Use of X-ray Absorption Spectroscopy to Distinguish Between Inner and Outer-sphere Pb Adsorption Complexes on Montmorillonite

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Adsorption behavior of Pb on montmorillonite as a function of pH was highly dependent on ionic strength. At $I = 0.1 \, M$ the removal of Pb from solution increased from ~40% to ~80% at pH = 6 and pH = 7, respectively. This pH dependent behavior suggests inner-sphere complexation on the functional groups at the edges of the montmorillonite. At $I = 0.002 \, M$ Pb absorption was less dependent on solution pH, with ~97% removed from solution at pH = 4 and nearly 99% removed from solution at pH = 7. The lack of pH dependence at $I = 0.002 \, M$ suggests that adsorption is primarily via an outer-sphere mechanism. The XANES spectrum of Pb sorbed on montmorillonite at pH = 4.40 ($I = 0.002 \, M$) was similar to the XANES spectrum of a Pb$^{2+}$ (aq) sample, suggesting that the adsorbed Pb is coordinated by water molecules. At pH = 6.40 ($I = 0.002 \, M$ and $I = 0.1 \, M$) the XANES spectra for Pb sorbed on montmorillonite are similar to a Pb solution containing predominantly $[\text{Pb}_4 (\text{OH})_4]^{4+}$ complexes, indicating that sorbed Pb is predominantly coordinated by OH$^{-}$ ligands.