

## Comparative Study of Cu<sup>2+</sup> Adsorption on Goethite, Hematite and Kaolinite: Mechanistic Modeling Approach

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The mechanisms of Cu<sup>2+</sup> adsorption onto goethite, hematite and kaolinite are different. Goethite and hematite showed a similar adsorption behavior (ionic-strength independent), but kaolinite gave somewhat different result (ionic-strength dependent). These experimental results were successfully simulated using a surface complexation model, TLM, which defines the inner- or outer-sphere complex. The chemical nature of Cu<sup>2+</sup> adsorption onto kaolinite was qualitatively identified by EPR spectroscopy.

### Introduction

Adsorption of metal ions in aqueous solution onto oxides and clay minerals has been a subject of interest in chemistry field and other research areas.<sup>1</sup> It is known to be an important process in various natural water systems<sup>2</sup> and becoming an increasingly important environmental issue in many countries. Iron oxides and kaolinite are widespread throughout the near-surface aquatic natural environment and play an important role to the fate of pollutant metal ions.

Although Cu<sup>2+</sup> adsorption on some minerals has been studied previously,<sup>3</sup> the mechanisms of adsorption have not been well understood because of the complex nature of adsorption phenomena at mineral/solution interfaces. Experimental sorption data have been described by various empirical means, including partition coefficients, isotherm equations, and conditional equilibrium constants.<sup>4</sup> Recently much effort has been made to develop a theoretical model for the adsorption at the mineral/water interface, and was successfully applied to several systems.<sup>5</sup> This approach might allow one to understand the adsorption mechanisms involved.

In this work, the effects of ionic strength on the adsorption of Cu<sup>2+</sup> onto goethite ( $\alpha$ -FeO(OH)), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and kaolinite were investigated, and the results were interpreted using surface complexation modeling (SCM) approach.

### Experimental

**Batch Sorption Experiment.** A number of mixtures were prepared with single minerals (2.0 g/L), copper nitrate ( $1.0 \times 10^{-4}$  M) and potassium nitrate (0.1 or 0.01 M) in 150 mL beakers. Goethite and hematite were purchased from High Purity Fine Chemical Inc. (Japan), and kaolinite (Georgia china clays) was supplied by Ward's company. All solutions were prepared from AR grade reagents and water with the resistivity of 18.3 M $\Omega$  cm (Milli-Q, Millipore).

The mixtures were allowed to stand overnight after the half an hour sonication (Decon, Ultrasonics Ltd.). The pH of the samples was then adjusted by the addition of KOH or HNO<sub>3</sub>. After a week equilibrium period, the final pH was determined, and an aliquot of the samples was withdrawn with a 10 mL plastic syringe then expressed through

a 0.22  $\mu$ m Millipore filter. The copper concentration in the filtrate was determined using ICP-AES (JY 50 P, Jobin yvon).

**EPR Measurements.** The aqueous solution containing kaolinite was transferred with syringe into a flat quartz cell, and the solution EPR spectra were recorded at room temperature on a Bruker 200 X-band spectrometer.

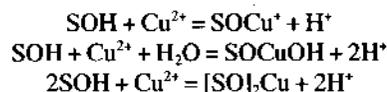
### Results and Discussion

**Surface Complexation Modeling.** The adsorption of metal ions onto mineral surfaces has been described by surface complexation modeling (SCM) approach.<sup>6</sup> The key of the SCM is to count chemical reactions between sorbing ions and surface functional groups in a manner similar to complexation reactions in a solution. The SCM used in this work is the modified version of the triple-layer model (TLM), which allows model analogues of both inner-sphere (placed in the  $\alpha$ -plane) and outer-sphere (placed in the  $\beta$ -plane) complexes to be formulated (see Figure 1).<sup>7</sup> In the TLM, weakly bonded ions are modeled as outer-sphere (ion-pair) complexes and strongly bonded ions as inner-sphere (surface coordination) complexes.<sup>8</sup>

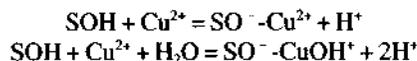
The surface complexation constants of Cu<sup>2+</sup> on goethite, hematite and kaolinite were fitted by the FITEQL program<sup>9</sup> from the sorption experimental data at a ionic strength of 0.01 M. The goodness of fit was quantified by the overall variance which is the weighted sum of the square residuals divided by the degree of freedom,  $\text{ss}/\text{df}$ .

For Cu<sup>2+</sup> sorption modeling, different sets of equilibria are tested. These equilibria are:

#### Inner-sphere complexes

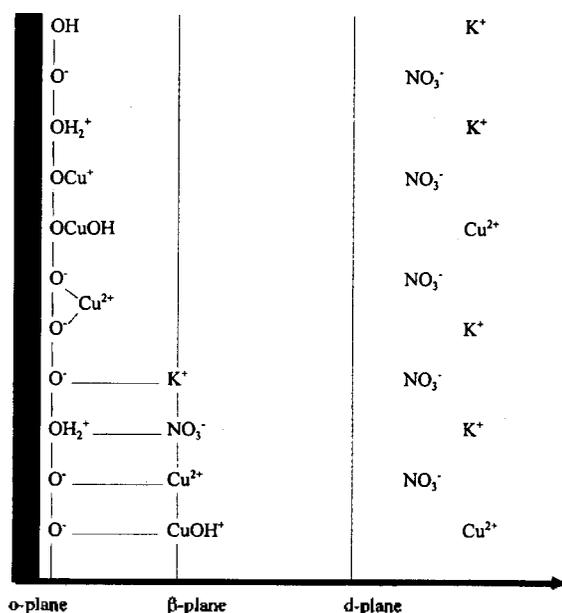


#### Outer-sphere complexes



where, SOH is the surface of the minerals.

The fitting results are given in Table 1, and the input parameters used for the FITEQL fitting are shown in Table



**Figure 1.** Schematic representation of inner- and outer-sphere  $\text{Cu}^{2+}$  complexes considered in this work; o-plane is mineral surface and location of inner-sphere complex.  $\beta$ -plane is location of outer-sphere complex. d-plane is distance of closest approach for freely moving ions in the diffuse layer.

2. These parameters were taken from the literature.<sup>10-13</sup> Using the best value determined, the percentage of adsorbed  $\text{Cu}^{2+}$  is calculated at both 0.1 M and 0.01 M  $\text{KNO}_3$  conditions.

**Adsorption on goethite.** The experimental results and modeling simulations of the adsorption of  $\text{Cu}^{2+}$  onto goethite are shown in Figure 2. An increase in ionic strength from 0.01 M to 0.1 M  $\text{KNO}_3$  had little effect on the adsorption of  $\text{Cu}^{2+}$  onto goethite. The simulated results using the inner-sphere complex only were in good agreement with the experimental data (see Figure 2a). Including the outer-sphere complex, however, the agreement is not as good as the inner-sphere case (see Figure 2b). These results indicate that  $\text{Cu}^{2+}$  forms strong bond (coordinative complex) with goethite surface. Kooner also found that the adsorption of  $\text{Cu}^{2+}$  onto goethite was not affected by the change in ionic strength.<sup>14,15</sup> Since the copper(II) ions which form inner-sphere complex are located in the o-plane, the change of background electrolyte ion (placed in the  $\beta$ -plane) con-

**Table 1.** Surface complexation constants of  $\text{Cu}^{2+}$  on goethite, hematite and kaolinite

Minerals	Reaction considered	log K	sos/df
<b>Goethite</b>			
model 1	$\text{SOH} + \text{Cu}^{2+} = \text{SOCu}^+ + \text{H}^+$	0.941	1.544
model 2	$\text{SOH} + \text{Cu}^{2+} = \text{SOCu}^+ + \text{H}^+$	0.4976	0.8613
	$\text{SOH} + \text{Cu}^{2+} + \text{H}_2\text{O} = \text{SO}^- - \text{CuOH}^+ + 2\text{H}^+$	-8.856	
<b>Hematite</b>	$\text{SOH} + \text{Cu}^{2+} = \text{SOCu}^+ + \text{H}^+$	0.2662	3.037
<b>Kaolinite</b>	$\text{AlOH} + \text{Cu}^{2+} = \text{AlOCu}^+ + \text{H}^+$	-4.443	10.01
	$\text{SiOH} + \text{Cu}^{2+} = \text{SiO}^- - \text{Cu}^{2+} + \text{H}^+$	0.1658	

AlOH aluminol site on kaolinite surface. SiOH silanol site on kaolinite surface.

centration does not influence the adsorption (see Figure 1).

**Adsorption on hematite.** The result of the  $\text{Cu}^{2+}$  adsorption on hematite is similar to that of goethite (see Figure 3). The adsorption was ionic-strength independent, and the experimental data were well simulated using the inner-sphere complex only. The adsorption edge (narrow range of pH where adsorption goes from near zero to almost complete adsorption) of hematite shifted slightly to a higher pH than that of goethite, and the surface complexation constant of  $\text{Cu}^{2+}$  for hematite is lower than that for goethite (see Table 1). These indicate that the affinity of hematite for  $\text{Cu}^{2+}$  is lower than that of goethite.

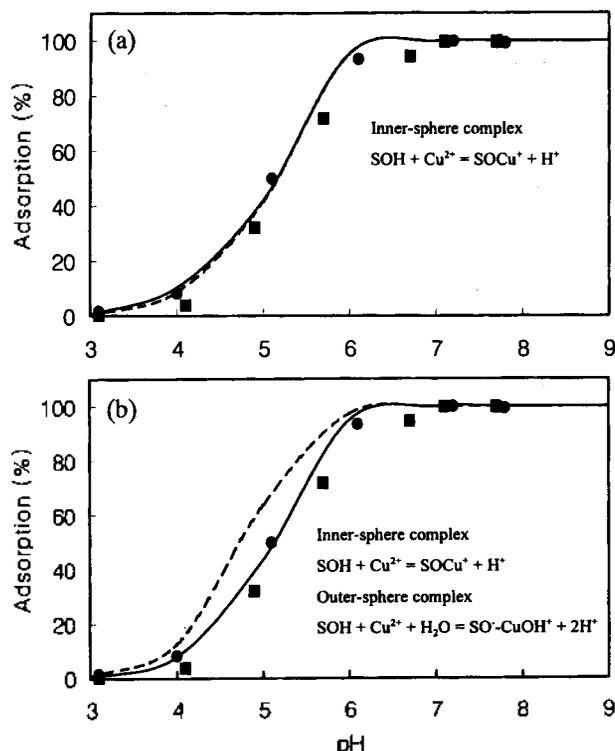
**Adsorption on kaolinite.** Contrary to the results of goethite and hematite, increasing the ionic strength substantially reduced the adsorption of  $\text{Cu}^{2+}$  onto kaolinite (see Figure 4). Kaolinite is a representative layered aluminosilicate mineral with the structure of tetrahedral (Si center) and octahedral (Al center) sheet in a 1:1 ratio.<sup>16</sup> The permanent structural charge of kaolinite is minor, hence cation adsorption takes place mainly at the proton-bearing surface functional groups such as silanols and aluminols exposed at the edge of the sheets.<sup>17,18</sup> And the pH dependent surface charge on kaolinite can be explained by proton donor-acceptor reactions occurring simultaneously on these groups.<sup>19,20</sup> Because of the above observations, two kinds of surface functional groups were used to fit the experimental data. And the silanol groups are assumed not to protonate at the pH values of the experiment.<sup>12</sup>

The best fit to the experimental data was obtained by using a combination of inner-sphere complex on the Al site and outer-sphere complex on the Si site (see Figure 4). The different complex types of the aluminol and silanol groups

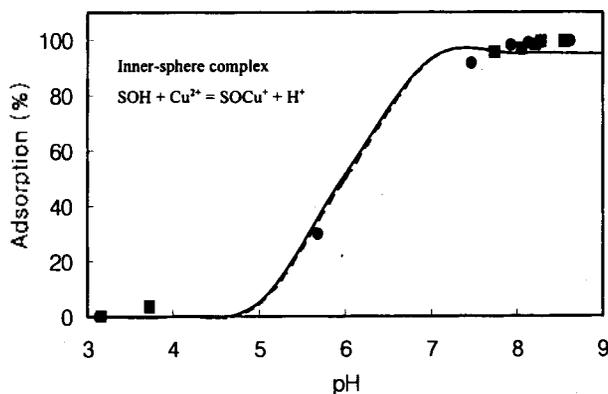
**Table 2.** The input parameter values of the FITEQL program

Parameter	Goethite	Hematite	Kaolinite	
<b>Surface reactions (log K)</b>				
$\text{SOH} + \text{H}^+ = \text{SOH}_2^+$	4.2	6.7	Aluminol 2.33	Silanol -NC
$\text{SOH} - \text{H}^+ = \text{SO}^-$	-10.5	-10.3	-5.28	-8.23
$\text{SOH} + \text{K}^+ - \text{H}^+ = \text{SO}^- - \text{K}^+$	-9.0	9.5	9.15	-1.75
$\text{SOH} + \text{NO}_3^- + \text{H}^+ = \text{SOH}^+ - \text{NO}_3^-$	6.2	7.5	NC	NC
<b>Inner-layer capacitance (<math>\text{F/m}^2</math>)</b>				
	1.1	0.9		2.4
<b>Outer-layer capacitance (<math>\text{F/m}^2</math>)</b>				
	0.2	0.2		0.2
<b>Surface area (<math>\text{m}^2/\text{g}</math>)</b>				
	48.0	44.6		7.99
<b>Site density (mol/l)</b>				
	$2.68 \times 10^{-3}$	$8.22 \times 10^{-4}$	$5.0 \times 10^{-4}$	$5.0 \times 10^{-4}$

NC not considered.

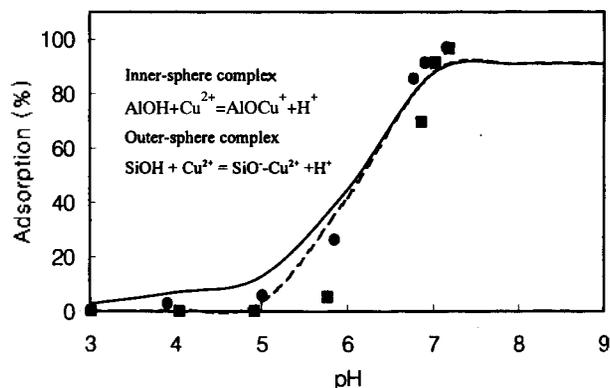


**Figure 2.** Adsorption of  $\text{Cu}^{2+}$  on goethite (a) model 1 (b) model 2; Points are experimental data;  $\bullet$  0.01 M  $\text{KNO}_3$ ,  $\blacksquare$  0.1 M  $\text{KNO}_3$ . Lines are data calculated using FITEQL; — 0.01 M  $\text{KNO}_3$ , --- 0.1 M  $\text{KNO}_3$ .



**Figure 3.** Adsorption  $\text{Cu}^{2+}$  on hematite; Points are experimental data;  $\bullet$  0.01 M  $\text{KNO}_3$ ,  $\blacksquare$  0.1 M  $\text{KNO}_3$ . Lines are data calculated using FITEQL; — 0.01 M  $\text{KNO}_3$ , --- 0.1 M  $\text{KNO}_3$ .

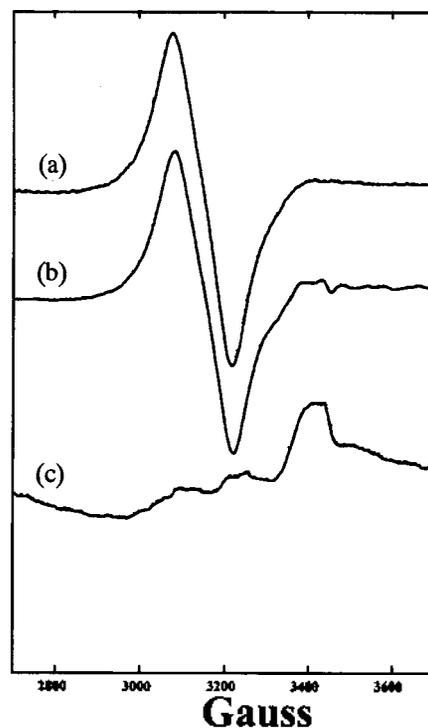
may be caused by the local crystal structure.<sup>12</sup> This result can be supported by recent work demonstrating the spectroscopic evidence of inner- and outer-sphere  $\text{Co}^{2+}$ -kaolinite complexes.<sup>21</sup> The simulations predicted the decrease of the  $\text{Cu}^{2+}$  adsorption with increasing ionic strength. This can be explained by the fact that outer-sphere complex is more sensitive than inner-sphere complex to ionic strength change since the outer-sphere complex is weakly bound to the surface. In the TLM, the background electrolyte ions are modeled to form outer-sphere complex, thus the electrolyte ions compete with the metal ions which form outer-sphere complex (see Figure 1). This phenomenon was also ob-



**Figure 4.** Adsorption of  $\text{Cu}^{2+}$  on kaolinite; Points are experimental data;  $\bullet$  0.01 M  $\text{KNO}_3$ ,  $\blacksquare$  0.1 M  $\text{KNO}_3$ . Lines are data calculated using FITEQL; --- 0.01 M  $\text{KNO}_3$ , --- 0.1 M  $\text{KNO}_3$ .

served in the case of  $\text{Sr}^{2+}$  and  $\text{UO}_2^{2+}$  adsorption onto kaolinite.<sup>22,23</sup>

**EPR Identification of Adsorption Reaction.** Adsorption can markedly affect the spectrum which is due to a change in the coordination environment and structure of the adsorbed metal complex. Copper(II) ion exists as the hexaquo species under normal natural water conditions. EPR spectroscopy can easily distinguish between free tumbling  $\text{Cu}^{2+}$  and immobilized adsorbed species. In free  $\text{Cu}^{2+}$  solution, the anisotropic contributions to the  $g$  and hyperfine coupling constants are averaged, resulting in simple isotropic peak (see Figure 5-a). However, in the adsorbed state, the anisotropic interactions contribute fully to the spectra, resulting in spectra more complex. EPR spectra in Figure 5 clearly show the main features of *in-situ*  $\text{Cu}^{2+}$  adsorption



**Figure 5.** EPR spectra (a) free  $\text{Cu}^{2+}$  solution, and  $\text{Cu}^{2+}$  in kaolinite suspensions. (b) at pH 4.5. (c) at pH 7.4.

reaction at  $\text{Cu}^{2+}$ /kaolinite interface. It allows a direct distinction between free  $\text{Cu}^{2+}$  and immobile adsorbed  $\text{Cu}^{2+}$  species (see Figure 5-b, c) in the *in-situ* reaction system. Small absorption peak ( $g_{\perp} \approx 2.07$ ) in Figure 5-b may be attributed to a formation of immobile  $\text{Cu}^{2+}$ -kaolinite surface complex at pH 4.5. The peaks from  $g_{\parallel}$  components are hidden in the main free  $\text{Cu}^{2+}$  peak. The results indicate that  $\text{Cu}^{2+}$  becomes more immobile (adsorbed) as pH increases. Complete analysis of EPR spectra has not been achieved because of its complex nature (due to different types of adsorption and peak broadening by inter ion interactions) of the system studied. However, EPR spectroscopy may be used as an aid in identifying the chemical nature of  $\text{Cu}^{2+}$  adsorption on mineral substrate in well defined systems.<sup>24,25</sup>

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