XAFS studies on surface coordination of Pb\textsuperscript{2+} on birnessites with different average oxidation states

Wei Zhao\textsuperscript{a,b}, Wenfeng Tan\textsuperscript{a,b}, Xionghan Feng\textsuperscript{a,*}, Fan Liu\textsuperscript{a}, Yaning Xie\textsuperscript{c}, Zhi Xie\textsuperscript{d}

\textsuperscript{a} Key Laboratory of Subtropical Agricultural Resource \\ & Environment, Ministry of Agriculture of China, Huazhong Agricultural University, Wuhan 430070, China
\textsuperscript{b} State Key Laboratory of Soil Erosion and Dryland Farming in the Loess Plateau, Institute of Soil and Water Conservation, Chinese Academy of Sciences, Yangling, Shaanxi 712100, China
\textsuperscript{c} Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China
\textsuperscript{d} National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

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**A B S T R A C T**

The adsorption of Pb\textsuperscript{2+} on birnessites was investigated by X-ray absorption fine structure (XAFS). Two Pb–O and two Pb–Mn shells were detected in the birnessites with Pb loading. For the same birnessite at low Pb loading (600 mmol/kg) the two Pb–O shells consisted of 3.1 O atoms at 0.227 nm and 8.2 O atoms at 0.399 nm, respectively. The two Pb–Mn shells consisted of 2.8 Mn atoms at 0.357 nm, and 6.1 Mn atoms at 0.377 nm. At high load loading (2344 mmol/kg) O atoms number decreased to respectively 1.2 at 0.226 nm, and 3.0 at 0.397 nm in the two Pb–O shells, and Mn atoms number decreased to respectively 1.0 at 0.356 nm and 2.8 at 0.375 nm in the two Pb–Mn shells. This is indicative of the distortion of the Pb\textsuperscript{2+} coordination environment with increased loading of Pb. The amount of Pb\textsuperscript{2+} adsorbed increased with increasing values of the average oxidation state (AOS) of birnessite, also in this case the distortion of the Pb\textsuperscript{2+} coordination environment led to a decrease in the Pb–O coordination numbers in both the Pb–O shells and in the Pb–Mn coordination numbers in both the Pb–Mn shells. Based on the XAFS analyses, three bonding mechanisms of Pb\textsuperscript{2+} adsorbed on the birnessites with different Mn AOS were proposed: a single-corner-sharing complex on particle edges along the u axis of Mn\textsubscript{0} layers, a double-corner-sharing complex on particle edges along the a or b axis, and a triple-corner-sharing complex in the interlayer above or below vacant sites.

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1. Introduction

The heavy metal lead is toxic to animals and vegetations and it can damage the nervous system of humans. Adsorption is one of the important processes that affect the transfer of lead and other heavy metals from the aqueous phase to the solid phase and, thus, influences the distribution, mobility, and bioavailability of heavy metal ions [1]. Manganese (Mn) oxides are widely distributed in soils, sediments, and ocean manganese nodules; they are characterized by low points of zero charge, high negative charge, large surface areas, and they are actively involved in various chemical reactions. They are considered as important lead adsorbents in the environment [2–4]. Birnessite is one of the most common Mn oxides. Feng et al. [5] found the adsorption affinity and capacity of birnessite for different heavy metal ions are unlike. Especially, birnessite had the greatest adsorption affinity and amount for Pb\textsuperscript{2+}. Understanding the mechanism of Pb\textsuperscript{2+} adsorption on birnessite, is important for an accurate thermodynamic and kinetic description of Pb\textsuperscript{2+} transport in the environment.

The basic building blocks of Mn oxides are the MnO\textsubscript{6} octahedra. These octahedra can be joined together by sharing corners or edges into layer structures (or phyllomanganates) [6]. The phyllomanganate birnessite can be denoted as $H_xK_yH_2O_xMn_{z-e}^{2-3+}[(Mn_{d}^{3+}, Mn_{e}^{4+})]P_1O_2$, where the interlayer species are written to the left of the square brackets and tc refers to interlayer Mn in triple corner-sharing positions above or below vacant Mn octahedral sites (T1) in the layer (enclosed in square brackets, except for the O atoms) [7,8]. The MnO\textsubscript{6} octahedral layers may have significant Mn vacancies with up to one site out of every six Mn octahedra in hexagonal birnessites. Interlayer water molecules and the cations that compensate the charges created by defects in the Mn octahedral layers have a profound influence on the resulting structures [6]. Many Mn oxides can be synthesized by direct or indirect transformation of birnessite [9,10].

Birnessite synthesis can be achieved by the reduction of potassium permanganate in a strong acidic medium [11], the product is termed “acid-birnessite” [12]. The acid birnessite has a hexagonal layer symmetry with layers comprising edge-sharing Mn(IV)O\textsubscript{6}...
octahedra, Mn(III)O₆ octahedra and vacant Mn octahedral sites [13]. Some Mn²⁺ and Mn³⁺ ions are located above or below vacant Mn octahedral sites in birnessites [6]. Many studies have indicated that the birnessite structural vacancies account for the negative layer charges [14–20], that they are associated with adsorption of heavy metals [16–18], with oxidation of Co²⁺ and Cr³⁺ [14,21] and with structural rearrangements of birnessite [9,22,23]. Based on X-ray diffraction measurement, Lanson et al. [24] concluded that around 75% of adsorbed Pb ions on birnessite were located either above or below the vacant Mn sites. These Pb ions shared three layer-oxygen atoms with three layer-Mn atoms, thereby forming tridentate corner-sharing (TC) interlayer complexes. The rest of the adsorbed Pb ions were located above or below the empty tridentate cavities, sharing three edges with neighbouring MnO₆ in the layer, thereby forming a tridentate edge-sharing (TE) interlayer complexes, as in quenselite. Villalobos et al. [25] also found that a portion of Pb ions formed double-corner-sharing complexes at particle edges of birnessite.

As the Pb adsorption capacity is determined largely by the amount of vacant Mn structural sites in birnessite, the density of vacant Mn structural sites is important. According to Zhao et al. [26] the amount of vacant sites increases with an increase of the average oxidation state of Mn (Mn AOS) of birnessite. Though the binding mechanisms of Pb²⁺ adsorbed on birnessites have been studied [24,25], there is little knowledge on how the binding mechanism varies with the amount of Pb²⁺ adsorbed and what the influence is of the amount of vacant Mn structural sites in birnessites on the binding mechanism. Therefore, in the present paper the binding mechanism of Pb²⁺ adsorbed on Mn oxide was investigated by varying the Pb loading and investigating the structure of the adsorbed complex with EXAFS spectroscopy. The experiments were carried out on the same birnessite sample with loading different amounts of Pb²⁺ adsorbed and on the birnessites with different Mn AOS loading maximum amount of Pb²⁺ adsorbed.

2. Materials and methods

2.1. Water and chemicals

Water used in the experiments was deionized and subsequently distilled. All chemicals were of analytical grade.

2.2. Preparation of the birnessite samples

Birnessites were synthesized in acidic medium, according to the method described by McKenzie [11] and Feng et al. [5]. Birnessites designated HB1, HB2 and HB3, were prepared using, respectively 45.0, 53.3 and 66.7 mL aliquots of 6 mol/L HCl added dropwisely at a speed of 0.7 mL/min to a boiling solution of 0.2 mol KMnO₄ in 45.0, 53.3 and 66.7 mL aliquots of 6 mol/L HCl added dropwisely designated HB1, HB2 and HB3, were prepared using, respectively octahedra, Mn(III)O₆ octahedra and vacant Mn octahedral sites [6]. Many studies have indicated that the birnessite structural vacancies account for the negative layer charges [14–20], that they are associated with adsorption of heavy metals [16–18], with oxidation of Co²⁺ and Cr³⁺ [14,21] and with structural rearrangements of birnessite [9,22,23]. Based on X-ray diffraction measurement, Lanson et al. [24] concluded that around 75% of adsorbed Pb ions on birnessite were located either above or below the vacant Mn sites. These Pb ions shared three layer-oxygen atoms with three layer-Mn atoms, thereby forming tridentate corner-sharing (TC) interlayer complexes. The rest of the adsorbed Pb ions were located above or below the empty tridentate cavities, sharing three edges with neighbouring MnO₆ in the layer, thereby forming a tridentate edge-sharing (TE) interlayer complexes, as in quenselite. Villalobos et al. [25] also found that a portion of Pb ions formed double-corner-sharing complexes at particle edges of birnessite.

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The AOS was measured using the oxalic acid-permanganate back-titration method [27]. The measurements were performed in triplicate and averaged.

2.4. Lead adsorption experiments

The Pb²⁺ adsorption experiments to birnessite were made at 25 °C. First 5 g/L HB suspensions at pH 5.00 were prepared. The pH of the suspensions was adjusted by addition of 0.1 mol/L HNO₃ or 0.1 mol/L NaOH under stirring until the pH value was stable at pH 5.00 ± 0.05. Then, 40 mL of HB suspension was mixed with 80 mL of Pb(NO₃)₂ solution in 0.15 mol/L NaNO₃ in a 150 mL triangle bottle (solid content 1.67 g/L; ionic strength 0.1 mol/L), after capping the bottles were stirred magnetically. To reach the adsorption saturation a Pb(NO₃)₂ concentration of 4.5 mmol/L was applied for the samples HB1, HB2 and HB3. For sample HB2 also an experiment with 1.0 mmol/L Pb(NO₃)₂ was carried out. The pH of the reaction system was maintained at 5.00 ± 0.05 by regular addition (every hour) of 0.1 mol/L NaOH or HNO₃ using a pH-stat technique. After 24 h reaction time the triangle bottles were centrifuged at 14,000 rpm for 10 min in a J2-MC Super-speed refrigerated centrifuge (Beckman, USA). The supernatants were collected and analyzed for the final Pb²⁺ concentration using an atomic absorption spectrometer (Varian AAS 240FS, Australia). The amounts of Pb²⁺ adsorbed were obtained from the difference between the initial amount and the final amount of Pb²⁺ in solution. Under the given conditions the partial CO₂ pressure in the air was not big enough to form PbCO₃ precipitates (chemical speciation calculation).

The precipitates of the centrifugation were washed with pure water for three times to remove free Pb²⁺ ions and the samples designated HB1Pb, HB2Pb, HB3Pb and HB2Pb low were preserved in the capped tubes at low temperature for the XAFS measurements.

2.5. XAFS data collection and analysis

PbO (orthorhombic, analytical solid reagent) and 0.1 mmol/L Pb(NO₃)₂ at pH 3.0 were used as model compounds. XAFS spectra were collected at the 4W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). The storage ring was operated at 2.2 GeV with a beam current of 80 mA. A Si(1 1 1) double crystal monochromator was used to provide an energy resolution of 1.5 eV. To suppress the unwanted harmonics, the monochromatic crystal faces were adjusted through reducing the incident beam by 30%. The incident and output beam intensities were recorded using ionization chambers filled with nitrogen gas and a 50% argon-doped nitrogen mixture, respectively. All adsorption samples were recorded at the Pb L₃-edge (E = 13035 eV).

Spectra for PbO (orthoro) powder and HB1Pb, HB2Pb, HB3Pb and HB2Pb low samples were collected with transmission mode because of their high Pb content. Spectra for the reference compound of Pb²⁺ (aq) solution and the HB2Pb low sample were measured in fluorescence mode due to their low Pb content. All spectra were measured at room temperature.

Two scans (minimum) were collected per sample with the following scan settings: −200 to −20 eV (relative to the Pb edge) in 4 eV steps and 1 s count time; −20 to 50 in 0.5 eV steps at 1 s count time; 50–200 eV in 2 eV steps at 1 s count time; 200–400 eV in 3 eV steps at 1 s count time; 400–500 eV in 4 eV steps at 1 s count time. Data reduction steps were performed using IFEFFIT program [28]. In extracting the χ(k) function, the XAFS signal was isolated from the absorption edge background by using a cubic spline function fit. The k¹-weighted χ(k) function was then Fourier transformed over k = 0.2–1.0 nm⁻¹ to yield the radial structure function (RSF). Data fitting was done in R space with a multishell fit routine and with an amplitude reduction factor (S₀²) fixed at 0.95 derived from PbO (ortho) spectral data fitting by use of the FEFF7 code with
single-scattering paths. The FEFF7 code reference [29] was utilized to calculate single scattering theoretical spectra and phase shifts for Pb–O and Pb–Mn backscatterers using an input file based on a structural model of PbO (ortho) [30], with Pb atoms at 0.354 and 0.373 nm replaced by Mn.

3. Results and discussion

3.1. Characterization of the birnessite samples

Powder XRD patterns indicate that HB1, HB2, and HB3 had four characteristic peaks at 0.721, 0.361, 0.246, and 0.142 nm (Fig. 1). These primary peaks are characteristic of birnessite without any impurities.

3.2. Amount of Pb²⁺ adsorbed on birnessites

For the same amount of Pb²⁺ added the amount of Pb²⁺ adsorbed increased from 2010 to 2438 mmol/kg with the increase of Mn AOS values from 3.83 to 3.92, see Table 1.

3.3. Pb L₃-edge XANES spectra

The Pb L₃-edge XANES spectra (Fig. 2a) are sensitive to the Pb²⁺ 1st-shell coordination environment and can be used to deduce the molecular structure of the Pb²⁺ adsorption complexes on the birnessite surface. Small differences in the degree of distortion and number of 1st-neighbour oxygen atoms around Pb²⁺ give rise to substantial differences in XANES spectra. HB₉₀ sample spectra are distinctly different from the Pb²⁺ (aq) spectrum (Fig. 2a), for which the main-edge is narrower, has greater amplitude, and occurs at lower energy than in the HB₉₀ sample spectra. In addition, in the Pb²⁺ (aq) spectrum occurs a pronounced broad peak at 13,060–13,100 eV, which is not present in the HB₉₀ sample XANES spectra. These spectral differences suggest that the molecular structures of Pb²⁺ adsorbed on birnessites are different from Pb²⁺ bound to water molecules; Pb²⁺ is likely adsorbed on birnessites by means of chemical bonds with oxygen atoms on the surface of birnessite besides electrostatic interaction. HB₉₀ sample spectra are also distinctly different from the PbO (ortho) spectrum (Fig. 2a), for which the main-edge feature is narrower, has greater amplitude, and occurs at higher energy than in the HB₉₀ sample spectra. In addition, there is a pronounced shoulder peak at 13,080–13,120 eV, which has less amplitude in the HB₉₀ sample XANES spectra. These spectral differences suggest that the molecular structures of Pb²⁺ ions adsorbed on birnessites are different from that in PbO (ortho): distorted tetragonal pyramids with oxygen atoms as ligands.

The profile and the energy of the absorption edge of the HB₉₀ sample spectra (Fig. 2a) are similar to the Pb₄(OH)₄⁴⁺(aq) spectrum (Fig. 2b) taken from the literature [31], despite the fact that Bargar used a higher standard energy of the Pb L₃-edge: 13055 eV compared to 13035 eV in the present experiments. This suggests that the 1st-shell coordination environment of Pb²⁺ in the HB₉₀ samples will be similar to that in Pb₄(OH)₄⁴⁺(aq): distorted trigonal pyramids with hydroxide ions as ligands. Therefore, adsorbed Pb ions on birnessite shared three layer-oxygen atoms with three layer-Mn atoms, thereby forming tridentate corner-sharing (TC) interlayer complexes, which is consistent with earlier results reported by Manceau et al. [16].

In the light of the discussion by Bargar et al. [31], a weak shoulder at ≈13027 eV in some of the Pb-L₃ edge spectra shown in Fig. 2a can be assigned to a 2p → 6s electronic transition, and the main absorption edge at ≈13035 eV can be assigned to a 2p → 6d electronic transition. This can further be illustrated by considering the 1st derivative of the XANES spectra (Fig. 3). The energy difference between the Pb 6s and Pb 6d levels in the Pb²⁺ compounds corresponds according to Bargar et al. [31] to the energy separation

![Fig. 1. Powder XRD patterns of three birnessites with different Mn AOS.](image1)

![Fig. 2. Pb L₃-edge XANES spectra of the samples and three reference materials. The spectra in panel (a) are measured in this study; the spectrum in panel (b) is taken Bargar et al. [31].](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>AOS</th>
<th>Pb²⁺ added (mmol/L)</th>
<th>Pb²⁺ adsorbed (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB₁₉₀₀</td>
<td>3.91</td>
<td>1.0</td>
<td>600</td>
</tr>
<tr>
<td>HB₂₉₀₀</td>
<td>3.91</td>
<td>4.5</td>
<td>2438</td>
</tr>
<tr>
<td>HB₃₉₀₀</td>
<td>3.83</td>
<td>4.5</td>
<td>2344</td>
</tr>
<tr>
<td>HB₁₉₀₀</td>
<td>3.91</td>
<td>4.5</td>
<td>2010</td>
</tr>
</tbody>
</table>
3.4. Pb L3-edge EXAFS spectra

Between the 2p → 6s and 2p → 6d peaks in the 1st-derivative spectrum. If the Pb–O bond lengths or O–Pb–O angles differ slightly among adsorption or solution complexes, then their Pb 6s–6p splittings should also differ, which will cause the 2p → 6s transition feature to become broadened or even disappearing [31]. Accordingly, the weak and broadened 2p → 6s peaks in some of the spectra may account for the distortion of the Pb2+ coordination environments.

**Fig. 3.** Normalized first derivative of the XANES spectra of two reference materials and the samples.

**Fig. 4.** Pb L3-edge EXAFS oscillation function χ(k) of the samples and two reference materials.
These Pb$^{2+}$ ions are located above and/or below the center, C, of a vacant Mn structural site and coordinated with the triangle of the three closest O atoms (Fig. 6). The distance Pb–Oa is 0.227 nm (EXAFS data analysis). The separation distance between two oxygen atoms in a layer in the idealized hexagonal layer structure of birnessite is $d(O–O) = d(Mn–Mn) = d(Mn–C) = 0.288$ nm [13]. The distance from the center C of the triangle $O_aO_bO_c$ to $O_a$ equals 0.166 nm \( \sqrt{\left(0.288/2\right)^2 + \left[0.288/2 \times (\sqrt{3}/3)\right]^2} = 0.166 \) nm.

Now the elevation of Pb$^{2+}$ above the O layer can be calculated: 
\[
\text{elevation of Pb above O layer} = \sqrt{(0.227)^2 - (0.166)^2} = 0.155 \text{ nm}
\]

Using the C–Oa distance and Pb–Oa distance (0.166 nm) and the thickness of the Mn layer (0.2 nm) [16], the Pb–C distance (0.155 nm) (Fig. 6) and the thickness of the Mn layer ($d(Mn–C) = 0.288$ nm), the Pb–G1 distance is 0.155 + 0.2 = 0.355 nm calculated from the elevation of Pb$^{2+}$ above the O layer and have the thickness of the Mn layer (0.2 nm) [16].

The distance of Pb–Mna, calculated from the elevation of Pb above the O layer and have the thickness of the Mn layer (0.2 nm), is $\sqrt{(0.255)^2 + (0.288)^2} = 0.385$ nm. To reconcile the calculated Pb–O and Pb–Mn distances found in our simulations of the trigonal corner sharing complex (Fig. 6) with the measured values (Table 2), it is necessary to move the corner oxygen atoms a small distance away from the 3-fold axis of the vacant Mn structural site (dilation of the vacancy hole) as occurs in chalcophanite, or into the sheet, along the (short) shared edges [25]. A similar shift along the shared edges was also suggested by Manceau et al. [16] for Zn-birnessite, and is commonly observed in dioctahedral layer structures [33]. In our model, moving the oxygen atoms 0.008 nm along the edges allows a shortening of the Pb–Mn distance from 0.385 nm to the 0.377 nm obtained from the EXAFS simulations. It is the backscattering of the six Mn atoms that contributes to the amplitude of the Mn shell composed of the 6.1 Mn at 0.377 nm.

\[ \text{In the best fit, } R^2 = 0.92. \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb–O1</th>
<th>Pb–Mn2</th>
<th>Pb–Mn3</th>
<th>Pb–O4</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$ (nm)</td>
<td>$N$</td>
<td>$\sigma^2$</td>
<td>$R$ (nm)</td>
<td>$N$</td>
</tr>
<tr>
<td>HB1m</td>
<td>0.229</td>
<td>1.4</td>
<td>0.018</td>
<td>0.360</td>
<td>0.9</td>
</tr>
<tr>
<td>HB2m</td>
<td>0.226</td>
<td>1.2</td>
<td>0.006</td>
<td>0.356</td>
<td>1.0</td>
</tr>
<tr>
<td>HB3m</td>
<td>0.227</td>
<td>2.7</td>
<td>0.019</td>
<td>0.357</td>
<td>1.7</td>
</tr>
<tr>
<td>HB2pm low</td>
<td>0.227</td>
<td>3.1</td>
<td>0.014</td>
<td>0.357</td>
<td>2.8</td>
</tr>
<tr>
<td>SEM</td>
<td>0.226</td>
<td>4.3</td>
<td>0.023</td>
<td>0.357</td>
<td>1.0</td>
</tr>
<tr>
<td>HRTEM</td>
<td>0.253</td>
<td>8.2</td>
<td>0.028</td>
<td>0.357</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$\sigma^2$ is Debye–Waller factor, $R_f$ is the figure of merit of the spectral fit.
In order to quantify the relative stability of the bonding arrangements of surface oxygen atoms with Pb^{2+}, Pauling’s electrostatic valence principle can be used: the sum of the bond valences around a given ion in the crystal structure equals the absolute value of its charge or it is very near to this value. Furthermore, the bonding configurations for metal ions (M^{z+}) bound to surface oxygen atoms on oxides are plausible when the sum of the M–O bond valences is less than 2.16 \[31\]. The likely configurations for Pb complexes predicted by Villaloobos et al.\[13\] at the possible sites are:

1. (Mn_2–O)_3Pb^0 as in the triple-corner-sharing complex deduced from EXAFS; the sum of Pb–O bond valence is 1.97–2.09. This complex is discussed above.
2. Mn_2–O–PbOH^{1/3} a monodentate complex at doubly coordinated oxygen atoms; the sum of Pb–O bond valence is 1.97–2.09.
3. (Mn–OH)_2PbOH^{1/3} a bidentate complex as in the double-corner-sharing complex from EXAFS; the sum of Pb–O bond valence is 1.98–2.10.

The Pb–Mn distance of 0.353 nm for the double-corner-sharing complex at particle edges is crystallographically possible by placing the Pb atom in an intermediate alignment between the center of the cavity and the plane of the sheet structure formed by the two bound oxygen atoms (Fig. 8a). Therefore, (Mn–OH)_2PbOH^{1/3} is a likely configuration for a Pb complex.

There are also about three Mn atoms in Pb–Mn shell located at a distance of 0.357 nm from Pb for the single-corner-sharing complex (Fig. 8b): therefore Mn_2–O–PbOH^{1/3} is also a likely configuration for a Pb complex besides (Mn–OH)_2PbOH^{1/3}.

The amount of Pb^{2+} adsorbed on the HB2Pb low is significantly more than that on HB2Pb low. The Pb^{2+} coordination environment in HB2Pb low (surface saturation with Pb) is distorted due to the electrostatic repulsion and the steric hinderence between adsorbed Pb^{2+} ions, therefore the coordination numbers are decreased (Table 2). The amount of vacant Mn structural sites increases with the Mn AOS of birnessite and largely determines the amount of Pb^{2+} adsorbed \[36\]. Therefore, for HB1Pb low, HB2Pb low, and HB3Pb low, the amount of adsorbed Pb^{2+} increased (same amount of Pb^{2+} added) according to the order of the Mn AOS values. In HB1Pb low and HB2Pb low the content of vacant Mn structural sites is large and the Pb adsorption is high. This will lead to a strong electrostatic repulsion between adsorbed Pb^{2+} ions. In this case the degree of distortion of the Pb^{2+} coordination geometry becomes so large that the coordination number is significantly lower than in HB2Pb low and HB3Pb low.

4. Conclusions

Two Pb–O and two Pb–Mn shells were detected by XAFS in the birnessites with Pb loading. For the same birnessite, at low loading (600 mmol/kg), Pb–O coordination numbers in the two Pb–O shells were 3.1 at 0.227 nm, and 8.2 at 0.399 nm and Pb–Mn coordination numbers in the two Pb–Mn shells were 2.8 at 0.357 nm, and 6.1 at 0.377 nm. At high Pb^{2+} loading (2344 mmol/kg), Pb–O coordination numbers in the two Pb–O shell decreased to 1.2 at 0.226 nm, and 3.0 at 0.397 nm, respectively, and Pb–Mn coordination numbers in the two Pb–Mn shells decreased to 1.0 at 0.356 nm, and 2.8 at 0.375 nm, respectively, due to the distortion of the Pb^{2+} coordination environment by other adsorbed Pb^{2+} ions. For birnessites with different Mn AOS, the amount of Pb^{2+} adsorbed increased in the same order as the Mn AOS values when the same amount of Pb^{2+} was added. With high adsorption values, the degree of distortion of the ideal Pb^{2+} coordination geometry is relatively large and the decrease in coordination number is relatively large. Independent of the AOS of a birnessite the same three bonding mechanisms for adsorbed Pb^{2+} have been proposed: a single-corner-sharing complex on particle edges along u axis, a double-corner-sharing complex on particle edges along a or b axis, and a triple-corner-sharing complex in the interlayer above or below vacant sites.

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