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Cu(II) adsorption onto ammonia-oxidizing bacteria and archaea

DREW GORMAN-LEWIS[1], WILLM MARTENS-HABBENA[2] AND DAVID A STAHL[1]

[1]University of Washington
[2]University of Florida / IFAS
Presenting Author: dgormanl@uw.edu

Copper plays an important role in the first step of nitrification during the aerobic oxidation of ammonia to nitrite. The enzyme that catalyzes ammonia oxidation to hydroxylamine, ammonia monooxygenase, requires Cu(II) as an essential cofactor in ammonia-oxidizing archaea and bacteria. Cu(II) also plays a role in shuttling electrons in ammonia-oxidizing archaea. In the environment, Cu (II) can easily form complexes with organic matter in soil pore water, freshwater, and seawater, limiting the amount of bioaccessible free Cu2+. Therefore, the acquisition of copper is a critical step for the metabolic functioning of ammonia-oxidizing archaea and bacteria. In this work, we describe the adsorption of Cu(II) onto the bacterial species *Nitrosococcus oceani* C-107 (*N. oceani*) and *Nitrosomonas europaea* C-31 (*N. europaea*) and the archaeal species *Nitrosopumilus maritimus* SCM1 (N. maritimus). We used surface complexation modeling and isothermal titration calorimetry to quantify the Cu(II) adsorption reactions. The results of the modeling indicated that Cu(II) adsorption onto bacterial species could be described with one reaction, while *N. maritimus* required two reactions to adequately describe adsorption. Copper adsorption enthalpies derived from isothermal titration calorimetry combined with surface complexation modeling revealed slightly exothermic enthalpies for *N. maritimus* and thermoneutral to endothermic enthalpies for bacterial species. Entropies of copper adsorption were positive and indicative of entropy-driven inner-sphere complexation reactions. Thermodynamic parameters describing the adsorption of copper onto *N. maritimus* are consistent with those describing the adsorption onto a mixture of phosphorous-bearing anionic oxygen and reduced sulfur ligands. Thermodynamic parameters describing Cu(II) adsorption onto *N. oceani* and *N. europaea* were consistent with Cu(II) adsorption onto phosphorous-bearing anionic oxygen ligands. The surface complexation models derived in this work can be used to predict Cu(II) partitioning in theoretical systems to better understand the selectivity of ammonia-oxidizing archaea and bacteria cell surfaces for Cu(II).