

# Effects of aggregation, ligand complexation and time on metal adsorption/retention to iron oxyhydroxide nanoparticles

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Nanoscale iron oxyhydroxides, which are commonly found in surface aqueous systems, can act as effective sorbents for dissolved metals due to their chemical reactivity, small size and high surface area which allow them to sequester ions from the aqueous and into the solid phase. However, they also rapidly aggregate under natural geochemical conditions, thus affecting their metal sorption capabilities. The broad range of particle aggregation mechanisms and states possible in the environment, in addition to variations in exposure/reaction time and other environmental factors (such as the increase in salinity associated with the transition from fresh water to seawater), substantially increases the complexity and variety of interactions between metal ions and nanoparticle aggregates.

We have conducted an array of macroscopic batch experiments, kinetic rate measurements, and spectroscopic analyses using synchrotron X-rays to explore Cu(II) and Zn(II) adsorption, desorption, and retention processes associated with aggregated and dispersed iron oxyhydroxide nanoparticles, including: 1) as a function of aggregation state induced by ionic strength (0.001-1.0 M), pH (5.0-10.0), and temperature (25°C-75°C); 2) in real-time (1 hr-5 weeks) using ion selective electrodes; 3) in the presence of chloride (0-0.6 M) and sulfate (0-0.09 M), two common inorganic ligands found in surface waters; and 4) using extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate metal speciation on sorbed/desorbed samples resulting from the prior studies.

Findings include: 1) aggregation state generally reduces initial metal uptake due to lowered surface area but increases metal retention due to inter-particle nanoporosity; 2) exposure time both lowers kinetic desorption rates and increases metal retention; 3) the presence of chloride and sulfate has varying effects that are concentration- and metal-dependent, but in both cases show evidence for the formation of ternary surface complexes; and 4) quantifiable variations in metal speciation at the solution-solid interface reveal dynamic changes in surface complexation that inform our understanding of fundamental sorption/desorption processes and potential applied remediation strategies in contaminated systems.