

Molecular-scale investigation using XAFS and QC for the reductive transformation of Cr(VI) by vivianite

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To obtain fundamental knowledge on oxidation-reduction process of hexavalent chromium (Cr(VI)) coupling with natural materials, especially Fe(II)-bearing minerals, is essential to comprehensively understand and precisely predict Cr(VI) fate in the subsurface. In this study, we have investigated reduction mechanism of aqueous Cr(VI) by vivianite ($\text{Fe}^{\text{II}}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$) in the presence of major competing ions (Ca^{2+} , HCO_3^-) at pH 5 – 9. Different removal kinetics of Cr(VI) by vivianite were observed with respect to the different pHs (pH5: 100% in 1 min.; pH 7: 100% in 12 hr; pH 9: 100% in 24 hr), which is resulted from electrostatic interaction between charged vivianite surface ($\text{PZC}_{\text{vivianite}}: 5.3$) and dominant Cr(VI) species (CrO_4^{2-} , HCrO_4^-) under the pHs. Presence of competing ions influenced the formation of different Cr(VI) species (CaCrO_4 , CrO_4^{2-}), however, did not affect the Cr(VI) removal kinetic by vivianite. Binding energies between Cr(VI) species on the vivianite surface were estimated by Quantum Calculations (Maestro and Cerius 2). The results have shown that Cr and O atom of Cr species are strongly bound with Fe and O atom of vivianite surface, respectively. Regardless of Cr(VI) specie type, Cr(VI) can be removed by vivianite via form of Cr-Fe, Cr-O, and O-Fe bindings. EXAFS analysis results can verify the reaction mechanism by showing the similar binding properties (binding distance and angle) of Cr(VI) with vivianite surface. The molecular scale investigations using XAFS and QC showed that Cr(VI) bound on the vivianite surface was reduced to Cr(III)-oxide by receiving electrons from Fe(II) of vivianite surface.