Copper and zinc adsorption by Chernozems of different textures

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Abstract. The dependence of Cu2+ and Zn2+ adsorption by Chernozems of the Rostov region on the soil texture was examined. The thermodynamic parameters of the Langmuir equation (K and C∞) were calculated for all the studied samples. According to the adsorption parameters, the metal cations were arranged in the order Cu2+ > Zn2+. The adsorption of the studied heavy metals and the strength of their fixation on the surface of soil particles decreased with a decrease in the percent of the clay fraction in the particle size distribution of the soils. A correlation analysis of the relationships between the adsorption parameters and the contents of particles <0.01 and <0.001 mm in the soil samples showed that the maximum adsorption (C∞) of the metals mainly depends on the particle size, whereas the strength of adsorption is largely controlled by the chemical and mineralogical composition of the soil particles.

1. Introduction

The pollution with heavy metals (HMs) poses a serious hazard to the environment. Copper and zinc are the priority pollutants of the biosphere among HMs. Entering the environment from the technogenic sources, they actively affect all its components. However, the greatest load is experienced by soils [1]. This is due to the soil capacity for strong binding and accumulation of HMs in the form of low-mobile compounds. Thus, soils serve as a natural buffer and detoxification agent in the environment.

All main components of the soil solid phase—clay minerals; amorphous and crystallized hydroxides of Fe, Mn, and Al; carbonates; and organic matter—contribute to strong fixation of HMs entering the soil from various technogenic sources. Their role and significance depend on the type of soil and the strength of the soil bonds with the metals. The multicomponent and polydisperse nature of the soil adsorption complex and the intrinsic properties of the HM cations determine the complex mechanisms of ion-exchange processes on the surface of soil particles.

Immobilization of HMs in soils is mainly due to their adsorption on the surface of fine soil particles and depends on their mineralogical and chemical composition and, hence, their physicochemical properties. Soil texture is very important for the adsorption of HMs. Silt and clay fractions are the most active adsorbents because of their high specific surface [2]. They are characterized by the high adsorption capacity regarding HMs. According to the adsorption capacity of HMs on the surface of iron hydroxides and clay minerals, HM cations are arranged into the following sequence: Cd2+ > Pb2+ > Cu2+ > Zn2+ [3]. However, according to the strength of bonds between the adsorbed cations and clay particles,
the sequence is different: Pb^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+} [3]. According to the capacity for Zn^{2+} sorption, the following sequence of soils was found: clayey calcareous soil > sandy calcareous soil > sandy acid lateritic soil [4]. This sequence demonstrated the key role of the soil texture in the sorption of HM cations.

Simultaneously, the data presented in the literature were obtained by different authors for different soils. The goal of this work is to study the adsorption of Cu and Zn by soils of the same genetic type, but with different particle size distributions. This will allow a better understanding of the role of the main components of soil adsorption complex (SAC) in the adsorption of heavy metal cations.

2. Objects and methods

The upper humus horizons (0–20 cm) of the clay loamy Haplic Chernozem, clay loamy Calcic Chernozem, silt loamy Calcic Chernozem, and loamy sandy Calcic Chernozem from the Rostov region were chosen as study objects.

The main physicochemical properties of the soils presented in table 1 were determined by the following methods: the pH of soil water suspension (soil to water ratio 1:2.5), by potentiometry; the organic carbon content, by titrimetry using wet combustion (bichromate oxidation) procedure (Tyurin’s method) [5]; the content of calcium carbonates, by the method of Kudrin [5]; the cation exchange capacity (CEC) and the exchangeable Ca^{2+} and Mg^{2+}, by the method of Shaimukhambetov [6]; and the soil particle size distribution, by the pipette method with pyrophosphate pretreatment [7].

| Indicators                  | Clay loamy Haplic Chernozem | Clay loamy Calcic Chernozem | Silt loamy Calcic Chernozem | Loamy sandy Calcic Chernozem |
|-----------------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|
| Particles <0.01 mm, %       | 48.1                        | 53.9                       | 31.4                        | 12.4                        |
| Particles <0.001 mm (clay), % | 28.6                        | 31.0                       | 19.1                        | 8.0                         |
| Organic carbon (C_{org}), %  | 3.7                         | 2.3                       | 2.0                          | 1.8                         |
| pH                          | 7.3                         | 7.4                       | 7.5                          | 7.2                         |
| CaCO_{3}, %                 | 0.1                         | 0.5                       | -                            | -                           |
| Ca^{2+}+Mg^{2+}, cmol(+)/kg | 35.0                        | 33.9                      | 29.5                        | 24.9                        |
| CEC, cmol(+)/kg             | 36.0                        | 35.2                      | 31.8                        | 25.9                        |

To study the adsorption of Cu and Zn by the Chernozems, nitrate salts solutions of these metals were used in concentrations of 0.05, 0.08, 0.1, 0.3, 0.5, 0.8, and 1.0 mmol L^{-1}. Behavior of HM cations in solutions depends on the concomitant anions due to association. However, it has been shown that NO_{3}^{-} anions have a weak effect on the behavior of Cu^{2+} and Zn^{2+} cations in heterogeneous systems. Specifically, Zhang and Sparks [8] demonstrated that Na-montmorillonite equally adsorbed the Cu^{2+} cations from 0.25 M chloride, perchlorate, nitrate, and sulfate solutions at pH from 4.31 to 4.54. The samples of soils were crushed and passed through a 1-mm sieve and treated with the Cu(NO_{3})_{2} and Zn(NO_{3})_{2} solutions in different concentrations. The soil-to-solution ratio was 1:10. The range of Cu^{2+} and Zn^{2+} concentrations in the system under study corresponded to various geochemical situations and real levels of soil contamination with these metals [9].

The suspensions were shaken for an hour and then left for 24 h, after which they were filtered. The concentration of HMs in the filtrates was determined by atomic absorption spectrometry (AAS). The amount of adsorbed HM cations was calculated from the difference between the concentrations of the metals in the initial solution and in the equilibrium solutions after interaction with the soil.
The experiments were performed in triplicate. Statistical treatment of the obtained data and calculation of the coefficients of determination were made using SigmaPlot 12.5 and MS Excel 2007 software at the confidence level of 0.95.

3. Results and discussion

The adsorption isotherms of HMs by the Chernozems of different textures are presented in figure 1. As seen from this figure, in all the experimental variants, the adsorption isotherms have the form of convex curves and, therefore, can be described by the Langmuir equation (1):

$$C_{ad} = \frac{C_\infty K_i C_{eq}}{1 + K_i C_{eq}}$$

(1)

where $C_{ad}$ is the amount of adsorbed cations, mmol kg$^{-1}$; $C_\infty$ is the maximum adsorption of HM cations, mmol kg$^{-1}$; $C_{eq}$ is the HM concentration in the equilibrium solution, mmol kg$^{-1}$; and $K_i$ is the Langmuir constant, L mmol$^{-1}$, characterizing affinity SAC to adsorbing cation (energy of cations interaction with soil adsorbing sites).

![Figure 1](image_url)

**Figure 1.** Adsorption isotherms of Cu$^{2+}$ and Zn$^{2+}$ added as nitrate salts to (1) clay loamy Haplic Chernozem, (2) clay loamy Calcic Chernozem, (3) silt loamy Calcic Chernozem, and (4) loamy sandy Calcic Chernozem.

The initial part of isotherm in the area of low equilibrium concentrations characterizes the high affinity of the soil for the studied metal cations. It passes into a smoother curve in the region of the high concentrations. The amount of adsorbed metals increases with an increase in the degree of the soil contamination, but the strength of bonds between the adsorbed HM cations and the soil decreases because of the decrease in the affinity of HM cations for the remaining adsorption sites [10]. This is reflected in the increase in the slope of the isotherms to the abscissa axis. During adsorption, the
adsorption sites with the highest affinity for the HM cations are filled first, which is reflected by the initial parts of the isotherms \[11, 12\]. Then, the sites with a lower affinity for the HM cations participate in the adsorption, which corresponds to the final parts of the isotherms (figure 1).

The values of the thermodynamic parameters of the Langmuir equation calculated from the experimental isotherms are presented in table 2. The high values of the correlation coefficients \(R^2 = 0.94–0.99\) attest to a good agreement between the experimental isotherms and the Langmuir equation.

The values of the adsorption constants \(K_i\) for the studied metal cations from nitrate salt solutions characterize the energy of interaction between the adsorbed cations and the soil adsorption sites; in all cases, they are significantly higher for \(\text{Cu}^{2+}\) than for \(\text{Zn}^{2+}\). Hence, the chemical features of the metal cation itself have a significant impact on the energy of its interaction with the surface of the soil particles. We can argue that the \(\text{Cu}^{2+}\) adsorption by the soils is characterized by more specific interaction with the soil adsorption complex than the \(\text{Zn}^{2+}\) adsorption. This result corresponds to the values of electronegativity of the studied metals \[13\]. The higher the electronegativity of an HM, the stronger its interaction with the surface of soil particles, i.e., stronger bonds with functional groups of the surface of soil particles are formed, and the mobility of the adsorbed HM cations decreases. Thus, the affinity of HMs for the particles of iron and aluminum hydroxides changes consistently with the electronegativity of HMs composing the following range \[13\]: \(\text{Cu} > \text{Ni} > \text{Co} > \text{Pb} > \text{Cd} > \text{Zn} > \text{Mg} > \text{Sr}\).

The maximum adsorption value \(C_\infty\) of \(\text{Cu}^{2+}\) calculated by the Langmuir equation is higher than that of \(\text{Zn}^{2+}\). Simultaneously, the differences in \(C_\infty\) of these metal cations are less significant than the differences in their \(K_i\) values (table 2)

| Adsorption parameters | \(\text{Cu}^{2+}\) | \(\text{Zn}^{2+}\) |
|-----------------------|------------------|------------------|
| **Clay loamy Haplic Chernozem** | | |
| \(C_\infty\) (mmol kg\(^{-1}\)) | 13.3±1.3 | 14.6 ±0.6 |
| \(K_i\) (L mmol\(^{-1}\)) | 93.7±20.7 | 5.3±0.2 |
| \(R^2\) | 0.94 | 0.99 |
| **Clay loamy Calcic Chernozem** | | |
| \(C_\infty\) (mmol kg\(^{-1}\)) | 23.7±3.5 | 13.5 ±0.5 |
| \(K_i\) (L mmol\(^{-1}\)) | 58.3±13.2 | 4.1±0.4 |
| \(R^2\) | 0.99 | 0.99 |
| **Silt loamy Calcic Chernozem** | | |
| \(C_\infty\) (mmol kg\(^{-1}\)) | 20.6±9.2 | 12.5 ±0.6 |
| \(K_i\) (L mmol\(^{-1}\)) | 54.5±21.9 | 3.9±0.3 |
| \(R^2\) | 0.98 | 0.99 |
| **Loamy sandy Calcic Chernozem** | | |
| \(C_\infty\) (mmol kg\(^{-1}\)) | 19.0±1.0 | 11.1 ±0.9 |
| \(K_i\) (L mmol\(^{-1}\)) | 25.9±2.4 | 2.6±0.3 |
| \(R^2\) | 0.99 | 0.99 |

The difference between the adsorption parameters of the Haplic and Calcic Chernozems of the same texture (clay loam) can be explained by the differences in the chemical properties and mineralogical compositions of similar particle-size fractions of the studied soils \[14\]. Specifically, the \(K_i\) value...
calculated from the adsorption isotherm of Cu\(^{2+}\) for the clay loamy Haplic Chernozem is significantly lower than the \(K_l\) value for the clay loamy Calcic Chernozem (table 2).

For the Calcic Chernozems, there is a clear tendency for a decrease in the adsorption parameters (\(C_\infty\) and \(K_l\)) of the studied HM cations from the clay loamy soil to the loamy sandy soil (Figure 1). This tendency is especially noticeable for Cu\(^{2+}\) adsorption. The decrease in \(C_\infty\) in the soils with a coarser texture is evidently due to a decrease in the specific surface area in this direction.

Simultaneously, the \(K_l\) value is much more dependent on the contents of the clay and silt fractions than the value of \(C_\infty\), especially for Cu\(^{2+}\) ions. In this context, we can argue that the adsorption constant \(K_l\) is more sensitive to the composition of the adsorbent than the maximum adsorption capacity.

This is confirmed by a fairly close correlation between the \(K_l\) values of individual ions and the contents of particles <0.01 mm (\(r = 0.73–0.78\)) and <0.001 mm (\(r = 0.73–0.80\)) in Chernozems of different textures. An even closer correlation between the same variables is observed for Calcic Chernozems (\(r = 0.89–0.90\) for particles <0.01 mm and \(r = 0.91\) for particles <0.001 mm).

The composition of the clay (<0.001 mm) fraction in the studied soils includes mainly secondary mineral components: clay minerals (illite, chlorite), coagels, iron and aluminum oxides, allophanes, mono- and polysilicic acids, as well as organic and organomineral substances [15]. A distinctive feature of the clay fraction particles isolated from the Chernozems is the presence of significant amounts of organic matter and organomineral compounds of various natures [16]. Thus, it can be supposed that these compounds are responsible for the observed differences between the sorption capacities of the studied soils. The analysis of the X-ray absorption near edge structure (XANES) data demonstrated that the formation of octahedral intrasphere chelate complexes is possible upon the interaction of Cu\(^{2+}\) ions with soil humic acids [17, 18]. With a decrease in the soil humus content, the strength of bonds between metal ions and the surface of soil particles decreases.

A less close correlation exists between the \(C_\infty\) values of metals and the particles <0.01 and <0.001 mm in the studied soil samples (\(r = 0.52\) for Cu\(^{2+}\) and \(r = 0.48–0.56\) for Zn\(^{2+}\)). Consequently, the particle size and the associated specific surface area mainly affect the \(C_\infty\) value, whereas the strength of bonds between the HM cations and the surface of soil particles characterized by the \(K_l\) value is largely controlled by the chemical and mineralogical compositions of the soil.

4. Conclusions
The differences in the adsorption characteristics of Cu\(^{2+}\) and Zn\(^{2+}\) ions by the Chernozems of different textures and different physicochemical and chemical properties were shown in the experiment. In all cases, the adsorption parameters of the HM cations followed the order Cu\(^{2+}\) > Zn\(^{2+}\). The experimental results corresponded to the thermodynamic adsorption parameters \(C_\infty\) and \(K_l\) calculated according to the Langmuir equation. An increase in the content of clay and silt fractions in the same genetic type of soil (Calcic Chernozem) led not only to an increase in the amounts of adsorbed metals but also to their stronger fixation on the surface of these particle size fractions.

A correlation analysis of \(C_\infty\) and \(K_l\) relationships with the contents of particles <0.01 and <0.001 mm in the soil samples showed that the amount of the adsorbed Cu\(^{2+}\) and Zn\(^{2+}\) cations mainly depends on the particle size, whereas the strength of adsorption is greatly affected by the chemical and mineralogical compositions of the soil particles. The tightness of the correlation between the adsorption constants \(K_l\) of the metals and the contents of the fine (<0.01 and <0.001 mm) particles in the soil samples is higher for the soils of the same genetic type (Calcic Chernozem) differing in their textures than for the soils of different genetic types (Haplic and Calcic Chernozems) having the same (clay loamy) texture.

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