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Sorption of heavy metals by humic acids of chestnut soils

The purpose of this article is to study the sorption of heavy metals by humic acids of light and dark chestnut soil. The objects of research are the samples of dark and light chestnut soils, selected from an ecologically clean area of East Kazakhstan. Humic acids (HA) were separated from the soil at different pH values. At the same time the yield of HA was 0.075 % from dark chestnut soil at pH 1.0, and it was 0.017 % from light chestnut at pH = 7.0. Further, the dependence of the sorption degree on the medium acidity was established. It was found that zinc and cadmium are better sorbed in a strongly acidic medium (pH < 1.0; 84.14 %), while lead is preferably sorbed at pH 6.0, and the degree of its sorption is higher (93.54 %). It was established that metals have a mutual effect, suppressing or enhancing the sorption of each other in bi- and polyelement variants. It was shown that cadmium significantly suppresses lead sorption in neutral media. Zinc more often increases the sorption of both cadmium and lead by 3 times. It was concluded that the binding of heavy metal ions by the organic fraction of the soil occurs due to the complexation with humic acids.

Keywords: heavy metals, dark chestnut soils, light chestnut soils (Kastanozems), organic fraction of soil, humic acids, sorption, zinc, lead, cadmium, East Kazakhstan, Borodulikha.

Introduction

Currently, the biosphere receives a huge amount of various pollutants, including heavy metals (HM), as a result of industrial and anthropogenic human activities. One of the most important parts of the biosphere is the soil cover, since in many cases it acts as a buffer, preventing or localizing contamination of other parts of the biosphere. The entry of HM into the biosphere leads to their accumulation in the soil in quantities that repeatedly exceed the background level, which reduces soil productivity and negatively affects the animal and plant world, as well as ultimately the human body [1–3].

Technogenic contribution in to the urban megalopolis soils is mainly manifested in a sharp increase in the specific concentration of mobile forms of Zn, Pb, Cu, and in a lesser extent of Cd, V, Co, Ni [2–4]. Toxic elements in soils are found in the form of light-exchange ions, colloidal particles, complex compounds, isomorphous impurities, complexes with humic acids, adsorbed complexes on iron and manganese hydroxides, on clay dispersed minerals, and carbonates [5–6].

It is known that soils differ in their sorption capacity in relation to heavy metals [7–11]. At the same time, it is believed that the ability to sorption of heavy metals is associated with the presence of specific high-molecular polyfunctional natural ligands in the organic part of the soil-humic acids (HA), fulvic acids and humin. Soils with a large supply of humic acids can bind a large amount of heavy metals. This is facilitated by the presence of a large number of different functional groups in the HA (carboxylic, alcoholic, phenolic, amine, amide, etc.), which provide the formation of strong complexes of these acids with heavy metal ions [12–14]. The interaction between humic acids and metals can occur by forming ionic, covalent, and chelated compounds [15].

The phenomena of ion exchange, surface sorption, coagulation and peptization play an important role in the sorption of HM by the soil fraction. The ratio of the mass fraction of organic matter to metal is important. HM sorption by the organic part of the soil can occur with the participation of carboxyl (–COOH) and phenolic (–OH) groups, this happens by replacing hydrogen with metal ions. Chelate complexes are formed as a result. The metal binds by chelating coordination (homeopolar) bonds and does not behave like a cation. Metal complex: organic matter can also be formed by replacing metal with a hydrogen cation outside the functional groups [16–17].

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Consequently, metals can enter both the cationic and anionic parts of humic acid molecules. It should be noted that the molecules of humus compounds of different soils differ in the number of functional groups and the degree of the «core» condensation. Therefore, sorption is influenced not only by the properties of metals, but also by the structure of humus compounds [18].

Contamination of the soil of East Kazakhstan with heavy metals has been studied by other scientists of Kazakhstan [19–21]. However the sorption degree of heavy metals (Zn, Cd, Pb) by the main components of the organo-mineral matrix of dark and light chestnut soil under conditions of mono- and polyelement pollution will be studied for the first time.

Data on the adsorption capacity of soils can serve as a basis for the development of methods for controlling the transformation of forms of chemical element compounds in areas that have been confirmed by technogenic pollution.

This paper presents the results of studying the processes of zinc, lead, and cadmium sorption in mono- and polyelement variants by humic acids of dark and light chestnut soil from the East Kazakhstan region.

Experimental

The objects of research are the samples of dark and light chestnut soils, selected from an ecologically clean area Borodulikha district of East Kazakhstan.

Borodulikha district is located in the North of the East Kazakhstan region. The total area is 7.2 thousand square meters, bordering the Altay region of the Russian Federation, as well as with Shemonaikha, Beskaragay districts and Semey city. Soils are saline and chestnut in the West of the district, and black earth (Chernozem) in the East of the district.

There is the Zhezkent mining and processing plant on the territory of the district, which is engaged in the extraction of polymetallic ores, and a number of reprocessing enterprises.

The organic part of dark and light brown was isolated according to the standard method [9], by three-fold extraction with 0.1 M NaOH solution. The soil suspension was filled with an extractant solution and shaken on a rotator for one hour. The resulting suspension was filtered, and the remaining soil in the flask was filled with a new portion of 0.1 M alkali solution. The extraction of organic matter was repeated three times.

Humic acids were separated from the filtrate by adding a 10 % solution of sulfuric acid to pH=1. The resulting precipitate was filtered and washed with water, and then dissolved in 0.1 M sodium hydroxide solution. Separate fractions of humic acids were deposited from the resulting solution by addition of 1 % sulfuric acid solution drop by drop to the resulting solution of humic acids to pH=7. The precipitate was separated by centrifugation after 2 hours of settling. A 1 % solution of sulfuric acid was added to the centrifuge again drop by drop to pH=7. All operations for separation of sediment were repeated similarly according to the above method.

Similar operations were performed by depositing fractions at pH 5.0; 4.0; 3.0; 2.0; 1.0 and at pH<1.0. The resulting fractions were dried on pre-dried paper filters to a constant weight. The mass of fractions was determined by the difference in the mass of «clean» filters and filters with organic matter after drying.

Thus, 7 organic fractions of dark chestnut soil at pH=7.0; 6.0; 4.0; 3.0; 2.0; 1.0 and <1.0, 8 organic fractions of light chestnut soil at pH=7.0; 6.0; 5.0; 4.0; 3.0; 2.0; 1.0 and <1.0 were isolated. The organic fraction at pH=5.0 for the dark chestnut soil was not considered due to the negligible allocation of humic acids into a separate fraction.

The study of sorption processes of heavy metals in mono-, bi- and polyelement variants of organo-mineral matrix of dark chestnut and light chestnut soil was carried out in accordance with [1]. Solutions of $Zn(NO_3)_2$, $Pb(CH_3COO)_2$, and $Cd(CH_3COO)_2$ salts were used for the model test. The salt concentration was 2.5 mmol/ml for mono- and bi-element variants and 1.25 mmol/ml for poly-element variant.

The solution of humic acids isolated at pH=7.0 was divided into 7 equal parts, in which a certain volume of zinc, lead, cadmium salts or their mixtures was added. The following options for applying HM solutions were used:

1. **mono-element** $(Zn(NO_3)_2; Pb(CH_3COO)_2; Cd(CH_3COO)_2)$
2. **bi-element** $(Zn(NO_3)_2 + Pb(CH_3COO)_2);$
 $(Zn(NO_3)_2 + Cd(CH_3COO)_2);$
 $(Pb(CH_3COO)_2 + Cd(CH_3COO)_2)$
3. **poly-element** $(Zn(NO_3)_2 + Pb(CH_3COO)_2 + Cd(CH_3COO)_2)$

A 10 % solution of sulfuric acid was added to the resulting solutions to pH=1.0. Humic acids were precipitated in all studied solutions. Then the solutions were infused for a day and centrifuged. The content of heavy metals (zinc, lead, cadmium, zinc-lead, zinc-cadmium, lead-cadmium, zinc-lead-cadmium) was determined in the centrifugate. The percentage of sorption was determined by the difference in concentration in the initial standard solution and the extract obtained after the sorption process.

Gross content and concentration of water-soluble, acid exchange forms of zinc, cadmium and lead in the analyzed solution was determined by extraction photometric method with ditizone using a photometer.

Results and Discussion

7 well-separated fractions have been formed by the triple extracted organic part of dark chestnut soil and 8 well-separated fractions have been formed by the light chestnut soil. Their isoelectric points correspond to the following pH values of the medium: 7.0; 6.0; 5.0; 4.0; 3.0; 2.0; 1.0 and <1.0.

In all fractions, the content of humic acids and organic fractions from the total content of organic matter was determined by gravimetry (Tables 1, 2).

Table 1

Content of humic acids and organic substances in the dark chestnut soil

| Fractions at pH | Humic acids content, % | Organic substances content, % |
|-----------------|------------------------|-------------------------------|
| <1.0 | 0.075±0.001 | 29.00±2.15 |
| 1.0 | 0.050±0.002 | 18.50±1.02 |
| 2.0 | 0.025±0.001 | 9.15±0.98 |
| 3.0 | 0.013±0.001 | 3.20±0.24 |
| 4.0 | 0.020±0.001 | 6.24±0.25 |
| 5.0 | – | – |
| 6.0 | 0.034±0.001 | 11.71±1.13 |
| 7.0 | 0.061±0.002 | 25.07±1.89 |

As can be seen in Table 1, the content of humic acids and organic substances prevails in fractions with pH <1.0 (0.075 % and 29.00 %), 1.0 (0.050 % and 18.50 %) and 7.0 (0.061 % and 25.07 %), which indicates that these fractions are enriched with organic substances.

Table 2

Content of humic acids and organic substances in the light chestnut soil

| Fractions at pH | Humic acids content, % | Organic substances content, % |
|-----------------|------------------------|-------------------------------|
| <1.0 | 0.012±0.001 | 19.00±1.67 |
| 1.0 | 0.013±0.002 | 14.25±1.19 |
| 2.0 | 0.010±0.001 | 13.00±1.14 |
| 3.0 | 0.009±0.002 | 9.55±1.05 |
| 4.0 | 0.009±0.002 | 12.20±1.17 |
| 5.0 | 0.008±0.001 | 10.70±1.12 |
| 6.0 | 0.011±0.001 | 1.85±0.12 |
| 7.0 | 0.017±0.002 | 20.25±1.53 |

As can be seen in Table 2, the content of humic acids and organic substances prevails in fractions with pH <1.0 (0.012 % and 19.00 %), and 7.0 (0.017 % and 20.25 %), which indicates that these fractions are enriched with organic substances.

Thus, the highest yield of humic acids and organic substances was obtained at pH 1.0; pH<1.0; pH 7.0 for dark chestnut soil, and at pH<1.0; pH 7.0 for light brown soil.

The isolated fractions of humic acids were studied by IR spectroscopy to determine the identification of functional groups included in the composition.

Figure 1 presents the IR spectrum of humic acids isolated from dark chestnut and light chestnut soils of the Borodulikha region.

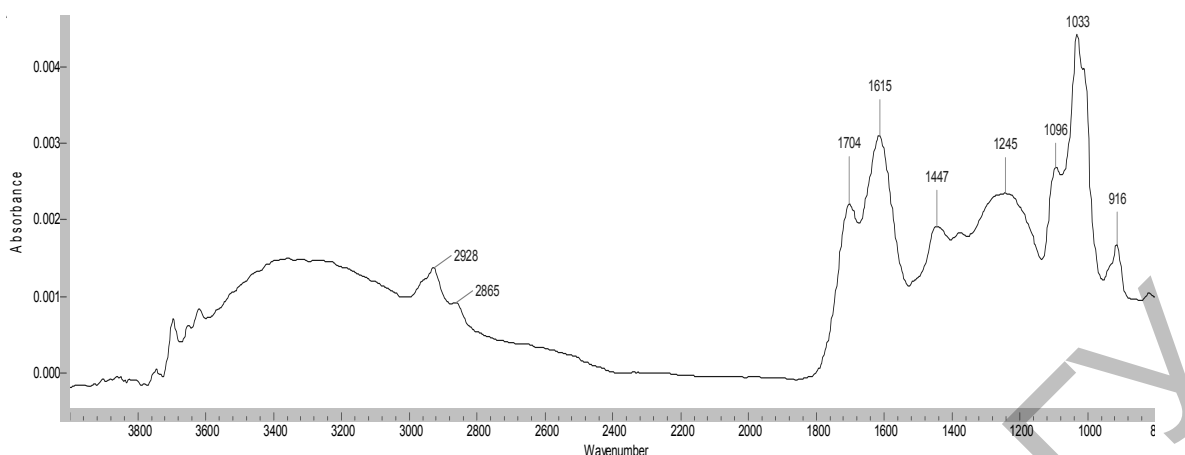


Figure 1. IR spectrum of humic acids

All absorption bands are presented in the IR spectra of the studied humic acids, which is confirmed the presence of the aromatic part (core) and external aliphatic chains in macromolecules. The characteristic absorption bands are in the range of 1000–1800 cm^{-1} . Absorption bands with maxima at 1033 cm^{-1} are caused by fluctuations in the O–H bond of primary alcohol groups. Absorption bands with maxima at 2865 and 2928 cm^{-1} are caused by valence fluctuations of $-\text{CH}_3$ and $-\text{CH}_2$ groups of the side chain. The narrow band with a maximum at 1704 cm^{-1} belongs to the carboxyl group $-\text{COOH}$. Aromatic and aryl-alkyl esters correspond to the absorption band at 1245 cm^{-1} . The absorption peak at 2865 cm^{-1} indicates the presence of alicyclic compounds. The presence of aromatic rings in humic acid molecules is indicated by the absorption band at 1615 cm^{-1} , which is caused by valence vibrations of the skeletal bonds of the aromatic rings.

The results of zinc, cadmium and lead sorption by organic fractions of dark and light chestnut soil in mono-, bi- and poly-element variants are presented in Tables 3, 4 respectively.

Table 3

Degree of metal sorption by organic fraction of dark chestnut soil in mono-, bi- and poly-element variants

| Variant | Degree of sorption, % | | | | | | |
|----------|-----------------------|------------|------------|------------|------------|------------|------------|
| | pH 7.0 | pH 6.0 | pH 4.0 | pH 3.0 | pH 2.0 | pH 1.0 | pH<1.0 |
| Zn | 52.06±0.01 | 55.06±0.03 | 56.00±0.01 | 76.59±0.01 | 72.21±0.01 | 74.55±0.01 | 84.14±0.01 |
| Pb | 85.71±0.01 | 93.54±0.02 | 41.91±0.01 | 34.57±0.01 | 37.38±0.01 | 35.58±0.01 | 14.14±0.01 |
| Cd | 29.02±15.03 | 56.56±0.01 | 24.28±0.02 | 27.29±0.01 | 22.05±0.01 | 15.75±0.01 | 78.06±0.01 |
| Zn/Pb | Zn | 76.17±0.01 | 77.45±0.02 | 78.17±0.02 | 54.19±0.01 | 42.13±0.01 | 19.97±0.01 |
| | Pb | 76.97±0.02 | 77.39±0.02 | 67.54±0.03 | 65.11±0.01 | 71.46±0.01 | 59.38±0.01 |
| Zn/Cd | Zn | 76.76±0.03 | 77.56±0.02 | 63.15±0.02 | 66.03±0.01 | 45.11±0.01 | 21.78±0.01 |
| | Cd | 81.09±0.06 | 81.70±0.06 | 82.20±0.12 | 79.42±0.01 | 54.78±0.02 | 48.61±0.01 |
| Pb/Cd | Pb | 13.62±0.02 | 11.10±0.12 | 49.77±0.01 | 47.93±0.01 | 73.52±0.01 | 75.19±0.01 |
| | Cd | 28.77±0.07 | 39.08±0.04 | 53.68±5.77 | 92.48±0.01 | 93.18±0.01 | 73.89±0.01 |
| Zn/Pb/Cd | Zn | 84.25±0.02 | 84.52±0.01 | 73.76±0.01 | 37.18±0.02 | 62.09±0.01 | 57.12±0.01 |
| | Pb | 84.49±5.78 | 84.35±0.02 | 80.80±0.01 | 78.63±0.02 | 47.88±0.01 | 11.41±0.01 |
| | Cd | 90.49±0.02 | 90.65±0.02 | 90.04±0.01 | 88.69±0.02 | 47.22±0.01 | 73.48±0.01 |

As can be seen in Table 3, the sorption of zinc was almost identical (sorption degree 52.06 %; 55.06 % and 56.00 %) by organic fractions with pH 7.0; 6.0; 4.0 in mono-element variant. The sorption of zinc was increased with further acidification, for example, it was increased by 1.5 times at pH=3.0 (76.59 %) compared to the value at pH=7.0 (52.06 %).

The degree of zinc sorption increased at pH 7.0; 6.0; 4.0 (76.17 %; 77.45 %; 78.17 %) with equivalent enrichment of each fraction with zinc and lead, except for highly acidic environments.

The cadmium presence also increased the zinc absorption, for example, the sorption degree was increased by 1.5 times at typical for this soil reaction medium pH 7.0–6.0 in comparison with the mono-element experiment. The same results were obtained with the combined presence of lead and cadmium.

The character of lead sorption in various versions of the experiment is similar to that in fractions with isoelectric points at pH 7.0; 6.0; 3.0 and is radically different from fractions with pH 2.0; 1.0; <1.0. The sorption patterns shown at pH 4 are intermediate.

The greatest absorption of lead was observed in pH 7.0; 6.0 fractions; the degree of sorption was decreased with acidification of the medium, for example, it decreased by 2 times at pH 4.0; 1.0 compared to pH 6.0. In the presence of an equivalent amount of zinc, lead sorption was slightly suppressed in fractions with pH 7.0; 6.0; 3.0; 2.0, and Vice versa, it was enhanced by the pH 4.0 and 1.0 medium reaction. Cadmium was even more deactivated processes of lead enrichment:

- by 6.3 times compared to the mono-element experiment in the fraction with pH 7.0;
- by 8.4 times at pH 6.0.

The absorption of lead was not affected by the presence of cadmium in fractions with pH 4.0 and 2.0. The combined presence of zinc and cadmium did not lead to any changes in the lead sorption as compared with mono-element variant reaction by organic fraction of dark chestnut soil (pH 6–7). Consequently, both zinc and cadmium reduce the degree of sorption, but the influence of zinc is more predominant in their combined presence.

Fractions at pH 7.0; 6.0; 4.0, as well as at pH 3.0 and 2.0, showed general regularities in the cadmium sorption in different versions of the experiment. The absorption dynamics is not unequal when the acidity increases.

The presence of zinc has a «catalyzing» effect on the cadmium sorption (approximately 3 times compared to the values of the mono-element variant in fractions with pH 7.0; 6.0; 4.0 and 1.0). The presence of lead does not have significant changes at pH 7.0; 6.0 and slightly increases sorption in more acidic fractions. In poly-element absorption variant, the sorption of cadmium is influenced more by the presence of lead, since sorption is comparable to those regularities that were deduced in the bi-element experiment in the presence of lead alone. Thus, the maximum values of the sorption degree belong to fractions with pH 7.0; 6.0; 4.0 in poly-element absorption variant. The degree of absorption increases almost 3 times compared to the mono-element experiment in these fractions.

Table 4

Degree of metal sorption by organic fraction of light chestnut soil in mono-, bi- and poly-element variants

| Variant | Degree of sorption, % | | | | | | | |
|----------|-----------------------|------------|------------|------------|------------|------------|------------|------------|
| | pH 7.0 | pH 6.0 | pH 5.0 | pH 4.0 | pH 3.0 | pH 2.0 | pH 1.0 | pH<1.0 |
| Zn | 23.70±0.01 | 39.62±0.01 | 32.08±0.02 | 33.12±0.01 | 55.03±0.01 | 56.11±0.01 | 53.25±0.02 | 84.10±0.02 |
| Pb | 82.17±0.01 | 88.21±0.01 | 27.04±0.01 | 25.01±0.02 | 13.13±0.01 | 18.64±0.2 | 23.11±0.01 | 25.70±0.01 |
| Cd | 56.23±0.01 | 40.24±0.02 | 22.61±0.01 | 14.51±0.01 | 13.42±0.01 | 17.93±0.01 | 78.04±0.01 | 83.65±0.02 |
| Zn/Pb | Zn | 64.81±0.01 | 72.40±0.01 | 10.03±0.03 | 16.95±0.01 | 11.46±0.02 | 37.91±0.01 | 79.21±0.01 |
| | Pb | 11.30±0.01 | 56.72±1.71 | 65.02±0.01 | 60.41±0.01 | 54.36±0.02 | 51.71±0.01 | 10.95±0.01 |
| Zn/Cd | Zn | 72.13±0.02 | 70.81±0.01 | 16.94±0.01 | 6.43±0.01 | 5.73±0.01 | 9.34±0.02 | 18.81±0.01 |
| | Cd | 63.00±0.02 | 57.11±0.01 | 51.82±0.01 | 62.22±0.01 | 54.93±0.01 | 58.81±0.01 | 51.74±0.01 |
| Pb/Cd | Pb | 55.64±0.02 | 54.21±0.02 | 66.00±0.02 | 53.36±0.01 | 53.04±0.02 | 56.81±0.01 | 36.07±0.01 |
| | Cd | 32.11±0.02 | 73.73±0.01 | 43.60±0.01 | 53.23±0.01 | 59.27±0.02 | 36.00±0.02 | 12.40±0.01 |
| Zn/Pb/Cd | Zn | 79.93±0.01 | 73.55±0.01 | 34.21±0.01 | 36.42±0.01 | 19.42±0.02 | 23.83±0.02 | 49.86±0.01 |
| | Pb | 67.84±5.77 | 53.94±0.02 | 70.12±0.01 | 73.90±0.01 | 67.90±0.02 | 72.82±0.01 | 69.63±0.01 |
| | Cd | 83.00±0.02 | 69.21±0.01 | 82.84±0.02 | 76.52±0.01 | 75.04±0.01 | 68.43±0.01 | 59.62±0.01 |

The sorption of zinc by the organic fraction of light chestnut soil was slightly different from dark chestnut soil. Dynamics of pollutant absorption within all factions in mono-variant naturally increased. By the nature of zinc sorption in the presence of lead or cadmium and in the simultaneous presence of lead and cadmium, the fractions can be combined into several microgroups: 1) with pH 7–6; 2) with pH 5; 4; 3; 2; 3) with pH 1; <1. The first group of fractions is active in normal natural conditions, it is increased its sorption in both in bi- and poly-element variants of the experiment. Moreover, the action of lead and cadmium is almost the same.

Lead and cadmium inhibited the sorption of zinc in the second group of humic acids in light chestnut soil. The cadmium had more competitive action there. For example, at pH 2 the sorption of zinc was suppressed by 1.5 times in the presence of lead and it was suppressed by 6 times in the presence of cadmium in

comparison with mono-element variant. Zinc absorption was increased in the presence of lead, and it was suppressed in the presence of cadmium in the group represented by fractions with pH 1 and <1.

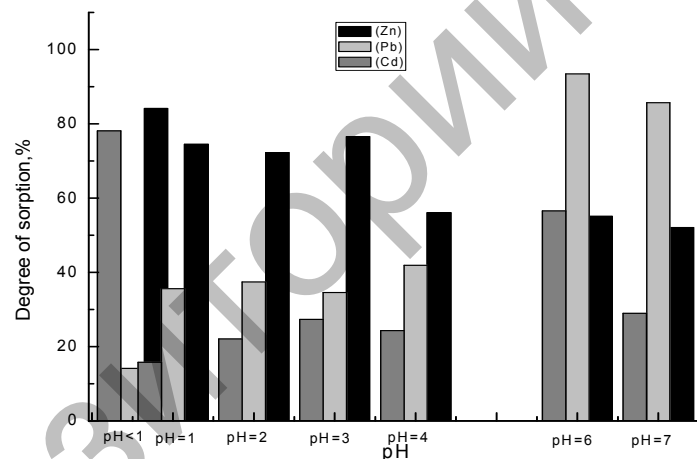
Lead absorption was suppressed with acidification of fractions in the mono-element version of the experiment. Thus, at pH 5, sorption decreased by about 3 times when compared with the fraction with an isoelectric point at pH 7.0.

Data obtained during bi-element and poly-element experiments indicates that, the lead sorption have been suppressed at pH 7.0; 6.0 and have been increased at pH from 5 to <1 by both zinc and cadmium, and their combined presence. The same dynamics of cadmium sorption have been shown by fractions with pH 6.0; 5.0; 4.0; 3.0; 2.0 relative to the presence of both zinc and lead.

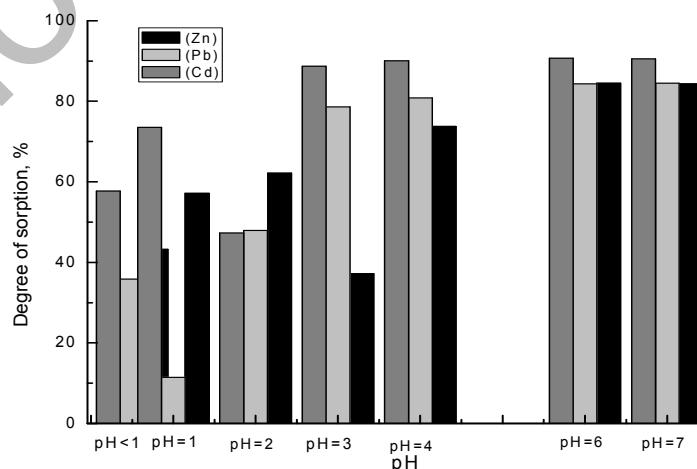
Zinc have been demonstrated a greater activating effect. For example, at pH 5.0 the presence of zinc increased the cadmium absorption by 2.3 times compared to the mono-element experiment, and by 1.9 times in the presence of lead alone. The character of cadmium sorption in poly-element enrichment was more influenced by the presence of zinc in all fractions except pH<1.

In general, the cadmium sorption was suppressed when acidified to pH 2.0 (by 3.1 times compared to pH 7.0) in mono-element version; it did not change significantly in poly-element enrichment. Almost all fractions increased the cadmium sorption at 2.7 times level compared to the average value of the mono-element experience of these fractions.

It was shown by the comparison of zinc, lead, and cadmium sorption degree values in a mono-element experiment (Fig. 2), that fraction with pH of 7.0, and 6.0 are indicators for lead (its sorption is more than 1.6 times the sorption of zinc and 3 times more the sorption of cadmium), more acidic fractions are indicators for cadmium (for example, the cadmium sorption is 1.3 times higher sorption of lead and 5.9 times higher sorption of zinc in fraction with pH 3.0).



a) specific sorption (multi-element variant)



b) competitive sorption (poly-element variant)

Figure 2. Comparison diagram of heavy metals sorption by the organic matrix of dark chestnut soil

Fractions with the same structure showed similar absorption patterns in the experiment. All the selected fractions can be divided into two groups: 1) pH 7.0; 4.0; 3.0 and 2) pH 1.0. Although the structure of the pH 6.0 fraction differs in spectrum from all others, it is characterized by similarity of the sorption character with the first group of fractions mentioned above. Humic acids with pH 1.0 active medium are in this series separately: the individual spectrum also characterizes the distinctive features in the sorbed capacity. It was shown by the comparison of all three metals sorption values (Fig. 3), that the fraction with a neutral medium showed greater affinity to lead, and the acidified medium showed greater affinity to zinc in the mono-element version.

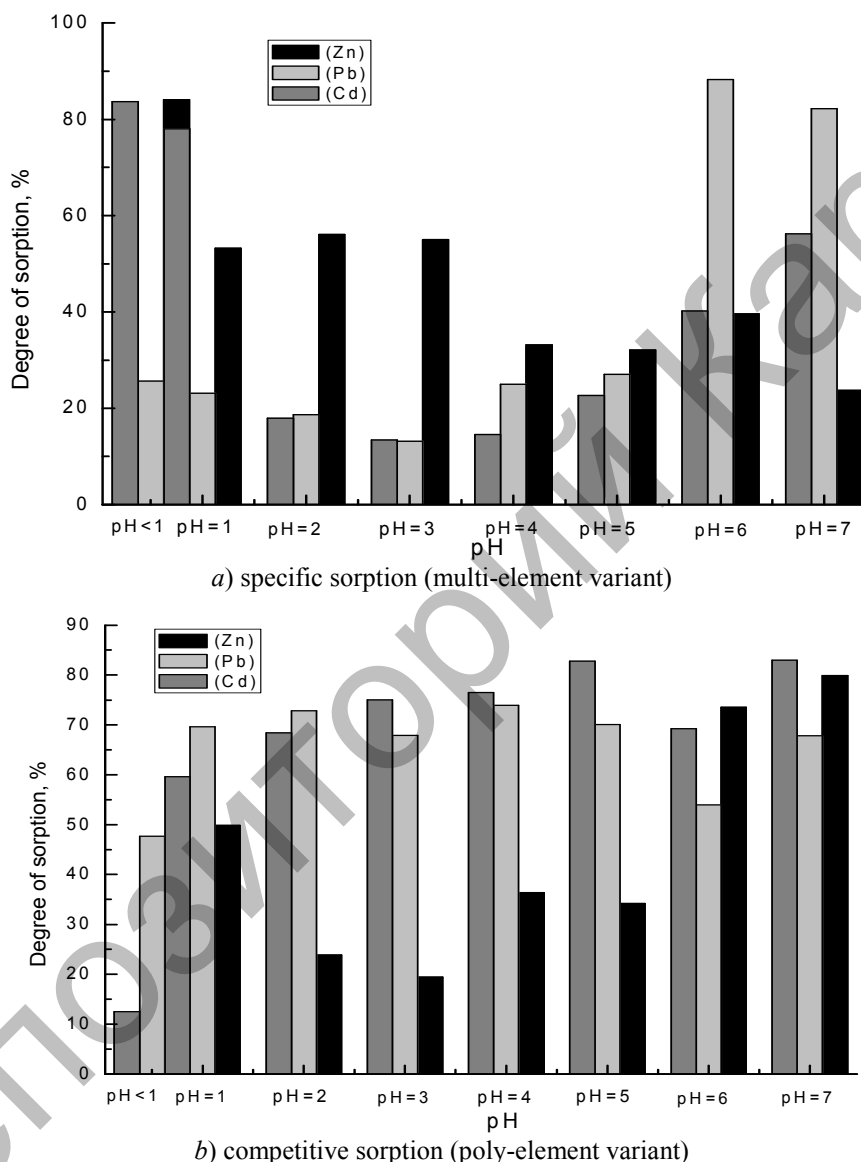


Figure 3. Comparison diagram of heavy metals sorption by the organic matrix of light chestnut soil

As can be seen in Figure 3, the percentage of sorption was highest for zinc and cadmium at pH < 1.0. The sorption processes were enhanced for all metals, and lead had a competitive effect on zinc and cadmium with the combined presence of all three ions. Similar dynamics of pollutants absorption were shown by fractions with pH 6.0; 5.0; 4.0; 3.0, which have approximately the same character of spectral curves.

The two studied soils showed different sorption activity. The fractions at pH = 7.0 (the active fraction for these soils) and at pH = 6 of the two soils absorbed the introduced pollutants differently (Figs. 4–6): dark chestnut soil absorbed more zinc than light chestnut soil under equivalent conditions. This can be explained by the low content of organic matter, and, accordingly, by the small percentage (%) of fractions in light chestnut soil (Tables 3, 4).

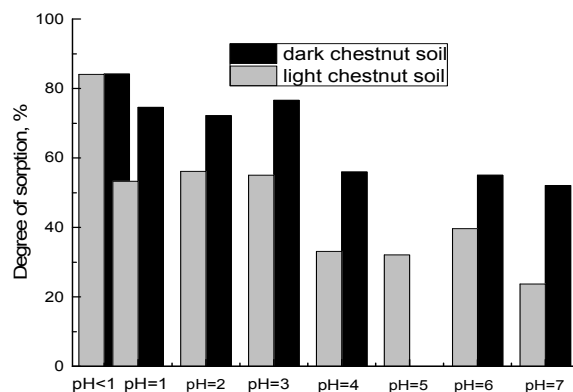


Figure 4. Comparative diagram of zinc sorption in the mono-element experiment

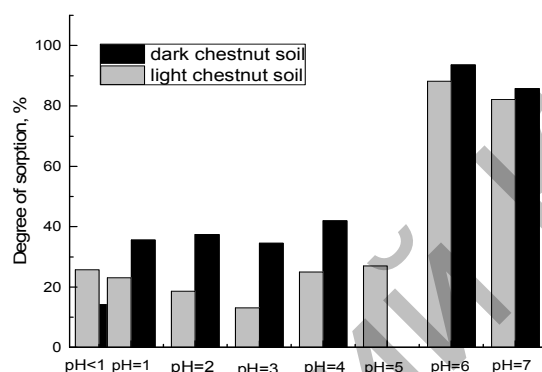


Figure 5. Comparative diagram of lead sorption in a single experience

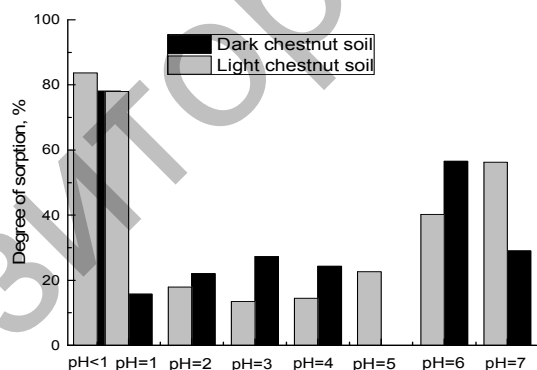


Figure 6. Comparative diagram of cadmium sorption in the mono-element experiment

Thus, since chestnut soils have a slightly alkaline reaction ($pH\ 7.2-7.5$) under normal conditions, all three metals have a high affinity for the organic fraction in poly-element contamination conditions. The sorption intensity is suppressed by acidification.

Conclusions

Thus, it was shown by the IR spectroscopy data, that extracted from the dark brown and light brown soils of the Borodulikha region humic acids contain primary and secondary alcohols, aromatic hydrocarbons, carboxylic acids, aromatic and aryl-alkyl esters. The presence of such functional groups as $-COOH$, $-OH$ in humic acids makes it possible to bind heavy metals to the organic fraction of the soil by forming chelate complexes.

The sorption of heavy metals by the organo-mineral matrix of dark chestnut and light chestnut soil of the ecologically clean Borodulikha region of East Kazakhstan was studied. Soil samples were selected in the Western part of Borodulikha district, where are no industrial enterprises. However, there is deforestation as a

result of forest fires. Today about 15 % of the district's territory is occupied by pine forest, whereas previously the area of the forest was 50 %. Therefore, the study of the degree of soil contamination is relevant.

It was established that the process of zinc, cadmium and lead sorption by organic fractions of dark chestnut and light chestnut soil proceeds differently in mono- and poly-element variants. For mono-element enrichment of the soil, lead is more sorbed by humic acid fractions of the studied soils at pH 7.0 and 6.0, its sorption degree reaches 93.54 %; zinc is more sorbed at acidic pH from 3.0 to < 1 uncharacteristic for these soils; cadmium is more sorbed by pH 1.0 and < 1 fractions, their sorption degree at pH 1.0 is 84.14 %. Sorption of zinc, lead, and cadmium by humic and hymetomelanic acids of organic matter of chestnut soils under conditions of poly-element enrichment is accompanied by the oppression of one heavy metal by another.

Data obtained on the sorption of heavy metals by soils can be used in assessing the impact of anthropogenic emissions on the environment, in developing practical recommendations to reduce the toxic effect of heavy metals. The results of the work can also be practically applied in rationing systems.

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Күрең топырақтың гумин қышқылдарының ауыр металдарды сорбциялауы

Мақаланың мақсаты ашық және қою-күрең топырағының гумин қышқылдарымен ауыр металдардың сорбциясын зерттеу. Зерттеу объектілері Шығыс Қазақстанның экологиялық таза ауданынан алынған қою және ашық-күрең топырақ үлгілері болып табылады. Гумин қышқылдары (ГК) топырақтан әр түрлі рН мәндерінде бөлініп алынды, бұл ретте ГК қою-күрең топырақтан ГК шығымы рН 1.0 кезінде 0.075 %; рН=7.0 кезінде ашық-күрең топырақтан 0.017 % құрады. Бұдан әрі сорбция деңгейінің орта қышқылдығына тәуелділігі анықталды. Мырыш пен кадмий күшті қышқыл ортада сорбцияланатыны анықталды (рН 1.0–84.14 %), ал қорғасын рН 6.0 — 93.54 % кезінде жақсы сорбцияланады және оның сорбция дәрежесі жоғары. Би- және полиэлементті нұсқаларда металдар бір-бірінің сорбциясын басу немесе күшейту арқылы өзара әсер ететіні анықталды. Кадмий нейтрал ортада қорғасынның сорбциясын едәуір басадыны көрсетілген. Мырыш кадмий мен қорғасын сорбциясын 3 есе арттырады. Ауыр металдар иондарының топырақтың органикалық фракциясымен байланысуы гумин қышқылдарымен комплекс түзілу есебінен болады деген қорытынды жасалды.

Кілт сөздер: ауыр металдар, қою-күрең топырақ, ашық-күрең топырақ, топырақтың органикалық фракциясы, гумин қышқылдары, сорбция, мырыш, қорғасын, кадмий, Шығыс Қазақстан, Бородулиха.

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Сорбция тяжелых металлов гуминовыми кислотами каштановых почв

Целью данной статьи является изучение сорбции тяжелых металлов гуминовыми кислотами (ГК) светло- и темно-каштановых почв. Объектами исследования являются образцы темно- и светло-каштановых почв, отобранные из экологически чистого района Восточного Казахстана. Гуминовые кислоты выделены из почвы при различных значениях рН, при этом выход ГК из темно-каштановой почвы при рН<1,0 составил 0,075 %, из светло-каштановой при рН=7,0 — 0,017 %. Далее была установлена зависимость степени сорбции от кислотности среды. Выявлено, что цинк и кадмий сильнее сорбируются в сильно-кислой среде (рН<1,0; 84,14 %), тогда как свинец лучше сорбируется при рН 6,0, причем степень его сорбции выше (93,54 %). В би- и полиэлементных вариантах выявлено, что металлы оказывают взаимное влияние, подавляя или усиливая сорбцию друг друга. Показано, что кадмий значительно подавляет сорбцию свинца в нейтральных средах. Цинк чаще усиливает сорбцию и кадмия и свинца в 3 раза. Сделано заключение, что связывание ионов тяжелых металлов органической фракцией почвы происходит за счет комплексообразования с гуминовыми кислотами.

Ключевые слова: тяжелые металлы, темно-каштановая почва, светло-каштановая почва, органическая фракция почвы, гуминовые кислоты, сорбция, цинк, свинец, кадмий, Восточный Казахстан, Бородулиха.

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