

Development of Surface Complexation Models of Cr(VI) Adsorption on Soils, Sediments and Model Mixtures of Kaolinite, Montmorillonite, γ -Alumina, Hydrous Manganese and Ferric Oxides and Goethite

University-Led Research

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Cr(VI) is a toxic contaminant that has been introduced into aquifers and shallow sediments and soils via many anthropogenic activities. Cr(VI) contamination is a problem or potential problem in the shallow subsurface at several DOE sites, including Hanford, Idaho National Laboratory, Los Alamos National Laboratory and the Oak Ridge Reservation (DOE, 2008). To accurately quantify the fate and transport of Cr(VI) at DOE and other contaminated sites, robust geochemical models, capable of predicting changes in chromium speciation resulting from sorption, dissolution, precipitation and redox reactions, are required. The objectives of this study are to: (1) measure Cr(VI) adsorption kaolinite, montmorillonite, hydrous manganese oxide, γ -alumina as a function of ionic strength, pH, $p\text{CO}_2$ and sorbate/sorbent ratio, (2) develop surface complexation model descriptions of Cr(VI) sorption for these systems, (3) test component additivity predictions for Cr(VI) adsorption on mixtures of six well-characterized sorbents, (4) measure Cr(VI) adsorption on four bulk natural soils and sediments before and after four step-wise sequential extractions, and (5) develop methods for extending the component additivity approach to natural soils and sediments.

Significant adsorption of Cr(VI) occurs on γ -alumina (5 g/L solid; 10^{-4} or 10^{-5} M Cr) at low pH, with 50% of the Cr(VI) adsorbed between pH 6.5 and 8. Adsorption is suppressed with increasing ionic strength, especially at high $p\text{CO}_2$. Surface complexation models provide adequate fits to individual adsorption edges, but generally fail to reproduce the full range of observed ionic strength and sorbate/sorbent ratio dependence of sorption. Significantly less Cr(VI) occurs on hydrous manganese oxide, although 100% of 10^{-5} M Cr(VI) is sorbed on 20 g/L HMO at low pH. Increasing ionic strength (0.001 to 0.1 M NaNO_3) significantly decreases Cr(VI) sorption. Cr(VI) sorption is slow, failing to reach steady state after 2 weeks, and nearly irreversible with pH changes from 3 to 10 on untreated kaolinite. Pretreatment with 0.5 M HCl, 0.4 M hydroxylamine HCl or 30% H_2O_2 greatly increase the rate of adsorption, as well as the total quantity of sorbed Cr(VI). Cr(VI) is similarly irreversible on untreated montmorillonite, but is much more rapid than on kaolinite. Pretreatment with 30% H_2O_2 dramatically decreases the quantity of Cr(VI) sorbed on montmorillonite. These data suggest that Fe(II) in the lattice of these clay minerals is responsible for the irreversible sorption of Cr(VI), presumably by promoting reduction to Cr(III). Adsorption edges were measured on an organic-rich soil from Kleinstuck Marsh, MI, before and after stepwise removal of four target fractions (exchangeable, carbonate, reducible and oxidizable) for periods of 24 hrs to 2 weeks. For all sediments except those with the oxidizable portion removed, Cr(VI) sorption increases with time below pH 7, reaching a maximum of 100% sorbed at pH 3 and decreasing with increasing pH. Below pH 7, all Cr remaining in solution is Cr(VI), but above pH 7, dissolved Cr(III) increases with time, with the largest increases occurring at the highest pH, demonstrating reduction of Cr(VI) in contact with sediments. Cr(VI) sorption is greatly diminished after removal of the oxidizable fraction, suggested that the bulk of the Cr(VI) binds to organic matter or Fe(II)-bearing clays.