CAN METAL SORPTION TO MINERAL-ORGANIC PARTICLES BE PREDICTED BY AN ADDITIVE MODEL?

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Introduction: Mineral surfaces in soil and aquatic environments are often coated to a large extent with natural organic matter, such as adsorbed humic and fulvic acids. Since humic and fulvic acids are negatively charged polyelectrolytes, they can profoundly alter the surface charge of oxide mineral particles. Previous studies on the effects of organic coatings on metal cation adsorption to mineral surfaces come to contradicting conclusions. Some studies suggested that the effects of adsorbed humic substances on metal sorption is purely additive, that is, humic substances merely add additional binding sites to the mineral surface without affecting metal sorption to the mineral surface itself. Other studies provide evidence for more specific interactions leading to either an enhancement or a decrease in metal sorption relative to a purely additive behavior. In this paper, we discuss the effects of adsorbed fulvic acid on the sorption of Cu(II) and Pb(II) to colloidal hematite (α-Fe_2O_3) particles.

Materials and Methods: Fulvic acid was extracted from an organic surface horizon of a forested Humic Gleysol in northern Switzerland and purified using IHSS standard methods. Colloidal hematite particles with 0.12 µm average diameter were synthezised by aging a concentrated $Fe(OH)_3$ gel at 100 °C. Proton, Cu(II), and Pb(II) binding to fulvic acid was investigated with potentiometric titration experiments using pH and ion selective electrodes. The pH-dependent sorption of Cu(II) and Pb(II) to pure and fulvic-acid coated hematite particles was studied in batch experiments.

Modeling: Sorption of protons and metal cations to fulvic acid was modeled using the non-ideal competitive adsorption equation combined with the Donnan electrostatic model (NICA-Donnan) [1]. Metal sorption to hematite was described with a basic Stern surface complexation model (BSM). A linear combination of both models was used to predict metal sorption in ternary systems, in which hematite and fulvic acid were present. The experimental data are compared with the calculations based on linear additive behavior in order to obtain information about possible specific interactions.

Results and Discussion: Addition of Cu (22 µM) had little effect on adsorption of fulvic acid (38 mg/L) to hematite (2 g/L). Adsorption of fulvic acid decreased from about 90% at pH 3 to less than 50% at pH 10 (in 0.1 M $NaNO_3$). At high pH, adsorption of humic acid to hematite also decreased with decreasing ionic strength (0.1 to 0.01 M $NaNO_3$).

The NICA-Donnan and BSM models provided excellent descriptions of the sorption behavior of protons, Cu(II), and Pb(II) to fulvic acid and hematite at various ionic strengths. Thus, the data and models for the single-sorbent systems should be well suited to test the linear additivity hypothesis. Figure 1 shows an adsorption edge for Cu(II) to pure hematite (open symbols) and fulvic acid-coated hematite (closed symbols).

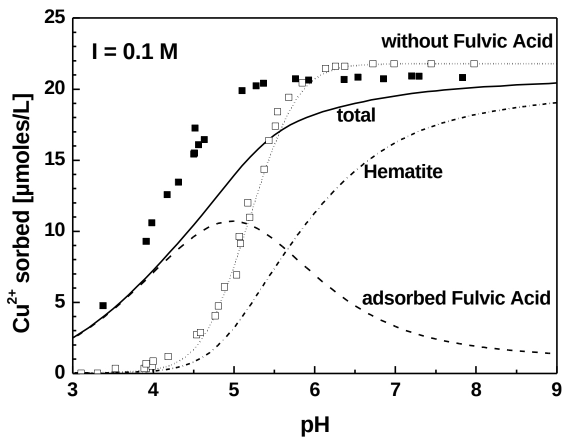

Figure 1. Sorption of Cu(II) in a hematite-fulvic acid system.

At low pH, addition of 38 mg/L fulvic acid to a suspension containing 2 g/L hematite increases Cu(II) sorption. At high pH, addition of fulvic acid leads to a reduction of Cu(II) sorption by about 5%. The solid line in Fig. 1 shows the prediction of Cu(II) sorption in the ternary system based on the linear additivity approach. This model underestimates Cu(II) sorption in the presence of fulvic acid by up to 25%, suggesting that the presence of fulvic acid on the hematite surface enhances Cu(II) sorption. Two possible explanations may be responsible for this non-additive behavior: (i) fulvic acid may add negative surface charge to the hematite surface and thereby increase the Cu(II) activity at the hematite surface, and (ii) the fulvic acid may be fractionated into a more reactive fraction, preferentially adsorbing to the hematite surface, and a less reactive fraction remaining in solution. Very similar results were obtained for Pb(II).

References: [1] Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., and Avena, M.J. (1999) *Colloids and Surfaces A* 151: 147-166.

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