ADSORPTION OF Cu ONTO ILLITE SURFACES: KINETICS AND METAL-ORGANIC ACID INTERACTIONS

M.A. Gonçalves

Departamento de Geologia y CREMINER, Faculdade de Ciências da Universidade de Lisboa, Edifício C6, Piso 4, Campo Grande, 1749-016 Lisboa, Portugal; mgoncalves@fc.ul.pt

INTRODUCTION

Adsorption of metals onto the surface of natural materials is a subject with relevance for the understanding of metal dispersion and retention in the environment, as well as for the evaluation of materials as retention barriers for remediation strategies. Metals are potentially toxic chemical elements depending on several factors such as concentration levels, oxidation state, and speciation in aqueous environments. Unlike organic pollutants that can undergo degradation, metals have in adsorption and precipitation their most important natural attenuation mechanisms, which control their bioavailability. Metal precipitation is most likely to occur under reducing and alkaline conditions. However, under the most common oxidising and near-neutral surface environments, adsorption becomes the major limiting mechanism controlling their concentration in the natural waters.

This work will focus on the adsorption kinetics of Cu onto illite surfaces at a pH range 4.5 – 6.5 and different ionic strengths. Adsorption of Cu will be also investigated in the presence of organic acids: hexanoic and citric acids.

EXPERIMENTAL CONDITIONS

The experimental study used the IMt-1 illite from the CMS repository. Pre-treatment of illite included grinding, washing, and sample separation to obtain a grain size fraction in the range of 0.4 – 20 μm. Carbonates, iron oxides, and organic matter were removed, and X-ray diffraction and SEM showed a relatively homogeneous $2M_d$ non-expanding illite with a perfectly platy morphology. Quartz (5% or less) and kaolinite (< 1%) were also detected. The illite has an N_2-BET surface area of 38.04 ± 0.04 m^2/g.

Surface protonation constants as well as the reactive surface site concentration were determined by titration of a 10 g/L illite suspension in a 0.1 M KNO_3 solution and of an acid blank solution. A chemical equilibrium model for surface speciation was fitted to the experimental results using FITEQL (Herbelin and Westall, 1999).

Experiments to study the adsorption kinetics of Cu were done in a continuous stirred flow-through reactor. Details of the experimental set-up are given in Gonçalves (2004). The experimental conditions were as follows: solution flow of 0.76 mL.min^{-1}; T = 25ºC; 500 mg of illite. Reacting solutions had Cu concentrations ranging from 50 to 150 mM, ionic strengths of 10^{-4} M $KClO_4$ and 10^{-3} KNO_3, and pH values of 4.5, 5.5, and 6.5. Experiments done included initial adsorption experiments and break through curve (BTC) experiments. In the latter, a blank solution is initially flowed through the reactor, which is then replaced by the Cu solution; once Cu saturation is achieved inside the reactor, the blank solution is again introduced in the system. The reacted solution was sampled regularly, and the pH was measured *ex-situ* during each sampling interval. Copper was analysed in a Philips Pye Unicam SP9 Atomic Absorption Spectrophotometer. Calibration was done in each analytical session by the external standard method. The detection limit for Cu, under these conditions, was 100 ppb, but eventually it was possible to pre-concentrate the more diluted samples and reach 20 ppb detection limit with less than 20% uncertainty.

CHEMICAL SYSTEM

The chemical speciation model fitted to the experimental titration curves with FITEQL is summarised in the table that follows (relevant equilibrium constants were taken from Du *et al.*, 1997a).

FITEQL optimised parameters		
Total Al^{3+} (M)	$6.24 \pm 0.15 \times 10^{-5}$	
Total Si (M)	$3.46 \pm 0.05 \times 10^{-3}$	
Total ≡SOH (mol/g)	$5.05 \pm 0.09 \times 10^{-4}$	
pK_{a1}	-2.94 ± 0.11	≡SOH + H$^+$ = ≡SOH^{2+}
pK_{a2}	3.98 ± 0.14	≡SOH = ≡SO$^-$ + H$^+$
V_y (FITEQL GoF parameter)	18.33	

The general equation for Cu uptake at aqueous illite surfaces where there are n surface sites, m copper ions, and p protons is (Du *et al.*, 1997b):

$$n(\equiv SOH) + mCu^{2+} + (p-n)H_2O \Leftrightarrow (\equiv SO)_n Cu_m(OH)_{(p-n)}^{(2m-p)} + pH^+ \quad (1)$$

having an intrinsic adsorption constant

$$K_{n,m,-p}^{int} = \frac{\left[(\equiv SO)_n Cu_m(OH)_{(p-n)}^{(2m-p)}\right]\left[H^+\right]^p}{\left[(\equiv SOH)\right]^n \left[Cu^{2+}\right]^m} \exp\left(-(2m-p)\frac{F\psi_0}{RT}\right) \quad (2)$$

In this equation, F is the Faraday constant, y_0 is the surface potential, R is the perfect gas constant, and T is the temperature (in Kelvin).

The equilibrium speciation as a function of pH (Figure 1) shows that for the concentration range of the adsorption experiments, Cu adsorbs according to
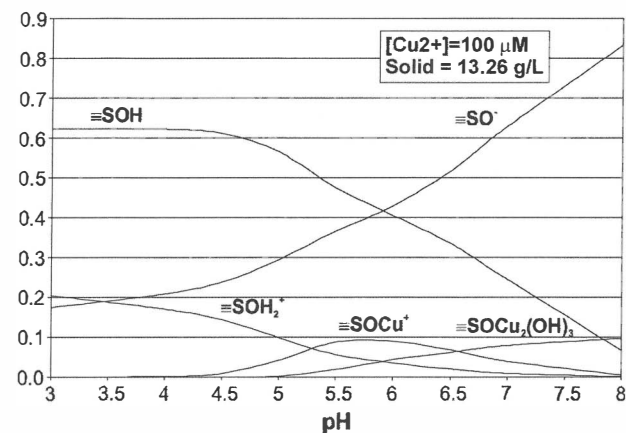

Figure 1: Surface equilibrium speciation of the illite suspension (13.26 g/L) with Cu (100 mM). The phase $^oSOCu_2(OH)_3$ is a surface precipitate. All relevant equilibrium constants were taken from Du et al. *(1997b).*

equation (1) with n, m, and $p = 1$. The remaining relevant reactions, in particular (1, 1, 2) and (1, 2, 3) for the triplet (n, m, p) are not significant for these conditions.

KINETICS OF Cu ADSORPTION ONTO ILLITE

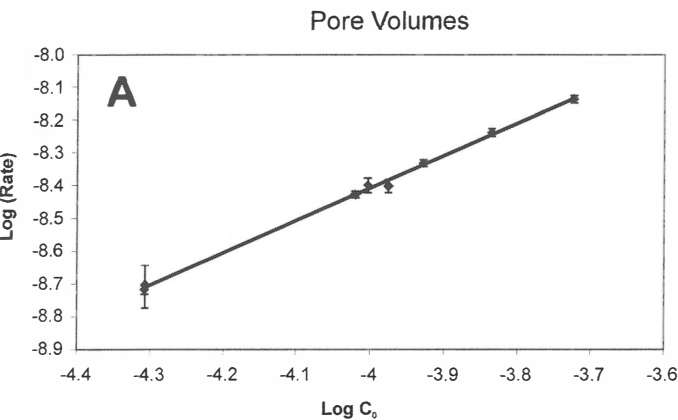The material balance for continuous stirred flow-through reactors, with a constant density solution, is

$$\frac{dn_j}{dt} = q(C_{j,in} - C_{j,out}) - R_j \quad (3)$$

where n_j is the number of moles of element j, t is the time, $C_{j,in}$ and $C_{j,out}$ are the input and output concentrations, q is the volumetric flow rate, and R_j is the extensive rate of adsorption of element j. For a reactor of volume V, the extensive rate of adsorption can be obtain, at any point in the experiment, by rearranging equation (3) as follows

$$R_j = -\frac{dC_{j,out}}{dt}V + q(C_{j,in} - C_{j,out}) \quad (4)$$

If the system is in steady-state, $\frac{dC_{j,out}}{dt} = 0$, and equation (4) is much simplified. Intensive rates of
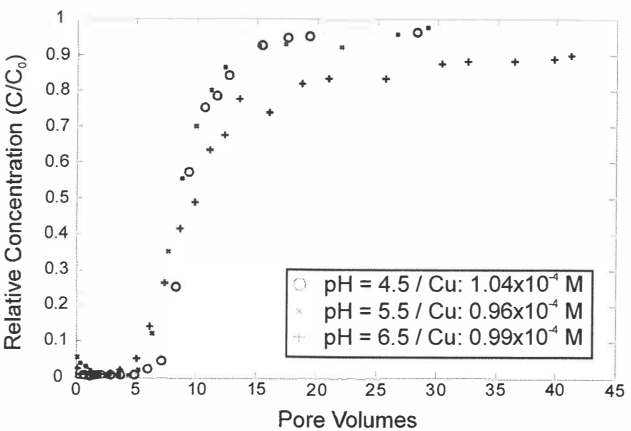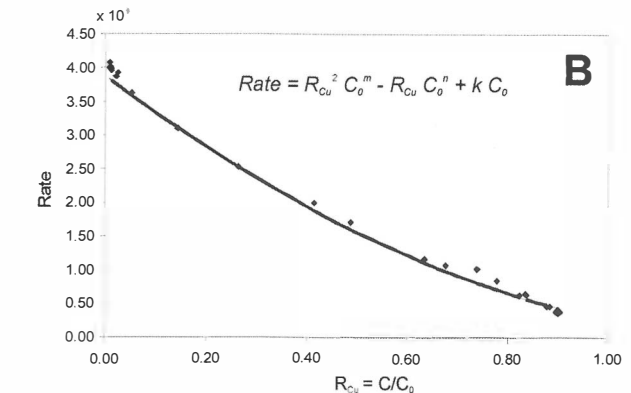

Figure 2: Outflow Cu concentrations (relative to inflow concentration, $C_0 \approx 10^{-4}$ M), as a function of pore volume (t=V/q) for different input solution pH. Ionic strength 10^{-4} M $KClO_4$ (pH = 4.5 and 5.5) and 10^{-3} M KNO_3 (pH = 6.5).

adsorption, r_j, are related to R_j by, $r_j = R_j/Nq$, where Nq is a normalising quantity such as surface area, volume of reactor, or mass of adsorbent. Computed rates in this work are all surface area normalised.

Initial adsorption experiments (Figure 2) show as main results the following: a) the system requires 1 to 2 h before reaching an initial steady state in which, independently of experimental initial conditions, Cu

*Figure 3: A: Least-squares fitting to the experimental steady-state adsorption rates as a function of initial Cu concentration, C_0; **B**: Non steady-state adsorption rates as a function of the ratio between outlet and inlet Cu concentrations; the rate decays according to an empirical model where* m *and* n *are exponents close to 2, and the zeroth order term is the steady-state adsorption rate (equation 5).*

adsorption rates are kept constant for 2 to 4 h, and the pH inside the reactor reaches 6 to 6.5; b) after this initial stage, the adsorption edge develops and the system attains an output Cu concentration equal to its input concentration within 20 to 30 h (for initial solutions with pH = 4.5 and 5.5); c) the higher the pH of the initial solution, the higher the adsorption capacity, and the longer the initial steady state; d) the adsorption edge curves for the experiments with pH 6.5 input solution and higher ionic strength develops earlier, but in these experiments the system did not reach saturation after 40 h (formation of surface precipitates is a likely hypothesis).

At steady state, and using equation (4), the surface area (SA) normalised rates of Cu adsorption were computed. A first order kinetics was adjusted to the computed values by least-squares fitting (Figure 3A):

$$(5)$$

$$r_{SA,Cu} = 3.50 \pm 0.56 \times 10^{-5} C_{Cu}^{0.99 \pm 0.02} \ (mol.m^{-2}.min^{-1}), \ r^2 = 0.997.$$

Non steady-state adsorption rates were also computed, and in all experiments the rate decays with the ratio between output and input Cu concentrations following an empirical second order polynomial with variable parameters m (2.08 – 2.19) and n (1.98 – 2.11) (Figure 3B).

INTERACTION WITH ORGANIC ACIDS AND DESORPTION RATES OF Cu

Monocarboxylic acids are among the most important organic components of landfill leachates, and for such reason have been a matter of interest for this and previous work (Gonçalves *et al.*, 2004). Experiments were done with hexanoic acid (5x′ 10⁻⁵ M), and no noticeable effect on Cu adsorption rates has been observed with solutions having an initial pH of 4.5 and 5.5. However, a slight decrease in Cu uptake has been noticed in the experiments at pH 6.5, nevertheless too close to experimental uncertainty to be taken as clear evidence for strong organic acid interaction in the Cu adsorption process.

The BTC experiments used both Cu solutions, and Cu and citric acid (both 50 mM) solutions in the same conditions, at pH 4.5 and 5.5, and ionic strengths of 10⁻³ M and 10⁻⁴ M (Figure 4). In these experiments, it is possible to compute steady-state desorption rates.

For the pH used in the BTC experiments, Cu forms predominantly the Cu(OH)Cit²⁻ complex, and in lesser amounts the CuCit⁻ complex. At pH 4.5 it is verified that although the presence of the citric acid decreases Cu adsorption, this decrease is not much different from the experiments with only Cu. Besides, at 10⁻⁴ M ionic strength the presence of citric acid caused an increase in total Cu adsorption. At pH 5.5 there is a markedly decrease in Cu adsorption. This is somewhat expectable since illite has a pH_{zpc} = 3.46, and the solution complex is likely to feel greater repulsion from the surface. Besides, the shape of the curve suggests that adsorption becomes diffusion controlled probably due to both electrostatic effects of the surface and the complex being a much larger molecule. In this case, ionic strength of the solution also controls the adsorption behaviour of Cu as one can see by inspection of both curves for the citric acid solution. The presence of citric acid also reduces the desorption rates of Cu relative to the same experimental conditions with only Cu. This somewhat difficulty in desorbing the complex, even at ionic strengths as low as 10⁻⁴ M suggests that the complex is more tightly bound to the surface than is Cu in the same conditions. The overall results are summarised in the table that follows.

ACKNOWLEDGMENTS

REFERENCES

Du Q., Sun Z., Forsling W. and Tang H (1997a). J. Colloid Interf. Sci., 187, 221-231.

Du Q., Sun Z., Forsling W. and Tang H (1997b). J. Colloid Interf. Sci., 187, 232-242.

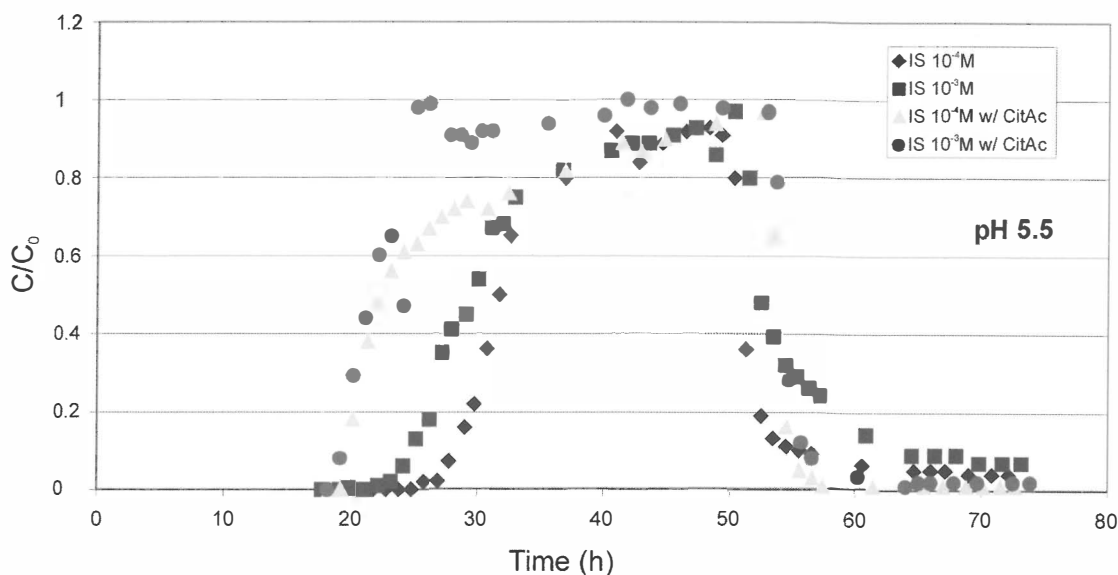Gonçalves M. A. (2004). PhD Thesis, Universidade de Lisboa, 211 pp. (unpublished)

Figure 4: Break through curves for the experiments at pH 5.5 and Cu solution with and without citric acid.

Gonçalves M. A., Nogueira J. M. F., Figueiras J., Putnis C. V. and Almeida C. (2004). Appl. Geochem. 19, 137-151.

Herbelin A. L. and Westall J. C. (1999) FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data. Dept. Chemistry, OSU.