Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Wei Zhao [a,b], Wenfeng Tan [a,b], Xionghan Feng [a,*], Fan Liu [a], Yaning Xie [c], Zhi Xie [d]

[a] Key Laboratory of Subtropical Agriculture Resource & Environment, Ministry of Agriculture of China, Huazhong Agricultural University, Wuhan 430070, China
[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
[c] Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China
[d] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

ARTICLE INFO

ABSTRACT

The adsorption of Pb^{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 lead 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^{2+} coordination environment with increased loading of Pb. The amount of Pb^{2+} adsorbed increased with increasing values of the average oxidation state (AOS) of birnessite, also in this case the distortion of the Pb^{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^{2+} adsorbed on the birnessites with different Mn AOS were proposed: a single-corner-sharing complex on particle edges along the *u* axis of MnO_6 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.

© 2010 Published by Elsevier B.V.

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^{2+}. Understanding the mechanism of Pb^{2+} adsorption on birnessite, is important for an accurate thermodynamic and kinetic description of Pb^{2+} transport in the environment.

The basic building blocks of Mn oxides are the MnO_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 $H_aK_b^+H_2O_cMn_{tc}^{2+,3+}[(Mn_d^{3+}, Mn_e^{4+}), \Pi_f]O_2$, 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 (Π) in the layer (enclosed in square brackets, except for the O atoms) [7,8]. The MnO_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_6

octahedra, Mn(III)O_6 octahedra and vacant Mn octahedral sites [13]. Some Mn^{2+} and Mn^{3+} 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 Co^{2+} and Cr^{3+} [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 MnO_6 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 Pb^{2+} adsorbed on birnessites have been studied [24,25], there is little knowledge on how the binding mechanism varies with the amount of Pb^{2+} 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 Pb^{2+} 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 Pb^{2+} adsorbed and on the birnessites with different Mn AOS loading maximum amount of Pb^{2+} 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 $KMnO_4$ in 300–400 mL of pure water. Vigorous stirring was used during the reaction. After further boiling for 30 min, the products were aged for 12 h at 60 °C in the reaction solution in order to achieve good degree of crystallinity. After aging the birnessite samples were purified by electro dialysis at a voltage of 150–220 V until the supernatant conductivities were <20 μS/cm and then the samples were dried at 40 °C and stored in air-tight bottles.

2.3. Characterization of the birnessite samples

X-ray diffraction (XRD) analyses were performed using a D/Max-3B diffractometer (Rigaku, Japan) using monochromatic Fe Kα radiation (λ = 0.19373 nm). The diffractometer was operated at a tube voltage of 40 kV and a tube current of 20 mA. Intensities were measured at 2θ = 10–90° using an interval of 2θ = 0.02° and a 0.2 s counting time per step.

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 Pb^{2+} 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 HNO_3 or 0.1 mol/L NaOH under stirring until the pH value was stabile at pH 5.00 ± 0.05. Then, 40 mL of HB suspension was mixed with 80 mL of $Pb(NO_3)_2$ solution in 0.15 mol/L $NaNO_3$ 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 $Pb(NO_3)_2$ 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 $Pb(NO_3)_2$ 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 HNO_3 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 Pb^{2+} concentration using an atomic absorption spectrometer (Varian AAS 240FS, Austrilia). The amounts of Pb^{2+} adsorbed were obtained from the difference between the initial amount and the final amount of Pb in solution. Under the given conditions the partial CO_2 pressure in the air was not big enough to form $PbCO_3$ precipitates (chemical speciation calculation).

The precipitates of the centrifugation were washed with pure water for three times to remove free Pb^{2+} ions and the samples designated $HB1_{Pb}$, $HB2_{Pb}$, $HB3_{Pb}$ and $HB2_{Pb\ low}$ 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 $Pb(NO_3)_2$ 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 L_3-edge (E = 13035 eV).

Spectra for PbO (ortho) powder and $HB1_{Pb}$, $HB2_{Pb}$, $HB3_{Pb}$ samples were collected with transmission mode because of their high Pb content. Spectra for the reference compound of Pb^{2+} (aq) solution and the $HB2_{Pb\ low}$ sample were measured in fluorescence mode due to their low Pb content. All presented 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 $\chi(k)$ function, the XAFS signal was isolated from the absorption edge background by using a cubic spline function fit. The k^1-weighted $\chi(k)$ 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 (S_0^2) fixed at 0.95 derived from PbO (ortho) spectral data fitting by use of the FEFF7 code with