



Organic Ligand Enhanced Cr(VI) Treatment in Pyrite Permeable Reactive Barriers

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Permeable reactive barriers (PRB), installed in subsurface in the path of flowing groundwater can offer a viable option for in situ remediation of Cr(VI)-contaminated subsurface systems. In this study, batch and column experiments were performed to determine the effects of organic ligands (L) on Cr(VI) treatment in PRBs containing pyrite. The organic ligands used include citrate, tartrate, oxalate, EDTA and salicylate. The results indicate that in the absence of organic ligands, the Cr(VI) removal by pyrite occurred only under acidic conditions (e.g., pH > 5). However, organic ligands led to a significant increase in Cr(VI) removal with pyrite depending on the type of organic ligand used, Cr(VI)/LT ratio and water chemistry (e.g., pH). While salicylate had no effect on Cr(VI) removal relative to non-ligand systems, the organic ligands including citrate, tartrate and oxalate significantly improved Cr(VI) removal under acidic to alkaline pH range. On the other hand, EDTA only improved Cr(VI) removal by pyrite under alkaline pH conditions relative to non-ligand conditions. In general, the efficiency of organic ligands on Cr(VI) removal decreased in the order: citrate > tartrate > oxalate > EDTA > salicylate. The X-ray photoelectron spectroscopy (XPS) and zeta potential measurements suggest that the Cr(VI) removal by pyrite occurred due to the reduction of Cr(VI) to Cr(III), coupled with the oxidation of Fe(II) to Fe(III) and disulfide (S₂²⁻) to sulfate (SO₄²⁻) at the pyrite surface as well as in aqueous phase. However, the precipitation of sparingly soluble Fe(III)-Cr(III)(oxy) hydroxide phases on pyrite surface led to surface passivation, which, then, inhibited further Cr(VI) reduction. The addition of organic ligands increased Cr(VI) reduction by pyrite due to: 1) the removal of the surface oxidation products by forming highly soluble Cr(III) and Fe(III)-ligand complexes as well as 2) the ligand promoted dissolution of Fe(II) from pyrite, which, subsequently, reduced Cr(VI) to Cr(III) in aqueous phase.