MODELING OF Cr(VI) ADSORPTION ON MIXTURES OF SELECTED SOIL MINERALS

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Introduction

Quantification of redox sensitive metals such as Cr(VI) in soils at contaminated sites is necessary for preventing and handling additional pollution (Dhal et al., 2013; Hsu et al., 2015). This study investigates the mechanisms of Cr(VI) adsorption on mixtures of natural and synthetic soil minerals using quantitative thermodynamically based mechanistic surface complexation models (SCMs). The main aim is to test a diffuse layer model (DLM) and a triple layer model (TLM) in order to develop a suitable model, which could be able to capture the process of Cr(VI) adsorption in natural heterogenic systems like soils. The component additivity (CA) approach is used when applying SCMs to describe the process of Cr(VI) adsorption in multi-component mixtures of selected soil minerals. CA approach was already applied to predict the metal adsorption in multi-component systems (Alessi and Fein, 2010). The SCMs could represent useful tool for investigating of soil mineral mixtures responsible for Cr(VI) retention in soils, and improving the handling and remediation processes.

Methods

The adsorption edge experiments were conducted for individual soil minerals as well as for their mixtures under atmospheric conditions at different solution pH (3–10), solid-solution ratio (2-20 g/L), total Cr(VI) concentrations (10^{-4}, 10^{-5}, and 10^{-6} M) and ionic strengths (using 0.001, 0.01, and 0.1 M KNO_3 as the background electrolyte). Suspensions consisting of different ratios of soil minerals were prepared in order to generate the multi-component systems according to the mineralogical composition of real contaminated soils. The adsorption edge data were used to calibrate the two-pK DLM and TLM. Titration data were used to optimize values of adjustable model parameters, using the programs ProtoFit and FITEQL 4.0 (Herbelin and Westall, 1999; Turner and Fein, 2006). The Cr(VI) surface complexation constants for individual minerals were determined in FITEQL 4.0 and they were included into the thermodynamic database program Visual MINTEQ in order to obtain a final DLM or TLM for Cr(VI) adsorption. A component additivity approach was tested for modeling the Cr(VI) adsorption on multi-component soil mineral mixtures using Visual MINTEQ. The goodness of fit of each calculated edge to experimental data was assessed using the WSOS/DF ratio produced by the software.

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Results

Cr(VI) was adsorbed insignificantly on pure quartz. Thus, the presence of quartz as one of the most common soil mineral phase, has a little effect on Cr(VI) adsorption on mixtures of soil minerals. On the other hand, results from mixtures containing different percentages of various soil minerals show a preferential effect of Fe (oxy)hydroxides on Cr(VI) adsorption. For instance, the single DLM provides more reasonable prediction for Cr(VI) adsorption onto mixture of ferrihydrite and kaolinite in comparison with only kaolinite surface, capturing the formation of single monodentate inner-sphere complexes (Figure 1).
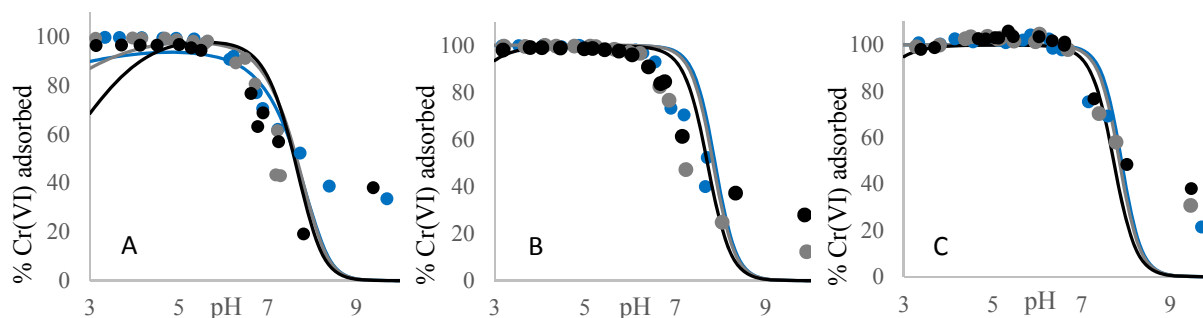
Figure 1. *Adsorption of Cr(VI) onto ferrihydrite-kaolinite mixture (Fe (oxy)hydroxid:clay mineral ratio = 1:3.3) at 10^{-4} M (A), 10^{-5} M (B) and 10^{-6} M (C) Cr(VI) and with 0.1 M (black), 0.01 M (grey) and 0.001 M (blue) KNO_3. Symbols represent experimental data; DLM edges are represented by solid lines.*

The presence of other mono- and bi-dentate complexes of chromate and dichromate as well as presence of outer-sphere complexes, which are not captured by DLM, would explain the model underestimation at pH<4 at 10^{-4} M Cr(VI) and pH>7 at all Cr(VI) concentrations. Dissolution of solid phases needs to be also considered for better SCMs fits.

Conclusion

The results are of general importance for further investigation of redox sensitive metal adsorption in natural soil systems. In addition, the role of humic acids is crucial in evaluation of adsorption processes in natural soils, which are strongly affected by interaction between organic substances and inorganic soil components.

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