

COPPER ADSORPTION ON BENTONITE AND SOIL AS AFFECTED BY pH

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ABSTRACT

The adsorption of Cu by bentonite and by soils high in iron oxides, and the effect of pH were the subject of this investigation. These processes were studied in the presence of 0.01 M K₂SO₄ under different initial concentrations of Cu (12–20 mg.cm⁻³ of bentonite or soil solution) and pH (4.0–8.0). Parameters characteristic of the isotherm models recorded for each pH value were used to compare the copper sorption processes examined at various pH values. In the course of this work the Langmuir isotherm model was employed. Using the parameters of these separate models, a model suitable for the description of the pH dependence of sorption was elaborated. This model, which is a logistic function containing an additive member, provides a good description of the pH dependence of both the adsorption maximum and the steepness of the initial section of the adsorption isotherm. Models using either the adsorption maximum or the initial steepness proved to be equally suitable for the description of the copper adsorption taking place on bentonite. In soil a linear correlation was found at all pH values between the quantity of adsorbed copper and the concentration of the equilibrium solution. These straight lines can be regarded as the section of the Langmuir equations, which can be approximated with an initial straight line. The slope of the straight lines equals to the product of the adsorption maximum and the energetic constant. With the help of the model it is possible to calculate the pH value at which copper adsorption changes to the greatest extent as the result of changes in pH. In the cases examined, this value was around pH 7, which correlates well with the fact that the copper ion forms adsorbed on the surface exhibit the most intensive change at a pH of around 7.

INTRODUCTION

The contribution of the copper (Cu) concentration in soils and soil components to plant nutrition and pollution control has been studied by many authors (1,2,3). Copper becomes adsorbed on the soil, forming associations with organic matter, Fe and Mn oxides, soil minerals, etc., thus making it one of the least mobile of the trace metals. The usual source of copper fertiliser is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (bluestone).

Studies were made on the sorption of anions and cations by bentonite and soils (4, 5, 6, 7, 8, 9, 10, 11). All these authors agree that the main factors influencing the movement of anions and cations and their availability to plants are soil composition, supporting electrolyte concentration, the initial concentration of the anion or cation adsorbed, and the solution pH. Copper adsorption was found to increase with a rise in pH (4) and was completed at pH values less than $\text{pK}_1 = 7.2\text{--}8.1$ (K_1 is the first hydrolysis constant of the metal):



The other two hydrolysis constants for Cu^{2+} at 25 °C were summarised by Leckie and Davis (12) as:



The values reported for pK_2 ranged from 13.7 to 17.3 and for pK_3 from 10.3 to 10.95.

The pH also influences the surface charge of soil colloids. At the isoelectric point the surface charge is zero, while at lower values of pH they have a net positive charge and at higher pH a net negative charge.

In the course of the present work studies were made on the pH dependence of Cu sorption on bentonite and soil.

MATERIALS AND METHODS

The studies were performed on soil located in Northern Greece. The taxonomic classification is given in *Table 1* and the physical and chemical properties of the soil in *Table 2*. The sample was air-dried and crushed to pass a 2 mm sieve. Particle size analysis was carried out using the pipette method (13). Organic matter was determined by the Walkley–Black method (14) and cation exchange capacity (C.E.C.) by MgCl_2 saturation with subsequent displacement by CaCl_2 (15,16). The exchangeable K was determined following extraction by 1 N ammonium

acetate, pH 7.0, and the available P by the method of Bray and Kurtz (17). The electrical conductivity (E.C.) was measured in a saturated soil paste and the pH measurements were made in a 1:2 soil/water mixture. The CaCO₃ equivalent was determined by treatment with dilute acid and the volume of released CO₂ using a Bernard calcimeter. Oxalate-, pyrophosphate- and CBD-extractable oxides were determined by the methods of (18, 19, 20), respectively.

Table 1. Soil taxonomic classification and particle size distribution of the soil.

Taxonomic Classification	Depth cm	Sand %	Silt %	Clay %
Alfisol Rhodoxeralf	0 - 50	22	16	62

Table 2. Physical and Chemical properties of soil.

Sample	Liquid Limit%	E.C Mmhos cm ⁻¹	pH 1:2	C.E.C. Meq 100 ⁻¹ g ⁻¹	CaCO ₃ Equiv.%	Ca* %	Organic matter, %
Alfisol Rhodoxeralf	56	<3	4.8	27.6	1.0	0.21	0.2

Exchangeable K Meq 100 ⁻¹ g ⁻¹	Available P (Bray-Kurtz) ppm	Total Salt %	Fe ₂ O ₃ %			Mn* ppm	Cu* ppm	Mg* %
			CBD [†]	Oxal. [‡]	Pyr. [§]			
0.32	7.5	<0.14	3.37	0.275	0.115	535	29.1	1.51

[†]CBD = citrate-bicarbonate-dithionite

[‡]Oxal.= oxalate

[§]Pyr.=pyrophosphate

*total concentration

Table 3 presents the physical and chemical properties of bentonite. The pH was measured in a 1:11 bentonite/water mixture and was found to be 6.00. The cation exchange capacity (C.E.C.) of bentonite was determined by MgCl₂ saturation with subsequent displacement by CaCl₂ (15, 16). The surface area of bentonite was determined using a Sorptomatic 1900 Carlo Erba porosimeter as described by Borggard (21, 22), while the total metal concentrations were measured with the method given in the ISO Standards Compendium (23).

Table 3. Physical and chemical properties of bentonite.

Sample	Mg.E.C. Mmol 100 ⁻¹ g ⁻¹	Specific Surface m ² g ⁻¹	Cu* ppm	Mn* ppm	Ca* %	Mg* %	pH
Bentonite	65.57	616.4	27.1	975	2.12	1.51	6.00

* Total metal concentration

Triplicate samples of soil and bentonite (< 2μ) were used for the adsorption studies. To each sample CuSO₄ solution was added, with K₂SO₄ as electrolyte and HNO₃ or KOH for pH adjustment. The Cu adsorption by soil and bentonite (4 g dm⁻³) was studied for five different initial concentrations of Cu (12, 14, 16, 18 and 20 mg Cu/dm³ of solution) with an electrolyte concentration of 0.01 N K₂SO₄ and five pH values (4.0, 5.0, 6.0, 7.0 and 8.0). The samples were incubated for a week at constant temperature (25°C) until equilibrium was reached and then centrifuged for twenty minutes at 15000 g and filtered. The quantity of Cu²⁺ in the solutions was measured using a SpectrAA-300 Varian Atomic Absorption Spectrometer.

Function fitting was carried out using an iterative, non-linear regression program based on a simplex stepping algorithm (24). The accuracy of fitting was characterised by the residual variance (res.) between the measured (Cu_{ads.meas.}) and calculated (Cu_{ads.calc.}) values using the following equation:

$$res. = \sqrt{\frac{\sum (Cu_{ads.calc.} - Cu_{ads.meas.})^2}{FG}}$$

where FG = number of data pairs – number of calculated parameters.

The linear correlation coefficient (r) values between the measured and calculated values were also calculated.

RESULTS AND DISCUSSION

The quantity of Cu adsorbed depended to a considerable extent on the acidity of the solution. *Figure 1* illustrates the quantity of copper adsorbed on bentonite and soil from a solution with a Cu concentration of 16 mg/dm³ as a function of solution pH. It can be seen from the figure that the quantity of Cu adsorbed (Cu_{ads.}) rose with pH in the pH range tested.

Parameters characteristic of the isotherm models recorded at each pH value can be used to compare the copper sorption processes taking place at various pH values.

The surface charge, and consequently the adsorption capacity, can be expected to change as a function of pH can the adsorption energy. The ion

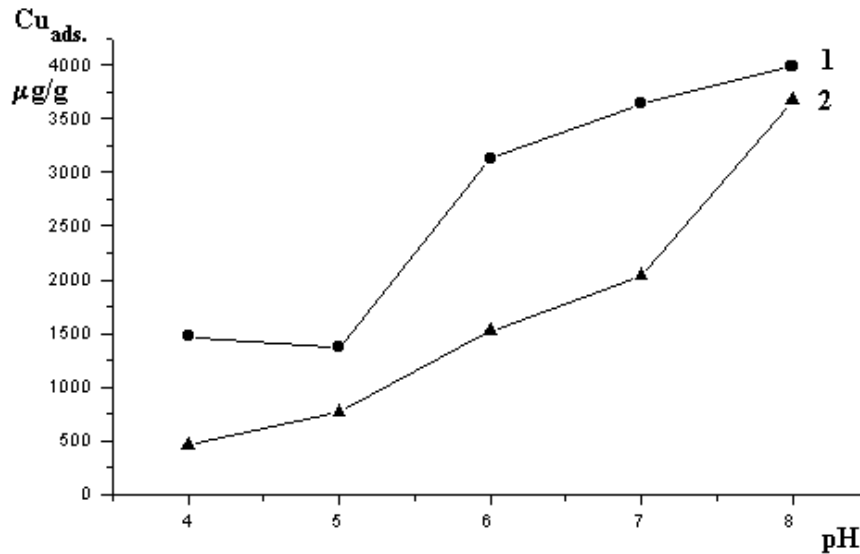


Figure 1. Quantity of copper adsorbed on bentonite (1) or soil (2) as a function of the pH of the solution. The initial concentration of the solution was 16 mg Cu dm⁻³

complex form of copper, the sorbed material, changes as a function of pH, as can be seen in Table 4. The data in this table were calculated using the MINTEQ program, based on a solution model using chemical equilibrium correlations.

Table 4. The Cu ion forms (calculated with the Minteq model).(Cu 12 mg dm⁻³)

Cu ion forms (Cu %)					
PH	Cu ²⁺	CuSO ₄ aq	CuOH ⁺	Cu(OH) ₂ aq	Cu ₂ (OH) ₂ ²⁺
4	65.8	34.2	-	-	-
5	65.7	34.3	-	-	-
6	64.7	33.8	-	-	-
7	33.8	17.7	2.1	36.5	9.9
8	-	-	-	97.4	-

The basis of this new model for the description of adsorption is the Langmuir isotherm model, the two parameters of which reflect both quantitative and qualitative aspects of surface adsorption.

$$Cu_{ads.} = \frac{A}{1 + \frac{1}{k} \cdot \frac{1}{c}}$$

where: Cu_{ads.} is the quantity of Cu adsorbed on bentonite or soil,
 c is the concentration of the equilibrium solution,
 A is the maximum quantity of Cu adsorbed at the given pH,
 k is the energetic constant.

Function fitting carried out using the linearised form of the equation may substantially deform the values of estimated parameters, depending on the variance of the data (25), so non-linear regression was applied.

The variance of the data did not allow either the energetic constant (k) or the adsorption maxima (A) to be accurately determined. The effect of deviation could have been reduced in this experiment by changing the experimental conditions and by increasing the number of measuring points. However, this will not be possible if the model is later applied for large numbers of soil samples.

For this reason the number of parameters in the model had to be further reduced. A model was thus sought with which adsorption at each pH value could be characterised with a single parameter. Experiments were carried out in two directions:

1. using an energetic constant (k) independent of pH,
2. using a linear isotherm model, interpreted with the aid of the Langmuir isotherm model.

Although it is clear that the quality of surface adsorption and consequently the value of k depends on the pH, ignoring the changes in pH nevertheless only causes a relatively small error in the model.

This is illustrated in *Table 5* by means of the parameters of models fitted to the data obtained for bentonite at pH 6 using various energetic constants (k). For each of these energetic constants (k) the values of the adsorption maximum (A), the residual variance (res.) and the correlation coefficient (r) were calculated and it was found that the parameters characteristic of accuracy of fitting (res., r) showed hardly any deviation in the case of models constructed using different parameters.

Table 5. Parameters of the models fitted to the data obtained on bentonite at pH 6 using various values of k.

k	cm ³ μg ⁻¹	0.5	0.8	1.0	2.0	5
A	μg g ⁻¹	4333	3825	3650	3289	3062
Res.	μg g ⁻¹	369	339	334	344	371
r		0.99	0.99	0.99	0.99	0.99

It is clear that in this case, even if the value of k changes by an order of magnitude (10 x), there will only be a 40 % change in the value of A.

Consequently, Langmuir isotherm equations with the same energetic constant (k) were fitted to the Cu adsorption data obtained at different pH values. In this way the effect of pH on adsorption could be characterised with a single parameter: the change in the adsorption maximum (A).

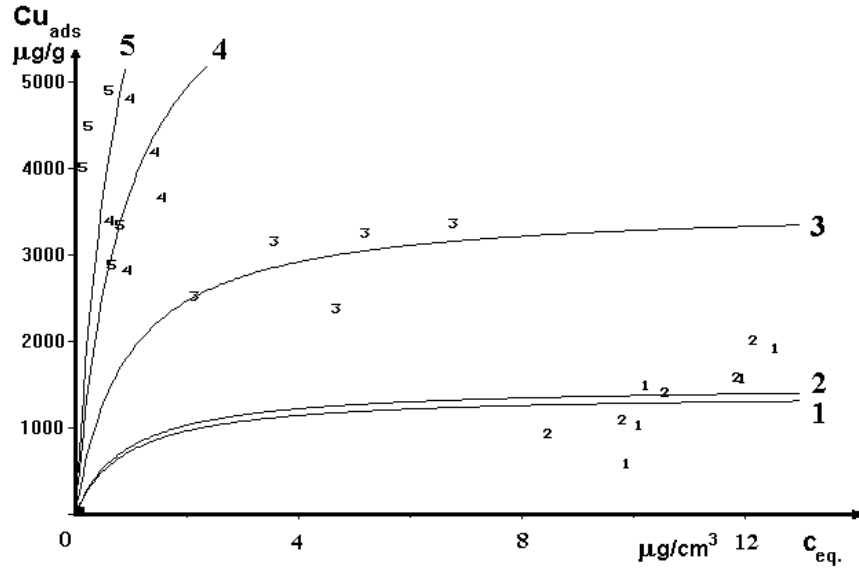


Figure 2. Langmuir isotherms as applied to Cu adsorption on bentonite at the pH values tested. No.1 = pH 4, No.2 = pH 5, No.3 = pH 6, No.4 = pH 7, No.5 = pH 8.

The value of the common energetic constant characteristic of Cu adsorption was $k = 1.114 \text{ cm}^3 \mu\text{g}^{-1}$ in the case of bentonite. This value gave the smallest values of residual variance (res.). The fitted sorption curves are illustrated in Figure 2, while the adsorption maximum (A) and residual variance values and the correlation coefficient (r) between the measured and calculated values are presented in Table 6.

Table 6. pH dependence of the parameters of the Langmuir function fitted to Cu adsorption data obtained on bentonite. The energetic constant is the same in each case ($k = 1.114 \text{ cm}^3 \mu\text{g}^{-1}$)

pH		4	5	6	7	8
A	$\mu\text{g g}^{-1}$	1400	1497	3578	7153	10316
res.	$\mu\text{g g}^{-1}$	456	365	333	807	2206
r		0.94	0.97	0.99	0.98	0.48

When the adsorption maxima (A) are plotted as a function of pH an S-shaped curve is obtained (Fig. 3). The best model for the curve is a logistic function. This is known as an autocatalytic model in reaction kinetics (26) and as a growth model in plant physiology (27):

$$A = \frac{\Delta A}{1 + e^{-b \cdot (pH - pH_{infl.})}} + A_{\min.}$$

where ΔA is the increment between the maximum and minimum of the pH-dependent A value, A_{\min} is the minimum value of A, $pH_{infl.}$ is the pH value at the inflection point of the curve, and b the growth constant.

The values of the parameters, determined with the aid of non-linear regression, were as follows: $\Delta A = 10617 \mu\text{g}\cdot\text{g}^{-1}$, $A_{\text{min}} = 1129 \mu\text{g}\cdot\text{g}^{-1}$, $b = 1.559$, $\text{pH}_{\text{infl}} = 6.81$ and the residual variance (res.) = $295 \mu\text{g}\cdot\text{g}^{-1}$. The fitted curve can be seen in *Figure 3*.

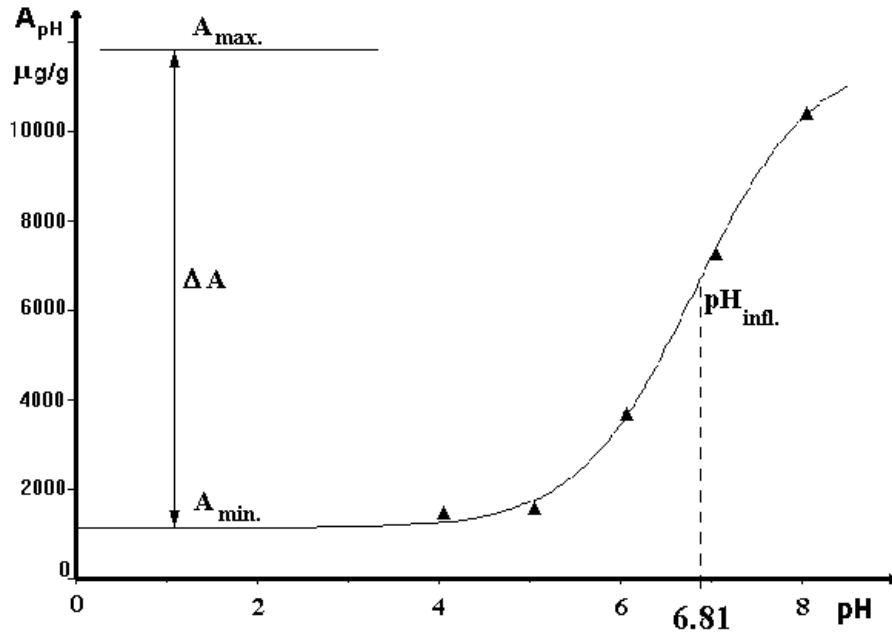


Figure 3. pH dependence of adsorption maximum (A_{pH}) values on bentonite.

The adsorption maxima rose almost tenfold as a function of pH. The steepest increase was observed at the inflection point of the curve, at pH 6.81.

Another approach to model development is to use a linear isotherm model and to interpret this with the aid of the Langmuir isotherm model. In this case a straight line starting from the origo was fitted to each of the points depicted on *Figure 2* for each pH value.

These straight lines can be regarded as the portions of the Langmuir functions which can be approximated with an initial straight line. This initial section of the adsorption isotherm can in practice be fitted to a tangent drawn through the point on the adsorption curve at which the equilibrium concentration is zero. The slope of the tangent can be calculated using the derivate calculated for the given point of the function. The correlation obtained after the derivation of the Langmuir function is:

$$\frac{dCu_{\text{ads.}}}{dc} = \frac{A \cdot k \cdot (1 + k \cdot c) - k \cdot A \cdot k \cdot c}{(1 + k \cdot c)^2} = \frac{A \cdot k}{(1 + k \cdot c)^2}$$

If the value of the equilibrium solution concentration is taken as 0 for the initial stage, the slope of the derivate, i.e. the tangent drawn at the initial point, is the product of the adsorption maximum (A) and the energetic constant (k):

$$\frac{dCu_{\text{ads.}}}{dc} = A \cdot k$$

Table 7. Slope (A*k) of the initial nearly straight section of the Langmuir functions fitted to the Cu adsorption data measured on bentonite as a function of pH.

pH		4	5	6	7	8
A*k	cm ³ g ⁻¹	121.3	133.0	606.0	3387.5	6503.4
res.	μg g ⁻¹	362	219	813	1235	2447
r		0.86	0.95	0.76	0.66	0.97

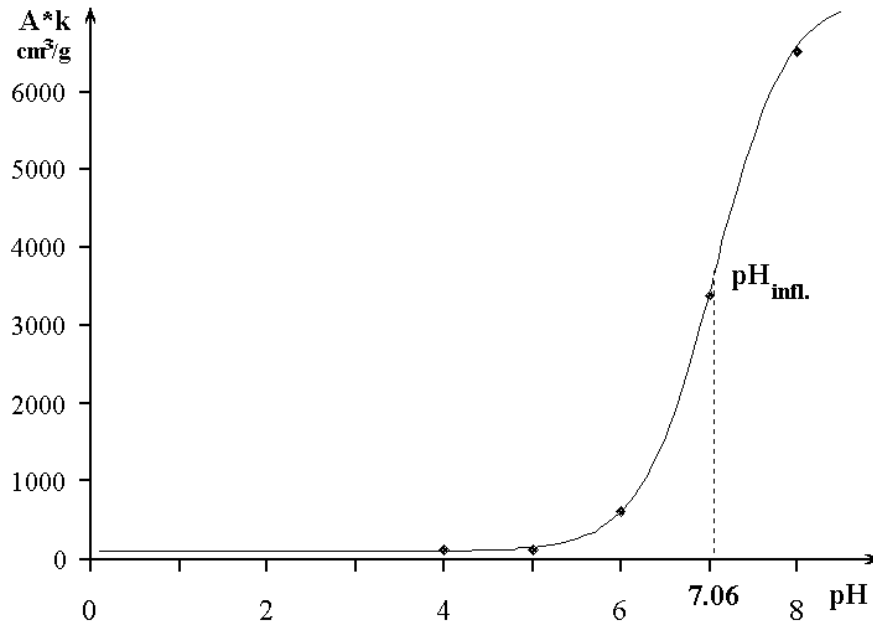


Figure 4. pH dependence of the $A_{pH} * k$ values corresponding to the slope of the initial – approximately linear – section of the adsorption isotherms on bentonite.

The values of A*k, the residual variance and the correlation coefficient (r) are presented in Table 7. If the values of A*k are plotted as a function of pH the points are located, as in the case of the other method of calculation, along the S-shaped curve given by the values of the adsorption maximum (A) (Fig. 4). This was to be expected, since if the value of k again exhibits no substantial pH dependence, the two quantities (A*k and A) differ only in the constant multiplier (k), which has no effect on the shape of the curve. An attempt was thus made to describe the pH dependence by means of a logistic function. If the values found at pH 8 are omitted, a model well fitted to the points is obtained:

$$A * k = \frac{\Delta A * k}{1 + e^{-b(pH - pH_{inf.})}} + A_{min.} * k$$

where $\Delta A * k$ is the increment between the maximum and minimum of the pH-dependent A*k value, $A_{min} * k$ is the minimum value of the pH-dependent A*k, pH_{inf} is the pH value at the inflection point of the curve, and b the growth constant.

This model corresponds mathematically with that derived for the other method of calculation. This becomes obvious if all the terms of the equation (both sides of the equation) are divided by k .

The values of the parameters, determined using non-linear regression (*Fig. 4*), were as follows: $\Delta A^*k = 7142.1 \text{ cm}^3 \cdot \text{g}^{-1}$, $A_{\text{min}}^*k = 103.2 \text{ cm}^3 \cdot \text{g}^{-1}$, $b = 2.438$, $\text{pH}_{\text{infl}} = 7.06$, the residual variance (*res.*) = $371.9 \text{ cm}^3 \cdot \text{g}^{-1}$ and $r = 0.999$.

The pH dependence of Cu sorption was also examined on soil. In this case a clear linear correlation was found between the quantity of adsorbed copper (Cu_{ads}) and the concentration (c) of the equilibrium Cu solution at all pH values (*Fig. 5*). As can be seen in the figure, the steepness of these straight lines depends on the pH of the solution. The values of A^*k , the residual variance and the correlation coefficient (r) are presented in Table 8.

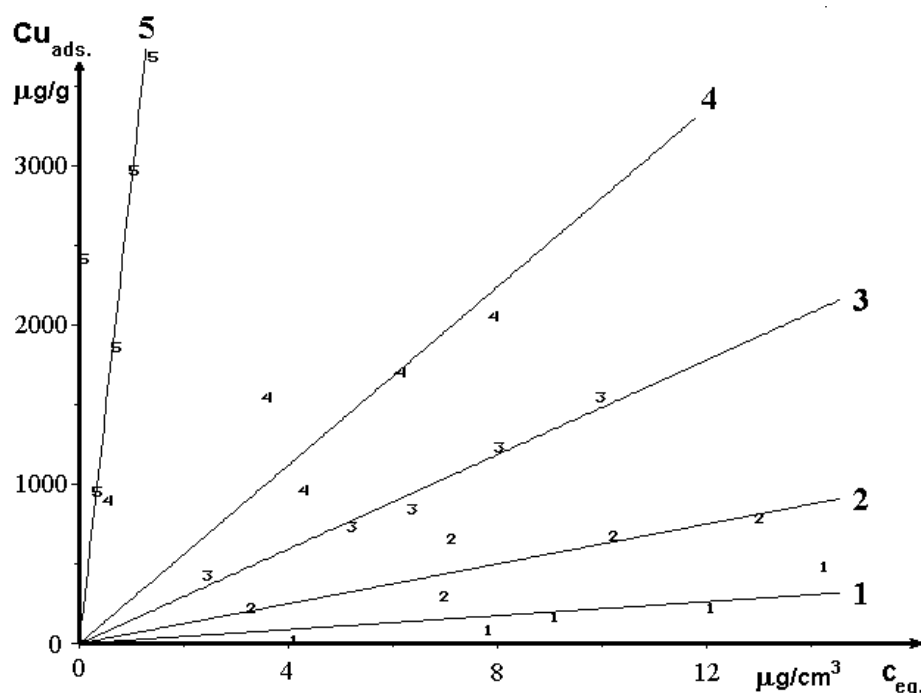


Figure 5. The Cu adsorption of the soil in the concentration range investigated can be described by linear functions, in all the experiments carried out at all pH values.

No.1=pH 4, No.2=pH 5, No.3=pH 6, No.4=pH 7, No.5=pH 8.

Table 8. Slope (A^*k) of the initial nearly straight section of the Langmuir functions fitted to the Cu adsorption data measured on soil as a function of pH.

pH		4	5	6	7	8
A^*k	$\text{cm}^3 \text{ g}^{-1}$	21.9	62.6	148.5	280.1	2907.6
<i>res.</i>	$\mu\text{g g}^{-1}$	108	128	71	487	1209
r		0.99	0.99	0.99	0.99	0.99

The values of the parameters, determined using non-linear regression (Fig. 6), were as follows: $\Delta A \cdot k = 503.5 \text{ cm}^3 \cdot \text{g}^{-1}$, $A_{\text{min}} \cdot k = 0 \text{ cm}^3 \cdot \text{g}^{-1}$, $b = 1.095$, $\text{pH}_{\text{infl}} = 6.79$, the residual variance (res.) = $0.96 \text{ cm}^3 \cdot \text{g}^{-1}$ and $r = 1.0$.

The sudden increase of Cu sorption on soil was at the same pH as on bentonite. This pH seems to be independent of quality of adsorbent.

In the pH 6–8 range a radical change in the sorption parameters can be observed as the result of the joint effect of two processes: a rapid increase in the negative charge mass close to the isoelectric point, and a change in ion form in the solution phase in this pH range. This latter means that while at pH 6 the quantity of Cu^{2+} ions (65 %) and of dissociated CuSO_4 (34 %) is approximately constant, at pH 7 the quantity of these two ion forms drops to half, while the $\text{Cu}(\text{OH})_2 \cdot \text{aq}$ form exhibits a decisive increase (37 %). At pH 8 the proportion of any form other than $\text{Cu}(\text{OH})_2 \cdot \text{aq}$ (97 %) becomes negligible (Table 4). It is a well-known fact that metal oxocomplexes are much more strongly bound to the surfaces of the adsorbents found in the soil.

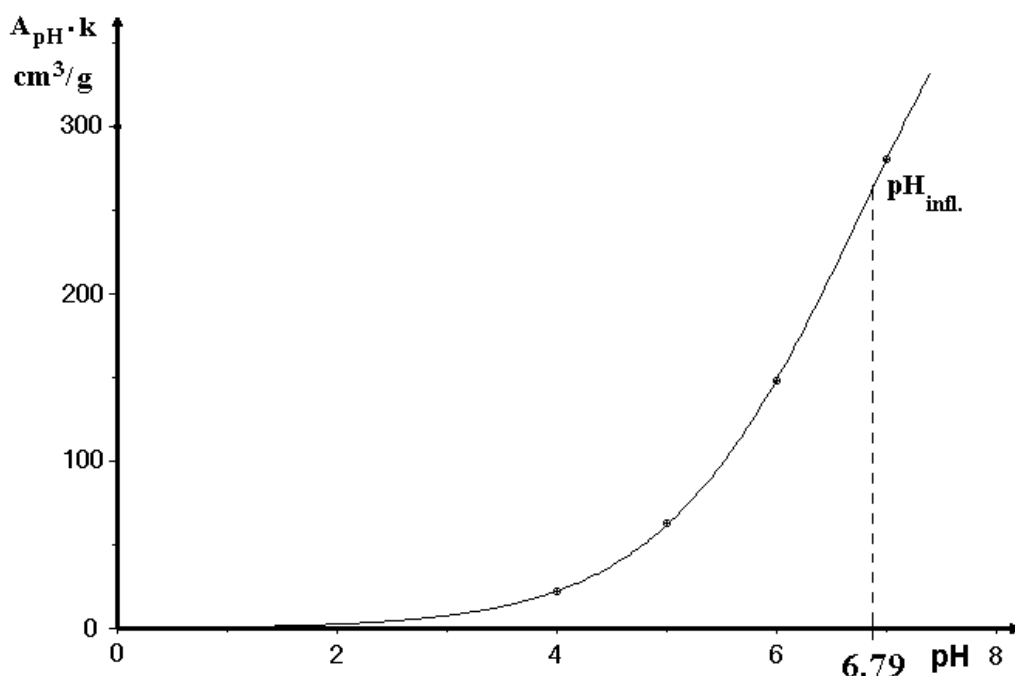


Figure 6. pH dependence of the $A_{\text{pH}} \cdot k$ values corresponding to the slope of the initial – approximately linear – section of the adsorption isotherms on soil.

CONCLUSIONS

The model descriptive of pH dependence is a logistic function containing an additive member. This model gives a good description both of the adsorption maxima of the Langmuir isotherm at various pH values and of the pH dependence of the steepness of the initial phase of the adsorption isotherm. With the aid of the model it is possible to calculate the pH value at which copper adsorption changes to the greatest extent due to changes in pH.

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