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Chromate Coordination on Lepidocrocite Facets Affects its Adsorption Behavior: *in Situ* ATR-FTIR, DFT+U methods and Theoretical Frequency Calculations

XIAOFEI LI, CHULING GUO, ZHI DANG*

School of Environment and Energy, South China University
of Technology, Guangzhou 510006, China
(*correspondence: chzdang@scut.edu.cn)

Chromium widely exists in soil and aquatic systems, and easily absorb on iron oxides. The coordination of chromate on different facets of iron oxides can significantly influence its mobility, reactivity and bioavailability in natural environment, but the relevant adsorption mechanisms remain ambiguous. In this study, macroscopic adsorption experiments combined with in situ ATR-FTIR spectroscopy, the DFT+U methods and theoretical frequency calculations were used to investigate how different chromate coordination on lepidocrocite facets affect its absorption behavior. In situ ATR-FTIR spectroscopy analysis showed the presence of single inner-sphere complexes (C3v symmetry) of chromate on lepidocrocite nanoplates with exposed {010} facet, and while the C3v and C2v species were formed on lepidocrocite nanorods with exposed {010} and {001} facets. Based on the experimental spectroscopy, DFT+U methods combined with theoretical frequency calculations for the typical lepidocrocite {010} and {001} facets model confirmed that monodentate binuclear inner-sphere on {010} facet and monodentate mononuclear and bidentate binuclear on {001} facets, which were further verified by thermodynamics and frequency fitting. The macroscopic adsorption kinetic and isotherms analysis revealed that the lepidocrocite nanorod with high proportion {001}/{010} facets had higher efficiency and capabilities of adsorption than lepidocrocite nanoplates with exposed {010} facet. Therefore, the chromate adsorption behavior on lepidocrocite was strongly dependent on the chromate surface complexes formed on the lepidocrocite facets. This study will help us to clarify the roles of lepidocrocite on the mobility and the bioavailability of chromate in the environment.