

# Competitive sorption of $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ at the hematite-water interface: Surface complexation modelling

D. I. Christl  
R. Kretzschmar  
H. Sticher

Institute of Terrestrial Ecology, Swiss Federal Institute of  
Technology, Grabenstrasse 3, CH-8952 Schlieren, Switzerland

Oxides and oxyhydroxides of iron and aluminum are important sorbents for heavy metal cations in aquatic and terrestrial environments. The sorption of metal cations has therefore been subject of many investigations. In the majority of studies, sorption of single metals as a function of pH and electrolyte concentration has been investigated. Little information is available on competitive sorption effects between strongly sorbing metal cations. This information is essential, however, if surface complexation models are to be applied successfully to more complex, multi-component systems such as contaminated soils or sediments. The objectives of the present study were to (i) investigate competitive sorption effects between two strongly sorbing heavy metals,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , to colloidal hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) particles, and (ii) to test various surface complexation models for their ability to predict competitive sorption from acid-base titration and single-metal sorption data.

## Materials and methods

Submicron sized hematite particles were prepared by aging a condensed Fe(III)-hydroxide gel for 72 h at  $100^\circ\text{C}$  (Sugimoto and Sakata, 1992). Excess salts were removed by washing and extensive dialysis. The particles were characterized by transmission electron microscopy (TEM),  $\text{N}_2$ -BET surface area measurements, and powder X-ray diffraction analysis (XRD).

Acid-base titrations of hematite colloids suspended in  $\text{NaNO}_3$  electrolyte solutions (0.005 to 0.5 M) were carried out under nitrogen atmosphere using a fully automated titration set-up (Schudel *et al.*, 1997).

The pH-dependent adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  to pure hematite was investigated with batch experiments. Solid concentrations and total metal concentrations ranged from 0.2 to 2 g/L and 4 to 300  $\mu\text{M}$ , respectively. The pH values were adjusted by adding either  $\text{HNO}_3$  or  $\text{NaOH}$ . Most experiments were performed in 0.1 M  $\text{NaNO}_3$  background electrolyte. All samples equilibrated under nitrogen gas for 21 h

at  $25^\circ\text{C}$  were filtered through a 0.1- $\mu\text{m}$  membranes prior to chemical analysis.

The single-metal sorption data were modeled using classical surface complexation models, such as the constant capacitance (CCM), diffuse double layer (DLM), and triple layer models (TLM). The program FITEQL 3.2 was used for parameter optimization (Herbelin and Westall, 1996). In a first step, the acid-base titration data of the hematite colloids were modeled to obtain best-fit parameters for surface protonation, ion-pair formation, surface capacitance, and site density. However, the site density cannot be reliably determined from acid-base titration data and was therefore also systematically varied. In the second step, the single-metal sorption data were modelled based on the models calibrated for protonation behaviour. In the third step, the obtained surface complexation constants were used to predict competitive sorption in the presence of both  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ . Precipitation of oversaturated solids was also considered.

## Results and discussion

The hematite particles were approximately spherical and  $122 \pm 29$  nm in diameter. The specific surface area of the particles was  $28.3 \text{ m}^2/\text{g}$ , as measured by the  $\text{N}_2$ -BET method. Analysis by XRD and TEM showed that the particles consisted of well-crystallized hematite. No impurities were detected.

Acid-base titration curves of the hematite particles at different ionic strengths exhibited a common intersection point near pH 9.2. This pH corresponds to the (pristine) point of zero charge (PZC) of the hematite surface in the absence of specifically adsorbing ions. The titration data were described very well by any of the surface complexation models.

As reported in the literature,  $\text{Pb}^{2+}$  was sorbed more strongly to hematite than  $\text{Cu}^{2+}$  and sorption of both metals increased sharply with increasing pH. The adsorption edges of both metals were nearly unaffected by the concentration of background electrolyte used. For example, sorption of  $\text{Cu}^{2+}$  as a

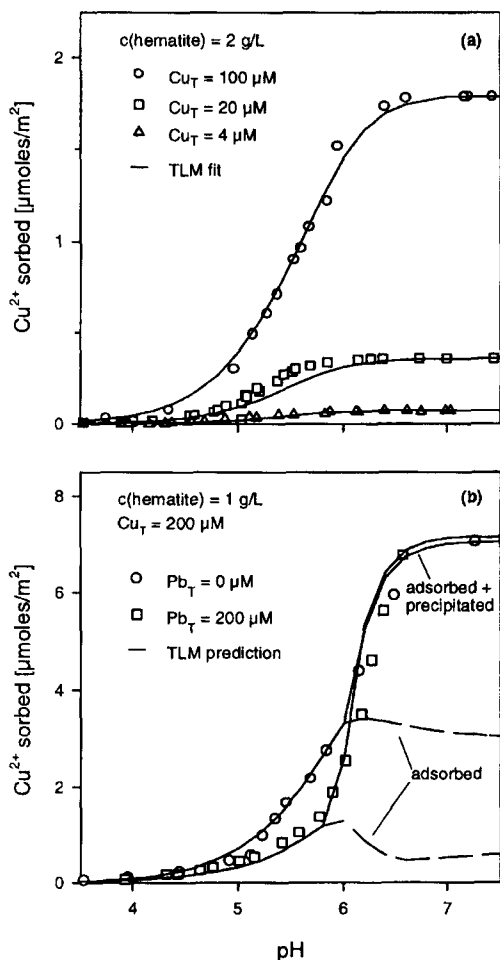


FIG. 1. Sorption of  $\text{Cu}^{2+}$  to hematite as affected by the presence of  $\text{Pb}^{2+}$  (in 0.1 M  $\text{NaNO}_3$ ). (a) Single-metal sorption data for low to medium surface coverage used to calibrate surface complexation models. Solid lines represent the best fit of the TLM (b) Competitive sorption of  $\text{Cu}^{2+}$  at high surface coverage in the presence of 100  $\mu\text{M}$   $\text{Pb}^{2+}$ . Solid lines represent predictions based on the calibrated TLM.

function of pH and total  $\text{Cu}^{2+}$  concentration is shown in Figure 1a. The maximum surface coverage (at 100% sorbed) in these experiments ranged from 0.07 to 1.77  $\mu\text{moles}/\text{m}^2$ . Similar results were obtained for  $\text{Pb}^{2+}$ . The data from these single-metal sorption

experiments were used to calibrate the surface complexation models. As an example, results based on the TLM are presented here. Three types of surface complexes were considered: (i) inner-sphere complexes, (ii) outer-sphere complexes, and (iii) outer-sphere complexes of singly hydrolyzed metal species (e.g.  $\text{PbOH}^+$ ). The solid lines in Figure 1a represent the best fit of the TLM with 7.2 sites/ $\text{nm}^2$ , which was the best-fit site density obtained from proton titration. Satisfactory description of the single-metal sorption data was also obtained using the DLM and CCM models, respectively.

At low to medium surface coverage ( $\leq 1.77 \mu\text{moles}/\text{m}^2$ ), almost no competitive effects between  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were observed. However, when the total metal concentrations were further increased, competition between  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  became clearly evident, although these effects were limited to a rather narrow pH range. A typical example is shown in Figure 1b, along with TLM predictions assuming 7.2 sites/ $\text{nm}^2$ . Competitive sorption can only be observed below pH 6. At higher pH values, precipitation of  $\text{Cu}(\text{OH})_2$  is predicted to occur. Since precipitation of  $\text{Cu}(\text{OH})_2$  does not depend on the presence of  $\text{Pb}^{2+}$ , competitive effects are overshadowed in macroscopic sorption data as soon as precipitation sets in. The onset of  $\text{Cu}(\text{OH})_2$  precipitation near pH 6.5 was verified by EXAFS spectroscopy.

The TLM predictions shown in Fig. 1b are in good agreement with experimental data. Model predictions of competitive sorption were extremely sensitive to the site density used. Lowering the site density resulted in strong overestimation of competitive effects, while increasing the site density had the opposite effect. Thus, we suggest that competitive sorption experiments provide valuable information about the site density relevant to metal complexation at oxide mineral surfaces.

## References

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