SURFACE COMPLEXATION MODELS FOR COPPER(II) ADSORPTION ON KAOLINITE

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Abstract : Adsorption experiments of Cu(II) to kaolinite were conducted to investigate the adsorption behavior of Cu(II) at a variety of aqueous conditions. Three electrostatic surface complexation models (i.e., Constant Capacitance Model (CCM), Diffuse Layer Model (DLM), and Triple Layer Model (TLM)) were used to simulate and predict the adsorption behavior of Cu(II) to kaolinite using MINTEQA2 program. The experimental data for adsorption edges of Cu(II) to kaolinite were compared to the modeling results predicted by surface complex models. The TLM among three surface complexation models showed excellent fitting results for Cu(II) adsorption data. These results suggest that TLM surface complexation model can successfully describe the adsorption behavior of Cu(II) to kaolinite. The speciation of copper ion at different pH conditions was calculated to investigate the dominant Cu ion species that lead to Cu(II) adsorption to kaolinite. The dominant species that caused the Cu(II) adsorption to kaolinite were $\equiv AlOCu^+$, $\equiv AlOHCu^{2+}$, and $\equiv(AlO)_2Cu$ for CCM and DLM, and $\equiv AlOCuOH$, $\equiv AlOCu^+$, and $\equiv AlOHCu^{2+}$ for TLM. The aluminol sites ($\equiv AlOH$) of kaolinite may have much stronger affinity of Cu(II) adsorption than silanol sites ($\equiv SiOH$). The hydrolytic complexes of Cu(II) on the kaolinite surfaces can be of much importance in Cu(II) adsorption to kaolinite.

Key Words : adsorption, constant capacitance model, copper(II), diffuse layer model, kaolinite, surface complexation model, triple layer model

INTRODUCTION

Adsorption onto mineral surfaces can play an important role in controlling the fate and transport of trace metals in natural aquatic systems. Adsorption behaviors of copper ion are of much concern because copper is not only widespread toxic metal in many contaminated subsurface environments but are also "soft or intermediately soft" toxic metals, which may contribute greatly to a high adsorptive preference of the metal on mineral surfaces. Cu(II) can be a potential metal to make a significant influence on adsorption behavior of organic and inorganics in aqueous

environments. A comprehensive understanding of adsorption of metal such as Cu(II) would be helpful in elucidating the biogeochemical behavior because adsorption reactions greatly affect their mobility, chemical reactivity, bioavailability and toxicity in biogeochemical systems. In addition, the studies of Cu(II) adsorption behavior can provide important information for remediating the sites contaminated with these pollutants.

A variety of attempts have been made to describe metal adsorption to environmental solids. Surface complexation models have been shown to be able to successfully describe the physicochemical properties of mineral surfaces and adsorption behavior of trace metals onto mineral surfaces. The surface complexation models used in describing metal adsorption to minerals generally consist of two types of models: electro-

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static surface complexation model (ESCM) and nonelectrostatic surface complexation model (NSCM). The ESCM describes electrostatic interactions as well as chemical reactions between solute and functional groups at solid surfaces while the NSCM represents only chemical reactions of interface region, excluding electrostatic interactions. An ESCM generally uses one of the following three conceptualizations of the structure of the electric double layer: constant capacitance model (CCM), diffuse layer model (DLM), and triple layer model (TLM), which are different in representing the interface of solid and liquid phases. Several researchers have applied the ESCM to the Cu(II) adsorption on mineral surfaces or natural sediments.[1-6] Shindler et. al. studied the Cu(II) adsorption to kaolinite and modeled the Cu(II) adsorption behavior to kaolinite.[1] In their study, however, the author did not consider the hydrolytic complexes (i.e., $\equiv$ SOCuOH) due to the hydrolysis reaction on the ampholytic surfaces of kaolinite. Hence, in their work, no hydrolytic complexes were included in the dominant species leading to the Cu(II) adsorption to kaolinite. Holm and Zhu also assumed hydrolytic complexes could not exist on the surfaces of kaolinite, which is about sorption of Cu(II) by kaolinite from landfill leachate-contaminated groundwater.[5] Recently, the hydrolytic complexes of Cu(II) have been reported to be important complex forms that lead to the Cu(II) adsorption on mineral surfaces such as calcium-montmorillonite and calcium-alginate.[2,3] In the present work, an attempt was made to assume all possible surface-metal complex species including hydrolytic complexes due to hydrolysis reaction of Cu ion to adequately simulate the Cu(II) adsorption behavior on kaolinite and investigate the dominant complex species affecting Cu(II) adsorption on kaolinite.

In this study, the adsorption behavior of Cu(II) to mineral surfaces was investigated at a variety of aqueous conditions. Three electrostatic surface complexation models (i.e., CCM, DLM, and TLM) were used to simulate and predict the

adsorption behavior of Cu(II) to kaolinite using MINTEQA2 Program. The experimental results of Cu(II) adsorption to kaolinite were compared to modeling results obtained by surface complex models to investigate how well the surface complexation model can predict the Cu(II) adsorption behavior to kaolinite.

MATERIAL AND METHODS

Sodium perchlorate ($NaClO_4$, crystals, 99.0%, EM Science, Gibbstown, NJ) was used to prepare pretreatment and background electrolyte solutions. In this study, perchlorate salts (i.e., $NaClO_4$) were employed in lieu of chloride salts (i.e., NaCl or KCl) to minimize the complexation of Cu(II) with anions in solution because perchlorate ion contains a low affinity with Cu(II) ion relative to chloride ion. Copper perchlorate ($Cu(ClO_4)_2$, crystals, Aldrich Chemical, Milwaukee, WI) was used as adsorbent. All solutions were prepared using double-distilled water (Mega-Pure System MP-6A, Corning, NY). The mineral used in this study was kaolinite (Kga-1b, Source Clay Minerals Repository, Univ. of Missouri Columbia, MO). The mineral was pretreated to remove amorphous iron oxides, and organic matter using dithionite-citrate-bicarbonate (DCB) and hydrogen peroxide.[7,8] In DCB treatment, 20 g of mineral was weighed into 250 mL plastic bottles and 80 ml of 0.3 M Na-citrate and 10 mL of 1 M $NaHCO_3$ were added. When the temperature in the water bath was brought to 75°C, 2 g Na-dithionite ($Na_2S_2O_4$) was added and stirred constantly. After the minerals were heated for another 15 min, they were then centrifuged for 30 min at 3,000 rpm to separate the soil and clear solution. The treated minerals with DCB treatment were used in H_2O_2 treatment. The 10 mL of 30% H_2O_2 was added to the sample in 250 mL plastic centrifuge tube. The minerals were allowed to stand overnight. Additional 10 ml of 30% H_2O_2 were added and placed into a water bath at a temperature slightly below 100 °C. When the reaction has subsided, the treated minerals were centrifuged for 30 min at 300

rpm.

Experimental Methods

The experiments for Cu(II) adsorption to mineral were performed in batch reactor systems. Fifty-milliliter polystyrene centrifuge tubes were used as batch reactors. Sorbent and background solution were added to the tubes as a suspension whose pH was previously adjusted to target pH with 0.5 N HClO$_4$ or NaOH, as required. The suspension equilibrated for at least four hr, enough time to hydrate the mineral surfaces, and the pH and ionic strength were readjusted, if necessary. Triplicate mineral suspensions were spiked with an appropriate amount of metal stock solutions. Control samples (metal + background solution, no sorbent) were prepared to quantify Cu(II) adsorption to the tube walls. All centrifuge tubes were agitated in the dark on an orbital shaker at 370 rpm and 20°C for 24 hr. Following equilibration, reactors were centrifuged

at 7,000 rpm for 30 min. Copper concentrations were analyzed by flame atomic absorption spectrometry using a Varian$^{®}$ Spectra AA 20 Plus spectrometer. The wavelength for copper was 327.4 nm.
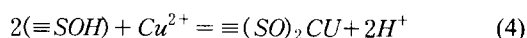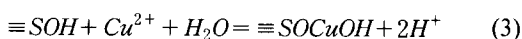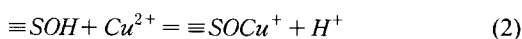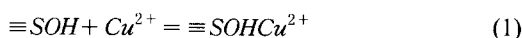
Modeling Methods

The experiments for adsorption edges of Cu(II) to kaolinite were conducted in the pH range of pH 3.5 to pH 7.0. Three electrostatic surface complexation models (i.e., CCM, DLM, and TLM) were used to predict and investigate the adsorption behavior of Cu(II) to kaolinite. The surface complexation modeling was conducted using MINTEQA2 program.[9] The experimental data for adsorption edges of Cu(II) to kaolinite were compared to the modeling results predicted by MINTEQA2 program. The model parameters (e.g., surface site density and equilibrium constants for surface reactions) for Cu(II)

Table 1. Surface complexation parameters incorporated into MINTEQA2 program for modeling Cu(II) adsorption on kaolinite.

Species	Value	Source
Surface area (m^2/g)	9.47	This study
Surface site density (sites/nm^2)	0.6	Sposito [10]
Inner layer capacitance (C$_1$, F/cm^2)	240	Riese [11]
Outer layer capacitance (C$_2$, F/cm^2)	20	Davis [12]
Surface complexation reactions		
	Log K	
$\equiv$SiOH^{2+} = $\equiv$SiOH + H$^+$	- 1.75	Riese [11]
$\equiv$SiOH = $\equiv$SiO$^-$ + H$^+$	- 6.25	Riese [11]
$\equiv$SiOH + Na$^+$ = $\equiv$(SiO$^-$ - Na$^+$)^0 + H	- 3.50	Riese [11]
$\equiv$AlOH^{2+} = $\equiv$AlOH + H$^+$	- 5.70	Davis and Leckie[12]
$\equiv$AlOH = $\equiv$AlO$^-$ + H$^+$	- 11.4	Davis and Leckie[12]
$\equiv$AlOH + Na$^+$ = $\equiv$(AlO$^-$ - Na$^+$)^0 + H$^+$	- 9.15	Davis and Leckie[12]
$\equiv$AlOH + ClO$_4^-$ + H$^+$ = $\equiv$(AlOH^{2+} - ClO$_4^-$)^0	- 7.90	Davis and Leckie[12]
$\equiv$SiOH + Cu^{2+} = $\equiv$(SiOH - Cu^{2+})^0	0.92	Stadler and Schindler[3]
$\equiv$SiOH + Cu^{2+} = $\equiv$(SiO$^-$ - Cu^{2+})+ + H$^+$	- 5.52	Schindler et. al.[1]
$\equiv$SiOH + Cu^{2+} + H$_2$O = $\equiv$(SiO$^-$ - CuOH$^+$)^0 + 2H$^+$	- 11.71	Stadler and Schindler[3]
2($\equiv$SiOH) + Cu^{2-} = $\equiv$(SiO$^-$)^2 - Cu^{2-})^0 + 2H$^+$	- 11.19	Schindler et. al.[1]
$\equiv$AlOH + Cu^{2+} = $\equiv$(AlOH - Cu^{2+})^0	4.34	Schindler et. al.[1]
$\equiv$AlOH + Cu^{2+} = $\equiv$(AlO$^-$ - Cu^{2+})$^-$ + H$^+$	- 2.1	Schindler et. al.[1]
$\equiv$AlOH + Cu^{2+} + H$_2$O = $\equiv$(AlO$^-$ - CuOH$^+$)^0 + 2H$^+$	- 8.29	Schindler et. al.[1]
2($\equiv$AlOH) + Cu^{2+} = $\equiv$((AlO$^-$)^2 - Cu^{2+})^0 + 2H$^+$	- 7.0	Schindler et. al. [1]
$\equiv$SiOH + Na$^+$ = $\equiv$(SiO$^-$ - Na$^+$)^0 + H$^+$	- 3.50	Schindler et. al.[1]

adsorption on kaolinite were retrieved from other literatures.[1,3,10~12] The model parameters incorporated into MINTEQA2 for modeling Cu(II) sorption on kaolinite were listed in Table 1. For adsorption model of Cu(II) to kaolinite, it was assumed that the Cu(II) could adsorb to both aluminol (=AlOH) and silanol (=SiOH) sites of kaolinite. In addition, the adsorption of Cu(II) on kaolinite was assumed to occur through several surface reactions as below;

$$\equiv SOH + Cu^{2+} = \equiv SOHCu^{2+} \tag{1}$$

$$\equiv SOH + Cu^{2+} = \equiv SOCu^{+} + H^{+} \tag{2}$$

$$\equiv SOH + Cu^{2+} + H_2O = \equiv SOCuOH + 2H^{+} \tag{3}$$

$$2(\equiv SOH) + Cu^{2+} = \equiv (SO)_2CU + 2H^{+} \tag{4}$$

Where $\equiv$SOH represents intrinsic surface functional group and $\equiv$SOHCu$^+$, $\equiv$SOCu$^+$, $\equiv$SOCuOH, $\equiv$(SO)$_2$Cu denote various types of Cu(II) sorbed surface sites

The hydrolytic complexes due to hydrolysis of metal are excluded in the mass law expression for the CCM and DLM because all surface complexes of CCM and DLM are assumed to be formed on the inner-sphere plane. Based on the theoretical hypotheses of CCM, DLM, and TLM, equations (1), (2), and (4) were used in the CCM and DLM calculations, while all equations (1), (2), (3), and (4) were used in the TLM calculations.

RESULTS AND DISCUSSION

Adsorption Model of Cu(II) to Kaolinite

Adsorption experiments of Cu(II) to kaolinite were conducted to investigate the adsorption behavior of Cu(II) at a variety of aqueous conditions. Figure 1 exhibits the experimental data and the model fitting curves for adsorption edges of Cu(II) with different Cu(II) concentration. The results of Cu(II) pH edges in Figure 1
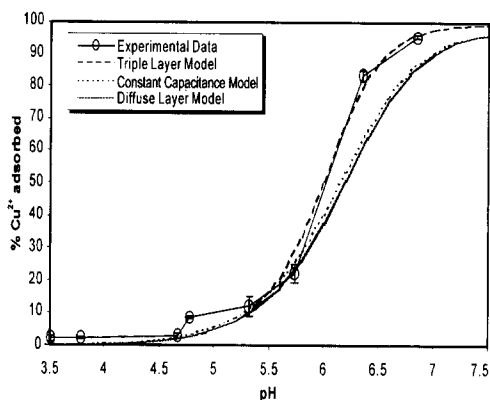

Figure 1. Fitting curves for the adsorption edges of Cu(II) with the three different surface complexation models for kaolinite. Some error bars for triplicate samples are shown smaller than the symbols.

indicate that the adsorption of Cu(II) to kaolinite is strongly pH dependent. At higher zone than pH 7.0, the most amount of Cu(II) in solution were adsorbed to kaolinite mineral. The TLM surface complexation model in Figure 1 shows excellent fitting results for Cu(II) sorption data. The calculated Cu(II) adsorptions with CCM and DLM, however, were in poor agreement with the experimental data. These results suggest that TLM surface complexation model can more adequately describe the adsorption behavior of Cu(II) to kaolinite than other surface complexation models, CCM and DLM. The presence of hydrolytic complexes considered in complexation equations of the TLM might account for more adequate prediction of TLM because the hydrolytic complexes due to hydrolysis reaction are not included in CCM and DLM.

The major species affecting Cu(II) adsorption to kaolinite were investigated with varying the complexation equations in mass law equilibria of TLM. The TLM surface complexation models without hydroxo complexes, silanol complexes, and bidentate complexes were assumed to evaluate the influence of the major Cu ion species on simulating the Cu(II) adsorption to kaolinite. The Cu(II) adsorbed % data from experiments were compared with the calculated results using TLM with variously assumed complexation equations.

The comparison results were represented in Figure 2. The surface complexation models without equation (3), (4), and silanol surface complexes represent the TLM surface complexation models without hydroxo complexes, bidentate complexes, and silanol complexes, respectively. Figure 2 shows that the model calculations by surface sites without hydrolytic reactions are not in good agreement with the experimental data. This result indicates the importance of the hydrolytic complexation of Copper ion for Cu(II) adsorption to kaolinite. A pivotal role of hydrolytic complexes for the Cu(II) adsorption to kaolinite might be attributed to high hydration energy of Cu ion in solution. Ions with higher hydration energy tend to have highly coordinated forms with water.[13] Copper ion with high hydration energy is so reactive that it is readily able to form hydrated complexes in aquatic systems. Hence, the presence of the hydrated forms of Cu ion in solution can lead to the predominant hydrolytic complexation of Cu ion on kaolinite surfaces.

In Figure 2, it is shown that the adsorption edge graphs of the TLMs without silanol and bidentate complexes nearly fell down on that of the original TLM including all assumed surface complexes, which means that the predicted models by surface sites without bidentate and silanol complexes were almost same as the original TLM surface complexation model. These observations suggest that bidentate complexes form to a very small extent in comparison to 1:1 monodentate complexes. In addition, these results imply that aluminol surface sites can be of more importance in Cu(II) adsorption to kaolinite than silanol surface sites. This modeling result indicates that TLM surface complexation model simulating hydrolytic complexation reactions of Cu ions can provide a good representation of the experimental data.

Speciation and Complexation of Cu ion on Kaolinite Surfaces

The species of Cu ion with varying pH condition were investigated to understand what Cu species were adsorbed to kaolinite at different pH condition. The speciation of Cu ion at different pH conditions was calculated based on the modeling results using MINTEQA2 program. Figure 3, 4, and 5 show the speciation diagram of Cu ion in the system Kaolinite-Cu^{2+}-H^+ for CCM, DLM, and TLM, respectively. The dominant species that caused the Cu(II) adsorption to kaolinite were $\equiv AlOHCu^{2+}$, $\equiv (AlO)_2Cu$, and $\equiv AlOCu^+$ for CCM and DLM and $\equiv AlOHCu^{2+}$, $\equiv AlOCuOH$, and $\equiv AlOCu^+$ for TLM. The three figures indicate that aluminol sites ($\equiv AlOH$) have much stronger affinity of Cu(II) adsorption than silanol sites ($\equiv SiOH$). In other words, this fact means that most adsorption of Cu(II) to kaolinite may occur on aluminol sites. This strong affinity of aluminol sites for Cu(II) adsorption was found in other studies,[3,14] which is about Cu(II) adsorption to Ca-montmorillonite with both aluminol and silanol sites. At pH < 6.0 ~6.5, Copper ion exists in the from of free Cu^{2+}. At pH > 6.5, $\equiv AlOCuOH$ was predominant species on the kaolinite surface for TLM. This result suggests that $\equiv AlOCuOH$ species can greatly control the Cu(II) adsorption to kaolinite at pH > 6.5 condition. Although the intermediate species $\equiv AlOCu^+$ and $\equiv AlOHCu^{2+}$ also affected the adsorption behavior of Cu(II) to kaolinite, their effects were small relative to the species $\equiv AlOCuOH$ at pH > 6.5.
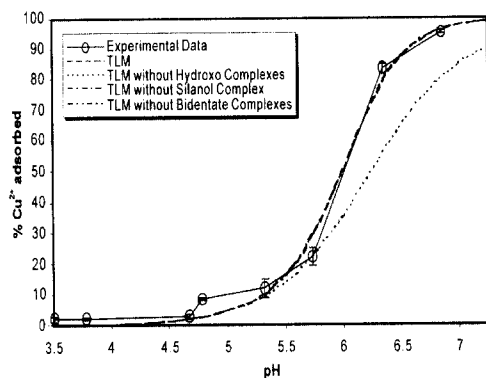

Figure 2. Fitting curves for the adsorption edges of Cu(II) with TLM surface complexation model including different type of complexation equations for kaolinite. Some error bars for triplicate samples are shown smaller than the symbols.

In Figure 3 and 4, the dominant Cu ion species for CCM and DLM become $\equiv AlOHCu^{2-}$, $\equiv AlOCu^+$, and $\equiv (AlO)_2Cu$ in the range of pH 6~6.5, pH 6.5~8, and pH > 8, respectively. Both CCM and DLM showed different speciation of Cu ion at a wide range of pH compared with TLM. These observations might result from the electrostatic difference of the surface complexation models. The CCM and DLM define specific adsorption of all ions on the inner-sphere plane.
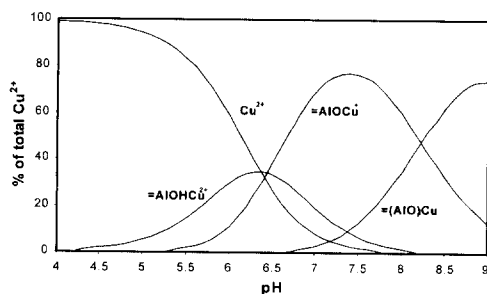

Figure 3. Speciation diagram of the system Kaolinite - Cu^{2+} - H^+ with varying pH condition for Constant Capacitance Model.
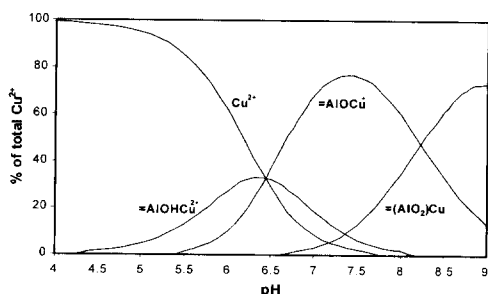

Figure 4. Speciation diagram of the system Kaolinite - Cu^{2+} - H^+ with varying pH condition for Diffuse Layer Model.
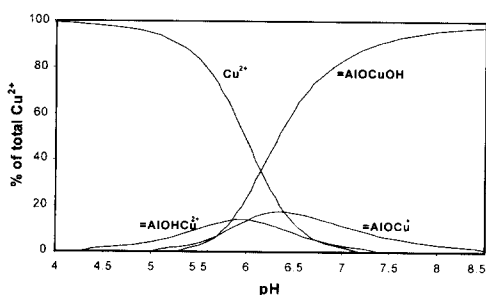

Figure 5. Speciation diagram of the system Kaolinite - Cu^{2+} - H^+ with varying pH condition for Triple Layer Model.

However, in TLM, protonation and deprotonation of surface sites are assigned to the inner-sphere plane and specifically adsorbed ions assigned to the outer-sphere planes.

Schindler et. al. reported that the dominant species leading to the Cu(II) adsorption to kaolinite were mono-dentate (i.e., $\equiv SOCu^+$) or bi-dentate surface complexes (i.e., $\equiv (SO)_2Cu$) on the kaolinite surfaces in the pH range of 6~7.[1] The dissimilarity of Cu ion species between our calculations and his calculations might result from the differently assumed Cu(II) surface complexation reactions in mass law expressions for the Cu(II) adsorption to kaolinite. In his study, the hydrolytic complexes such as $\equiv AlOCuOH$ were not included in the surface equilibria. Davis and Leckie showed that calculations with surface reactions involving hydrolytic complexes of metal ions were more consistent with experimental adsorption data than complexation by surface sites without hydrolytic surface reactions.[12] The results of this study as to the dominant Cu ion species affecting Cu(II) adsorption are supported by his observation. Hence, it can be concluded that the hydrolytic complexes of Cu(II) can be of much importance in Cu(II) adsorption on kaolinite.

CONCLUSIONS

Three electrostatic surface complexation models (i.e., CCM, DLM, and TLM) were used to simulate and predict the adsorption behavior of Cu(II) to kaolinite. The TLM among three surface complexation models (i.e., CCM, DLM, and TLM) showed excellent fitting results for Cu(II) adsorption data. These results suggest that TLM surface complexation model can successfully describe the adsorption behavior of Cu(II) to kaolinite. The speciation of Cu ion at different pH conditions was calculated to investigate the dominant Cu ion species that lead to Cu(II) adsorption to kaolinite. The dominant species that caused the Cu(II) adsorption to kaolinite were $\equiv AlOCu^+$, $\equiv AlOHCu^{2+}$, and $\equiv (AlO)_2Cu$

for CCM and DLM and $\equiv AlOCuOH$, $\equiv AlOCu^+$, and $\equiv AlOHCu^{2+}$ for TLM. The aluminol sites ($\equiv AlOH$) of kaolinite may have much stronger affinity of Cu(II) adsorption than silanol sites ($\equiv SiOH$). The hydrolytic complexes of Cu(II) on the kaolinite surfaces can be of much importance in Cu(II) adsorption to kaolinite.

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