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Ecosorbent Based On Modified Biochar from Rice Husk for Strong Binding Of Heavy Metals in Soil

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Abstract
The peculiarities of obtaining carbon ecosorbent from rice husk for strong binding of heavy metals (Cd (II), Cu (II) ions) and their detoxification in soils have been studied. It is established that the modification of biocarbon can significantly improve the structural-porous and ion-exchange properties of the material, which increases its sorption capacity. The obtained results show that the modified ecosorbents from rice husk have a fairly high exchange capacity for Cu (II) and Cd (II) ions. Sorption binding of ecosorbents reaches values of 80-90%. The introduction of such an ecosorbent into the soil leads to a strong binding of toxic heavy metals in stationary sulfide forms, prevents migration, which prevents their accumulation in plants. Sulfur-containing ecosorbents from pyrolyzed plant raw materials are environmentally friendly and have the potential for detoxification of heavy metals in the root zone of the soil.

Key words: *carbon ecosorbent, pyrolyzate, sorption, metals, plants, soil, bioaccumulation.*

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I. Introduction

Currently, the main and dangerous pollutants are heavy metals. This is due to their high toxicity to living organisms in relatively low concentrations, as well as the ability to bioaccumulate [1-3]. Heavy metals, in contrast to organic pollutants, are not destroyed, but only pass from one form of existence to another, in particular, are part of salts, oxides, organometallic compounds. Increasing their concentration in the soil leads to a violation of agrocenoses. The ability of plants to accumulate heavy metals limits the use of contaminated areas for growing crops [4]. Depending on the sources of pollution (natural or man-made) there are noticeable differences in the profile distribution of heavy metals in the soil. At a natural high level of these elements there is an increase in the metal content in depth along the soil profile. In man-made pollution, heavy metals, on the contrary, are concentrated closer to the surfaces. Various methods, including sorption, are used to clean ecosystems from heavy metals. If you are considering ways to clean contaminated soil, it is advisable to use the most environmentally friendly and safe methods. You can precipitate heavy metals in the form of sparingly soluble deposits. use their leaching from the soil profile, use the extraction of metals from soils by plants and microorganisms and sorption by minerals with high cation exchange capacity and sorbent composites.

Physical soil removal is the oldest method of reclamation of contaminated soil. The method involves complete removal of contaminants and relatively rapid cleaning of the infected area of soil [5.6]. Disadvantages include the fact that contaminants simply move to another location where they need to be controlled. There may be a risk of spreading contaminated soils and dust particles when removing and transporting contaminated soil.

Heavy metal removal methods, including chemical precipitation, oxidation or reduction, filtration, ion exchange, reverse osmosis, membrane technology, evaporation, and electrochemical treatment, become ineffective when heavy metal concentrations are less than 100 mg / L. Most salts of heavy metals are soluble in water and wastewater, where they cannot be separated by physical methods. In addition, physicochemical methods are inefficient or expensive when the concentration of heavy metals is very low. Biological methods, such as biosorption or bioaccumulation to remove heavy metals, may be an attractive alternative to physicochemical methods. One of the possible methods is electromelioration [7]. Leaching of heavy metals [8] outside the soil profile with water is inefficient due to their low solubility and significant strength of their bond in the soil absorption complex. It is possible to clean by washing the soil with solutions of surfactants or solutions containing strong oxidants. When leaching, the content of heavy metals (Zn, Pb, Cd, Ni, Cu, As) is reduced by 85 - 95%.

Some plant species can take heavy metals and concentrate them in their biomass. Phytoextraction shows good results in cleaning the soil of heavy metals. Indian mustard, alfalfa, cabbage, tall fescue, juniper can be used for this purpose. Reclamation of soils or their purification from contamination by plants is an ecological and progressive method [9, 10]. Purification of soils from heavy metals by growing plants - phytomellants on contaminated soils requires their complete removal from the soil before the end of flowering and the beginning of death of the lower leaves with subsequent disposal. For effective removal of heavy metals from the soil, it is necessary to provide several cycles of growing crops. Ash obtained after incineration is considered hazardous waste and must be disposed of. It is shown that when grown on contaminated soils, even hyperaccumulants, the content of metals such as lead, cadmium and copper in plant samples on the aboveground part does not exceed 1.2; 0.5-1 and 10-12 mg / g dry weight, respectively [11].

Sorption methods of soil cleaning occupy an important place in a set of measures aimed at eliminating man-made pollution. Sorbents based on activated carbon, zeolites, natural materials and minerals with a high cation exchange capacity, etc. are used to clean ecosystems from heavy metals. Reducing the toxicity of heavy metals in soils is possible by binding their mobile forms of sparingly soluble compounds (sulfides, carbonates, phosphates, hydroxides, etc.) on the surface of sorbents when introduced into the soil. Depending on the level of pollution and the purpose of the soil, there are different ways to implement sorption treatment. For example, in the case of minor contamination of agricultural soils, sorbents are applied to the depth of the fertile layer and are not subject, as a rule, to be removed from the treated soil [12].

The use of secondary plant raw materials is a promising direction for obtaining on its basis ecosorbents with specified properties. Conversion of plant residues into biochar by pyrolysis is beneficial for the environment compared to their direct combustion. Biochar is a stable, carbon-rich product that is synthesized as a result of pyrolysis (carbonization) of plant biomass. Potential uses of biochar include improving soil fertility, restoring contaminated soils, and processing by-products such as agricultural waste. The main parameters that control its properties include pyrolysis temperature, time, heat transfer rate and type of raw material. The efficiency of biochar in the disposal of contaminants depends on its surface area, pore size distribution and ion exchange capacity. Relatively high pyrolysis temperatures usually lead to the formation of biochar, which is effective in the sorption of organic pollutants by increasing the surface area, microporosity and hydrophobicity. Biochar obtained at low temperatures are more suitable for removing inorganic contaminants. However, due to the complexity of the soil-water system in nature, the effectiveness of biochar in the recovery of various pollutants still remains uncertain [13,14].

The high adsorption capacity of biochar is due to high aromaticity and low polarity. Pyrolysis temperature affects the properties of biochar and is a critical factor for assessing the effectiveness of removal of toxicants from the environment. So in the pyrolysis of pine needles was obtained biochar at different pyrolysis temperatures of 300, 500 ° C. The pyrolysis temperature showed a pronounced effect on the properties of biochar. Biochar obtained at a higher temperature has a higher efficiency of removal of toxicants from water due to its high surface area, microporosity and the degree of carbonization. Biochar can be used to remove pollutants in the environment, as a fertilizer for the soil, providing long-term sorption [15].

In the study of structural-porous, sorption and ion-exchange properties of the original and modified lignocellulosic biomass, both conventional and special methods were used. Sorption experiments were performed under static conditions on aqueous extracts of soils contaminated with heavy metal ions. The concentration of heavy metal ions was determined on an atomic adsorption spectrometer after atomization of the sample in an air-acetylene flame.

II. Experimental

Carbon sorbents obtained by pyrolysis of cellulose-containing raw materials (rice husks) in a strictly functional mode were selected as objects of study. Rice husk contains: lignin - 0.5%; cellulose -48.2%; hemicellulose - 35.1%; substances insoluble in water -2.6%. Pyrolysis was carried out in a stain less steel reactor with an inner diameter of 60 mm and a height of 50 mm with a lid. He was placed in a muffle furnace, the power of which was automatically adjusted to maintain a given temperature in the reactor. Research results show that heat treatment of rice husks is accompanied by the destruction of cellulose and lignin, leading to weight loss (up to 70%). For the rapid course of the pyrolysis process, the source material must be ground into fractions not exceeding 3 mm. Under different conditions of pyrolysis may change the composition of the pyrolyzate (table 1).objects of study were selected carbon sorbents obtained by pyrolysis of cellulosic materials (wood, corn cobs) in a strictly functional mode. Pyrolysis was carried out in a reactor made of stainless steel with an internal diameter of 60 mm and a height of 50 mm with a lid. It was placed in a muffle furnace, which capacity is automatically regulated to maintain the desired temperature in the reactor.

The properties of carbon material surface were evaluated according to the determinants under the standard methods of indicators: specific surface; content of acid and carbonyl groups and regeneration capability. The concentration of absorbed substance was determined by the weight method and according to calibration schedule by photometry and UV-spectrometry method.

Based upon the results obtained the physic-chemical parameters of the pyrolysis process of initially raw materials were calculated and optimal conditions of carbon material obtainment were determined.

The sorption properties of sorbents were evaluated according to such criteria as floatability, hydrophoby, oil-receptivity and range of working temperatures.

For the bio-activation of the sorbent used complex microorganisms-destructors of oil of natural origin. Table 1 shows the number of oil-oxidizing microorganisms in samples of samples taken from different objects, where oil pollution is constantly present. Studies have shown that the largest number of OOM up to 38 × 105 cl / g (cells per gram) is found in soils with aging oil pollution.

To select strains of microorganisms-destructors of oil samples have been selected from the contaminated areas and were obtained pure cultures of microorganisms-destructors which then has been grown on dense nutrient medium.

Table 1.
The composition of pyrolysis products of rice husk
(biochar - C, silicon dioxide - SiO2).

Pyrolysis temperature, ° C	Process duration, min	Content of pyrolysis products, %	
		C	SiO_2
250	10 40 60	20 25 37	30 35 27
300	10 40 60	60 65 72	40 35 28
400	10 40 60	78 89 87	22 11 13
450	10 40 60	82 79 77	18 21 23
500	40 60	55 57	45 43

The purpose of heat treatment in an oxygen-free atmosphere is to obtain amorphized biochar from rice husk. At average pyrolysis temperatures in the range of 300-450oC, the biomass of plant raw materials passes through exothermic processes and releases the maximum amount of carbon material. Pyrolysis at high temperatures (usually above 700oC) is not suitable for obtaining biochar because a small amount of biochar is obtained. The process of biochar formation ends at the end of the release of gaseous decomposition products. By its structure, biochar belongs to the class of carbonized substances with a characteristic structure [16]. Elements H, O, N, P and S are included in the structure as heteroatoms, which explains the reactivity of biochar.

Our proposed method of obtaining sulfur-containing biocarbon ecosorbent from rice husk is a one-stage pyrolysis of raw materials together with sulfur-containing reagents at a temperature of 350-400 ° C. The result is sulfur-modified biochar. Sodium thiosulfate Na2S2O3 was used as a modifier. The obtained ecosorbent has heat resistance and mechanical strength. Ecosorbent does not contain components that can pass into water during use.

III. Results and Discussion

The temperature regime of processing and the composition of the mixture of starting materials (rice husk and sodium thiosulfate) were substantiated experimentally after determining the optimal sorption capacity of the obtained ecosorbents relative to Cd (II), Cu (II) ions. X-ray phase analysis of the obtained samples of the sorbent showed the presence on its surface of 23-35% bound sulfur. The sulfur-containing biocarbon sorbent (biochar) has the ability to strongly bind Cd (II) and Cu (II) ions to the surface of the sorbent in insoluble sulfide form, which neutralizes them in aqueous and soil media.

Fractographic studies were performed to determine the effectiveness of the obtained ecosorbents against heavy metals. In Fig.1, table.2. the quantitative elemental composition of ecosorbent particles obtained by scanning electron microscopy and micro-X-ray spectral analysis based on an analytical complex consisting of a scanning electron microscope and a spectrometer is shown. The spectra of the sorbent particles indicate the binding of Cd (II) ions to the surface of the particles.

Studies of the efficiency of the obtained ecosorbents in soils were performed in special vegetation containers on model soil systems. In the course of experimental research, medium loamy and chernozem soils were selected as objects. After removing foreign inclusions (plant residues, large mineral inclusions, etc.), the soil was ground to a fraction of less than 1.0 mm. Solutions of CuSO4 x 5 H2O and Cd (NO3) 2 x 4H2O salts were used for soil contamination. The solution was mixed with the soil to achieve a given concentration of heavy metals (Cd (II) from 2 to 6 mg / kg of soil, Cu (II) from 132 to 396 mg / kg of soil).

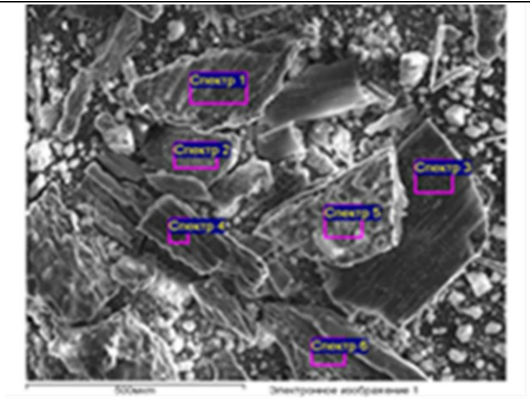

Fig.1. Electronic image of sulfur-containing ecosorbent particles after sorption of Cd (II) ions from aqueous solutions.

The contaminated soil mixture was mixed, sealed and maintained at constant humidity. Sulfur-containing ecosorbent was then added to the contaminated soil in an amount in accordance with the sorption capacity of the ecosorbent relative to the studied ions on model aqueous media. Ecosorbents were added to contaminated soil at the rate of 150 gr. sorbent per 1.5 kg. soil. The samples were kept under static conditions at a temperature of 20 ± 5 ° C for 60 days. The moisture content in the soil-ecosorbent mixture during the experiment was maintained at 40%.

Table 2.
Elemental composition of sulfur-containing ecosorbent particles (%)
after sorption of Cd (II) ions from aqueous solutions.

Specter	C	O	Si	S	P	Ca	Cd
Specter 1	57.15	30.16	5.53	0.98	0	2.32	1.99
Specter 2	66.20	24.31	2.70	1.50	0	1.80	2,39
Specter 3	81.58	11.94	0.96	1.38	0	2.15	1.30
Specter 4	70.04	21.06	2.75	2,1	0	0.15	2,65
Specter 5	10.22	41.94	11.32	10.84	0	14.62	7.66
Specter 6	32.00	39.55	21.93	1.42	0	1.72	2.00

Table 3. presents the results of the detoxification effect of the ecosorbent on the content of Cd (II) and Cu (II) ions in the aqueous soil extract. A significant decrease in the concentration of ions during tillage with sulfur-containing ecosorbent has been established.

Table 3.
The content of Cd (II) and Cu (II) ions in the aqueous soil extract

Sample	Cd (II), mg / kgгрунта	Decreased concentration Cd(II), %	Cu(II), mg / kg гоунта	Decreased concentration Cu(II) , %
Control. Soil	----	----	----	----
Soil + Cd (II)	6.2	----	----	----
Soil + Cd (II) + pyrolyzate	0.9	85	----	----
Soil + Cd (II) pyrolyzate $Na_2S_2O_3$ 10%	0.14	98	----	----
Soil + Cd (II) + pyrolyzate + $Na_2S_2O_3$ 20%	0.21	97	----	----
Soil + Cu (II)	----	----	397	----

Soil + Cu (II) + pyrolyzate	----	----	100	74
Soil + Cu (II) + pyrolyzate + $Na_2S_2O_3$ 10%	-----	----	54	86
Soil + Cu (II) + pyrolyzate + $Na_2S_2O_3$ 20%	----	----	26	93

When assessing the ecotoxicological parameters of soils on mobile forms of heavy metals, it is not enough to check only the aqueous soil extract.

Metals in different forms in the soil have different mobility, migration ability and accessibility for plants. Therefore, in researches of efficiency of ecosorbents plant phytotesters are used. The advantage of these metal testers is the reaction rate in research. In indicator plants, the metal content in the cells correlates with the content in the soil. Oats (Avena sativa L.) and watercress (Lepidium sativum) were used as phytoindicators of metals.

Toxicological indicators during the vegetation experiment prove that the introduction of ecosorbents based on rice husk in soil contaminated with cadmium and copper ions prevents the transition of these metals into plants in terrestrial plant biomass and phytotester root biomass when treating contaminated soil with ecosorbent in the separate presence of heavy metals and in their joint presence.

Table 4
The content of Cd (II) and Cu (II) ions in the green biomass of phytotester (oats).

Sample	Cd(II) , mg / kg of biomass	Decrease Cd(II) , %	Cu(II), mg / kg of biomass	Decrease Cu(II), %
Control, The soil is uncontaminated	----	----	----	----
Soil + Cd(II)	0,193	----	----	----
Soil + Cd(II) + pyrolyzate	0,173	10	----	----
Soil + Cd(II) + pyrolyzate + $Na_2S_2O_3$ 10%	0,094	51	----	----
Soil + Cd(II) + pyrolyzate + $Na_2S_2O_3$ 20%	0,027	78	----	----
Soil + + Cu(II)	----	----	1,870	----
Soil + + Cu(II) + pyrolyzate	----	----	1,010	14
Soil + + Cu(II) + pyrolyzate + $Na_2S_2O_3$ 10%	----	----	0,750	36
Soil + + Cu(II) + pyrolyzate + $Na_2S_2O_3$ 20%	----	----	0,050	86

The results of tests of ecosorbents based on rice husk pyrolyzate for detoxification of soils contaminated with cadmium and copper ions using oat phytotester and watercress convincingly prove the high efficiency of the obtained ecosorbents for detoxification of heavy metals in the root layer of the soil.

IV. Conclusions

The possibility of obtaining an ecosorbent based on biochar from rice husking, modified with cottage cheese for strong bonding of important metals (Cd (II) and Cu (II) ions and their detoxification in soils, has been studied. Due to the connection, the movement of ions of important metals in the group decreases and, as a result, reduces their accumulation in terrestrial plant biomass. The advantage of sulfur-containing biocarbon ecosorbent is its environmental friendliness, because it uses lignin-cellulose-containing raw materials - plant waste and harmless sulfur-containing components in small quantities.

Studies show that ecosorbents based on sulfur-modified rice husk biochar can be used as an effective, affordable, environmentally friendly and inexpensive sorption material for detoxifying copper and cadmium ions in soils, restoring and improving soil agrochemicals.

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