The mechanistic view of Cu(II) adsorption and desorption kinetics on illite surfaces: to which 2:1 clay surfaces metals adsorb?

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Metal adsorption on mineral surfaces is a topic extensively pursued by researchers to improve the understanding of the environmental fate of metals, and provide natural low-cost adsorbents for remediation and other technological applications. Despite the wealth of available information, few studies were devoted to metal adsorption mechanisms and its stability as a surface complex, which depends on the ionic strength of the solution. Few surface running waters have ionic strengths in excess of 10^{-3} M. We present a review of studies on Cu adsorption/desorption kinetics and adsorption isotherms on illite surfaces using flow-through and batch reactors, respectively. The solution pH was 4.5 – 6.5 with ionic strengths of 10^{-4} M and 10^{-3} M. The influence of organic molecules on Cu adsorption was also investigated using citric acid as a proxy for poly-functional natural organic matter. These results were complemented by ab-initio DFT and molecular dynamics simulations to calculate the energy of the hydroxylated clay edge surfaces to select which are the most stable and hence the most likely for metal surface complex formation.

Results show that Cu adsorbs in a two-step Eigen-Wilkins-Werner type mechanism (fast formation of an outer-sphere complex followed by a much slower inner-sphere complex). Published EXAFS data show that Cu and Co surface complexes bind to clay edge surfaces as the ionic strength increases. The (001) surface becomes relevant for infinitely diluted solutions. Flow-through and batch reactor experiments indicate that ionic strength does not affect significantly the total adsorption capacity of illite, but the rates and stability of the adsorbed complex are considerably affected. Adsorption rates decrease with increasing ionic strength, while desorption rates increase. Steady-state adsorption rates are 1-2 orders of magnitude higher than the corresponding desorption rates, (0.9 – 2 x 10^{-10} mol/m^2/min). Initial non-steady state adsorption rates differ by 3-4 orders of magnitude. These desorption rates are linked to the rate-limiting step of inner-sphere complex hydration following the reverse path of the proposed mechanism. An order of magnitude increase in the ionic strength doubles the amount of desorbed Cu. Clay edge surface sites are amphoteric, therefore surfaces develop a charge in response to pH, and Cu adsorption increases with increasing pH. The negatively charged CuCit- ion behaves differently, but since it can form multiple surface bonds the amount desorbed is half the value measured for Cu in the same conditions. However, the Cu citrate complex is more sensitive to ionic strength, which reduces its total adsorption.

Classical modeling of the clay-edge surface hydration showed that from a larger set of Miller index planes, the (110), (-110), (010), and (100) faces are the most stable, and a pseudo-hexagonal crystal shape is generated with the first three surface planes, as documented for phyllosilicates.

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