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Adsorption of heavy metals by soils of East Kazakhstan

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Abstract

The article describes the results of environmental sustainability and absorption capacity of the most common soil of the Republic of Kazakhstan. The types of soils, the most resistant to contamination with lead. It was found that the absorption of lead studied soils process occurs as a result of joint actions such as cation exchange mechanism and the mechanism of surface complexation. The dynamics of the process of absorption, calculated the rate of absorption of lead soil. Determined that the absorption of single-element soil accumulate more lead than the Polyelement and single-element contamination is less of an environmental threat. The dependence of the processes of absorption of lead from the physical and chemical properties of soils and the correlation coefficients were calculated. On the basis of the detected absorption processes depending on the concentration of lead source solutions for Langmuir equations calculated figures lead the thermodynamic state in the soil - the value of the maximum absorption and bond strength. Calculated potential buffer capacity of soils.

Keywords: ecology, pollution, heavy metals, lead

Introduction

As a result of the rapid development of the industry a negative impact on the environment has become global in nature, leading to contamination of large areas [1,2,5]. Currently, one of these problems is the pollution of soils of different kinds of pollutants, especially dangerous - stable soil pollution, toxic components as heavy metals (HM) [3,4,8]. A large proportion of emissions of gas and dust are deposited on the surface of the soil, and the polluted upper, most fertile layer. In soil, the transformation processes are carried out of various compounds, wherein the conversion occurs as toxic compounds chemically inert, low-toxicity to plants and inaccessible products and increase the level of toxicity of chemical compounds by dissolving in an acid or alkaline medium [6].

As of the metal lead is selected because it is a priority pollutant in East Kazakhstan [7]. Lead belongs to the HM I hazard class, is highly toxic, mutagenic and carcinogenic, bioaccumulative [11].

Among the most important processes controlling the migration ability of HM in the soil-plant system are absorption processes, so the study of the absorption properties of soils at various levels of anthropogenic impact - is a serious problem of soil ecology, an important scientific and practical aspect. Its solution allows evaluating and predicting the ecological condition of the soil, developing measures to reduce or eliminate the toxic and environmental effects of pollution. The absorptive capacity of the soil in relation to the lead depends on their physico-chemical composition, the content of humus and carbonates, pH, cation exchange capacity [9].

Subjects and Methods

The objects of the study were used humus horizons (0-20 cm) of chestnut soils, widespread in eastern Kazakhstan: the typical low-humus leached sandy loam, typical low-humus leached medium loamy and alkaline leached medium loamy low-humus (soil classification is given by LL Shishova and others, 1997) [10].

Selection and determination of physico-chemical properties of the test conducted on the soil conventional methods. Determination of total content of chemical elements in soils, determined by atomic emission spectroscopy method with inductively coupled plasma (instrument "Spectroflame-ICP", Germany). Mobile forms of lead removed most common and accepted extractants: bidistilled water, ammonium acetate buffer solution with pH 4.8

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and 1.0N. HCl. The concentrations of water-soluble and acid-form ion exchange lead was determined as follows. A weighed sample of soil (3 g) was poured into a solution of the appropriate extractant relation soil / solution = 1/ 10, was shaken on a rotator for 1 hour, filtered and analyzed. Analysis of the concentration of Pb²⁺ ions carried photocolimetry dithizonal method for prescribing of G.Y. Rinkis (1972). The sensitivity of the method - 0.01 microgram / ml, characteristic measurement error - ± 4,6%. In the study of lead uptake kinetics into the flask capacity of 1 liter was placed 50 g of soil were added to 500 ml of a 5 mM solution of Pb(NO₃)₂, and the flask was placed on a magnetic mixer, at intervals indicated below Time pipetted to 10 ml, filtered and the filtrate was determined by ion concentration of Pb²⁺. At the same time, measurements of pH (potentiometric method). aliquots sampling time (after 0 taken during the addition to the soil solution) was as follows: 1, 3, 5, 7, 10, 15, 20, 30, 45, 60, 75, 90, 120, 150, 180, 300, 480, 720, 1440 and 2280 minutes.

To characterize the absorption sites on the surface of the soil 2 series of experiments were performed: 1) at various concentrations of Pb²⁺ ions in solutions and constant pH and 2) at different pH conditions, and the same concentrations of Pb²⁺ ions.

pH was adjusted to the desired level (pH 4, 5 and 6), the surging of 0.1 M HNO₃ or 0.1 M KOH and was monitored throughout the process.

In determining the parameters of competitive absorption of copper, lead and zinc soil sample weighing 5 g was placed in a flask and added with 50 ml solution containing all three elements (in the form of nitrate) in equivalent amounts (1, 2.5, 5, 7.5 and 10 mmol / l). The flasks were

shaken on a rotator for 1 hour, 48 hours asserted, filtered and analyzed. Analysis of the concentration of ions Cu²⁺, Pb²⁺ and Zn²⁺ was carried out by the above method of G.Y. Rinkis. The number of absorbed soil HM ions calculated by the difference between the model and the concentration of the test solutions. For comparison investigated absorption capacity of the soil contamination with single-element copper, lead and zinc. An experiment was conducted similarly, except that the model solutions contained only one of the above elements.

To investigate the absorption processes lead soils prepared solutions Pb(NO₃)₂ different concentrations - 0.5; 1.0; 1.5; 2.5; 5.0; 7.5; 10.0 mmol / l. Soil sample soi-weight 3 g was placed in the flask was added 30 ml solutions Pb(NO₃)₂ concen-trations above, was shaken on a rotator for 1 hour and allowed to stand for 48 hours. The solutions were then filtered off and the filtrate was determined by equilibrium concentration Pb²⁺ ions. As the saline solution in the stripping of lead ions were used KCl, Ca(NO₃)₂ and (NH₄)₂SO₄. The number of absorbed soil ions calculated by the difference between the initial concentration and the test solutions.

Experiments were performed in triplicate. Processing of the results carried out using Microsoft Excel program.

Results

Physical and chemical characteristics of soils studied are presented in Table. 1. In general, the soil is neutral - pH of about 7; poor in humus, are composed of time-the number of private and physical clay silt. Relevant differences are revealed in the cation exchange capacity.

Table 1 Physico-chemical composition of the studied soils

Soil	pH	Humus, %	sludge, %	Physical clay, %	cation exchange capacity, mg- equivalent /100 g
1	7,2	0,9	10,1	15,2	9,5
2	7,0	2,5	15,3	26,1	17,8
3	6,9	2,3	19,5	28,9	20,4

Note:here and after: 1 - Brown leached typical little humus loamy; 2 - Brown leached typical little humus medium loamy; 3 - Brown weakly alkaline leached humus medium loamy

Gross lead content varies from 14 to 17 mg / kg. Most are rich in gross lead leached alkaline low-humus medium-loamy soils, the least - typical low-humus leached sandy soils. Mobile fund lead compounds ranged from 10.5 to

11.5% of the total content, and at a fraction of water-soluble forms of accounts 0.5-0.6%, exchange forms - 2.5-3%, acid-soluble forms - 7 5.8%.

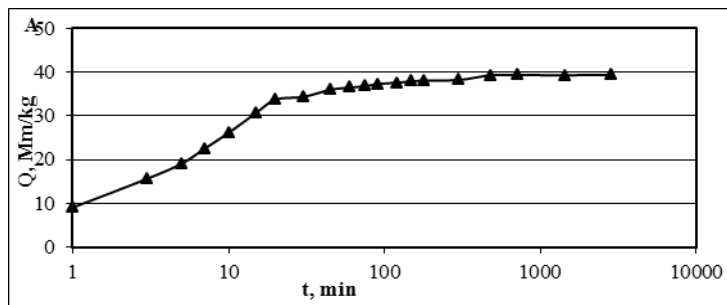


Fig. 1: The kinetics of lead absorption by soils (▲ - typical leached medium-low-humus soil)

The data obtained in the study of the absorption kinetics of the process are shown in Fig. 1. Up to a point with increase in reaction time of solid-liquid separation amount of lead absorbed increases. After 5-8 h. System "soil-solution" comes into balance, the amount of lead absorbed stops

changing. Lead absorption rate (calculated according to the value of the slope angles allocated for the curves of linear plots) as fickle and over time gradually decreases (Table. 2).

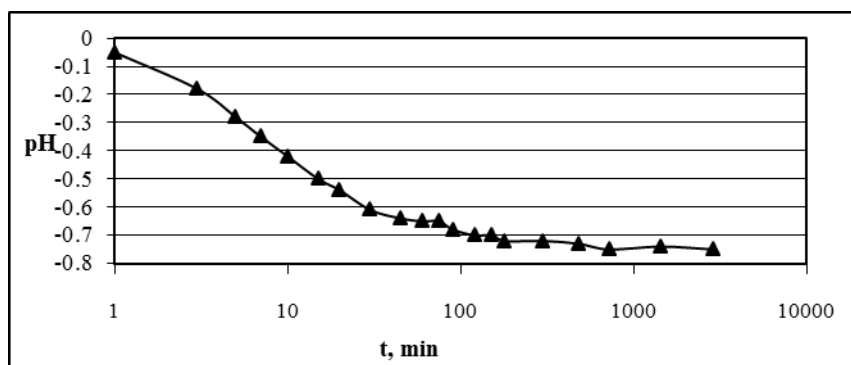
Table 2 The rate of absorption of lead by soil

The plot on Chart	The rate of absorption, mM/g in a minute		
	typical	leached weakly	humified medium loamy soils
I			1,467
II			0,073
III			0,0055

In the first 15 min. interactions lead uptake rate in the first 15 minutes of its interaction with the soil is 20 times higher than in the subsequent 45 minutes, and 266 times higher compared to pre-equilibrium period.

This is because in the initial moments of the soil solution to interact with the surface of the solid phase present a wide

variety of adsorption-vacancy centers of different nature, the number of which increases with decreasing contact time *etsya* as binding ions of Pb^{2+} . Simultaneously the solution decreases equal Spring Pb^{2+} ion concentration as a result of their absorption soil.

**Fig. 2:** Changes in pH in the soil absorption of lead

Upon absorption of lead decreases soil pH solutions (Fig. 2). The most dramatic decrease in pH occurs in the first 15 min. interaction with the soil solution, between 15 minutes. to 1 hr. is characterized by a smooth change of pH. Acidification may be due to hydrolysis of Pb^{2+} and the cations with subsequent absorption hydrolyzed forms soil-absorbing complex (Zyrin et al, 1986;. Ladonin, 2002; Pinsky, 1998). Another mechanism involves the in-drive in the exchange process additional exchange centers, saturated with H^+ ions and reach of Ca^{2+} , of NH_4^+ and alkali metal (Pinsky., 1998; Ponizovskii et al, 1999; Sposito, 1981).

Determination of lead absorption mechanism soil can be carried out on the basis of these laws. Lead absorption by the mechanism of cation exchange is described to be linearly-isotherm absorption and is characterized by a high degree of positive-New depending on the absorption capacity of the solid phase of the metal concentration in the water dis-create and weak dependence on pH conditions. Lead uptake mechanism is characterized by a high-surface complexation positive degree depending on pH conditions of the medium and low dependence on ionic strength (Malinowski, 2002; Baeyens et al, 1997). Linear character isotherm absorption lead soils in experiments with a constant pH, and at different concentrations of the solutions, as well as increasing the absorptive capacity of the soil with increasing pH allow us to conclude that the absorption of lead researched soils results from the joint action of the cation exchange and surface mechanisms complexation.

When single-element contamination there are marked differences in the absorption of HM by soil.

According to the number of absorbed substances investigated elements can be arranged in the following decreasing series: $Pb \gg Cu > Zn$. In the process of absorption of lead accumulates soil 6.5 times greater than copper, and 9.5 times greater than that of zinc.

When Polyelement lead contamination absorbed 5 times less copper - 2 times, zinc - 4 times. The order of the elements on the amount absorbed, the previous: $Pb > Cu > Zn$. Lead absorbed 3 times more than copper, and 8.5 greater than zinc. Polyelement TM soil pollution is a major environmental threat than the single-element contamination.

Physical and chemical properties of soils can be arranged in a series of descending-patient coefficients of correlation between these properties and the amount of lead absorbed: physics-cal clay> silt> EKO> Humus> rNvodn. The maximum value of the coefficient of correlation-tion found between the amount of lead absorbed by Q and the content in the soil INDIVIDUALS-tion of clay, minimal - between the amount of absorbed lead and pH. The results are consistent with data in the literature: it is well known that soil contamination TM heavy particle size distribution, for example, clay and loam, is significantly lower environmental risk than pollution sandy loam and sandy soils.

In addition, it should be noted that revealed a very weak relationship between the pH of the soil and the rest of the parameters, in some cases, the correlation is negative. Close to one correlation coefficients are observed between the EWC and the content in the soil and humus sludge. Attempts to establish a mathematical relationship between the various physical and chemical soil parameters and to evaluate the potential environmental risk of soil contamination by these parameters were made by many researchers. Identified in our work patterns are valid only in specific cases and can only be applied for similar soils and conditions.

The study has revealed the dependence of absorption processes of lead from solutions $Pb(NO_3)_2$ on the physico-chemical properties of soil (Fig. 3).

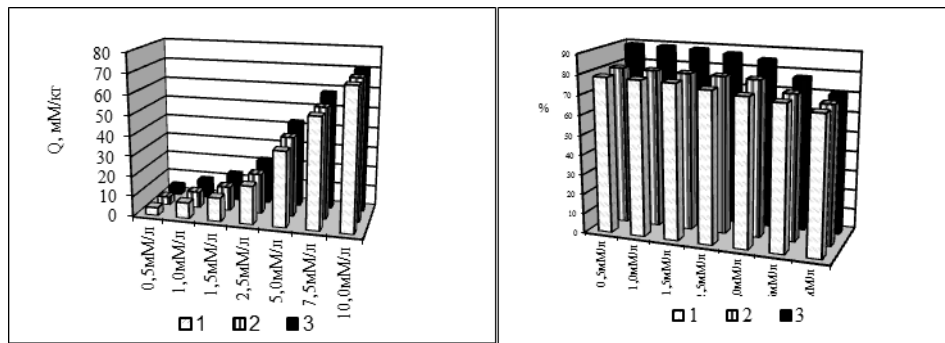


Fig. 3: The amount of lead absorbed by the soil solution of Pb (NO₃)₂

The amount of absorbed soil lead is in direct proportion to the concentration of initial solutions - with increasing concentration on the order quantity is increased absorption of lead - in 8-9 times. With the change in the concentration of model creates dis-changing as the proportion of absorbed lead with respect to the number of introduced. When the concentration of the lead nitrate solutions lead percentage of absorbed soil gradually decreases, although the decrease is very weakly expressed - 9-18%, depending on soil type. Reduced absorption rate may be due to a decrease in the number of available adsorption sites in the soil-absorbing complex. It can also explain the minimal impact on the ionic strength of lead uptake, because the lead has an

affinity for the soil organic matter, and the reaction occurs with the formation of coordination compounds. It was found that the greatest absorption capacity with respect to Pb²⁺ ions have a low-humus leached brown alkaline medium loamy soil below the absorption capacity of Brown leached typical little humus medium loamy soils and the lowest absorbency exhibit a brown alkaline low-humus leached medium-loamy soils. It should be noted that this relationship is stored using the solutions of concentrations. To more clearly present the experimental results were plotted between the amount of absorbed lead source and Q (1) and the equilibrium (2) solution concentration C (Figure 4).

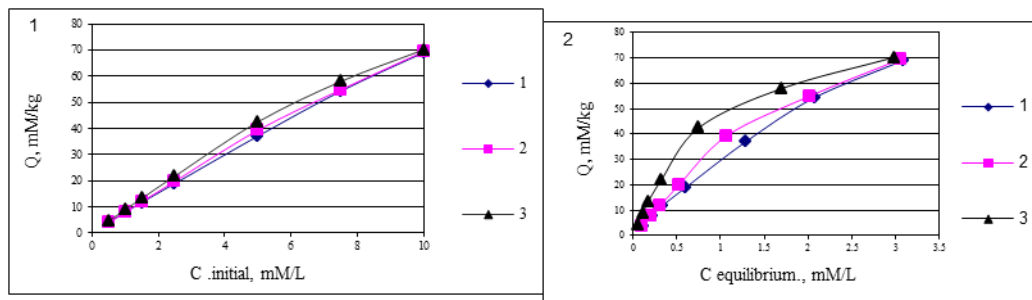


Fig. 4: The total absorption of lead from the soil solutions Pb (NO₃)₂

According to Fig. 4 shows that the amount of absorbed soil lead gradually increases with increase in model Pb²⁺ ion concentration solutions. With the change in the concentration of model solutions and changing the proportion of absorbed lead with respect to the number of introduced. With increasing concentration solutions Pb (NO₃)₂ lead percentage of absorbed soil decreases, and this decrease occurs smoothly and uniformly in all soil types. Reduced absorption intensity due presumably decrease the amount of free absorption centers in the soil-absorbing complex. The reason may also be a change in the surface of the particles as a result of the absorption of the soil certain amount of co-member. This phenomenon is explained by the fact that the effect of ionic strength on the uptake of lead and minimal interaction occurs primarily to form coordination compounds.

cations in these soils may be no more than 3-4% of the lead absorbed by the soil. The findings suggest a relatively high bond strength of lead ions with components soil-absorbing complex, rich in humus and exchangeable cations. Data obtained from the desorption shows that the lead forms compounds with soil and extremely strong bonds very weakly desorbed. When using the results of the experiments directly on natural ecosystems, there are some difficulties with the forms of metals revenues influence of living organisms, as well as the processes of transformation of the HM joints in natural conditions, which are not included in the experiments. The results of our research allow us to reveal the patterns of behavior of the HM in the contaminated soil and use them in the standardization systems in the preparation of the forecast in the feasibility of using commercial facilities for the dosage of anthropogenic load on agricultural buildings. The absorptive capacity of soils can be quantified using the Langmuir equation:

The results obtained in the study lead desorption show that the desorption ability to form the following salt solutions decreasing number (for all of the soils): (NH₄)₂SO₄ > Ca (NO₃)₂ > KCl.

$$C / Q = 1 / (Q_{max} * K) + (1 / Q_{max}) * C, (1)$$

The highest capacity for stripping soil has chestnut (NH₄)₂SO₄, extracting from 1 to 4% absorbed lead, the lowest - KCl, which removes from 0.4 to 3% of lead ions. Differences between saline minor and the experimental results can be sound so that the composition of exchange

where C - equilibrium concentration of the element in the solution; Q - the number of absorbed element per unit weight of the sorbent; Q_{max} - absorptive capacity of the

sorbent; K - coefficient, which reflects the strength of the bond between the component and the sorbent reaction centers.

The observed dependence of the C / Q from C really is almost a monotone, though somewhat unevenly, increasing.

Thus, absorption of lead chestnut soils proceeds in accordance with the Langmuir equation. To quantify the absorption of lead studied soil types for the end (linear) plots isotherms Langmuir equation parameters were calculated (Table. 3).

Table 3 The parameters of the Langmuir equation

Options	Soils		
	1	2	3
Q _{max} , mM/kg	145,7	148,6	98,5
K, L/mM	0,3	0,2	0,8

It may be noted that several different lead to the potential absorptive capacity from that which has been revealed in the experiment. This may be due not sufficiently wide range of concentrations of the solutions used in this work. It is clearly seen that the inverse relationship (the more soil absorbs lead, the weaker it is retained) for the lead between Q_{max} and K is shown.

Discussion

For the first time investigated the absorption of lead chestnut soils of East Kazakhstan, depending on a number of external and internal factors (the time factor, the pH of reacting with the soil solution, the presence of other ions in solution HM, physico-chemical characteristics of the soils, the initial concentration of the solution. According to the content of humus, silt, physical clay, cation exchange capacity and the pH of the studied soils are characterized by the average buffering and background for East Kazakhstan gross of lead-containing, in the range of 14 to 17 mg / kg. in the mobile fund share of the lead compounds to water-soluble forms have to 0, 5-0, 6%, the exchange forms - 2.5-3%, acid-soluble forms - 7.5-8% of the total content. A direct negative correlation between soil lead absorption values in the series:

Physical clay> silt> cation exchange capacity> humus> pH

In single-element quantity absorbed soil pollution metal decreases among: Pb> Cu> Zn, Pb and absorbed 6.5 times greater than Cu, and 9.5 times more than Zn. When Polyelement pollution the absorption capacity of the soil is sharply reduced: Pb absorbed 5 times less, Cu - 2 times, Zn - 4 times. The order of the elements on the amount absorbed, the previous: Pb> Cu> Zn. Polyelement pollution of soil by HM is a large environmental risk than single-element pollution.

Soil reacting with a solution of lead nitrate in time, amount of absorbed metal increases within 5-8 hours, then the system "soil-solution" reaches equilibrium.

In the absorption of lead soil pH is a decrease of model solutions, the stronger, the greater the initial concentration of the metal ions.

Removing the lead from the soil absorption complex of soils investigated by time-personal physical and chemical composition allows arranging them in the following decreasing number by the number of desorbed metal: 3> 2> 1, and this dependence is maintained at all concentrations used, creates races. Saline solutions for stripping lead capacity of soils located in the decreasing number (for all of the soils): (NH₄)₂SO₄> Ca (NO₃)₂> KCl.

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