

The effect of natural and anthropogenic factors on sorption of copper in chernozem

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The aim of this work was to study the effect of the attendant anions and particle-size distribution on the adsorption of copper by ordinary chernozem. Solutions of HM nitrates, acetates, chlorides, and sulfates were used to study the effect of the chemical composition of added copper salts on the adsorption of copper by an ordinary chernozem. Samples of the soil sieved through a 1-mm sieve in the natural ionic form and soil fraction with different particle size (clay - the particle with size $< 1\mu\text{m}$ and physical clay $< 10\mu\text{m}$) were treated with solutions of the corresponding copper salts at a soil : solution ratio of 1:10. The concentrations of the initial copper solutions were 0.02, 0.05, 0.08, 0.1, 0.3, 0.5, and 1.0 mM/L. The range of Cu^{2+} concentrations in the studied system covers different geochemical situations corresponding to the actual levels of soil contamination with the metal under study. The suspensions were shaken for 1 h, left to stand for 24 h, and then filtered. The contents of the HM in the filtrates were determined by atomic absorption spectrometry (AAS). The contents of the adsorbed copper cations were calculated from the difference between the metal concentrations in the initial and equilibrium solutions.

The isotherms of copper adsorption from the metal nitrate, chloride, and sulfate solutions have near linear shapes and, hence, can be satisfactorily described by a Henry or Freundlich equation:

$$C_{ads} = K_H \cdot C_{eq}, (1)$$

$$C_{ads} = K_F \cdot C_{eq}^n, (2)$$

where C_{ads} is the content of the adsorbed cations, mM/kg soil; C_{eq} is the concentration of copper in the equilibrium solution, mM/L; K_H and K_F denote the Henry and Freundlich adsorption coefficients, respectively, kg/L.

The isotherm of Cu^{2+} adsorption by ordinary chernozem from acetate solutions is described by the Langmuir equation:

$$C_{ads} = C_{\infty} \hat{E}_L C / (1 + \hat{E}_L C), (3)$$

where C_{ads} is the content of the adsorbed cations, mM/kg soil; C_{∞} is the maximum adsorption of the HM, mM/kg soil; \hat{E}_L is the affinity constant, L/mM; C is the concentration of the HM in the equilibrium solution, mM/L.

According to the values of K_H , the binding strength of the copper cations adsorbed from different salt solutions decreases in the series: $\text{Cu}(\text{Ac})_2(1880,5 \pm 76,2) > \text{CuCl}_2(1442,8 \pm 113,5) > \text{Cu}(\text{NO}_3)_2(911,4 \pm 31,1) >> \text{CuSO}_4(165,3 \pm 12,9)$. Thus, copper is most strongly adsorbed from the acetate solution and least strongly from the sulfate solution.

The adsorption of copper by clay and physical clay fractions from the ordinary chernozem was of limited character and followed the (3) equation. In the particle-size fractions separated from the soils, the concentrations of copper decreased with the decreasing particle size. The values of \hat{E}_L and C_{∞} characterizing the HM adsorption by the chernozem and its particle-size fractions formed the following sequence: clay ($80,20 \pm 20,29$ and $28,45 \pm 0,46$) > physical clay ($58,20 \pm 14,54$ and $22,15 \pm 1,22$) > entire soil ($38,80 \pm 12,33$ and $17,58 \pm 3,038$).

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