NEW GEOCHEMICAL BARRIER TO DETOXIFYOF SOIL FROM ARSENIC AND MERCURY

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Abstract - **The given article reveals a problem of weeding soil from heavy metals, in particular from arsenic and mercury. Authors got a new geochemical barrier, consisting of a mixture of the utilized bird's dung, a marble crumb and a peroxide of calciumwith the high absorbent activity. The research results allow to eliminate undesirable influence of heavy metals on plants and to get ecological clear products.**

Keywords: Geochemical barrier, peroxide of calcium, utilized bird's dung, detoxication

INTRODUCTION

The negative impact of hazardous substances on objects of biogeocenoses appears in different ways, especially with respect to the soil, which is the main component and the foundation of operation of all terrestrial ecosystems.

Every year there is an increase of the intensity of soil environment pollution by heavy metals, so the search and development of effective environmental and economic methods of providing access to clean crop production is a challenge for the agricultural sector. The certain scientific and practical interest about thesolution to this issue is the creation of geochemical barriers in the soil system to inhibit the translocation of heavy metals in plants.

It is known that the toxic components are adsorbed by organic substances and many mineral components of soils, as a result there is a change in the level of their toxicity and bioavailability. Manifestation of the adverse effects of polluting substances in agroeco-system depends on the solubility of the pollutants, their mobility in soil and species characteristics of crops.

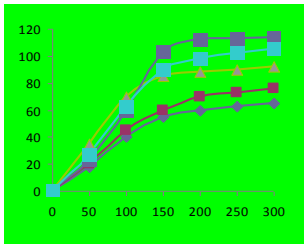
Analyzing data from the literature [1-3] and the results of our experiments [4] to study the sorption capacity of different materials for the management of migration, the translocation of As and Hg we have selected the geochemical barrier consisting of a mixture of recycled bird droppings, marble chips and calcium peroxide, which have high sorption.

METHOD

Calcium peroxide is a well-known commercial product which is manufactured on an industrial scale. It is widely used. The main decomposition products are hydrogen peroxide, oxygen, and thus it is used for bleaching, eliminating bad smells, as a local disinfectant. It is also known the use of calcium peroxide for agriculture to improve the growth of various crops at the expense of aeration as a result of the collapse of hydrogen peroxide to oxygen. When you add hydrogen peroxide it accelerates the process of decay. In addition the introduction of calcium peroxide into the soil makes it possible to adjust the pH value in the ecosystem due to the formation of $Ca(OH)_2$.

The use of calcium carbonate and hydrogen peroxide, bird droppings reducesignificantly the flow of heavy metals into plants due to their adsorption properties.

Figure 1 shows the experimentally obtained data describing sorption processes which take place with the participation of the components.



A mg / g

CaCO3 : CaO2 1) 1:4; 2) 1:3; 3) 1:2; 4) 4:1; 5) 5:1

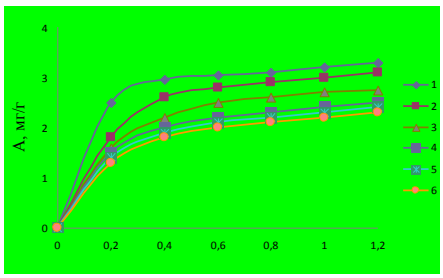
Figure 1 - Adsorption of mercury isotherm with a mixture of calcium carbonate and hydrogen peroxide at different ratios of components.

As it is seen from Figure 1, a mixture of calcium carbonate and hydrogen peroxide in the ratio of 4:1, respectively has the best adsorption capacity with respect to mercury. The same sorbent ratio was also the best during the sorption processes with arsenic. In this regard, further research is taken as a basis for our present composition of sorbents. On the basis of experimental studies it is also found that the balance in the system occurs within 10-20 minutes and it is a good indicator for operating conditions.

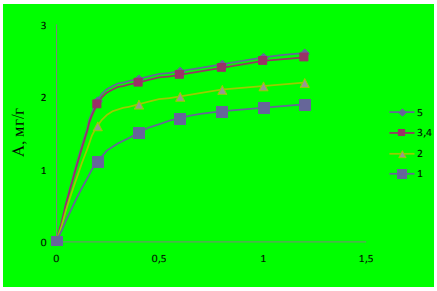
Fairly steep rise in the adsorption isotherms of both arsenic and mercury indicates free inner and outer surfaces of sorbents the sorbents to bind heavy metals. A mixture of carbonate and hydrogen peroxide has a high adsorption capacity with respect to arsenic and mercury.

Figure 2 presents data on the basis of these results, by which we can judge about the dependence of sorption processes on the pH of theenvironment from which the heavy metals are extracted. The data obtained are consistent and understandable in the light of the forms of arsenic and mercury in aquatic systems as a function of pH. Thus, with increasing of pH from 4 to 7 the intake of mercury in the plant is reduced by five times. The reason may lie in the formation of carbonate sediment, or the accumulation of hydroxo complexes $HgOH^+$ and $Hg(OH)_2$ in the solution, or in the decrease in the activity of free Hg^{2+} ions due to their partial binding of ion pairs.

a)



b)



The pH value**,** s: 1 - 0 2 - 1.5-4.0; 3 - 6,8-8,0 4 - 8.0-10.0 5 - 10,0-12,0 6 - 13 , 0

Figure 2 - Adsorption isotherms of mercury (a) and arsenic (b) with a mixture of calcium carbonate and hydrogen peroxide (4:1) at different values of pH.

The sorption of arsenic decreases rapidly with decreasing acidity of the solution, which is associated with a form of existence of this element in the anionic form. Besides, the change in pH has an effect on the cation exchange capacity of the adsorption complexes, which occur when using a mixture of poultry manure, calcium carbonate and hydrogen peroxide (Table 1).

Given the above identified laws to inhibit the migration of arsenic and mercury in plants, along with calcium carbonate and peroxide, studies of adsorption processes with the additional introduction of a system of soil bird droppingswere carried out. For this purpose, the mixture of these three components was introduced into the soil and the extraction from ammonium acetate-buffered saline with pH = 4.8 was carried out in 3 days.

Table 1: Value of a cation exchange capacity of adsorption complexes of organic compounds and metals, with application to the soil the mixture of poultry manure, carbonate and hydrogen peroxide calcium mg-ekv/100 gram of soil (gray soil)

object	Cation exchange capacityat different pH values		
	4,5	7,0	8,3
Soil + $CaCO_3$	81,2	90,4	102,3
Soil + $CaCO_3$+ CaO_2	82,8	93,5	112,6
Soil + $CaCO_3$+ CaO_2+ bird droppings	118,7	130,0	148,4

To assess the migratory ability of arsenic and mercury in the soil system by introducing a mixture of poultry manure, calcium carbonate and hydrogen peroxide (4:1:0,1) the rate of immobilization is applied. To calculate this ratio we used the following formula:

$$K_{imm.} = [(C - Cc) / C]. 100\%$$

where C is concentration of mobile forms of heavy metals in the soil prior to the introduction of sorbents;

Cc is the concentration of mobile forms of heavy metals in the soil after application of sorbents.

Tables 2-3 show the calculated values of the coefficients of immobilization and experimental data characterizing the process of translocation of heavy metals in the presence of a soil system of an artificial geochemical barriers.

As it can be seen from the data when introducing of calcium compounds together with bird droppings, which contain various organic compounds, immobilization ratio increases (Table 2). In the presence of calcium carbonate and hydrogen peroxide, arsenic and mercury compounds are converted into particles of insoluble form and accumulated in the solid phase of soil system. Increase in the immobilization in the presence of bird droppings can be explained by the formation of complex compounds of humic acids, which they contain, with metals. Metals may be included both in anionic and cationic moiety in humic acid. Carboxyl and phenolic hydroxy groupsare responsible for the formation of stable complexes with metal ions. Humic acid, having a high sorption capacity with respect to heavy metal ions behave as complexing sorbents. In addition, the heavy metals with a variable valence are able to interact with the N-and S-containing functional groups of organic compounds. This gives a basis to determine the role of poultry manure as a powerful geochemical barrier responsible for the concentration of metals in soils. This accumulation can not be considered definitive, since under the influence of various anthropogenic factors the metals can move into mobile and immobile form.

Table 2: Values of the coefficients of immobilization upon application to the soil the mixture, consisting of calcium carbonate and hydrogen peroxide, as well as recycled bird droppings in their mass ratio (4:1:0,1)

Soil	Soilsorbents	immobilization ratio of heavy metal,%	
		As	Hg
Greysoil	$CaCO_3$	82	72
Greysoil	CaO_2	70	81
Greysoil	$CaCO_3$ + CaO_2 +birddroppings	96	93
Blackearth	$CaCO_3$	95	98
Blackearth	CaO_2	93	95
Blackearth	$CaCO_3$ + CaO_2 +birddroppings	100	100

Table 3: Content of As and Hg in soils and plants without and with the introduction of the sorption mixture - bird droppings, $CaCO_3$, CaO_2, mg / kg

Object	Withoutintroduction ofsorbents				With the introduction of mixture of sorbents in the plants of As and Hg	
	In the soils As and Hg		In plants As and Hg			
	Greysoil	Greysoil	Greysoil	Greysoil	Greysoil	Greysoil
Arsenic						
corn	156,2	160,5	80,4	15,3	0.08	0,04
mustard	156,2	160,5	91,4	22,7	0,09	0,3
clover	156,2	160,5	75,6	14.2	1,8	notdetected
Mercury						
Corn	120,4	125,9	91,3	9,9	0,02	notdetected
Mustard	120,4	125,9	111,0	98,0	0,08	notdetected
Clover	120,4	125,9	70,3	60,6	1,3	0,01

These obtained experimental dependences can be taken as the theoretical basis for the selection of sorption processes to develop a series of environmental measures.

As it follows from the experimental data presented in Table 3, the number of heavy metals arriving at plants to create geochemical barrier does not exceed regulatory levels (Hg - 0,5 mg / kg, As - 0,3 mg / kg in food). The presence of peroxide calcium in geochemical barrier not only helps to detoxify the soil from heavy metals and to detoxify the bacterial, fungal, parasitic and viral microorganisms.

CONCLUSION

Thus, the introduction of arsenic and mercury contaminated soil mixture of poultry manure, calcium carbonate and hydrogen peroxide can eliminate the undesirable effects of heavy metals on the plants and grow the environmentally friendly products.

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