Comparative study: Metal adsorption onto *Bacillus subtilis* and Fe-oxidizing *Leptothrix cholodnii* SP-6SL bacterial cells

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Fe-oxidizing bacteria (FeOB) form bacteriogenic iron oxides (BIOS) as a result of iron oxidation. These minerals occur as nanoparticles or mineral coatings, and have highly reactive surfaces, which may affect contaminant fate and transport through adsorption reactions. Although the mechanisms governing the formation of BIOS particles are widely studied, there is little consensus on the mechanism(s) and kinetics controlling bacterial iron oxidation in general. Adsorption of ferrous iron cations onto bacterial cell walls may represent the rate-controlling step for biotically induced ferrous oxidation, but there are no studies that quantify either the extent of Fe^{+2} adsorption onto bacterial cells or the thermodynamic stabilities of the important Fe(II)-bacterial complexes.

In this study, we took a two pronged approach: 1) experiments were conducted to measure Fe adsorption onto a sheathless variant of FeOB *Leptothrix cholodnii* SP-6SL cells directly, and 2) adsorption experiments were performed using a range of metals onto both *L. cholodnii* and *B. subtilis* in order to determine if both bacterial surfaces interact with metals similarly. Linear free-energy relationships using stability constant values for aqueous metal-anion complexes were first proposed in an effort to supplement thermodynamic data. We apply a linear free-energy approach to estimate Fe^{+2} binding constants with sites on *L. cholodnii* and *B. subtilis* cells, deriving a relationship between metal binding constants involving the cell surface and those involving acetate. In order to calibrate this relationship, we measured Sr^{+2}, Zn^{+2}, Cd^{+2}, Ni^{+2}, Cu^{+2}, Fe^{+2}, and Pb^{+2} adsorption onto both bacterial species. The experiments for both species were performed aerobically for all metals except Fe, which was conducted under a nitrogen/hydrogen atmosphere; ionic strength was held constant with 0.1 M $NaClO_4$; experiments were conducted as a function of pH over the range of 2 to 11, and biomass and metal concentrations were held at 10 g/L and 2 ppm, respectively. Non-adsorbed Sr, Zn, Cd, Ni, Cu, and Pb concentrations were analyzed using ICP-OES, with non-adsorbed Fe concentrations determined via GFAA.

We observed enhanced removal of all metals under all pH conditions relative to abiotic controls. The adsorption measurements conducted as a function of pH constrain which cell envelope functional groups are involved in metal binding, and we used the adsorption measurements to determine equilibrium constants for the important adsorption reactions. The thermodynamic parameters determined here not only improve quantitative models of Fe(II) distribution and speciation in geologic systems, but they also can be used to construct quantitative models of Fe(II) bioavailability in bacteria-bearing systems as well, allowing the effects of competing cations and complexing ligands to be accounted for in each model.