

# Studies of Competitive $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ and $\text{Cr}^{3+}$ Sorption in Grey-Brown Podzolic Soils

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## Abstract

Studies of competitive sorption were carried out using the three-component solution  $\text{CuCl}_2$ ,  $\text{CoCl}_2$  and  $\text{CrCl}_3$  in two grey-brown podzolic soils saturated with  $\text{Ca}^{2+}$  cations. In most cases in batch experiments the Freundlich equation was the best to describe the sorption process. The linear sorption equation was successfully applied to describe  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  sorption in column experiments. A significant effect of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  on  $\text{Co}^{2+}$  sorption was found in both column and batch experiments. Sorption of ions of the studied heavy metals was not equivalent to  $\text{Ca}^{2+}$  desorption from soil.

**Keywords:** heavy metals, soils, competitive sorption

## Introduction

Knowledge of various interactions between the solid phase components and the substances in the solution is of significant importance to many environmental science disciplines [5, 6]. In soil science this information is indispensable to determine the sorption processes and mobility of such pollutants as heavy metals or organic substances in soil profiles and groundwater aquifers.

Metal ions are bonded by layer silicate clays with permanent negative charge by ion exchange reactions. Clays have high preference for higher-charge cations. In the case of the same charge, preference is generally higher for cations with the largest ionic radii and the lowest hydration energies [17]. Metal oxides and hydroxides of Fe, Mn and Al as well as amorphous aluminosilicates provide sorption sites for specific sorption. Preference of oxides and hydroxides for heavy metals often correlates with the first hydrolysis constant of the metal ions. Bonding such cations as  $\text{Cd}^{2+}$  or  $\text{Co}^{2+}$  on organic matter can be viewed as an ion exchange process. The high degree of selectivity shown by organic matter for such metals as  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  suggests that they are also specifically sorbed [17, 18].

A large part of studies meant for obtaining adsorption isotherms was made using batch experiments [5]. The results of these studies showed that the heavy metal sorption in soils is well described by the Freundlich equation [10, 12]. Various forms of the Langmuir equation were often successfully applied [8, 24]. Column experiments can be an alternative for batch experiments. A column is considered as a model for natural displacement of dissolved substance in the soil [27]. As column experiments are much closer to field conditions [13], recently they have been the most frequently applied method to study sorption [19].

Studies of heavy metal sorption are focused mainly on one-component systems [18], though it has been known for a long time that competition between heavy metal ions for soil sorption sites can cause an increase of their mobility and bioavailability [20]. However, there are only few papers concerning sorption of heavy metal ions in multi-component systems [3].

Therefore, research concerning the course and range of sorption of heavy metal ions ( $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) in multi-component systems in Polish mineral soils was undertaken. This paper presents part of

these studies. Knowledge of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  sorption processes is important in soil sciences because metals are of moderate or high toxicity for plants and mammals, and human activity may result in increases of their contents in soils [17].

The aim of these studies was to determine the course of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  sorption in the three-component system in selected soils and their description by means of sorption equations commonly used in soil sciences. The experiments were performed also in order to have insight into the leading chemical processes between the metal ions and the solid phase of soils. To accomplish this objective detailed batch and column experiments were carried out.

## Materials and Methods

### Soils

The studies were carried out using the samples taken up from  $A_p$  level of grey-brown podzolic soils derived from slightly loamy silty sand as well as that derived from clay silt (referred to as sandy and loess soil in the paper). In Poland the area of grey-brown podzolic soil derived from clays and loamy sands is 24%, the area of that derived from loess and loess-like formations is 2.69% [28]. The soil samples were air-dried, sieved using a 1 mm mesh diameter sieve and averaged. The basic physicochemical properties of sandy and loess soils were as follows: floating fraction contents - 10 and 39%, colloidal clay contents - 2 and 3%, pH in KCl - 3.9 and 4.3, specific (total) surface area - 8.67 and 20.05  $\text{m}^2 \text{g}^{-1}$ , humus contents - 1.24 and 1.52%, total sorption capacity - 41.4 and 77.5  $\text{mmol}_c \text{kg}^{-1}$ .

### Column Experiments

Soil samples were uniformly packed to the polypropylene columns of the inner diameter 2.75 cm and length 5.55 cm. The soil column was saturated with water at the velocity rate determined for a given experiment, maintained by means of a peristaltic pump. Then the soil was saturated with  $\text{Ca}^{2+}$  cations by passing 60  $\text{cm}^3$  of  $\text{CaCl}_2$  solution of a concentration 0.05  $\text{mol dm}^{-3}$ . The effluent from the column was collected in 5  $\text{cm}^3$  portions by means of a fraction collector. The contents of  $\text{Cl}^-$  anions in the effluent portions were determined by the Mohr method. Then 50  $\text{cm}^3$  of deionized water and the three-component solution including 0.0166  $\text{mol dm}^{-3}$   $\text{CuCl}_2$  and  $\text{CoCl}_2$  as well as 0.0111  $\text{mol dm}^{-3}$   $\text{CrCl}_3$  were passed through the column. Solution pH was 2.9 and it was not buffered due to the effect of buffer ions on sorption. The amounts of ions of individual metals in the solution were chemically equivalent. The last stage was passing 50  $\text{cm}^3$  of deionized water through the column. pH was measured in the portions of the effluent from the column. Contents of Cu, Co, Cr and Ca in the portions were determined by means of Flame Atomic Absorption Spectrometry (FAAS). Ionic equi-

libria of the solution were calculated using the program MINEQL<sup>+</sup> [26].

Changes of the substance concentration in the solution introduced with the constant velocity of flow into the soil column (whose pores are completely filled with liquid) on the column outlet are described by the breakthrough equation [29]:

$$C(T)/C_0 = 1/2 \operatorname{erfc}[\sqrt{P/4RT}(R-T)] + 1/2 e^P \operatorname{erfc}[\sqrt{P/4RT}(R+T)], \quad (1)$$

where:

$C_0$  and  $C$  - the concentrations of the substance in the influent and effluent from the column [ $\text{mol}_c \text{dm}^{-3}$ ],

$T$  - the pore volume ( $T = ut/L$ ),

$P$  - the Peclet column number ( $P = uL/D$ ),

$R$  - the retardation factor,

$L$  - the column length [cm],

$t$  - the time [h],

$u$  - the mean interstitial velocity [ $\text{cm h}^{-1}$ ],

$D$  - the dispersion coefficient [ $\text{cm}^2 \text{h}^{-1}$ ].

In equation (1)  $\operatorname{erfc}(x)$  is the complementary error function which can be calculated numerically [1].

The values of  $u$  and  $D$  were calculated (Solver tool of Excel 2000 package) from eq. (1) based on the concentration  $C_{exp}^c(T)$  for  $\text{Cl}^-$  anions for which  $R = 1$  [22]. The results of calculations correspond to the maximum of squared correlation coefficient ( $r^2$ ) for  $C_{eq}^c(T)$  versus  $C_{exp}^c(T)$  relationships. Calculation accuracy was checked using experimental data obtained by Elprince et al. [7] and the calculated values of  $u$  and  $D$  were compared with their results and those of Yamaguchi et al. [30].

Sorption in soils is most frequently described by the Freundlich equation [10, 12]:

$$S_e = k_F C_e^n, \quad (2)$$

where:

$k_F$  and  $n$  are the equation coefficients,

$S_e$  and  $C_e$  are the sorption and equilibrium concentrations in  $\text{mol}_c \text{kg}^{-1}$  and  $\text{mol}_c \text{dm}^{-3}$ , respectively.

In the column experiments the retardation factor  $R$  is described by equation [14]:

$$R = 1 + \frac{\rho_b}{\varepsilon} n \frac{S_e}{C_e} = \frac{\rho_b}{\varepsilon} k_F n C_e^{n-1}, \quad (3)$$

where:

$\rho_b$  is the bulk density [ $\text{g cm}^{-3}$ ],

$\varepsilon$  is the soil porosity in the column [ $\text{cm}^3 \text{cm}^{-3}$ ].

The  $R$  value changes depending on  $C_e$ . The coefficients  $n$  and  $k_F$  can be calculated solving numerically the classical advection-dispersion equation (ADE). The MCMFIT program can be used here [2].

When  $n=1$  the Freundlich equation simplifies to the linear form  $S_e = K_D C_e$ , where  $K_D$  is the linear sorption distribution coefficient. Value  $R$  is then constant and independent of concentration [14]:

Table 1. Parameters of the soil columns used in the experiments.

Soil	$\rho_b$ $\frac{\text{g}}{\text{cm}^3}$	$\varepsilon$ $\frac{\text{cm}^3}{\text{cm}^3}$	$u$ $\frac{\text{cm}^2}{\text{h}}$	$D$ $\frac{\text{cm}^2}{\text{h}}$	$P$	$r^{2*}$	$R_c$	$r^{2**}$
Sandy soil	1.58	0.46	7.29	3.95	10.2	0.9993	1.003	0.9993
	1.58	0.45	3.42	1.59	11.9	0.9987	0.987	0.9987
Loess soil	1.27	0.57	3.59	0.13	151.4	0.9999	1.002	0.9999
	1.27	0.56	1.87	0.05	190.8	0.9994	0.999	0.9994

$\rho_b$  = bulk density;  $\varepsilon$  = porosity;  $u$  = mean interstitial velocity;  $D$  = dispersion coeff.;  $P$  = Peclet number;  $r^{2*}$  = squared correlation coeff. - assumption  $R_c = 1$ ;  $R_c$  = retardation coeff.;  $r^{2**}$  = squared correlation coeff. - assumption  $R_c \neq 1$ .

$$R = 1 + \frac{\rho_b}{\varepsilon} K_D \quad (4)$$

In this case  $R$  can easily be calculated by estimation for the sorbed substance  $a$  such a value  $K_D^a$  that gives the best correlation between the experimental points and those determined from equation (1).

Sorption  $S$  [ $\text{mol}_c \text{ kg}^{-1}$ ] of the substance  $a$  in the column can be calculated from the following equation:

$$S^a = \left( \sum_{i=1}^j (C_0^a \frac{C_i^c}{C_0^c} - C_i^a) v_i \right) / m, \quad (5)$$

where:

$m$  [kg] is the soil mass in the column,

$i$  is the number of the effluent portion of the volume  $v$  [ $\text{dm}^3$ ],

$C_i^a$  and  $C_0^a$  are the concentrations of the substance  $a$  in this portion and in influent [ $\text{mol}_c \text{ dm}^{-3}$ ],

$C_i^c$  and  $C_0^c$  are the respective concentration of the conservative element [ $\text{mol}_c \text{ dm}^{-3}$ ].

To obtain the adsorption isotherms from the column experiments the local equilibrium assumption must be satisfied. The existence of physical equilibrium was checked in each experiment by means of Maraqua, et al. [15] method, which makes use of the property that the presence of stagnation water in the column shifts the breakthrough curve for the conservative element to the left and changes the value of the retardation factor ( $R \neq 1$ ). The maintenance of the chemical equilibrium was tested applying the two methods: each experiment was carried out with two different flow velocities [5] and another one worked out by Brusseau et al. [4] when flow interruption was used.

### Batch Experiments

Soil samples were placed in columns, saturated with  $\text{Ca}^{2+}$  ions by passing  $60 \text{ cm}^3$   $\text{CaCl}_2$  solution of a concentration  $0.05 \text{ mol dm}^{-3}$ , washed with  $50 \text{ cm}^3$  deionized water then moved onto the Petri plates and air-dried. After breaking up, 5 g samples were weighed and shaken for 24 hours with  $5 \text{ cm}^3$  (sandy soil) or  $10 \text{ cm}^3$  (loess soil) of the three-component solutions  $\text{CuCl}_2$ ,  $\text{CoCl}_2$  and  $\text{CrCl}_3$ . In the solutions the concentration ranges between  $0.0014$  and  $0.0166 \text{ mol dm}^{-3}$  for  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ , and be-

tween  $0.0009$  and  $0.0111 \text{ mol dm}^{-3}$  for  $\text{Cr}^{3+}$  (7 levels). After centrifugation and determination of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ca}^{2+}$  contents in the equilibrium solution by means of the atomic absorption spectrometry the metal sorption was calculated from the concentration differences of the introduced and equilibrium solutions. The experiments were repeated three times. The results were subjected to statistical analysis using Statgraphics Plus V.3.1. software. The methods of simple and nonlinear regression were applied.

### Results

The column experiments were carried out with the two flow velocities:  $7.29$  and  $3.42 \text{ cm h}^{-1}$  in the sandy soil as well as  $3.59$  and  $1.87 \text{ cm h}^{-1}$  in the loess soil (Tab. 1). For each velocity  $u$  there was obtained a very good correlation between the experimental points determined from  $\text{Cl}^-$  concentrations and the points determined from equation (1) for the  $P$  values from Table 1. The column Peclet differences of the experiments in individual soils are not large and comparable to the limits of  $\text{Cl}^-$  determination accuracy. Therefore, it can be assumed that the breakthrough curves ( $\text{BTC}_s$ ) for the conservative element overlap in each soil.

The values of retardation coefficients  $R_c$  for the breakthrough curves of conservative element determined from equation (1) are practically equal to 1 (the values  $r^2$  for  $D$  and  $u$  with the assumption  $R_c = 1$  are identical with the values  $r^2$  assuming  $R_c \neq 1$ ). This means that the condition of the physical equilibrium is maintained [15]. Large dispersion and small Peclet values of the columns with the sandy soil were caused by as much as 64% contribution fraction of particles of  $1.0 - 0.1 \text{ mm}$  diameter in the granulometric composition. In the loess soil contribution of this fraction was only 6.5%.

The course of sorption in the columns with sandy soil is presented in Fig. 1. For clarity the experimental points with lower velocity were plotted only in the essential parts of the  $\text{BTC}_s$ . The  $\text{BTC}_s$  for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  determined using the linear model of sorption (values  $K_D^{Me}$  in Table 2) from the points of experiment carried out with  $u = 7.29 \text{ cm h}^{-1}$  are marked with broken lines. Taking into account the values of correlation coefficients for the determined sorption distribution coefficients  $K_D^{Me}$  it can be assumed

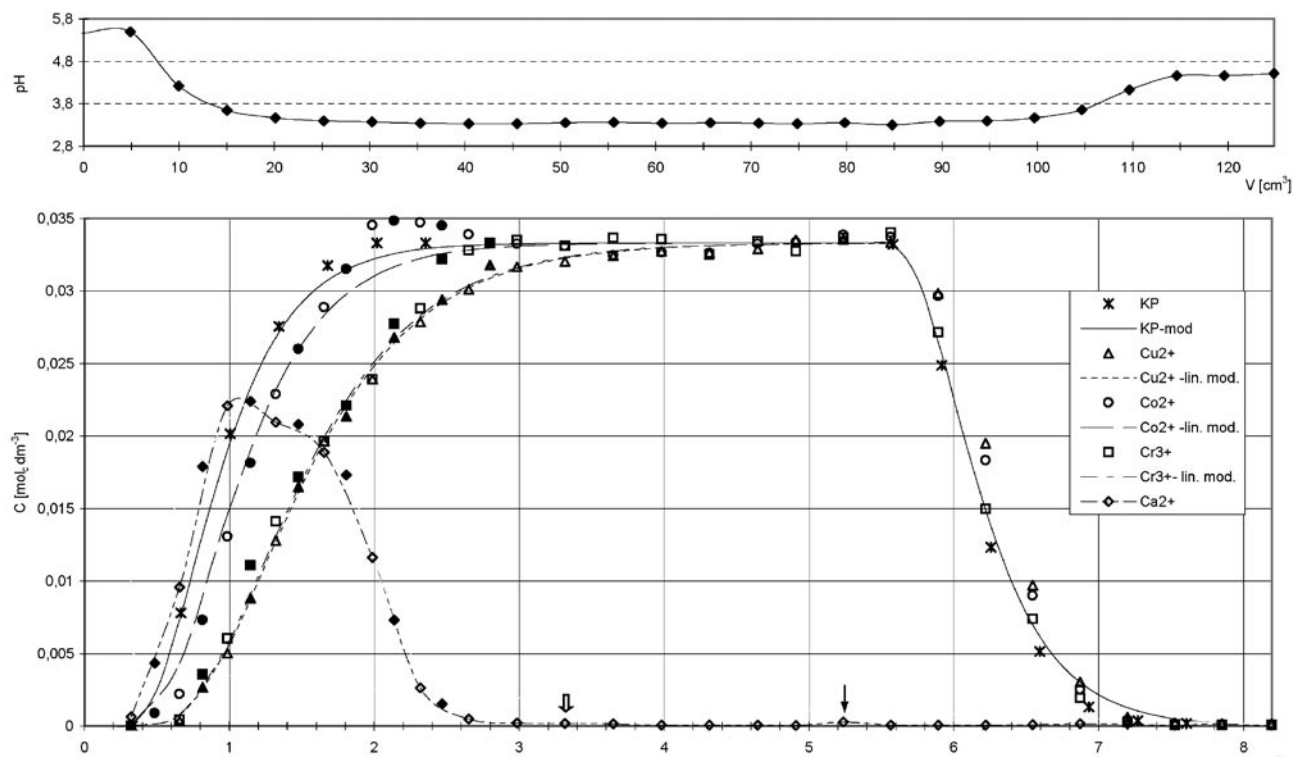


Fig. 1. Measured and predicted BTCs for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions in the sandy soil at  $u = 7.29 \text{ cm h}^{-1}$  (light points) and  $u = 3.42 \text{ cm h}^{-1}$  (black points). In the upper part - pH of the effluent.

that the linear model describes sorption in the columns very well, which is confirmed by small differences in sorption extent determined from these coefficients ( $S_D^{Me} = K_D^{Me} C_0^{Me}$ ) and sorption  $S^{Me}$  determined from equation (5), after achieving the sorption saturation ( $C^{Me} = C_0^{Me}$ ). Small differences in the partition coefficient values for the experiments made with different velocities (differences within the limit of method accuracy) and overlapping of the breakthrough curves indicate that the sorption processes proceeded quickly enough for the chemical equilibrium to be established. The existence of this equilibrium was confirmed by the flow interruption method - the position of points after interrupting the three-component solution flow through the column and

resumption after 24 h did not change (points in Fig. 1 to the right of  $\Downarrow$ ).

Experimental points for  $\text{Co}^{2+}$  cations in the range  $2 < T < 3$  (Fig. 1) are found somewhat above their model curve and the level  $C = 0.0332 \text{ mol}_c \text{ dm}^{-3}$  - concentration in the influent. It means that after the initial sorption some  $\text{Co}^{2+}$  ions were displaced from the soil sorption sites due to competition with  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions. Therefore, the correlation of model BTC<sub>s</sub> for  $\text{Co}^{2+}$  to the experimental points was the smallest (Table 2).

The sorption process in the column with loess soil is presented in Fig. 2. In the figure besides the  $\text{Ca}^{2+}$  ions desorption peak there can be seen a similar peak of  $\text{Co}^{2+}$  ions, the effect of competition with  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  for

Table 2. Parameters of metal ion sorption in the column experiments.

Soil	$u$ $\frac{\text{cm}}{\text{h}}$	$K_D^{Cu}$ $\frac{\text{mol}}{\text{kg}} \frac{\text{mol}}{\text{mol}} \frac{\text{mol}}{\text{dm}^3}$	$S_{CuD}$ $\frac{\text{mol}_c}{\text{kg}}$	$r^{2*}$	$S_{Cu}$ $\frac{\text{mol}_c}{\text{kg}}$	$K_D^{Co}$ $\frac{\text{mol}}{\text{kg}} \frac{\text{mol}}{\text{mol}} \frac{\text{mol}}{\text{dm}^3}$	$S_{CoD}$ $\frac{\text{mol}_c}{\text{kg}}$	$r^{2**}$	$S_{Co}$ $\frac{\text{mol}_c}{\text{kg}}$	$K_D^{Cr}$ $\frac{\text{mol}}{\text{kg}} \frac{\text{mol}}{\text{mol}} \frac{\text{mol}}{\text{dm}^3}$	$S_{CrD}$ $\frac{\text{mol}_c}{\text{kg}}$	$r^{2***}$	$S_{Cr}$ $\frac{\text{mol}_c}{\text{kg}}$
Sandy soil	7.29	0.189	0.0063	0.9995	0.0066	0.047	0.0016	0.9878	0.0014	0.188	0.0063	0.9973	0.0056
	3.42	0.183	0.0061	0.9987	0.0060	0.049	0.0016	0.9927	0.0012	0.164	0.0055	0.9942	0.0050
Loess soil	3.59	0.384	0.0128	0.9904	0.0129	0.202	0.0067	0.8408	0.0032	0.518	0.0173	0.9972	0.0212
	1.87	0.391	0.0130	0.9636	0.0123	0.225	0.0075	0.7705	0.0025	0.546	0.0181	0.9952	0.0260

$u$  = mean interstitial velocity;  $K_D^{Cu}$ ,  $K_D^{Co}$ ,  $K_D^{Cr}$  = linear sorption distribution coefficients;  $S_{CuD}$ ,  $S_{CoD}$ ,  $S_{CrD}$  = sorption from the equation  $S_D^{Me} = K_D^{Me} C_0^{Me}$ ;  $r^{2*}$ ,  $r^{2**}$ ,  $r^{2***}$  = squared correlation coeff. for the respective  $K_D^{Me}$ ;  $S_{Cu}$ ,  $S_{Co}$ ,  $S_{Cr}$  = sorption calculated from equation (5).

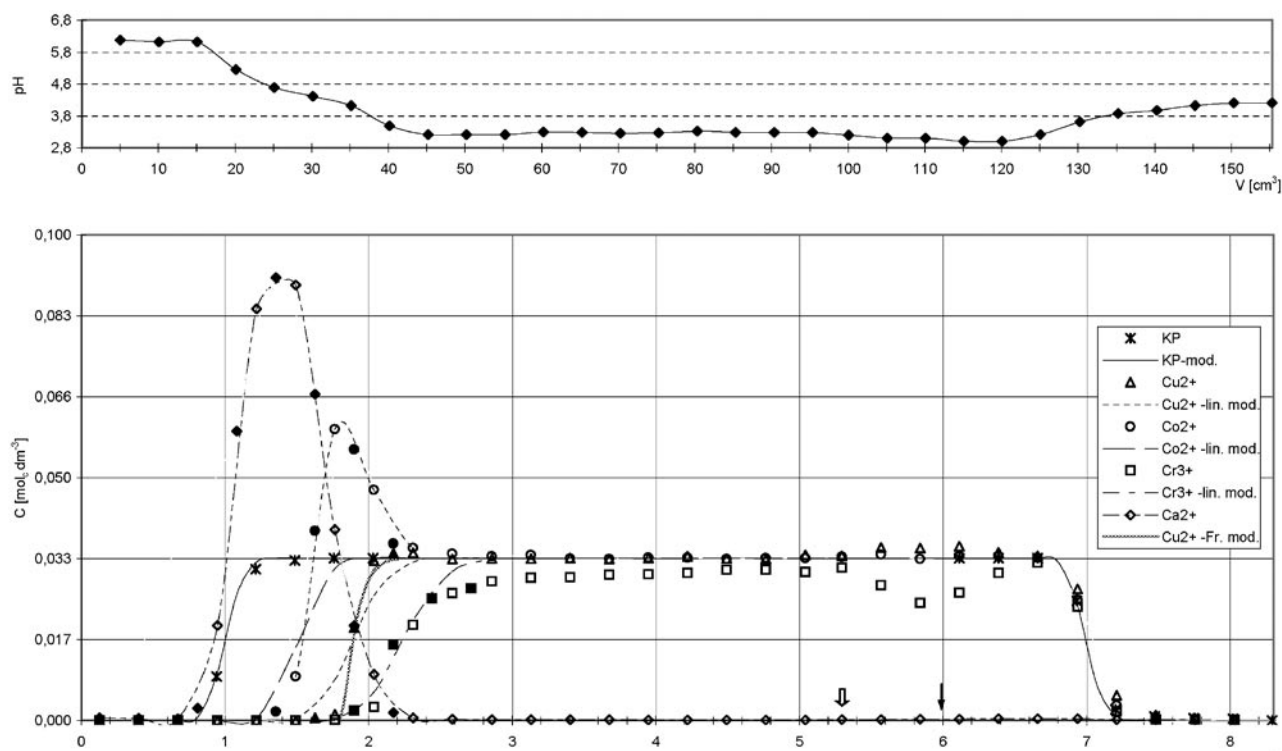


Fig. 2. Measured and predicted BTCs for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions in the loess soil at  $u = 1.87 \text{ cm h}^{-1}$  (light points) and  $u = 3.59 \text{ cm h}^{-1}$  (black points). In the upper part - pH of the effluent.

sorption sites. The linear sorption equation was used again to describe the process. The adsorbed  $\text{Co}^{2+}$  amount calculated from it is much greater compared to the real value calculated using equation (5) (values  $S_D^{\text{Co}}$  and  $S^{\text{Co}}$  in Table 2) because the value  $K_D^{\text{Co}}$  calculated by means of the maximization method of the correlation coefficient  $r^2$  does not take into account desorption due to competitive interactions. The model BTC<sub>s</sub> for  $\text{Cu}^{2+}$  ions is well correlated with the experimental points (Fig. 2) and there are no greater differences between  $S_D^{\text{Cu}}$  and  $S^{\text{Cu}}$  (Table 2). However, a better correlation was achieved determining BTC<sub>s</sub> based on the retardation factor from equation (3) (for  $k_F = 0.402$  and  $n = 0.717$  the  $r^2$  value was 0.9991). The BTC<sub>s</sub> for  $\text{Cr}^{3+}$  determined using  $K_D^{\text{Cr}}$  (Table 2) describes well the ion sorption for both velocities when  $T \leq 2.4$ . With greater values  $T$  a distinct deviation of the model curve from the experimental points can be observed. After flow interruption and restart after 24 h (points to the right of ↓) a significant increase of  $\text{Cr}^{3+}$  sorption combined with a small desorption of  $\text{Cu}^{2+}$  from the sorption sites and a decrease in the effluent pH take place. This indicates that besides the process of a very fast sorption, which is well characterized by the determined sorption distribution coefficients (Table 2) another process in which  $\text{Cr}^{3+}$  ions were very slowly sorbed proceeds. It follows from the shapes of BTC<sub>s</sub> after the flow interruption (Fig. 2) that slow sorption of  $\text{Cr}^{3+}$  ions isn't combined with  $\text{Ca}^{2+}$  desorption. The difference  $S^{\text{Cr}}$  and  $S_D^{\text{Cr}}$  for the experiment carried out with the velocity  $1.87 \text{ cm h}^{-1}$  is  $0.0079 \text{ mol}_c \text{ kg}$ ,

this approximate value can be taken as the quantity sorbed due to the time-dependent mechanism. The difference  $S^{\text{Cr}}$  and  $S_D^{\text{Cr}}$  for the experiment carried out with the velocity of  $3.59 \text{ cm h}^{-1}$  is smaller, which is caused by the lack of flow interruption and greater velocity of liquid flow through the column.

The results of batch experiments in sandy soil are presented in Fig. 3. Sorption of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions is well described by the Freundlich equation (values of  $k_F$  and  $n$  coefficients in Table 3); the application of the Langmuir equation gave much worse correlation coefficients. However, the dependence between  $S_e$  and  $C_e$  for  $\text{Co}^{2+}$  sorption was approximately linear. It is well enough described by the equation  $S_e = a C_e + b$  with the negative value of coef-

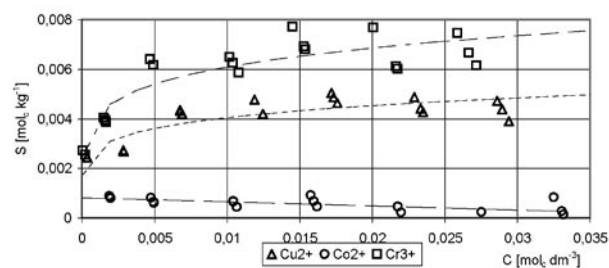


Fig. 3. Sorption isotherms of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions in the sandy soil - batch experiments.

Table 3. Parameters of the sorption equations in the batch experiments.

Soil	Metal ion	Values of coefficients	Standard error	r <sup>2</sup>	p
Sandy soil	Cu <sup>2+</sup>	$k_F = 0.0086$ $n = 0.16$	0.098 0.019	0.7918	0.0000
	Co <sup>2+</sup>	$a = -0.0165$ $b = 0.00082$	0.0038 0.000074	0.4999	0.0003
	Cr <sup>3+</sup>	$k_F = 0.013$ $n = 0.17$	0.084 0.0015	0.8742	0.0000
Loess soil	Cu <sup>2+</sup>	$k_F = 0.016$ $n = 0.17$	0.087 0.017	0.8350	0.0000
	Co <sup>2+</sup>	$k_F = 0.0029$ $n = 0.046$	0.0078 0.017	0.2817	0.0133
	Cr <sup>3+</sup>	$k_F = 0.024$ $n = 0.12$	0.045 0.0068	0.9395	0.0000

$k_F$ ,  $n$  = coefficients from the Freundlich equation;  $a$ ,  $b$  = coefficients from the linear equation; r<sup>2</sup>, p = statistic parameters from the simple regression method.

efficient  $a$  (Table 3). The relationships between  $S_e$  and  $C_e$  in this soil are statistically significant at the 99% confidence level because p-values are less than 0.01 in all cases. The unusual shape of Co<sup>2+</sup> sorption isotherm can be explained by the effect of competitive interactions: an increase of heavy metal ions concentration in the solution caused an increase of their competition for sorption sites, which resulted in the sorption decrease of ions of the smallest affinity.

The sorption isotherms obtained from the batch experiments in the loess soil are of non-linear character for the ions of each metal (Fig. 4). It follows from the analysis of the correlation coefficients (Table 3) that the process is well described by the Freundlich equation. The relationships between  $S_e$  and  $C_e$  are for Cu<sup>2+</sup> and Cr<sup>3+</sup> significant at the 99 %, and for Co<sup>2+</sup> at the 95 % confidence level (p-value for this element is less than 0.05).

In all column experiments the total sorption of heavy metal ions was greater than the amount of Ca<sup>2+</sup> desorbed. For example the total sorption of 0.0122 mol<sub>c</sub> kg<sup>-1</sup> heavy metal ions (sum  $S^{Me}$  in Table 2) in the experiment in sandy soil carried out with the velocity 3.42 cm h<sup>-1</sup> caused desorp-

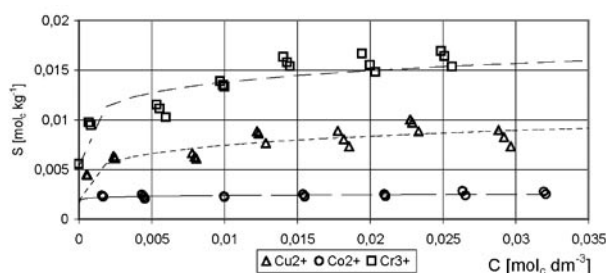


Fig. 4. Sorption isotherms of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> ions in the loess soil - batch experiments.

tion of 0.0056 mol<sub>c</sub> Ca<sup>2+</sup>. In the experiment in loess soil with the velocity 3.59 cm h<sup>-1</sup> sorption of 0.0373 mol<sub>c</sub> kg<sup>-1</sup> heavy metal ions caused desorption of 0.0302 mol<sub>c</sub> kg<sup>-1</sup> Ca<sup>2+</sup>. Also in the batch method the mean value from the experiments for the total sorption of heavy metal ions was in both soils larger than the desorbed amount of Ca<sup>2+</sup> (Fig. 5).

In sandy soil in the batch experiments (Fig. 3), the total amount of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> sorbed from the solutions of the greatest concentrations was practically the same as in the column experiments (sum  $S^{Me}$  in Table 2). In the loess soil the amount sorbed in the batch experiments (Fig. 4) was considerably smaller.

The curves of elution with water of individual heavy metals (points in Figs. 1 and 2 to the right of ↓) in all experiments run very close to the conservative curves (with the exception of Cu<sup>2+</sup> curves, they practically overlap). This indicates that in both soils the contribution to binding of heavy metal ions of sorption forces weaker than ion exchange was mostly insignificant.

## Discussion

In all the experiments the number of desorbed Ca<sup>2+</sup> ions was smaller than the total sorption of heavy metal ions. From the works by Randle and Hartmann [25] one can suppose that heavy metal ions can combine with organic substance by means of physical sorption. The contribution of this kind of sorption can be clearly seen only in the case of Cu<sup>2+</sup> - in both soils the points for Cu<sup>2+</sup> are above the conservative curve and the points for ions of other metals (Figs. 1 and 2).

Sorption non-equivalent to Ca<sup>2+</sup> desorption can also indicate sorption of ions in the hydrolyzed form. As it follows from the calculations of ion equilibria of the solution used in the experiment made with the program MINEQL<sup>+</sup> [26], there were about 90% free Cu<sup>2+</sup> and Co<sup>2+</sup> ions but the remaining were CuCl<sup>+</sup> and CoCl<sup>+</sup> ions. In the case of chromium, besides Cr<sup>3+</sup> ions there were 2-17% Cr(OH)<sup>2+</sup> ions in the solution. There is little probability that chromium ions sorbed in the Cr(OH)<sup>2+</sup> form and occupied only two sorption sites of soil. It follows from the earlier studies [23] of competitive sorption from the three-component solutions including equivalent numbers

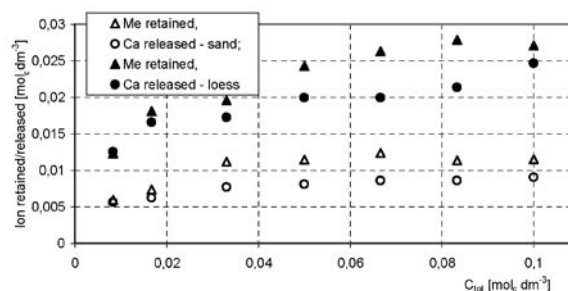


Fig. 5. Relationship between total Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> sorption and Ca<sup>2+</sup> release as a function of total concentration of metal ions in solutions added to the system - batch experiments.

of ions that total sorption of  $\text{Cr}^{3+}$  with other heavy metal ions expressed in  $\text{mol}_c$  was not greater than sorption from  $\text{Cr}^{3+}$  free solutions.

Sorption non-equivalent to  $\text{Ca}^{2+}$  desorption can indicate the existence of a specific sorption process, which is connected with  $\text{H}^+$  desorption from the sorption sites [11]. In experiments specific sorption should exhibit pH decrease in the effluent from the column below the pH of the introduced solution (i.e. pH 2.9). However, in the experiments (Figs 1 and 2) this effect was not observed. A lack of distinct pH decrease can be explained by a neutralizing effect of  $\text{OH}^-$  released due to sorption of  $\text{Cr}(\text{OH})^{2+}$  ions in the non-hydrolyzed form. The only evidence for specific sorption occurrence was a distinct decrease of effluent pH to 3.0 in the loess soil during flow interruption (Fig. 4).

The result of above inquiries is that the leading sorption process of examined heavy metals in soils was exchangeable sorption (evidence is displacement of a large quantity of  $\text{Ca}^{2+}$  ions). There are also data suggesting occurrence of physical and specific sorption.

The observed differences in the sorption extent in the batch and column experiments are of moderate value (in comparison with literature [5, 14, 15]) and do not diminish applicability of these results. It seems that one of the most important reasons affecting ionic equilibria in the experiments is the fact that in the column experiments ions undergoing desorption from the sorption sites left the reaction medium but in the batch experiments they still remained in the solution being in contact with soil.

Partial desorption of the substance characterized by small affinity for the sorbent during the competitive sorption is scarcely described in literature. Martin and Al Bahrani [16] observed this studying adsorption of organic compound including aromatic rings on the activated carbon. Mohan and Chandler [21] described similar behaviour of  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  cations during common sorption with  $\text{Fe}^{2+}$  on the activated carbon. This paper is one of the few [9], which describe a similar course of competitive sorption of heavy metal ions in soils. Application of Freundlich equation or its linear form gave good results in the case of metal ions with high affinity for soils ( $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ) both in the batch and column experiments. In the case of  $\text{Co}^{2+}$  ions, which have small affinity for soils, usefulness of these equations was little. Competitive interactions had too great an effect on the course of sorption ions of this element. Necessity of solving this problem is one of the reasons for continuing of the investigations concerning competitive sorption.

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