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The adsorption mechanisms of heavy metal ions by meadow soil

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Introduction

Soil is one of the key elements for all terrestric ecosystems. The ability of soils to adsorb metal ions from aqueous solution is of special interest and has consequences for agricultural issues as remediation of polluted soils. The aim of this work was to study the mechanisms of Cu and Zn adsorption by meadow soil in the Rostov region (Russia).

Materials and Methods

The objects of study was the upper humus horizon (0–20 cm) of meadow heavy loamy soil (Fluvisol) on alluvial deposits (**Table 1**). The studied soil was selected in the area without anthropogenic impact.

Table 1. Physical and chemical properties of the studied soil

pHwater	C_{org}	$CaCO_3$	Physical clay (<0.01 mm)	Clay (<0.001 mm)	Exchangeable Ca^{2+}+ Mg^{2+},	Cu	Zn
	percent (%)				cmol(+)/kg	mg/kg	
7.5	4.3	0.6	55.8	32	38.1	37	110

Heavy metal adsorption procedure

Air-dried aliquots (5 g) of the studied samples were flushed with 50 ml of metal solutions ($Cu(NO_3)_2$ and $Zn(NO_3)_2$) with the following Cu^{2+} and Zn^{2+} concentrations (mM·L⁻¹): 0.05, 0.08, 0.1, 0.3, 0.5, 0.8, and 1.0. Heavy metals were added separately or simultaneously. Suspensions were stirred for 1 h, left in the calm state for 24 h. The pH values of the equilibrium solutions were determined by potentiometry. The suspension was then centrifuged and filtered. The content of the metal in the filtrates was determined by AAS. The amount of metal absorbed by the solid phase was deduced from the difference between the added amount and the concentration measured in the equilibrium solution.

The adsorption of metals can be described by the Langmuir equation:

$$C_{ads} = C_{\infty} K_L C_{eq} / (1 + K_L C_{eq}),$$

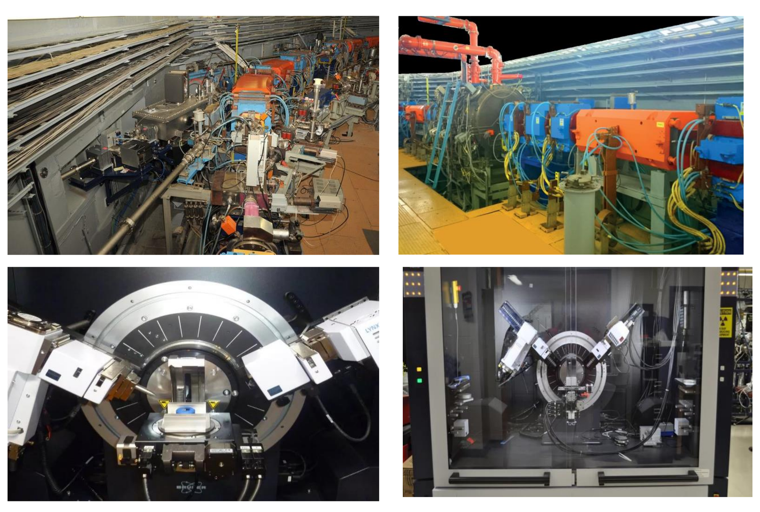
where C_{ads} is the concentration of the adsorbed cations; C_{∞} is the maximum sorption capacity of a soil, mM kg^{-1}; K_L is the affinity constant, L·mM^{-1}; C_{eq} is the concentration of the metal in the equilibrium solution, mM L^{-1}.

Adsorption mechanisms

The montmorillonite and calcite samples were saturated with Cu^{2+} and Zn^{2+} ions using a saturated solution of metal nitrate during a week. This solution, kept at constant pH, was changed twice a day. The calcite sample was collected in the studied Fluvisol using MBS-10 binoculars. The montmorillonite sample (GSO 8694-2005) is standard reference material.

X-ray Absorption Spectroscopy (XANES)

X-ray Diffraction (XRD)



CONCLUSIONS

Thus, regularities in the absorption of Zn and Cu by meadow soil in the Rostov region (Russia). Combination of both physico-chemical and direct physical methods can provide a large amount of real information about the solid phases that retain heavy metals.

Results and Discussion

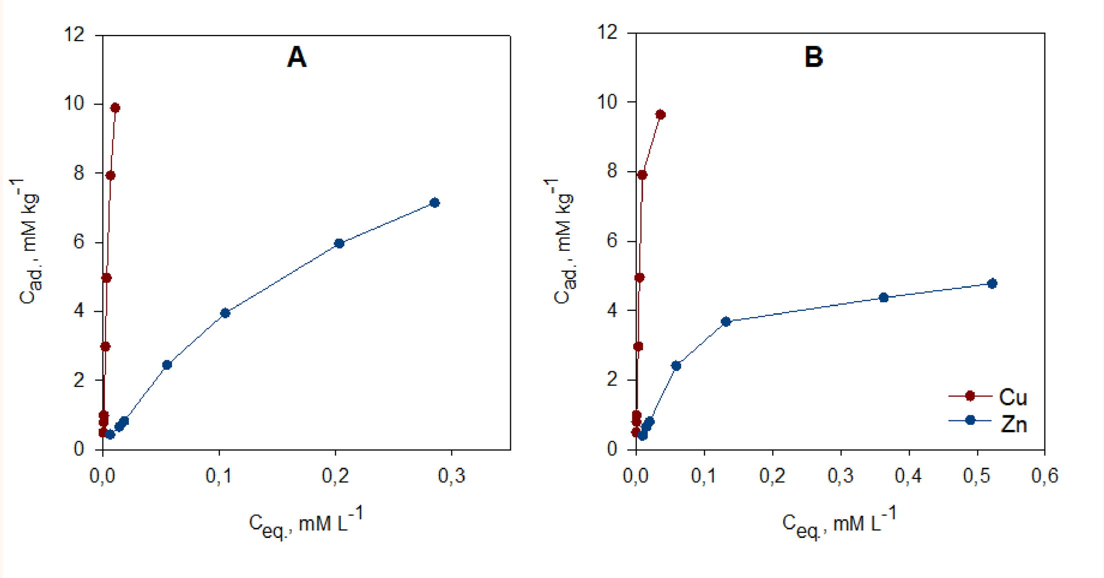


Fig. 1. Adsorption isotherms of heavy metals by the Fluvisol at at the (A) mono- and (B) polyelement addition.

Table 2. Parameters of heavy metals adsorption by Fluvisol during the mono- and polyelement pollution

Variation	C_{∞}, mM·kg^{-1}	K_L, L·mM^{-1}	R^2
monoelement pollution			
Cu	19.15±1.72	103.76±6.30	0.99
Zn	13.18±0.48	3.95±0.35	0.99
polyelement pollution			
Cu	12.30±1.33	126.72±33.53	0.98
Zn	5.60±0.29	11.57±1.90	0.99

In all cases, Cu had the higher ranges of values parameters of the adsorption process relative to of Zn. The values of C_{∞}) of individual cations at the polyelement contamination was always lower than at the monoelement contamination because of the mutual competition. At the same time, the values of K_L for the polyelement adsorption were higher than those for the monoelement adsorption because metals interact with most of the specific adsorption centers.

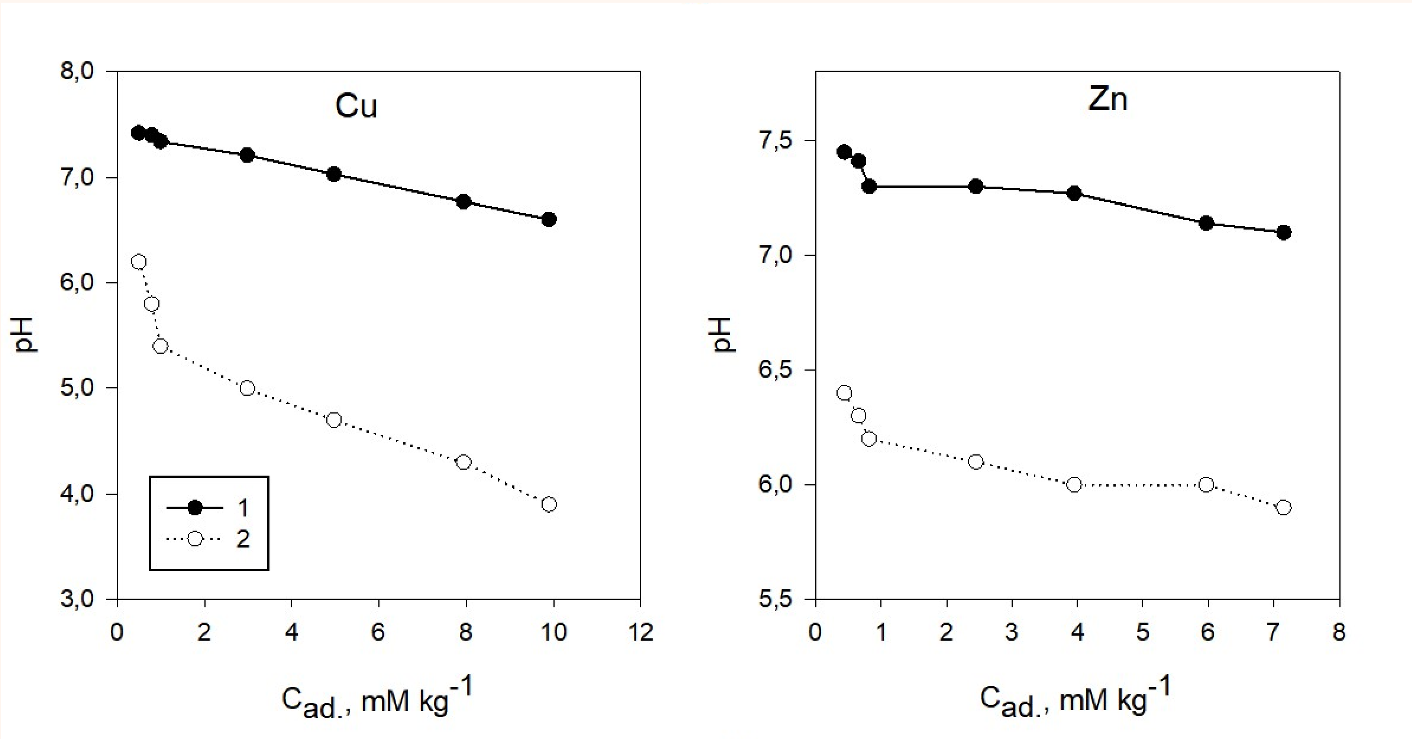


Fig. 2. Variation of pH equilibrium (1) and respective initial solutions (2) at heavy metals adsorption by the Fluvisol from nitrate salt solutions

Dissolution of salts $Cu(NO_3)_2$ and $Zn(NO_3)_2$ provokes variation of pH values in the initial solutions due to processes of hydrolysis. Character of the dependence of pH from the adsorbed metal amount is governed mainly by the composition of the solid phase: the presence of carbonates and hydrogen, which can exchange with HM cations.

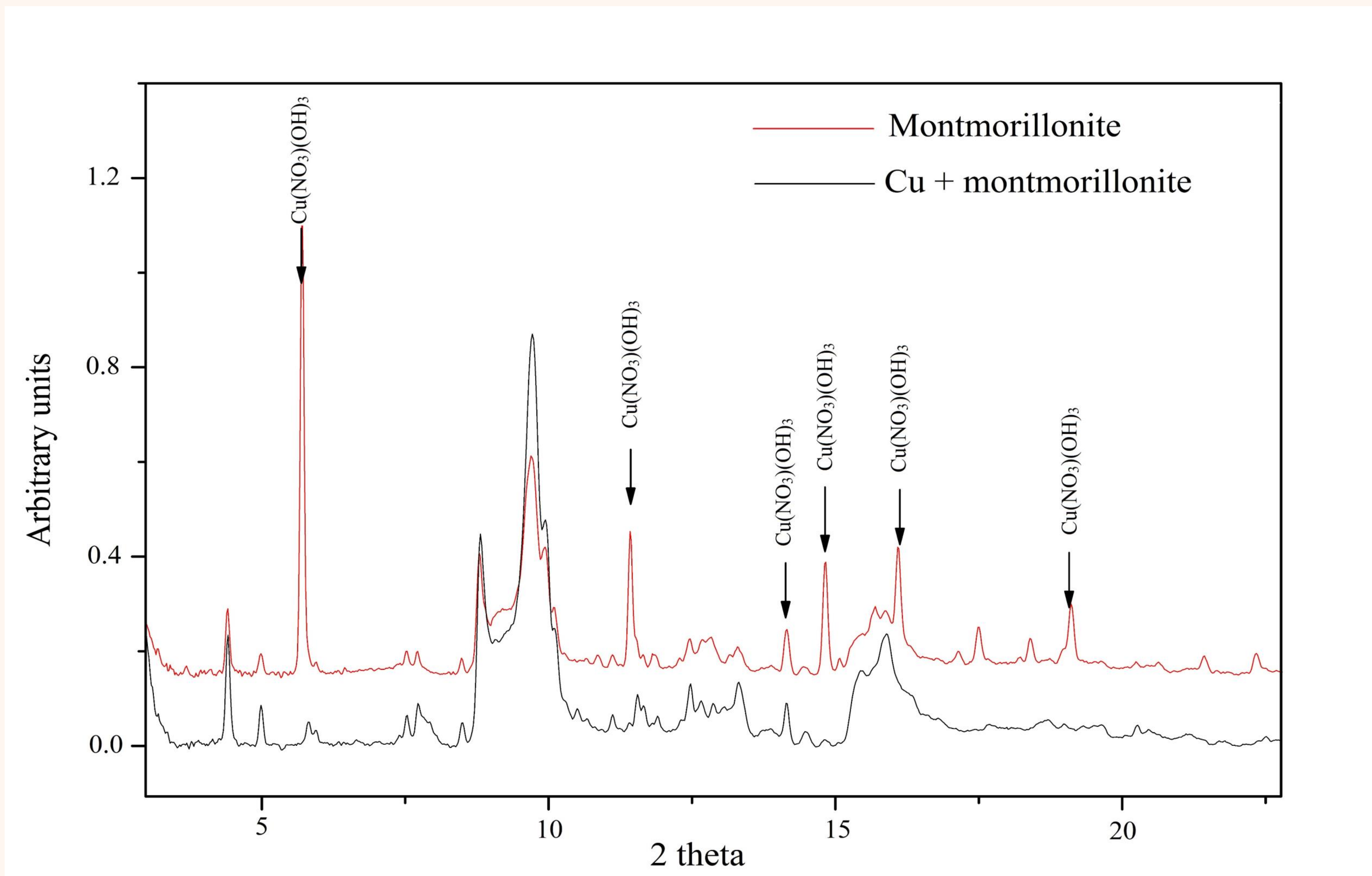


Fig. 3. Comparative analysis of X-ray powder diffractograms of the initial sample of montmorillonite mineral phase and after saturation with $Cu(NO_3)_2$.

Application of recent XRD methods of the X-ray identification of the montmorillonite, the dominant mineral hydromorphic soils, saturated with Cu^{2+} ions revealed that concentrations of metal ions decrease because of the formation and precipitation of the coarse-crystalline phase $Cu(NO_3)(OH)_3$ (**Fig. 3**).

Analysis of the K-edge XANES spectra of Zn adsorbed by soil carbonates revealed that the metal ions replace Ca ions at octahedral sites of calcite (**Fig. 4**).

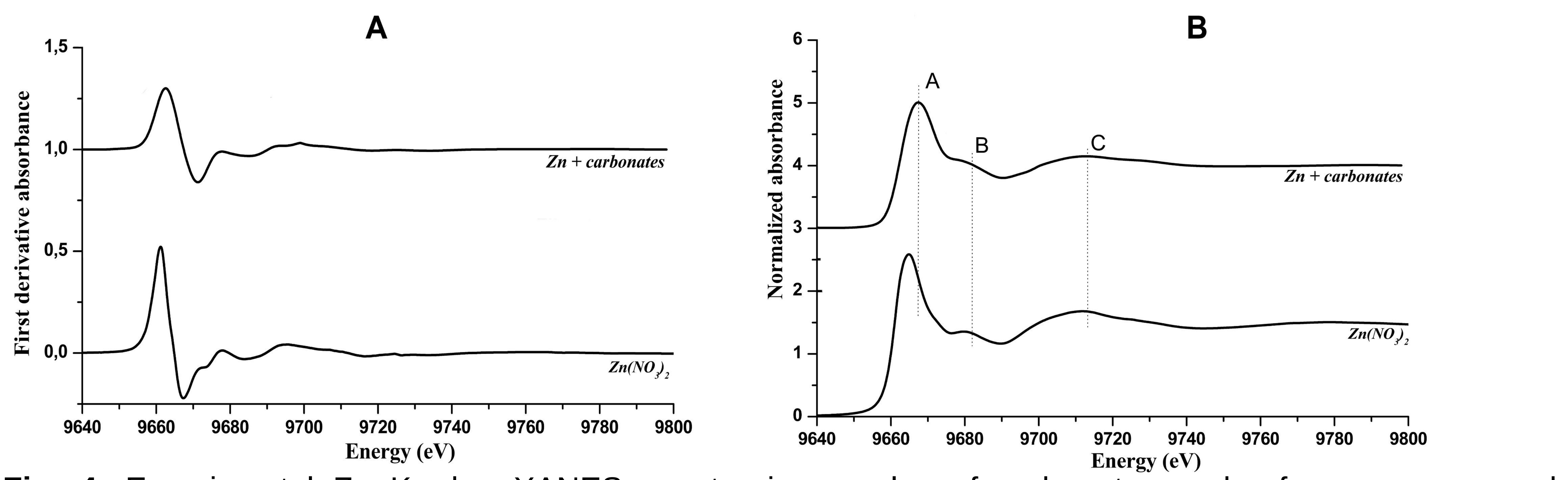


Fig. 4. Experimental Zn K-edge XANES spectra in samples of carbonates and reference compounds $Zn(NO_3)_2$ (a); first derivative of the Zn K-edge XANES spectra (b)

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