

Adsorption of sulfate to ferrihydrite: surface complexation modeling and in-situ infrared spectroscopy

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Sulfate, a major anion in nature, can affect the mobility of coexisting dissolved toxic trace elements by influencing the adsorption properties of the species on mineral surfaces. Ferrihydrite is an important scavenger for trace elements in natural water because of its adsorption capacity and its ubiquitous formation in surface conditions. To elucidate the adsorption behavior of the trace elements in natural water, it is important to construct a predictive model of sulfate adsorption on ferrihydrite that can predict the adsorption behavior of sulfate quantitatively under widely various environmental conditions based on the spectroscopic information of sulfate adsorption.

In-situ infrared spectra for sulfate adsorption on ferrihydrite as a function of pH (3-7), ionic strength ($I = 0.01$ and 0.1) and sulfate loading ($[\text{SO}_4^{2-}] = 0.1$ and 0.2 mM) were obtained to constrain the surface speciation of sulfate on ferrihydrite. The shape of the spectra was pH-dependent. The degree of *nu*3 band splitting decreases with pH. Little difference of the spectra was found between different ionic strengths and sulfate loadings for the same pH. The little influence of ionic strength on the IR spectra indicates that the inner sphere and outer sphere species most likely do not exist simultaneously at the same pH condition. Based on the IR spectra obtained from lower pH showing the splitting of *nu*3 band to two peaks with activation of *nu*1 band, the surface species is identified to be single inner sphere monodentate sulfate. The changes of spectra with pH are most likely attributable to the changes of the electric field strength posed to the sulfate on ferrihydrite surface, which is strongly pH-dependent.

The predictive model for sulfate adsorption was constructed using an extended triple layer model (ETLM). The pH adsorption edges and proton surface charges in the presence of sulfate as a function of ionic strength and sulfate concentration were obtained, respectively, from batch adsorption and acid-base titration experiments. The sulfate adsorption on ferrihydrite increases continuously with decreasing pH and ionic strength. These macroscopic adsorption data were analyzed using ETLM to retrieve the sulfate adsorption reaction and the equilibrium constant. Results of ETLM analyses showed that adsorption of sulfate on ferrihydrite is a single monodentate inner sphere process that is consistent with in-situ infrared spectroscopic observation.

Batch adsorption data from earlier studies of sulfates on ferrihydrite were reasonably reproduced using ETLM with the same adsorption reaction and equilibrium constant.

Keywords: ferrihydrite, sulfate, surface complexation modeling, in-situ infrared spectroscopy