RELATIONSHIP BETWEEN Pb$^{2+}$ ADSORPTION AND AVERAGE Mn OXIDATION STATE IN SYNTHETIC BIRNESSITES

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Abstract—The relationship between vacant Mn structural sites in birnessites and heavy-metal adsorption is a current and important research topic. In this study, two series of birnessites with different average oxidation states (AOS) of Mn were synthesized. One birnessite series was prepared in acidic media (49.6–53.6 wt.% Mn) and the other in alkaline media (50.0–56.2 wt.% Mn). Correlations between the Pb$^{2+}$ adsorption capacity and the $d_{110}$ interlayer spacing, the AOS by titration, and the release of Mn$^{2+}$, H$^+$, and K$^+$ during adsorption of Pb$^{2+}$ were investigated. The maximum Pb$^{2+}$ adsorption by the birnessites synthesized in acidic media ranged from 1320 to 2457 mmol/kg with AOS values that ranged from 3.67 to 3.92. For birnessites synthesized in alkaline media, the maximum Pb$^{2+}$ adsorption ranged from 524 to 1814 mmol/kg, with AOS values between 3.49 and 3.89. Birnessite AOS values and Pb$^{2+}$ adsorption increased as the Mn content decreased. The maximum Pb$^{2+}$ adsorption to the synthetic birnessites calculated from a Langmuir fit of the Pb adsorption data was linearly related to AOS. Birnessite AOS values apparently reflect the quantity of vacant sites which largely account for Pb$^{2+}$ adsorption. Therefore, the Pb$^{2+}$ adsorption capacity of birnessite is mostly determined by the Mn site vacancies, from which Mn$^{2+}$, H$^+$, and K$^+$ released during adsorption were derived.

Key Words—Adsorption, Birnessite, Mn Average Oxidation State, Pb$^{2+}$, Vacant Mn Structural Site.

INTRODUCTION

Lead is an environmental heavy metal that has always attracted much attention. Examination of the mechanisms that determine Pb and soil-component interactions is crucial to understanding the fate of Pb in soils, sediments, and water. A greater understanding of Pb interaction mechanisms could also help in water purification and in remediation efforts in Pb-contaminated soil (Matocha et al., 2001).

Manganese oxides are extensively distributed in soils, sediments, and ocean Mn nodules. Manganese oxides commonly have a low point of zero charge, large surface area, large negative charge, and are very active in various chemical reactions; they are also considered to be important adsorbents of Pb (McKenzie, 1980; O’Reilly and Hochella, 2003; Post, 1999). The phyllosilicate mineral, birnessite, is the most common type of manganese oxide in soils. Many Mn oxides can be synthesized by direct or indirect transformation of birnessite (Golden et al., 1987; Tu et al., 1994). Birnessites are usually synthesized in acidic or alkaline media using one of two approaches. Firstly, birnessites can be synthesized by the reduction of KMnO$_4$ in a strongly acidic medium (McKenzie, 1971). The resulting birnessite has hexagonal layer symmetry with layers consisting of edge-sharing Mn(IV)O$_6$ octahedra, Mn(III)O$_6$ octahedra, and vacant Mn octahedral sites (Villalobos et al., 2006). Some Mn$^{2+}$ and Mn$^{3+}$ are located above or below vacant Mn octahedral sites in birnessites (Webb et al., 2005). The number of vacant Mn octahedral sites can reach up to 12% (Villalobos et al., 2006). Secondly, birnessites can be synthesized by the oxidation of manganese hydroxide in a strong alkaline medium (Luo and Suib, 1997; Villalobos et al., 2003; Feng et al., 2004). In the structure of this synthetic birnessite, Mn$^{3+}$-rich rows parallel to the $b$ axis are separated from one another along the $a$ axis by two Mn$^{4+}$ rows (Drits et al., 1997; Lanson et al., 2002a). The amount of vacant Mn octahedral sites can reach up to 5% (Manceau et al., 2002; Post and Veblen, 1990). Birnessite structural vacancies account for a negative layer charge and relate to the adsorption of Pb, Zn, Cu, Cd, and Ni, to the oxidation of Co$^{2+}$ and Cr$^{3+}$, and to the transformation of minerals (Appelo and Postma, 1999; Burns, 1976; Lanson et al., 2002b; Manceau and Charlet, 1992; Peacock and Sherman, 2007; Villalobos et al., 2006). Surface-adsorbed Pb on birnessite was octahedrally coordinated and ~75% of the Pb was located either above or below vacant Mn sites. The rest of the Pb was located above or below empty tridentate cavities, sharing three edges with neighboring MnO$_6$ in the layer (Lanson et al., 2002b). A proportion of the Pb forms double-corner-sharing complexes at particle edges of birnessite (Villalobos et al., 2005).

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