The Mechanisms of Lead Absorption of Soil Particles Depending on Metal Composition Applying from Anthropogenic Sources

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Abstract: The effect of Cl^-, CH_3COO^- and NO_3^- anions on the adsorption of lead by an ordinary chernozem has been studied. It has been shown that the attendant anions affect the shape of the adsorption isotherms, which are described by the Langmuir, Freundlich, or Henri equations. The greatest influence on the constants of lead has anion CH_3COO^-, on the magnitude C_{max}^- anions Cl^- and NO_3^-. The assessment of the mobility of the adsorbed cations from the extraction with ammonium acetate (pH 4.8) has shown that the content of the desorbed metals is always lower than the content of the adsorbed cations. The extraction of lead significantly depends on the composition of the salt added and decreases in the series: zinc chlorides > acetates > nitrates.

Key words: Adsorption · Lead · Chernozem · Attendant anions · Adsorbed cations

INTRODUCTION

It is known that most of heavy metals (HMs) emitted by industrial enterprises and motor vehicles as aerosols arrive into the soil in the form of oxides, oxyhydroxides, carbonates, chlorides, sulfates and phosphates [1]. However, problems related to the effect of the chemical form of a HM on its adsorption by the soil remain to be studied. The authors think that, in calcareous soils, the $H_2PO_4^-$ anion present in the solution acidifies the soil liquid phase and a significant amount of $CaCO_3$ is dissolved. The adsorption of copper, lead and cadmium by soils increased in the presence of calcium phosphate $(Ca(H_2PO_4)_2*H_2O)$ [3]. HMs were more strongly fixed in the soil surface–phosphorus–metal complexes. At the equal ionic strengths of the solutions, the sorption of HMs decreased depending on the attendant anion in the series $ClO_4^- > SO_4^{2-} > NO_3^- > Cl^-$ [2]. The anions present in the soil solution (HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, OH^-), can not only relate to HMs and form insoluble salts with them but also shift the equilibrium of the ion exchange toward the transition of HMs into solution due to their binding into soluble complexes [3]. Almost all the anions present in the natural solution, as well as water, have complexing capacities.

The aim of this work was to study the effect of the chemical composition of added lead salts on their adsorption and the retention strength of HM cations by an ordinary chernozem.

MATERIALS AND METHOD

The object of the study was the upper 0 to 20 cm horizon of a clay loamy ordinary chernozem on loess-like loam in Rostov oblast (the South of Russia), which had the following physical and chemical properties: Corg, 2.3%; pH, 7.3%; and the CEC, 37.1 mmol(+)/100 g. The exchangeable cations were as follows: Ca^{2+}, 29.5; Mg^{2+}, 5.5; Na+, 0.1; K_{ex}, 22.8 mg/100 g; $CaCO_3$, 0.1%; and P_2O_{5mob}, 1.6 mg/100 g. The physical clay was 53.1% and the clay was 32.4% [4].

Solutions of lead nitrates; acetates; chlorides; and sulfates were used, except for sulfate because of its low solubility in water. To study the adsorption of the metal, samples of the soil sieved through a 1-mm sieve in the natural ionic form were treated with solutions of the corresponding HM salts at a soil : solution ratio of 1 : 10. The concentrations of the initial lead solutions were 0.02, 0.05, 0.08, 0.1, 0.3, 0.5 and 1.0 mM/L. Each concentration corresponded to one point on the adsorption isotherm.

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The selected range of the HM concentrations was based on the actual levels of the soil contamination with Pb. 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. The contents of the adsorbed HM cations were calculated from the difference between the metal concentrations in the initial and equilibrium solutions.

The desorption of the adsorbed HM in the soil (their mobile form) was assessed by their extraction with a 1 N ammonium acetate solution at pH 4.8 with a soil : solution ratio of 1 : 5. The time of the extraction was 18 h [4].

RESULTS AND DISCUSSION

The adsorption of HMs by the soils is most frequently described by the Langmuir or Freundlich equation. The Langmuir equation is derived from the model concept of the adsorption process and has the form

$$C_{ads.} = C_{\infty} K_L C / (1 + K_L C), \tag{1}$$

where C_{ads} is the content of the adsorbed cations; C_{∞} is the maximum adsorption of the HM, mM/kg soil; K_L is the affinity constant, L/mM; and C is the concentration of the HM in the equilibrium solution, mM/L [5].

This equation describes limited adsorption. In the region of low concentrations of adsorbates (low filling of the adsorbent's surface), it is transformed into a linear equation passing through the origin. This region is referred to as the Henry region, because the isotherm in this concentration range is described by a linear equation ($C_{ads} = C_{\infty} K_L C$) referred to as the Henry isotherm. At high concentrations of cations in the solutions, the surface is saturated with the adsorbate and the adsorption ceases ($C_{ads} = C_{\infty}$).

The Freundlich equation is purely empirical:

$$q = K_F C^{1/n}, \tag{2}$$

where q is the content of the substance adsorbed by the solid phase normalized to its mass; C is the equilibrium concentration of the substance in the solution; K_F is the Freundlich adsorption coefficient characterizing the energy of the interaction between the adsorbed cations and the solid phase, L/kg; and $1/n$ is the empirical
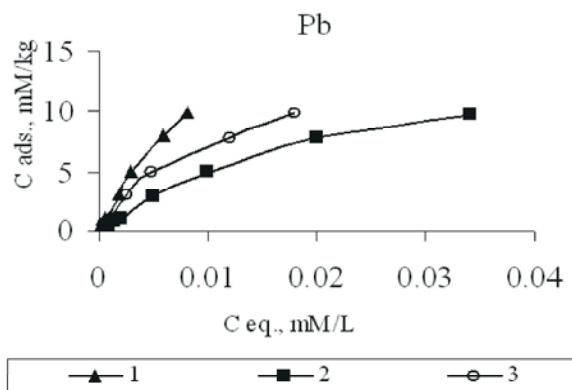

Fig. 1: Isotherms of the adsorption of Pb by an ordinary chernozem at their addition in the form of (*1*) chlorides, (*2*) nitrates, (*3*) and acetates

exponent in the Freundlich equation. At $n = 1$, the Freundlich equation is also transformed into the Henry equation.

The Freundlich equation better describes the adsorption on poorly crystallized or amorphous adsorbents with the almost continuous distribution of surface areas with different adsorption activities [6].

The adsorption isotherms of HM cations from chloride, nitrate, acetate and sulfate solutions are given in the Figure 1. The isotherms have different shapes, from almost linear to strongly convex ones. The isotherm's shape is determined by the character of the adsorbate–adsorbent interaction: the more convex the isotherm, the stronger the adsorbate is retained by the adsorbent [7].

The analysis shows that one equation is insufficient to describe the isotherms obtained. All three equations – the Henry, Langmuir and Freundlich equations – should be used. The adsorption of lead from chloride solutions is best described by the Langmuir and Henry equations. The isotherms of lead adsorption from acetate and nitrate solutions are best described by the Langmuir and Freundlich equations. The quality of the approximation is similar [8].

The parameters of the HMs' adsorption calculated from these equations are given in Tables 1.

The approximation quality of the experimental isotherms by these equations is characterized by determination coefficients (R^2) 0.99 (Table 2). Adsorption constants vary over a wide range and do not show a clear relationship with views of the cation, which is explained by the nature of both the empirical equations [9].

Table 1: Parameters of the Langmuir equation for the adsorption of Pb from different salt solutions by an ordinary chernozem

Metal application form	C_{max}, мM•Kg^{-1}	K_L, l•мM
Chloride	33,4±9,7	52,4±20,2
Acetate	14,2±2,1	76,1±23,9
Nitrate	16,8±1,1	40,9±4,8

Table 2: Parameters of the Henry and Freundlich equations for the Pb adsorption from different salt solutions by an ordinary chernozem

Metal application form	K_F, мM/Kg)/ (мM/l)$^{1/n}$, K_g, л/Kg	n	R^2
Chloride	1299,6±53,7	1,0	0,98
Acetate	150,1±40,6	0,7±0,1	0,98
Nitrate	98,8±24,1	0,67±0,06	0,98

Table 3: Contents of the lead cations from an ordinary chernozem contaminated with different metal salts

Chlorides		Acetates		Nitrates	
The adsorbed, mM/kg	The extracted, mM/kg	The adsorbed, mM/kg	The extracted, mM/kg	The adsorbed, mM/kg	The extracted, mM/kg
0,50	0,18	0,496	0,05	0,49	0,03
0,99	0,21	0,989	0,15	0,98	0,11
2,98	0,85	2,975	0,93	2,95	0,35
4,97	1,98	4,951	1,73	4,90	0,86
9,92	3,80	9,820	3,74	9,66	1,90

However, the comparison of the calculated parameters reveals ten dencies similar to those found for the adsorption parameters calculated from the Langmuir equation. According to the effect on the binding strength between lead and soil from the Henry equation the value of KF decreases in the series $CH_3COO^- > NO_3^-$ [10].

Thus, the effect of the attendant anions on the adsorption of HM cations by soils generally is retained and corresponds to the stability constants of the complexes formed by the studied metals with the ligands present in the liquid phase of the studied systems [4, 8]: $CO_3^{2-} > OH^- > HCO_3^- > SO_4^{2-} > CH_3COO^- > Cl^- > NO_3^-$. The most stable complexes are formed at the interaction of lead with анионами CO_3^{2-} и OH^- anions. The complexes with $Cl-$ and NO_3^- anions are the least stable.

In general, the behavior of the metal in the soil, the solution greatly depends on the individual circumstances. Soluble complexes investigated lead cations from nitrate ions, the least stable and hence less likely affect the behavior of the metal in the adsorption process, while the anions of acetic acid to form sufficiently stable complexes with lead.

Chemical properties of the anions associated not only affect the adsorption characteristics HM quantitative, but also on the mechanisms of their interaction with the surface of soil particles and metals in the form of finding the solid phase [5, 9]. To answer this question studied desorption exchange forms of zinc cations adsorbed from soil solutions of chlorides, acetates and nitrates, ammonium acetate buffer (pH 4.8).

The data of Table 3 shows that in all cases the amount of desorbed cations substantially less than the amount absorbed. Hence, the single extraction of the exchangeable HM cations by this extracting agent does not ensure their total transfer into the solution [20]. Sadovnikova [11] noted that a single treatment with 1 N NH4Ac does not completely displace the exchangeable forms of Pb and Zn, because it extracts no more than 50% of the exchangeable alkaline_earth cations, which are significantly weaker retained by the soil than the HMs.

When the content of the adsorbed cations increases, both the absolute amount of the desorbed cations and the percentage of their desorption increase. This fact confirms the common idea that the binding of the adsorbed cations to the soil particles becomes weaker because of the energetic heterogeneity of the surface and the mutual effect of the adsorbed cations. As far as the surface is filled with adsorbed cations, they occupy positions with progressively lower affinities for these cations, which increases their mobility and availability to plants and microorganisms.

For the effect of the anions on the extraction of the adsorbed cations from the soil, it could be noted that the extraction of lead progressively decreases in the series $Cl^- > CH_3COO^- > NO_3^-$.

CONCLUSION

The influence of anions Cl^-, CH_3COO^- and NO_3^- on lead absorption of chernozem ordinary. It is shown that, depending on the accompanying anion adsorption isotherms are shaped differently and are described by Langmuir, Freundlich, or Henry. The greatest influence on the bond strength of the metal to the surface of soil particles having an anion of acetic acid, the smallest - anions nitric and hydrochloric acids.

With an increasing amount of the absorbed metal cations increases not only the absolute amount of desorbed cations, but also the desorption rate. Extraction of lead depends strongly on the composition of salt introduced and decreases in the order: $Cl^- > CH3COO^- > NO3^-$.

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