictions of the extent of sorption based on the sum of the sorption capacities of the individual soil constituents may result in serious deviation from the reality (Khan, 1980). Consequently, sorption predictions from soil composition would be greatly improved with a better understanding of how interactions between individual soil constituents affect the sorption behavior of naturally occurring soil colloids (Cowan et al., 1992).

Traditionally, the importance of the different soil components in contaminant sorption has been evaluated by determining the sorption behavior of selected soil

fractions or by investigating changes in sorption after removing selected soil constituents (Huang et al., 1984; Zachara et al., 1993; Laird et al., 1994; Gray et al., 2000; Li et al., 2001). An alternative approach has been the use of model sorbents. Extensive literature exists on the interaction of inorganic and organic contaminants with synthetic or purified soil constituents, such as clay minerals, metal oxides, or humic acids (Bailey et al., 1968; Laird et al., 1992; Zachara et al., 1993; Cox et al., 1995; Sarkar et al., 1999, 2000; Hundal et al., 2001). Information on the interaction of contaminants with multiple or polyphasic sorbents is more scarce, although in the last years increased attention has been given to studying the behavior of multicomponent model sorbents to achieve a more realistic interpretation of the sorption process in soil (Tipping et al., 1983; Pusino et al., 1992; Fusi et al., 1993; Taylor and Theng, 1995; Payne et al., 1996; Celis et al., 1996; Sannino et al., 1999; Alcacio et al., 2001). Most of these studies revealed that the behavior of complex sorbents could be far from that expected for the sum of their individual constituents.

Heavy metals are important environmental pollutants threatening the health of human populations and natural ecosystems. Like other inorganic and organic contaminants, the fate of heavy metals in the environment is largely controlled by sorption reactions with soil colloids. The three main active soil colloidal constituents, clay minerals, metal oxides, and organic matter, are important sorbents of heavy metals owing primarily to their cation-exchange capacity (CEC) and their ability to form inner-sphere complexes through surface reactive groups, such as carboxylic and hydroxyl groups (Mercier and Detellier, 1995; Jelinek et al., 1999; Sheng et al., 1999; Ponizovskii and Mironenko, 2001; Weng et al., 2001). Mutual interactions between clay minerals, Fe oxides, and organic matter can greatly alter the sorptive properties of these soil constituents for heavy metals because such interactions usually involve cation exchange sites and carboxyl and OH surface groups, that is, potential sorption sites for heavy metals (Rengasamy and Oades, 1977; Gu et al., 1994; Cornejo and Hermosín, 1996). In the present work, the sorption-desorption of Pb(II) and Hg(II) ions by binary and ternary model sorbents containing SW, Ferrih, and HA is reported and compared with the sorption behavior of the individual model sorbents. Experiments were conducted at high metal ion concentrations and low pH to simulate a worst-case scenario of contamination by heavy metals. A recent example is the accident occurred in Aznalcóllar

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Abbreviations: AAS, atomic absorption spectrometry; CEC, cation-exchange capacity; d_{001} , basal spacing; Fe_o , oxalate-extractable Fe; Fe_d , dithionite-citrate-bicarbonate-extractable Fe; Ferrih, ferrihydrite; FTIR, Fourier-transform infrared; HA, humic acid; MW, molecular weight; SSA, specific surface area; SW, Wyoming montmorillonite.

Table 1. Characteristics of the humic acid (HA).

C	H	O†	N	S	ash	Total acidity	-COOH	Phenolic OH
						mmol kg ⁻¹		
52.9	4.7	36.2	4.3	0.5	1.4	8190	4440	3750

† Calculated by difference.

(Spain) in 1998, where 4.5 hm³ of acid sludge containing high metal ion concentrations contaminated the Guadamar River and surrounding soils (van Geen et al., 1999). The information provided in this work may be helpful for a better understanding of the role of the three main soil colloidal components in heavy metal sorption when associated in naturally occurring soil aggregates, and for soil remediation studies as well.

MATERIALS AND METHODS

Single Sorbents

The single model sorbents used in this work were SW, poorly crystallized Ferrih, and soil HA. The HA was extracted from the A (0–15 cm) horizon of a histosol with 0.5 M NaOH according to the International Humic Substances Society (IHSS) standard method (Swift, 1996). After extraction, the HA was precipitated with 6 M HCl, washed with 0.1 M HCl and 0.3 M HF, dialyzed (molecular weight [MW] cut-off: 3.5 kDa; final conductivity <3 μS cm⁻¹), and then freeze-dried. Physicochemical characteristics of the HA are given in Table 1. The <2-μm fraction of Na-SWy2, SWy-2 (The Clay Minerals Society, Columbia, MO), was separated by sedimentation and then lyophilized. Isomorphous substitutions in the octahedral layer of SWy-2 result in a CEC of 76 cmol_c kg⁻¹, compensated mainly by Na⁺ as principal exchangeable cation. Ferrihydrite was synthesized in the laboratory by neutralizing a 0.1 M Fe(NO₃)₃ solution (1 L) with NaOH to pH of 7.5. The precipitate was washed three times with deionized water, dialyzed for 5 d (MW cut-off: 10 kDa; final water conductivity <3 μS cm⁻¹), and then freeze-dried. The X-ray diffractogram of Ferrih showed only the two *hk* lines at about 0.254 and 0.150 nm, respectively, and its N specific surface area (SSA) was 346 m² g⁻¹ (Table 2). These data indicated the poor crystallinity of the Fe oxyhydroxide obtained (Schwertmann and Taylor, 1989).

Binary and Ternary Model Sorbents

Binary and ternary model sorbents containing SW, Ferrih, and HA were prepared according to the procedure previously described by Celis et al. (1998). This consisted of Fe(III) precipitation in the presence of SW and shaking of dissolved HA in the presence of clay or Ferrih particles, followed by lyophilization. The three main differences between the complexes prepared here and those used in Celis et al. (1998) were: (i) the HA was extracted from a different soil, (ii) we used the untreated Na-SW instead of the Ca-saturated clay, and (iii) to favor association, we added the HA solution to just-precipitated Ferrih instead of to the lyophilized sample.

Montmorillonite-Ferrihydrite Binary Associations (SW-Ferrih)

Aliquots of 10 g of SW were treated with 500 mL of aqueous Fe(NO₃)₃ solutions containing two different Fe(III) concentrations (15 and 30 mM). The suspensions (pH 2.5 due to the hydrolysis of Fe³⁺) were stirred for 10 min, neutralized with NaOH up to pH 7.5, and shaken for 16 h. The resulting SW-Ferrih binary associations were dialyzed (MW cut-off: 10 kDa), freeze-dried and stored at room temperature until used. The amounts of Fe(III) used in the synthesis corresponded to final Ferrih contents of about 8 and 16% (SW-Ferrih₈ and SW-Ferrih₁₆). A blank clay sample (SW-Ferrih₀) was also prepared by treating 10 g of SW with 500 mL of HNO₃ (pH 2.5), neutralizing with NaOH to pH 7.5, shaking for 16 h, and then freeze-drying. This sample, without Fe(NO₃)₃ treatment, served as a control and helped distinguish the effects of Fe treatment from those due to the low pH of the Fe(III) solutions used (Celis et al., 1998).

Montmorillonite-Humic Acid Binary Associations (SW-HA)

SW-HA binary associations were obtained by adding 10 g of SW to 400 mL of aqueous solutions (pH 6.5) containing

Table 2. Characteristics of the model sorbents†.

Sorbent	Sorbent composition‡			Fe _e /Fe _d	pH§	SSA	d ₀₀₁ (25°C/200°C)
	SW	Ferrih	HA				
%							
m ² g ⁻¹							
nm							
Single model sorbents	SW	0	0	–	7.0	25	1.50/0.97
	Ferrih	100	0	0.99	5.8	346	–
	HA	0	100	–	2.3	<1	–
Binary associations	SW-Ferrih ₀	100	0	–	6.3	25	1.41/0.98
	SW-Ferrih ₈	92.7	7.3	0.98	4.7	58	1.41/0.98
	SW-Ferrih ₁₆	86.3	13.7	0.93	4.8	83	1.41/0.98
	SW-HA ₀	100	0	–	6.5	43	1.56/0.98
	SW-HA ₄	95.7	0	–	5.2	4	1.56/0.99
	SW-HA ₈	93.3	0	–	5.2	3	1.56/0.99
	Ferrih-HA ₀	0	100	1.03	6.6	348	–
	Ferrih-HA ₄	0	96.3	1.00	6.0	334	–
	Ferrih-HA ₈	0	93.1	0.99	6.4	290	–
Ternary associations	SW-Ferrih-HA ₀	85.2	14.8	0	0.94	82	1.56/1.00
	SW-Ferrih-HA ₄	82.5	14.6	2.9	0.92	57	1.56/1.00
	SW-Ferrih-HA ₈	81.0	13.5	5.5	0.96	32	1.56/1.00

† SW: Wyoming montmorillonite; Ferrih: ferrihydrite; HA: humic acid; Fe_e: oxalate-extractable Fe; Fe_d: dithionite-extractable Fe; SSA: specific surface area; d₀₀₁: basal spacing at room temperature and after heating at 200°C.

‡ The Fe and organic C contents of the binary and ternary associations were converted to Ferrih and HA contents using the Fe and organic C contents of pure Ferrih and pure HA, respectively.

§ Measured in suspensions containing 1 g of sorbent and 50 mL of 0.01 M CaCl₂ solution.

0.4 or 0.8 g of HA previously dissolved by bringing the suspensions to pH 10 using NaOH. Once dissolved, the HA solution was brought to pH 6.5 using HCl, and then the 10 g of SW were added. The amounts of HA used in the preparation of the SW-HA binary associations corresponded to final HA contents of 4 and 8% (SW-HA₄ and SW-HA₈). A blank clay sample (SW-HA₀) was also prepared by treating 10 g of SW identically, but without HA addition. After shaking for 16 h, the SW-HA binary associations and the blank clay were dialyzed (MW cutoff: 10 kDa), freeze-dried, and stored at room temperature until used.

Ferrihydrite-Humic Acid Binary Associations (Ferrih-HA)

Suspensions containing 10 g of just-precipitated Ferrih were centrifuged, the supernatants were removed, and then 400 mL of aqueous solutions (pH 6.5) containing 0.4 or 0.8 g of dissolved HA were added. The suspensions (Ferrih-HA₄ and Ferrih-HA₈) along with a HA-free control Ferrih sample (Ferrih-HA₀) were shaken for 16 h, dialyzed (MW cut-off: 10 kDa), freeze-dried, and stored at room temperature until used.

Montmorillonite-Ferrihydrite-Humic Acid Ternary Associations (SW-Ferrih-HA)

SW-Ferrih-HA ternary associations were obtained from the SW-Ferrih₁₆ binary complex. Suspensions containing the just-precipitated SW-Ferrih₁₆ binary complex (approximately 10 g) were centrifuged, the supernatant was removed, and then 400 mL of aqueous solutions (pH 6.5) containing 0.4 or 0.8 g of dissolved HA were added. The suspensions (SW-Ferrih-HA₄ and SW-Ferrih-HA₈) along with a HA-free control sample (SW-Ferrih-HA₀) were shaken for 16 h, dialyzed (MW cut-off: 10 kDa), freeze-dried, and stored at room temperature until used.

Sorbents Characterization

The Fe content of the sorbents was determined by oxalate-extraction (Fe_o) and also by dithionite-citrate-bicarbonate extraction (Fe_d) following the procedures described by McKeague and Day (1966). Elemental analyses (C, H, N, S) were performed using a Perkin-Elmer elemental analyzer, model 1106 (Perkin-Elmer Corp., Norwalk, CT). Acidity of HA was measured according to Swift (1996). Specific surface areas of the sorbents were obtained by N₂ adsorption at 77 K using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan). The samples were out gassed at 80°C and equilibrated under vacuum for 15 h before measuring the N₂ adsorption isotherm. Basal spacing values of SW samples were obtained by X-ray diffraction on oriented specimens using a Siemens D-5000 diffractometer (Siemens, Stuttgart) with CuK_α radiation. Fourier-Transform infrared (FTIR) spectra were obtained on KBr disks in a Nicolet 5 PC spectrometer (Nicolet Instr. Corp., Madison, WI).

Heavy Metal Sorption-Desorption Experiments

Lead(II) and Hg(II) sorption isotherms on the different sorbents were obtained using the batch equilibration procedure. As described above, all sorbents were freeze-dried before reacting with the metal ions. Duplicate 10-mg sorbent samples were equilibrated at 20 ± 2°C for 24 h with 10 mL of aqueous solutions of Pb(NO₃)₂ or Hg(NO₃)₂ (Sigma, ACS reagent) with metal ion concentrations ranging from 0.25 to 1 mmol L⁻¹. For HA, higher metal ion concentrations (up to 5 mmol L⁻¹) were used to reach the "plateau" of the sorption isotherm, which allowed us to determine the maximum sorp-

tion capacity of the sorbent. Initial heavy metal solutions were prepared in 0.001 M HNO₃ (pH = 3) to avoid precipitation and to simulate a worst-case scenario of heavy metal mobilization. For all sorbents, the pH of the suspensions remained 3.0 ± 0.3 after a 24-h equilibration. After equilibration, the suspensions were centrifuged and 5 mL of the supernatant solution was removed for analysis. The concentration of heavy metal in the supernatant was determined by atomic absorption spectroscopy (AAS) using a Perkin-Elmer 1100B atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT). The amount of metal sorbed was calculated by difference between the initial and final solution concentrations. Metal solutions without sorbent were also shaken for 24 h and served as controls. For the experimental conditions used, the sensibility of AAS for Pb(II) and Hg(II) analysis was about 0.002 and 0.025 mM, respectively. Due to the high concentrations used in the sorption experiments (initial concentrations ≥ 0.25 mM), errors associated with metal analysis were in general < 10%. For spectroscopic analysis, HA samples (10 mg) treated with 10 mL of 1 mM heavy metal solutions (pH 3), along with a heavy metal-free HA control sample, were washed once with 10 mL of distilled water and then air-dried and analyzed by FTIR spectroscopy as KBr disks. The heavy metal-free HA control sample consisted of 10 mg of HA treated with 10 mL of 1 mM HNO₃ (pH 3) to avoid spectroscopic differences due to pH effects on the HA sample.

Desorption was measured immediately after sorption from the 1 mmol L⁻¹ initial concentration point of the sorption isotherms. The 5 mL of supernatant removed for the sorption analysis were replaced with 5 mL of HNO₃, NaNO₃, or Ca(NO₃)₂ at different concentrations. Then, the suspensions were shaken at 20 ± 2°C for 24 h, centrifuged, and the metal concentration determined in the supernatant. This desorption procedure was repeated three times. All sorption and desorption studies were conducted in duplicate.

Heavy metal sorption isotherms were fit to the Langmuir equation: $C_e/C_s = C_e/C_m + 1/C_m \times L$, where C_s (mmol kg⁻¹) is the amount of heavy metal sorbed at the equilibrium concentration C_e (mmol L⁻¹), C_m (mmol kg⁻¹) is the maximum sorption capacity of the sorbent, and L (L mmol⁻¹) is the Langmuir constant, which is related to the free energy of adsorption (Gu et al., 1995). C_m and L can be calculated from the linear plot of C_e/C_s vs. C_e .

RESULTS AND DISCUSSION

Characteristics of the Sorbents

Table 2 summarizes the most relevant characteristics of the single, binary, and ternary model sorbents, along with those of the blank samples prepared for each type of binary and ternary association. It should first be pointed out that the amounts of Ferrih and HA in the binary and ternary sorbents were very close to those expected from the amounts of clay, Fe(NO₃)₃, and HA introduced during the synthesis. In addition, the Fe_o/Fe_d ratio, very close to unity, indicated that most of the Fe present in the associations was amorphous or of very low crystallinity (McKeague and Day, 1966).

The changes in pH, SSA, and basal spacing (d_{001}) values observed on association of SW, Ferrih, and HA (Table 2) were similar to those reported for analogous binary and ternary model associations (Celis et al., 1998). Thus, Fe precipitation on SW led to an increase in the SSA measured by N₂ adsorption, whereas associa-

tion of HA with SW and Ferrih gave rise to a decrease in SSA (Table 2). This effect was less evident for the Ferrih-HA associations, most likely because much of the microporosity of Ferrih was not accessible for the large humic macromolecules, thus remaining unblocked during the N adsorption measurement (Celis et al., 1998, 1999). In agreement with the results reported by Celis et al. (1998) for their binary and ternary model associations, d_{001} of our complexes (Table 2) did not show evidences for penetration of Fe or HA polymers in the interlayers of SW during the synthesis.

As mentioned in the preceding section, the main differences between the complexes prepared in this work and those used by Celis et al. (1998) were the different origin of the HA (Table 1), the nature of the exchangeable cation in SW (Na^+ vs. Ca^{2+}) and the addition of HA to freshly precipitated Ferrih instead of to the lyophilized sample. Based on Celis et al. (1998), we performed an estimation of the degree of HA association with SW and Ferrih in binary and ternary particles from the measurement of the UV absorption (285 nm) of the HA solution before and after its interaction with the minerals during the preparation of the complexes. The results showed that the association of HA with Na-SW was $<10\%$ of the HA added, which is in contrast to the value of 52% reported by Celis et al. (1998) for Ca-SW. On the other hand, association of HA to sorbents containing freshly precipitated Ferrih was always $\geq 80\%$ of the HA added, compared with the values of 35 to 46% reported by Celis et al. (1998) for soil HA association to lyophilized Ferrih. Although the different nature of the HA may have contributed to the observed differences, these results strongly indicate that Ca^{2+} , as interlayer cation in SW, favors the interaction of humic acid with the clay and that freshly precipitated ferrihydrite particles are more reactive in binding HA than lyophilized Ferrih particles.

Heavy Metal Sorption Experiments

Sorption by Single Sorbents

Heavy metal sorption isotherms on single sorbents showed high sorption of Pb(II) by HA, moderate sorption by SW and negligible sorption by Ferrih, whereas Hg(II) was sorbed by all three single sorbents following the sequence: $\text{HA} \gg \text{Ferrih} > \text{SW}$ (Fig. 1). All sorption isotherms had a strong Langmuir-character, which suggests that a limited number of sorption sites exists and that as more sites in the sorbent are occupied it becomes increasingly difficult for the sorbing species to find a vacant site available (Giles et al., 1960). Lead(II) and Hg(II) sorption data were, therefore, well described by the Langmuir equation with regression coefficients $R^2 > 0.98$ (Tables 3 and 4). Both the Langmuir maximum sorption capacities (C_m) and the affinity coefficients (L) decreased in the order: $\text{HA} > \text{SW} > \text{Ferrih}$ (for Pb) and $\text{HA} > \text{Ferrih} > \text{SW}$ (for Hg).

The high sorption measured for Pb(II) and Hg(II) on HA can be related to the strong affinity of heavy metals for carboxylic and phenolic groups of humic substances

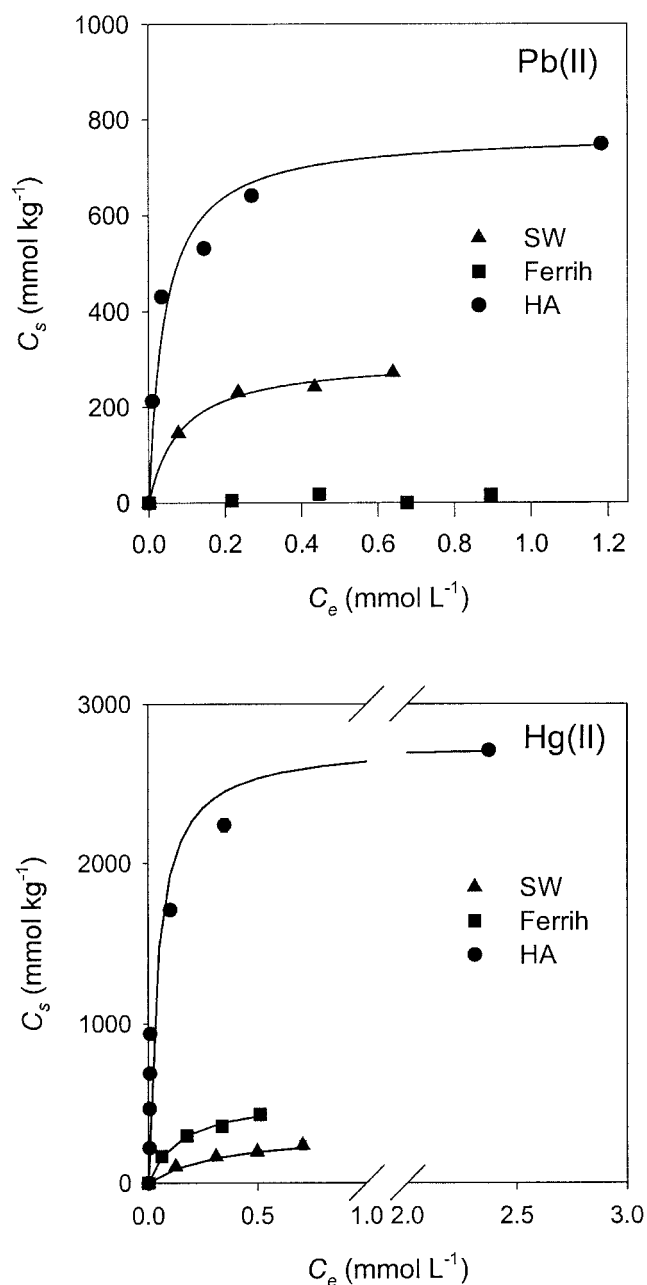


Fig. 1. Lead (II) and Hg(II) sorption isotherms (pH = 3) on single model sorbents. Symbols are experimental data points whereas lines are the Langmuir-fit sorption isotherms.

(Sauvé et al., 1998; Ponizovskii and Mironenko, 2001). Sorption of Hg(II) on HA was even greater than that observed for Pb(II), probably reflecting the ability of Hg(II) to bind a greater amount of those groups. Although the maximum sorption capacities measured for Pb(II) and Hg(II) on HA ($C_{m-\text{Pb}} = 771$, $C_{m-\text{Hg}} = 2750$) were lower than the total acidity (carboxylic + phenolic groups) of the HA used ($8190 \text{ mmol kg}^{-1}$, Table 1), it should be noted that both Pb(II) and Hg(II) are divalent cations and their sorption may have consumed two carboxylic/phenolic groups of HA. In addition, pK_a for phenolic groups and carboxylic groups in organic matter is typically higher than 3 and the low pH of the suspensions during the sorption experiments (pH = 3) proba-

Table 3. Langmuir parameters for Pb(II) sorption on model sorbents.

Sorbent	Pb(II)			C_{m-calc}^{\dagger}
	C_m	L	R^2	
	mmol kg ⁻¹	L mmol ⁻¹		
SW	302 (287–318)‡	12 (9–16)	0.995	–
Ferrih	0§	–	–	–
HA	771 (755–787)	24 (18–34)	0.999	–
SW-Ferrih ₀	267 (255–280)	7 (6–9)	0.996	267
SW-Ferrih ₈	296 (275–319)	4 (3–5)	0.989	248
SW-Ferrih ₁₆	264 (237–299)	4 (3–7)	0.978	230
SW-HA ₀	270 (256–286)	12 (9–19)	0.994	270
SW-HA ₄	315 (310–320)	12 (11–13)	1.000	291
SW-HA ₈	337 (324–350)	14 (11–19)	0.997	303
Ferrih-HA ₀	0	–	–	0
Ferrih-HA ₄	0	–	–	31
Ferrih-HA ₈	0	–	–	54
SW-Ferrih-HA ₀	248 (228–272)	8 (6–13)	0.985	248
SW-Ferrih-HA ₄	241 (237–245)	8 (7–9)	1.000	263
SW-Ferrih-HA ₈	249 (223–282)	7 (4–13)	0.974	277

† Calculated from the composition of the associations and the sorption capacity of the individual constituents.

‡ Values in parenthesis are standard error ranges about the mean.

§ Negligible sorption.

bly resulted in considerable competition between the metal ions and H⁺ ions for acidic sorption sites.

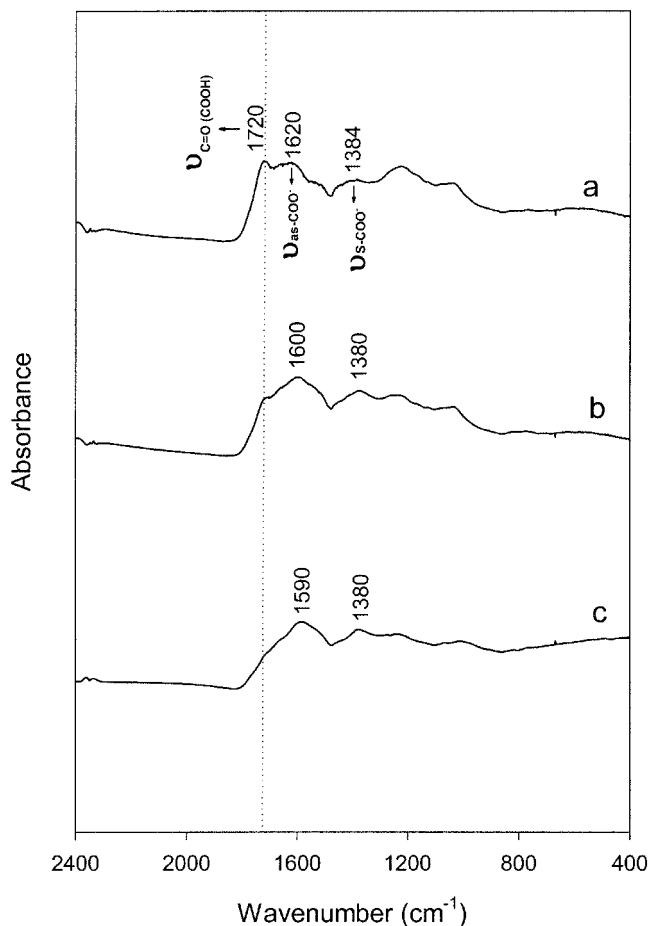
Fourier-transform infrared spectra of HA and its complexes with Pb(II) and Hg(II) clearly revealed the role of carboxylic groups in the retention of the heavy metals by HA (Fig. 2). The band at 1720 cm⁻¹ in the FT-IR spectrum of HA is assigned to the C=O stretching vibration of protonated carboxylic groups (Bellamy, 1975). On Pb(II) and especially Hg(II) treatment, the intensity of this band was greatly reduced and a great increase in the intensity of the bands at about 1600 and 1380 cm⁻¹ was observed. These bands are assigned, respectively, to the antisymmetric and symmetric stretching vibrations of ionized COO⁻ groups (Bellamy, 1975), thus demonstrating the involvement of carboxylic groups of HA in the retention of Pb(II) and Hg(II) and revealing that sorption occurred mainly through ionized COO⁻ groups. The shift of the COO⁻ stretching vibration band at 1620 cm⁻¹ to lower wave numbers on HA interaction with the metals reveals a decrease in the

Table 4. Langmuir parameters for Hg(II) sorption on model sorbents.

Sorbent	Hg(II)			C_{m-calc}^{\dagger}
	C_m	L	R^2	
	mmol kg ⁻¹	L mmol ⁻¹		
SW	319 (296–346)‡	4 (3–5)	0.988	–
Ferrih	536 (501–577)	7 (6–9)	0.990	–
HA	2750 (2700–2815)	23 (18–32)	0.999	–
SW-Ferrih ₀	331 (289–386)	2 (1–3)	0.960	331
SW-Ferrih ₈	275 (238–326)	2 (1–3)	0.953	345
SW-Ferrih ₁₆	246 (236–256)	4 (3–5)	0.996	360
SW-HA ₀	273 (239–318)	3 (2–5)	0.961	273
SW-HA ₄	369 (356–383)	13 (10–16)	0.997	372
SW-HA ₈	454 (418–497)	19 (11–42)	0.985	446
Ferrih-HA ₀	490 (439–553)	11 (7–20)	0.974	490
Ferrih-HA ₄	376 (342–418)	11 (7–20)	0.981	580
Ferrih-HA ₈	459 (411–520)	13 (7–28)	0.973	648
SW-Ferrih-HA ₀	462 (348–686)	2 (1–3)	0.824	462
SW-Ferrih-HA ₄	525 (495–560)	3 (2–4)	0.992	528
SW-Ferrih-HA ₈	474 (436–519)	9 (6–14)	0.985	589

† Calculated from the composition of the associations and the sorption capacity of the individual constituents.

‡ Values in parenthesis are standard error ranges about the mean.

**Fig. 2. Fourier transform infrared spectra of Humic acid (a); Pb(II)-treated HA (b); and Hg(II)-treated HA (c).**

strength of the C-O bond, probably due to a strong interaction of the carboxylate groups with the metal ions. Nevertheless, besides carboxylic groups, other functional groups with strong affinities for heavy metals, such as the thiol or amino functionalities, may have also contributed to the uptake of Pb(II) and Hg(II) by the HA (Guentzel et al., 1996; Pardo, 2000). In fact, elemental analysis of the HA revealed N and S contents of 4.3 and 0.5%, respectively (Table 1), which correspond to about 3071 mmol N kg⁻¹ and 156 mmol S kg⁻¹. In particular, the strong affinity of Hg(II) for the thiol-SH functionality has been stressed by a number of authors (Mercier and Detellier, 1995; Xia et al., 1999; Skyllberg et al., 2000; Celis et al., 2000; Lagadic et al., 2001).

The Langmuir maximum sorption capacities, C_m , obtained for Pb(II) and Hg(II) sorption on SW (Tables 3 and 4) were very similar ($C_m \approx 300$ mmol kg⁻¹), although the higher L constant associated with the Langmuir sorption isotherm of Pb(II) appeared to indicate a greater affinity of this metal ion for the SW surface compared with Hg(II). In contrast, Hg(II) displayed much greater affinity for Ferrih than Pb(II) (Fig. 1). The different speciation of Hg(II) and Pb(II) in aqueous solution at pH 3, as a result of the greater hydrolysis constant of Hg²⁺ ($K_1 = 10^{-2.7}$) compared with Pb²⁺ ($K_1 = 10^{-7.71}$), may account for the different sorption behavior

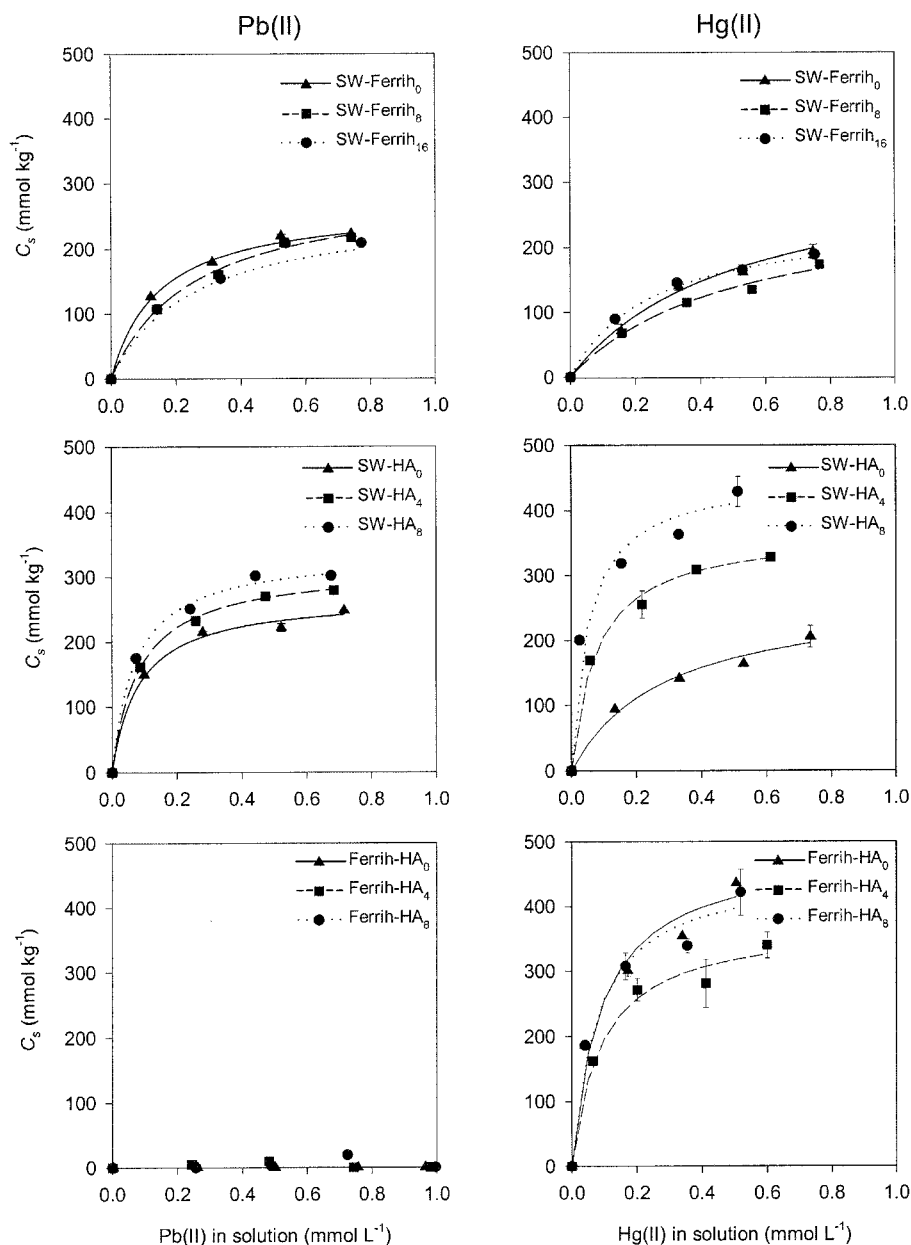


Fig. 3. Lead (II) and Hg(II) sorption isotherms (pH = 3) on binary model sorbents. Symbols are experimental data points whereas lines are the Langmuir-fit sorption isotherms.

observed for Hg(II) and Pb(II) on SW and Ferrih (Sarkar et al., 1999; Shen et al., 1999; Ritchie et al., 2001). Using the MINTEQA2 chemical equilibrium model (Gustafsson, 2002), we estimated that at our experimental conditions Pb(II) exists mainly (>97%) as Pb^{2+} aqueous species, which should be greatly attracted by the negatively charged SW surface and repelled by the positively charged Ferrih surface. In the case of Hg(II), however, not only Hg^{2+} (approximately 54%) but also considerable amounts of $Hg(OH)^+$ (approximately 18%) and $Hg(OH)_2^0$ (approximately 28%) species are predicted by MINTEQA2 at $[Hg(NO_3)_2] = 0.5 \text{ mM}$ and $[HNO_3] = 1 \text{ mM}$. It appears that hydrolyzed Hg species has less affinity for SW and greater affinity for Ferrih than the unhydrolyzed one. These results agree with those of Schwertmann and Taylor (1989) who found that the pH

of maximum increase in heavy metal sorption on Fe oxides was linearly related to the first hydrolysis constant of the metal ion, strongly indicating that the hydrolyzed species (MOH^+) is preferentially sorbed by Fe oxides over the unhydrolyzed one (M^{2+}). This would explain the observed affinity of Hg(II) for Ferrih in contrast to the low affinity observed for Pb(II). Several reactions in which mono- and binuclear complexes are formed at the hydroxylated surface of the Fe oxide have been proposed as heavy metal sorption mechanisms on Fe oxide surfaces (Schwertmann and Taylor, 1989).

Sorption by Binary Model Associations

Lead (II) and Hg(II) sorption isotherms on binary associations containing SW, Ferrih, and HA were in

general well described by the Langmuir equation, with regression coefficients $R^2 > 0.95$ (Fig. 3, Tables 3 and 4). While Pb(II) and Hg(II) sorption on SW was little affected by Fe precipitation, sorption of both heavy metals on SW-HA associations was significantly increased by the presence of HA in the associations (Fig. 3). The increase in Hg(II) sorption was even greater than that observed for Pb(II), in accordance with its greater sorption on pure HA (Fig. 1). It is interesting to note that the maximum sorption capacities, C_m , of the SW-HA associations for Pb(II) and Hg(II) were close or even greater than the values expected (C_{m-calc}), from the composition of these associations and the individual sorption capacities of SW and HA for the metal ions (Tables 3 and 4). As mentioned before, association between HA and SW was low due to predominance of negative charges in both constituents and the presence of Na as interlayer cation in SW. As a result of this low association, most of the binding sites of SW and HA in the SW-HA complexes seem to have remained available for heavy metal sorption.

In contrast to the behavior of the SW-HA associations, the presence of HA in the Ferrih-HA complexes did not result in any increase in Pb(II) or Hg(II) sorption by Ferrih. Sorption of Pb(II) remained negligible, whereas low amounts of HA even reduced the sorption of Hg(II) by the Fe oxide (Fig. 3). Correspondingly, the Langmuir maximum sorption capacities measured for Pb(II) and Hg(II) sorption by Ferrih-HA particles (Tables 3 and 4) were significantly lower than the values expected (C_{m-calc}) from the composition of these particles and the sorption capacities of their individual constituents (i.e., Ferrih and HA). These results can be related to the intimate association of HA with Ferrih (approximately 100%), which apparently resulted in blockage of many functional groups responsible for heavy metal sorption. Interaction of acidic functional groups of humic substances with the hydroxylated surface of Fe oxides is known to be a major mechanism of association (Day et al., 1994; Gu et al., 1995; Leone et al., 2001), and it appears that the availability of these groups for heavy metal sorption is considerably reduced after association. This reduced availability can be due not only to direct blockage of sorption sites, but also to a reduction in the accessibility to those sites. In any case, it follows that prediction of heavy metal sorption by organic matter-Fe oxide particles based on the sum of the sorption capacities of the individual constituents may result in an overestimation of the extent of sorption and in turn in an underestimation of the soluble (available) fraction of heavy metals in the environment.

Sorption by Ternary Model Associations

Sorption isotherms on ternary model sorbents containing SW, Ferrih, and HA (Fig. 4) revealed different sorption patterns for Pb(II) and Hg(II). Similarly to the behavior of the Ferrih-HA binary associations, the expected increase in Pb(II) sorption by the presence of HA in ternary particles was not observed (Fig. 4). Even though the amounts of Ferrih in ternary particles were

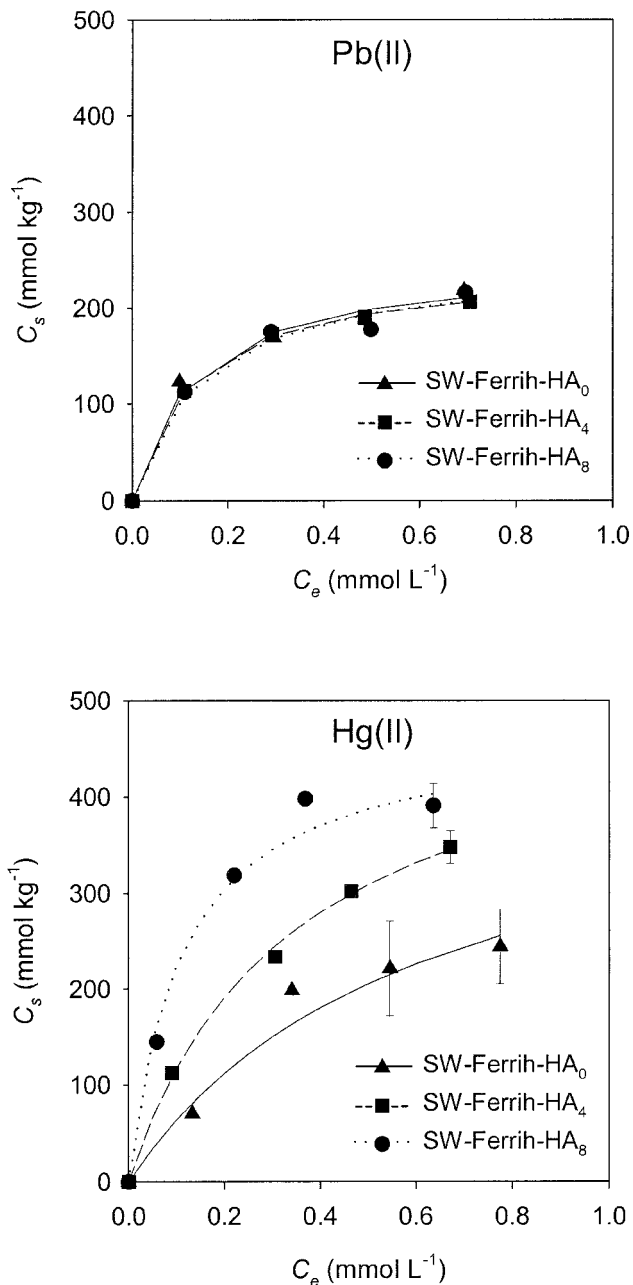


Fig. 4. Lead (II) and Hg(II) sorption isotherms (pH = 3) on ternary model sorbents. Symbols are experimental data points whereas lines are the Langmuir-fit sorption isotherms.

relatively low (Table 2), it appears that association of HA with the Ferrih coatings still blocked most of the functional groups of HA responsible for Pb(II) sorption. Interestingly, this behavior was less evident for Hg(II) (Fig. 4), suggesting that many functional groups of HA responsible for Hg(II) uptake were not involved in the interaction of HA with the minerals, and thus remained unblocked for heavy metal sorption. This could have been the result of the low amount of Ferrih present in the ternary particles together with the large amount of functional groups of HA able to bind Hg(II). These results illustrate that not only the amount and nature of the surface that remains available after interassocia-

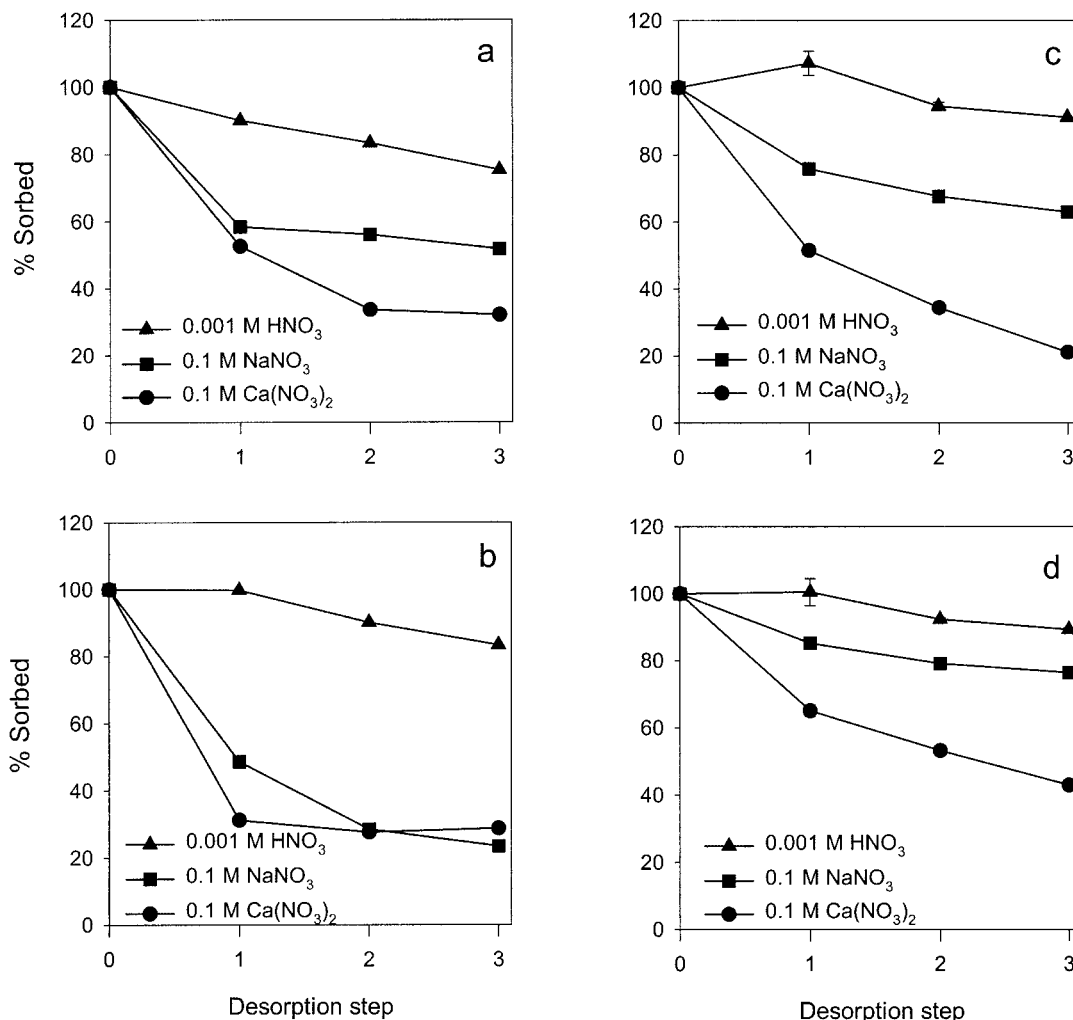


Fig. 5. Lead (II) and Hg(II) desorption from model sorbents: (a) Pb(II) from SW-Ferrih-HA₀, (b) Pb(II) from SW-Ferrih-HA₈, (c) Hg(II) from SW-Ferrih-HA₀, and (d) Hg(II) from SW-Ferrih-HA₈.

tion of single soil constituents, but also the nature of the sorbing species are critical parameters in determining the sorptive behavior of organomineral soil colloids.

Desorption Experiments

Desorption of Pb(II) and Hg(II) from mineral (SW-Ferrih-HA₀) and organomineral (SW-Ferrih-HA₈) model particles was investigated by successive treatments with HNO₃, NaNO₃, and Ca(NO₃)₂ solutions (Fig. 5). Enhanced desorption by higher ionic strength solutions was observed, indicating that much of the Pb(II) and Hg(II) sorbed by the mineral and organic surfaces was in an exchangeable form. In the case of Hg(II), desorption from samples containing HA was lower than that observed from samples without HA. This suggests stronger sorption of Hg(II) by organic matter than that by mineral surfaces, which is in agreement with the high affinity of Hg(II) for pure HA observed in sorption experiments.

CONCLUSIONS

The three main active soil colloidal constituents, clays, Fe oxides, and HAs are important sorbents for heavy

metals, but mutual interactions between these constituents can alter their sorptive behavior when associated in organomineral soil colloids. The great affinity of HA for Ferrih, for instance, reduced considerably the ability of Ferrih-associated HA to bind Pb(II) and Hg(II), while this behavior was less evident in SW-HA binary associations because of the much lower affinity of HA for SW compared with that for Ferrih. It appeared that the intimate association of HA with Ferrih involved many functional groups of HA (such as carboxylic groups) which were responsible for heavy metal sorption. Furthermore, the different behavior of ternary model particles containing SW, ferrihydrite, and humic acid in sorbing Pb(II) and Hg(II) indicated that the amount and nature of the surface that remains available after interassociation of single soil constituents together with the nature of the sorbing species are both critical parameters in determining the sorptive behavior of organomineral soil colloids. The results of this study confirmed, in summary, that the sorptive behavior of complex particles may not be directly derived from the simple sum of the contributions of the single constituents, and illustrated the usefulness of considering pol-

yphasic model sorbents to achieve a more accurate interpretation of the sorption process in soil.

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