Adsorption of Cu onto illite surfaces: The effects of ionic strength and organic acids

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Copper is one of the most representative transition metals in landfill leachate-derived polluted waters. Besides, these waters are heavily loaded with several groups of organic acids, namely monocarboxylic acids with 6 to 10 C atoms [1]. Previous studies [2] concluded that octanoic acid had little influence in the uptake of Cu by kaolinite surfaces.

The performed experiments used a flow-through reactor loaded with 0.5 g of the IMt-1 illite from the CMS repository, where the Cu (50–150 μM) solutions had 0.5×10^{-5} M of hexanoic acid. The pH of the solutions was 4.5, 5.5 (both 10^{-4} and 10^{-3} M IS), and 6.5 (10^{-3} M IS). A chemical equilibrium model was fitted to the experimental data of the illite suspension titration using FITEQL [3]. Surface dissociation constants were optimised, and the values obtained were $pK_{a1} = -2.94\pm0.11$ (surface protonation, $\equiv SOH_2^+$) and $pK_{a2} = 3.98\pm0.14$ (surface deprotonation, $\equiv SO^-$). Total site concentration was $5.05\pm0.09\times10^{-4}$ M.

Experiments at pH 4.5 and 5.5 reached saturation with respect to Cu adsorption, and the introduction of hexanoic acid did not show any discernible differences in the experiments. However, at pH 6.5 and higher ionic strength a slight decrease in the adsorption capacity was observed. It is presently unclear if this is an ionic strength or acid effect because ionic strength alone has a similar effect and at these pH values the amount of dissociated hexanoic acid in solution is very similar 81% (5.5) and 98% (6.5). Higher ionic strength increased the rates of Cu desorption by 65% and 57% at pH 4.5 and 5.5 respectively. It also increased the initial amount of desorbed Cu from 23% to 37% at pH 4.5, and from 6% to 29% at pH 5.5. Further experiments will use poly-functional organic acids as these are known to form more stable complexes with Cu.

References

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[3] Herbelin, AL, and Westall, JC. (1999) FITEQL 4.0 User's Manual. Dept Chemistry, Oregon State University.

Travertine terrace growth dynamics

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Calcium carbonate precipitate from hydrothermal and karst-derived water often grows as terraces or carbonate rims holding pools of water. The rim height ranges from 5 mm to meters and the pool areas range from square millimeters to tens of square meters. We describe a model of the formation and growth of travertine terraces and compare the predictions with the present surface topography of an active travertine site and with vertical cuts through travertine beds.

The numerical model is based on an empirical relationship between flow rate and precipitation rate. Water flow in the evolving travertine pool geometry is calculated using a 2D fluid dynamics model. The dynamics of the system are complicated, with constant redirection of flow as the topography changes. Consequently, precipitation rate at each point fixed in space is highly variable through time. Modelling results are compared with pool shapes and pool size distribution derived from aerial photographs and laser profiling at the Troll Spring site, Svalbard. An observed minimal rim height is explained as an effect of surface tension, which is not included in the model. The model describes the emergence and coarsening of large-scale pattern from a small-scale mechanism.

The travertine quarries at Rapolano Terme, Italy, have been described in detail by Guo and Riding. We visited the quarries Cava Campo Muri and Cava la Chiusa in August 2004. The exposed walls of the quarries were up to 15 meters high and up to 100 meters long. Most walls showed flat deposits with only periodic growth of small terraces that died off again or they showed large, sloping features caused by pre-existing topography. On some walls that were cut at a favourable direction with respect to a gentle slope we could directly observe how small terraces grew in size both vertically and horizontally while the travertine was deposited. Terrace coarsening is shown to occur by rim inundation as in our numerical model and not by "step bunching" of microterracettes.