MOLECULAR BINDING MECHANISMS OF AQUEOUS Cd AND Pb TO SIDEROPHORES, BACTERIA AND MINERAL SURFACES

Abstract

by

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Recent studies have shown that diverse groups of bacteria adsorb metals to similar extents and uptake can be modeled using a universal adsorption model. In this study, XAFS has been used to resolve whether binding sites determined for single species systems are responsible for adsorption in more complex natural bacterial assemblages. Results obtained from a series of XAFS experiments on pure Gram positive and Gram negative bacterial strains and consortia of bacteria as a function of pH and Cd loading suggests that every bacterial strain has a complex physiology and they are all slightly different from each other. Nevertheless from the metal adsorption chemistry point of view, the main difference between them lies in the site ratio of three fundamental sites only - carboxyl, phosphoryl and sulfide. Two completely different consortia of bacteria (obtained from natural river water, and soil system with severe organic contamination) were successfully modeled in the pH range 3.4 – 7.8 using the EXAFS models developed for single species systems. Results thus obtained can potentially have very high impact on the modeling of the complex bacterial systems in realistic geological settings, leading to further refinement and development of robust remediation strategies for metal contamination at macroscopic level.
In another study, solution speciation of Pb and Cd with DFO-B has been examined using a combination of techniques (ICP, TOC, thermodynamic modeling and XAFS). Results indicate that Pb does not complex with DFO-B at all until about pH 3.5, but forms a totally caged structure at pH 7.5. At intermediate pH conditions, mixture of species (one and two hydroxamate groups complexed) is formed. Cd on the other hand, does not complex until pH 5, forms intermediate complexes at pH 8 and is totally chelated at pH 9.

Further studies were conducted for Pb sorption to mineral surface kaolinite with and without DFO-B. In the absence of DFO-B, results suggest outer sphere and inner sphere sorption of Pb on kaolinite surface at acidic and circumneutral pH conditions respectively. In the presence of DFO-B, bulk sorption studies indicated that Pb sorption is enhanced in the presence of DFO-B around pH 6 and inhibited above pH 6.5. This was confirmed by x-ray fluorescence measurements. Extended XAFS study clearly indicated unwrapping of DFO-B molecule at the surface. Our study has unambiguously recognized it as a ”Type A” ternary complex (”Type A” complex means surface-metal-ligand type of interaction). Taken together, bulk adsorption measurements and XAFS experiments represent a powerful approach for determining and modeling metal speciation and adsorption.