ADSORPTION CHARACTERISTICS OF Cu(II) ON HUMUS–KAOLIN COMPLEXES

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Abstract—The sorption of Cu(II) was investigated on synthetic humus–kaolin complexes. Two groups of humic fractions were compared to investigate the effect of molar mass on the Cu(II) adsorption capacity. Another approach was to compare the capacities of humic acid (HA) and fulvic acid (FA) to adsorb Cu(II). The adsorption capacity of fulvic acid on kaolin is smaller than that of humic acid. The adsorption behavior of fulvic acid on kaolin can be described by a Langmuir-type isotherm. However, the adsorption isotherm of humic acid on kaolin exhibits non-Langmuir behavior. The results showed the affinity of Cu(II) on humic acid was greater than by fulvic acid. However, the affinity of Cu(II) adsorption by humic acid with large molar mass was equal to that by humic acid with small molar mass. A modified model incorporating a proton competition coefficient can differentiate the competitive effect from Cu(II) adsorption. A constant (K_m) independent of pH was derived from this model. HA–Kaolin complex has a greater Cu(II) affinity constant that FA–Kaolin complex according to models with either a single-site or a continuous distribution.

Key words—adsorption, copper, humic acid, kaolin

INTRODUCTION

The composition of natural soil varies depending on geochemical and climatic environments. Soils from varied sources have varied adsorption characteristics. The importance of organic matter (humus) is clearly recognized to be a major factor to control the physical and chemical properties of soils (Wershaw, 1993). Therefore, it is difficult to compare experimental data from metal adsorption in soils without controlling the consistency of organic coatings on the soil. The intensity of metal sorption is dependent on the origin, the molar mass (MM), and the molecular configuration of the humic coatings on the soil. As metal stability constants differ by several orders of magnitude for the mass experimental conditions (Stevenson and Fitch, 1986).

The artificial preparation of soil in order to represent a substitute for general soil has been made in the measurement of chemical adsorption in recent years. Preparations for this purpose include the adsorption/coating method (Kishi, 1988; Murphy *et al.*, 1990) and the evaporation method (Rebhun *et al.*, 1992). However, work on the interactions between hydrophobic organic compounds and artificial soils has been limited.

In this work, an attempt has been made to use commercially available substances to prepare "synthetic" soils with known and controlled compo-

sitions, and to replace natural soil in the adsorption experiment. A known humic acid has been separated into two fractions according to the molecular size. Humic substances of four varied mass or sources were coated into kaolin surfaces with adequate methods in order to prepare artificial humus–kaolin complexes. Complexes containing the same organic content have been compared for their Cu(II) affinity. The competition of hydrogen ion and the heterogeneity of humus–kaolin surface is included in modelling Cu(II) adsorption in these systems.

MODEL DEVELOPMENT

The metal ion becomes adsorbed onto the soil surface, that is, onto a complex-forming group on the soil surface (mostly onto organic coatings). Adsorption equilibria that are in principle similar to oxide surfaces can describe the extent of metal affinity to soil surfaces:

$$S + H^+ = S-H \tag{1}$$

$$S + M^{2+} = S-M \text{ or}$$

$$2S + M^{2+} = 2S-M. \tag{2}$$
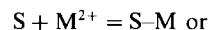
After metal ions adsorb onto the solid surface, the surface site may be classified as unoccupied (free) site {S}, proton-occupied {S–H}, and metal-occupied (S–M and 2S–M). In fact, H^+ behaves as a competitive ion in this metallic adsorption system for a potentially active site. Hence, pH is a major parameter

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to control metallic adsorption. Equations (1) and (2) present metal ions and proton ions that compete for the free affinity site, S, which including 1:1 or 2:1 binding type. In this scheme, we assume that one metal ion can occupy one site or two sites.

According to equations (1) and (2), one can define the corresponding equilibrium constants, K_h (proton affinity) and K_m (metal affinity) under assumption that the affinities of hydrogen ion and metal ions toward all sites are identical:

$$K_h = \frac{\{S-H\}}{\{S-\}[H]} \tag{3}$$

$$K_m = \frac{\{S-M\}}{\{S-\}[M]}. \tag{4}$$

Na^+ in a solid–liquid system is excluded from the vicinity of the adsorbent due to the Donnan potential and the inability of Na^+ to compete with proton and metal ions for the adsorption sites (Gamble et al., 1983). Alkali metal ions form complex with few ligand (Tobin et al., 1984). As mentioned before, metal-binding sites in soil may be classified into three groups in a metal–soil system: an unoccupied (free) site, a site occupied by metal, and a site occupied by a proton (Huang et al., 1991). Therefore, it is assumed that no cations other than M^{2+} and H^+ can occupy the sites; the total number of sites, Γ_{max}, is defined as

$$\Gamma_{max} = \{S-M\} + \{S-H\} + \{S-\}. \tag{5}$$

Combining equations (3), (4) and (5) gives an adsorption model for a single-site as follows:

$$\{S-M\} = \frac{\Gamma_i K_{mi}[M]}{1 + K_{mi}[M] + K_{hi}[H]}. \tag{6}$$

According to a Scatchard plot (mass/law plot), i.e. $\{S-M\}/[M]$ vs $\{S-M\}$, equation (6) becomes rearranged as

$$\frac{\{S-M\}}{[M]} = \frac{\{S-M\}K_m}{1 + K_h[H]} + \frac{\Gamma_{max}K_m}{1 + K_h[H]}. \tag{7}$$

The conditional stability constant K_m^c is a function of proton concentration, i.e. $K_m^c = K_m/1 + K_h[H]$. The term $1 + K_h[H]$ is called the proton competition coefficient. The proton stability constant, K_h, can be derived from equation (8), as

$$\frac{\{S-H\}}{[H^+]} = -K_h\{S-H\} + K_h\Gamma_{max}. \tag{8}$$

Organic coatings on soil consist of adsorption sites of several types. When a metal ion is introduced into the soil system, adsorption may occur at any site, either a mineral or an organic site. Those sites with high affinity for the metal ions become occupied first. In this case, the Scatchard plot of equation (7) may not give a linear relationship; more than one linear relationship may occur. With the assumption that each specific site has a binding constant, K_m, and with each corresponding capacity denoted Γ_i, a split Langmuir isotherm refers to separate linear isotherm regions representing distinct sites, which may be summed up into a single isotherm [equation (9)] as

$$\{S-M\} = \Sigma\left\{\frac{\Gamma_i K_{mi}[M]}{1 + K_{mi}[M] + K_{hi}[H]}\right\}. \tag{9}$$

When metal adsorption occurs at a constant pH, K_{hi} may be replaced by an apparent constant K_h^a that is obtained from the gradient of the proton titration curve at a given proton concentration (pH).

EXPERIMENTAL

Preparation of humic and fulvic acid

A humic acid concentrate (Na-salt from Aldrich Chemical Co., U.S.A.) was prepared by dissolving humic acid powder in pure water (Millipore Q-water), adjusted to pH 10 with NaOH (5 N). After stirring one hour, the solution was then filtered through 0.45-μm filter paper. This procedure presumably reduced the concentration of any dissolved metal impurities by alkaline precipitation of the metal hydroxide species. Chemical analysis of humic acid available from Aldrich performed by Narkis and Rebhun (1975) gave the composition as shown in Table 1.

Humic acid in the concentrate was divided into two fractions by gel permeation chromatography (GPC) with Sephadex G-75 (medium, Pharmacia, Sweden) packed as a wet slurry in a 2.6-cm dia column of 40-cm length. The eluent (10^{-4} M NaClO$_4$ solution adjusted to pH 7.0) flowed

Table 1. Chemical properties of Aldrich's humic acid and IHSS reference humic substances

	Humic acid (Aldrich)	Soil humic acid (IHSS)	Soil fulvic acid (IHSS)
Carboxyl C (190–165 ppm)	—	18	25
Aromatic C (90–165 ppm)	—	50	30
Aliphatic C (0–90 ppm)	—	22	31
C	58.99	57.47	50.08
H	3.95	3.75	3.98
O	36.35	33.39	42.26
N	0.60	4.14	2.66
S	—	0.41	0.62
P	—	0.32	0.05

Unit is in percentage.
—: Data not available.

at 24 ml/h. An aliquot (2 ml) of the concentrate was injected into the column and collected in two fractions, which were called the high and low molar mass of humic acid [Ha(H) and HA(L), respectively]. In addition to Na-salt of humic acid, well characterized soil humic acid and soil fulvic acid obtained from the International Humic Substances Society (IHSS) [represented as HA(S) and FA(S), respectively] were used without further purification. The distributions of carbon functional groups and the elemental analysis of those humic and fulvic acid are also shown in Table 1.

The quantities of humic acid were determined by the measurement of total organic carbon with a TOC analyzer (Dohrmann DC-180). The adsorption experiment was conducted with kaolin of constant content (50 mg/100 ml) and the humic acid with varied content.

Synthetic soil preparation

Dissolved humic acid (Aldrich Chemicals), either large or small molar mass, resulted in partial flocculation at pH < 5.5. In order to prepare synthetic soil with two fractions of humic acid, a precalculated amount of HA(H) or HA(L) concentrate was added to a suspension of kaolin, and mixed on a hot plate. Following adjustment of the suspension to 5.5 with $HClO_4$, the suspension was evaporated to dryness on a vacuum rotary evaporator. The residuals crushed to a homogeneous brown powder were regarded as the "synthetic" soil.

Another method to prepare synthetic soils was coating of humic [HA(S)] and fulvic acid [FA(S)] onto kaolin in a batch adsorption experiment. A parallel blank test was also conducted to assure the dissolved condition of humic acid during the adsorption experiment. In this experiment we found that the two acids maintained the dissolved condition about pH 5.5. According to the adsorption isotherm, it was possible to design an operation condition to acquire the same amount of organic substance coated on kaolin. "Synthetic" soils prepared according to this method are denoted HA(S)-kaolin and FA(S)-kaolin. After coating was completed, the suspensions were centrifuged at 6000 rpm for 10 min. The precipitates were collected, dried in an oven at 45°C, and stored for further experiments. The organic content of this "synthetic" soils was then obtained according to its adsorption capacity.

Adsorption of Cu(II) onto humus–kaolin complex

The capacity of adsorption by Cu(II) onto the humus–kaolin complex was assayed by alkalimetric/metal titration with the increment of Cu(II) loading (from 10^{-6} M to 10^{-4} M) in the ionic strength solution ($NaClO_4$ to give $I = 0.01$ M), distilled-deionized water and humic–kaolin solution. The pH was kept at 5.5 ± 0.02 throughout the experiment with the addition of $HClO_4$ or NaOH. During pH adjustment, the sample was purged with N_2 gas to eliminate the carbonate effect in solution. The samples were then agitated in a temperature-controlled reaction cell (200 ml) at 25 + 1°C. After addition of each increment of Cu(II) ion, at least 10 min passed to allow to obtain a stable electrode potential.

RESULTS AND DISCUSSION

Figure 1 illustrates the distribution of molar mass of humic acid. The chromatogram shows a continuous distribution in the range of isolation by Sephadex G-75 (MM. 3000–MM. 80000 g). However, it was reasonably successful in isolating compounds having MM. >6000 g and those with MM. between 3000 and 6000 g. Two fractions are denoted according to MM. of humic acid to be large [HA(H)] or small [HA(L)]. The humic acid was found to be partially flocculated below pH 6.5. Therefore, "synthetic soil"
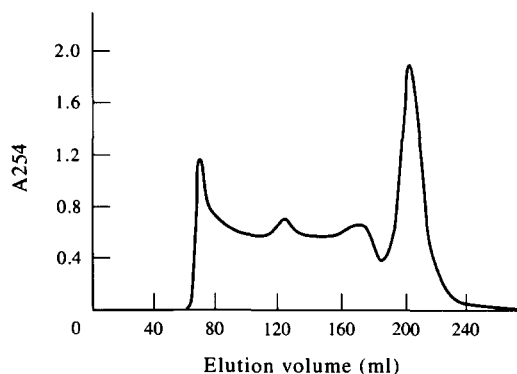

Fig. 1. Fraction of Aldrich's humic acid on GPC with Sephadex G-75.

was prepared according to the evaporation method rather than the adsorption method. The synthetic soils were prepared containing 1% of organic matter.

Adsorption isotherms of IHSS reference humic acid [HA(S)] and fulvic acid [FA(S)] on kaolin are shown in Fig. 2. The adsorption behavior of fulvic acid is described as an isotherm of the Langmuir type; it indicates that fulvic acid was coated onto the kaolin as a monolayer adsorption. The adsorption isotherm of humic acid on kaolin exhibited a non-Langmuir behavior; this phenomenon occurs since hydrophobic end of dissolved humic acid can interact with that of adsorbed humic acid, thereby resulting in further adsorption (Murphy et al., 1990).

Figure 2 also shows that the adsorption capacity of fulvic acid on kaolin was smaller than humic acid at a small surface coverage. With increasing surface coverage, the adsorption strength of humic acid decreased because of the shielding effect from the coated humic acid on the neighboring site. After covering as a first layer on kaolin, humic acid then forms a second layer outside the first layer with the hydrophobic interaction. Unlike humic acid, fulvic acid adsorbed onto kaolin according to Langmuir behavior to reach a maximum adsorption capacity. The "synthetic" soils were then prepared according to
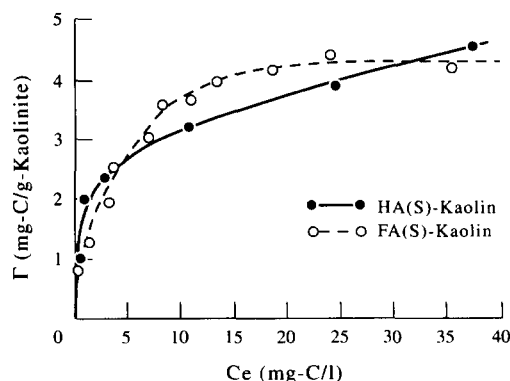

Fig. 2. Adsorption isotherms of IHSS reference humic acid and fulvic acid on the kaolin: HA(S), humic acid; FA(S), fulvic acid.
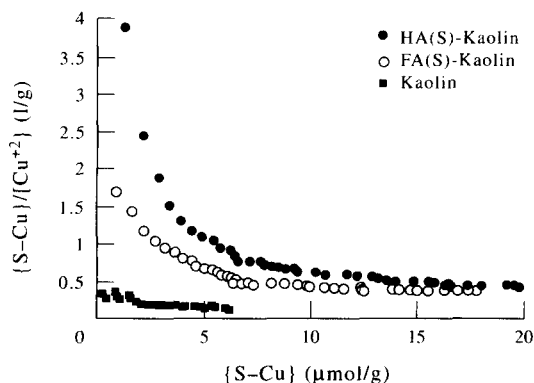
Fig. 3. The Scatchard plot for Cu(II) affinity with kaolin, HA(S)-kaolin complex, and FA(S)-kaolin complex.

Fig. 4. The relationship between K_m^c and {S–Cu} of Cu(II) affinity with the HA(H)-kaolin complex and the HA(L)-kaolin complex.

adsorption isotherms. The intersection point of two isotherms was applied to design experimental conditions, so as to prepare an equal carbon amount of two organic on kaolin. After adsorption, HA(S)- and FA(S)-complexes were washed by using NaClO₄ (0.01 M, 100 ml). TOC of the washing reagent is < 1 ppm, which is near TOC value of the blank test. Hence humic substances adsorbed onto kaolin are not desorbed (washed out) by NaClO₄ solution (0.01 M). The organic content of those synthetic soils is calculated to be 0.43% from the data in Fig. 2.

The approach of a Scatchard plot is the most popular method for graphical analysis of metal adsorption experiments. Adsorption of Cu(II) by four humus–kaolin complexes was performed at a given pH and ionic strength. Typical adsorption data were analyzed by a Scatchard plot shown in Fig. 3. The concave-up curves of the Scatchard plots for HA(S) and FA(S) show that adsorption of the first metal ion has a greater apparent affinity than that of subsequent metal ions. A reasonable explanation is that the presence of multiple classes of sites or an electrostatic effect causes this phenomenon (Stevenson and Chen, 1991). Figure 3 also shows a straight line of a Scatchard plot for Cu(II) affinity with kaolin, indicating a homogeneous surface of kaolin.

In order to describe the Cu(II) adsorption strength from this heterogeneous surface system, various values of K_m^c were acquired from the slope of Scatchard plots at varied extents of Cu(II) binding. The relationships between K_m^c and {S–Cu} were arranged and plotted as illustrated in Figs 4 and 5. Hence, adsorption constants decrease with increasing extent of adsorption. These constants acquired from the plot involve functions of pH and surface coverage (i.e. they are not thermodynamic constants). The result also shows that adsorption behaviors of both HA(H)-kaolinite and HA(L)-kaolinite are similar. However, the adsorption constants of HA(S)-kaolin are significantly greater than FA(S)-kaolin over the whole range of surface coverage. Non-linear regression (Wilkinson, 1988) was applied to generate the polynomial equations to relate log K_m^c to {S–Cu}
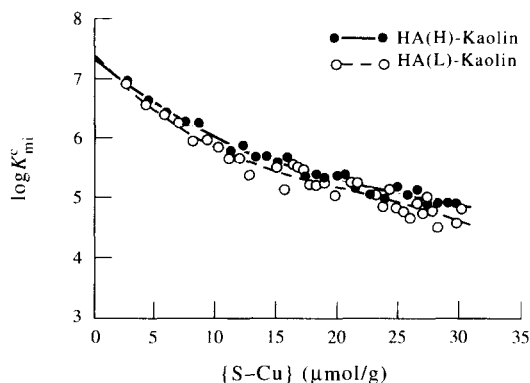
(Table 2). These equations simply describe the change of adsorption energy, but failed to indicate the type of binding. For instance, monodentate binding of Cu(II) with a carboxyl group and a bidentate complex of Cu(II) with two carboxyl groups may occur simultaneously.

Table 2 shows the Cu(II) affinity constant K_m^c or K_{mi}^c, maximum affinity capacity of pure kaolin and an organic-coated kaolin at a given condition. Only a single-site model was applied to describe the affinity of Cu(II) onto kaolin due to its homogeneous surface. Humic coatings of high molar mass [HA(H)] contain greater Cu(II) affinity capacity than humic coatings of low molar mass [HA(L)], but these affinity constants are almost equal. Hence both HA(H) and HA(L) containing similar functional groups result in an equal affinity constant; HA(H) contains a greater density of sites, thereby resulting in a greater maximum affinity capacity. The affinity of Cu(II) toward an amino group is greater than toward a carboxyl or phenolic group, and the binding of Cu(II) toward phosphate groups is also significant (Motschi, 1987; Motschi and McEvoy, 1985). According to the binding result (Table 2), the greater constant for adsorption of Cu(II) on HA(S)-kaolin than on
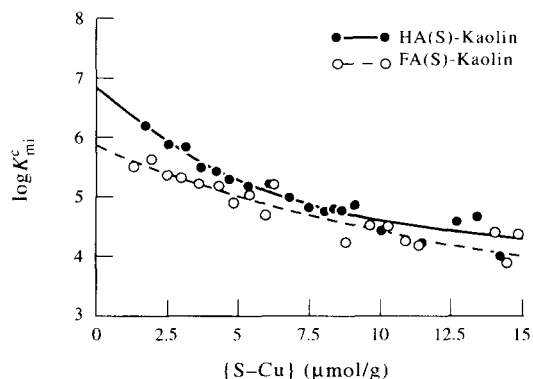

Fig. 5. The relationship between K_m^c and {S–Cu} of Cu(II) affinity with the HA(S)-kaolin complex and the FA(S)-kaolin complex.

Table 2. The analysis of Cu(II) adsorption constant for the humus–kaolin complex at pH 5.5

Humus–kaolin complexes	Single-site model		Continuous distribution model $\log K^c_{mi} = f(v)$
	Γ_{max}	$\log K^c_m$	
Kaolin	13.064	4.26	—
HA(H)–kaolin	40.951	5.12	$\log K^c_{mi}$ 7.342 $- 0.1693v + 0.00426v^2 - 0.00004565v^3$
HA(L)–kaolin	32.003	5.185	$\log K^c_{mi} = 7.41 - 0.2242v + 0.00802v^2 - 0.000122v^3$
HA(S)–kaolin	31.694	4.481	$\log K^c_{mi} = 6.89 - 0.43v + 0.02706v^2 0.0006612v^3$
FA(S)–kaolin	34.852	4.255	$\log K^c_{mi} = 5.888 - 0.1995v + 0.006381v^2 - 0.00009174v^3$

Γ_{max}, μmol/g; K^c_m, (M)$^{-1}$, v, μmol-Cu(II)/g-complex.

FA(S)–kaolin is a result of the contribution of nitrogen and phosphate functional groups on humic acid. Fulvic acid contains a greater fraction of carboxyl or phenolic groups. However, the smaller Cu(II) affinity of oxygen functional groups than nitrogen and phosphate functional groups, results in a lower Cu(II) affinity on kaolin coated with fulvic acid. Another evidence in the table indicates that the Cu(II) affinity of FA(S)–kaolin is almost equivalent to that of inorganic kaolin. It is because both surfaces abound with oxygen atoms.

Potentiometric titration is a simple measure to describe interaction of protons and a solid surface. Figure 6 shows data from net proton adsorption calculated from the potentiometric titration data of both suspension and supernatant. The initial titration point was set about pH 7; at that pH the acidic groups may be assumed to be almost dissociated. Hence, the capacity of proton adsorption may be neglected at pH 7. The simple Langmuir isotherm may be used to describe the proton adsorption of 1:1 type. Using nonlinear regression (NLR) with computer iteration, the total number of proton adsorption sites and average proton adsorption constant were calculated at 45.92 μmol/g and 4.146 $(\mu M)^{-1}$ for HA(S)–kaolin and at 200.98 $(\mu$mol/g and 3.477 $\mu M)^{-1}$ for FA(S)–kaolin, respectively. The greater capacity to adsorb protons on the FA(S)–kaolin complex results from the abundant carboxyl and phenolic (–OH) groups in fulvic acid. The acidity constants of N– and P– ionizing groups are smaller than that of the carboxyl and phenolic functional group. Therefore, like the Cu(II) affinity, the greater

content of N- and P-functional groups leads to increase proton affinity to humic acid relative to fulvic acid. The same trend of adsorption behavior for Cu(II) and H$^+$ on humus–kaolinite substance indicates their competition for adsorption on the same site. Further graphic analysis is necessary to describe proton adsorption on these heterogeneous surfaces. The proton affinity data of HA(S)- and FA(S)-complex were plotted according to the Scatchard plot (Fig. 6). Except for small surface coverage, for which the proton affinity of both surfaces is large and independent of surface coverage. The graphic analysis demonstrates that a single-site Langmuir model applied to proton affinity produced a better fit than Cu(II) affinity.

K^c_m listed in Table 2 is the adsorption constant at a specific pH. As mentioned, protons compete with Cu(II) ions for the same site. The modified model presented here incorporated a proton competition coefficient, which can differentiate the effect of competition from Cu(II) adsorption. Therefore, a constant (K_m) independent of pH may be derived from this model; the results are listed in Table 3. The HA(S)–kaolin complex has a greater Cu(II) affinity constant than FA(S)–kaolin complex for either a single-site model or a continuous distribution model. By means of these adsorption constants, from either model, one can predict the Cu(II) adsorption capacity over a diverse Cu(II) loading conditions at various pH values. However, the high molecular weight of humic acid has similar Cu(II) affinity as the low molecular weight of humic acid. It indicates that the molecular size of humic acid has no effect on the Cu(II) affinity.
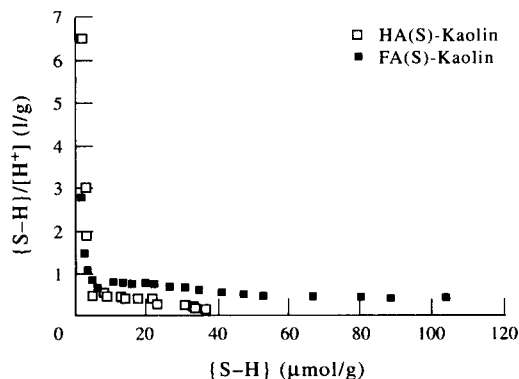

Fig. 6. The Scatchard plot for proton affinity with HA(S)–kaolin complex and FA(S)–kaolin complex.

CONCLUSIONS

The adsorption capacity of fulvic acid on kaolin is smaller that of humic acid. The adsorption behavior of fulvic acid on kaolin can be described by a Langmuir-type isotherm (monolayer adsorption). However, the adsorption isotherm of humic acid on kaolin exhibits non-Langmuir behavior (multilayer adsorption). Various K^c_m values were derived from the slope of Scatchard plots at varied extent of Cu(II) binding. The results indicate that apparent adsorption constants decrease with increasing extent of adsorption, and humic acid with a large molar mass has an affinity strength for Cu(II) similar to humic acid with a small molar mass.c acid with a large molar

Table 3. The Cu(II) adsorption constant for the humus–kaolin complex with the exclusion of pH effect

Humus- kaolin complexes	Single-site model $\log K_m$	Continuous distribution model $\log K_{mi} = f(v)$
HA(H)–kaolin	5.154	$\log K_{mi} = 7.607 - 0.1693v + 0.00426v^2 - 0.00004565v^3$
HA(L)- kaolin	5.217	$\log K_{mi} = 7.672 - 0.2242v + 0.00802v^2 - 0.000122v^3$
HA(S)–kaolin	4.500	$\log K_{mi} = 6.91 - 0.43v + 0.002706v^2 - 0.006612v^3$
FA(S)–kaolin	4.259	$\log K_{mi} = 5.892 - 0.1995v + 0.006381v^2 - 0.000099924v^3$

K_m, $(M)^{-1}$; v, μmole-Cu(II)/g-complex.

mass can however offer more affinity sites than humic acid with a small molar mass. Hence the molecular size of humic acid has an effect on the maximum capacity of Cu(II) affinity apart from the strength of affinity.

The results also show that adsorption behaviors of HA(H)–kaolin and HA(L)–kaolin are similar. However, the adsorption constants of HA(S)–kaolin are significantly greater than those of FA(S)–kaolin over the whole range of surface coverage. Polynomial equation relating $\log K_m^c$ to $\{S–Cu\}$ simply describes the variation of adsorption energy, but provides no information about the type of binding.

The intrinsic proton affinity of synthetic soils is easily described with a Langmuir isotherm for a single-site model. The total number of affinity sites and the average proton affinity constant were calculated to be $45.92 \, \mu\text{mol/g}$ and $4.146 \, (\mu M)^{-1}$ for HA(S)–kaolin and at $200.98 \, \mu\text{mol/g}$ and $3.477 \, (\mu M)^{-1}$ for FA(S)–kaolin, respectively. The similar trend of adsorption behavior for Cu(II) and H^+ on kaolin–humic substance indicates that they compete for adsorption on the same site. Except for small surface coverage, the proton affinity is independent of surface coverage.

A modified model incorporating a proton competition coefficient can differentiate the competitive effect from Cu(II) adsorption. A constant (K_m) independent of pH was derived from this model. HA(S)–kaolin complex has a greater Cu(II) affinity constant than FA(S)–kaolin complex according to models with either a single-site or a continuous distribution.

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