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Mechanism of Cu Sorption Onto Iron Oxides: Results from Sorption Isotherms and Spectroscopy

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In soils and sediments, the mobility and bio-availability of aqueous metal cations is often controlled by sorption onto iron oxides and oxide hydroxides such as goethite, hematite and ferrihydrite. A molecular understanding of how metals sorb onto mineral surfaces is needed before we can reliably model equilibria from sorption isotherm measurements. Sorption of ions onto mineral surfaces may occur via outer-sphere complexes, inner-sphere complexes, surface precipitates or via ion exchange. The aqueous chemistry of copper is strongly controlled by sorption onto iron oxides. A number of studies have been directed towards understanding the mechanism of Cu sorption onto goethite (α-FeOOH). Grossl and Sparks (1995) argue that copper forms a monodentate inner-sphere complex on the goethite surface. Consistent with the inner-sphere complex, Kooner (1992) and Jung et al. (1998) find that sorption is independent of ionic strength. Ali and Dzomback (1996) find that sulphate enhances Cu^{+2} sorption but they attribute this to the formation of a ternary complex. Although Grossl and Sparks (1995) proposed a single monodentate surface complex, Robertson and Leckie (1998) modelled the sorption of Cu in terms of two surface sites with very different Cu affinities. However, the combination of surface sites that fit the data depended upon the model for the electrostatic potential at the goethite-water interface. A further complication is that copper forms a variety of polynuclear complexes. Rodda et al. (1996) argue that both monomeric $CuOH^+$ and dimeric $Cu_2(OH)_2^{2+}$ complexes sorb onto goethite at pH = 5.0.

In the work reported here, we measured the sorption of Cu on goethite, hematite and ferrihydrite as a function of ionic strength and pH and fit the resulting isotherms to a set of surface complexes using FITEQ. We also obtained EXAFS spectra to determine the mechanism of Cu sorption on goethite at low and high pH. At pH= 4.6, the sorption of Cu is strongly enhanced by increasing the ionic strength from 0.1 to 1.0 M. EXAFS spectra suggests that, at pH = 4.6, Cu sorbs via an outer sphere complex insofar as there is no evidence for any Cu-Fe or Cu-Cu interaction. In contrast, sorption of Cu at pH = 6.27 shows no strong enhancement with increasing ionic strength and the EXAFS spectra shows strong evidence for an inner sphere complex with a Cu-Fe distance of 3.8 Å. Moreover, the sorbed Cu atoms are forming hydroxo-bridged Cu-Cu dimers with a Cu-Cu distance of 2.9 Å. The same structure in seen in freshly precipitated $Cu(OH)_2$. It is difficult, therefore, to spectroscopically distinguish a polynuclear inner sphere complex from a surface precipitate. However, a good fit of the sorption isotherms on goethite, hematite and ferrihydrite were obtained (using FITEQ) to a model corresponding Cu-Cu dimers on the goethite surface rather than a $Cu(OH)_2$ precipitate.

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