Surface Complexation Modeling of cation adsorption by TiO_2 nanoparticles

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Surface Complexation Models (SCM) provide a means to quantify the specific adsorption of ions, the interaction of electrolyte ions, and the pH-dependent charging at mineral-aqueous solution interfaces. Additionally, SCMs provide a thermodynamic framework for predicting surface protonation equilbria. The charge distribution (CD) and MUSIC model facilitates the integration of molecular-scale information with macroscopic data to describe the interface behavior of ion-mineral systems.

In this presentation, we will dicuss the application of the CD and MUSIC model to provide a thermodynamic description of the primary charging behavior of a suite of monodisperse, nanocrystalline anatase particles in NaCl media. Additionally, the CD-MUSIC model has been used to evaluate the interaction of Sr^{2+} and Ca^{2+} ions with the same suite of nano-anatase samples.

The adsorption of cations onto nano-anatase was evaluated over a wide range of pH, surface loading, and ionic strength. Complementary DFT-MD molecular simulations were also completed to evaluate the bonding geometries of all cations on the predominant (101) anatase surface. The adsorption behavior for the two divalent cations onto the anatase surface are broadly similar; although, Ca^{2+} first adsorbs at slightly low pH values and has slightly steeper charging curves than Sr^{2+}. The variations in the macroscopic charging curves for the interaction of Sr^{2+} and Ca^{2+} with anatase reflect the differences in binding geometries identified at the molecular-level. The DFT-MD optimizations show inner-sphere binding for all cations; however, the most stable binding geometries are different for each ion. The Na^+ and Sr^{2+} ions have bidentate coordination geometries, with Na^+ ions coordinated to two bridging oxygen (BO) surface sites and Sr^{2+} coordinated to two terminal oxygen surface sites. Conversely, Ca^{2+} ions are coordinated to three BO sites. This molecular-scale information was used explicitly to constrain all CD-MUSIC model fits.

Organic carbon and trace element mobilization from a biochar amended arable soil: A soil column study

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The addition of charred biomass (biochar) to agricultural soils is currently attracting attention as a means for sequestering carbon and as a potentially valuable method to improve soil fertility. Because some uncertainty remains about the possible impacts of biochar additions on organic carbon and trace element cycling in arable soils we conducted a soil column study to investigate the mobilization of trace elements (Mn, Fe, Cu, Zn) and organic carbon.

Amendments of 1% (w/w) of grounded and finely dispersed biochar resulted in a net reduction of organic carbon, Cu and Zn leaching from the saturated soil columns. The organic carbon leaching from the amended soil was less phenolic indicating that sorption to biochar was compound specific. A more detailed characterization of the organic matter with ultra-high resolution mass spectrometry revealed that the most non-polar compounds detectable with this method were retained by the biochar likely because of hydrophobic interactions.

Cu and (to a lesser extend) Zn were associated with the organic matter retained by the biochar as revealed by gel-permeation liquid chromatography hyphenated with inductively coupled plasma mass spectrometry. Complexation with organic matter may therefore play an important role in the interactions of some metals with biochar in soils. The elution behavior of Fe and Mn was almost unaffected.

After two weeks of flow interruption the water-logged soil columns had turned anoxic. Under these conditions the elution behavior of the trace elements changed markedly. Mobilization of Fe and Mn increased strongly, but the increase was less pronounced for the biochar amended soil indicating that sorption of Fe(II) and Mn(II) to the biochar had occurred. Zn and organic carbon on the other hand showed almost no difference to the oxic elution indicating no redox sensitivty.

Our results show that charred biomass affects the quantity and quality of organic matter as well as the quantity and speciation of trace elements leaching from agricultural soils.

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