

Reactivity of chromate, molybdate, and tungstate on ferrihydrite by XAFS and molecular orbital calculation

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Hexavalent Chromium (Cr(VI)) has serious toxicity and carcinogenicity with high mobility in aquatic system. Therefore, fundamental understanding of the adsorption mechanism of chromate to ferrihydrite, an important adsorbent in natural systems, is essential to discuss their scavenging behavior. Although molybdenum (Mo) and tungsten (W) are congeners with Cr, the adsorption mechanisms (inner- or outer-sphere complexation) on ferrihydrite are different: molybdate forms outer-sphere complex, but tungstate forms inner-sphere complex (1). However, adsorption mechanisms of Cr(VI) on ferrihydrite is unknown. In this study, we performed extended X-ray absorption fine structure (EXAFS) analysis and *ab initio* molecular orbital (MO) calculations to reveal adsorption mechanisms of chromate and the results were compared with those for molybdate and tungstate.

Based on the adsorption experiments, adsorption amount of chromate was determined using inductively coupled plasma mass spectrometry (ICP-MS). EXAFS analysis was used to clarify coordination environment of chromate on ferrihydrite measured at BL-12C in Photon Factory (Tsukuba, Japan). In addition, *ab initio* MO calculations were performed for the oxyanions (chromate, molybdate, tungstate) with Fe-(oxyhydr) oxide cluster model to obtain adsorption energy of outer-sphere complex and hydration energy of these oxyanions.

From the EXAFS analysis, Cr-Fe shell was observed for chromate on ferrihydrite in pH 4 and pH 6 spectra, while the spectrum at pH 8 was almost identical to that of chromate solution. However, the contribution of Cr-Fe shells at pH 4 and pH 6 are considered small degree because of low coordination number (CN) value. Hence, it is suggested that chromate mainly forms outer-sphere complex on ferrihydrite. Adsorption amount of chromate decreased as the ionic strength increased, which can be regarded as another evidence of the formation of outer-sphere complex. From *ab initio* MO calculations, stabilities of hydration complex in water and outer-sphere complex on ferrihydrite decreased in the order of chromate > molybdate > tungstate. Based on these results, it is suggested that it is relatively less stable for tungstate to form hydration and outer-sphere complexes, which allows us to conclude that chromate and molybdate prefer to form outer-sphere complexes, whereas tungstate to inner-sphere complex.

(1) Kashiwabara et al (2011) *Geochim. Cosmochim. Acta* **75**, 5762-5784.

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