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## Use of nanostructured materials for the sorption of heavy metals ions

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**Abstract.** Recently, carbon materials containing fullerenes have been used as sorbents. The purpose of the study was to explore and compare the sorption properties with respect to heavy metal ions of fullerene-containing materials. This will allow to obtain in the most effective way the fullerene-containing sorbents for use in processes of cleaning of environmental objects. Several types of sorbents obtained from shungite and graphite were selected for our research. For a month, the soil had been contaminated with the lead and zinc salts in a concentration exceeding the maximum permissible value of 30 times. Sorbents had been then added in a ratio of 1: 5. A week later, the soil extracts were analyzed for salt and pH content. The results indicated that fullerene-containing sorbents bind a significant part of pollutants and reduce the toxicity of the soil. Nevertheless, complete purification from metals was not observed. The obtained results are the basis for the further studying of sorption properties of carbon nanomaterials and are of practical importance in the field of nanotechnology, ecology, ecotoxicology, chemical technology of inorganic substances and others.

### Introduction

Over the last 100 years, the speed of development of technology and industry has increased in several times, which has led to a tremendous growth in the number of enterprises around the world. It is obvious that with increasing volumes of production of all kinds of goods, the technogenic impact that humanity exerts on the environment grows, which leads to a number of environmental changes, some of which have an impact not only on the local level but also in the world.

One of the results of an active industrial impact in a region is the accumulation of heavy metals into the environment, which content exceeds the maximum of permissible level in many times. Most often, this problem is associated with inadequate technologies and methods of cleaning of industrial waste, which, is released into the environment, and mainly into water and soil, and then, as a result brings to the contamination. The regions are mostly exposed to the heavy metal contamination including cities and large industrial areas due to the activity of thermal power stations and road transport. Particularly



damaging effects are caused by ash dumps formed as a result of the operation of the CHP plant, since the ash can be carried by the wind over many kilometers around, having a detrimental effect on water structure, rivers and soil

Heavy metals are one of the most harmful types of pollution and, according to the state standards, they are ranked as second in terms of the degree of danger, staying in one line with pesticides. These include elements such as vanadium, germanium, manganese, fluorine, nickel, zinc, molybdenum, strontium, mercury, lead, etc. – all in all more than 40 elements of periodic table.

At present, the negative impact of heavy metals is not fully taken into account in comparison with radioactive substances. Therefore, in the future they can become more dangerous due to excessive accumulation in the environment and can destabilize the ecosystems of different territories and then the planet itself.

Soil is mainly encountered medium in which heavy metals are absorbed, as well as atmosphere and hydrosphere. It serves as a source of secondary pollution entering from the surface air and water into the ocean. From the soil, heavy metals are assimilated into the plants, then they are found in food and in the light of an increase in the anthropogenic effects on soils, the question of quick and effective methods for cleaning soils from various pollutants is topical and justified. Therefore, great attention is paid to the search for universal means for cleaning soils from polluting substances based on both natural and technogenic origin.

The volume of wastewater formation at enterprises and the number of harmful components contained there define the requirements for clearing methods. These methods should be located in the first place on technological and hardware registration, providing increase of degree of sewage treatment. At the same time, the initial raw materials used in the course of extraction of harmful components should be effective enough, extended and have a low cost. The methods of sewage treatment with natural sorbents find their distribution at the preliminary and final stages of the technological purification chain. They are also used as separate methods.

The purpose of scientific work is research the effectivity in sorption of ions of heavy nonferrous metals from water solutions of the new carbon – mineral sorbents of a natural origin. The final stage of the research is to find the sorbents with the mostly effective sorption properties. They should interact weakly with water molecules and well with organic substances, being relatively large-porous. During the short time being in contact with water, they must have a high sorption capacity, high selectivity and low retention capacity while regeneration. In this case, the cost of regeneration should be low. Sorbents must be strong and not abrade, quickly wetted with water, and they have a certain granulometric composition.

In addition, they must have low catalytic activity with respect to oxidation reactions and condensation. Finally, their production should be low of cost as well as their sorption capacity after regeneration should vary insignificantly and provide a large number of work cycles.

At the moment porous materials with a high specific surface area are used as sorbents for a wide range of substances. Among them the most frequent are carbon materials, sometimes referred to as "active coal", as well as silica gel, alumogel and a number of others. The porosity of carbon materials can be increased by activation, for example by steam treatment, which increases their specific surface area and appropriately increases their sorption capacity. At the same time, there is an upper limit of the specific surface achieved in such activation processes, which creates limitations on the sorption properties of these carbon materials. Recently, carbon materials containing fullerenes-spherical molecules of several dozen carbon atoms have been used as sorbents. Such fullerene-containing carbon materials exhibit increased sorption properties with respect to a number of sorbed substances. At the same time, there are many ways of obtaining fullerene raw materials - by burning graphite, enriching shungite rocks, etc.

Meanwhile, despite the wide interest in fullerenes in various fields, the study of sorption properties with respect to metal ions is carried out a little.

The purpose of the study was to explore and compare the sorption properties with respect to heavy metal ions of fullerene-containing materials. For this purpose, the following tasks were identified:

1) to make the contamination of soil samples with zinc and lead salts of known concentration in the laboratory;

2) to make a comparative analysis of the sorption efficiency of different types of fullerene-containing carbon sorbents.

### Materials and Methods of research

The following types of sorbents were selected for the investigation: initial shungite (Shr) (VKO, Bakyrchik deposit), shungite concentrate after flotation process (SHF), readyshungite sorbent (Shs), fullerene soot (F), birch activated carbon (BAC) and pharmacy activated charbon (AC).

Fullerene soot was formed by burning a graphite rod in a fullerene synthesis reactor operated in the National Nanotechnology Laboratory of an open type.

The concentration of metal ions before and after sorption was determined by electrochemical analysis method on the INESA DDSJ-308a TDS meter, the hydrogen indicator was determined on Mettler Toledo G20, the toxicity of the soil extract before and after sorption measured by the biotesting method.

For the model of pollution, zinc and lead were taken as the most common pollutants. A week later, the soil extracts were analyzed and found out the total dissolved solids and pH level.

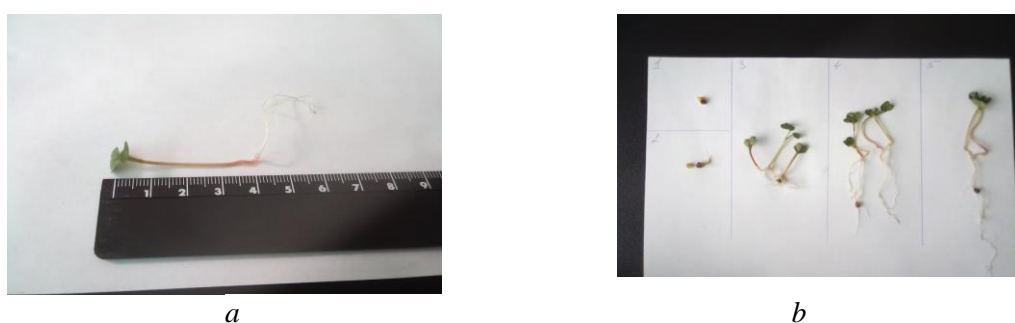
### Results and Discussion

According to the results, the most effective sorbent in an aqueous solution of zinc is AC, then group of materials in series of descending: AC –Shf– BAC – Shs– Full – Shr. The best sorption in solutions containing lead fractions was shown by flotation-concentrated shungite, then others in descending order: Shf-BAC-AC-Full-Shs-Shi. Generally, the concentration of salts was decreased in all solutions. So, the crushed raw shungite proved to be the worst sorbent. Shungite sorbent is lagging behind the indicators due to the smaller surface area as compared with the fleet-concentrated shungite.

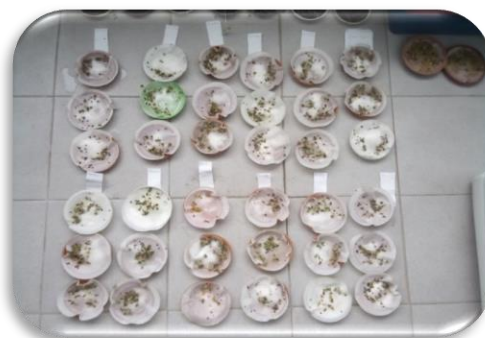
Flotation-concentrated shungite lowered the acidity and removed the color of the extract, which indicates the absorption of organic matter from the soil.

The acidity of soil solutions decreased to the optimum values (pH 6.5-7.5) by all sorbents.

The soil was tested for phytotoxicity. Radish (*Raphanus Sativus*) "18 days" and "ultra-early" was used as an object test to determine the phytotoxicity of the soil. Radish seeds were soaked in soil extracts. Radish was germinated. Repetition of germination was threefold. After the service life soil solutions with sorbents were compared with the reference value (figures 1-5).

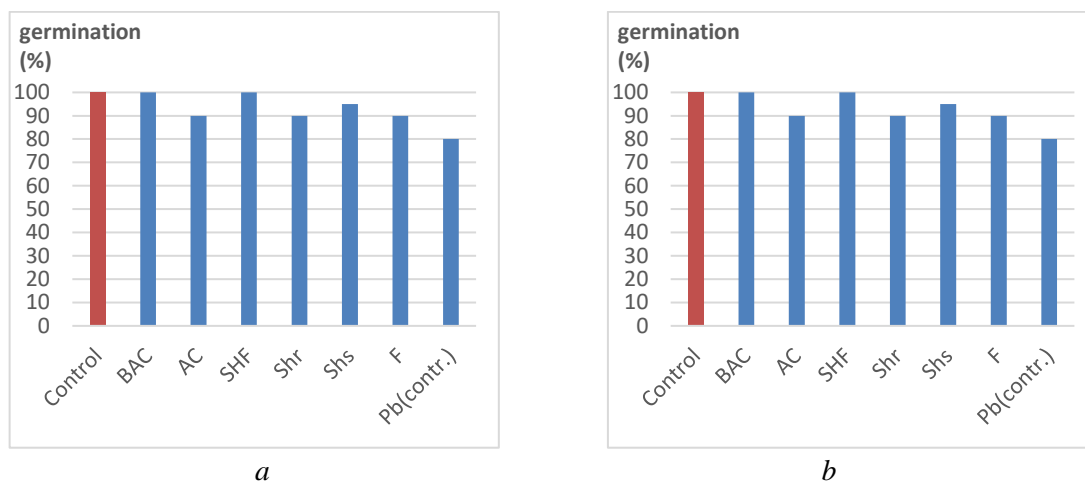


**Figure 1.** Measuring the length of the shoots: (№1 0-0.49 cm, №2 - 0,5-0,9 cm, №3 - 1-4,9 cm, №4 - 5-9cm, №5 - 10-20 cm).



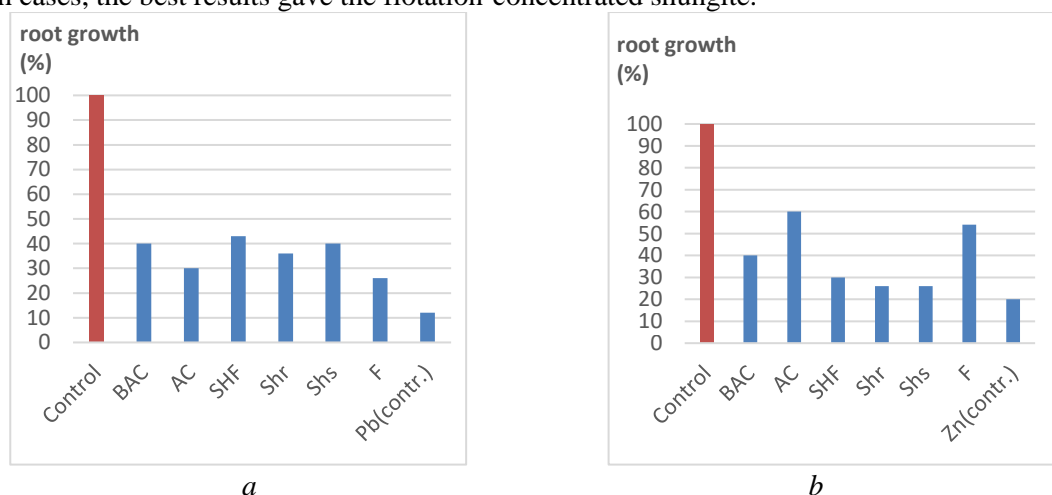
**Figure 2.** Bioindication of soil extracts by *Raphanussativus*.

Proceeding from the diagrams, one can clearly trace the decrease in germination, strength and speed of germination, as well as the effect of the presence of sorbents in contaminated soils on these parameters.



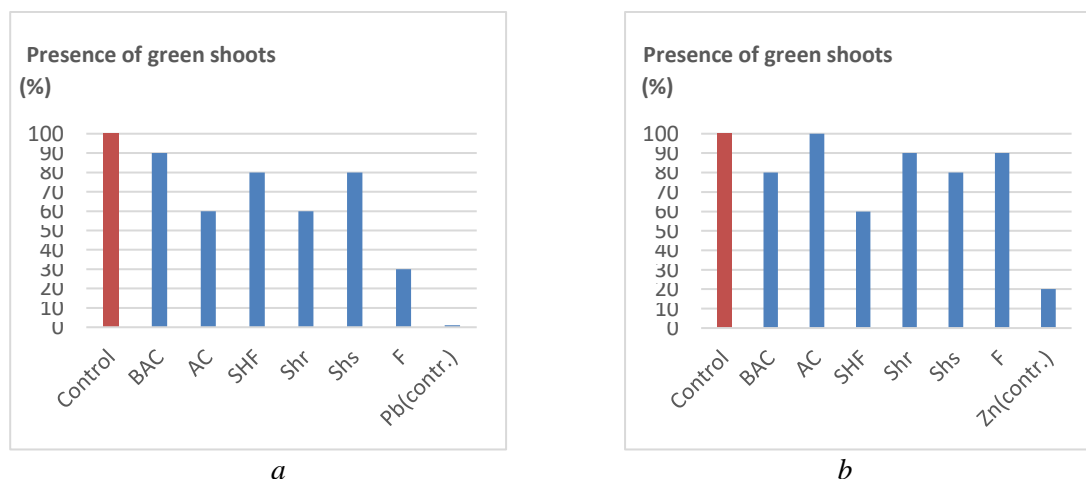
**Figure 3.** General germination of plants in mixed with sorbents of contaminated soils Pb (a) and Zn (b).

On average, compared to control contaminated soil, all samples with sorbents gave inflated indices. In both cases, the best results gave the flotation-concentrated shungite.



**Figure 4.** Correlation of root growth in mixed with sorbents of contaminated soils Pb (a) and Zn (b).

When comparing the length of the roots of contaminated samples with a net control blank value, the best performance there were demonstrated by samples with activated carbon and fullerene soot (in exemplary zinc contamination). In soils contaminated with lead, there is a general decrease in root growth. The best performance was distinguished by shungite floto-concentrated and shungite sorbent.



**Figure 5.** Presence of green shoots grown in mixed with sorbents of contaminated soils with lead (a) and zinc (b).

## Conclusion

Currently, a large number of studies on the methods of obtaining and use of fullerenes are being carried out. The initial raw material for obtaining fullerenes can be both graphites and shungites. There are two opposing opinions about the properties of fullerene materials. The majority of researchers believe and prove by scientific experiments that solutions, insisted on fullerene-containing materials, become not just pure drinking water, but also a molecular-colloidal solution of fullerenes. This water is attributed to a new generation of medical and preventive agents with a multifaceted effect on the body. Other researchers argue that water infused simply with a piece of carbon-containing mineral can be harmful, because it brings to a chemical reaction and has a possibility to form a low-concentration acid solution.

Based on figure 3, it is evident that fullerene-containing sorbents bind a significant part of pollutants and reduce the toxicity of the soil. Nevertheless, despite the presence of nanoparticles, complete purification of soils from metals is not observed and the soil remains toxic to plants.

Among the shungite materials, flotation-concentrated shungite was the most effective cleaning agent in the aggregate of indices. Next comes the shungite sorbent and crushed raw shungite. However, when compared with activated carbons, shungite demonstrates lower efficiency in soil cleaning.

The results of our studies showed that aqueous solutions with fullerenes obtained by infusion of water do not have highly effective cleaning properties.

Most likely, it is necessary to change the procedure for using fullerene-containing materials in sorption processes. Perhaps one can get positive results when passing water or soil extracts contaminated with heavy metals through a fullerene sorbent under dynamic conditions. To do this, the contaminated working solution passes through a sorption column filled with fullerene-containing materials. However, this method is no longer suitable for cleaning soil samples.

In the future, it is necessary to determine the content of metals in the soil and in plants entirely to obtain a complete overview. It is also necessary to investigate the cleaning rate of each sorbent containing fullerenes for the development of further recommendations.

## References

- [1] Hirsch A 2005 *Fullerenes: Chemistry and Reactions* (Weinheim: WILEY-VCH) p 423

- [2] Mosin O, Ignatov I 2013 Composition and structural properties of the natural fullerene-bearing shungite mineral *Biotekhnospera* ISSN: 2073-4824
- [3] Piotrovsky L B, Kiselev O I 2004 Fullerenes and viruses *Fullerenes, nanotubes, and carbon nanostructures* vol 12 pp 397–403
- [4] Wharton T 2001 New non-ionic, highly water-soluble derivatives of C60 designed for biological compatibility *Tetrahedron Lett.* vol 42 pp 5159–5162
- [5] Khamitova K K, Ismailov D V, Sultangazina M N, Kanat R 2018 Sorption Extraction of Heavy Metal Ions from Industrial Sewage Key Engineering Materials vol 769 pp 187–192.
- [6] Khamitova K K, Kerimbekov D S, Ismailov D V, Gabdullin M T, Schur D V 2018 Analysis of the toxic effects of fullerene soot on radish seedlings *Modern problems of condensed matter physics* pp 159-163