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DECONTAMINATION OF HARMFUL HEAVY METALS IN SOILS USING AGRO-ORES AND HUMATES

Boynazarov Baxron Raimovich
Tashkent State Agrarian University, docent E-mail: boynazarovbaxrom73@mail.ru
Usanboyev Najmiddin Khalmirzayevich
Deputy Director of Scientific Affairs of the Institute of General and Inorganic Chemistry
Khudayarov Makhmasaid Makhmarajabovich
Senior Lecturer, Tashkent State Agrarian University

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Abstract. The article presents the results of determining the total and soluble forms of heavy metals in industrial soils. It was found that the addition of potassium humate and natural bentonite clay isolated from coal oxidized in a solution of H2O2 to soils contaminated with heavy metals significantly reduces the soluble forms of heavy metals.

Key words: humate, organic substances, heavy metals, bentonite, toxic substances, soil, trace elements.

INTRODUCTION

The extraction, processing of natural resources, the intensification of agriculture and other anthropogenic activities are leading to widespread environmental pollution. Pollution of soils, groundwater and air with hazardous heavy metals and toxic chemicals is one of the most important problems facing the world today. For this reason, there is a need to develop technologies that prevent harmful substances from entering the food chain during the processing of natural resources and the cultivation of agricultural crops [1,2].

Environmental pollution by chemicals not only leads to the destruction of the biosphere, but also reduces the quality of food products produced. The impact of harmful substances is determined by many factors, including the nature and concentration of the element, the physicochemical properties of the soil, the activity of soil microorganisms, the form of heavy metal compounds in the soil, and the presence of substances that form complex compounds that reduce the absorption of heavy metals by plants [3].

In the study of soils and their productivity, there is great interest in trace elements, including heavy metals. While elements such as cobalt, copper, iron, manganese, molybdenum, nickel, and zinc are essential for the vital activity of living organisms in small concentrations, their toxicity increases with increasing concentration in the cell. For this reason, these elements are often referred to as trace elements in small concentrations, and as heavy metals in high concentrations. Metals such as cadmium, lead, and mercury are toxic even at low concentrations [4,5]. Soil minerals and humic substances have the most important properties in controlling the mobility and biological properties of elemental compounds in terrestrial ecosystems [6,7]. Humic substances react with cations, anions, neutral molecules, radionuclide mixtures, and other environmental pollutants and reduce their harmful effects [8].

Humic substances in the soil can form complexes with metal ions and change the availability of nutrients to plants. They can form complex complexes in the form of metal-humate and metal-humate-mineral, and also reduce the availability of heavy metals to plants by forming chemical bonds with heavy metals depending on the pH of the soil solution [9].

In the biosphere, humus substances perform the following functions: 1. Accumulative function - accumulates various chemical substances and energy, which are subsequently assimilated by living organisms. Humus substances contain the following substances in their composition: 40-60% carbon; 3-5% nitrogen, 20-40% oxygen, as well as sulfur, phosphorus, and various metal ions. As a result of their assimilation, living organisms and plants receive the elements they need in the required amount. 2. Transport or migration function of humic substances - humic substances can form with metal cations, along with poorly soluble, stable compounds, stable, but soluble compounds capable of geochemical migration of compounds. It is known that iron is almost stationary at normal pH values for most soils. The dominant form of iron hydroxide, which is a solubility product, cannot cause a significant movement of iron ions in the soil profile. However, it is true that iron migration is well organized. For iron, as well as for cations of many other metals, their dominant migration form is represented by complex organomineral compounds, in which fulvic acids play the main role. In this way, many trace elements migrate, as well as the main part of phosphorus and sulfur. 3. The regulatory function of humic substances - combines many phenomena and processes in soils. The regulatory function of humic substances is divided into several main parts: 1) formation of soil structure and water-physical properties of soils; 2) regulation of ion exchange reactions between solid and liquid phases; 3) influence on acid-base and oxidation-reduction regimes; 4) regulation of nutritional conditions of living organisms; 5) regulation of the thermal regime of the soil and atmosphere. 4. The protective function of humic substances is known, but not sufficiently studied. In general, it can be noted that humic substances protect or preserve soil biota in various adverse and extreme conditions. It is known that humus-rich soils are better able to withstand drought or excessive moisture and are less prone to erosion. Humic substances bind sufficiently strong radionuclides, detergents, and pesticides, thereby preventing their penetration into plants or other negative effects. The physiological function of humic substances is associated with their role as carriers of amino acids, some vitamins, and antibiotics [10-14].

In this work [15] an attempt was made to understand the effect of humic acids on the differential release of cations from silicates (olivine and tourmaline), their relative stability order, the kinetics of solubilization processes and the nature of residual products. The kinetic dissolution curves of both minerals are distinctive, consisting of successive peaks and troughs, indicating an alternating cycle of dissolution and reprecipitation. The removal of cations from the structure depends on its appropriate position in the crystal lattice, which in turn determines the entry of humic acid into it; moreover, the stability of the chelate formed between the humic acid and the individual cation is a decisive factor. The study of mineral-humic acid reaction residues showed that not only in the easily crystallized olivine, but also in the stable tourmaline, a decrease in $Fe^{2+/3+}$ and Si^{4+} and an enrichment of Al^{3+} and Mg^{2+} (only in olivine) were observed. The appearance of new crystalline phases indicates the precipitation of humic acids on the mineral surface due to their complex formation with cations. From this it can be concluded that humic substances not only form insoluble complex complexes with cations, but also cause their transition to some solution.

The following work [16] showed that the destruction of causative microorganisms by chemicals is limited by the presence of toxic ions, therefore, the treatment of agricultural crops with 50-90 mg/l humic acid was more effective in reducing causticity and mortality than a mixture of formaldehyde and methylene blue. Humic acids improve the conditions for plant growth and increase disease resistance, and moderate the solubility of cations in the soil and the pH of the soil. A solution obtained by extraction from plant-based compost with 0.1 normal sodium hydroxide was precipitated at pH 2 and applied to three types of soils with a thickness of 15 cm and an area of 0.12 m^2. The results showed that the application of 100-200 ml of humic acid per 0.12 m^2 gave an acceptable yield and improved the physicochemical properties of the soil. It showed that the pH level of the soil is 7-8, cation exchange is 60%, and the volume density of the soil reaches 1.1-0.97 g/cm^3.

From the above data, it can be concluded that the application of humic substances and agro-ore bentonites to soils contaminated with heavy metals not only reduces the harmful effects of heavy metals, but also increases soil fertility and creates the opportunity to obtain high and high-quality yields from plants. Therefore, currently, the study of the processes of obtaining fertilizers containing humic substances, the development of their technologies and their application in agriculture are of great importance for obtaining environmentally friendly and high yields from agricultural crops [17-19].

In this work, studies were carried out on the decontamination of soils from harmful substances using humic substances and bentonites in the vicinity of the Almalyk Mining and Metallurgical Combine (Joint Stock Company) located in the Tashkent region and in the agricultural crops grown on the farm of the combine. The selection of soil samples was carried out at the end of the growing season in accordance with GOST 17.4.4.02-84.

In order to convert heavy elements in the soil into a form that cannot be absorbed by plants by sorption and complex formation, mixture samples were prepared by adding potassium humate and bentonite in different amounts to 7 soil samples taken from 100 grams. The samples were stored in a humidified state for 7 days. After that, the samples were dried at a temperature of 40°C, and the amounts of elements in total and water-soluble forms were determined. The chemical composition of the potassium humate and bentonite used is given in Tables 1 and 2.

Table 1.

Humate potassium content, %

Humidity	Ash	Total organic matter	Including	
			Humic acids	Fulvic acids
97,17	0,11	2,72	1,42	0,24

Table 2

Bentonite chemical composition, % (Tashkent region)

SiO_2	T_1O_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5	SO_3	H_2O	CO_2
50,34	0,73	15,21	5,67	2,3	0,03	4,76	2,31	2,36	0,13	1,48	5,42	3,41

Potassium humate was oxidized from Angren coal with hydrogen peroxide, and then the oxidized product was isolated by extraction with 1% KOH solution. Its concentration was diluted to 0.1% and added to the soil in various proportions. The amount of heavy metals in the soil was determined using the methods “Determination of the elemental composition of rocks, soil, soil and subsoil sediments by inductively coupled plasma atomic emission method and inductively coupled plasma mass spectrometry” using the 7500 Series device (ICP-MS). The degree of soil contamination is characterized by the abundance of REM and Clark and the degree of affinity of biochemical elements.

$$K_{\mathrm{uz}} = \frac{\mathrm{C_{uz}}}{\mathrm{C_y}}\, 100\%$$

K_{uz} – the level of absorption of the element.
C_y – the total amount of elements in the soil.
C_{uz} – the concentration of water-soluble forms of the element [20-22].

The obtained data were processed using generally accepted mathematical statistical methods using MS Excel and Statistica-10.0. The reliability of the differences in mean values was assessed using the Fisher-Student test. The results are presented in Table 3.

Table 3

Changes in water-soluble forms of heavy metals in the soil under the influence of

potassium humate and bentonite. g/t

№	Options		Pb	Cd	Zn	Cr	Ni	Cu	Co
1	Soil sample (SS)	Total	180	2,60	500	43,0	29,0	190,0	9,20
		absorption	6,0	0,084	25,0	4,10	3,70	25,0	0,640
		K*	3,3	3,23	5,0	9,53	12,76	13,15	6,95
2	SS, 0.15 ml Humate potassium	absorption	3,60	0,067	16,0	1,70	3,0	23,0	0,450
		K*	2,0	2,57	3,2	3,95	10,3	12,11	4,89
3	SS, 0.3 ml Humate potassium	absorption	2,80	0,055	13,4	1,90	3,0	22,0	0,340
		K*	1,55	2,11	2.,68	4,4	10,3	11,58	3,69
4	SS, 0.5 ml Humate potassium	absorption	2,50	0,037	17,0	1,55	2,5	19,0	0,295
		K*	1,38	1,42	3,4	3,6	8,62	10,0	3,20
5	SS, 1.5 g of bentonite	absorption	1,60	0,047	21,0	1,40	2,80	19,0	0,430
		K*	0,89	1,80	4,2	3,25	9,65	10,0	4,67
6	SS, 0.15 ml humate potassium, 1.5 g bentonite	absorption	2,90	0,039	16,2	1,10	2,70	17,0	0,440
		K*	1,61	1,5	3,24	2,55	9,3	8,9	4,78
7	SS, 0.3 ml humate potassium 3 g bentonite	absorption	3,10	0,037	12,0	2,10	2,60	18,2	0,470
		K*	1,72	1,4	2,4	4,88	8,96	9,57	5,10

K* is the absorption level of the metal

It was found that the introduction of potassium humate and bentonite in small amounts into soil contaminated with heavy metals leads to a decrease in the water-soluble form of heavy metals. When 0.15 ml of 0.1% potassium humate was added to 100 g of soil sample, the mobility level of heavy metals (K*), that is, water-soluble forms of Pb 3,3%; Cd 3,23%; Zn 5,0%; Cr 9,53%; Ni 12,76%; Cu 13,15%; Co 6,95%, respectively, to Pb 2,0%; Cd 2,57%; Zn 3,2%; Cr 3,95%; Ni 10,3%; Cu 12,11%; Co 4,89%, with the addition of 0.3 ml of Pb 1,55%; Cd 2,11%; Zn 2,68%; Cr 4,4%; Ni 10,3%; Cu 11,58%; Co 3,69%; Co showed a decrease of up to 3.69%. We can also see a partial decrease in the soluble form of heavy metals in samples where bentonite clay was added to the soil sample. For example, when 1.5 g. bentonite clay was added to 100 g of soil, the soluble form of heavy metals showed a decrease of Pb 0,89%; Cd 1,80%; Zn 4,2%; Cr 3,25%; Ni 9,65%; Cu 10,0%; Co 4,67% compared to the control.

Metal humates form stable complexes at low concentrations. This process occurs with the participation of the strongest donor centers. At high concentrations, on the contrary, weak binding centers participate, as a result of which the stability of the resulting compounds decreases.

As mentioned above, the introduction of potassium humate and bentonite in various amounts into soils with a high REM (permissible norm) of heavy elements leads to a decrease in the soluble forms of heavy metals. Studies have shown that the application of humates and bentonite from natural agrominerals to the soil in small quantities reduces the amount of harmful substances in the form that is absorbed by plants, that is, salts of humic acids react with cations of metals in the form that are absorbed, forming complex complexes that are insoluble in water and the soil environment, and these complex compounds improve the physical state of the soil.

The addition of humate and bentonite to the soil significantly changes the available forms of Pb, Cd and other elements in its composition. The results of studies on the study of potassium humate showed that its use in soils contaminated with heavy metals gives a positive effect. Experiments on the introduction of bentonite and humates into soils contaminated with heavy metals show their effectiveness.

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