Evaluation of the biochar effect on co-contaminated soils by the fitotesting method

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Abstract. In the conditions of the adjacent location of agricultural land with industrial land, there is a continuous soil contamination of the territories adjacent to the emission sources. There is a threat of hazardous ecotoxicants migration, including heavy metals and benzo[a]pyrene, one of the main persistent compound, the marker of soil PAHs pollution, along trophic chains, which can be dangerous for a public health. In this study, the technology of biochar manufacturing from sunflower husks tested for improving the territories adjacent to technogenic emissions sources of heavy metals and PAHs. Using scanning electron microscopy showed that the resulting sorbent has a high specific surface area. With the help of phyto-testing, the optimal dose of the sorbent introduction into the combined contaminated soil was determined in the level of the 1% and 2%. The use of a sorbent in an amount of 1% significantly increased the root length of the test culture by 3.5 times as compared to the variant without adding the sorbent. The biochar applying into the contaminated soil contributed to an increase in the length of the barley root that confirms the effectively of the developed sorbent remediation of the co-contaminated soils.

1 Introduction

As a result of technogenesis the persistent toxicants concentrates in the environment. Chemical pollution is second the most important reason for the soil cover degradation [1]. Every year, once fertile soils are removed from the category of agricultural land, being unsuitable for the production of high-quality and safe products. Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) are one of the most common chemical pollutants upcoming into the environment under the technogenic contamination and accumulated in the increasing content year by year.

There are a number of large industrial enterprises in the Rostov Region. Monitoring studies showed that the soils of the Novocherkasskaya Power Station, one of the largest power producing enterprises all over the Russia, are contaminated with the Cu content in soils reached 200 mg kg\(^{-1}\), and benzo[a]pyrene reaches 400 μg kg\(^{-1}\) [14, 15], in the soils of the former storage of liquid industrial effluents 500 mg kg\(^{-1}\) Cu, benzo[a]pyrene - more than 500 μg kg\(^{-1}\) [16, 17]. At the same time, the agricultural production produced in the region.

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The above-mentioned contamination conditions can contribute to a decrease in the quality and productivity of agricultural crops, and this problem requires the development of methods and systems for remediation of contaminated soils. Thus, the study of the biochar using effectiveness on the co-contaminated soils is of particular relevance.

To prevent the above-mentioned problem, many researchers [2-4] are developing methods for contaminated soils remediation. Sorption bioremediation is one of the most widespread systems for removing the ecotoxicants from soil. The background of this method is based on the sorbent applying into the chemically contaminated soils for the HM and PAHs immobilization by chemisorption and adsorption on the sorbent surface [5-7]. In addition to the sorbate properties itself, the important factors affecting the sorption potential of the sorbent include the physical characteristics of the specific surface area and porosity. The use of mineral sorbents is advisable in areas close to the field of raw chemicals extraction, while the use of such sorbents in remote areas prone to chemical pollution will require additional costs for the ameliorant transportation. The use of a carbon sorbent activated carbon is widespread [8]. Some researchers have shown the effectiveness of using biochars – the products of various plant materials pyrolysis produced from food industry waste, for example: biochar from banana peel [9], coffee residue [10], nutshell [11] or apricot kernels [12] can be used as sorbents for HM and PAHs remediation on contaminated soils. The economic efficiency of chemically contaminated soils remediation with biochar is higher than activated carbon [13]. In addition, the use of carbon sorbents is available in developing agricultural production areas with a great potential for utilization of agricultural by-products.

2 Methods

2.1 The biochar properties

In this work, the raw material using for obtaining the biochar was sunflower husk, since in the Rostov Region there are large-tonnage reserves of sunflower processing waste. Experimental biochar samples were obtained as a result of thermal decomposition of sunflower husks in a steel reactor by varying the temperature from 250°C up to 750°C with a heating rate of 30°C/min and a biomass holding time of 30 minutes. The porosity of biochar was measured on a volumetric analyzer "ASAP 2020" Micromeritics by the method of low-temperature nitrogen adsorption [18]. The calculation of the specific surface area and porosity parameters was carried out by the BET method for N\textsubscript{2} in the range of equilibrium values P/P\textsubscript{0}=0.05–0.97 [19]. The determination of the micro-, meso- and macropores volumes of sorbents was carried out using the comparative t-method using the Hurkins-Jura equation to calculate the thickness of the adsorbate statistical layer. The pore size distribution was calculated using the density functional theory (NLDFT) method [20]. The surface area of the biochar, in addition to low-temperature nitrogen adsorption – desorption methods, was studied using laser scanning confocal microscopy (Keyence VK-9700 microscope) [21].

2.2 Fitotesting of the biochar produced

To select the doses of sorbent introduction into the combinedly contaminated soil, phytotesting was carried out on soil samples containing different amounts of biochar. The phytotest scheme included: control (without adding pollutants), control + different doses of biochar (0.5%, 1%, 1.5%, 2%, 2.5%), also variants of the experiment with the various doses of the sorbent application into the soil containing 550 mg kg Cu\textsuperscript{-1} in the form of an acetate acid salt of the metal and 400 ng g\textsuperscript{-1} benzo[a]pyrene, which corresponds to exceeding the maximum permissible concentration of Cu and benzo[a]pyrene by 20 times by 10 times [22].
Benzo[a]pyrene was selected as the most persistent PAHs compound characterizing the whole PAHs class, because only benzo[a]pyrene content in soil is officially regulated in Russian Federation form all of the PAHs. These concentrations of pollutants correspond to their content in the soils of impact zones in the Rostov Region. The original uncontaminated soil used for setting up the experiment was sampled from the specially protected natural area of the Persianovskaya reserved steppe [23] and represents Haplic Chernozem with the following properties: physical clay content - 52%, silt - 30%, humus - 4.2%, pH of water extract - 7.5, CaCO₃ content - 0.4%, cation exchange capacity - 33 cmol(+)kg. The soil selected for the experiment was cleaned of plant residues and other inclusions, grounded in a porcelain mortar and passed through a sieve with a hole diameter of 1 mm. Weighed portions of soil (50 g) were transferred into Petri dishes and pollutants were added according to the experimental scheme. After the applying of the chemical contaminants, the soil was incubated for a week. Then biochar was added for the 1 week incubation period in the contaminated soil. Sowing of plants was carried out with tweezers in each cup of 15 previously germinated seeds of spring barley varieties "Ratnik" The seeds were germinated in crystallizers between two layers of moistened filter paper in a thermostat at a temperature of 250°C [23]. The moisture content in the studied soil samples was maintained at a level of 60% of the total field moisture capacity during the entire time of the experiment [24]. Sampling of plants was carried out after 7 days from the moment of sowing. The plants were carefully removed from the Petri dishes and the root part was cleared of soil. The length of the roots was measured, since this parameter is most sensitive to stress caused by soil pollution [25]. The experiment was repeated four times.

2.3 Statistical processing of the obtained results

Statistical processing of the results obtained, as well as presentation of graphic material was performed using the SigmaPlot 12.5 program. The significance of differences in the length of barley roots in different variants of the experiment was calculated using the Student's test at P-level <0.5.

3 Results and Discussion

The biochar sample is a coarse, highly porous material with a large surface area. The particle size and structure was determined by the characteristics of the feedstock. Biochar particles have an anisotropic structure of pores, which are long cylindrical cavities located along the longitudinal axis of sunflower husk particles. On the sagittal perspective (Fig. 1A), a developed surface with many cracks and slit-like invaginations 1-2 μm wide is visible. Segmental cleavage (Fig. 1B) contains many rounded pores with a size of 10-30 μm, as well as pores with a size of 0.5-1 μm (Fig. 1B).
The physical characteristics of the specific surface area and porosity of the obtained sorbent (Table 1) from sunflower husk correspond to biochar made from other materials [26, 27]. This material has a high specific surface area, which is important for its use as a remediation agent for chemically contaminated soils.

Table 1 - Characteristics of the specific surface area and porosity of biochar

| Granule/particle size (mm) | Specific surface area (m²/g) | Pore volume (cm³/g) |
|---------------------------|-----------------------------|---------------------|
|                           |                             | total        | macro >500nm | meso 2-500nm | micro >2nm |
| 1-5                       | 440                         | 0.81         | 0.14         | 0.04        | 0.63       |

Phytotesting showed that biochar does not have a toxic effect on the root part of spring barley at application rates from 0.5% to 2%. However, with the presence of 2.5% sorbent in the soil, there is a tendency for a slight decrease in the length of plant roots (Fig. 2).
Soil contamination with 10 MPC CuO and 20 MPC benzo[a]pyrene showed a 7.8-fold decrease in the length of the barley root (Fig. 3).

The applying of biochar into the contaminated soil contributed to an increase in the length of the barley root. At the same time, the most effective doses of the sorbent were 1% and 2%. The use of a sorbent in an amount of 1% significantly increases the root length of the test culture by 3.5 times as compared to the plant of the experiment variant without adding the sorbent to the contaminated soil. No statistically significant differences in the length of the barley roots of the experimental variants with the applying of 1% and 1.5% biochar into the contaminated soil were revealed. The next significant increase in the length of plant roots was observed with the applying of 2% sorbent, where this indicator is 7.3 times higher than in the variant experience without biochar. A further increase (up to 2.5%) of the sorbent content in the contaminated soil detected as ineffective, and the root length of the test culture is slightly reducing.

4 Conclusions

The obtained sorbent based on sunflower husk has a large specific surface, which allows it to be used on soils exposed to chemical pollution. Contamination of ordinary chernozem with copper acetate (10 MPC) and benzo[a]pyrene (20 MPC), led to the suppression of seedlings of spring barley. The presence of the sorbent in the studied doses in uncontaminated soils does not have a toxic effect on the growth of barley seedlings. The optimal dose of sorbent introduction into combined contaminated soils was 1% and 2% of biochar application.

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