

THE SORPTION MECHANISMS OF METAL IONS (CADMIUM AND LEAD)  
TO BACTERIAL BIOMASS, SIDEROPHORES AND MINERALS

Abstract

by

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Metal pollution has a negative, even fatal, impact to the environment and human health. Developing better remediation strategies has long been a challenge. The fate of heavy metals in the environment is determined by the surrounding substances, surface and interfaces. Because of the abundance of bacterial biomass, minerals and natural organic matter (*e.g.* siderophores), they play a critical role in the fate of metals in the environments and in the contaminated sites. It is essential to understand the processes and mechanisms of interaction between them at both macroscopic and microscopic scales. The work presented in this dissertation used a synchrotron based technique, X-ray absorption fine structure (XAFS), to obtain information on molecular-scale structure knowledge of metals in different conditions.

Most bacteria live in the community form, biofilms, instead of the planktonic (free-swimming) form. Biofilms are complex communities of bacteria enclosed in an extracellular polymeric substance (EPS) matrix which is composed of extracellular polysaccharide, proteins and DNA secreted by bacteria. EPS is the dominant

component of the total organic matter in a biofilm. Since both cell walls (of Gram-negative and Gram-positive bacteria) and EPS are negative charged and have functional groups that can bind metals at most pH values, they are capable of adsorbing metals in the solutions. Therefore to quantify the capacity and mechanism of metal sorption by bacterial biomass is essential to understand the fate of metals in the environment. The comparison of sorption capacities and mechanisms between planktonic and biofilm biomass has a critical impact on the modeling of metals' fate at different conditions. Metal (cadmium) sorption experiments were conducted for both planktonic and biofilm biomass. The sorption capacities and mechanisms were compared for both biomass. Comparable metal sorption capacities and similar behaviors were found for both planktonic and biofilm biomass when pH and metal concentrations changed in the solutions. The surrounding structural information obtained from the XAFS measurements and analysis revealed that the same binding sites were occupied for both biomass with slightly different component ratios, which supported the sorption behavior observed in the bulk experiment.

Siderophores are low molecular weight organic ligands that are exuded by aerobic microorganisms and graminaceous plants to acquire Fe(III) from the environment. Besides their significant binding capacity of Fe(III) with reaction constants  $10^{25}$  -  $10^{50}$ , they can also bind other metals such as Al, Cd, Pb, etc. Minerals, especially the swelling clays, can sorb significantly both metals and siderophores. Therefore the fate of metals is determined by the complex interactions among metals, siderophores and minerals. Lead interactions with siderophores (Desferroxamine B, DFO-B) and swelling clays (montmorillonite, MMT) were investigated by XAFS measurements.

The chelation of lead by DFO-B increases with increasing pH. At pH less than 3, there is no chelation between lead and DFO-B. At pH greater than 7.5, lead ions are completely chelated by DFO-B as a hexadentate complex. In the absence of DFO-B, it is observed that hydrocerussite precipitation is the dominant lead sorption mechanism by MMT at high pH (7.5). At the lower pH (4.0 and 5.5), there was no precipitate observed, and the outer-sphere complex dominates. When the pH value increases from 4.0 to 5.5, the number of outer-sphere sites decreases and inner-sphere sites increases. The addition of DFO-B increases the lead sorption of MMT for the low pH samples. There was no precipitate observed in the presence of DFO-B at any of the pH values. DFO-B chelation, along with inner-sphere and outer-sphere complex, contributes to lead sorption to MMT at all pH values.