
POLLUTION

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THE SORPTION CAPACITY OF NATURAL SOILS IN RESPECT OF COPPER IONS (II) FROM SOLUTIONS $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Research article

Abstract

The paper describes a new technique for processing experimental data on sorption capacity (E) of variously composed natural soils in relation to heavy metals in aqueous solutions. The calculation scheme is based on an inhomogeneous system of equations, compiled from the data on mineral composition of soils and the E values. Such a system of equations was compiled for the experimental data on the sorption characteristics of natural soils (as suspensions) with respect to Cu^{2+} ions (of up to 1000 mg/l) from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions. The highest sorption characteristics with respect to Cu^{2+} ions from solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were associated with uneven-grained aggregates of calcite and chlorite followed by quartz and montmorillonite; dolomite and hydromica had the lowest sorption characteristics.

Keywords: suspension, copper, natural soils, sorption capacity, mineral composition.

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СОРБЦИОННАЯ ЕМКОСТЬ ПРИРОДНЫХ ГРУНТОВ В ОТНОШЕНИИ ИОНОВ МЕДИ (II) ИЗ РАСТВОРОВ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Научная статья

Аннотация

Разработана методика обработки экспериментальных данных сорбционной емкости природных грунтов (E) различного состава в отношении тяжелых металлов (ТМ) из водных растворов. Расчетная схема основывается на неоднородной системе уравнений, составленной по данным минерального состава грунтов и значениями величины E . Подобная система уравнений была составлена для опытных данных сорбционных характеристик природных грунтов (в виде суспензий) в отношении ионов Cu^{2+} из растворов $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ вплоть до 1 г/л. Оказалось, что наиболее высокими сорбционными характеристиками по отношению к ионам Cu^{2+} из растворов $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ обладают совокупности разнозернистых частиц кальцита и хлорита, достаточно высокими – монтмориллонита, кварца и весьма низкими - доломита и гидрослюда.

Ключевые слова: суспензия, медь, изотерма, природные грунты, сорбционная емкость, минеральный состав, корреляционная зависимость, система уравнений.

1. Introduction

The majority of the data on the determination of the parameters of the sorption process in natural soils with respect to heavy metals (HM) from aqueous solutions were obtained in laboratory experiments under a static mode of operation with constant or intermittent mixing of the suspension. In these conditions and from the most general point of view, the total exchange (sorption) complex with respect to HM of a polymineral natural soil suspension is characterized by the resultant sorption interaction (capacity) of exchange complexes of the sets of heterogeneous particles of each mineral.

The main factors influencing the sorption capacity of natural soils (E) are: mineral composition of the soil (m , wt%), structural characteristics of the mineral (degree of particles dispersion, nature and size of their surface, etc.), volume of the

solution (V), weight of the sample (P), equilibrium concentration of HM in the solution (C , and initial — C_o), its composition (W), and temperature. Thus, calculation of the sorption capacity of a lithological variety (E , mg/g), in the most general form, is carried out by the equation $E = (C_o - C) \times V/P$. Correlation between the values of E and V , P , W , C is determined through a series of experiments.

Correlations between E and the lithological composition of natural soils and subsoils have been studied to a lesser extent. Most of these correlations were obtained considering the influence of only a single factor or using model samples [1], [2]. The dependence of E on the granulometric composition was studied using different fractions of a certain mineral; the dependence of E on the mineral composition was studied using different minerals of a certain fraction [1], [3], [4], [5], [6], [7]. To a lesser extent, similar dependencies were studied under the combined effect of these factors on the process of HM absorption by natural soils from aqueous solutions, i.e., without sorting and handling samples. Processing of parameters obtained under these conditions using the traditional statistical methods (for example, multiple correlation) may encounter fundamental difficulties associated with insufficient quantity and quality of data. As a rule, it takes at least 20 to 50 tests to calculate statistical characteristics [8], [9].

One possible solution of such a task is the compilation of a system of equations using the previously established data on mineral composition of soils and the coefficients (not yet known — see explanation below) which characterize the structural characteristics of each set of mineral particles. A similar approach was used for the scalar physical-chemical properties of subsoils [2].

We have compiled the equations for each lithological variety based on the general concepts of the sorption characteristics of natural soils and individual minerals in relation to HM from aqueous solutions. The following premises were considered: (1) the general (resultant) structural characteristics of the aggregate of heterogeneous particles of a given mineral are represented by a single dimensionless coefficient ξ ; (2) $(m \times \xi)_i$ is the surface area of the sorption reaction of *all* particles of the i -th mineral that has the strongest sorption capacity with respect to HM from solutions; and (3) $(m \times \xi)_j$ is the area of the reaction surface of particles of the j -th mineral with the minimal sorption capacity with respect to HM. In this case, the coefficient of the effective surface of the soil sorption reaction (F) is directly proportional to the total surface area of the sorption reaction of the

particles of the "active" minerals ($\sum_i (m \times \xi)_i$) and inversely proportional to the surface area of the practically inert ("passive") particles ($\sum_j (m \times \xi)_j$), that is:

$$F = \frac{\sum_i (m \times \xi)_i}{\sum_j (m \times \xi)_j} \quad (1)$$

It was assumed that, from the most general point of view, E of natural soils in relation to HM is directly proportional to F . For a specific sample of experimental data an inhomogeneous system of equations of the form $E(F)$ and the solution for the ξ values was compiled, meeting the condition that $\sum_i m_i + \sum_j m_j = 100$ wt%. The form of equation (1) was chosen so as to obtain a linear dependence $E(F)$ with a high level of correlation coupling.

Thus, the determined ξ values characterize the structural features of the aggregate of particles of each mineral within the framework of only the desired set of experimental data. When new data are added to this data set, the system of equations is solved with respect to the new values of ξ and meeting the conditions $\xi_N \approx \xi_{N+1}$ (where N is the number of updates).

2. Methods

We used sorption isotherms of Cu^{2+} ions from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions as the experimental data. The samples included 16 unprocessed, unsorted Paleogene, Neogene, and Quaternary natural soils collected in Russia, Ukraine, Uzbekistan, and Slovakia (suspensions of clays, loams, and loess-like clays and loams). The experiments were carried out under static conditions at C_o , up to 1000 mg/l and $P:V = 1:100$ g/ml. The composition of the studied soils is presented in Table 1. Some of the most characteristic isotherms are shown in Fig 1. A more detailed description of the samples and the experimental procedures are described in [10].

For certain C_o values (with an interval of 50 mg/l for each isotherm), the systems of equations were constructed so that $F_{1-16} = E_{1-16}$ (where, 1-16 are the samples numbers, tab. 1). For example, at $C_o = 100$ mg/l: $F_1 = 11$, $F_6 = 8.5$, $F_9 = 3.4$, $F_{16} = 5.5$ (Fig. 1a),

The general form of the dependencies was constant (relative to C_o), while m_i and m_j varied. The values of the coefficients (ξ_i and ξ_j) were determined by solving the system of inhomogeneous equations (2). The coefficients obtained were related through dependencies $\xi_i(C_o)$ and $\xi_j(C_o)$ which were selected using the method of least squares.

$$\left\{ \begin{array}{l} F_1 = 11 \\ \dots \\ F_6 = 8.5 \\ \dots \\ F_9 = 3.4 \\ \dots \\ F_{16} = 5.5 \end{array} \right. \quad (2)$$

Table 1 – Mineral composition of the samples (wt%)

Sample №	Montmorillonite	Hydromica	Kaolinite	Chlorite	Quartz	Feldspar + plagioclase	Hornblende	Muscovite + biotite	Calcite	Dolomite
1	7,3	7,8	0,5	0,8	44,2	18	0,3	-	11,8	8,1
2	6,0	6,8	1,5	3,2	46,3	19,3	-	-	10,6	6,3
3	-	2,2	1,4	-	70,5	15,0	-	-	10,9	-
4	91,4	-	-	-	0,35	-	0,3	0,05	7,9	-
5	-	-	97,6	-	-	0,4	-	2,0	-	-
6	-	96,1	-	2,1	0,4	0,6	-	0,9	-	-
7	-	33,0	-	12,2	31,0	8,4	1,7	-	3,8	9,9
8	5,4	9,5	-	2,2	65,1	11,4	0,3	-	2,5	3,6
9	6,9	25,7	1,5	-	50,4	15,5	-	-	-	-
10	3,5	3,1	0,8	-	80,4	11,4	-	-	-	-
11	0,6	25,3	-	4,6	37,6	13,2	-	-	7,6	8,7
12	2,3	15,6	-	4,0	63,1	13,5	-	-	-	-
13	3,9	2,9	0,5	-	78,3	14,4	-	-	-	-
14	0,4	21,3	-	5,1	34,0	13,3	-	-	10,6	14,2
15	-	8,1	-	4,3	54,4	9,4	-	-	7,7	16,0
16	0,6	4,6	-	2,4	79,2	13,2	-	-	-	-

Note: sample 1 contains 1.2 wt% of siderite; sample 11 contains 2.4 wt% of gypsum; sample 12 contains 1.6 wt% of halite; and sample 14 contains 1.2 wt% of pyrite.

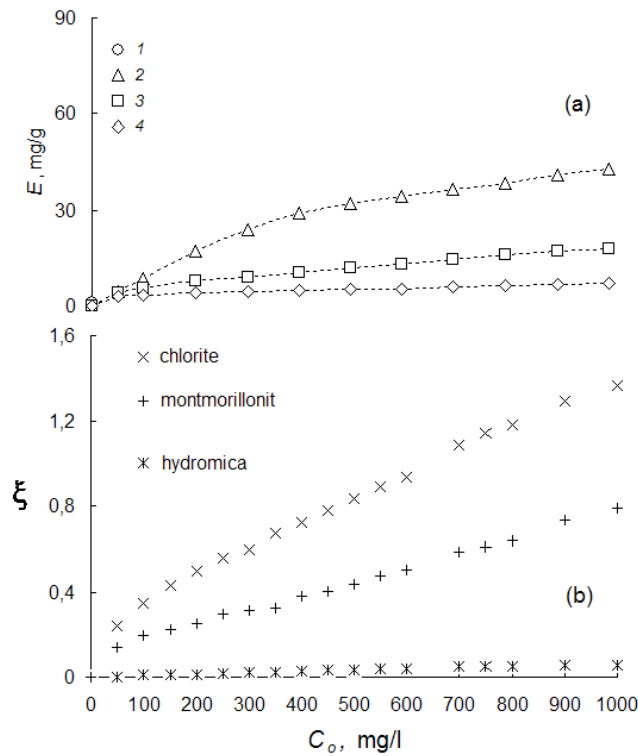


Figure 1 – Relationship between E (a), ξ (b), and C_o ; the experimental data are shown with “no-fill” symbols; calculated values are shown with lines; ξ values were calculated; 1 — sample 1, 2 — sample 6, 3 — sample 16, 4 — sample — 9

Taking into account the regression equations and the coefficients, a computer program was compiled (*BARIT16*). By changing the program input data (m_i , m_j , and C_o) it is possible to calculate the predicted E values (mg/g) depending on the share of each mineral in natural soils, in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions of up to 1000 mg/l.

3. Results and Discussion

The general form of equations (1) remained unchanged at C_o of up to 1000 mg/l. The values of E calculated with *BARIT16* agreed with the experimental data for samples 1-3 and 7-16. It was not possible to select the values of ξ for mono-mineral soils (samples 4-6). The graphs of the dependencies of ξ on C_o for some minerals are given in Fig. 1b. Dependence of E on the composition of soils is shown in Figs. 2-4.

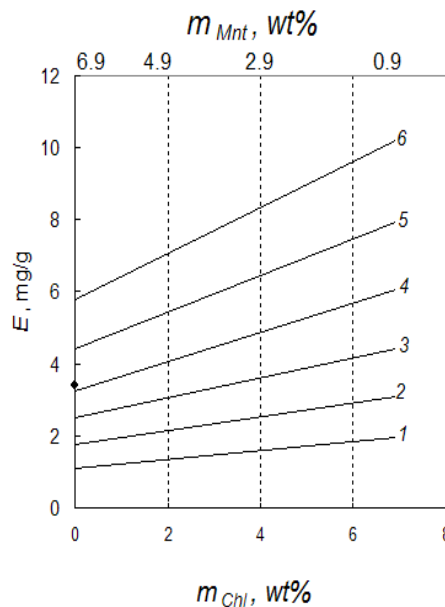


Figure 2 – Relationship between E , m_{Chl} , and m_{Mnt} at $C_o = 100$ mg/l. In sample 9 (“fill” symbol), m_{Chl} and m_{Mnt} were modified inversely to the contents of quartz and hydromica; 1 — quartz 20.4 wt% and hydromica 55.7%; 2 — quartz 30.4 wt%

and hydromica 45.7 wt%; 3 — quartz 40.4 wt% and hydromica 35.7 wt%; 4 — quartz 50.4 wt% and hydromica 25.7 wt%; 5 — quartz 60.4 wt% and hydromica 15.7 wt%; 6 — quartz 70.4 wt% and hydromica 5.7 wt%.

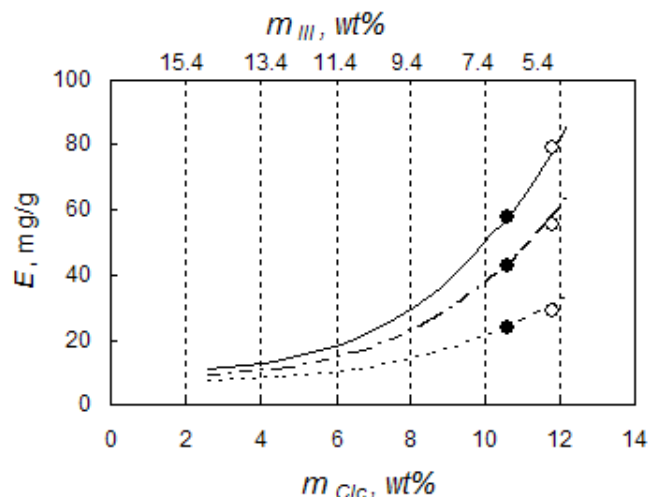


Figure 3 – Relationship between E , m_{Clc} , and m_{III} at $C_o = 300, 600,$ and 900 mg/l shown, respectively, with dashed, dot-dash, and solid lines. The m_{Clc} values in the composition of sample 2 (“fill” symbol) were modified inversely to the values of m_{III} . Sample 1 (“no-fill” symbol) represented the verification sample; its composition was close to that of sample 2.

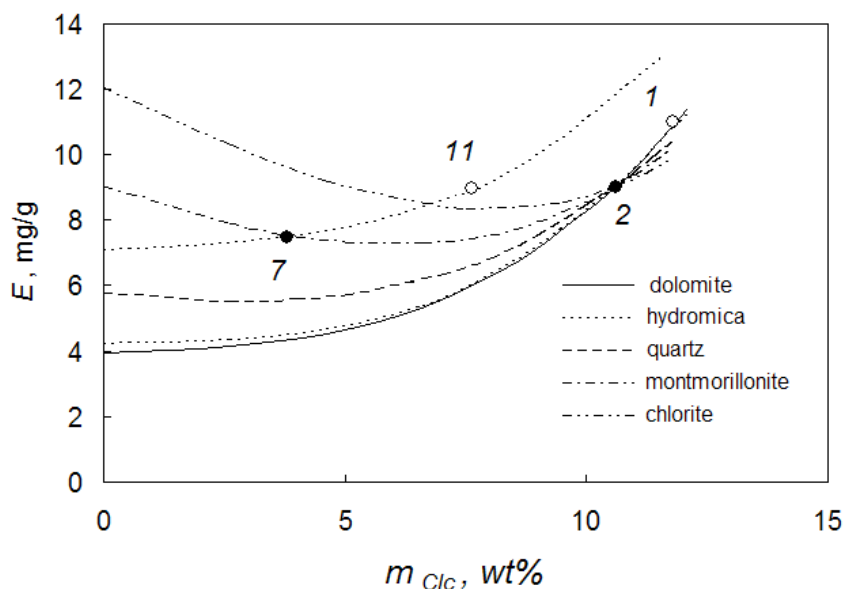


Figure 4 – Relationship between E and m_{Clc} at $C_o = 100$ mg/l. The m_{Clc} values were modified inversely to the contents of dolomite, hydromica, quartz, montmorillonite, and chlorite in samples 2 and 7 (“fill” symbols); the calculated values are shown with lines; the data for samples 1 and 11 (verification samples) are shown with “no-fill” symbols — the composition of these samples is similar to that of samples 2 and 7.

Figure 2 shows the results of predictive calculations of dependence of E on the share of four minerals that compose sample 9. The contents of quartz (20.4-70.4 wt%) and chlorite (m_{Chl} , 0-6.9 wt%) were modified inversely to the values of, respectively, hydromica and montmorillonite (m_{Mnt}). It appears that with every 1% increase in the content of chlorite or quartz, E increases by an average of ≈ 5 -7% — up to: $\approx 40\%$ for chlorite and up to $\approx 80\%$ for quartz.

Reliability of the obtained results was evaluated by comparing the E values of soils with the known composition (Table 1) and the calculated values of the modified samples. In the modified soil samples, the values of the relative mineral content were changed inversely: for example, 2% increase by weight of calcite (m_{Clc}) was associated with 2% decrease by weight of hydromica (m_{III}). When m_{Clc} and m_{III} were changed (Fig. 3) but kept within generally the same composition range (“fill” symbol in Figs. 3 and 4), we obtained a similar to the verification samples (in terms of the content of these minerals) modified sample (“no-fill” symbol in Figs. 3 and 4 was used for the verification samples).

It appears that E values of the modified soil samples corresponded better to the natural soil samples when changes in the relative composition of minerals occurred in the samples with high and low sorption characteristics.

Thus, Fig. 4 shows the results of E calculations ($C_o = 100$ ml/l) for samples 2 and 7 when the relative content of calcite was altered. For sample 2, an increase in m_{Clc} from 10.6 to 11.8 wt% (10.6-11.8 wt%) and a decrease in dolomite (6.3-5.1 wt%) or hydromica (6.8-5.6 wt%) were associated with the calculated E values that actually corresponded to the E values of sample 1 (with a difference of $\Delta \approx 2\%$). Similar results were obtained for the entire range of the C_o values (Fig. 3). In sample 7, when

the relative contents of calcite and hydromica were altered, the calculated E values corresponded to the values of sample 11 ($\Delta < 1\%$).

When the contents of quartz, chlorite, and montmorillonite changed, the minimum values of E coincided with the inflection points of the graphs; Δ increased to 10% with a calcite content of 11.8 wt% (Fig. 4). This shape of the graphs can be explained by the greater sorption capacity of the particles of these minerals compared with the calcite particles when its content is respectively below 2.6, 6.6, and 8.6 wt%, and their lower sorption characteristics when the content of calcite is respectively greater than 2.6, 6.6, and 8.6 wt%. The dependence of E on the amount of quartz, (i.e., a mineral with a low sorption capacity for cation exchange) is associated with the size of its reaction surface area — apparently it is so large that it can significantly control the sorption of Cu^{2+} ions.

The calculations of the E values (Figs. 2 and 4) show that the highest sorption characteristics are associated with the particles of calcite and chlorite, followed by montmorillonite, quartz; hydromica and dolomite have very low sorption characteristics. This conclusion may be explained by the dependence of the values of ξ on C_0 ; i.e., chlorite and montmorillonite have higher values of ξ than hydromica (Fig. 1b).

Thus, equations of the form (1) and the obtained values of ξ can serve as the basis for the calculation schemes in studies of the effect of the soil composition and the structural features of minerals on E .

4. Conclusions

The method for processing experimental data on the sorption capacity of suspensions of natural soils (E) of various compositions with respect to heavy metals is based on the inhomogeneous system of equations which are solved by finding the coefficients characterizing the common structural features of the particles aggregates (ξ).

This treatment of the experimental data (E) with respect to Cu^{2+} ions from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions (of up to 1000 mg/l) was used to construct a linear dependence of E on the coefficient of the effective reaction surface of the particles (F). The values of F were calculated by the equation, the terms of which are the shares of each mineral with the corresponding coefficients ξ .

The highest sorption characteristics with respect to Cu^{2+} ions from solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were associated with uneven-grained aggregates of calcite and chlorite particles followed by quartz, montmorillonite; dolomite and hydromica had the lowest sorption characteristics.

Conflict of Interest

None declared.

Конфликт интересов

Не указан.

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