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METHOD OF SOILS ENVIRONMENTAL REMEDIATION POLLUTED MAINLY BY CADMIUM, LEAD, ZINC AND CHROMIUM

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The method of contaminated soils remediation from technogenic polyelemental pollution of Cd, Pb, Cr, Zn is substantiated, where in using of ferrous sulphate with addition of vermicompost as a soil activator self cleaning and soils improver prolonged effects, according to the level of soil contamination is provided by restoring its natural properties and an allowance nutrients in the soil, which helps to restore the productivity of plants and environmental rehabilitation of contaminated soil-plant system. The technical result of the designed method is the acceleration of microbiological processes, physical and chemical adsorption of heavy metals of different classes of hazards in the soil by complementary introducing additional soils structure improves combinations of organic and inorganic nature, which ensures effective remediation of polluted soils, expanding the range of heavy metals spectrum, that are unable to migrate into adjacent to the soil environment, protection and optimization, and restore of soil humus status.

***Key words**: heavy metals (cadmium, lead, zinc and chromium), technogenic pollution of soils, the method of remediation.*

Introduction. Soil fertility restoring and their protection from pollution is relevant and one of the most complex scientific challenges. Improving the environmental situation in polluted soils by conducting effective remediation requires addressing a range of questions of the methodological, technological and legal measures for the development and implementation of the complex of physical, physical-chemical, chemical, and biological measures to reduce the intensity of the soil degradation processes on the impact of chemical industrial pollution. Therefore, an important and significant both in theoretical terms and in terms of the application is the elaboration of new methods of remediation of polluted with heavy metals (HM) soil conditions for improving their ecological condition and to prevent reduction of soil productivity and plant deterioration of their quality.

State of the problem knowledge. Analysis and ranking of all known modern methods of soil - plant system remediation, mono - and polyelemental contaminated by HM presented in the previous scientific articles as a result of the execution of fundamental research [1-5].

The analysis of patents on methods of environmental rehabilitation of contaminated by HM soil shows that in the near (for the technical nature) to developed method have we known method using an aqueous solution of humic acids (HA), excluded from the lowland peat [6]. Reducing the toxicity of contaminated soils is achieved by chemical binding of HM cations into insoluble compounds with the HA. However, the initial HA are usually of low activity (as a consequence of low hydrated and dispersion, blocking their active centers of various components), which requires the inclusion of an additional stage of obtaining HA water-soluble and significantly complicates and increases the cost of operations for HM detoxification in soil. The method does not take into account the composition and nature of the pollution and the buffer properties of soils, which reduces the effectiveness of their remediation.

It is well known another way to restore fertility (optimization of the structural condition, increase microbial activity) of low buffer capacity sand contaminated soil [7].

The method involves the introduction into the soil of peat and organic fertilizers protein 4 % in a weight ratio of 1:1-2, the suspension of activated sludge in the amount of 0,05-0,3 % in the the ratio of C:N:P exactly equal to 100:5:1. The disadvantage of this method is the complexity of its implementation and resource-expensive, preservation of ecological risk of secondary contamination of soil due to high content of HM in activated sludge.

The closest to the technical nature and the result achieved, there is a way, involving the use of water-soluble ferrous salts in combination with nitrogen fertilizers at a certain ratio [8]. The effectiveness of HM detoxification is achieved by physical-chemical adsorption and reduction of mobility HM in technogenic soils with neutral and alkaline properties, formed stable organic-mineral complexes that are unavailable to plant roots. This approach provides the efficient use of soils improvers, but because of HM pollution in the areas of sustainable action is polyelemental character, from the entire HM spectrum reduced mobility only Pb and Cd. In addition, ferrous are an antagonist of phosphorus, zinc and manganese, and therefore the risk of stagnation receipt of phosphorus and trace elements to plants increase.

Moreover, on the background of long-term application of nitrogen fertilizers, there is a reduction of amorphous ferrous content in the soil, decreases the efficiency of ferrous sulphate as a detoxifier, there is peptidase and remove of clay colloids, which could lead to the destruction of soil absorption complex, loss of agronomical valuable soil structure and soil fertility. Together with the loss of clay minerals are lost and resistance of soils to HM pollution.

The purpose of investigations – is to elaborate a method of remediation of soil contaminated mainly by Cd, Pb, Cr, Zn, through acceleration of microbiological processes, physical and chemical adsorption HM different hazard classes through complementary making structurebased soils improvers of organic and inorganic type. The method is aimed at the effective remediation of contaminated soils, expanding the range of HM that are unable to migrate to neighbouring sites soil protection and optimization and recovery of humus soil conditions, affecting the activation of self-purification of soil from the HM, contributing to the improvement of the ecological state of soils in areas with intensive influence of atmospheric-technical pollution for simultaneous increase bioenergy potential and buffer capacity of soils; providing prolongation of action detoxicants, the creation of a reserve of nutrients in the soil, increasing the plant resistance to contamination for the restoration of their productivity.

Objects and methods. The method of elaboration include: patent searching in accordance with ДСТУ 3575-97; *field stage* - soil-geochemical survey on local and regional levels, including in the context of a sustained impact sources of atmotechnogenic emissions of inorganic nature pollution of Zmievskaya TES "Centrenergo" NAC "Energy company of Ukraine" in Kharkiv region and "Ukrzinc" Donetsk region, and a series of microfield experiments; *analytical stage* - definition of the mobile forms of trace elements (TE) and HM content in chernozem soils of different buffer capacity used as extractants acetate ammonium buffer solution with pH 4.8 and 1N HCl in accordance with ДСТУ 4770.1:2007 **–** ДСТУ 4770.9:2007; *laboratory stage* – assessment of trace element status of soils on expert evaluation of the documentation, statistical data processing.

Objects of patent search - objects of copyright, which is patented in Ukraine and CIS countries, the EU in the plane of the goal. The subject of search - method in general; separate operations (stages) of the method is independent of patentable subject; the methods of their production and application; equipment used to implement the process. Methods of research - expert evaluation, analysis, comparison.

The objects of research – soils Forest-steppe and Steppe climatic zones of Ukraine on the effects of pollution by HM and for his absence; activatory toxicity of organic and inorganic nature; the ways, methods and measures for remediation of contaminated soils. Research methods – universal scientific methods, methods of theoretical analysis, system and ecosystem approaches, landscape-geochemical, laboratory and analytical; statistical methods of data processing, expert assessment of the documentation.

Soil improvers (ferrous sulfate, biohumus) at the same time applied to the soil according to the established levels of polyelemental soil contamination by HM (Cd, Pb, Cr, Zn): at moderate levels of pollution, a lump sum for 5 years – ferrous sulphate ($FeSO_4$ x$7H_2O$) – 300-500 kg/ha, biohumus – 2000 kg/ha; at a dangerous level of pollution, a lump sum for 2-3 years – 800-1500 kg/ha, biohumus – 4000 kg/ha; for extremely dangerous level of pollution, once annually – 2500-3000 kg/ha, biohumus – 6000 kg/ha.

Soil improvers' applying carried out according to the guidelines on the substantiation of chemical substances in the soil norms [9], ferrous sulphate in dry form and consistent introduction of biohumus the use of existing guidelines [10]. The method of application of biohumus as of concentrated organic fertilizers of prolonged action - surface, in the spring of pre-sowing soil cultivation affecting the activation of self-purification of soil from the HM, efficiency of ferrous sulphate action of remediation.

Used a ready biohumus (vermicompost) is a product of physical and biochemical transformation of manure of cattle, as organic substrate with a term vermicomposting in 6 months, which is formed as a result of the interaction of earthworms and microorganisms. Applied biohumus was characterized by such compound: humus - 8 %; the total content of organic substances – 40 %; humic substances - 25 %; pH - 7,1+0,4; N total – 0,5 %; P total – 0,8 %; K total – 1,5 %; Ca – 4 %; Mg –0,8 %; ash – 35 %; humidity – 14 %). The contents of the HM in biohumus below the maximum permissible concentration for soils and does not exceed the normative values and the well-known requirements regarding the contents of the HM in organic fertilizers (Table 1).

Table 1. Requirements to the contents of the HM limit in organic fertilizers

Normative document	The contents of the HM in organic fertilizer (mg/kg of dry substance)					
	Cd	Cu	Pb	Zn	Ni	Cr
Biohumus (vermicompost)	0,15	5,22	1,90	41,2	6,36	3,96
ТУ 9819-238-00008064-98	2	132	130	220	-	-
Norm (*Справочная книга, 2001*)	20	1000	750	2500	300	750
Permissible concentrations (*ГОСТ Р17.4.3.07-2001*)	30	1500	500	3500	400	1000

Assessment of the ecological state of soils by trace element status and content of the HM conducted in accordance with valid regulations to current standards and methodical basis, using the total pollution index (*Zc*) and background levels of HM content for soils Forest-steppe and Steppe climatic zones of Ukraine [11]. These values characterize the local zones of soil pollution on the content of the total and mobile forms HM (extremely hazardous pollution – maximum permissible concentrations HM>5; $Zc_{\text{total form}}$ = 178 (8); $Zc_{\text{AAB with pH 4,8}}$ = 265(8); $Zc_{\text{1нHCl}}$ = 89,4 (7);

the dangerous level of maximum permissible concentrations HM - 2-5; $Zc_{total\ form}$ = 16,7 (8); $Zc_{AAB\ with\ pH\ 4,8}$ = 185 (9); $Zc_{1нHCl}$ =29,7 (6); a moderate level of pollution - maximum permissible concentrations of HM - 2; $Zc_{total\ form}$ = 10,8 (8); $Zc_{AAB\ with\ pH\ 4,8}$ = 8,4 (5); $Zc_{1нHCl}$ = 7,3 (5)).

Evaluation of the effectiveness of soil remediation on the content of mobile forms of elements-contaminants carried out on the coefficients of the protective properties of the soil (*Kz*,%), and soil pollution by mobile forms HM (*Kzg,* time) that define in accordance with the formula 1 and 2.

$$Kz = 100 - C\ mf / C\ tf \times 100\ \%, \quad (1)$$

where: *C mf* – the content of mobile forms of HM in the soil after cleaning (extractant 1N HCl mg/kg),

C tf – the total content of the HM in the soil (mg/kg).

The coefficient of the protective properties of soils (Kz) characterizes the share of mobile acid-soluble forms of a chemical element in the total content in the soil, which is conjugate form and is available for plants.

$$Kzg = C\ mf / C_{background}, \quad (2)$$

where: *C mf* – the content of mobile forms of VMS in the soil after cleaning (extractant buffer solution ammonium acetate with pH 4,8; mg/kg),

$C_{background}$ – the background content of HM mobile forms (mg/kg of soil).

The coefficient of soil contamination by HM mobile forms (*Kzg*) characterizes the number of mobile forms of a particular chemical element that exceed natural background levels in the soil.

The necessity of corresponding coefficients introduction due to expediency of transition to dimensionless variables for objectivity in evaluation of the effectiveness of remediation of contaminated soils by HM belonging to different classes of hazard (Cd, Pb, Zn - 1 class; Cr - 2 class), characterized by different levels of total natural content in the soil (Cd 1, Pb - 10, Zn - 53; Cr - 52 mg/kg) and different mobility in polluted soils (Cd - 26,7-92,3 %, Pb - 21,7-74 %, Zn - 16,8-47 %; Cr - 3,9-7,8 %).

Assessment of the complex of remediation of contaminated by HM soil effectiveness are also conducting *in vivo.* Test culture barley *(Hordeum).* The productivity of agrophytocenoses determine at the end of the vegetation period. Test reactions - biological activity of soil (cellulolytic and nitrification activity, CO_2 emissions) in connection with the known methods of microbiological and biochemical studies of contaminated soils: the method by *Д.Г. Звягинцев* (1980); application methods by *Е.Н. Мишустин* (1971); determination of the levels of soil CO_2 emissions on techniques by *И.Н. Шарков* (1987) and *В.Н. Макаров* (1988). Studies of the soil colloids and their fractions spent on methods by *Н.И. Горбунов* (1957), *А.Ф. Тюлин* (1958). The data processing was performed using the methods of mathematical statistics in the framework of the software package *Statistica 10.*

Results. Based on the results of long-term field investigations in areas of tehnogenic impact, it was found that the ferrous sulphate and biohumus, which applied separately on contaminated HM soils for inactivation of their toxicity at different, interact with metals-toxicants. The performance impact is actually enhanced combining with their appling in accordance with the level of contamination soil with neutral or alkaline reaction of the soil environment. However, biohumus as organic fertilizer and structurebased polluted by HM soil increases the efficiency of the ferrous sulphate action period, which helps extend their joint impact on the contaminated soil - plant system. Under such conditions formed stable organo-mineral complexes that include HM, enhanced oxidative processes; biohumus activates the functioning of bacterial microflora with the growth of microorganism's biomass, which results in improving the process of biological absorption metals and their involvement in the biomass of soil's microorganisms. A necessary condition, while, is its high intensity compared with mineralization of soil organic matter, which contributes sorption HM amorphous colloids hydroxides and oxides of ferrous, which have a large capacity of absorption. Fixed by microorganisms HM are less accessible to plants, in comparison with the HM, adsorbed to soil clay minerals. So, by influencing to the processes of salinity and humification of organic matter in the soil system is provided by the technical result - environmental remediation of polluted HM soils.

It is established that the combination of the complex structurebased different nature of soils have provided positive influence on the activation as microbiological (cellulolytic and nitrification activity, CO_2 emissions) and physico-chemical processes in the soil (ion exchange, adsorption and absorption, joint coagulation, transformation of soluble HM compounds in insoluble), evidenced by the results of research (Table 2-4, Fig.1).

Physical and chemical changes that occur in the soil for making ferrous sulphate and as a result of influence of low-molecular organic compounds composed of biohumus and the neutral and alkaline environment of the soil, promote comprehensive coagulation of colloidal solution of ferrous hydroxide with soil organic matter than is reduced HM mobility (Table 2), which are connected with water-soluble organic substances; ensures the promotion of physical-chemical adsorption HM from the soil solution. Thus, the calculated values of the estimated coefficients, according to Table 2, characterizing the degree of purification of soil from the HM after using ferrous sulphate and biohumus as measures detoxification at different levels of soil contamination and is a confirmation of their effective combination.

Thus, the coefficient of soil contamination mobile forms of Cd is reduced to 0.5-3 -11 compared with the control, where the levels were 1,5-5-15. A similar trend is also installed for mobile forms of Pb, Zn and Cr in soil. The result of that is the high purification from the HM in soi, the formation of stable compounds with mineral and organic colloids in the soil; intensification of the processes of humus mineralization by increasing the content of water-soluble carbon in the soil (Table 3), up to certain limits that are positive for improving the ecological state of soils in areas with intensive atmotehnogenic pollution by HM.

However, we found that as a result of effective environmental remediation for the introduction structurebased as part of the complex that features increases the risk of excessive mineralization of humus, which may lead to violation of the carbon balance of the soil and the leveling effect of soil remediation of contamination. In addition, it was determined that without appling of biohumus ferrous sulphate limited dose of 600 kg / ha,

Table 2. Assessment of the remediation effectiveness of polluted soil on the coefficients of pollution and protective properties of soils

Options for remediation respectively to levels of HM contaminated soils	The coefficient of soil contamination by HM mobile forms (*Kzg*)				The coefficient of the protective properties of soils relative to HM (Kz, %)			
	Cd	Pb	Zn	Cr	Cd	Pb	Zn	Cr

The moderate level of pollution								
Control (contaminated soil)	1,5	4	3	2	69	59	75	96
$FeSO_4$x7H_2O 300-500 kg/ha + biohumus 2 t/ha	0,5	3	2,5	1,5	76	62	78	97
The dangerous level of pollution								
Control (contaminated soil)	5	54	7	6	50	46	64	94
$FeSO_4$x7H_2O 800-1500 kg/ha + biohumus 4 t/ha	3	53	6	4,5	59	47	68	95
The extremely dangerous level of pollution								
Control (contaminated soil)	15	171	218	18	32	51	53	92
$FeSO_4$x7H_2O 2,5-3 t/ha + biohumus 6 t/ha	11	165	200	14	36	55	54	92,8

for the excess of which there are negative effects - increased the content of soil colloids that peptidase by water and, consequently, reduced the proportion of soil compounds which are not amenable to soil peptization.

By results of the soil colloids and their fractions researches, it was found that the introduction of biohumus is an effective lever of influence on the ecological carbon balance in the soil, restoration and improvement of its structure (including by reducing the intensity of the processes of humus mineralization), fixation HM by colloids and soil organic matter of biohumus, increasing the absorption capacity of the soil and pH, reduction of water-soluble carbon content (Table 3).

Therefore, reduction of soil contamination factor stated increases the protective properties of soils relative to the HM, and thus confirmed the effectiveness of the proposed method of environmental remediation and its benefits. Also, the results of microbiological and biochemical studies have found increased activity of the biological component of the soil, particularly cellulolytic and nitrification activity and soil CO_2 emissions (Table 4).

To intensify the natural biological soil potential and on the background of the decrease of the negative impact of HM, improving the ecological state of the soil, which has a positive influence on the productivity of barley plants (Fig. 1, options 1-4 compared with the control - variant 5). This is an additional confirmation of the proposed method effectiveness of the complementary appling of ferrous sulphate and biohumus provides the ability to implement them as effective soils improvers for restore of contaminated by HM soils.

The elaborated method of HM polluted soil remediation is reasonable to use in the agro-ecology, ecotoxicology of soil, environmental assessment, to develop a complex of measures for remediation of soils contaminated territories and, consequently, to reduce the intensity of the processes of soil degradation on the impact of chemical pollution, for creating conditions for improving the ecological condition of soil and prevent reduce plant productivity, degradation of their quality.

Table 3. The impact of soils improvers on the state of colloids and their fractions in the polluted soil

Options for remediation of contaminated soils	Colloids of the I fraction of fine particles (1H NaCl), %	Colloids of the II fraction of fine particles (0,004н NaOH), %	Colloids of the III fraction of fine particles (0,05n HCl), %	The residual	Water-soluble C, mg/100 g soil layer 0-20 cm	
					1-th year of validity	2-nd year of validity
According to prototype						
Control (contaminated soil)	38,90	1,64	2,73	48,41	8,1	-
$FeSO_4x7H_2O$	37,94	1,01	3,12	49,79	9,71	-
$FeSO_4x7H_2O$ + nitrogen fertilizers	38,20	1,45	5,35	51,10	11,21	-
According to the proposed method						
Control (contaminated soil)	33,33	2,46	2,79	53,17	7,9	8,15
$FeSO_4x7H_2O$	34,42	5,26	4,53	55,63	10,44	11,05
$FeSO_4x7H_2O$ + biohumus	40,40	5,89	3,6	57,26	9,2	8,40

Table 4. Influence of soil improvers combination on indicators of biological activity of contaminated soil

Combination options of soils improvers	Soil CO_2 emission intensity, mg/m^2		Cellulolytic activity, %		Нітрифікаційна активність, NO_3^- мг/100 г ґрунту	
	Lim	M	Lim	M	lim	M
Control (contaminated soil)	129,32 - 138,40	133,86	15,5 - 20,5	18,0	3,15 - 6,14	4,64
$FeSO_4x7H_2O$ 500 kg/ha	135,99 - 152,1	144,05	14,90 - 25,77	20,33	3,29 - 7,1	5,19
$FeSO_4x7H_2O$ 500 kg/ha + biohumus 2 t/ha	144,89 - 162,92	153,90	16,55 – 26,0	21,28	4,5 - 5,9	5,2
$FeSO_4x7H_2O$ 1500 kg/ha	135,58- 149,99	142,78	21,1 - 52,0	36,55	3,42 - 6,01	4,71
$FeSO_4x7H_2O$ 1500 kg/ha + biohumus 2 t/ha	159,64 - 180,78	170,21	26,6 - 62,1	46,0	3,41 - 7,85	5,63

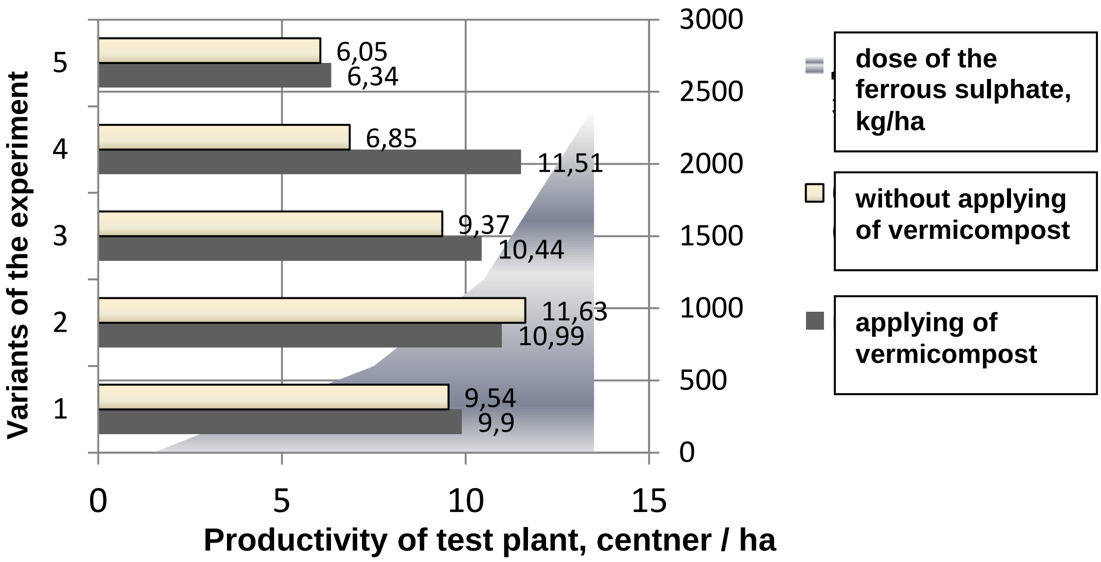

Fig.1. - The influence of ferrous sulphate and vermicompost on Hordeum plant productivity

Conclusions. Distinctive features and benefits of the proposed technical solution, compared with conventional methods and approaches are the following:

- activation of soils self-purification with different levels of contamination mainly by Cd, Pb, Cr, Zn, in the areas of intensive influence sustainable sources of technogenic emissions for the acceleration of microbiological and physico-chemical processes of soils for simultaneous increase bioenergy potential and buffer capacity of soils;
- reduction of resources consumption of remediation of contaminated soils procedures through the restoration of the soil natural properties, provide prolongement actions detoxicants for the creation of a reserve of nutrients in the soil, increasing the plant resistance to contamination for the restoration of their productivity;
- the objective assessment of the effectiveness of contaminated soils remediation of different hazard classes of HM and levels of industrial pollution for the using of the coefficients of the soil protective properties and soil pollution mobile forms of HM.

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