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USE OF MODIFIED BIOCHARB FROM BAGASSA TO REMOVE HEAVY METALS

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Abstract

Today, the development of environmentally friendly technologies for the detoxification of heavy metals in environmental objects is relevant. One of the promising areas is the production of carbon sorption materials (biochar) from lignocellulosic waste. Plant waste is a promising natural renewable material for ecosorbents. Biochar is a stable carbon-containing product that is synthesized as a result of pyrolysis (carbonization) of plant biomass. In this study, the possibility of obtaining an ecosorbent from bagasse (vegetable waste from sugarcane production) was studied. When obtaining ecosorbents for the absorption of complex compounds of heavy metal ions, chemical and biological modification of biochar was used. Sulfur-containing biochar was obtained by chemical modification by one-stage pyrolysis of raw materials together with sulfur-containing reagents. Sulfur-containing biochar has a high absorption capacity compared to the original biochar. Its specificity is due to the formation of insoluble heavy metal sulfides on the surface and in the pores of the sorbent. Microbiological modification leads to the creation of a biosorption material for the strong binding of heavy metal ions. Sulfate-reducing bacteria immobilized on the surface of biochar are able to convert sorbed heavy metals into insoluble sulfide forms. A comprehensive study of the structural-porous and sorption properties of the original and modified bagasse biochar has been carried out. Comparative analysis of the adsorption capacity of the original bagasse, biochar from bagasse, biochar modified with sulfur, and biochar with sulfate-reducing bacteria immobilized on its surface showed that chemically and biologically modified biochar from sugar cane bagasse can strongly bind heavy metal ions. It was noted that sulfur-containing biochar and biochar with immobilized sulfate-reducing bacteria have a high absorption capacity (more than 90 %) with respect to Cd(II), Cu(II), Pb(II) and Zn(II) ions at an initial concentration of 2 to 5 MPC. The studies show that chemically and biologically modified sugarcane bagasse biochar can be used as effective ecosorbents for heavy metal detoxification in water and soil environments. Their main property is the ability to form insoluble sulfide forms of metals on the surface and in the pores of the ecosorbent.

Keywords: adsorption; metals; bagasse; pyrolysis; biochar; sulfides; sulfate-reducing bacteria.

ВИКОРИСТАННЯ МОДИФІКОВАНОГО БІОВУГІЛЛЯ З БАГАСИ ДЛЯ ВИДАЛЕННЯ ВАЖКИХ МЕТАЛІВ

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Анотація

Рослинні відходи – перспективний відновлюваний природний матеріал для екосорбентів. Біовугілля – стабільний вуглецевмісний продукт, який синтезується в результаті піролізу (карбонізації) рослинної біомаси. Вивчена можливість отримання екосорбенту з багаси (рослинних відходів виробництва цукрової тростини). У процесі отримання екосорбентів для поглинання комплексних сполук іонів важких металів використовували хіміко-біологічну модифікацію біовугілля. Сірковмісний біовугілля отримували хімічною модифікацією шляхом одностадійного піролізу сировини спільно з сірковмісними реагентами. Його специфічність зумовлена утворенням нерозчинних сульфідів важких металів на поверхні та в порах сорбенту. Мікробіологічна модифікація призводить до створення біосорбційного матеріалу для міцного зв'язування іонів важких металів. Імобілізовані на поверхні біовугілля сульфатредукуючі бактерії здатні переводити сорбовані важкі метали в нерозчинні сульфідні форми. Проведено комплексне дослідження структурно-пористих та сорбційних властивостей вихідного та модифікованого біовугілля. Порівняльний аналіз адсорбційної здатності вихідного багаси, біовугілля з багаси, біовугілля, модифікованого сіркою, та біовугілля з іммобілізованими на його поверхні сульфатредукуючими бактеріями показав, що хімічно та біологічно модифіковане біовугілля з багаси цукрової тростини здатне міцно зв'язувати іони важких металів. Хімічно і біологічно модифіковане біовугілля з багаси цукрової тростини може використовуватися як ефективні екосорбенти для детоксикації важких металів у водних та ґрунтових середовищах.

Ключові слова: адсорбція; метали; багаса; піроліз; біовугілля; сульфіді; сульфатредукуючі бактерії.

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Introduction

As a result of human anthropogenic activity, an excess amount of toxic metal ions is released into the environment, namely into water, air and soil. Heavy metals such as Cd, Cu, Hg, Ni, Pb and Zn are toxic, not biodegradable, and accumulate in the environment [1–3]. Wastewater is the largest source of pollution. Methods for the removal of heavy metals, including chemical precipitation, oxidation or reduction, filtration, ion exchange, reverse osmosis, membrane technology, evaporation, and electrochemical purification, become ineffective when the concentration of heavy metals is less than 100 mg/l [4; 5]. One of the possible methods is electroremediation [6]. During leaching, the content of heavy metals (Zn, Pb, Cd, Ni, Cu, As) decreases by 85–95 % [7].

Cleaning is possible by washing the soil with solutions of surfactants or solutions containing strong oxidizing agents [8; 9].

Some plant species can absorb heavy metals and concentrate in their biomass. Phytoextraction shows good results in cleaning the soil from heavy metals [10]. Reclamation of soils or their purification from pollution by plants is an ecological and progressive method [11; 12]. Cleaning the soil from heavy metals by growing plants – phytomeliorants on contaminated soils requires their complete removal from the soil before the end of flowering and lower leaves beginning to die off, followed by disposal. To effectively remove heavy metals from the soil, it is necessary to provide for several cycles of growing crops. Ash from incineration is considered hazardous waste and must be disposed of. It has been shown that when grown on contaminated soils, even hyperaccumulants, the content of such metals as lead, cadmium and copper in plant samples of the aerial part does not exceed 1.2; 0.5–1 and 10–12 mg/g dry weight, respectively [13; 14].

Sorption methods occupy an important place in the set of measures aimed at eliminating technogenic pollution of the environment. To clean ecosystems from heavy metals, sorbents based on natural materials and minerals with high cation exchange capacity are used [15; 16].

A promising direction is the creation of technologies for the production and use of ecosorbents from plant waste. The conversion of plant residues into biochar by pyrolysis has opened up new possibilities for wastewater and soil treatment. Carbon materials are used as adsorbents for water purification, since they have

a porous structure and a large surface [17]. The advantages of using plant waste as a raw material are low cost, infinitely renewable secondary raw materials, availability, and environmental friendliness. The main parameters that determine the properties of biochar include the temperature and time of pyrolysis, preparation methods and the type of raw material. The efficiency of biochar in neutralizing pollutants depends on its surface area, pore size distribution, and ion exchange capacity [18]. In the formation of carbon material during the pyrolysis of cellulose-containing material, reactive groups are created on the coal surface, which determine the possibility of chemical and biological modification of the biochar surface to improve its sorption and detoxifying properties [19].

Materials and Methods

The objects of the study were: cake - vegetable waste from the production of sugar cane; pyrolyzed bagasse - biochar; biochar modified with sulfur; biochar with immobilized sulfate-reducing bacteria.

The composition of lignocellulose-containing plant waste justifies the possibility of obtaining carbon material (biochar) from them. In this study, the features of obtaining and chemical and biological modification of biochar have been studied. The composition of the sugar cane pulp: cellulose 47.59 wt.%; hemicellulose 26.92 % by weight; lignin 21, 53 wt.%. The research results show that the heat treatment of cake is accompanied by the destruction of cellulose and lignin. At medium pyrolysis temperatures (low temperature pyrolysis), the biomass undergoes exothermic processes and releases the maximum amount of carbon material. The generally accepted term for obtaining carbon material by pyrolysis (heat treatment without air-oxygen access) from plant biomass is biochar.

The structural element of carbonized substance is the atomic network of polymerized carbon [20]. The elements H, O, N, P, and S included in the structure explain the reactivity of the resulting biochar. The presence of micro- and mesopores in biochar determines its high internal specific surface area. Macropores facilitate the access of biomolecules during the microbiological modification of biochar. The properties of the carbon material surface were evaluated according to generally accepted methods for determining the indicators: specific surface area; the content of acid and carboxyl groups. Based on the results obtained, the physicochemical parameters of the raw material

pyrolysis process were calculated and the optimal conditions for obtaining the carbon material were determined. When studying the structural-porous, sorption and ion-exchange properties of the original and pyrolyzed lignocellulosic biomass, both traditional and special methods were used. Sorption experiments were carried out under static conditions on solutions of metal salts and water extracts from soils contaminated with heavy metal ions.

The specific surface area and pore volume are determined from the nitrogen adsorption-desorption isotherm at 77K. Nitrogen adsorption-desorption isotherms were measured using a gas-adsorption analyzer AUTOSORB-6B (Quantachrome, USA). The parameters of the porous structure were calculated using AUTOSORB-1 software (Quantachrome, USA). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method in the range of relative pressures of 0.05–0.3. The specific surface area of mesopores was determined by comparing the adsorption isotherm with adsorption on a non-porous adsorbent with close surface chemistry (t-method). The specific surface of micropores and the volume of micropores were determined by the Dubinin-Radushkevich method. The total pore volume was determined by calculating the maximum nitrogen adsorption (at a relative pressure of about 1) per pore volume using the molar volume of liquid nitrogen at 77 K (0.03467 cm³/mmol). The average pore radius was determined assuming a cylindrical pore shape according to the formula $R=2V/S$, where V is the total pore volume, S is the specific surface area determined by the BET method.

The specific surface area characterizes the surface area of the adsorbent on which adsorbates of a molecular nature can be absorbed. The maximum specific surface area of biochar under various pyrolysis conditions reached 450 m²/g.

The characteristic is important for comparing different adsorbents with each other, as well as for evaluating the absorption capacity of the adsorbent. The pore volume characterizes the available volume in the adsorbent in which adsorbates can be absorbed. According to the IUPAC classification, pores in adsorbents are divided into the following categories: micropores (pores with a size of less than 2 nm), mesopores (pores with a size of 2–50 nm), and macropores (pores with a size of more than 50 nm). Therefore, the volume of micropores characterizes the volume of porous space in

which molecules with a size of no more than 2 nm can be absorbed.

The method of determining the static exchange capacity

consists in determining the number of ions absorbed from a constant volume of the working solution per unit mass of the adsorbent.

Samples of sorbents were dried at a temperature of 110 °C for 2 hours.

The sorbents were weighed on analytical balances with an accuracy of 0.0001 g.

The weight of 0.5 g was placed in a dry conical flask with a capacity of 100 ml, and 25 ml of working solution (0.1 M HCl) was added. The flask was closed and periodically stirred for 4 hours. After that, the solution was drained and an aliquot (5 ml) was titrated with 0.1 M NaOH solution. The equivalence point was determined using an indicator (phenolphthalein).

The values of the static exchange capacity indicate the ability of the material to bind ions due to ion exchange.

Chemical modifiers contribute to the development of the cellular structure of biochar. The sulfur-containing modifier used in our case diffuses into the internal structure of the carbon matrix during pyrolysis, expanding existing pores and creating new pores. Modification of biochar with sulfur makes it possible to obtain sulfur-containing biochar. Carbon disulfide-containing materials are sorption-selective with respect to a number of heavy metals due to the formation of insoluble metal sulfides on their surface. The proposed method for obtaining sulfur-containing biocarbon ecosorbent from bagasse is a one-stage pyrolysis of raw materials together with sulfur-containing reagents at a temperature of 350–450 °C. Sodium thiosulfate Na₂S₂O₃ was used as a modifier. X-ray phase analysis of the obtained samples of sulfur-containing biochar showed the presence of up to 35 % of bound sulfur on its surface, which determines the ability to firmly bind metal ions to the surface of the sorbent in an insoluble sulfide form and neutralize heavy metals in water and soil environments. The resulting ecosorbent has thermal stability and mechanical strength.

Microbiological modification leads to the creation of a biosorption material. Sulfate-reducing bacteria (SRB) immobilized on the surface of biochar are also capable of converting sorbed heavy metals into insoluble sulfide forms. SRB was isolated from galvanic drains, oil drains and cultivated on an elective medium with the composition (g/cm³): Na₂CO₃ – 0.1; CaCl₂ – 0.01; MnSO₄ – 0.02; NaCl – 3.0; Na₂HPO₄ – 1.5; KH₂PO₄

- 1.0; K_2HPO_4 - 1.0; nutrient agar for SRB inoculation - 20.0 g; distilled water up to 1 dm³. The SRB complex was identified in a specialized laboratory and assigned to the genera *Desulfotomaculum*, *Desulfosporomusa*, *Desulfosporosinus*, *Thermodesulfobium*, *Desulfobacter*, *Desulfobacterium*, *Desulfobulbus*, *Desulfococcus*, *Desulfomicrobium*. The presence of functional (carboxyl and phenolic) groups on the surface of the carbon ecosorbent determines the ability of the material to retain biomolecules on the surface due to a covalent bond or due to -COOH, COCl-, -NH₂-, -N₂⁺ groups. A sufficient number of immobilized cells on the surface of the sorbent is 120–200×10⁴ cells/g.

Results and discussion

Under laboratory conditions, the development and adaptation of the parameters of the process of pyrolysis of sugar cane bagasse with subsequent chemical and microbiological modification was carried out. The optimal technological parameters for obtaining biochar from bagasse biomass have been determined.

Structural-pore and ion-exchange characteristics of the original bagasse, biochar, sulfur-containing biochar, and biochar with SRB were determined (Table 1).

The specific surface characterizes the surface area of the adsorbent on which adsorbates of molecular nature are capable of adsorbing. The characteristic is important for comparing different adsorbents with each other, as well as for assessing the absorbency of the adsorbent. The pore volume characterizes the available pore volume of the adsorbent in which the adsorbates are able to be absorbed. The static exchange capacity (SEC) values indicate the ability of a material to bind ions of toxic substances. The method for determining the static exchange capacity consists in determining the amount of ions absorbed from a constant volume of the working solution per unit mass of the sorbent. The specific surface of biochar is higher than that of sulfur-containing biochars and biochars with SRB, which is explained by the immobilization of sulfur or microorganisms on the biochar surface.

Table 1

Structural-pore and ion-exchange characteristics of the original bagasse, biochar, sulfur-containing biochar, and biochar with SRB.

Indicator	Sorbent type			
	The original bagasse	Biochar from bagasse	Sulfur-containing biochar	Biochar With SRB
Bulk density, g/cm ³	0.6	0.5	0.6	0.7
Specific surface area, m ² /g	2	420-450	399-410	403-420
Total pore volume, cm ³ /g	0.14	0.38	0.33	0.28
Static exchange capacity for cations (Na ⁺). mg-eq / g	1.6	3.17	3.02	2.99
Static anion exchange capacity (Cl ⁻). mg-eq / g	0.28	0.54	0.47	0.44

The studies of toxic heavy metal ions sorption by original bagasse, biochar, sulfur-containing biochar, and biochar with SRB were carried out under static conditions from aqueous solutions of salts: chlorides of lead, cadmium, zinc and copper. The sorption kinetics was studied by the limited volume method: 0.1 dm³ of a model solution with an initial concentration of 100 mg/dm³ was poured into a series of flasks with 0.2 g portions of the sorbent and left there for 100 min at 20°C. At certain intervals, the

solutions were filtered and the equilibrium concentration of metal ions was determined by atomic absorption spectroscopy. The sorption value was estimated from the decrease in the content of the studied ion in the volume of the solution before and after sorption. Figure 1 shows the sorption isotherms of heavy metal ions by the ecosorbent from native bagasse, pyrolyzate (biochar), sulfur-modified biochar, and SRB-modified biochar.

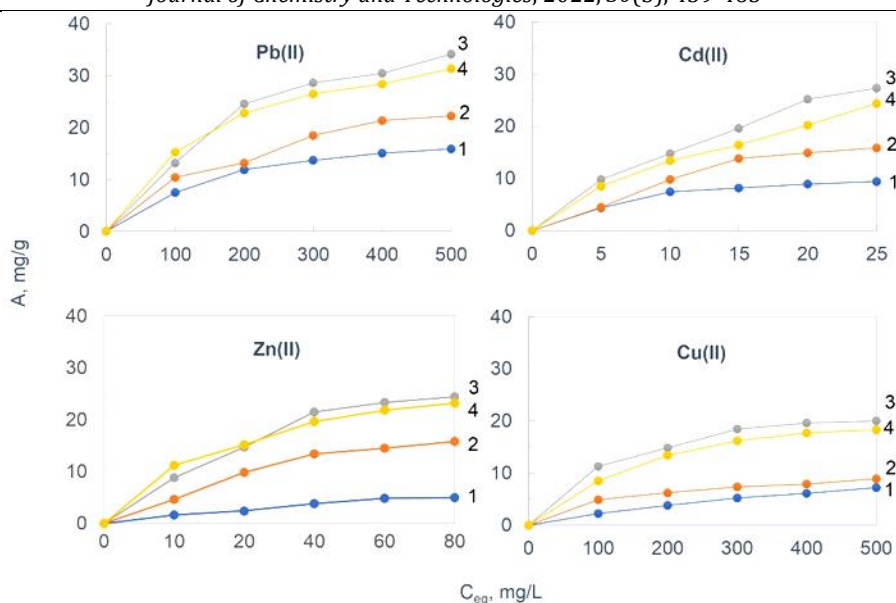


Fig. 1. Sorption isotherms of heavy metal ions by ecosorbent based on bagasse: 1-original bagasse; 2- biochar; 3 - sulfur-modified biochar; 4- biochar modified SRB.

Sulfur-modified bagasse biochar has a high ability to absorb heavy metal ions Pb(II)-37mg/g, Cd(II)-29mg/g, Cu(II)-30mg/g, and Zn(II)-27 mg/g compared to the original biochar. On the surface of the sulfur-containing sorbent there are sulfide, hydrosulfide, and C-S-C groups, which determine its specific formation on the surface and in the pores of the sorbent of poorly soluble sulfides of heavy toxic metals.

Sulfate-reducing bacteria immobilized on the surface of biochar also cause the formation of sulfide forms of metals on the surface and in the pores of the ecosorbent. The sorption performance of such a biosorption complex with

respect to heavy metal ions is practically at the level of the absorption capacity of sulfur-containing biochar.

The effect of the initial concentration of metal ions on the process of binding and their detoxification was studied. The initial concentration of heavy metal ions ranged from 2 to 5 MPC (maximum allowable for drinking water). Based on the obtained results of the concentrations of metal ions before and after treatment of the saline solution with an ecosorbent, the effectiveness of its action for their detoxification was assessed (Table 2).

Table 2

The efficiency of sorption of heavy metal ions by ecosorbents based on bagasse from aqueous solutions

Sorbent type	The amount of sorption. %			
	Cu (II)	Zn (II)	Cd (II)	Pb (II)
The original bagasse	13.1	17.0	19.1	17.2
Biochar from bagasse	37.1	39.1	32.3	37.4
Sulfur-containing biochar	97.0	94.1	95.0	96.3
Biochar with SRB.	92.0	90.0	92.0	94.6

It has been established that sulfur-containing biochar and biochar with immobilized sulfate-reducing bacteria have a high absorption capacity (more than 90%) with respect to Cd (II), Cu (II), Pb (II), and Zn (II) ions. The influence of solution pH on the adsorption capacity of the ecosorbent was studied. Optimal sorption conditions were recorded at pH 5.0. Optimal pH values were experimentally proven. Low pH values negatively affect the processes of sorption and binding (Table 3). A decrease in sorption removal at pH

higher than 6.0 may be associated with solvation and hydrolysis of metal ions.

The results of the study show that ecosorbents based on sugarcane pulp biochar with immobilized sulfate-reducing bacteria can strongly bind Cd (II), Cu (II), Pb (II), and Zn (II) ions and be used as Cd (II) and Zn (II) ions effective sorbents for cleaning aqueous solutions. Their key property is the ability to form insoluble sulfide forms of metals on the surface and in the pores of the ecosorbent.

Table 3

Dependence of the degree of binding of Cu(II) and Cd(II) by the ecosorbent on solution pH (CCu = 390 mg/l, CCd = 6 mg/l, V = 50 ml; m of the ecosorbent = 1 g, $\tau = 1$).

The name of the sorbent	The amount of sorption. %									
	Cu(II)					Cd(II)				
	pH=2	pH=4	pH=5	pH=6	pH=7	pH=2	pH=4	pH=5	pH=6	pH=7
Biochar from bagasse	22.3	24.2	37.1	31.3	22.5	23.2	23.1	32.3	22.7	19.3
Sulfur-containing biochar	66.4	82.6	97.0	89.4	72.2	77.5	87.6	95.0	88.5	87.1
Biochar with SRB.	71.2	88.2	92.0	84.2	66.2	69.8	87.6	92.0	87.4	83.2

Fractographic studies were conducted to determine the efficiency of the obtained ecosorbents with respect to heavy metals. The quantitative elemental composition of ecosorbent particles after sorption (using the example of removal of Cd(II) ions) was established based on data from scanning electron microscopy and micro-X-ray spectral analysis (analytical complex of scanning electron microscope and spectrometer). The spectra of sulfur-containing particles indicate the binding of Cd (II) ions to the surface of the particles.

The results of the study show that ecosorbents based on sugarcane pulp biochar with immobilized sulfate-reducing bacteria can strongly bind Cd (II), Cu (II), Pb (II), and Zn (II) ions and be used as Cd (II) and Zn (II) ions effective sorbents for cleaning aqueous solutions. Their key property is the ability to form insoluble sulfide forms of metals on the surface and in the pores of the ecosorbent.

The possibility of using bagasse-based ecosorbents for detoxification of Cd (II), Cu (II),

Pb (II), and Zn (II) ions in soils has been studied. Vegetation studies during the detoxification of heavy metals in the basal layer of soil were carried out according to generally accepted methods.

Ecosorbent was introduced into the soil contaminated with ions of the studied metals at the rate of 150 g of sorbent per 1.5 kg of soil. The samples were kept under static conditions at a temperature of $20 \pm 5^\circ\text{C}$ for 2 months. The humidity of the soil-ecosorbent mixture during the experiment was maintained at the level of 30–40 %. Table 4 shows the results of the detoxification effect of the ecosorbent, estimated by the concentration of ions in the water extract from the soil.

A significant decrease in the concentration of ions in the water extract from soils was established when contaminated soil was treated with an ecosorbent containing sulfur and modified with sulfate-reducing bacteria.

Table 4

The content of Cd (II) and Cu (II) ions in aqueous soil extract

	Cd (II), mg / kg Soil	Decreased concentration Cd (II), %	Cu (II), mg / kg Soil	Decreased concentration Cu (II), %
Control. Soil	0.03 (BG)	0	0.09 (BG)	0
Soil + Cd (II)	6.2	0	0.09 (BG)	0
Soil + Cd (II) + pyrolyzate	1.2	85	0.09 (BG)	0
Soil + Cd (II) + pyrolyzate + Na ₂ S ₂ O ₃	0.23	97	0.09 (BG)	0
Soil + Cd (II) + pyrolyzate + SRB	0,21	0,22	0.09 (BG)	0
Oil + Cu (II)	0.03 (BG)	0	397.31	0
Soil + Cu (II) + pyrolyzate	0.03 (BG)	0	100.22	74
Soil + Cu (II) + pyrolyzate + Na ₂ S ₂ O ₃	0.03 (BG)	0	26	93
Soil + Cu (II) + pyrolyzate + SRB	0.03 (BG)	0	22	94

Note: BG- background pollution

However, when evaluating the ecotoxicological indicators of soils for mobile forms of heavy metals, it is not enough to check only the water extract from the soil. Metals in different forms in the soil have different mobility, migration ability, and availability for plants. Phytoindicators were used to assess the detoxifying effect of the ecosorbent. In indicator plants, the content of metals in the cells correlates with the content in the soil. Oats (*Avena sativa* L.) and watercress (*Lepidium sativum*) were used as phytoindicators of metals.

The toxicological indicators of soils and plants during vegetation studies confirm that the introduction of an ecosorbent based on bagasse into soil contaminated with Cd (II), Cu (II), Pb (II) and Zn (II) ions prevents the transfer of these metals to plants (to the ground biomass and biomass of phytotesters roots).

Clearing the soil from harmful substances occurs inside the soil as a result of their binding into sparingly soluble sulfide compounds. Ecosorbents are able to firmly bind up to 75 % of the studied metals in the soil.

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