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Sorption of cadmium on humic acid: Mechanistic and kinetic studies with atomic force microscopy and X-ray absorption fine structure spectroscopy

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Humic acids (**HA**) constitute a major fraction of the organic matter in soils and sediments. Little is known about the kinetics and mechanisms of Cd sorption by HAs, especially those pertaining to the surface features and structure of the Cd-humate complexes. We investigated Cd sorption by HA using the conventional batch method, N_2-BET method, **atomic force microscopy** (**AFM**), and **extended X-ray absorption fine structure** (**EXAFS**) spectroscopy to gain a better understanding of the kinetics and mechanisms. Cadmium sorption by HA can be described by the parabolic diffusion equation. The increase in the apparent diffusion coefficient with an increase in the initial Cd concentration was less pronounced at higher initial Cd concentrations, apparently due to an enhancement in aggregation of the Cd-humate complexes. The HA before and after Cd sorption at Cd concentrations $\leq 10^{-6}$ M in different reaction times was spheroidal in shape. The Cd-humate complexes formed at 10^{-4} and 10^{-3} M Cd gradually changed to resemble the shape of a bean with increasing reaction time, thereby substantially decreasing their specific surface. Cadmium ions raveled the spheroidal HA particles into a bean-like structure by coordinating to six O atoms from the functional groups of HA, with a Cd-O distance of 2.297(2) Å. The Cd-O bond strength decreased with increasing initial Cd concentration.

Key words: Cadmium, humate complexes, conformation, atomic force microscopy, EXAFS

Liu, C., Frenkel, A. I., Vairavamurthy, A. et Huang, P. M. 2001. **Étude de la mécanique et de la cinétique de la sorption du cadmium par l'acide humique au moyen de la microscopie à force atomique et de la spectroscopie des structures fines par absorption des rayons X**. Can. J. Soil Sci. **81**: 337–348.
Les acides humiques (AH) constituent une bonne partie de la matière organique présente dans le sol et les sédiments. On sait peu de choses sur la cinétique et la mécanique de la sorption du Cd par les AH, surtout en relation avec les propriétés de la surface et la structure des complexes Cd-humate. Les auteurs ont étudié la sorption du Cd par les AH selon la méthode par lots traditionnelle, la technique N_2-BET, la microscopie à force atomique (MFA) et une variante de la spectroscopie des structures fines par absorption des rayons X (EXAFS) dans l'espoir de mieux comprendre la cinétique et la mécanique du phénomène. L'équation de diffusion parabolique décrit la sorption du cadmium par les AH. La hausse du coefficient de diffusion apparent associée à l'augmentation de la concentration initiale de Cd est moins importante quand la concentration initiale de Cd est plus élevée. On le doit apparemment à une meilleure agrégation des complexes Cd-humate. Les AH présentent une forme sphéroïdale avant et après la sorption du Cd (concentration $\leq$ ^{10}-6 M) à divers temps de réaction. Les complexes Cd-humate qui voient le jour aux concentrations de 10^{-4} et de 10^{-3} M de Cd changent graduellement de forme pour prendre celle d'un haricot quand le temps de réaction augmente, ce qui réduit sensiblement leur surface spécifique. Les ions cadmium emmêlent les particules sphériques de AH pour leur donner la forme d'un rein en s'associant à six atomes d'oxygène des groupes fonctionnels de l'acide, avec un espacement Cd-O de 2,297(2) Å. La liaison Cd-O s'affaiblit à mesure qu'augmente la concentration de Cd.

Mots clés: Cadmium, complexes d'humate, conformation, microscopie à force atomique, EXAFS

Humic acids are among the most widely distributed organic materials in soils and sediments (Stevenson 1994). They have a profound effect on the speciation and mobility of heavy metals in soils and aquifers because they carry a large number of functional groups on their surface that can complex with the metals (Stevenson 1976; Herndorff and Schnitzer 1980; Benedetti et al. 1995). Research on Cd pollution has received increasing international attention as Cd is toxic and can cause severe human health problems such as bronchitis, kidney disorders and itai-itai disease (Webb 1979; Alloway 1995). Humic acids have a substantial capacity to complex metal ions, and the complexation process may affect the solubility of the metal ions (Zhang et al. 1996). Studies on the speciation of particulate-bound Cd in temperate (Krishnamurti et al. 1995) and tropical (Onyatta and Huang 1999) soils indicate that the metal-organic com-

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plex-bound Cd is highly correlated with the bioavailability index of Cd. On the other hand, it was reported that adding HA to soils reduces the bioavailability of Cd (Taylor and Theng 1995; Shuman 1998); the nature of the soil's organic matter apparently influences this attribute.

Much previous work on the interaction between Cd and HAs focused on their complexes using titration methods and sorption modeling (Stevenson 1976; Manunza et al. 1995; Benedetti et al. 1995; Bolton et al. 1996; Crist et al. 1999). Recently, the surface features of HAs and Cd-humate complexes were investigated by AFM (Liu and Huang 1999). The AFM of the standard soil HA obtained from the International Humic Substances Society shows that under ambient conditions HA consists of spheroidal particles with a diameter of ca. 50–150 nm and a thickness of ca. 10–30 nm. Humic acid aggregation increased with an increase in the amount of Cd complexed with it. The spheroids assembled into large particles with bean-like shapes at initial Cd concentrations of 10^{-4} and 10^{-3} M. The aggregation state of the Cd-humate complexes may affect the release of Cd from them.

Although many studies have investigated the equilibrium of Cd sorption by soil constituents and soils (Schulte and Beese 1994; Pardo and Guadalix 1995; Sakurai and Huang 1996; Filius et al. 1998; Naidu et al. 1997; Naidu and Harter 1998), little is known of the kinetics and mechanisms of Cd sorption by HA, especially those pertaining to the surface features and structure of the Cd-humate complexes. The objective of the present study was twofold: to investigate the kinetics of Cd sorption by HA and the associated surface changes of the Cd-humate complexes using AFM and measurement of specific surface area, and to explore the binding mechanisms of Cd in Cd-humate complexes using extended X-ray absorption fine structure (EXAFS) spectroscopy.

MATERIALS AND METHODS

Sorption of Cadmium by Humic Acid

Fifty milligrams of standard soil HA (1S102H) from the International Humic Substances Society were dispersed in 40 mL deionized distilled water by ultrasonification (Sonifier, Model 350, Danbury, CT) at 150 W for 2 min in an ice bath. The HA suspension was adjusted to pH 5.0 with 0.01 M NaOH, and diluted to 50 mL. An aliquot of 50 mL of 2×10^{-8}, 2×10^{-7}, 2×10^{-6}, $2 \times 10^{-4,}$ or 2×10^{-3} M $Cd(NO_3)_2$ containing 0.02 M $NaNO_3$ at pH 5.0 then was mixed with the HA suspension, bringing the final volume of the mixture to 100 mL. The final Cd concentration was 10^{-8}, 10^{-7}, 10^{-6}, 10^{-4}, and 10^{-3} M and the $NaNO_3$ concentration was 0.01 M. The Cd-HA suspension was shaken for 0.083, 0.25, 0.5, 1, 2, 4, 8, and 24 h at 298 K. At the end of each reaction time, the suspension was filtered through a Millipore membrane (0.025 μm pore size) using a 100-mL syringe. The concentration of Cd remaining in the filtrate was determined at 248.3 nm by graphite furnace atomic absorption spectrometry (GFAAS) (Model HGA-600, Perkin Elmer Corp., Norwalk, CT) or AAS (Perkin Elmer atomic absorption spectrophotometer, Model 3100, Perkin Elmer Corp., Norwalk, CT). The solid sample was dialyzed with deionized distilled water until the conductivity of the water outside the dialysis tube was less than 5×10^{-3} dS m^{-1}, and then the sample was freeze-dried. The HA in the same volume (100 mL) of deionized distilled water also was shaken for 0.083 and 24 h at 298 K as the control. Each experiment was done in duplicate.

Atomic Force Microscopy

After the sample was freeze-dried, 5 mg of the HA or Cd-HA complexes were dispersed in 15 mL deionized distilled water using ultrasonification at 150 W for 2 min in an ice bath. One drop of the HA or Cd-HA complex suspension was deposited on a watch glass and air-dried overnight at room temperature (296.5 ± 0.5 K). The watch glass was then fastened with double-sided tape to a magnetized stainless-steel disk (diameter of 12 mm). Three-dimensional AFM images were recorded under ambient conditions at room temperature using a NanoScope™ III atomic force microscope (Digital Instruments, Inc., Santa Barbara, CA). The imaging area was 5×5 μm^2. The scanner type was 1881E and its size was 15 μm. A silicon-nitride cantilever with a spring constant of 0.12 N/m was used in contact mode. The scanning rate was 18.31–27.47 Hz. To eliminate experimental artifacts, the AFM cantilever was changed when necessary. Furthermore, the scanning area and scanning angle were often changed by entering different area and angle parameters to detect possible artifacts caused by HA particles adhering to the AFM tip.

Determination of Specific Surface Area

The **specific surface area** (**SSA**) of the freeze-dried HA and Cd-humate complexes formed at each reaction time was measured using a five-point BET N_2 sorption isotherm (Gregg and Sing 1982) obtained with a Quantachrome Autosorb-1 apparatus (Quantachrome Corp., Syosset, NY). Before N_2 adsorption, ca. 100 mg samples were outgassed for 24 h at 15 mTorr. During N_2 adsorption, the solids were thermostated in liquid N_2 (77–78 K).

EXAFS Analysis

The freeze-dried Cd-humate complexes used for EXAFS analysis were formed at initial Cd concentrations of 10^{-6} and 10^{-4} M at the end of a 24-h reaction time. The EXAFS experiment was done at the beamline X23-A2, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York. The intensity of the incident X-rays was measured by an Ar-filled ionization chamber. The intensity of the fluorescent radiation from the sample was measured with a Kr-filled Lytle ionization detector. The κ-weighted EXAFS function $\chi(\kappa)$ (κ is wavevector) was produced for the unknown Cd-humate and reference $Cd(ClO_4)_2$ experimental data. The non-linear least-squares fit of experimental data to theoretical curves was done in R-space by Fourier transformation (FT). The adjustable structural parameters were the Cd coordination numbers, the Cd-O distance, and any disorder in these distances (σ^2). The X-ray absorption spectra were treated following a standard procedure (Zabinsky et al. 1995).

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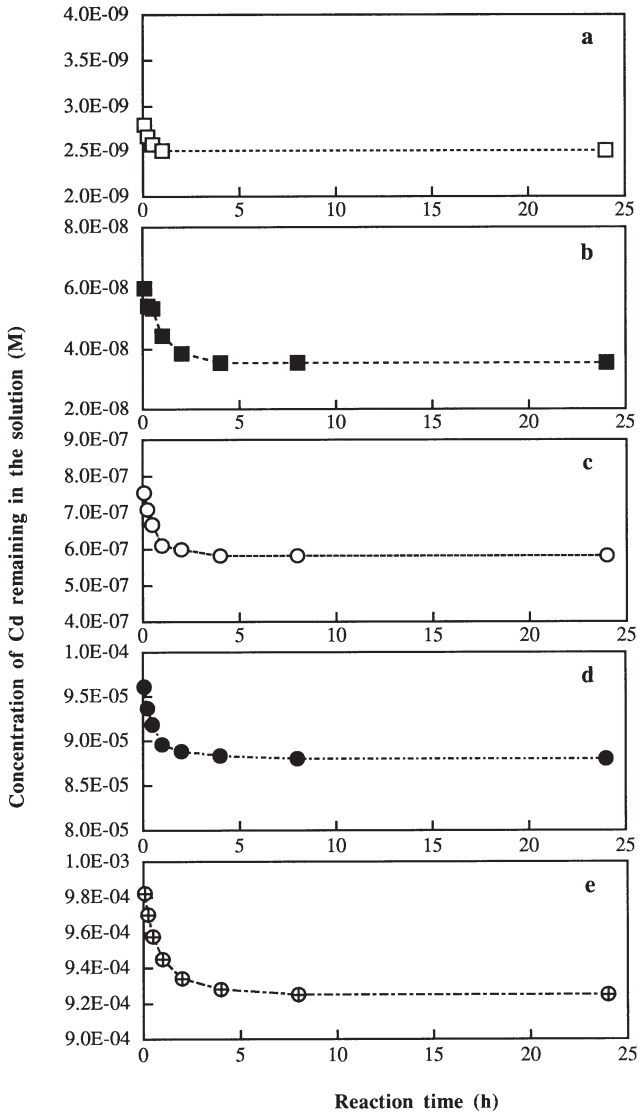

Fig. 1. The time function of the concentration of Cd remaining in solution after reaction with the HA at initial Cd concentrations of (a) 10^{-8}, (b) 10^{-7}, (c) 10^{-6}, (d) 10^{-4}, and (e) 10^{-3} M at pH 5.0 and $NaNO_3$ concentration of 0.01 M.

RESULTS AND DISCUSSION

Kinetics of Cadmium Sorption by Humic Acid

After mixing the $Cd(NO_3)_2$ solution with HA at pH 5.0, the concentration of Cd remaining in the solution decreased rapidly with reaction time (Fig. 1). The time required for Cd sorption by HA to reach equilibrium increased with an increase in the initial Cd concentration. At the end of a 1-h reaction time, sorption had reached equilibrium at an initial Cd concentration of 10^{-8} M, whereas it approached equilibrium after a 4-h reaction time at 10^{-7} and 10^{-6} M Cd concentrations; for initial concentrations of 10^{-4} and 10^{-3} M Cd, this time was 8 h (Fig. 1). The amount of Cd sorbed by HA at the end of 24-h substantially increased with increasing initial Cd concentration (Table 1).

Cadmium sorption at an initial Cd concentration of 10^{-8} M reached equilibrium at the end of an hour. Therefore, the kinetic and empirical equations, including the zero-order, first-order and second-order-rate equations, the Elovich equation, the modified Freundlich equation, and the parabolic diffusion equation, were used to fit the Cd sorption data at the end of reaction times from 0.083 to 1 h. The degree of fit of the rate equations to the data was examined using the correlation coefficient (r^2), probability (P), and standard error (SE) of linear regression analysis (Table 2). The parabolic diffusion equation better described Cd sorption by HA than did the other equations (Table 2). Therefore, we used the parabolic equation to fit the Cd sorption data:

$$q_t/q_{24} = B + kt^{1/2}$$

where q_t (g Cd kg^{-1} HA) is amount of Cd sorbed by HA at the reaction time t, q_{24} (g Cd kg^{-1} HA) is the amount of Cd sorbed by HA at the end of a 24-h reaction time (which is the maximum amount of Cd sorbed by HA at each initial Cd concentration), k ($h^{-1/2}$) is the apparent diffusion coefficient, and B is a constant. To compare the apparent diffusion coefficients of Cd sorption by HA at different initial Cd concentrations, this equation was used, rather than equation $q_t = B + kt^{1/2}$.

Figure 2 shows the fit of the Cd sorption data to the parabolic diffusion equation. The apparent diffusion coefficients of Cd sorption by HA rose with increasing initial Cd concentration (Table 3). However, the extent of this increase declined from a low initial Cd concentration to a high one. The apparent diffusion coefficients, respectively, increased by about 6.0, 1.7, and 1.3 times when the initial Cd concentration increased from 10^{-8} to 10^{-7} M, from 10^{-7} to 10^{-6} M, and from 10^{-6} to 10^{-4} M. When the initial concentration increased from 10^{-4} to 10^{-3} M Cd, the apparent diffusion coefficient of sorption did not rise significantly (Table 3).

The parabolic diffusion equation is often used to indicate that diffusion-controlled phenomena are rate-limiting (Sparks 1999). Several researchers applied the parabolic equation to study the kinetics of sorption of nutrients and

Table 1. Amount of Cd sorbed by HA at various initial Cd concentrations at pH 5.0 and $NaNO_3$ concentration of 0.01 M at the end of a 24-h reaction period

Initial Cd concentration (M)				
10^{-8}	10^{-7}	10^{-6}	10^{-4}	10^{-3}
		g Cd kg^{-1} HA		
0.0017 ± 0.0001	0.014 ± 0.001	0.094 ± 0.002	2.70 ± 0.07	16.9 ± 0.6

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Table 2. Comparison of the degree of fit of the kinetic equations to the data of Cd sorption by HA[z]

Rate equation	Initial Cd concentration (M)											
	10^{-8}			10^{-7}			10^{-6}			10^{-4}			10^{-3}		
	r^2	P	SE	r^2	P	SE	r^2	P	SE	r^2	P	SE	r^2	P	SE
Zero-order	0.857	7.41×10^{-2}	3.07×10^{-5}	0.986	4.69×10^{-3}	2.09×10^{-4}	0.965	1.76×10^{-2}	3.17×10^{-3}	0.933	3.43×10^{-2}	0.20	0.946	2.73×10^{-2}	1.02
First-order	0.905	4.89×10^{-2}	1.63×10^{-5}	0.984	8.02×10^{-3}	3.45×10^{-4}	0.979	1.07×10^{-2}	2.96×10^{-3}	0.942	2.94×10^{-2}	0.19	0.946	2.72×10^{-2}	1.00
Second-order	0.879	6.22×10^{-2}	2.53×10^{-5}	0.993	3.49×10^{-3}	1.73×10^{-4}	0.984	7.76×10^{-3}	2.26×10^{-3}	0.946	2.72×10^{-2}	0.18	0.948	2.66×10^{-2}	0.98
Parabolic diffusion	0.970	1.50×10^{-2}	1.06×10^{-5}	0.994	3.22×10^{-3}	1.63×10^{-4}	0.999	3.52×10^{-4}	1.42×10^{-3}	0.991	4.56×10^{-3}	0.07	0.995	2.63×10^{-3}	0.27
Elovich	0.962	1.91×10^{-2}	1.29×10^{-5}	0.983	8.47×10^{-3}	1.66×10^{-4}	0.983	8.61×10^{-3}	1.82×10^{-3}	0.991	4.40×10^{-3}	0.48	0.988	7.13×10^{-3}	0.31
Freundlich (Modified)	0.962	1.90×10^{-2}	1.33×10^{-5}	0.965	1.76×10^{-2}	2.63×10^{-4}	0.957	2.15×10^{-2}	3.08×10^{-3}	0.991	4.38×10^{-3}	0.07	0.982	9.03×10^{-3}	0.59

[z]The r^2 is the correlation coefficient; P is the probability; SE (g Cd kg^{-1} HA) is the standard error, which was calculated by the difference between measured amount of Cd sorbed A and calculated amount of Cd sorbed A* based on the equation $SE = [\Sigma(A - A^*)^2 / (n - 2)]^{1/2}$.

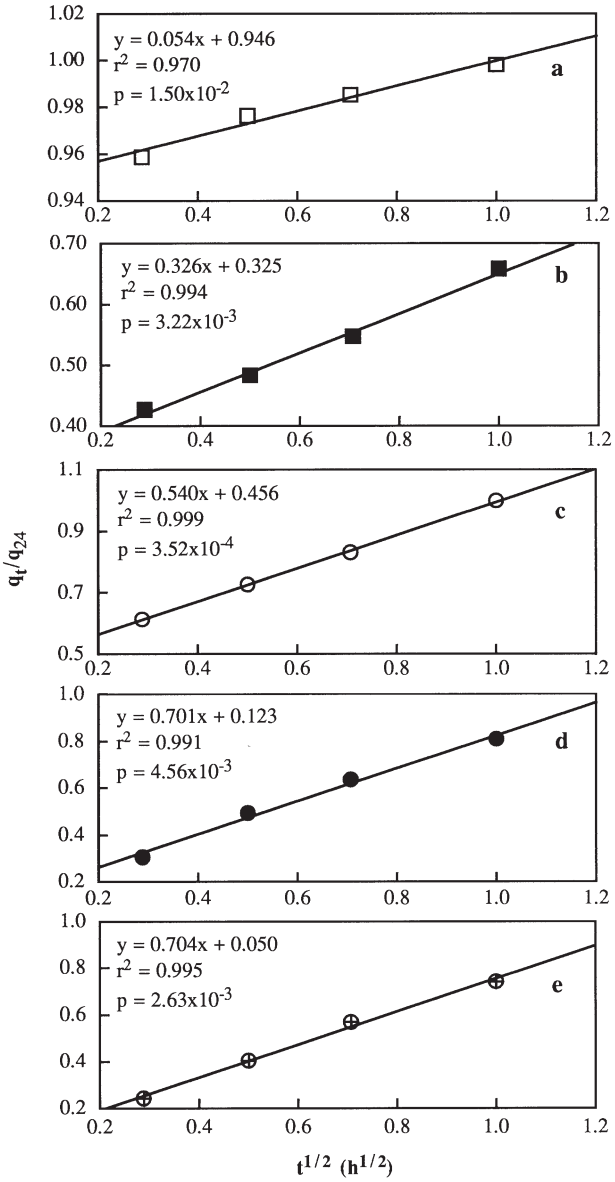

Fig. 2. Cadmium sorption by HA at the initial Cd concentrations of (a) 10^{-8}, (b) 10^{-7}, (c) 10^{-6}, (d) 10^{-4}, and (e) 10^{-3} M at pH 5.0 and an $NaNO_3$ concentration of 0.01 M based on the parabolic diffusion equation; q_t and q_{24} are the amounts of Cd sorbed by the HA (g Cd kg^{-1} HA) at reaction time t and at the end of a 24-h reaction period, respectively.

pollutants by soil constituents and soils (Cooke 1966; Chute and Quirk 1967; Alekseyev and Zyrin 1980; Jardine and Sparks 1984; Simard et al. 1992; Mengel and Uhlenbecker 1993; Dang et al. 1994; Ma and Liu 1997). Cadmium sorption by HA is well described by the parabolic diffusion equation in the present study, suggesting that its rate is limited by diffusion. The chemical reaction between Cd ions and functional groups (such as –COOH and –OH of HA) should be faster than diffusion processes. Apparently, the functional groups of HA have a high affinity for Cd ions, as

Table 3. Apparent diffusion coefficients of Cd sorption by HA at different initial Cd concentrations at pH 5.0 and $NaNO_3$ concentration of 0.01 M

Initial Cd concentration (M)				
10^{-8}	10^{-7}	10^{-6}	10^{-4}	10^{-3}
Apparent diffusion coefficient ($h^{-1/2}$)				
0.054 ± 0.007	0.326 ± 0.018	0.540 ± 0.010	0.701 ± 0.048	0.704 ± 0.036

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indicated by the high stability constant of Cd-humate complexes (log K = 6.9, assuming that one metal ion combines with two ligands) (Stevenson 1976).

Surface Features of Cadmium-humate Complexes

Atomic force micrographs of Cd-humate complexes were taken after the samples had been dialyzed to remove the free Cd salt in solution. The different amounts of Cd complexed by HA resulted in great variation of submicrometer surface features (Table 1 and Figs. 3, 4 and 5). The surface feature of HA without Cd treatment was similar at the end of reaction time of 0.083 and 24 h; HA was present as spheroids of diameter ca. 50–150 nm (Fig. 3a and b). After sorption of Cd ions by HA at initial Cd concentrations of 10^{-8} and 10^{-7} M, the surface feature of the HA at the end of reaction times of 0.083 and 24 h were similar, and did not differ greatly from those of HA alone (Fig. 3a–f), even though the apparent diffusion coefficient of Cd sorption by HA varied greatly with initial Cd concentration (Table 3); this is because these low levels of Cd from 10^{-8} M to 10^{-7} M did not cause much aggregation of HA. As the Cd concentration increased to 10^{-6} M, aggregation of Cd-humate complexes was slightly enhanced compared with pure HA (Fig. 3g and h).

However, the surface features of HA after Cd sorption at initial Cd concentrations of 10^{-4} and 10^{-3} M distinctly changed with the reaction time, and were different to pure HA and to HA after reacting with Cd from initial concentrations of 10^{-8} to 10^{-6} M (Figs. 3, 4 and 5). Humic-acid particles after Cd sorption from an initial concentration of 10^{-4} M still were present as spheroids at the end of a 0.083-h reaction time (Fig. 4a); however, the diameter of some spheroids had increased to ca. 175 nm. With a longer reaction time, aggregation of HA was greatly enhanced. The maximum diameter of spheroidal Cd-humate complexes increased from ca. 175 nm to 310, 420, and 520 nm, respectively, when the reaction time lengthened from 0.083 h to 0.25, 0.5, and 1 h (Fig. 4a, b, c, and d). Bean-like particles were imaged after a reaction time of 2 h (Fig. 4e). The atomic force micrograph (Fig. 4e) clearly shows that the bean-like particle is an aggregate of spheroids. As reaction time was extended to 4, 8, and 24 h, more bean-like particles were observed (Fig. 4f, g and h).

At a Cd concentration of 10^{-3} M, the aggregation of Cd-humate complexes was enhanced compared with complexes formed in the same reaction time from an initial Cd concentration of 10^{-4} M (Figs. 4 and 5). Complexes formed at the end of 0.083 and 0.25 h at an initial Cd concentration of 10^{-3} M were spheroidal, with maximum diameters of ca. 400 and 550 nm, respectively. After a reaction time of 0.5 h, Cd-humates were still present as spheroids. However, the spheroids had started to become arranged into bean-like structures (Fig. 5c). As the reaction time lengthened to 1 h, the bean-like structure of the aggregates was more evident (Fig. 5d). After 2- and 4-h, the bean-like particles were even more evident and the spheroidal particles were less apparent (Fig. 5e and f), until, after 8 h, the spheroids were almost completely assembled into massive bean-like particles, which contained some ring-structures (Fig. 5g). Cadmium-humate complexes formed by the end of 24-h had similar surface features to the complexes formed at the end of an 8-h reaction time (Fig. 5g and h).

The atomic-force micrographs of Cd-humate complexes (Figs. 3, 4 and 5), along with the apparent diffusion coefficient of Cd sorption (Table 3), indicate that the rate of Cd sorption by HA is greatly influenced by the surface features of the adsorbent. Apparently, Cd concentrations of 10^{-8} and 10^{-7} M were not high enough to cause major changes in the molecular conformation of the Cd-humate complexes (Fig. 3c–f). Therefore, the apparent diffusion coefficient of Cd sorption by HA, which was calculated from the kinetic data for periods from 0.083 to 1 h, increased by about six times when the initial Cd concentration increased from 10^{-8} to 10^{-7} M (Table 3). While the aggregation of Cd-humate complexes formed at the initial Cd concentration of 10^{-6} M was slightly enhanced (Fig. 3g and h), the apparent diffusion coefficient of Cd sorption by HA increased only by a factor of 1.7 (Table 3). The aggregation of Cd-humate complexes formed in the early part of the reaction period apparently retards the diffusion of Cd into HA particles during the later part. This trend was more pronounced when the initial Cd concentration was raised from 10^{-6} and 10^{-4} M, as the aggregation of Cd-humate complexes became further enhanced with increasing levels of Cd ions (Table 3 and Figs. 3 and 4). When the Cd concentration increased from 10^{-4} to 10^{-3} M, the apparent diffusion coefficient of Cd sorption by HA did not change significantly (Table 3); this is because the Cd-humate complexes formed at 10^{-3} M Cd were even more aggregated than those formed at 10^{-4} M Cd during the same reaction time (Figs. 4 and 5). Therefore, the extent of the increase in the apparent diffusion coefficient of Cd sorption by the HA fell with enhancement of Cd-humate complex aggregation.

Chen and Schnitzer (1976) used scanning electron microscopy (SEM) to observe the morphological conformation of metal-FA complexes and found that different metal ions affect the aggregation of FA to different extents, resulting in formation of long, thin fibers of Cu^{2+}-FA complex, thick and multi-layered aggregates of Al^{3+}-FA complexes, fibrous structures with many interconnections of Fe^{3+}-FA complexes, and finger-like protrusions of Fe^{2+}-FA com-

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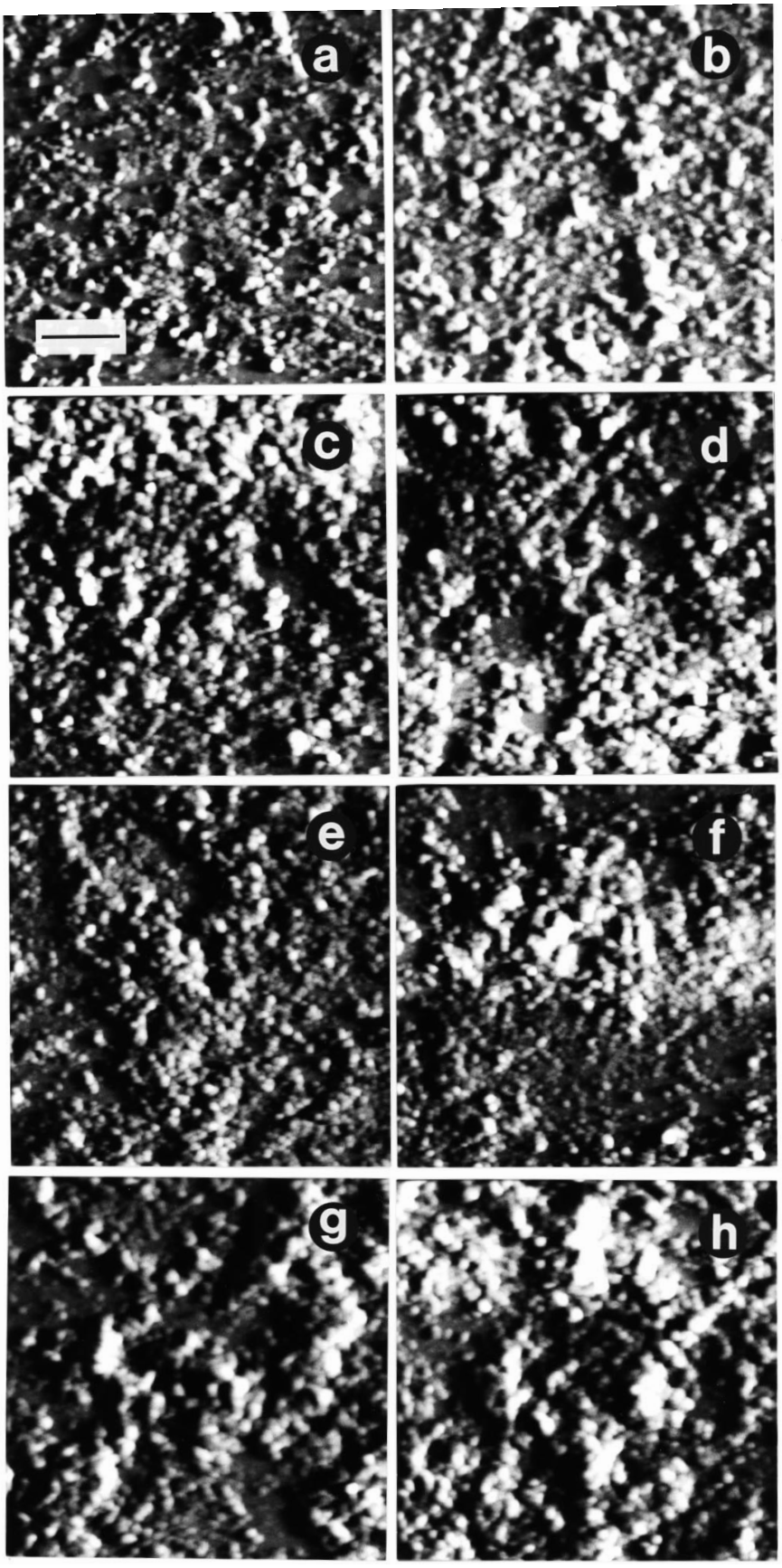

Fig. 3. Atomic force micrographs of Cd-humate complexes formed by treating HA with different concentrations of $Cd(NO_3)_2$ at the end of a 0.083-h and a 24-h reaction period at pH 5.0 and an $NaNO_3$ concentration of 0.01 M. The sample was dialyzed with deionized distilled water to remove the free Cd salt. (a) 0 M Cd and 0.083 h, (b) 0 M and Cd 24 h, (c) 10^{-8} M Cd and 0.083 h, (d) 10^{-8} M Cd and 24 h, (e) 10^{-7} M Cd and 0.083 h, (f) 10^{-7} M Cd and 24 h, (g) 10^{-6} M Cd and 0.083 h, and (h) 10^{-6} M Cd and 24 h. The bar represents 1 μm for all the images (a to h).

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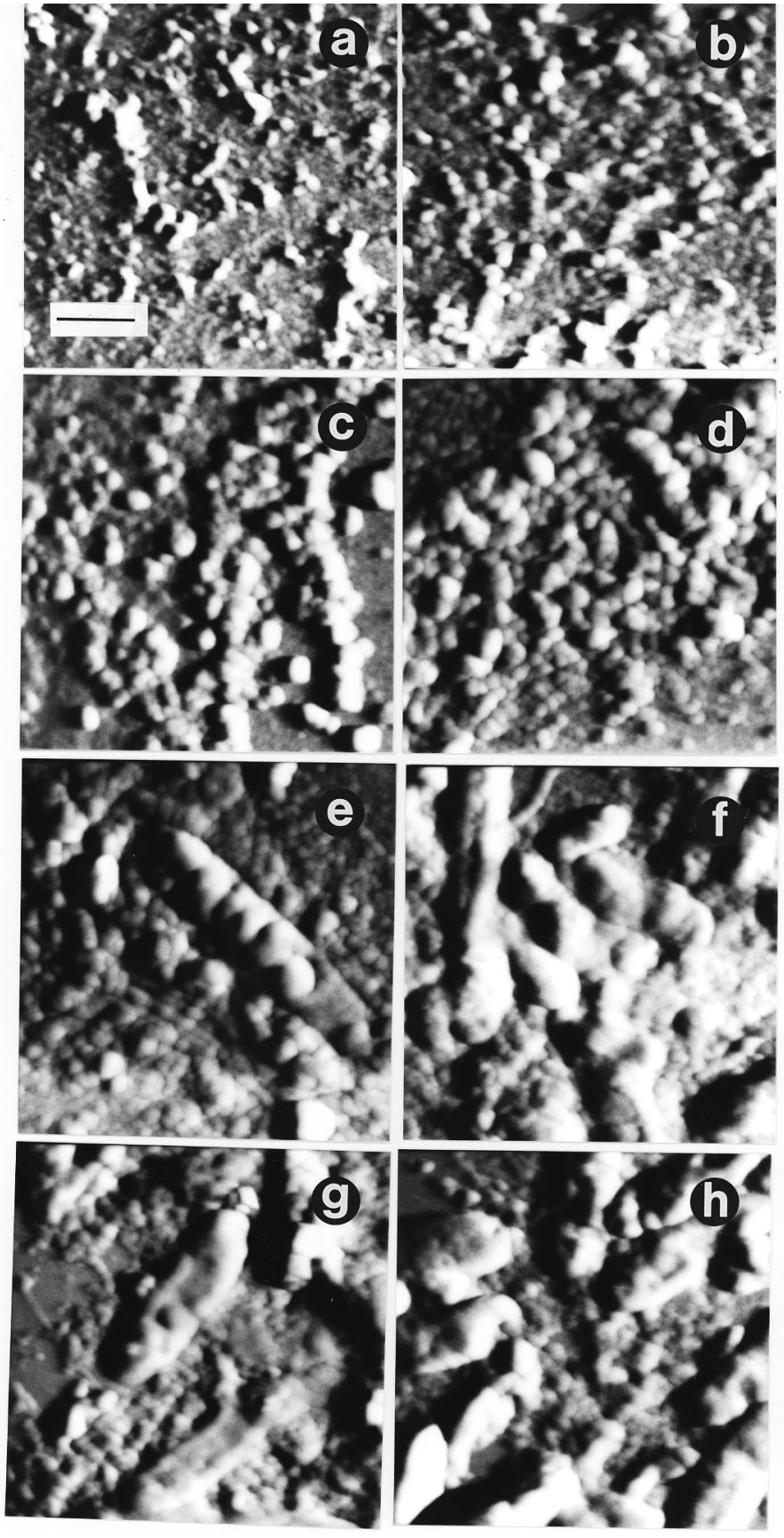

Fig. 4. Atomic force micrographs of Cd-humate complexes formed by treating HA with 10^{-4} M $Cd(NO_3)_2$ for various reaction periods at pH 5.0 and an $NaNO_3$ concentration of 0.01 M. The sample was dialyzed with deionized distilled water to remove the free Cd salt. (a) 0.083, (b) 0.25, (c) 0.5, (d) 1, (e) 2, (f) 4, (g) 8, and (h) 24 h. The bar represents 1 μm for all the images (a to h).

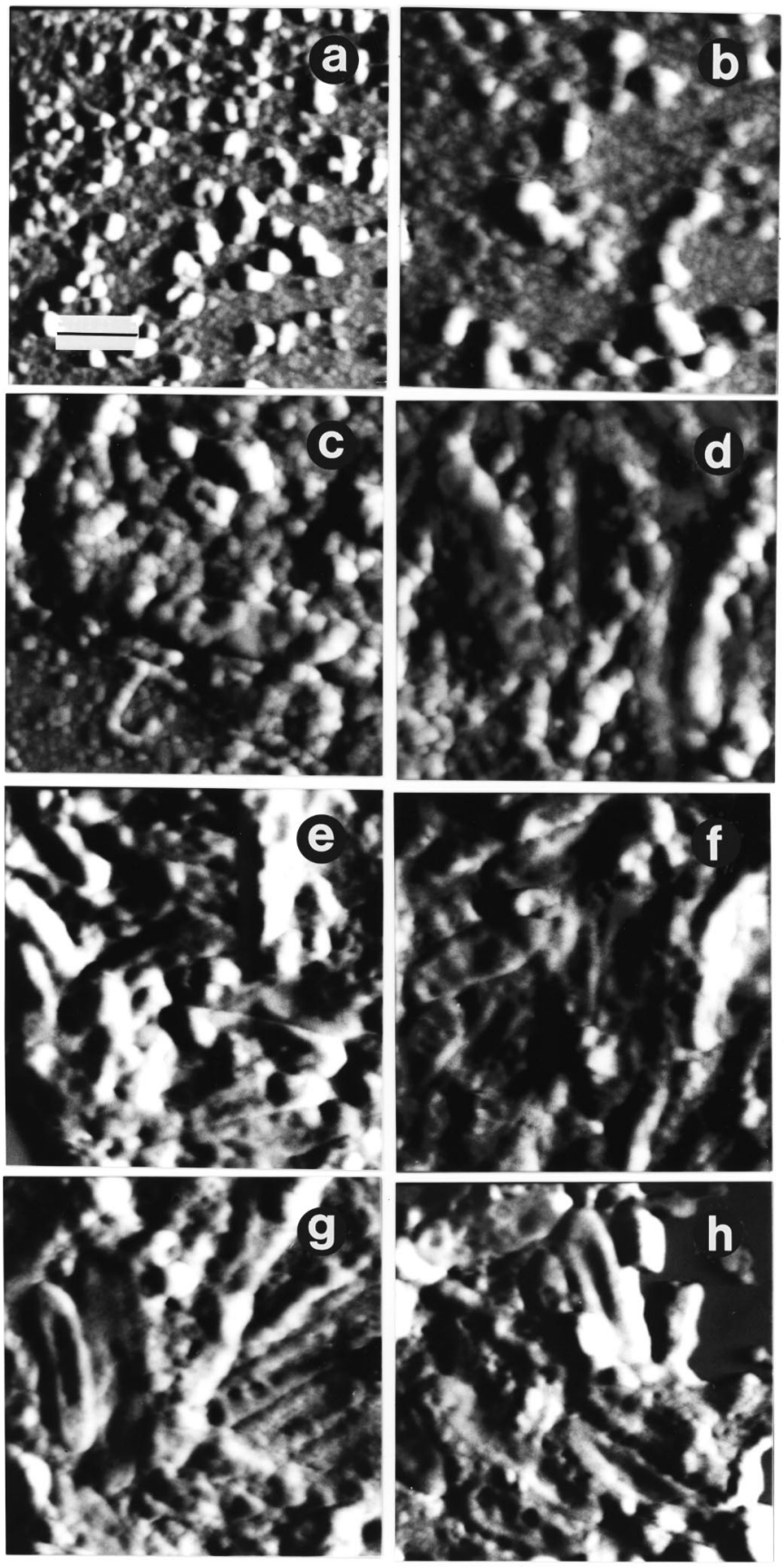

Fig. 5. Atomic force micrographs of Cd-humate complexes formed by treating HA with 10^{-3} M $Cd(NO_3)_2$ for various reaction periods at pH 5.0 and an $NaNO_3$ concentration of 0.01 M. The sample was dialyzed with deionized distilled water to remove the free Cd salt. (a) 0.083, (b) 0.25, (c) 0.5, (d) 1, (e) 2, (f) 4, (g) 8, and (h) 24 h. The bar represents 1 μm for all the images (a to h).

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Table 4. Specific surface area of Cd-humate complexes formed at various initial Cd concentrations at pH 5.0 and $NaNO_3$ concentration of 0.01 M[z]

Reaction period (h)	10^{-8}	10^{-7}	10^{-6}	10^{-4}	10^{-3}
			(m^2 g^{-1})		
0.083	21.3 ± 0.4	21.1 ± 0.5	20.2 ± 0.4	15.0 ± 0.6	12.4 ± 0.2
0.025	20.5 ± 0.6	20.7 ± 0.3	18.4 ± 0.2	12.1 ± 0.2	9.2 ± 0.1
0.5	20.4 ± 0.5	20.3 ± 0.2	17.2 ± 0.3	10.1 ± 0.5	6.6 ± 0.2
1	20.4 ± 0.3	19.9 ± 0.2	16.4 ± 0.1	8.2 ± 0.3	4.9 ± 0.4
2	ND[y]	19.7 ± 0.3	15.8 ± 0.3	6.4 ± 0.4	2.9 ± 0.5
4	ND	19.4 ± 0.7	15.3 ± 0.3	4.6 ± 0.1	2.6 ± 0.4
8	ND	19.5 ± 0.5	15.4 ± 0.2	4.3 ± 0.3	2.8 ± 0.3
24	20.2 ± 0.6	19.5 ± 0.4	15.2 ± 0.7	4.1 ± 0.3	2.8 ± 0.2

[z]The specific surface area of pure HA after reaction with deionized distilled water was, respectively, 22.4 ± 0.5 and 22.1 ± 0.7 at the end of 0.083-h and 24-h reaction periods.
[y]Not determined.

plexes. The Cu^{2+}-FA complexes seemed to have the highest orientation, followed by the Fe^{3+}-FA complexes. Liu and Huang (1999) showed that the conformation of Cd^{2+}-HA complexes is quite different from those of the metal-FA complexes. The present study shows that the conformation of Cd^{2+}-HA complexes varies with the reaction time for complexation. Cadmium-humate complexes with various degrees of aggregation have different surface features at the submicrometer-scale, which may affect the release of Cd from them.

Specific Surface Area of Cadmium-humate Complexes

The N_2-BET SSA of freeze-dried Cd-humate complexes formed at various initial Cd concentrations and different reaction times in the present study range from 22.4 to 2.6 m^2 g^{-1} (Table 4). At a Cd concentration of 10^{-8} M, the SSA values of Cd-humate complexes formed after 0.083 and 24-h are almost the same as those of pure HA similarly exposed in deionized distilled water. The SSA values of Cd-humate complexes formed at a Cd concentration of 10^{-8} M for different reaction times are not significantly different (Table 4); similar results were obtained at a Cd concentration of 10^{-7} M (Table 4). Apparently, the concentration of Cd ions (10^{-8} and 10^{-7} M) is not high enough to cause major aggregation of HA particles (as indicated by their atomic force micrographs, Fig. 3c–f).

The SSA of Cd-humate complexes formed at 10^{-6} M Cd decreased significantly compared to pure HA (Table 4). Furthermore, the SSA of Cd-humate complexes fell with increasing reaction time up to 2 h (Table 4). The kinetic data (Fig. 1) show that Cd sorption at 10^{-6} M reached equilibrium after a 4-h reaction. Therefore, before Cd sorption reached equilibrium, the longer the reaction time, the more Cd ions were adsorbed, resulting in higher aggregation of HA particles and lower SSA of the Cd-humate complexes formed.

Cadmium-humate complexes formed at Cd concentrations of 10^{-4} and 10^{-3} M had substantially lower SSAs than pure HA and Cd-humate complexes formed from 10^{-8} to 10^{-6} M Cd (Table 4). At the same reaction time, the SSA of Cd-humate complexes formed at a Cd concentration of 10^{-3} M was significantly lower than that of complexes formed at 10^{-4} M (Table 4). The Cd sorption data (Fig. 1) indicate that reaction at these initial Cd concentrations approached equilibrium at the end of 8-h. However, the SSA of Cd-humate complexes formed at initial Cd concentrations of 10^{-4} and 10^{-3} M decreased greatly with an increase in the reaction time only within the period from 0.083 to 4 h, and from 0.083 to 2 h, respectively (Table 4). The SSA of Cd-humate complexes, along with the atomic force micrographs (Figs. 4 and 5) suggest that Cd sorption at an initial Cd concentration of 10^{-4} M within the reaction time from 4 to 8 h, and at an initial Cd concentration of 10^{-3} M within 2 to 8 h took place inside the pores of the bean-like particles through slower diffusion processes. Cadmium sorption occurring inside the pores can also explain why the time required for Cd sorption by HA to reach equilibrium is longer at initial Cd concentrations of 10^{-4} and 10^{-3} M compared with an initial concentration of 10^{-8} to 10^{-6} M.

The SSA of HA is directly related to the exposure of functional groups on the surface, and thus influences sorption. However, no perfect method has been developed to measure the SSA of organic matter. Most information on the surface area of organic matter in soil was obtained from the difference between the EGME surface area of soils before and after removing organic matter. This method fails to provide consistent and reliable values for the surface area of soil organic matter (Chiou et al. 1990; Pennell et al. 1995). Chiou et al. (1990) used the N_2-BET method to determine the SSA of HA, and found that it was 18 m^2 g^{-1} for a freeze-dried soil HA and ca. 0.7 m^2 g^{-1} for an oven-dried sample. Oven drying apparently increases aggregation of HAs, and thus cannot give a reasonable value for the SSA. As the sample needs to be outgassed under high vacuum (15 mTorr) for the N_2-BET method, HAs could become dehydrated, causing the sample to collapse and shrink. Thus, the N_2-BET method might underestimate the SSA of HAs.

EXAFS Spectroscopy and Cadmium-sorption Mechanism

Cadmium ions, which are a Lewis acid, can bond to the functional groups of HAs, thus enhancing aggregation of HAs, and finally condensing the spheroidal HA particles into bean-like structures. Although the coordination of Cd ions by HAs was postulated in a previous study (Liu and

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Table 5. Cadmium-oxygen bonds in $Cd(ClO_4)_2$ and the Cd-humate complexes formed at the initial Cd concentrations of 10^{-6} and 10^{-4} M at pH 5.0 and $NaNO_3$ concentration of 0.01 M at the end of a 24-h reaction period

Sample	Coordination number of Cd	Cd-O bond distance (Å)	σ^2 (Å^2)[z]
$Cd(ClO_4)_2$	6	2.29	NA[y]
Cd-humate (10^{-6} M)	6.8 ± 0.7	2.295 ± 0.003	0.0006 ± 0.0018
Cd-humate (10^{-4} M)	6.1 ± 0.2	2.298 ± 0.006	0.0076 ± 0.0005

[z]The disorder value of the Cd-humate complexes.
[y]Not applicable.

Huang 1999), the actual mechanism of complexation was not known. This problem was examined here by EXAFS spectroscopy of Cd-humate complexes formed at initial Cd concentrations of 10^{-6} and 10^{-4} M at the end of a 24-h reaction time.

Table 5 shows the optimized structural parameters derived from the EXAFS analysis, which are illustrated in Fig. 6, along with the experimental spectra. To obtain the optimized parameters, the experimental functions were Fourier-transformed from wavevector (κ, Å^{-1}) to distance (Å) and then fitted with FEFF6 (Zabinsky et al. 1995) theoretical curves (Figs. 7 and 8). The nearest neighbor environment of Cd was modeled using Cd-O interactions. In principle, it is possible to discriminate oxygen, nitrogen or carbon atoms as first nearest neighbors to cadmium from the EXAFS analysis. In the present case, this task is complicated because the EXAFS's signal quality is limited by the low concentration of cadmium ions. Fortunately, the nitrogen and carbon atoms have very similar electron-scattering properties as oxygen, and choosing the Cd-O interaction to model interaction of Cd with its first nearest neighbors is a good first approximation. The Cd-O coordination numbers, bond lengths and their mean squared disorder (σ^2) varied in the fitting process. It should be noticed that the peak positions of the Fourier transform magnitudes in Figs. 7 and 8 are shifted by ca. 0. 5 Å toward lower distances from the actual bond lengths obtained from the EXAFS data (Table 5), because no corrections for photoelectron phase shift functions were made in Figs. 7 and 8.

The EXAFS results (Table 5) indicate that Cd is coordinated by six O atoms in the Cd-humate complexes formed at an initial Cd concentration of 10^{-6} M or 10^{-4} M. This substantiates Liu and Huang's (1999) proposed structural model for Cd-humates. The Cd-O bond distance for humate complexes formed at the initial Cd concentration of 10^{-4} M (2.298 Å) was not significantly larger than that in the complexes formed in the 10^{-6} M Cd system (2.295 Å) (Table 5). Therefore, the Cd-O bond distance in the complexes is 2.297(2) Å. However, the disorder value (σ^2) of Cd-humate complexes at 10^{-6} M Cd (0.0006 Å^2) was much smaller than that of the Cd-humate complexes formed at 10^{-4} M Cd (0.0076 Å^2). Because the bond length disorder is inversely proportional to the bond force constant (Frenkel and Rehr 1993; Fendorf et al. 1994), these results indicate that the Cd-O bonding was much stronger in the former than that in the latter. Even though the uncertainty in the disorder factor of Cd-O pair for the 10^{-6} M Cd sample was three times greater than its value, the difference in these factors, obtained for the samples with different Cd concentrations, was well outside the error bars.

CONCLUSIONS

Cadmium sorption by HA can be described by the parabolic diffusion equation, indicating that the rate of sorption is limited by diffusion-controlled processes. The apparent diffusion coefficient increased with a rise in the initial Cd concentration from 10^{-8} M to 10^{-3} M. However, the degree of

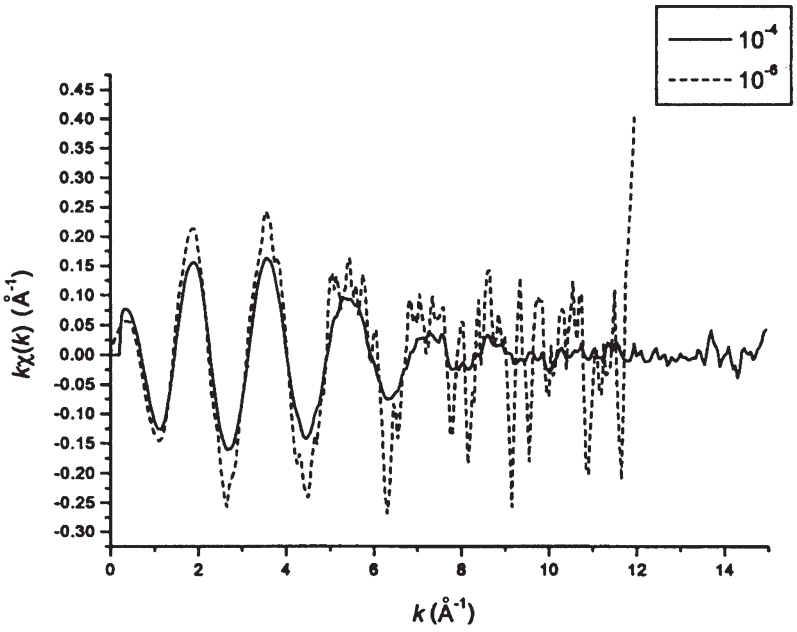

Fig. 6. Experimental κ-weighted EXAFS function $\chi(\kappa)$ for Cd-humate complexes formed at initial Cd concentrations of 10^{-6} and 10^{-4} M at pH 5.0 and an $NaNO_3$ concentration of 0.01 M at the end of a 24-h reaction period. The wavevector κ (Å^{-1}) is an energy-related unit defined as $\kappa = [2m(E–E_0)\,\bar{h}–2]^{1/2}$, where $\bar{h}$ is Planck's constant divided by 2π, m is the mass of an electron, E is the energy of the original X-ray photon, and E_0 is the electron- binding energy. The χ is the oscillatory portion of EXAFS. The κ-weighted EXAFS function $\chi(\kappa)$ (i.e., $\kappa\chi(\kappa)$) is the $\chi(\kappa)$ function multiplied by κ.

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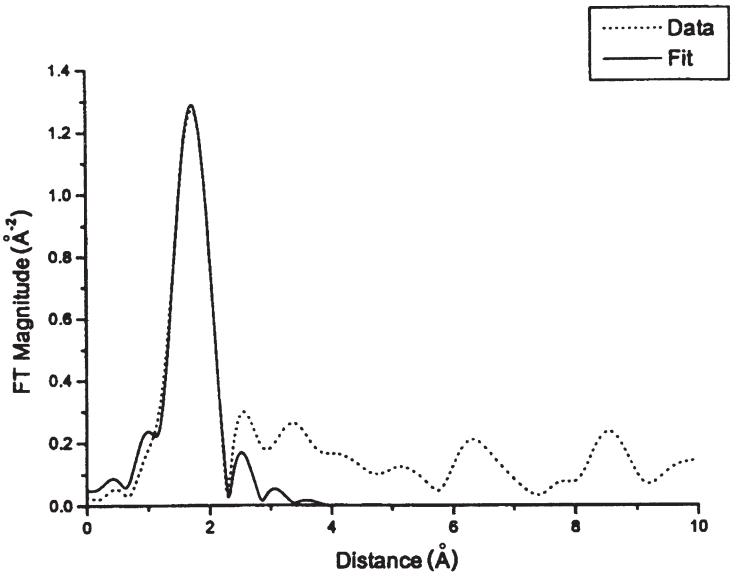

Fig. 7. Fourier-transformed (FT) functions (uncorrected for phase shifts) of κ-weighted EXAFS spectra (dashed line) and optimized theoretical curve (solid line) of Cd-humate complexes formed at an initial Cd concentration of 10^{-6} M at pH 5.0 and an $NaNO_3$ concentration of 0.01 M at the end of a 24-h reaction period. The FT magnitude is the intensity of Fourier-transformed $\kappa\chi(\kappa)$ spectra.

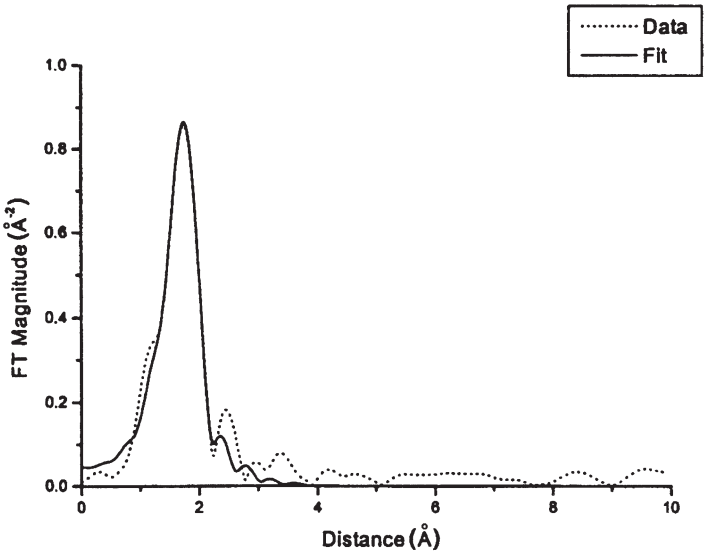

Fig. 8. Fourier-transformed (FT) functions (uncorrected for phase shifts) of κ-weighted EXAFS spectra (dashed line) and optimized theoretical curve (solid line) of Cd-humate complexes formed at an initial Cd concentration of 10^{-4} M at pH 5.0 and an $NaNO_3$ concentration of 0.01 M at the end of a 24-h reaction period. The FT magnitude is the intensity of Fourier-transformed $\kappa\chi(\kappa)$ spectra.

the increase declines from a low initial Cd concentration to a high one; this is due to enhancement of Cd-humate-complex aggregation at higher concentrations. The Cd-humate complexes formed at 10^{-4} and 10^{-3} M gradually changed from spheroids to bean-like particles with an increase in the reaction time and in the amount of Cd adsorbed, resulting in a decrease of the specific surface area. The kinetic, specific-surface, AFM and EXAFS data show that Cd enhanced aggregation of HA and finally raveled the spheroidal HA particles into the bean-like structure by coordinating to six O atoms of the functional groups of HA, with a Cd-O distance of 2.297(2) Å. Further, the disorder values of the Cd-humate complexes signify that the Cd-O bond strength decreases with an increase of the initial Cd concentration. The formation of Cd-humate complexes with different Cd-O bond strengths, specific surface, and surface features at the submicrometer-scale strongly influences the dynamics of Cd sorption, and may, thus, affect its bioavailability and mobility in soils and sediments.

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