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Real-time, in situ surface-specific studies of chromate binding to silica/water interfaces using second harmonic generation

A.L. MIFFLIN, C. KONEK, H. AL-ABADLEH AND
F.M. GEIGER

Department of Chemistry, Northwestern University, 2145
 Sheridan Road, Evanston, IL 60208
 (geigerf@chem.northwestern.edu)

Hexavalent chromium contamination in ground water is widespread and has received much attention in the past decades. Using the nonlinear optical laser spectroscopy surface second harmonic generation (SHG), we have studied chromate adsorption and desorption at the silica/water interface in real time, at room temperature and at chromate concentrations ranging from 1×10^{-6} to 2×10^{-4} M. A polarization analysis of the SHG signal is consistent with the electric dipole of the surface-bound chromate being directed along the surface normal. Adsorption isotherms recorded between pH 4 and 11 indicate hydrogen bond formation between chromate and the silica/water interface; its free energy of adsorption is 38(1) kJ/mol. The pH dependence of the free energies of adsorption is discussed in the context of the silica/water interfacial potential and pKa's measured between pH 1 and 14.

Real-time kinetic measurements of chromate adsorption and desorption in the submonolayer surface coverage regime show that chromate binding to the fused quartz/water interface is completely reversible, consistent with the high mobility of Cr(VI) in most soils and the measured free adsorption energies. Kinetic measurements carried out with varying chromate concentrations at a constant flow rate allow us to determine the adsorption and desorption rate constants, which yield binding constants that are in good agreement with the thermodynamic results obtained from the adsorption isotherms. Results obtained from chromate binding studies to acid-terminated organic silanes on silica were carried out as well and the laboratory data are applied to a simple chemical transport model.

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Ni immobilisation by Al-modified montmorillonite: A novel uptake mechanism deduced by P-EXAFS

M. NACHTEGAAL¹, A. SCHEIDEGGER² R. DÄHN²
 AND G. FURRER¹

¹Institute of Terrestrial Ecology, ETH Zürich, Switzerland
 (nachttegaal@env.ethz.ch; furrer@env.ethz.ch)

²Waste Management Laboratory, Paul Scherrer Institute,
 Switzerland (andre.scheidegger@psi.ch;
 rainer.daehn@psi.ch)

The sorption capacity of montmorillonite, a highly reactive 2:1 clay mineral, for small cations, such as Ni, Cu, Co and Zn, can strongly be improved by intercalating the clay mineral with Al species (such as the Al_{13} Keggin complex). These Al-modified clay minerals offer a great potential for gentle and cost-effective soil remediation and environmental engineering, including the use of the material as a liner for landfills and radioactive waste repositories [1].

Using polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy we succeeded to obtain the first spectroscopic data that allowed us to unequivocally propose a molecular-level picture of the Ni uptake mechanism onto Al-modified clay minerals. Samples were prepared by equilibrated Ni with Al intercalated montmorillonite for 1 month to 9 years, at pH 5-7 and initial Ni concentrations of 1000-3000 ppm. EXAFS data analysis revealed that Ni cations are surrounded by 6 oxygen atoms at ≈ 2.05 Å and 6 aluminum atoms at ≈ 3.02 Å. This finding suggests that Ni is incorporated into an Al hydroxide-like phase. Furthermore, the P-EXAFS data showed a pronounced angular dependency indicating that the Ni-doped Al hydroxide-like phase is highly oriented with respect to the montmorillonite platelets. Consequently, we propose the formation of a Ni-doped gibbsite-like monolayer in the interstitial space of the Al-modified montmorillonite.

The above finding represents the first spectroscopic evidence for a novel uptake mechanism for Ni by clay minerals, and explains the observed stability of sorbed Ni [1]. So far, the only Ni^{2+} uptake mechanism onto montmorillonite proposed in the literature are (1) the formation of surface complexes on edge sites and interlayer sites, or (2) the incorporation of Ni into neofomed phyllosilicates [2].

References

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