Abstract

This dissertation utilizes X-ray Absorption Spectroscopy (XAS) to investigate the binding mechanisms of Cd sorbed to iron-oxide mineral hematite (α-Fe₂O₃) nanoparticles and Cr bound to redox active 3, 5-di-tert-butyl-1, 2-quinone-1-(2-oxy-3, 5-di-tert-butylphenyl)imine or “ONO” ligand (Cr(ONO)₂).

Recent studies have shown that iron-oxide mineral structure, stability and reactivity with respect to environmental processes such as sorption (loss of Cd from solution through either adsorption or precipitation) and dissolution may be different when the size of particles is in the nano-sized range. This study investigates the effects of hematite (α-Fe₂O₃) nanoparticle (NP) size (8 nm versus 40 nm) on cadmium (Cd) sorption mechanism(s) using batch sorption experiments coupled with XAS. The extent of sorption (As percent sorbed or surface coverage to NPs) as well as sorption mechanism(s) indicate that as 8 nm and 40 nm NPs have substantially different specific surface areas, the results depend on whether the experiments are run normalized to NP surface area (Surface Area Normalized-SAN) or normalized to NP mass (Mass Normalized-MN) within reaction vessels. Cd sorption has increased to ~100% at pH 9.5 but the sorption edge has shifted to the right for larger NPs. XAS results indicate that at pH 7.5, Cd has adsorbed to 8 nm and 40 nm SAN NPs while more precipitation has been observed on 40 nm MN NPs. At pH 9, adsorption and minor precipitation in 8 nm NPs, a
more balanced mixture of adsorption and precipitation on 40 nm SAN NPs and more precipitation on 40 nm MN NPs have been observed.

In another study, differences between solid state and solution state Cr(ONO)$_2$ have been investigated using XAS. This investigation is part of a broad study of bonding and structure down group VI complexes of the “ONO” ligand. When metal complexes contain redox-active ligands, they are capable of adopting multiple stable oxidation states making it hard to define the oxidation of the central atom. X-ray Absorption Near Edge Structure (XANES) data indicate that Cr is more oxidized in Cr(ONO)$_2$ in the solid state than in solution but does not suggest any integer oxidation state. Extended X-ray Absorption Fine Structure (EXAFS) results indicate that Cr(ONO)$_2$ adopts shorter metal-ligand bond lengths in the solid in agreement with D$_2$ symmetric structure. However, in solution state, it possesses longer metal-ligand bond lengths similar to a D$_2$ symmetric structure with 0.022(±0.004) Å longer Cr-O and 0.066(±0.012) Å longer Cr-N distances than in the solid or a C$_2$ symmetric structure with one ligand at very similar distances as in the solid and the other with average bond elongations of 0.064 (0.008) Å. This result is in complete disagreement with similarities found in solid state and solution state complexes of Molybdenum (Mo) and Tungsten (W) with the “ONO” ligand.