Adsorption 6, 325–335, 2000

Thermodynamics of Copper Adsorption-Desorption by Ca-Kaolinite

M. DOULA
National Agricultural Research Foundation of Greece, Soil Science Institute of Athens 1,
Sof. Venizelou Str. Likovrissi, 14123, Attiki, Greece
mdoula@cc.uoa.gr

A. IOANNOU*
University of Athens, Department of Chemistry, Panepistimiopolis-Zografou, 15771, Athens, Greece
aioannou@cc.uoa.gr

A. DIMIRKOU
National Agricultural Research Foundation of Greece, Soil Science Institute of Athens 1,
Sof. Venizelou Str. Likovrissi, 14123, Attiki, Greece
aioannou@cc.uoa.gr

Abstract. The temperature effect on Cu adsorption and desorption on kaolinite has been investigated at four temperatures (8°C, 25°C, 30°C and 40°C). The clay sample was saturated with Ca. Copper was sorbed from solutions containing eleven Cu concentrations between 0.0010 and 0.0211 M, equilibrated for 2 days. Cu adsorption decreased, but desorption increased with increasing temperature, indicating that adsorption is an exothermic process while desorption is endothermic. These conclusions are confirmed by the values of ΔH^0 estimated for adsorption and desorption.

The initial copper concentration is a significant factor influencing mainly the adsorption process, which is spontaneous ($\Delta G^0 < 0$) only for low initial Cu concentrations. The desorption process is spontaneous for all Cu concentrations. ΔS^0 values have also been calculated. Experimental adsorption data were successfully fitted to the Freundlich isotherm and to the Gouy-Chapman model in order to express the process quantitatively.

Keywords: copper, ca-koalinite, adsorption, desorption, thermodynamics

Introduction

The extent to which a soil, or a soil constituent reacts with metal cations is important both for plant nutrition and for pollution control. For metals such as copper, zinc etc, these reactions have a large effect on their availability to plants and on the extent to which these metals pass into the food chain. The characteristics of these reactions have been measured on a range of absorbents (James and Barrow, 1981).

Copper is one of the important, essential elements for plants and animals. In nature, it forms sulfides, sulphates, sulfosalts, carbonates and other compounds and also occurs under reducing environments as the native metal. Copper is specifically adsorbed or "fixed" in soils, associating with soil organic matter, oxides of Fe and Mn, soil silicate clays and other minerals which makes it one of the trace metals which moves the least. Copper pollution can arise from Cu mining and smelting, brass manufacture, electroplating and excessive use of Cu-based agrichemicals. Anthropogenic inputs of copper to land are very diverse. Soil levels of copper are affected by soil and crop

---

*To whom correspondence should be addressed. A. Ioannou, 14 Thermopilon St., 15351, Pallini, Attiki, Greece.

treatments including fungicides, fertilisers not used to rectify copper deficiencies, livestock manures, sewage sludges and atmospheric deposition. For example, pig slurry containing up to 1990 mgkg^1 Cu has been reported (Alloway, 1990). The usual copper fertiliser source is $CuSO_4 \cdot 5H_2O$ (bluestone), although other compounds, mixtures and chelates are also used. Hydrated $CuSO_4$ is quite water soluble and is compatible with most fertiliser materials. Copper sulfate is used widely as an algicide in ornamental ponds and even in water supply reservoirs which are affected by blooms of toxic blue-green algae.

Copper has been subject to investigation by many researchers (McBride et al., 1998; Karathanasis, 1999; Vlasova, 2000). All of them agree that soil solution pH, supporting electrolyte concentration and soil solution constituents influence copper movement and its availability to plants. Generally the adsorption of copper has been found to increase with increasing pH (Forbes et al., 1974; Sparks et al., 1995). Because temperature is also an important factor influencing metal adsorption by clays and soils, the subject of the present investigation was to examine how adsorption and desorption of copper on Ca-kaolinite is affected by changing temperature.

Generally, the adsorption of metals on soils, clays and oxides causes the release of cations holed on the substrates or bound to them. For example, Padmanabham (1983), after research on synthetic goethite, supports the view that adsorption of Cu is accompanied by the release of one or two moles of hydrogen per mole of cation adsorbed. In the present experiment kaolinite was satured with Ca, meaning that all of its exchangeable cations were displaced by Ca ions. During the adsorption process, an exchange reaction occurs between Ca from clay and Cu from solution. In contrast, desorption is an exchange reaction between Cu holed on clay and H^+ from solution.

Materials and Methods

Experiment

The clay sample ($<2\mu$) used for this study was kaolinite (Lot No: 6325) which was calcium saturated by washing with 1 N $CaCl_2$ solution. The $CaCl_2$ excess was removed by washing with deionised water followed by dialysis until a negative chloride test (with $AgNO_3$) was obtained in the wash solution. Adsorption studies were carried out using triplicate samples (2.0 g) of Ca-kaolinite in 20.0 ml $CuSO_4$ solution added to the substrate at concentrations such that the mixture contained 0.0010, 0.0024, 0.0043, 0.0054, 0.0064, 0.0086, 0.0107, 0.0124, 0.0147, 0.0189, 0.0211 M of Cu.

Sample (Ca-kaolinite) pH, as measured in a 1 : 10 Ca-kaolinite/water mixture (ratio same as in experimental sample) was 5.2. After adding $CuSO_4$, solution pH varied from 4.9 to 5.6 depending on the $CuSO_4$ concentration. Samples were shaken in a waterbath at 8°C, 25°C, 30°C and 40°C for 48 hours. The equilibration period of 48 hours for adsorption and desorption of Cu by kaolinite assigned on the basis of previous experiments with shaking period of 12, 24, 36, 48 hours and of 5 to 150 days. According to the literature, the equilibrium for copper adsorption is reached within 24 hours (Cavallaro and McBride, 1978). After the equilibration period, the samples were centrifuged at 15000 g for 10 minutes and Cu in the supernatant was determined by using a SpectrAA-300 Varian Atomic Absorption Spectrometer (AAS). All experiments were carried out under a N_2 atmosphere.

A volume of deionized water equal to that of the adsorption solution was added to the remaining solid, and samples were shaken for 48 hours at 8°C, 25°C, 30°C and 40°C. After centrifugation Cu desorbed was also measured using AAS.

It should be noted that the pH reached at the equilibrium for the adsorption varied from 4.9 to 5.6, while for desorption it was the same for all samples. For this reason, the mean of the sample pH values, equal to 5.3, was used. It is known that the solution pH shifts to lower values when adsorption occurs, due to the exchange reaction between H^+ from the surface and metal ions from the solution.

In the present study, the substrate was Ca-saturated, meaning that the above reaction should have occurred between Ca^{2+} and H^+ before the Cu ions were added. Thus, the decrease in solution pH is considered to be negligible and the differences due mostly to the $CuSO_4$ solutions added.

Infrared spectrograms were recorded with a Perkin Elmer FT-IR. 16PC using 0.3 percent KBr pallets. Specific surface area (SSA) was determined by the BET method, using N_2 as adsorbate in Sorptomatic 1900 Carlo Erba Surface area analyser. X-ray power diffraction patterns were obtained from gently pressed specimens of random particle orientation using a D-500 Siemens Generator and CuKa-radiation. NMR spectra were obtained on a Bruker 400 MSL instrument using the software programs incorporated in the instruments. Thus, the inverse gated heteronuclear decoupling (HPDEC.PC) was used for silicon spectra and

Table 1. Some of kaolinite's characteristics.

Total Cu (ppm)	Specific surface^{a}	C.E.C. (meq/100 g)	pH (in H_2O)
18.85	12.07	10.20	5.2

$^{a}m^2g^{-1}$.

the quadruple one pulse acquisition with phase cycling (NUTATION.PC) for the aluminum. The most important parameters used for NMR spectra are given below:

The resonance frequency for silicon was 79.494 MHz. In these NMR spectra, the high power mode was used so the acquisition time was set as short as possible while long enough to record FID (D7 = 20 ms). The decoupler power (DP) used was 12 H and the relaxation delay used was 104 s. The data points (TD) were 4 K and the size (SI) of FID also 4 K. Trapezoidal multiplication TM (TM1 = 0 and TM2 = 400) was used in the processing with 2000 scans for the samples, but only 8 scans for the control sample.

The resonance frequency for aluminum was 104.262 MHz. The relaxation delay was 1.0, TD 1 K and SI 4 K. The dead time used was 8.0 μs and for the processing TM. D3 and D4 used were 8.0 μs and 0.6 μs respectively. The number of scans used for the sample was 8.

The cation exchange capacity (C.E.C.) of Ca-kaolinite was determined by $MgCl_2$ saturation with subsequent displacement by $CaCl_2$ (Okazaki et al., 1963; Rich, 1962). Sample Cu concentration was determined by the method described by ISO Standards Compendium (1994).

The chemical properties of kaolinite are shown in Table 1.

Theoretical Considerations

Adsorption of Cu is an exchange reaction between Cu^{2+} in solution and Ca^{2+} which is held by the solid substrate, and may be represented as follows:

$$\text{Kaol} > \text{Ca} + \text{Cu}^{2+}_{\text{sol}} \overset{K_{\text{eq}_{\text{ad}}}}{\longleftrightarrow} \text{Kaol} > \text{Cu} + \text{Ca}^{2+}_{\text{sol}} \qquad (1)$$

Initial	C_0	–
React	X	X
Equilibrium	$C_0 - X$	X

where C_0 is the initial Cu^{2+} concentration (mol l^{-1}) and X is the adsorbed Cu^{2+} concentration (mol l^{-1}) which is equal to the desorbed concentration of Ca^{2+}.

The equilibrium constant, $K_{\text{eq}_{\text{ads}}}$, for the above reaction is

$$K_{\text{eq}_{\text{ads}}} = \frac{[\text{Ca}^{2+}]_{\text{sol}}}{[\text{Cu}^{2+}]_{\text{sol}}} = \frac{X}{C_0 - X} = \frac{X}{C} \qquad (2)$$

where C is the concentration (mol l^{-1}) of Cu^{2+} remaining in the solution.

According to the literature, copper is adsorbed on a solid surface as Cu^{2+} or as $CuOH^{+}$, depending on environmental pH (Alloway, 1990). When copper is adsorbed as $CuOH^{+}$, the equilibrium of the exchange reaction is:

$$\text{Kaol} > \text{Ca} + 2\text{CuOH}^{+}_{\text{sol}} \overset{K'_{\text{eq}}}{\longleftrightarrow} \text{Kaol} > 2\text{CuOH}^{+} + \text{Ca}^{2+}_{\text{sol}} \qquad (3)$$

Initial	C_0	–
React	$2X$	X
Equilibrium	$C_0 - 2X$	X

The equilibrium constant, K'_{eq}, for the above reaction is

$$K'_{\text{eq}} = \frac{[\text{Ca}^{2+}]_{\text{sol}}}{[\text{Cu}^{2+}]^{2}_{\text{sol}}} = \frac{X}{(C_0 - 2X)^2} = \frac{X}{C^2} \qquad (4)$$

The above equilibrium, in the present experiment, could be ignored according to the calculations presented in the appendix.

The desorption process is an exchange between Cu^{2+} from the clay surface and H^{+} ions in solution (due to acidic solution conditions) and may be represented as follows:

$$\text{Kaol} > \text{Cu} + 2\text{H}^{+}_{\text{sol}} \overset{K_{\text{eq}_{\text{des}}}}{\longleftrightarrow} \text{Kaol} > 2\text{H}^{+} + \text{Cu}^{2+}_{\text{sol}} \qquad (5)$$

Initial	c	–
React	$2C_{\text{des}}$	C_{des}
Equilibrium	$c - 2C_{\text{des}}$	C_{des}

The equilibrium constant, $K_{\text{eq}_{\text{des}}}$, for the above reaction is

$$K_{\text{eq}_{\text{des}}} = \frac{[\text{Cu}^{2+}]_{\text{sol}}}{[\text{H}^{+}]^{2}_{\text{sol}}} = \frac{C_{\text{des}}}{(c - 2C_{\text{des}})^2} \qquad (6)$$

where c (mol l^{-1}) is the concentration of H^{+} ions before the start of the reaction and C_{des} is the concentration (mol l^{-1}) of Cu^{2+} desorbed. Reaction (5) is not the only one taking place at the time of Cu^{2+} desorption.

Calcium ions are also desorbed. The value of solution pH at the equilibrium was measured as equal to 5.3 for all samples. This specific value of pH results from both Cu^{2+} and Ca^{2+} desorption. Thus, the value for $[H^+]$ at equilibrium is $10^{-5.3}$ M; that is $[c - 2C_{des}] \approx 10^{-5.3}$ M.

The standard free energy, ΔG^0(kcal mol^{-1}), was calculated from the following equation (Doula et al., 1995, 1996):

$$\Delta G^0 = -RT \ln K_{eq} \tag{7}$$

where: R is the gas constant equal to 1.98×10^{-3} kcal mol^{-1}grad^{-1} and T is the absolute temperature (K).

The apparent heat of reaction-enthalpy, ΔH^0 (kcal mol^{-1}), was assumed to be constant for a constant surface coverage and was estimated using the equation (Doula et al., 1995, 1996):

$$\ln K_{eq} = -\frac{\Delta H^0}{R}\frac{1}{T} + D \tag{8}$$

where: D is a constant.

Equation (8) is represented by a straight line for most reactions and processes, with a slope equal to $(-\Delta H^0/R)$. For exothermic processes, the slope is positive ($\Delta H^0 < 0$), while it is negative for endothermic processes ($\Delta H^0 > 0$). The constant D is calculated from the line's intercept.

The entropy, ΔS^0(kcal mol^{-1}grad), of the system is calculated by using the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

For a quantitative description of the adsorption process, adsorption data were fitted to the Freundlich isotherm and to the Gouy-Chapman model (Ioannou et al., 1996). Freundlich isotherm:

$$X = KC^n, \quad \text{or} \quad \log X = \log K + n \log C \tag{10}$$

where X is the adsorbed Cu^{2+} concentration (mol l^{-1}), C is the concentration (mol l^{-1}) of Cu^{2+} remaining in solution and K(mol^{1-n}l^{n-1}) and n (no unit) are constants, with $n < 1$. Gouy-Chapman model (Ioannou et al., 1996):

$$\ln\frac{X}{C} = A + BX \tag{11}$$

where A (no unit) and B (l mol^{-1}) are constants.

Results and Discussion

Kaolinite used in the present study was identified as "pure" from its FT-IR spectrum (1a), ^{27}Al-MAS-NMR spectra (1b), ^{29}Si-MAS-NMR spectra (1c) and X-ray powder diffraction patterns (1d).

The infrared curve of pure kaolinite is characterized by two strong bands of octahedral OH-stretching vibrations between 3800 and 3600 cm^{-1} when the sample is mounted by the KBr pallet technique (Tan, 1983). The infrared curve of the kaolinite used is characterized by the sharp bands at 3688, 3652 and 3619 cm^{-1} of octahedral OH-stretching vibrations and water adsorbed (Fig. 1(a)). In addition, the lower frequency region (Fig. 1(a)) exhibits sharp bands at 1114, 1006 and 938–912 cm^{-1} attributed to O—Al—OH, to Si—O and Al—OH vibrations (Dimirkou et al., 1996).

Figure 1(b) (^{27}Al-MAS-NMR spectra) shows two peaks corresponding to the tetrahedrally (T) (ca. 40 ppm) and octahedrally (O) (ca. 10 ppm) coordinated Al. The calculated (from peak intensities) T/O ration for the kaolinite sample was found to be 1/38.55. In addition, a second order effect is verified in the sample (characteristic shape at 50 ppm).

The ^{29}Si-MAS-NMR spectra (Fig. 1(c)) shows a peak at ca. 90 ppm characteristic of the $(AlO)_3$—Si—OSi grouping in high siliceous materials. In addition, Fig. 1(c) shows a peak at −80 to −90 ppm characteristic of Si(4Al) and two peaks at −100 to −130 ppm characteristic of Si(1Al) and Si(0Al), respectively.

Figure 1(d) of the X-ray diffraction pattern exhibits the characteristic first order diffraction of kaolinite at the angle of $2\theta = 12, 4$ which corresponds to a d spacing of 7.14 Å.

As shown in Fig. 2, adsorption of Cu^{2+} on Ca-kaolinite increased with decreasing temperature, a phenomenon which has also been observed by Doula et al. (1996) for the adsorption of potassium on Ca-bentonite.

Adsorption equilibrium constants have been calculated for each of initial Cu^{2+} concentrations (Table 2). It should be noted that, according to theory, the equilibrium constant for a certain reaction depends only on temperature, while it is independent of reactant concentration. For metal adsorption (Cu^{2+}) on a colloid surface (Ca-kaolinite), the distribution of double-layer charge depends on solution ionic strength. In the present experiment, solution ionic strength varied with varying initial copper concentration, so a different equilibrium should be assumed for each concentration or, in other words, a different system for each of the copper concentrations with a different equilibrium constant.

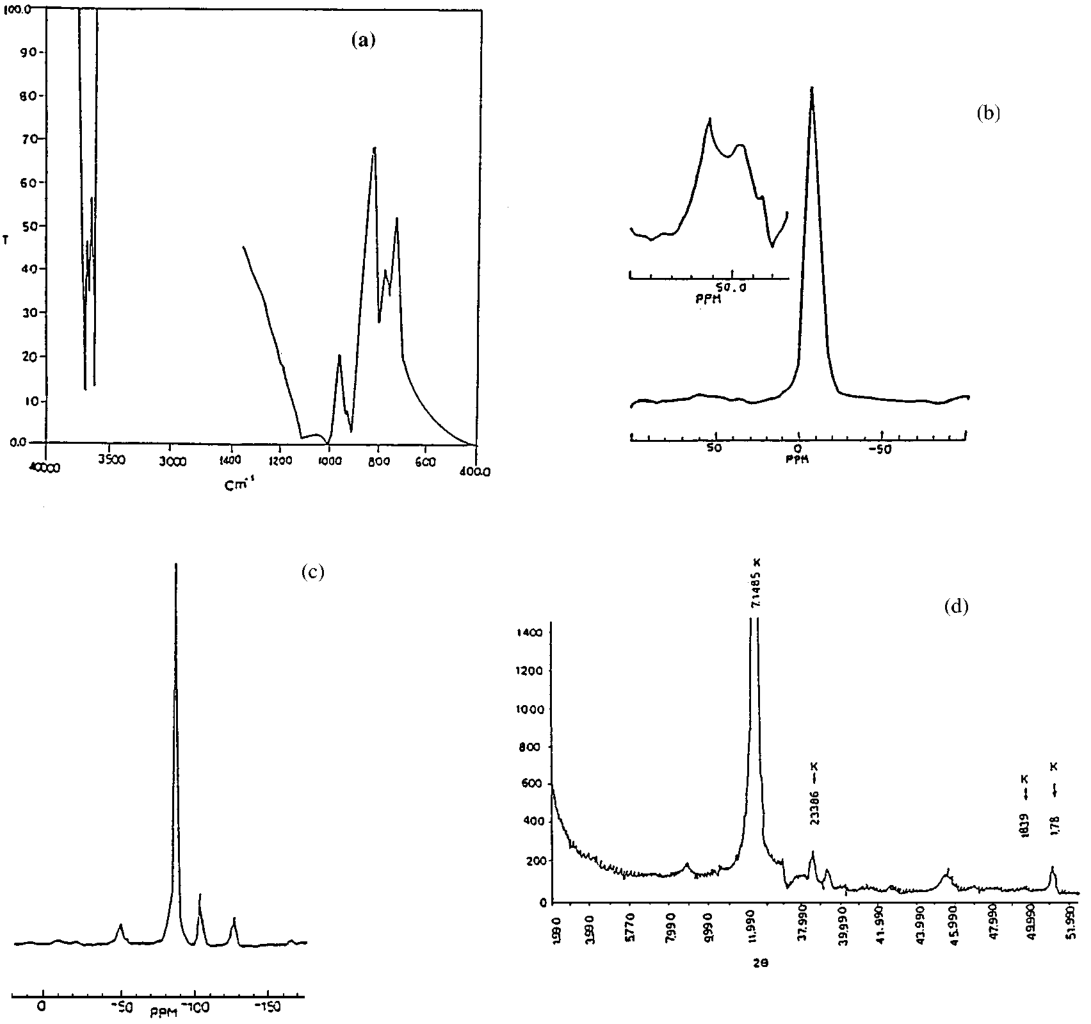

Figure 1. (a) Infrared transmittance (%T) of kaolinite spectra, (b) ^{27}Al-MAS-NMR spectra at 104.262 MHz of kaolinite, (c) ^{29}Si-MAS-NMR spectra at 79.494 MHz of kaolinite and (d) X-ray powder diffraction patterns of kaolinite.

For the adsorption process, equilibrium constants decreased with increasing copper concentration, indicating that an increase in copper concentration shifts equilibrium (1) to the left.

This conclusion is confirmed by the ΔG^0 values (Table 2), which increase with increasing initial copper concentration. For initial copper concentrations smaller than 0.0107 M for 25°C, 0.093 M for 30°C and 0.0085 M for 40°C, ΔG^0 values are negative (Fig. 3). These negative values of ΔG^0 mean that the reaction is spontaneous, while the positive ΔG^0 values for copper concentrations larger than those mentioned above indicate non-spontaneous reactions. At 8°C, negative values for ΔG^0 were observed for Cu concentrations smaller than 0.017 M Cu. (Fig. 3). It should be noted that a second-order polynomial function relates ΔG^0 and C_0 for Cu for each temperature with an extremely good fit, as shown in Fig. 3. From Fig. 4, where graphs of ln $K_{\mathrm{eq}_{\mathrm{ads}}}$ as a function of $1/T$ are presented, it can be seen that ΔH^0 values, for all conditions examined, are negative (Table 3) and that exchange reactions are all exothermic.

The value of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption. For chemical sorption, enthalpy values range from 20 to 200 kcal mol^{-1}, while for physical sorption

Table 2. Equilibrium constants ($K_{\mathrm{eq}_{\mathrm{ad}}}$) and free energy ($\Delta G^0$) values for Cu adsorption by Ca-kaolinite, at different temperatures.

C_0	8°C		25°C		30°C		40°C	
mol l^{-1}	$K_{\mathrm{eq}_{\mathrm{ads}}}$	ΔG^0	$K_{\mathrm{eq}_{\mathrm{ads}}}$	ΔG^0	$K_{\mathrm{eq}_{\mathrm{ads}}}$	ΔG^0	$K_{\mathrm{eq}_{\mathrm{ads}}}$	ΔG^0
0.0010	3.29	−0.663	1.93	−0.3876	1.74	−0.333	1.37	−0.1957
0.0024	3.08	−0.627	1.94	−0.3928	1.76	−0.339	1.60	−0.2911
0.0043	2.35	−0.475	1.53	−0.2495	1.56	−0.266	1.40	−0.2064
0.0054	2.09	−0.411	1.49	−0.2358	1.32	−0.166	1.25	−0.1394
0.0064	1.96	−0.375	1.33	−0.1684	1.28	−0.1496	1.06	−0.0373
0.0086	1.68	−0.290	1.21	−0.1116	1.11	−0.0632	1.04	−0.0237
0.0107	1.43	−0.200	0.997	0.001774	0.886	0.07266	0.787	0.1485
0.0124	1.17	−0.0893	0.966	0.02042	0.826	0.1148	0.722	0.202
0.0147	1.08	−0.0454	0.856	0.0918	0.763	0.1624	0.729	0.196
0.0189	0.968	0.0181	0.746	0.173	0.705	0.2098	0.579	0.338
0.0211	0.882	0.06991	0.655	0.2498	0.612	0.2952	0.533	0.3902

ΔG: kcal mol^{-1}, $K_{\mathrm{eq}_{\mathrm{ads}}}$: no unit.

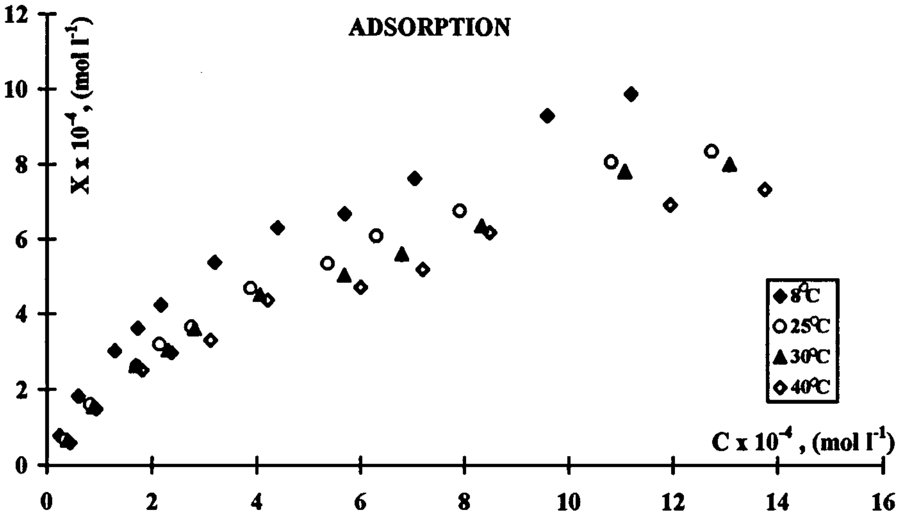

Figure 2. Isotherms for Cu^{2+} adsorption for all temperatures. X: Concentration of adsorbed Cu^{2+} and C: Equilibrium Cu^{2+} concentration.

they range from 2 to 6 kcal mol^{-1}. On the basis of the above distinction, we conclude that Cu sorption by Ca-kaolinite is a physical process.

In attempting to explain the adsorption of Cu on Ca-kaolinite at different temperature (from 8°C to 40°C) the following should be noted:

Firstly, the process is exothermic, so a decrease of temperature encourages Cu adsorption. In other words, it encourages the exchange of Ca from the clay surface for Cu from solution. Secondly, copper concentration is a significant factor influencing the adsorption process. The adsorption is spontaneous for copper concentrations smaller than a certain value, while this phenomenon is dramatically reversed for higher copper concentration, because of surface saturation and the larger percentage of copper remaining in the solution.

Thirdly, the variation of estimated ΔH^0 values (for adsorption) with increasing Cu concentration is limited. An exception occurs for the two lowest Cu concentrations, for which ΔH^0 and ΔG^0 have the highest negative values. This differentiation emphasises the ease of the exchange reaction when small amounts of Cu are present in the solution.

Table 3. ΔH^0 and ΔS^0 values for Cu sorption and desorption by Ca-kaolinite.

	Adsorption					Desorption				
C_0 mol l^{-1}	$\Delta H^{0\,a}$	$\Delta S^{0\,b}$ (8°C)	ΔS^0 (25°C)	ΔS^0 (30°C)	ΔS^0 (40°C)	ΔH^0	ΔS^0 (8°C)	ΔS^0 (25°C)	ΔS^0 (30°C)	ΔS^0 (40°C)
0.0010	−4.786	−0.0147	−0.0148	−0.0147	−0.0147	1.673	0.0396	0.0399	0.0400	0.0395
0.0024	−3.712	−0.0110	−0.0111	−0.0111	−0.0109	1.244	0.0393	0.0393	0.0393	0.0392
0.0043	−2.886	−0.0086	−0.0088	−0.0086	−0.0086	1.430	0.0407	0.0408	0.0408	0.0407
0.0054	−2.938	−0.0090	−0.0091	−0.0091	−0.0089	2.184	0.0438	0.0439	0.0438	0.0438
0.0064	−3.321	−0.0105	−0.0106	−0.0105	−0.0105	1.289	0.0411	0.0413	0.0410	0.0412
0.0086	−2.735	−0.0087	−0.0088	−0.0088	−0.0087	0.860	0.0399	0.0401	0.0400	0.0398
0.0107	−3.348	−0.0112	−0.0112	−0.0113	−0.0112	1.125	0.0414	0.0416	0.0415	0.0414
0.0124	−2.666	−0.0092	−0.0090	−0.0092	−0.0092	1.606	0.0435	0.0436	0.0436	0.0434
0.0147	−2.270	−0.0079	−0.0079	−0.0080	−0.0079	0.565	0.0404	0.0407	0.0408	0.0403
0.0189	−2.686	−0.0096	−0.0096	−0.0096	−0.0097	1.272	0.0434	0.0435	0.0437	0.0433
0.0211	−2.712	−0.0099	−0.0099	−0.0099	−0.0099	1.315	0.0440	0.0440	0.0441	0.0440

[a] ΔH^0: kcal mol^{-1}, [b] ΔS^0: kcal mol^{-1} grad^{-1}.

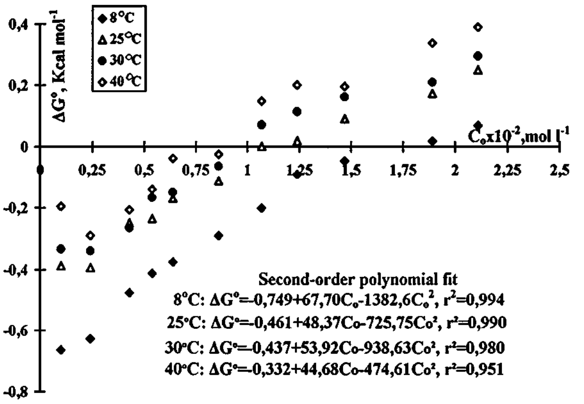

Figure 3. Standard free energy (ΔG^0) for Cu^{2+} adsorption on Ca-kaolinite as function of initial Cu^{2+} concentration (C_0) for all temperatures.

The formation of kaolinite >Ca is thermodynamically more stable than kaolinite >Cu and for this reason at high temperatures, when plenty of energy is offered to the system, a decrease of Cu adsorption is observed (kaolinite >Ca is favoured). It is also possible that kaolinite >Cu formation is kinetically favored because of the smaller ionic radius of Cu^{2+}, and consequently this formation appears at lower temperatures.

In order to express Cu adsorption by Ca-kaolinite quantitatively, adsorption data were fitted to the Freundlich isotherm and to the Gouy-Chapman model (Figs. 5(a) and (b)). Model constants are summarized in Table 4.

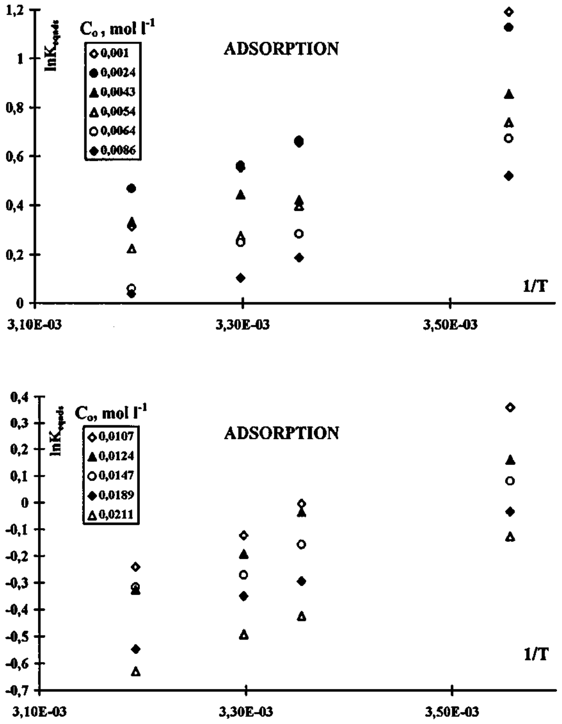

Figure 4. $\ln K_{\mathrm{eq}_{\mathrm{ads}}}$ as a function of $1/T$ for Cu^{2+} adsorption on Ca-kaolinite for all temperatures.

The fit to the linear form of the models was examined by calculation of the linearity coefficient (r^2). It is noteworthy that both the Freundlich and Gouy-Chapman models were found to describe adsorption successfully.

Table 4. Constants *K, n* for Freundlich isotherm *A, B* for Gouy-Chapman model and their linearity coefficients r^2, for Cu^{2+} adsorption by kaolinite.

	Freundlich			Gou-Chapman		
Temperature	K	n	r^2	A	B	r^2
8°C	7.78×10^{-2}	0.629	0.983	1.32	1.53×10^{3}	0.980
25°C	8.96×10^{-2}	0.680	0.982	0.822	1.44×10^{3}	0.984
30°C	8.03×10^{-2}	0.676	0.977	0.747	1.53×10^{3}	0.961
40°C	7.46×10^{-2}	0.680	0.962	0.625	1.64×10^{3}	0.915

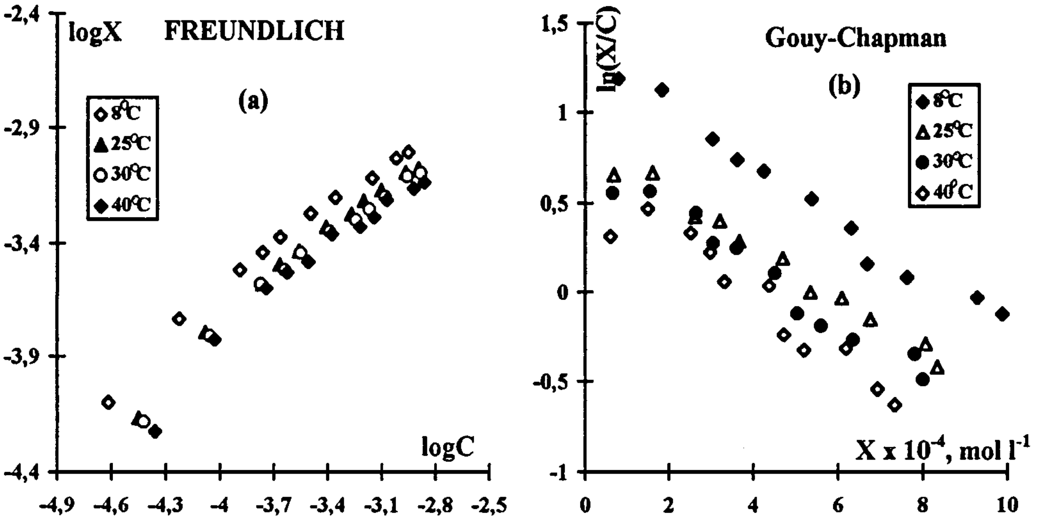

Figure 5. Freundlich (a) and Gouy-Chapman (b) isotherms for Cu^{2+} adsorption on Cakaolinite for all temperatures.

As a general result of the Cu^{2+} desorption study, the process is found to be endothermic, since an increase in desorption is observed with increasing temperature (although this increase is very small). (Fig. 6).

The concentrations of Cu desorbed are very low compared to those for the adsorption process. On the other hand, equilibrium constants $K_{\text{eq}_{\text{des}}}$ for desorption, according to Eqs. (5) and (6), (Table 5) are large. Since the $K_{\text{eq}_{\text{des}}}$ refers to the exchange process between Cu^{2+} and H^+, it may be concluded that Cu^{2+} exchanges its sites on clay for H^+ ions from the solution extremely easily.

Figure 7 presents $\ln K_{\text{eq}_{\text{des}}}$ as a function of $1/T$ in order to estimate ΔH^0 values for the desorption process. For all temperatures and initial Cu concentrations, ΔG^0 values for desorption are negative (Table 3), indicating that desorption is also a spontaneous physical process, despite the positive enthalpy ΔH^0 values for all conditions.

As indicated in Table 3, ΔS^0 values for the adsorption process are negative. These values are expected for ΔS^0, because during a physical sorption the degrees of internal freedom of the system are decreased. In contrast, for desorption ΔS^0 and ΔH^0 values should have the opposite sign, meaning positive.

At this point, it should be noticed that the calculated ΔH^0 values include the enthalpies of hydration, dilution, mixing and exchange. Because of uncertainties about the energy of hydration of the adsorbed-desorbed ions, most of these terms cannot be calculated with a high degree of accuracy (Udo, 1978; Doula et al., 1995). Consequently, the enthalpy of exchange itself cannot be adequately computed. Because of these limitations, the thermodynamic values in Table 3 have been used qualitatively in the above discussion.

Appendix

In considering Cu hydrolysis, we have

$$\begin{array}{ccccc} CuSO_4 & \rightarrow & Cu^{2+} & + & SO_4^{2-} \\ C_0 & & C_0 & & C_0 \end{array} \qquad (1)$$

Table 5. Equilibrium constants ($K_{\mathrm{eq_{des}}}$) and free energy (ΔG^0) values for Cu desorption by Ca-kaolinite, at different temperatures.

C_0	°C		25°C		30°C		4°C	
mol l^{-1}	$K^*_{\mathrm{eq_{des}}}$	ΔG^0	$K^*_{\mathrm{eq_{des}}}$	ΔG^0	$K^*_{\mathrm{eq_{des}}}$	ΔG^0	$K^*_{\mathrm{eq_{des}}}$	ΔG^0
0.0010	2.41	−9.464	3.35	−10.23	3.59	−10.44	3.10	−10.70
0.0024	4.38	−9.796	5.14	−10.48	5.25	−10.67	5.50	−11.05
0.0043	6.45	−10.01	7.78	−10.73	8.14	−10.94	8.30	−11.31
0.0054	7.92	−10.13	10.7	−10.92	11.0	−11.11	11.8	−11.52
0.0064	10.5	−10.28	12.9	−11.02	11.7	−11.16	13.7	−11.62
0.0086	12.0	−10.36	14.9	−11.11	14.4	−11.28	13.8	−11.62
0.0107	15.9	−10.51	20.1	−11.29	19.1	−11.45	19.4	−11.83
0.0124	19.2	−10.62	24.3	−11.40	25.1	−11.61	25.4	−12.00
0.0147	26.4	−10.80	32.6	−11.57	34.0	−11.79	27.8	−12.06
0.0189	33.4	−10.93	40.1	−11.70	45.7	−11.97	40.5	−12.29
0.0211	42.2	−11.06	48.2	−11.80	52.4	−12.05	53.1	−12.46

K_{eq}: l mol^{-1}(*: $\times 10^7$), ΔG: kcal mol^{-1}.

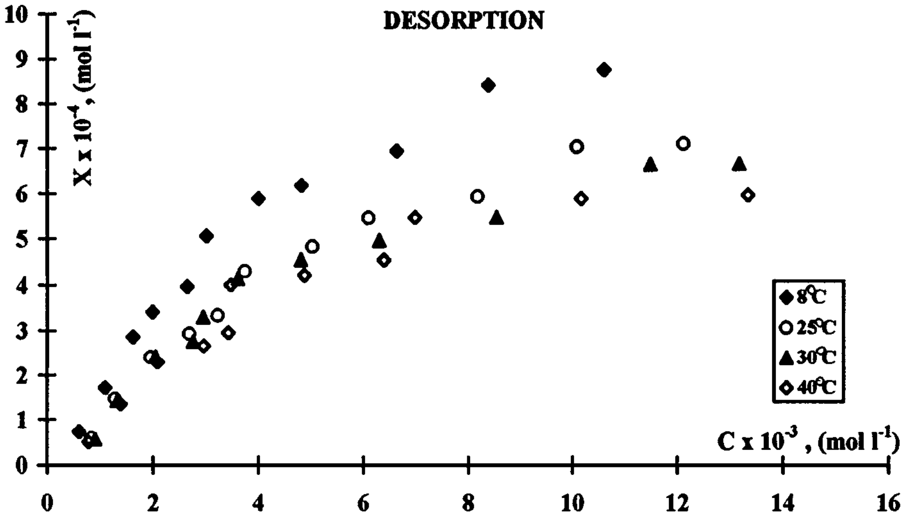

Figure 6. Isotherms for Cu^{2+} desorption for all temperatures. *X*: Concentration of adsorbed Cu^{2+} and *C*: Equilibrium Cu^{2+} concentration.

and

$$Cu^{2+} + H_2O \overset{K_h}{\longleftrightarrow} CuOH^+ + OH^- \tag{2}$$

Initial	C_0		
Hydrolyzed	aC_0	aC_0	aC_0
Equilibrium	$C_0(1-a)$	aC_0	aC_0

where C_0 is the initial Cu^{2+} concentration (mol l^{-1}), and a is hydrolysis degree.

- For $C_0 = 0.0010$ M, equilibrium pH was measured to be 5.19, so:

$$\begin{aligned} \mathrm{pH} = 5.19 &\Leftrightarrow [\mathrm{H}^+] = 6.5 \times 10^{-6}\,\mathrm{M} = aC_0 \\ &\Leftrightarrow 6.5 \times 10^{-6}\,\mathrm{M} = a10^{-3} \\ &\Leftrightarrow a = 6.5 \times 10^{-3}. \end{aligned}$$

The hydrolysis constant K_h is:

$$K_h = \frac{a^2 C_0}{1-a} = 4.225 \times 10^{-8} \quad \text{and} \quad pK_h = 7.37.$$

The percentage of hydrolyzed Cu^{2+} is:

$$\%\mathrm{CuOH}^+ = 0.65.$$

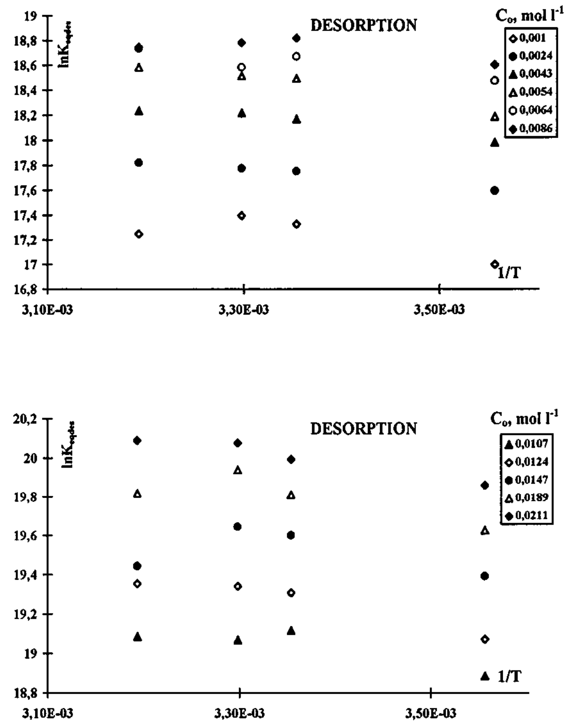

Figure 7. $\ln K_{\mathrm{eq_{des}}}$ as a function of $1/T$ for Cu^{2+} desorption for all temperatures.

- For $C_0 = 0.0211$ M where pH $= 4.86$, it is calculated in the same way that:

  $a = 6.5 \times 10^{-4}$, $K_{\mathrm{h}} = 8.97 \times 10^{-9}$, $pK_{\mathrm{h}} = 8.05$

  and %CuOH^{+} $= 0.065$.

From the above calculations, it is obvious that the hydrolysis of Cu^{2+} to produce $CuOH^{+}$ is negligible and may be ignored in the present investigation.

Nomenclature

N	solution normality (equiv. l^{-1})
C.E.C.	cation exchange capacity (meq (100 g)$^{-1}$)
C_0	initial copper concentration (mol l^{-1})
X	adsorbed copper concentration (mol l^{-1})
C	($:C_0 - X$) concentration of copper remains in solution (mol l^{-1})
$K_{\mathrm{eq_{ad}}}$	equilibrium constant for Cu^{2+} adsorption, no units
[. . .]	concentration (mol l^{-1})
K'_{eq}	equilibrium constant for $CuOH^{+}$ adsorption (mol l^{-1})
c	initial H^{+} concentration at desorption solution (mol l^{-1})
C_{des}	concentration of desorbed Cu^{2+} (mol l^{-1})
$K_{\mathrm{eq_{des}}}$	equilibrium constant for Cu^{2+} desorption (l mol^{-1})
ΔG^0	standard free energy (kcal mol^{-1})
R	gas constant (1.98×10^{-3} kcal mol^{-1}grad^{-1})
T	absolute temperature (K)
K_{eq}	equilibrium constant, generally
ΔH^0	apparent heat of reaction-enthalpy (kcal mol^{-1})
ΔS^0	entropy (kcal mol^{-1} grad^{-1})
a	hydrolysis degree, no unit
K_{h}	hydrolysis constant (mol l^{-1})
K	Freundlich isotherm constant (mol^{1-n} l^{n-1})
n	Freundlich isotherm constant, $n < 1$
A	Constant for Gouy-Chapman model
B	Constant for Gouy-Chapman model (mol^{-1} l)

References

Alloway, B.J., *Heavy Metals in Soils*, pp. 151–153, Blackie & Son, London, 1990.

Cavallaro, N. and M.B. McBride, "Copper and Cadmium Adsorption Characteristics of Selected Acid and Calcareous Soils," *Soil Sci. Soc. Am. J.*, **42**, 550–556 (1978).

Dimirku, A., A. Ioannou, and Ch. Kalliannou, "Synthesis-Identification of Hematite and Kaolinite-Hematite (k-h) system," *Commun. Soil Sci. Plant Anal.*, **27**(5–8), 1091–1106 (1996).

Doula, M., A. Ioannou, and A. Dimirkou, "Thermodynamics of Potassium Exchange in Calcium Bentonite (Ca-b)," *Commun. Soil Sci. Plant Anal.*, **26**(9–10), 1535–1545 (1995).

Doula, M., A. Ioannou, and A. Dimirkou, "Thermodynamics of Phosphate Adsorption–Desorption by Alfisols, Entisols, Vertisols and Inceptisols," *Commun. Soil Sci. Plant Anal.*, **27**(5–8), 1749–1764 (1996).

Forbes, E.A., A.M. Posner, and J.P. Quirk, "The Specific Adsorption of Divalent Cd, Co, Cu, Pb and Zn on Goethite," *J. Soil Sci.*, **27**, 154–166 (1974).

Ioannou, A., A. Dimirkou, and Th. Mavromoustakos, "Isotherms of Phosphate Sorption by Hematite and Bentonite-Hematite (b-h) system," *Commun. Soil Sci. Plant Anal.*, **27**(5–8), 1901–1924 (1996).

ISO Standards Compendium, *Environment Soil Quality* (1st edn.), ISO/TC 190, Chairman, 1994.

James, R.O. and N.J. Barrow, "Copper reactions with inorganic components of soils including uptake by oxide and silicate minerals." In *Copper in Soils and Plants*, Academic Press, Sydney, 1981.

Karathanasis, A.D., "Subsurface Migration of Copper and Zinc Mediated by Soil Collois," *Soil Sci. Soc. Am. J.*, **63**, 830–838 (1999).

McBride, M., C.E. Martinez, and S. Sauve, "Copper(II) Activity in Aged Suspensions of Goethite and Organic Matter," *Soil Sci. Soc. Am. J.*, **62**, 1542–1548 (1998).

Okazaki, R., H.W. Smith, and C.D. Moodie, "Hydrolysis and Salt-Retention Errors in Conventional Cation Exchange Capacity

Procedures," *Soil Sci*., **96**, 205–209 (1963).

Padmanabham, M., "Adsorption-Desorption Behavior of Copper (II) at the Goethite-Solution Interface," *Aust. J. Soil Res*., **21**, 309–320 (1983).

Rich, C.I., "Mineralogy of Soil Potassium," in *The Role of Potassium in Agriculture*, V. Kilmer, S.E. Younts, and N.C. Brady (Eds.), pp. 79–108, American Society of Agronomy, Madison, WI, 1962.

Sparks, M.K., D.J. Wells, and J.J. Johnson, "Characterizing Trace Metal Adsorption on Kaolinite," *European J. Soil Sci*., **46**, 633–640 (1995).

Tan, H.K., *Principles of Soil Chemistry* (2nd edn.), p. 183, Marcel Dekker, NY, 1993.

Udo, E.J., "Thermodynamics of Potassium-Calcium and Magnesium-Calcium Exchange Reactions on Kaolinitic Soil Clay," *Soil Sci. Soc. Amer. J*., **42**, 556–560 (1978).

Vlasova, N.N., "Adsorption of Cu^{2+} Ions onto Silica Surface from Aqueous Solutions Containing Organic Substances," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **163**, 125–133 (2000).