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Investigation of Nanohydrophobic Sand as an Insulating Layer for Cultivation of Plants in Soils Contaminated with Heavy Metals

M. Myrzabaeva[1]*, Z. Insepov[1], K.K. Boguspaev[2], D.G. Faleev[2], M. Nazhipkyzy[2,3], B.T. Lesbayev[2,3], Z.A. Mansurov[3]

[1]Nazarbayev University, 53 Kabanbay Batyr str, Astana, Kazakhstan
[2]Al-Farabi Kazakh National University, 71 al-Farabi Ave, Almaty, Kazakhstan
[3]Institute of Combustion Problems, 172 Bogenbay batyra str, Almaty, Kazakhstan

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Abstract

The paper presents the results of laboratory experiments to test hydrophobic sand, on the basis of soot as an insulating for growing plants-hyperaccumulators heavy metals – amaranth (*Amaranthus paniculatus*) and sunflower (*Helianthus annuus*) plants. For the first time in agriculture hydrophobic sand was used for the irrigation of water-saving experiments for growing palms in arid areas of the UAE. The hydrophobic sand was obtained from normal beach sand, which is covered by small particles of pure silica, pretreated pairs trimethylhydroxysilane, $(CH_3)_3SiOH$. After this treatment, the outer shell grains saturated groups of compounds insoluble in water, sand and exposes hydrophobic properties. Thus obtained nanohydrophobic sand is considered to be physiologically safe for plants and supplied by the manufacturer with 30-year warranty of the hydrophobic effect. In our experiments we used the conventional washed river sand, as adhesive bases used polyurethane glue SD-600 is dissolved in ethyl acetate. The sand thus obtained is added 1% superhydrophobic soot. The sand is obtained by using carbon black becomes hydrophobic properties, does not transmit moisture, it has virtually no adverse effect on plant growth. To test hydrophobic sand used plastic pots (volume 1 l). The lower layer of the moistened soil-ground containing various concentrations of heavy metals (TM), the next separation layer – nanohydrophobic sand, and the top layer – a layer of fertile soil enriched vermicompost for growing plants. When watering plants nanohydrophobic sand layer retains water and prevents migration of TM (Zn, Cd, Cu) of the lower contaminated layer to the upper, the mold.

1. Introduction

Company "DIME hydrophobic materials" for the first time reported production of hydrophobic granular compositions to be used in industry. Hydrophobic granular compositions (hydrophobic sand, HS) were proposed to be used for water proofing of building, constructions, foundations, elements of hydrotechtehnical units. At present time, there are quite many methods for production of hydrophobic granular material which include mainly thermal treatment of the initial mineral carrier followed by interaction of the latter with the hydrophobic agent and modifier [1].

In agriculture, in order to save irrigation water for growing palm-trees in arid zones of UAE, scientists used hydrophobic sand obtained from usual beach sand coated with small particles of pure silicon dioxide pretreated with vapors of trimethylhydroxysilane, $(CH_3)_3SiOH$. After such treatment, the external shell of a grain of sand is saturated with groups of compounds insoluble in water, this imparting hydrophobic properties to sand. Nanohydrophobic sand obtained in this way is considered to be physiologically safe for plants and is supplied by the producer with a 30 year' guarantee of the hydrophobic effect [2]. Also, hydrophobic sand can be used for growing flowers, seedlings,

*Corresponding author. E-mail: malika77780@mail.ru

etc. in pot cultures. In this case, hydrophobic sand is mixed with soil, thereby increasing access for air to the roots of plants and breathing of roots doesn't limited even with the excess of water. The layer of hydrophobic sand retains water but leaks air necessary for development of roots.

After placing the layer of hydrophobic sand, capillary is broken and if is used for salinated soils, the insulating layer will not allow the salts to migrate up to the root system [3]. In field conditions, when growing plants including cereals (rice), hydrophobic sand can be used as an interlayer under the fertile layer of soil to decrease losses of irrigation water. Moisture is retained in the upper fertile layer and, when using organic fertilizers, it is possible to achieve rich plant yield per the unit of area and decrease the amount of irrigation water 5–10 times.

In our experiments, hydrophobic sand obtained based of super hydrophobic soot was used as an insulating layer [4]. The advantage of this material was evaluated by the following parameters: – the degree of sand hydrophobicity; – the effect of hydrophobic sand on the growth and development of plants; – the level of migration of heavy metals (Helianthus annuus L.) through the layer of hydrophobic sand. To evaluate the level of migration of Helianthus annuus, in the experiments we used plants – hyperaccumulators of heavy metals and radionuclides – amaranth (*Amaranthus paniculatus* L.) and sunflower (*Helianthus annuus* L.) grown from seeds in the upper fertile layer.

Plants-hyperaccumulators are used for remediation of soils contaminated with heavy metals and radionuclides (Phytoremediation). Phytoremediation has become an effective and economically profitable method for purification of the environmental after the discovery of plants-hyperaccumulators of heavy metals which are able to accumulate damage to the plant up to 5% of nickel, zinc or copper in terms of dry weight – that is ten times more than usual plants. In our experiments it was shown that Amaranthus (*Amaranthus paniculatus*) can accumulate zinc (Zn) up to 568 mg/kg of the dry weight of plants, copper (Cu) – 83 mg/kg, and cadmium (Cd) – 32 mg/kg [5]. The possibility of soil remediation with the help of sunflower (*Helianthus annuus*) sprouts was successfully demonstrated by us in laboratory experiments [6]. Thus, in case of migration of HM through the layer of HS we can detect them when analyzing vegetative organs of plants for their content with the help of atomic-absorption spectrometry.

2. Material and methods

2.1. Plants-hyperaccumulators

Vegetation experiments were carried out according to the methods described in the manual Z.I. Zhurbitskogo [7]. In the experiments, we used two types of plants-hyperaccumulators: amaranth (*Amarantus paniculatus*) and sunflower (*Helianthus annuus*) grown in plastic pots with the volume of 500 ml. With the soil mixture (vermiculite/sand 1:1). Metals in the form of salts: $Cd(CH_3COO)_2$ $2H_2O$ (50 mg/kg); $Cu(CH_3COO)_2$ H_2O (100 mg/kg); $Zn(CH_3COO)_2$ H_2O (200 mg/kg) were introduced into soil mixture. Plants grown in soil without metal salts served as a reference. Experiments were repeated three times. Duration of the laboratory experiment was 45 days. Samples of plants (roots, leaves and stems) and soils for determination of HM content were taken in the end of the experiment.

2.2. Preparation of hydrophobic sand on the basis of soot

The method for production of super hydrophobic soot was described in detail in [3]. In the experiments, we used washed river sand, as glue basis we used polyurethane glue YP-600 dissolved in ethylacetate. The content of a glue mass does not exceed 5% of the sand mass. A glue layer is coated with the sand surface by deposition of polyurethane film from the solvent. For this, the sand with polyurethane glue solved in ethylacetate was intensively mixed, the volatile solvent was evaporated. As a result, a nanoscale film from polyurethane is formed on the surface of sand grains. 1% superhydrophobic soot of calcium was added to the sand, than the obtained mass was mixed with the velocity of 60 r/s during 30 min at 40–90 °C. In the course of mixing, the surface of sand grains is encapsulated into a nanoscale film from the mixture of hydrophobic soot and calcium stearate. The role of superhydrophobic soot is in increasing with the degree adhesion of a hydrophobic film on the surface sand grains, their hydrophobic properties and decreasing the time of solidification.

2.3. Determination of HM contents in samples of soil and plants by atomic-absorption method

Determination of HM was carried out on atomic-absorption spectrophotometer AAS-IN of the film Carl Zeiss using a flame sprayer. Extraction of HM from soil and plant samples was performed by wet and dry mineralization [5].

3. Discussion and Results

For investigations, we used annual plant-hyperaccumulators of heavy metals (HM) amaranth and sunflower (*Helianthus annuus* L.) – herbs with powerful root system and over ground part, with intensive growth and high productivity of biomass (5, 6). These types of plants are used in the technology for remediation of soils contaminated with heavy metals (Phytoremediation) where they exhibit their natural ability to accumulate in cells of root, stem and leaves ions of HM in the form of complexes in toxic for plants. In our experiments we carried out by us earlier, amaranth accumulate in vegetative organs (leaves) – Zn-548 mg/kg, Cd-36 mg/kg, Cu-86 mg/kg; (roots) Zn-175 mg/kg, Cd 32 mg/kg, Cu-91 mg/kg, which is quite comparable with the indices of such plants-hyperaccumulators as *Thlaspi caerulescens, Silene vulgaris* and *Alyssum* [8]. Sunflower (*H. annuus* L.) is a well-known plant – hyperaccumulator HM which is successfully used in experiments on phytoremediation of contaminated soils.

3.1. Study of the properties of hydrophobic sand

Before using hydrophobic sand in experiments on growing plants, it was tested under laboratory conditions and its properties are presented in Figs. 1 and 2.

Hydrophobic sand obtained based on the basis of soot was added to water in a beaker. Usual river sand was added to the second beaker with water for comparison. As is shown in Fig. 1, the obtained hydrophobic sand (10 g) is freely floating on the surface of water.

Fig. 1. Properties of hydrophobic sand: 1 – usual river sand on the bottom of glass; 2 – hydrophobic sand on the surface of water.

Figure 2 presents the results of experiments on comparison of characteristics of water absorption dynamics by the sample of river sand, the sand with polyurethane film coated on its surface and the hydrophobic sand on soot.

The initial of river sand and the sand with polyurethane coating absorb water instantly till complete wetting. Water poured onto the surface of the obtained hydrophobic sand spread on its surface in the form of droplets and is not absorbed by hydrophobic sand till its complete evaporation.

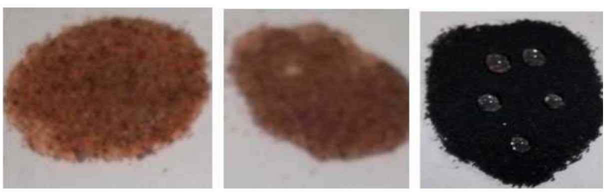

Fig. 2. The dynamics absorption of water: 1 – usual river sand, 2 – sand with polyurethane, 3 – hydrophobic sand.

3.2. Performance of experiments

The effect of hydrophobic sand on the growth of amaranth and sunflower was determined in the following experiments. The pots for growing the plants were filled by the mixture of vermiculite/river sand (1:1) / hydrophobic sand (10%) by weight. In the reference, the mixture vermiculite/river sand (1:1) was used. Settled water without chlorine was poured into the pots in the usual mode. Germination of seeds, height and habitus of plants were analyzed. The experimental results showed (Fig. 3) that hydrophobic sand obtained on the basis of soot mixed with usual river sand (10%) practically did not affect the growth of sprouts and in the course of vegetation a negative effect on the plant was not observed.

However, to get a full picture of the effect of hydrophobic sand on the growth of plants we used plants grown under conditions maximum to the experiment as the second reference. For this, 1/3 layer of hydrophobic sand was loaded into pots and ground for growing plants was placed onto it. In this case, consumption of irrigation water and the effect of sand on the growth of plants were considered (Fig. 4).

Fig. 3. The effect of hydrophobic sand on the growth of sunflower: 1 – the control, 2 – the experience (mixture of HS (10%) with river sand.

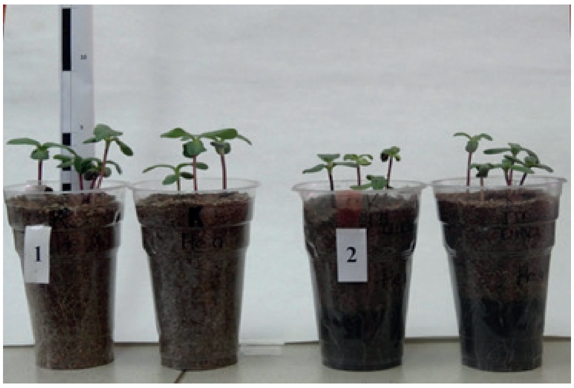

Fig. 4.The effect of hydrophobic sand support on the growth of sunflower. An arrow points at the support from hydrophobic sand: 1 – control plants, 2 – plants grown with the support from hydrophobic sand.

As is seen in Fig. 4, hydrophobic sand slightly decreases the intensity of sunflower growth at the first stages of plants development. To the end of the experiment the difference in growth was leveled.

The obtained results allow concluding that HS in small doses (10%), when being mixed with soil ground, does not practically exert a negative effect on the growth of sunflower sprouts. However, when using a support from hydrophobic sand, a slight delay in the growth of plants was observed. These facts were taken into account when analyzing the results obtained using an insulating layer of HS in the experiments with heavy metals (Zn, Cd, Cu) on evaluation of migration and accumulation of HM by amaranth and sunflower. Figure 5 presents examples of experiments with HM and the insulating layer of hydrophobic sand on the example with Cd.

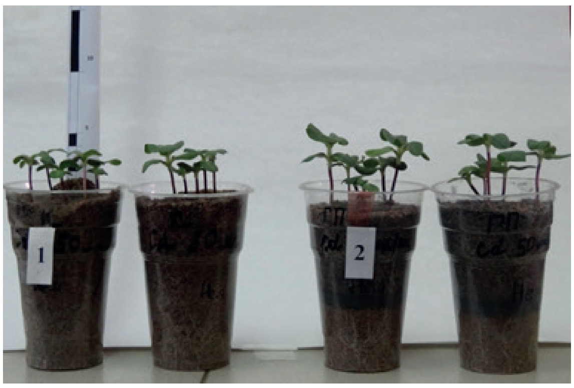

Fig. 5. The experiment with the use of an insulating layer of hydrophobic sand: 1 – control contains 50 mg/kg of Cd, 2 – the experiment the lower layer contains 50 mg/kg of Cd^{2+} and a layer of hydrophobic sand. The upper arrow points at a layer of hydrophobic sand. The lower arrow – soil ground with Cd^{2+}.

Fig. 6. A general view of experiments with the use of the insulating layer of hydrophobic sand and plants-accumulators of HM. On the example of sunflower (*Helianthus annuus*).

A general view of experiments with the use of plants accumulators of HM for evaluation of the insulating action of hydrophobic sand is shown in Fig. 6.

3.3. The content of HM in the vegetative plants-hyperaccumulators

First, it was supposed that the layer of hydrophobic sand, breaking capillarity, prevents the percolation of soluble salts of HM together with irrigation water upward to the root system of plants. In the ideal variant, the amount of HM in the upper layer must not exceed the values in reference plants. To determine the content of HM, the samples of leaves, roots and soil in the lower and upper layers were taken on the 45^{th} day. The content of Zn, Cd, Cu in the samples was determined by the atomic-absorption method.

3.4. Amaranthus paniculatus L.

Figure 7 presents the results of experiments on the effect of the insulating layer of hydrophobic sand on the level of heavy metal contents in amaranthus.

In the experiment, without introduction of metals, the content of HM in the plants corresponds to the background level. In the plants grown in pots with introduction of HM but without the insulating layer of HS we observed a considerable content of HM, this confirming the ability of amaranthus to accumulate them in its vegetative organs. In the experiments with the insulating layer of HS, a general picture on the content of metals (Zn, Cd, Cu) in the plants indicates a positive action of the insulating layer of hydrophobic sand that does not pass water and prevents migration of HM.

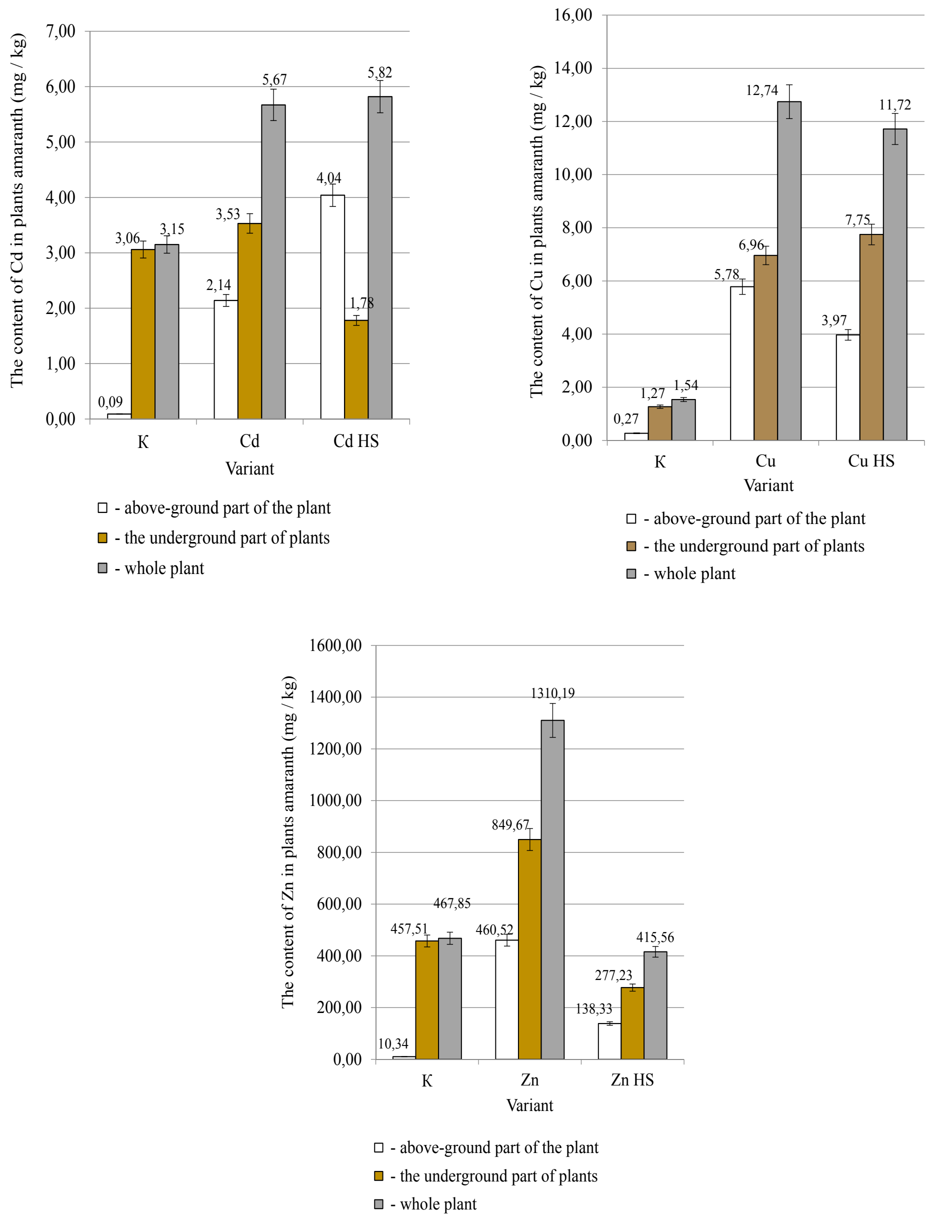

Fig. 7. The content of Cd (a), Cu (b), Zn (c) in the vegetative organs of amaranthus. This effect is vividly demonstrated in the experiments with Zn (Fig. 7b): K – control without hydrophobic sand; (Cd, Cu, Zn) – the experience with the introduced metals; Cd HS, Cu HS, Zn HS – the experience with the introduced metals under the layer of hydrophobic sand.

The distribution in the values of Cu and Cd content in the samples of leaves and roots of amaranthus in different variants of experiments is explained by the fact that in some cases, on account of positive geotropism, the roots of amaranthus shoot through the layer of hydrophobic sand and percolate into the soil ground contaminated with metals (Fig. 8).

Similar results are obtained in the experiments with sunflower. The layer of hydrophobic sand does not pass moisture and ions of heavy metals into the soil ground with the growing plants. However, as in case with amaranthus, the roots of sunflower penetrate through the sand layer and therefore, the content of heavy metals was detected in the samples of leaves and roots (Fig. 8).

Analysis of amaranthus cultivated soil: for following the series of experiments on analysis of the quality of hydrophobic sand, we took samples of ground in the upper and lower layer to determine the content of heavy metals in them. In case of percolation of moisture and HM ions together with it through the insulating layer of hydrophobic sand, moisture and HM in the upper (fertile) layer will be detected in sufficient concentrations. The results of experiments are presented in Figs. 9–11.

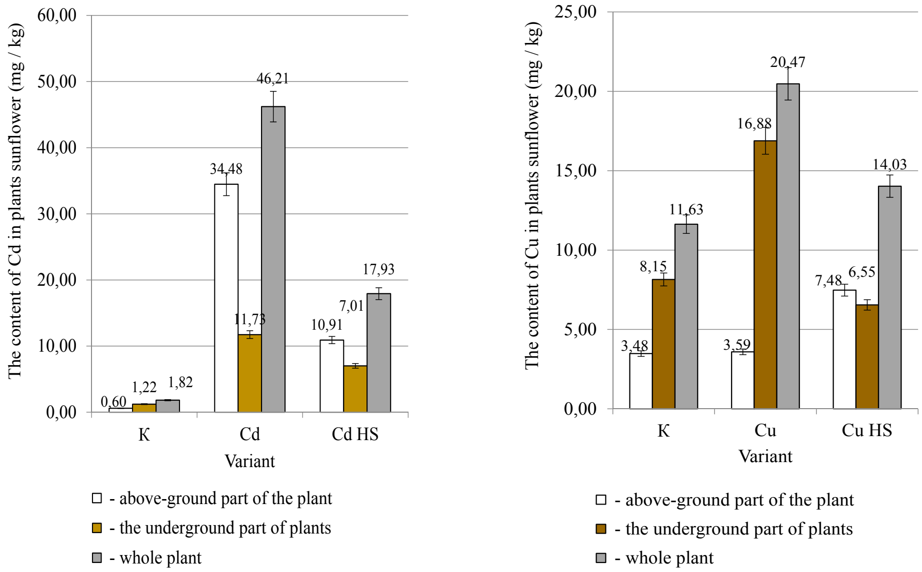

Fig. 8. The content of Cd (a), Cu (b) in sunflower plants: K – control without hydrophobic sand; (Cd, Cu) – the experience with the introduced metals; Cd HS, Cu HS, Zn HS – the experience with the introduced metals under the layer of hydrophobic sand.

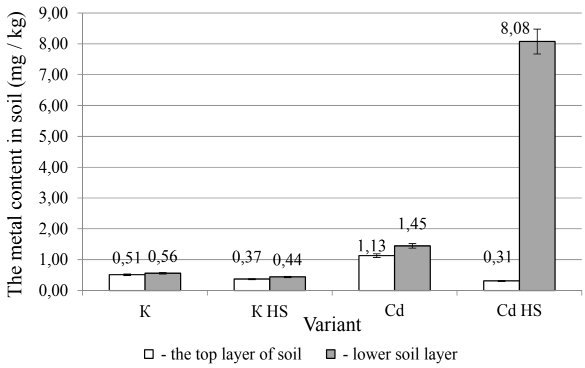

Fig. 9. Copper content in different layers of soil after removal amaranth.

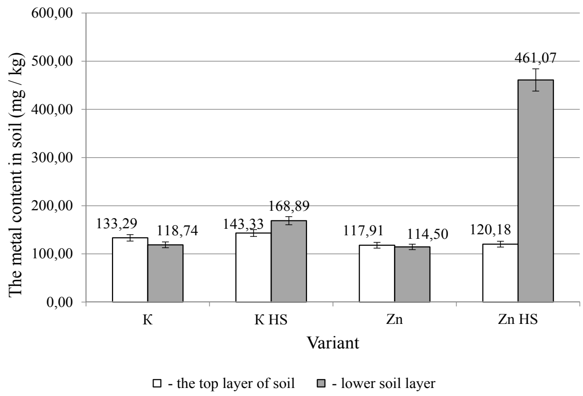

Fig. 11. The cadmium content in the different layers of soil after the removal of the amaranth plant.

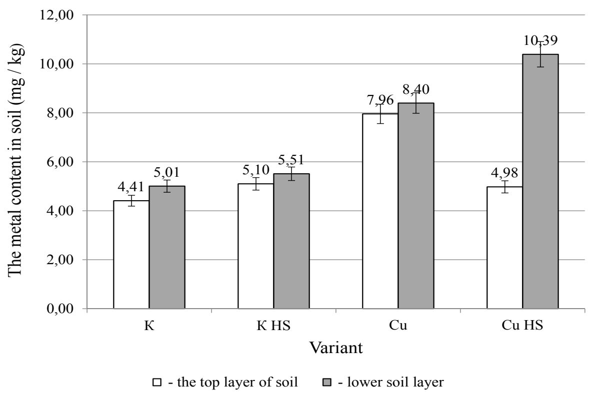

Fig. 10. The zinc content in the different layers of soil after the removal of the amaranth plant.

As is seen in the presented graphs, if some error are not taken into account (experiments with copper), the content of HM in the upper layer remained practically at the level of reference. In the lower layer, HM were detected in high concentrations considerably exceeding the reference. The obtained results allow supposing that the layer of hydrophobic sand functions as a barrier and does not pass moisture and, correspondingly HM to the upper (fertile) layer. Similar results are obtained in the experiments with sunflower (Figs. 12-14).

Analysis of sunflower (*H. annuus*) cultivated soil.

The obtained results in both the experiments with amaranth and experiments with sunflowers showed that the layer of hydrophobic sand on the basis of soot does not pass moisture and serves as a barrier on the path of migration of HM from the contaminated layer to the upper fertile layer of the ground. The growth of roots of amaranthus and sunflower through the layer of hydrophobic sand.

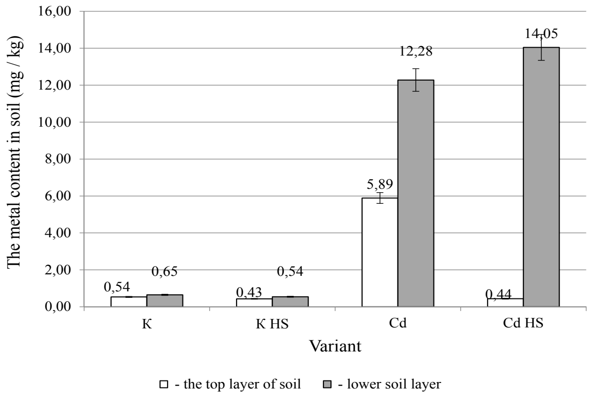

Fig. 12. The copper content in the different layers of soil after the removal of sunflower plants.

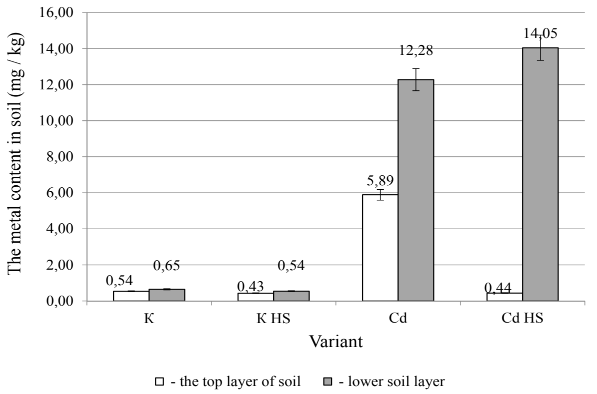

Fig. 13. The content of zinc in the different layers of soil after the removal of sunflower plants.

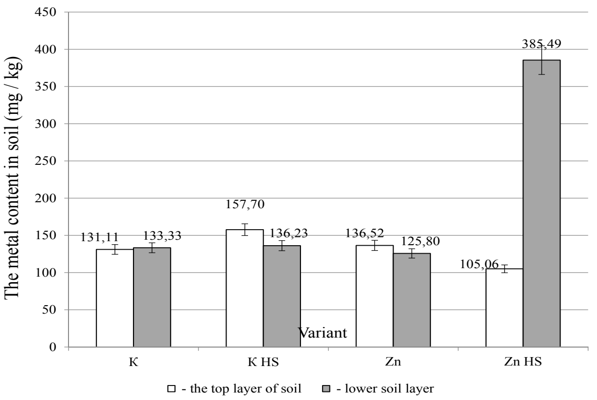

Fig. 14. The cadmium content in different layers of soil after the removal of the sunflower plants

Figure 15 presents the processes of growth and penetration of sunflower roots through the layer of hydrophobic sand.

As it was mentioned, on account of positive geotropism, roots of plants continuing their growth via the layer of hydrophobic sand and penetrate to the lower layer containing HM and accumulate them in vegetative organs.

(a) (b) (c)

Fig. 15. Development of the root system of sunflower sprouts through the layer of hydrophobic sand: (a) – control, without introduction of hydrophobic sand; (b) – the mixture of ground with hydrophobic sand; (c) – the layer of hydrophobic sand. Arrows point at the roots: shoot through the layer of hydrophobic sand.

As a result, in some cases, in samples of leaves and roots, metals are detected in the plants of amaranthus and sunflower grown in the experiments with the insulating layer of hydrophobic sand.

4. Conclusions

The carried out experiments on testing the hydrophobic sand obtained on the basis of soot showed:

- the obtained sand possesses hydrophobic properties, floats on the surface of water, does not sink. Water poured onto the surface of the obtained hydrophobic sand spreads on its surface in the form of droplets and is not absorbed by hydrophobic sand till its complete evaporation;
- 1.5 cm insulating layer from hydrophobic sand does not pass water and the moisture is retained in the upper fertile layer, this creating favorable conditions for the growth of plants;
- the used hydrophobic sand renders a minimal negative action on the growth and development of plants, however, to make a definite conclusion on its physiological safety, it is necessary to perform field tests using different kinds of plants including trees;
- the layer hydrophobic sand is a barrier for migration of heavy metals (Cu, Zn, Cd) from the contaminated layer to the fertile ground.

However, it should be noted that the layer of hydrophobic sand of 1.5 cm in laboratory experiments does not restrict the growth of roots (positive geotropism) and the roots penetrate the through the insulating layer. This fact was noted by the researchers, when growing palm trees with the 20 cm layer of hydrophobic sand in field experiments on regulation of irrigation water consumption [4].

To have a final evaluation of hydrophobic sand based on soot, it is necessary to consider the economic component-cost price, prospects of production and its longevity – the guarantee of retaining hydrophobic properties during a long period of 30 years. The most probable agricultural direction of using hydrophobic sand in Kazakhstan is rice growing in Kyzylorda region. Hydrophobic sand can be used to save of irrigation water for growing rice.

References

[1]. J.E. Fernandez, F. Moreno, J.M. Murillo, M.V. Cuevasa, and F. Kohler, Agricultural Water Management 51 (1) (2001) 29–51. DOI: 10.1016/S0378-3774(01)00118-4.

[2]. B.T. Lesbayev, M. Nazhipkyzy, N.G. Prikhodko, M.G. Solovyova, G.T. Smagulova, G.O. Turesheva, M. Auyelkhankyzy, T.T. Mashan, Z.A. Mansurov, Journal of Materials Science and Chemical Engineering 2 (1) (2014) 63–65. DOI: 10.4236/msce.2014.21011.

[3]. Mohammed A. Salem, Wasef Al-Zayadneh, Helmut Friedel Schulze and A.J. Cheruth, Journal of Food, Agriculture & Environment 11 (2) (2013) 591–595. Online ISSN: 1459-0263.

[4]. K.K. Boguspaev, Sh.E. Arystanov, Sh.Sh. Sadykov, A.T. Ivashchenko, Accumulation of heavy metals in vegetative organs of Amaranthus (A. tricolor, A. paniculatus) in the process of development of plants. Bulletin of KazGU, Biology series, 2 (14) (2001) 53–62.

[5]. K.K. Boguspaev, D.G. Faleev, I.A. Perova, D.A. Erezhepov. The effect of biohumus on absorption of heavy metals (Cd, Zn) by hyperaccumulators (Helianthus annuus) heavy metals. Bulletin of KazNU, Biology series 4 (56) (2012) 300–304.

[6]. Z.I. Zhurbickij. *Teorija i praktika vegetacionnogo metoda* [Theory and practice of the vegetative method], Moscow, Nauka 1968, 263 p. (in Russian).