CHARACTERIZATION OF Pb, Cu, AND Cd ADSORPTION ON PARTICULATE ORGANIC MATTER IN SOIL

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Abstract—Evidence exists for significant metal enrichment in particulate organic matter (POM) compared to other soil constituents, but the relevant mechanisms are poorly understood. In the present study, adsorption of the heavy metals Pb, Cu, and Cd on a loamy soil and on POM separated from this soil was investigated. The adsorption kinetic data can be well described with a pseudo-second order model, whereas the equilibrium data are well fitted by a Langmuir model. Adsorption isotherms and kinetics data, in addition to the influence of pH on metal adsorption, showed that POM had a much higher adsorption capacity for Pb, Cu, and Cd compared to the whole soil. Ionic strength effects on metal adsorption, Fourier transform infrared spectroscopy, x-ray absorption spectroscopy, x-ray absorption spectroscopy including x-ray absorption near-edge structure and extended x-ray absorption fine-structure spectroscopy were employed to elucidate the adsorption mechanisms. The results suggested that Pb and Cu adsorption on POM was mainly through inner-sphere complexes with carboxyl and hydroxyl groups. Cadmium was possibly adsorbed via outer-sphere complexation, indicated by the influence of ionic strength on Cd adsorption.

Keywords—Particulate organic matter Heavy metals Adsorption Fourier transform infrared spectroscopy X-ray absorption spectroscopy

INTRODUCTION

Increasing heavy metal loading on both agricultural and urban soils because of anthropogenic activities has led to extensive research concerning the chemistry of heavy metals in soils [1–3]. The metal concentration in soil solution (and, hence, the bioavailability or toxicity of heavy metals) most likely is controlled by reactions at the soil–solution interface. Therefore, a better understanding of the availability and fate of these elements depends on our knowledge of the adsorption reactions taking place at this boundary.

In soils, heavy metals may be adsorbed by many sorbent phases, such as metal (oxyhydr)oxides, clay minerals, and organic matter. Intensive studies have been carried out to investigate metal adsorption on these sorbents and to elucidate the sorption mechanisms [4,5]. Previous studies [6–8] have demonstrated that soil organic matter contains many important functional groups, such as -COOH and -OH, which can readily bind metal ions and form strong complexes that are resistant to desorption. Hence, soil organic matter is an important adsorbent for heavy metals.

Soil organic matter is a complex, heterogeneous medium. In addition to the well-known humic fractions, such as humic acid, fulvic acid, and humin, exist a large quantity of particulate organic matter (POM), consisting of light-density, sand-sized (>0.05 mm) organic debris with a relatively rapid turnover. Studies of POM have gained attention since the last decade. Elliott [9] suggested that POM was a key fraction influencing soil fertility and had the potential to be used as an

indicator of soil quality. More recently, researchers found a significant metal enrichment in POM compared to the other soil constituents. Besnard et al. [10] investigated vineyard soils with Cu contamination and found that among the two most Cu-enriched soil fractions, the POM accumulated up to 2,000 mg/kg of Cu, and the other corresponding clay fraction contained up to 500 mg/kg of Cu. An investigation of polluted soils from a former iron ore–processing site found that POM was responsible for 16 to 41% and for 12 to 32% of the accumulation of Cu and Zn, respectively, in soils. These studies [10,11] focused on metal enrichment in POM of heavily polluted soils. Balabane and Van Oort [12] investigated metal accumulation in the arable soils with low metal concentration. Their results indicated that Cd concentrations in POM were 5- to 11-fold higher than the corresponding values in the bulk soils. These studies give us a hint that POM plays an important role in metal accumulation in soils, but the interactions between POM and heavy metals in soil and the relevant mechanisms of heavy metal enrichment in POM remain poorly characterized.

To enhance our understanding of the relevant mechanisms of metal enrichment in POM, we examined the adsorption behavior of Pb, Cu, and Cd on POM. Metal adsorption on POM and the original soil from which the POM was separated were compared. Fourier transform infrared (FTIR) spectroscopy, x-ray absorption spectroscopy (XAS), XAS including x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine-structure (EXAFS) spectroscopy were employed to elucidate the binding sites and coordination environment of metal ions adsorbed on POM.

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MATERIALS AND METHODS

Adsorbent characteristics

A loamy soil (Alfisols) was collected from the surface (depth, 0–15 cm) of an experimental field previously amended with straw. The soil sample was air-dried, ground, and passed through a 2-mm, nylon-fiber sieve. Physical fractionation of POM was achieved using the method described by Ducaroir and Lamy [13] with some modifications. The soil was agitated in water with glass beads, leading to the complete dispersion of soil particles larger than 0.05 mm. The particle size fractions from 0.05 to 2 mm were separated by wet-sieving, and then the POM was separated by repeated flotation-panning in water and oven-dried at 55°C. Scanning-electron micrographs (S-3000N; Hitachi, Tokyo, Japan) of the POM were obtained with $\times 400$ magnification. The total C and N content was determined by dry combustion in an autoanalyzer (Vario EL; Elementar Analysensysteme, Hanau, Germany). The pH values of POM and soil suspensions were measured at a solid to water ratio of 1:1 (w/v). Cation-exchange capacity was determined using the method described by Rhodes [14]. Nitrogen-specific surface area of the POM and soil was measured by using a Flow-sorb II surface area analyzer (ASAP 2000; Micromeritics, Norcross, GA, USA) and by applying the Brunauer–Emmett–Teller equation to the sorption of N_2 at a relative partial pressure of 0.3 at 77 K.

Adsorption kinetics

Adsorption kinetic studies were conducted by a batch technique at 20°C. A 0.2-g portion of POM or soil was weighed into a 50-ml polyethylene centrifuge tube, and 20 ml of 4 mM $Pb(NO_3)_2$, $Cu(NO_3)_2$, or $Cd(NO_3)_2$ solution (prepared in a 0.01 M $NaNO_3$ electrolyte) were added. After the samples were shaken end-over-end for predefined time intervals, the suspensions were filtered. The concentrations of Pb, Cu, and Cd in the filtrate were determined by inductively coupled plasma–optical emission spectrometry (Optima 2000 DV; PerkinElmer, Wellesley, MA, USA). The quantity of metal adsorbed at time t (q_t) was deduced from the mass balance between the initial concentration and the concentration at time t in solution. All the measurements were carried out in triplicate. For each sample, a control without adsorbent was performed to account for any possible chemical precipitation.

Adsorption isotherms

The adsorption isotherm was performed using the same method as described above. The initial concentrations of dissolved metal ranged from 0.2 to 6 mM. The pH of the system was kept at 5.5. To examine the effect of ionic strength, adsorption of metals on POM was performed in a background electrolyte of 0.01 and 0.1 M $NaNO_3$.

Effect of pH on the adsorption of Pb, Cu, and Cd

Aqueous solutions (<20 ml) of 0.01 M $NaNO_3$ were mixed with 0.2 g of POM or soil. The suspension pH was adjusted to the desired pH, ranging from 2 to 8, by adding a small volume of dilute HNO_3 or $NaOH$. The suspension was then spiked with Pb, Cu, or Cd to yield a starting concentration (C_0) of both 1 and 4 mM for both Pb and Cu and of 0.5 and 2 mM for Cd, with a final volume of 20 ml. After 24 h of shaking, final pH values were measured, and suspensions were centrifuged at 7,200 g for 15 min, filtered, and analyzed for the metal concentrations.

Adsorption models

A pseudo–second order kinetic model [15,16] was used to fit the adsorption kinetic data. The equation is

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

where k is the rate constant for the pseudo–second order model and q_e and q_t are the amount of solute adsorbed per unit adsorbent at equilibrium and at time t , respectively. Herein, the initial adsorption rate (v_0) is calculated as $v_0 = kq_e^2$.

The equilibrium data were analyzed using a Langmuir sorption isotherm:

$$q_e = \frac{bq_m C_e}{1 + bC_e}$$

where q_m (mmol/g dry wt) is the maximum sorption capacity corresponding to the complete monolayer coverage, C_e (mM) is the equilibrium solute concentration, and b (L/mmol) is the equilibrium constant related to the energy of sorption. The parameters were obtained by nonlinear least-squares-regression analysis.

FTIR spectroscopic measurements

Infrared spectra were obtained using a GX2000 FTIR spectrophotometer (PerkinElmer) equipped with deuterated triglycine and mercury–cadmium–telluride detectors (Thermo Nicolet, Madison, WI, USA), a KBr beam splitter (Thermo Nicolet), and a sample bench purged with dry air. The resolution for the FTIR spectra was 4.0 cm^{-1} , and a total of 32 scans were collected for each spectrum. The FTIR spectra were recorded with pellets obtained by pressing a mixture of 1 mg of sample and 100 mg of KBr under reduced pressure.

XAS data collection and analysis

Wet pastes of POM, obtained by decanting the supernatant after the adsorption experiments described above with an initial concentration of 4 mM at pH 5.5, were loaded into Teflon® sample holders and sealed with Kapton tape. X-ray absorption spectra at the Cu K-edge (8,979 eV) and Pb L₃-edge (13,055 eV) were collected at the 4WIB beamline of the Beijing Synchrotron Radiation Facility using a Si (111) double-crystal monochromator. The storage ring was operated at 2.2 GeV, with an average beam current of 80 mA. To minimize harmonics, the monochromator crystals were detuned by approximately 30%. The XAS data for all adsorption samples were collected in fluorescence mode, whereas the reference compounds $Cu(OH)_2$, $Cu(CH_3CO_2)_2$, and $Pb(CH_3CO_2)_2 \cdot 3H_2O$, as well as the β -PbO powders and the solutions of $Cu(NO_3)_2$ and $Pb(NO_3)_2$, were in transmission mode at room temperature. The spectra were recorded using sampling steps of 0.6 eV for XANES and 3.0 eV for EXAFS. Data regarding three scans for the same sample were averaged to improve the signal to noise ratio. The energy was calibrated using a Cu or Pb metallic foil.

Data were processed using WinXAS2.1 [17] following standard procedures. The $x(k)$ functions were subtracted from data with a polynomial pre-edge and a cubic spline function and were normalized using the absorption edge jump. The resulting $x(k)$ functions were weighted with k^3 for Cu and k for Pb to compensate for the damping of the EXAFS amplitude with increasing k and were Fourier-transformed to obtain radial structure functions. The weighted k was used because of the

Table 1. Selected characteristics of particulate organic matter (POM) and soil^a

Characteristic	POM	Soil
pH	7.6	6.9
C (%)	32.31	1.95
N (%)	2.04	0.24
H (%)	3.76	0.47
CEC (cmol/kg)	57.6	13.7
OM (%)	52.68	3.38
Texture (sand/silt/clay)		32/45/23
BET surface area (m ² /g)	7.92	9.72

^a BET = Brunauer-Emmet-Teller; CEC = cation-exchange capacity; OM = organic matter.

noise by weighting with k^3 for Pb-POM EXAFS spectrum at $k > 6 \text{ \AA}^{-1}$. The radial structure functions were calculated by Fourier transforms $k^n x(k)$ over the range from 2 to $12 \text{ \AA}^{-1}$ for Cu and from 2 to $10 \text{ \AA}^{-1}$ for Pb ($n = 3$ for Cu, $n = 1$ for Pb). The fits were performed in k -space.

During the fitting procedure, the coordination number (N) was fixed, and the interatomic distance (R), energy shift (E_0), and Debye-Waller factor (σ^2) were varied until the best fit was achieved. Phase shifts and backscattering amplitudes were obtained from the theoretical calculation with the model compound $\text{Cu}(\text{OH})_2$ using FEFF7.0 [18].

RESULTS AND DISCUSSION

Characterization of POM

The characteristics of the POM and the original soil are shown in Table 1. The percentage of POM in the soil sample was 0.58%. The total C and N content was determined, and the C to N ratio was 15.8, typical of decomposing crop residues [12]. Scanning-electron micrographs indicated that the POM was composed of a heterogeneous range of components with a porous structure (figure not shown). The Brunauer-Emmett-Teller surface area of the POM was $7.92 \text{ m}^2/\text{g}$. This relatively low value probably resulted from the measurement method that we used, in which the adsorption of N_2 gas can only determine the external surface area of the POM [19].

Adsorption kinetics

The adsorption of Pb, Cu, and Cd on POM and the soil typically was characterized by a biphasic process for the initial metal concentration of 4 mM (Fig. 1). The initial rapid phase (first 10 min) accounted for a considerable portion of the sorption. During this stage, 89 to 98% of the adsorption of Pb, Cu, and Cd occurred for the POM, compared to 78 to 84% over the same period for the soil. This presumably resulted from a chemical reaction and film-diffusion process [19]. Adsorption in the subsequent 10 to 30 min was slower and probably resulted from the diffusion of metal ions into the porous structures of the adsorbent [20]. The initial adsorption rate for POM was much higher than that for the soil, suggesting the higher affinity of the metals studied for the POM than for the soil.

To evaluate the differences in the adsorption kinetic rates, the pseudo-first order model, pseudo-second order kinetic model, and intraparticle diffusion model were tested to fit the results. The rate law for a pseudo-second order kinetic model can best describe the experimental data (Fig. 1), with a correlation coefficient (r^2) of one. Successful fitting of the data with the second-order kinetic model suggests that chemisorption was the rate-controlling step [15,16]. Kinetic constants,

Fig. 1. Adsorption kinetics of Pb, Cu, and Cd on particulate organic matter (POM) and soil with an initial metal concentration of 4 mM. Dotted lines represent the modeled results using pseudo-second order equation. The terms t and q_t represent time and the amount of metal adsorbed per gram of POM or soil at time t , respectively. The second-order equation represents the pseudo-second order kinetic model fit.

including v_0 , k , and q_e were calculated from the slopes and intercepts of the plots, which are presented in Table 2. The initial sorption rate (v_0) values for POM were 134.41, 25.90, and 7.51 mmol/g/h for Pb, Cu, and Cd, respectively. Similar trends with the descending order of $\text{Pb} > \text{Cu} > \text{Cd}$ were observed for the bulk soil.

Adsorption isotherms

Sorption isotherms of Cu, Pb, and Cd on the POM and the soil are presented in Figure 2. The equilibrium data fit better to the Langmuir model than to the Freundlich model; therefore, the fit by the Langmuir sorption isotherm is given in Figure 2. The significant correlation coefficients (r^2) ranged from 0.947 to 0.995 ($p < 0.01$). Good agreement with the experimental data suggests that the adsorbed metal forms a monolayer coverage on the adsorbent surface. The values of q_m and b obtained from the plots are listed in Table 3. The greatest equilibrium fixation capacity (q_m) was obtained for Pb (0.501 mmol/g), which decreased to 0.475 mmol/g for Cu and 0.304 mmol/g for Cd. The corresponding values for the soil were 0.211, 0.108, and 0.085 mmol/g for Pb, Cu, and Cd, respec-

Table 2. Pseudo-second order kinetic model parameters for the adsorption of Pb, Cu, and Cd on particulate organic matter (POM) and soil^a

Metal-adsorbent	v_0 (mmol/g/h)	k (g/mmol/h)	q_e (mmol/g)	r^2	SE
Pb-POM	134.41	844.3	0.399	1.000	0.0096
Cu-POM	25.90	169.4	0.391	1.000	0.0292
Cd-POM	7.51	125.1	0.245	1.000	0.0345
Pb-soil	7.57	170.0	0.211	1.000	0.0093
Cu-soil	1.69	139.6	0.111	1.000	0.0185
Cd-soil	1.62	229.2	0.084	1.000	0.0152

^a v_0 = initial sorption rate; k = the rate constant for the pseudo-second order model; q_e = amount of solute added per unit adsorbent at equilibrium.

Fig. 2. Adsorption isotherms of Pb, Cu, and Cd on particulate organic matter (POM) and soil. Solid line denotes the adsorption isotherm predicted using the Langmuir model. The terms C_e and q_e represent the equilibrium metal concentration in solution and the amount of metal adsorbed per gram of POM or soil at equilibrium, respectively.

tively. Particulate organic matter showed a preferential binding capacity for the metal ions. These results also are in agreement with the previously obtained kinetic data.

Influence of pH

The solution pH plays a significant role in the sorption of heavy metals, because it affects the surface charge of the adsorbent, the degree of ionization, the speciation of the surface functional groups, and the ionic species of metals. Harter and Naidu [21] reported that the sorption edge (whereby sorption increases rapidly over a relatively narrow pH range) tended to become more distinct and shifted to a higher pH as the initial metal concentration increased. Therefore, two initial concentrations of each metal were used in the present work.

The adsorption of Pb, Cu, and Cd followed the expected trend of increased metal sorption with the increase of pH from 2 to 8, and the sorption edge shifted to a higher pH as the initial metal concentration increased (Fig. 3). Taking Pb as an example, POM adsorbed 73% of total Pb even at pH 2.5 (Fig. 3a). Ninety-eight percent of Pb was adsorbed on the POM at pH 3.9 and 5.9 for the initial aqueous concentrations of 1 and 4 mM, respectively. A similar proportion of Pb was adsorbed on the bulk soil at pH 5.5 and 6.6 for the initial dissolved Pb concentrations of 0.5 and 2 mM, respectively, indicating that POM has a higher affinity than the whole soil for Pb. We also observed that metal adsorption on POM was much less pH-

Fig. 3. Effect of pH on the adsorption of (a) Pb, (b) Cu, and (c) Cd on particulate organic matter (POM) and soil.

Table 3. Langmuir parameters for metal adsorption on particulate organic matter (POM) and soil^a

Metal-adsorbent	q_m (mmol/g)	b (L/mmol)	r^2
Pb-POM	0.501	48.93	0.972
Cu-POM	0.475	18.52	0.993
Cd-POM	0.304	2.90	0.995
Pb-soil	0.211	24.23	0.990
Cu-soil	0.108	11.05	0.947
Cd-soil	0.085	1.35	0.975

^a q_m = maximum sorption capacity corresponding to the complete monolayer coverage; b = equilibrium constant related to the energy of sorption.

dependent compared with soil, reflecting the high metal affinity toward POM. Among the metals investigated, Pb had the highest affinity toward POM, followed by Cu and Cd, a finding similar to the results of Appel and Ma [22] and of Reddad et al. [23], who investigated metal uptake by three tropical soils and polysaccharides in sugar beet pulp, respectively.

At a given pH, the adsorption percentages decreased with increasing initial metal concentrations. This can be explained by changes in the metal ion to adsorbent ratio. At low metal ion to adsorbent ratios, adsorption mainly occurs on the higher-energy sites. As the metal ion to adsorbent ratio increases, the higher-energy sites become saturated, allowing adsorption to take place on lower-energy sites, causing a reduction in the percentage uptake of the metal from solution [24].

Fig. 4. Effect of ionic strength on the adsorption of Pb, Cu, and Cd on particulate organic matter (POM). The C_e and q_e represent the equilibrium metal concentration in solution and the amount of metal adsorbed per gram of POM or soil at equilibrium, respectively.

Influence of ionic strength

The adsorption isotherms of Pb, Cu, and Cd on POM in 0.1 and 0.01 M NaNO_3 solutions are displayed in Figure 4. Adsorption was not significantly different for Pb and Cu between the two ionic strengths; however, differences in Cd adsorption could be observed, especially at high concentrations. The maximum fixation capacity (q_m) for Cd was 0.304 and 0.205 mmol/g for the 0.01 and 0.1 M NaNO_3 solutions, respectively. The effect of ionic strength on sorption relates to the binding sites that are available. The Na^+ in the background electrolyte can compete with the metal adsorbed on the outer-sphere sorption sites, whereas it does not compete for the inner-sphere sites. Therefore, the effect of ionic strength on metal adsorption often is used as indirect evidence for distinguishing between outer-sphere and inner-sphere adsorption. The lack of an ionic strength effect on the adsorption of Pb and Cu and the dependence of Cd adsorption on the ionic strength suggest that Pb and Cu primarily formed inner-sphere complexes with POM, whereas Cd adopted outer-sphere adsorption complexes with POM. The observation that Cd sorption mainly involved electrostatic coulombic interactions instead of chemical bonding is consistent with the fact that Cd is a closed-shell cation (valence orbital is full— d^{10}), which favors coulombic-type reactions at the adsorbent surface. Furthermore, Pb and Cu possess a higher hydrolysis constant, $\log K(\text{OH})$, than Cd; hence, they will have a lower degree of metal ion solvation, thus favoring the approach of Pb and Cu to the sorbent surface. As such, the impact that increases of ionic strength have on metal adsorption would diminish with an increasing metal hydrolysis constant [23,25].

FTIR spectrum analysis

The FTIR-spectra of the native POM and of POM with Pb and Cu adsorbed are shown in Figure 5. The FTIR spectrum of POM indicated the presence of carboxyl and hydroxyl groups. The broad bands at 3,300 to 3,400 cm^{-1} are dominated by -OH stretching vibrations. The peaks at 1,652 and 1,423 cm^{-1} are caused by the stretching band of carboxyl groups. The peaks at 2,933 cm^{-1} represent C-H stretching vibrations and - CH_3 wagging. The strong peak that appears at 1,032 cm^{-1} results from C-OH stretching vibrations. The absorbance of

Fig. 5. Fourier transform infrared spectra. The letters a, b, and c represent the spectra for native particulate organic matter (POM), Cu adsorbed on POM, and Pb adsorbed on POM, respectively.

the peaks at 3,300 to 3,400, 1,652, 1,423, and 1,032 cm^{-1} for POM with Pb and Cu adsorbed was slightly lower compared to the native POM, suggesting that the carboxyl and hydroxyl groups were responsible for the metal adsorption.

Cu K-edge XANES and EXAFS spectroscopic studies

The normalized K-edge XANES spectra and their first derivatives for Cu-POM and model compounds are shown in Figure 6a and b. The XANES spectra (Fig. 6a) appeared to be very similar, with white-line peaks at the energy of 8,975 eV. The first derivative spectra (Fig. 6b) showed that the absorption edges (Fig. 6a) had two different inflections, corresponding to derivative peaks at 8,986 eV (α peak) and 8,991 eV (β peak). The β peak represents the main absorption transition ($1s \rightarrow \text{continuum}$). The α peak on the low-energy side of the β peak in Figure 6b is influenced by the degree of axial distortion and the covalence of the equatorial ligands bonded to Cu ions [26–28] and, thus, provides information regarding the Cu-binding environment. As demonstrated by the Cu^{2+} (aqueous) spectrum (Fig. 6b), water molecules coordinated in the equatorial plane produce a strong α peak intensity. The diminished α peak intensity for Cu-POM in comparison with aqueous Cu^{2+} suggests that stronger field water molecules in the tetragonal plane associated with Cu were partly replaced with weak field organic groups (carboxyl and hydroxyl functions) in POM. The POM was much larger than the water molecule; therefore, Cu^{2+} was sterically hindered when it approached and could not bond in the equatorial plane with the same degree of angular overlap as that adopted by water. Based on the above results, one can draw a conclusion that Cu tends to form inner-sphere complexes with POM [29]. This finding is in agreement with the laboratory experiments conducted on ionic strength effect on Cu adsorption.

The k^3 -weighted EXAFS spectra of Cu-POM, $\text{Cu}(\text{OH})_2$, and $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ and its corresponding radial structural function derived from Fourier transformations are presented in Figure 6c and d. The position of the peaks in the radial structural function corresponds to relative distances (uncorrected for phase shift) between Cu and neighboring atoms in local coordination shells. The strongest peak, occurring at 1.54 Å (Fig. 6d), corresponds to the first shell of O atoms. For $\text{Cu}(\text{OH})_2$, the second peak may be caused by the effect of Cu-Cu bonds [28]. Quantitative EXAFS results were obtained by only fitting the filtered first-shell signal (in the 0.85–2.24 $\text{\AA}^{-1}$ range). The

Fig. 6. Normalized x-ray absorption near-edge structure (XANES) spectra (pre- and near-edge region) of Cu-particulate organic matter (POM) sample and the model compounds (a), corresponding first derivatives (b), extended x-ray absorption fine-structure (EXAFS) spectra (χ function) of the Cu adsorbed on POM and the model compounds (c), Fourier transformation of the EXAFS spectra (d), and first-shell fit of the EXAFS function of the Cu adsorbed on POM (e). Solid and dotted lines represent the experimental first-shell filtered data and the best fit, respectively. Experimental phase and amplitude functions were extracted from the EXAFS spectrum of the $\text{Cu}(\text{OH})_2$ as the model compound. E = x-ray energy (eV); R = interatomic distance ($\text{\AA}$); k = photoelectron wave vector unit ($\text{\AA}^{-1}$); μ = normalized absorbance (E); $k^3\chi(k)$ = normalized k^3 -weighed EXAFS signal; $F(R)$ = Fourier transform magnitude.

Cu-O phase shift and oxygen scattering amplitude were extracted from the $\text{Cu}(\text{OH})_2$ reference spectrum. Fitting of the first shell in the Cu-POM sample (Fig. 6e) indicated that the Cu was surrounded by four equatorial oxygen atoms and two axial oxygen atoms. The average bond length of Cu-O in the

equatorial and axial plane was 1.95 and 2.28 $\text{\AA}$, respectively, which is consistent with related studies [27,30]. The EXAFS spectrum of the Cu-POM sample exhibits similarities to that obtained for $\text{Cu}(\text{CH}_3\text{CO}_2)_2$, suggesting that the binding sites for Cu-POM involve carboxylic moieties on the POM surface.

The lack of features at higher R in the radial distribution function of the Cu-POM sample indicates that no high- Z backscatters are bound to the oxygen atoms of the first coordination shell of Cu. The Cu-POM EXAFS spectrum also is similar to the Cu^{2+} (aqueous) spectrum, possibly because both bonding environments have light elements (C and H) bound to the oxygen atoms in the first Cu coordination shell, which are poor backscatters. This is consistent with the assignment of Cu binding by carboxyl and hydroxyl groups.

Pb L_3 -edge XANES and EXAFS spectroscopic studies

To investigate further whether the local coordination environment of Pb in POM was similar to that of Cu, the Pb L_3 -edge XANES and EXAFS were examined. Many previous studies have demonstrated that Pb L_3 -edge XANES is very sensitive to the first-shell coordination environment [31,32]. The XANES spectra of Pb-POM and the model compounds are shown in Figure 7a. The XANES spectrum of Pb-POM has two prominent peaks at the energy of 13,043 and 13,083 eV. Similar peaks are observed for $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ and, to a lesser extent, for Pb^{2+} (aqueous). The spectrum for $\beta\text{-PbO}$ is somewhat different, with the peaks at 13,046 and 13,093 eV. The similarities in the XANES spectra of the Pb-POM and $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ samples demonstrate that the local atomic structure of the first shells of oxygen surrounding the Pb atoms are similar, indicating Pb coordination to oxygen atoms of POM through carboxyl functional groups, similar to the Pb coordination environment in $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$.

Background-subtracted, k -weighted EXAFS functions are presented in Figure 7b. For the χ structure of Pb-POM, a large decrease in the amplitude of the signal occurs at $k > 6 \text{ \AA}^{-1}$. This can be ascribed to the dampening of the EXAFS signal because of structural and thermal disorder and the absence of any heavy backscattering atoms in the local ($\sim 5 \text{ \AA}$) coordination environment of Pb. [32]. The first two oscillations of the Pb-POM EXAFS spectrum at 2.8 and $4.7 \text{ \AA}^{-1}$ have amplitudes relatively similar to those in the $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ EXAFS spectrum. To isolate the characteristic frequencies that exist in the χ structure, EXAFS data were Fourier transformed to yield radial structure functions (Fig. 7c). These spectra exhibit peaks that reflect the relative radial distances (not corrected for phase shift and amplitude) between Pb and the neighboring atoms. A single peak is observed at approximately $1.9 \text{ \AA}$ for the Pb^{2+} (aqueous) sample. Similar peaks at approximately $1.7 \text{ \AA}$ are observed for the Pb-POM sample and the model compounds of $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ and $\beta\text{-PbO}$. The shorter Pb-O bond distances for Pb-POM than that of Pb^{2+} (aqueous) suggests that Pb adsorbed on POM adopted inner-sphere complexes [31,32]. A comparison of the L_3 -edge XANES spectra (Fig. 7a), EXAFS spectra (Fig. 7b), and corresponding Fourier transform spectra (Fig. 7c) shows a good agreement between the Pb-POM and $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ spectra, lending further support to the binding of Pb by POM via oxygen bridges on surface functional groups, such as carboxyl.

No XAS study was carried out for Cd because of the practical limitations to the energy range available in the Beijing Synchrotron Radiation Laboratory.

CONCLUSION

The POM is typical of decomposing crop residues and has heterogeneous, porous structures. It plays a significant role in the retention of heavy metals in soils. The adsorption kinetics and adsorption isotherms indicated the high affinity of heavy

Fig. 7. Normalized Pb L_3 x-ray absorption near-edge structure (XANES) spectra for Pb adsorption sample and the model compounds (a), Pb L_3 -edge extended x-ray absorption fine-structure (EXAFS) spectra (b) and Fourier transforms of the EXAFS data (c). E = x-ray energy (eV); R = interatomic distance ($\text{\AA}$); k = photoelectron wave vector unit ($\text{\AA}^{-1}$); μ = normalized absorbance (E); $k\chi(k)$ = normalized k -weighted EXAFS signal; $F(R)$: Fourier transform magnitude; POM = particulate organic matter.

metals toward POM. The dependence of Cd adsorption on ionic strength suggested that the adsorption of Cd on POM occurred through outer-sphere complexes. The adsorption of Cu and Pb revealed no dependence on solution ionic strength, indicating inner-sphere complexation as the adsorption mech-

anism for these two metals. The XAS and FTIR spectroscopic studies provided further compelling evidence for the formation of inner-sphere complexes for Pb and Cu adsorbed on POM and suggested that the complexation was mainly through carboxyl and hydroxyl groups.

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