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Sorption of Cu and Pb to kaolinite–fulvic acid colloids: Assessment of sorbent interactions

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Abstract—The sorption of Cu(II) and Pb(II) to kaolinite–fulvic acid colloids was investigated by potentiometric titrations. To assess the possible interactions between kaolinite and fulvic acid during metal sorption, experimental sorption isotherms were compared with predictions based on a linear additivity model (LAM). Suspensions of 5 g L^{-1} kaolinite and 0.03 g L^{-1} fulvic acid in 0.01 M $NaNO_3$ were titrated with Cu and Pb solutions, respectively. The suspension pH was kept constant at pH 4, 6, or 8. The free ion activities of Cu^{2+} and Pb^{2+} were monitored in the titration vessel using ion selective electrodes. Total dissolved concentrations of metals (by ICP-MS) and fulvic acid (by UV-absorption) were determined in samples taken after each titration step. The amounts of metals sorbed to the solid phase, comprised of kaolinite plus surface-bound fulvic acid, were calculated by difference. Compared to pure kaolinite, addition of fulvic acid to the clay strongly increased metal sorption to the solid phase. This effect was more pronounced at pH 4 and 6 than at pH 8, because more fulvic acid was sorbed to the kaolinite surface under acidic conditions. Addition of Pb enhanced the sorption of fulvic acid onto kaolinite at pH 6 and 8, but not at pH 4. Addition of Cu had no effect on the sorption of fulvic acid onto kaolinite. In the LAM, metal sorption to the kaolinite surface was predicted by a two-site, 1-pK basic Stern model and metal sorption to the fulvic acid was calculated with the NICA-Donnan model, respectively. The LAM provided good predictions of Cu sorption to the kaolinite–fulvic acid colloids over the entire range in pH and free Cu^{2+} ion activity (10^{-12} to 10^{-5}). The sorption of Pb was slightly underestimated by the LAM under most conditions. A fractionation of the fulvic acid during sorption to kaolinite was observed, but this could not explain the observed deviations of the LAM predictions from the experimental Pb sorption isotherms. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Sorption to mineral surfaces and complexation by humic substances are two important processes influencing the cycling of potentially toxic trace metals in the environment (Adriano, 2001). In general, the bioavailability and mobility of trace metals depends strongly on chemical speciation (Traina and Laperche, 1999). The toxicity of a metal is commonly directly proportional to the activity of the free metal ion (Traina and Laperche, 1999; Brown and Markich, 2000). The mobility of trace metals in soils and aquatic environments is controlled mainly by their distribution between immobile solid phases, mobile colloidal particles and dissolved species (Kretzschmar et al., 1999). A quantitative assessment of the sorption behavior of trace metals in aqueous systems containing clays and humic substances is therefore essential for understanding the biogeochemistry of trace metals.

The sorption of metal cations to pure oxides and clay minerals has been studied extensively during the past. In many studies, experimental sorption data have been described using various surface complexation models, such as the triple layer model, the generalized two-layer model, the 1-pK basic Stern model, and the CD-MUSIC model (Dzombak and Morel, 1990; van Riemsdijk and Van der Zee, 1991; Goldberg, 1992; Hiemstra and van Riemsdijk, 1996; Venema et al., 1996). All these models describe the adsorption of ions onto mineral surfaces in terms of reaction equations for the formation of surface species and the corresponding equilibrium constants (Goldberg, 1992).

The binding of trace metals to purified humic substances has also been investigated in some detail (Benedetti et al., 1995; Benedetti et al., 1996b; Kinniburgh et al., 1996, 1998; Tipping, 1998; Christl et al., 2001; Milne et al., 2003). Humic substances are natural organic macromolecules with pH-dependent negative charge due to carboxylic and phenolic functional groups. Experimental data on competitive binding of protons and metals cations to humic substances has been accurately described by various modeling approaches, for example, Tipping's Model VI (Tipping, 1998) and the NICA-Donnan model (Kinniburgh et al., 1996; Christl et al., 2001; Milne et al., 2003). These models are based on affinity distributions for metal cation and proton binding sites and also take electrostatic interactions into account.

The application of sorption models developed and calibrated for isolated mineral and organic sorbents to soils and sediments is still difficult and often questionable. One potential problem is that reactive mineral surfaces in soils and aquatic systems are frequently coated to a large extent by adsorbed natural organic matter, such as humic substances (Davis, 1982; Sposito, 1984). Humic substances can bind to mineral surfaces by a variety of mechanisms, for example, ligand exchange, electrostatic interactions, cation and water bridging, and hydrophobic interactions. Specific adsorption by ligand exchange is considered to be the most important sorption mechanism of humic substances to oxides and edge-surfaces of clay minerals (Stumm et al., 1980; Gu et al., 1994; Schlautman and Morgan, 1994). Because of their negative charge, adsorbed humic substances strongly alter the net particle charge, zeta potential, and colloidal stability of clay and oxide particles (Amal et al., 1992; Tiller and O'Melia, 1993; Kretzschmar et al., 1997, 1998; Tombacz et al., 1998).

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Adsorbed humic substances also change the sorption of trace metal cations at the mineral-water interface (Dalang et al., 1984; Xu et al., 1989; Murphy and Zachara, 1995; Robertson, 1996; Schroth and Sposito, 1998; Vermeer et al., 1999; Christl and Kretzschmar, 2001a). However, the specific interactions between metal cations and adsorbed organic substances at mineral surfaces are still not well understood and partially contradicting results have been reported in the past. Several factors may play a role: (i) addition of high-affinity binding sites by organic functional groups, (ii) competition for reactive binding sites at the mineral surface, (iii) formation of ternary metal-organic surface complexes, (iv) alteration of surface charge and distribution of surface potentials, and (v) fractionation of humic substances during sorption to mineral surfaces. Zachara et al. (1994) suggested that adsorbed humic substances contribute additional binding sites for Co without affecting Co sorption to the mineral sorbents, which consisted mainly of gibbsite, Al-goethite, and kaolinite. Sorption of Co to the mineral-organic particles was therefore well predicted by a simple linear additive model (LAM), which essentially describes the system as a physical mixture of independent sorbent phases without specific interactions between the sorbents. In contrast, significant deviations of metal sorption from linear additive behavior were reported for other mixed mineral-organic sorbent systems (Robertson, 1996; Vermeer et al., 1999; Christl and Kretzschmar, 2001a). Robertson (1996) investigated the sorption of Cu in suspensions containing goethite and humic acid and found that the LAM overestimated Cu binding by a factor of up to 7. The greatest deviations were observed at low pH and low Cu^{2+} activities, where Cu was mainly bound to sorbed humic acid. Vermeer et al. (1999) examined the sorption of Cd to hematite in the presence of humic acid. The LAM overestimated Cd sorption by a factor of up to 10 at pH 4 and high Cd concentrations, where Cd was bound mainly to sorbed humic acid. At pH 9, however, where most Cd was sorbed to the mineral surface, the LAM underestimated Cd sorption systematically by about a factor of 2 with maximal deviations up to a factor of 10. Vermeer et al. (1999) explained the observed nonadditive effects by electrostatic interactions between positively charged mineral surfaces and negatively charged humic acid molecules. Christl and Kretzschmar (2001a) investigated the sorption of Cu in suspensions containing hematite and fulvic acid. In this case, the greatest deviations of observed Cu sorption from LAM predictions were found near pH 5, where the LAM underestimated Cu sorption by a factor of 1.4.

Sorbent interactions in mixed mineral-organic systems may lead to different nonadditive effects on metal sorption, depending on the nature and concentration of the metal cation, the pH of the suspension, and the surface chemistry of the mineral and organic sorbents. For example, iron oxide minerals such as goethite and hematite have rather high points of zero net proton charge (pH_{PZNPC}) near pH 8 to 9 (Stumm and Morgan, 1996). Therefore, their surfaces are strongly positively charged at low pH values resulting in strong electrostatic interactions between the oxide surface and fulvic or humic acid molecules (Vermeer and Koopal, 1999; Vermeer et al., 1999). Large deviations of metal sorption from linear additivity have been observed in such systems (Robertson, 1996; Vermeer et al., 1999; Christl and Kretzschmar, 2001a). In contrast, the edge-surfaces of clay minerals have a much lower pH_{PZNPC} and the face-surfaces have negative structural charge. Thus, we expect that the electrostatic interactions between clay edge-surfaces and fulvic or humic acid molecules are weaker and that cation-bridging on face-surfaces may influence fulvic or humic acid adsorption to the clay particles. It therefore seems likely that also the effects of sorbent interactions on metal sorption are different for oxide and clay minerals, but the mechanisms and effects are not yet understood. In addition, the charge and macromolecular properties of the organic matter may also affect the sorbent interactions. When comparing literature data, it must be kept in mind that also the quality of experimental data and model fits for the pure mineral and organic sorbents can influence the LAM predictions. To test the linear additivity assumption, it is necessary to study mixed mineral-organic sorbent systems and the respective single sorbent systems over wide ranges in metal concentration and pH, and to develop accurate models describing metal sorption to the pure sorbents.

In this study, we used kaolinite and fulvic acid as a mixed-sorbent system for the trace metals Cu and Pb. Kaolinite is a major component of the clay fraction of strongly-weathered soils in humid climatic regions. Kaolinite is also an interesting mineral sorbent, because it has significant amounts of pH-dependent charge on the edge-surfaces with a pH_{PZNPC} near pH 5 (Heidmann et al., 2005; Schroth and Sposito, 1997) and minor amounts of permanent negative charge on the face-surfaces (Brady et al., 1996; Heidmann et al., 2005). The origin of permanent negative charge in kaolinites can be due to some isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheets (Brady et al., 1996). However, also trace impurities of smectites or other 2:1 layer silicates may contribute some negative charge (Brady et al., 1996; Ma and Eggleton, 1999). The competitive sorption of protons, Cu and Pb to pure kaolinite was studied and modeled by Heidmann et al. (2005). The fulvic acid chosen as the organic sorbent was well-characterized (Christl et al., 2000) and model parameters for proton, Cu and Pb sorption were available from previous studies by Christl et al. (2001) and Christl and Kretzschmar (2001b). Furthermore, the same fulvic acid was also used in a previous study on the sorption of Cu and Pb in systems containing hematite and fulvic acid (Christl and Kretzschmar, 2001a). The objectives of this study were to (i) investigate the sorption of Cu and Pb in mixed kaolinite–fulvic acid suspensions over wide ranges in pH and metal concentrations, and (ii) compare the experimental sorption isotherms with LAM model predictions based on previously calibrated sorption models for the pure kaolinite (Heidmann et al., 2005) and fulvic acid (Christl and Kretzschmar, 2001b; Christl et al., 2001).

2. EXPERIMENTAL SECTION

2.1. Sorbents

The <1 μm size fraction of a well-characterized reference kaolinite (KGa-2, Source Clays Repository, The Clay Minerals Society) was used as the mineral sorbent. To separate the <1 μm size fraction, 10 g of the KGa-2 kaolinite were suspended in 250 mL of high-purity deionized water (18 MΩ, Milli-Q, Millipore). The suspension was adjusted to pH 9.5 by NaOH addition and treated for 15 s with an ultrasonic tip to facilitate particle dispersion. The <1 μm size fraction was then separated by repeated centrifugation, decantation, and redispersion steps. The kaolinite was saturated with Na^+ by washing it five times with a 1 M NaCl solution, followed by repeated washes with