Clays and Clay Minerals, Vol. 26, No. 2, pp. 101–106, 1978.

COPPER(II) INTERACTIONS WITH KAOLINITE: FACTORS CONTROLLING ADSORPTION

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(Received 10 June 1977)

Abstract—The adsorption of Cu^{2+} on kaolinite was studied at different ionic strengths following various treatments of the mineral surface in order to evaluate the conditions influencing adsorption. The data indicate a strong preference of the Na^+ exchange form of kaolinite for Cu^{2+} but a weak affinity of the natural kaolinite for Cu^{2+}. Protons are generated by Cu^{2+} adsorption, a result of the exchange of surface protons, and possibly the enhancement of Cu^{2+} hydrolysis at the kaolinite surfaces. The exchange of Na^+ by Cu^{2+} on the kaolinite is not described by the mass-action equation, but can be interpreted in terms of permanent charge sites on the surfaces when the additional factors of Na^+–H_3O^+ exchange and blockage of sites by Al ions are considered.

Key Words—Adsorption, Copper, Exchange, Hydrolysis, Kaolinite.

INTRODUCTION

Although Cu^{2+} adsorption on kaolinite has been studied previously (Menzel and Jackson, 1950; Farrah and Pickering, 1976), the mechanisms of adsorption have not been well defined, partially because of the lack of agreement concerning the nature of negative charge sites on kaolinite. Permanent charge on kaolinite surfaces resulting from isomorphous substitution has been suggested by a number of studies (Sumner, 1963; Follett, 1965). A recent investigation has shown that the pH-dependent component of surface charge on kaolinite is quite small when aluminum and hydrogen ion occupation of permanent charge sites is taken into account (Bolland et al., 1976). In addition, evidence has been presented to indicate that adsorbed Cu^{2+} on kaolinite largely occupies the planar external surfaces rather than edges of platelets (McBride, 1976). Thus, heavy metal ion adsorption at low concentrations should occur largely as a result of electrostatic interaction with permanent charge sites, and might be expected to fit an adsorption model similar to that used for smectites.

Adsorption data for Cu^{2+} on kaolinites have suggested that there is a surface affinity for $CuOH^+$ (Menzel and Jackson, 1950), and that at high Cu^{2+} concentrations, kaolinites enhance $Cu(OH)_2$ precipitation (Farrah and Pickering, 1976). However, proton release by clays in the presence of Cu^{2+} salt solutions is not sufficient evidence that Cu^{2+} hydroxy species have been formed. Numerous other sources of protons exist in the system, and detailed studies are required to separate and quantify certain of these proton sources. In addition, many kaolinites are contaminated with significant quantities of high-charge minerals (e.g. micas, smectites), and have adsorption properties more characteristic of the mineral impurities than the kaolinite. Thus, pure kaolinites have CEC values (1–2 mequiv./100 g) which make measurement of heavy metal adsorption difficult at realistically low solution concentrations, and adsorption data for kaolinite have been lacking when compared to ion adsorption on high-charge clays.

The purpose of the present study is to measure Cu^{2+} adsorption by a pure, low CEC kaolinite, at relatively low solution concentrations of Cu^{2+} under several conditions of pH and ionic strength. An attempt will be made to explain the data in terms of the surface properties of kaolinite.

METHODS

A well-crystallized Clay Minerals Source Reference kaolinite from Georgia was used for the Cu^{2+} adsorption studies, having a CEC as determined by Mn^{2+} adsorption of 1.2 mequiv./100 g. The CEC estimated by Cu^{2+} adsorption was 1.6 mequiv./100 g, suggesting excess adsorption as a result of hydrolysis (McBride, 1976). For the purposes of this study, the CEC was taken to be 1.2.

In the initial experiments, 100 mg samples of the untreated kaolinite were placed in flasks, and 25 ml of $CuCl_2$ solutions of varying concentrations ($1.25 \times 10^{-6} - 5 \times 10^{-4}$ M) were added to the clays. These systems, as well as all of the others described in this study, were equilibrated by shaking for 1 day, centrifuged, and the supernatants were analyzed for pH and Cu^{2+} concentration using a glass electrode and Cu^{2+} specific ion electrode. The pH values of the $CuCl_2$ solutions were also determined before they had been added to the clays. The experiment was repeated using $CuCl_2$ solutions containing 0.01 M NaCl.

For the natural kaolinites, the weak Cu^{2+} adsorption required that the experiment be repeated using 1.00 g of kaolinite in 25 ml of aqueous Cu^{2+} solutions containing 0.01 M NaCl. The greater quantity of clay allowed measurement of adsorption by the decrease in solution concentration of Cu^{2+}.

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https://doi.org/10.1346/CCMN.1978.0260204 Published online by Cambridge University Press

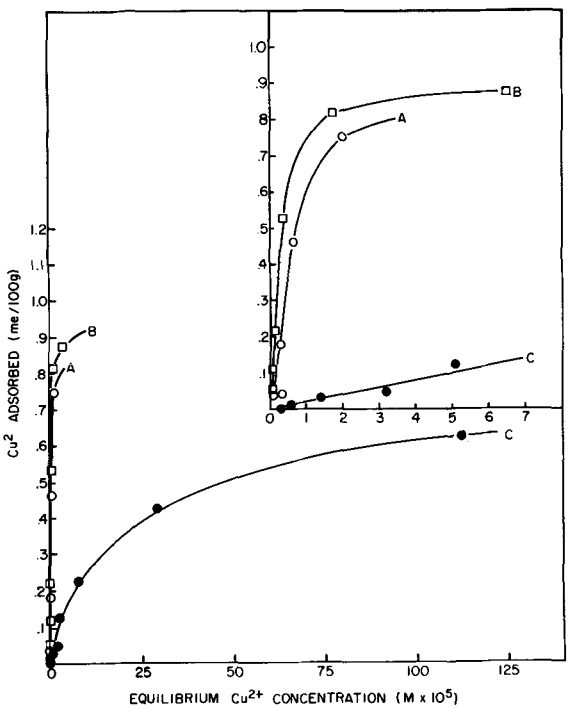


Fig. 1. Cu^{2+} adsorption isotherms for (A) Na^+-kaolinite in 0.01 M NaCl, (B) Na^+-kaolinite with no excess NaCl present, and (C) Natural (untreated) kaolinite in 0.01 M NaCl, 1 g clay in 25-ml solution. (Expanded scale isotherms are shown to illustrate the extent of adsorption at low Cu^{2+} concentration.)

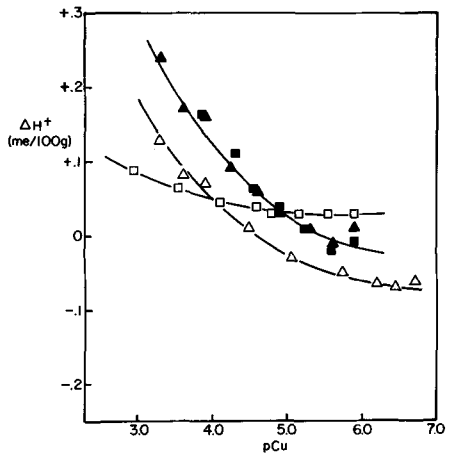


Fig. 2. Relationship between equilibrium concentration of Cu^{2+} and the change in quantity of protons in solution, ΔH^+, as a result of kaolinite addition to $CuCl_2$ solutions. The following systems are shown: Na^+-kaolinite with no NaCl added (△), natural kaolinite with no NaCl added (▲), natural kaolinite in 0.01 M NaCl (1.0 g in 25 ml) (□), and Al-saturated kaolinite with no NaCl added (■).

Similar experiments were conducted on kaolinites that had been washed twice with HCl-acidified NaCl (pH = 3.4), and then saturated with Na^+ using two washes in neutral NaCl. After removing the excess salt with several distilled water washes, the clays were dried at 60°C. These acid-washed Na^+-kaolinites were placed in flasks in quantities of 100 mg and equilibrated with 25 ml of $CuCl_2$ solutions, with and without 0.01 M NaCl. The pH values of the solutions before and after equilibration, and the amount of Cu^{2+} in solution, were determined as before. The Na^+ concentrations in the supernatants were determined by flame photometry in the experiments where excess NaCl was not added.

Finally, 100-mg samples of acid-washed Na^+-kaolinite were washed once with 10^{-3} M $AlCl_3$, then washed free of excess Cl^-. The pH of the 10^{-3} M $AlCl_3$ was 4.22, but the final water wash of the kaolinite had a pH of 5.58. These Al-treated kaolinites were equilibrated with 25-ml quantities of $CuCl_2$ solutions, and the equilibrium Cu^{2+} and pH values of the supernatants were measured.

RESULTS AND DISCUSSION

The Cu^{2+} adsorption isotherms (Figure 1) indicate that the Na^+ exchange form of kaolinite adsorbed Cu^{2+} much more strongly than the untreated kaolinite. A clay/solution ratio of 1 g/25 ml was required for the untreated kaolinite in order to produce measurable adsorption. The expanded scale isotherms of Figure 1 demonstrate a plateau in the adsorption of about 0.9 mequiv. Cu^{2+}/100 g for the Na^+ form of kaolinite, with the presence of 0.01 M NaCl in solution only slightly reducing Cu^{2+} adsorption. All exchange experiments involving 0.10-g samples of untreated or Al-exchanged kaolinite resulted in so little Cu^{2+} adsorption that isotherms could not be obtained, although pH data for these systems were recorded.

The change in the quantity of hydrogen ions in solution, ΔH^+, associated with the adsorption of Cu^{2+} on kaolinite, is plotted in Figure 2 as mequiv. H^+ per 100 g of kaolinite. The general trend, regardless of the previous treatment of the kaolinite, is an increasing proton release to solution with increasing Cu^{2+} concentration (i.e., greater adsorption of Cu^{2+}). The untreated and Al-exchanged kaolinites showed very similar behavior in terms of proton release, suggesting similar surface characteristics. However, the acid-washed Na^+-kaolinite had a proton release that was consistently 0.5–0.7 mequiv./100 g lower than that of the untreated and Al-exchanged forms (Figure 2). This can be understood on the basis of the amount of Na^+ released by the Na^+-kaolinite upon equilibration with the Cu^{2+} solutions. The Na^+ in solution varied only from 0.56 to 0.71 mequiv./100 g as the Cu^{2+} concentration was increased by more than three orders of magnitude. Evidently, most of the Na^+ was released to solution by proton exchange even before Cu^{2+} became significant in the exchange process. As a result, the proton release curve of Na^+-kaolinite (Figure 2) was lowered relative to the other curves by an amount equal to the quantity of Na^+ desorbed by solution protons (ca. 0.5 mequiv./100 g). The

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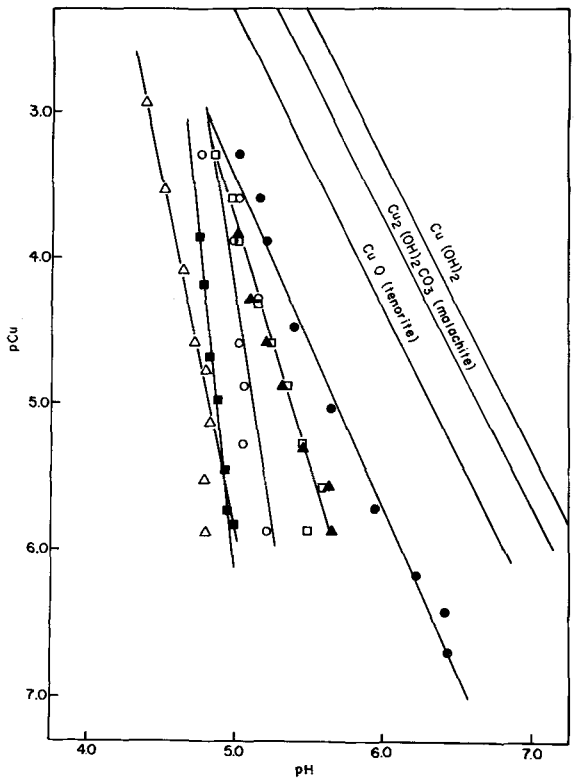


Fig. 3. The pH-pCu equilibrium relationship for the following kaolinite systems: Na^+-kaolinite with no NaCl added (●), Na^+-kaolinite in 0.01 M NaCl (■), natural kaolinite with no NaCl added (□), natural kaolinite in 0.01 M NaCl (○), natural kaolinite in 0.01 M with 1 g of kaolinite present (△), Al-saturated kaolinite with no NaCl added (▲). The solubility lines for copper hydroxide, malachite and tenorite are determined from the data of Baes and Mesmer (1976).

small remainder of adsorbed Na^+ was gradually released as the Cu^{2+} concentration was increased. The CEC as estimated by Na^+ (0.71 mequiv./100 g) is less than the value of 1.2 determined by divalent ions such as Mn^{2+} (McBride, 1976) because of the apparent strong preference of kaolinite surfaces for divalent ions. Removal of excess NaCl during the preparation of Na^+-saturated kaolinite results in hydrolysis, with the result that a significant portion of the exchange sites are occupied by protons. The hydrolysis effect seems to be more pronounced on kaolinites than on smectites as a result of the wider CEC/solution ratios generally used, producing a greater dilution of the exchanger in the case of kaolinite. This effect can easily be misinterpreted as evidence for pH-dependent charge sites on kaolinite.

The proton release curves (Figure 2) show changes in ΔH^+ values which indicate that about 0.25 mequiv. of protons per 100 g of clay were generated as a result of surface adsorption of Cu^{2+}. Thus, Cu^{2+} ions may have exchanged about 0.25 mequiv. of protons from the surface, or the process of Cu^{2+} adsorption may have involved hydrolysis, with the release of 0.25 mequiv. of protons. The data do not distinguish between these alternatives. However, the Cu^{2+}-saturated kaolinite has been shown to have a higher apparent CEC than the equivalent Mn^{2+}-saturated form by 0.4 mequiv./100 g (McBride, 1976), suggesting that surface hydrolysis may occur with the adsorption of Cu-hydroxy ions or $Cu(OH)_2$. Possibly, the proton release of this study involved a combination of Cu^{2+}–H_3O^+ exchange and Cu^{2+} hydrolysis upon adsorption. The maximum observed proton release could have resulted in the adsorption of 0.25 mequiv. of $CuOH^+$ or 0.125 mmol of $Cu(OH)_2$ by 100 g of kaolinite, producing an apparent CEC based upon Cu^{2+} adsorption that overestimated the quantity of permanent charges sites. The proton release curves of Figure 2 appear to have no maximum, and suggest that Cu^{2+} hydrolysis in the presence of kaolinite, rather than Cu^{2+}–H_3O^+ (or Cu^{2+}–Al^{3+}) exchange accounts for a large part of the proton generation at high Cu^{2+} concentrations. Farrah and Pickering (1976) have shown that kaolinite enhances the apparent precipitation of copper at high solution Cu^{2+} concentrations.

The equilibrium pH–Cu relationships in all of the kaolinite systems investigated (Figure 3) indicate that all systems were well undersaturated with respect to amorphous $Cu(OH)_2$($pK_{so} \simeq 19$), tenorite ($pK_{so} \simeq 20$) and malachite. However, the slope of the pH–pCu relationship for the acid-washed Na^+-kaolinite is near that of the precipitated Cu phases, suggesting a surface precipitation phenomenon. It is possible that $Cu(OH)_2$ is adsorbed on kaolinite in much the same way that $Al(OH)_3$ is precipitated in clay systems which are undersaturated with respect to amorphous alumina (Turner and Brydon, 1965). However, the data may also simply indicate Cu^{2+}–H_3O^+ exchange with the release of two protons for each Cu^{2+} ion adsorbed. The system is complicated by the carbonate equilibrium in the pH range of 5.5 so that the proton uptake data for Na^+-kaolinite in the absence of excess NaCl cannot be considered very accurate.

The acid-washed Na^+-kaolinite, in the presence of 0.01 M NaCl, showed a much different pH–pCu relationship (Figure 3), with the pH changing very little at different Cu^{2+} levels. The effect of the 0.01 M NaCl was to lower the equilibrium pH by exchange of H_3O^+ from surfaces, thereby replacing the Cu^{2+}–H_3O^+ exchange process to a large extent with Cu^{2+}–Na^+ exchange. The result is a system much more undersaturated with respect to amorphous $Cu(OH)_2$, having a pH only slightly dependent on the Cu^{2+} concentration in solution.

The untreated kaolinite showed a similar, but less pronounced effect of 0.01 M NaCl upon the pH–pCu relationship (Figure 3). In the absence of NaCl, the slope indicated that the adsorption of Cu^{2+} had less effect on the pH for the untreated clay than for the Na^+ exchange form. This would be a reasonable result if the natural kaolinite were largely saturated with ions other than H_3O^+. The same system, with 0.01 M NaCl pres-

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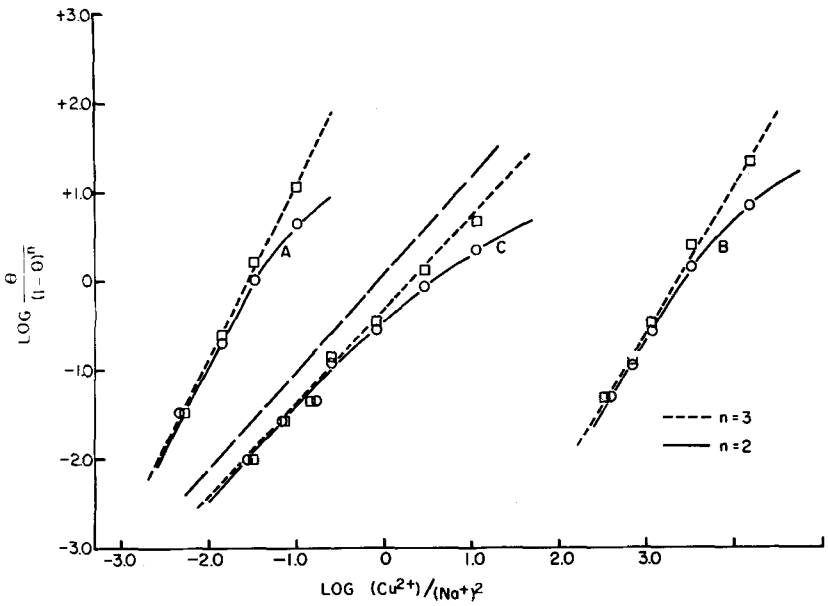


Fig. 4. Cu^{2+} adsorption isotherms for (A) Na^+-kaolinite in 0.01 M NaCl, (B) Na^+-kaolinite with no excess NaCl present, and (C) Natural (untreated) kaolinite in 0.01 M NaCl, 1 g of clay in 25 ml. The solid lines represent $\theta/(1-\theta)^2$ isotherms, the broken lines represent $\theta/(1-\theta)^3$ isotherms. The dashed line indicates the Cu^{2+} adsorption isotherm of acidified Na^+-montmorillonite (in 0.01 M NaCl) as a comparison.

ent, showed a general downward shift in pH which was much less than that observed for the Na^+-exchanged kaolinite, again suggesting that few protons on the natural kaolinite were available for exchange by Na^+.

The Al^{3+}-exchanged kaolinite and the untreated kaolinite had virtually identical pH–pCu relationships under similar experimental conditions (Figure 3). This is evidence that the natural kaolinite was largely saturated with Al ions, accounting for the similar proton release curves of the untreated and Al^{3+}-washed kaolinites (Figure 2), and the weak adsorption of Cu^{2+} by the natural clay (Figure 1). The adsorption of Cu^{2+} by 0.100-g samples of untreated (natural) and Al^{3+}-saturated kaolinites was not measurable under the exchange conditions of this study, a probable result of the strong affinity of charge sites for Al^{3+} ions compared to divalent metal ions (Nye et al., 1961).

The pH–pCu lines of Figure 3 appear to converge at high Cu^{2+} concentrations (pCu = 2.5–3.0), an indication that Cu^{2+} hydrolysis in solution, rather than an exchange mechanism, controls the equilibrium pH. This result is expected, since the quantity of H_3O^+ ions that can be released by exchange is small relative to the acidity generated by hydrolysis to form $Cu_2(OH)_2^{2+}$ and $CuOH^+$ in concentrated Cu^{2+} salt solution (Baes and Mesmer, 1976).

The pH–pCu relationship for 1.00 g of untreated kaolinite in 25-ml solution containing 0.01 M NaCl (Figure 3) is shifted to lower pH values relative to the relationship for 0.100 g of the same clay. Evidently, the greater clay/solution ratio results in the availability of more acidity for exchange by NaCl.

The data of this study suggest that Cu^{2+} adsorption at low Cu^{2+} activities in solution occurs mainly by exchange on permanent charge sites, since maximum adsorption levels are near the estimated CEC of the kaolinite. A similar conclusion regarding metal ion adsorption on kaolinite has been reached in some studies (Bolland et al., 1976) but not in others (Ferris and Jepson, 1975). It is evident that the preparation of the clay for the adsorption experiments greatly influences the adsorption of metals. The natural kaolinite of this study was apparently largely saturated with Al ions. Extraction of the natural kaolinite with 0.10 M NaCl (adjusted to pH 3.4 with HCl) released 0.4 mmol Al/100 g. This was about four times the amount of Al released by 0.10 M NaCl adjusted to one pH unit higher, and corresponds to 1.2 mequiv. Al adsorbed as Al^{3+}. These data, and the adsorption isotherms of Figure 1, are consistent with the concept that Al^{3+} (and probably Al-hydroxy) ions dominate the permanent charge sites of naturally occurring kaolinites. Divalent metals such as Cu^{2+} are weakly adsorbed on these clays as a result of the strong surface attraction for Al. The effect of adsorbed Al on the surface is to give the kaolinite the appearance of having a strongly pH-dependent charge (Bolland et al., 1976; Smith and Emerson, 1976).

The adsorption data for the three exchange experiments in which significant Cu^{2+} was removed from solution (Figure 1) were tested for their fit to ion exchange

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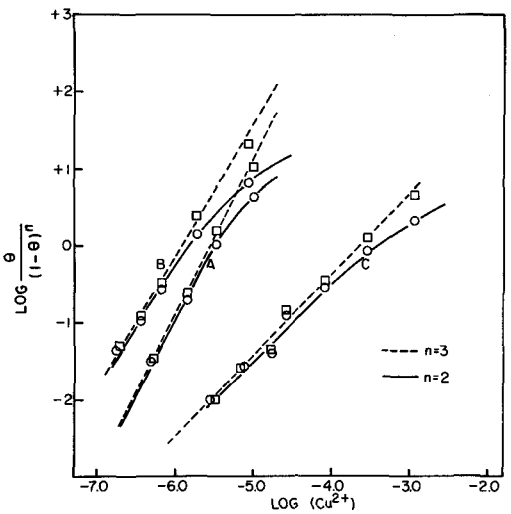


Fig. 5. Cu^{2+} adsorption isotherms for (A) Na^+-kaolinite in 0.01 M NaCl, (B) Na^+-kaolinite with no excess NaCl present, and (C) Natural (untreated) kaolinite in 0.01 M NaCl, 1 g of clay in 25 ml. The solid lines represent $\theta/(1-\theta)^2$ isotherms; the broken lines represent $\theta/(1-\theta)^3$ isotherms.

models. The equilibrium constant, K, for the mass-action form of the Cu^{2+}–Na^+ exchange equation can be given as:

$$K = \frac{\bar{f}_{Cu^{2+}}}{\bar{f}^2_{Na^+}} \cdot \frac{[\overline{Cu^{2+}}]}{[\overline{Na^+}]^2} \cdot \frac{(Na^+)^2}{(Cu^{2+})} \qquad (1)$$

where $\bar{f}_{Cu^{2+}}$ and $\bar{f}_{Na^+}$ are 'surface activity' coefficients, $[\overline{Cu^{2+}}]$ and $[\overline{Na^+}]$ are equivalent fractions of Cu^{2+} and Na^+ occupying the permanent charge sites of the kaolinite, and (Cu^{2+}) and (Na^+) are the solution activities. If $[\overline{Cu^{2+}}]$ is redefined as θ, then $[\overline{Na^+}]$ equals $1-\theta$ for the Cu^{2+} – Na^+ system, assuming that surface hydrolysis is negligible (i.e. few H_3O^+ ions occupy charge sites). By taking the logarithmic form of equation (1):

$$\log \frac{\bar{f}_{Cu^{2+}} \cdot \theta}{\bar{f}^2_{Na^+}(1-\theta)^2} = \log K + \log \frac{(Cu^{2+})}{(Na^+)^2}$$

it can be seen that a plot of $\log \theta/(1-\theta)^2$ against $\log (Cu^{2+})/(Na^+)^2$ will produce a straight line with slope one and intercept $\log K$ if $\bar{f}_{Cu^{2+}}/\bar{f}_{Na^+}$ remains constant for different levels of adsorption of Cu^{2+} on the kaolinite. The data plotted in this manner appear to be fairly linear (Figure 4), although the slopes of the Na^+-kaolinite isotherms are greater than unity. In contrast, the slope of the natural kaolinite isotherm is close to one. This difference is evidence that Na^+-kaolinite and natural kaolinite respond differently to a change of $(Cu^{2+})/(Na^+)$ in solution, the Na^+ form of the clay adsorbing more Cu^{2+} for a given increment of Cu^{2+} in solution. However, the fact that the Na^+-kaolinite isotherms plot in much different positions depending upon whether or not excess NaCl is present in solution (Figure 4), indicates that the exchange model poorly describes the system, since the model should predict the effect of $(Cu^{2+})/(Na^+)$ upon the level of adsorbed Cu^{2+}. The failure of the model could be a result of the surface hydrolysis mechanism on Na^+-kaolinite, which resulted in occupation of a large portion of the surface exchange sites by H_3O^+ rather than Na^+. In addition, the attraction of the surfaces for Cu^{2+} may be so strong that a mass-action treatment of the exchange is a poor approximation. This second possibility is suggested by the adsorption data when they are replotted without taking the concentration of Na^+ in solution into account (Figure 5). The Cu^{2+} adsorption isotherms for the Na^+-kaolinite then plot closely together, indicating that 0.01 M NaCl had a much less important effect upon the level of Cu^{2+} adsorption than predicted by the mass-action ion competition model. Farrah and Pickering (1976) also found little effect of the Na^+ concentration on Cu^{2+} adsorption by kaolinite; however, this is not a specific adsorption effect, since Mg^{2+} and Ca^{2+} showed strong competition with Cu^{2+} for adsorption sites. The additional factor of enhanced Cu^{2+} hydrolysis at the kaolinite surface would further cause the Na^+–Cu^{2+} exchange equation to be inaccurate.

The natural kaolinite adsorption plot (Figure 5) is displaced from the Na^+-kaolinite isotherms, a result of the much lower affinity of Al-occupied exchange sites for Cu^{2+}. A previous study of Ca^{2+}–Al^{3+} exchange on montmorillonite (McBride and Bloom, in press) has shown that Al^{3+} is not readily displaced from permanent charge sites with the addition of excess $CaCl_2$. In a similar way, the presence of Al^{3+} and hydroxy-Al ions on kaolinite surfaces tends to inhibit adsorption of divalent ions, and may appear to reduce the CEC of the clay.

It should be noted that the $\theta/[(1-\theta)^2]$ term is not unique in description of surface adsorption since it is derived from the assumption of solution-like behavior of adsorbed ions. If the activity coefficients, $\bar{f}_{Cu^{2+}}$ and $\bar{f}_{Na^+}$, are functions of the surface coverage term, θ, then the $\log \theta/[(1-\theta)^2]$ plot will not produce a straight line and the slope may not equal one. In fact, plots of $\log \theta/[(1-\theta)^3]$ against $\log (Cu^{2+})/(Na^+)^2$ [or $\log (Cu^{2+})$] for the Cu^{2+} adsorption data may be more linear than the $\log \theta/[(1-\theta)^2]$ plots (see Figures 4 and 5, broken lines). Assumptions other than those which regard surface-adsorbed ions as solution-like in all respects produce equations of different forms, and these will be discussed in a later paper. However, similar principles of adsorption should apply for different clay minerals with permanent charge, and this concept is suggested by the adsorption isotherm of Cu^{2+} on Na^+-montmorillonite in 0.01 M NaCl (low pH) shown in Figure 4 (dotted line). This $\theta/[(1-\theta)^3]$ adsorption line for the acidified montmorillonite is almost coincident with the analagous isotherm for natural kaolinite.

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CONCLUSIONS

Adsorption of Cu^{2+} by kaolinite is generally accompanied by proton release to solution, which appears to be mainly due to Cu^{2+}–H_3O^+ exchange at low Cu^{2+} concentrations. At higher Cu^{2+} concentrations, the clay may enhance hydrolysis of Cu^{2+} with the adsorption of hydrolyzed species. The proton balance is further complicated by the surface hydrolysis phenomenon, in which the Na^+ exchange form of kaolinite actually removes protons from solution with Na^+ release, thereby increasing the pH of dilute Cu^{2+} salt solutions added to the kaolinite.

The affinity of Cu^{2+} for natural kaolinite is quite low, a result of the fact that a large part of the exchange sites is occupied by Al ions. Very high affinity of kaolinite for Cu^{2+} can be induced by replacing surface Al ions with H_3O^+ and Na^+. The latter two ions are readily displaced from permanent charge sites by Cu^{2+}. Thus, kaolinites in acid soil environments are unlikely to strongly adsorb heavy metals such as Cu^{2+} because of the dominance of Al on exchange sites.

The combination of hydrolysis (Na^+–H_3O^+) in dilute suspensions of kaolinite and the occupation of exchange sites by Al^{3+} and Al-hydroxy ions produces the effect of apparent pH-dependent charge. However, the evidence from this study supports the concept that permanent charge sites resulting from isomorphous substitution (Al^{3+} for Si^{4+}, Mg^{2+} for Al^{3+}) are largely responsible for the CEC of pure kaolinite.

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Резюме- Изучалась абсорбция Cu^{2+} каолинитом при различной ионной силе,обусловленной разнообразными обработками поверхности минерала,проведенными,чтобы определить условия,влияющие на абсорбцию.Полученные данные показывают сильную способность Na^+ обменной формы каолинита к обмену на Cu^{2+}, но слабую способность к обмену на Cu^{2+} естественного каолинита.Протоны генерируются в результате абсорбции Cu^{2+} как результат обмена поверхностных протонов и возможно увеличения гидролиза Cu^{2+} на поверхностях каолинита.Обмен в каолините Na^+ на Cu^{2+}не описывается уравнением действия масс,а может интерпретироваться как места постоянных зарядов на поверхностях,если рассматривать дополнительные факторы обмена Na^+-H_3O^+ и блокирование этих мест ионами Al.

Kurzreferat- Um die Bedingungen unter welchen Adsorption stattfindet, zu finden, wurde, nach etlichen Behandlungen der Mineraloberfläche, die Adsorption von Cu(II) an Kaolinit bei verschiedenen Ionenstärken gemessen. Die Messdaten bringen eine starke Bevorzugung der Na^+Austauschform des Kaoliniten für Cu(II) hervor, aber nur eine schwache Affinität des natürlichen Kaoliniten für Cu(II). Protonen werden durch die Cu(II) Adsorption erzeugt, ein Resultat des Austausches von Protonen an der Oberfläche, und vielleicht eine Zunahme von Cu(II) Hydrolyse an den Kaolinitoberflächen. Der Austausch von Na durch Cu Ionen am Kaolinit kann nicht mit der Massen-Aktionsgleichung beschrieben werden, aber er kann als permanente Ladungsstellen an den Oberflächen interpretiert werden, falls die zusätzlichen Faktoren des Na^+-H_3O^+ Austausches und Blockierung der Stellen durch Al Ionen in Betracht gezogen werden.

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