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CHEMICAL-PHYSICAL FEATURES OF THE BIOCHAR-BASED OIL-DESTRUCTIVE SORBENT

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The main task and relevance of this work are to develop the most effective sorbents for cleaning oil pollution or accidental oil spills. A generalized criterion for evaluating the effectiveness of a sorbent is the local availability and fast renewability of raw materials for biochar.

The features of obtaining biochar from cellulose-containing plant raw materials of corn cobs are described. The effect was studied of the pyrolysis conditions of the selected plant material on the physicochemical properties of biochar, which are responsible for the intermolecular interaction of the sorbent with the adsorbed substance and for immobilization and viability of oil degrading bacteria, which indicates the possibility to control the properties of oil destructive sorbent at the production stage. The optimal mode of carbonization of such raw materials has been worked out to obtain a sorbent with porosity and chemical compatibility with oil-degrading bacteria.

Cultural cultivation for immobilization of oil-degrading bacteria was carried out in a nutrient medium and a concentrate was prepared. It is shown that biochar with oil-oxidizing microorganisms fixed on its surface has significant sorption and destructive properties.

Keywords: *oil contamination, oil destruction, bioactive sorbent, absorption, biodegradation bacteria, pyrolysis*

INTRODUCTION

The sorption process is one of the most effective methods for cleaning ecosystems from oil pollution. The experience of localization and clear oil pollution has led to the development of technologies using a special group of biosorbents, which possess not only physical absorptional activity to oil products but also a biological ability to decompose oil products using a biodegradation process [1–5].

The biodegradation process performs by a special group of bacteria destructors of hydrocarbon [6–10]. The mechanism of oil biodegradation using bacteria can be described in the outline as follows [6]. The bacterium capsule consists of chromosomes and a plasmid. A plasmid is a physically separate genetic element of a bacterium. The genes contained in the biodegradation plasmids allow them to encode independently the enzymes of oil hydrocarbon compounds and use their carbon and energy to increase the growth of bacterial biomass. Mass growth enhances oil-destructive colonies of bacteria's selective advantages over other bacteria and further accelerates the destruction of environmentally toxic oil pollutants. For example, the bacterium *Pseudomonas putida* has a biodegradation plasmid containing a number of enzymes that convert cyclic hydrocarbons toluene and xylene to benzoate [7]. Also important, *Pseudomonas putida* can exist under conditions when naphthenes are the only carbon source [8].

Such a type of microorganisms is well fixed and held on the cellulose-containing particles of biochars. The nature of biochar particle surface and the branched porosity affects both the physical sorption properties and the possibility of immobilization of oil-degrading bacteria. Also, the presence of micro- and mesopores in biochar forms its high internal specific surface, which plays an important role in chemical reactions occurring at relatively low temperatures. Macropores have a smaller contribution to the change in the specific surface area of biochar, but facilitate the access of bacteria during immobilization [1, 2].

Immobilization of bacteria is possible with chemical and biological compatibility with the sorbent material, which is ensured by the required concentration of carboxyl and phenol groups on the surface of its particles and is determined by the capability to retain bacteria due to covalent bonds with $-$COOH, –COCl, $-NH_2$, $-N_2^+$ and NCO$-$ groups. These groups are formed during the pyrolysis of the cellulose-containing material, so qualitative breakthroughs in technologies for the purification from oil pollution can be provided in the development of sorbents based on the most effective natural raw material, its special disperse shredding or granulation, and at the optimal regime of pyrolysis. An obtained “biosorption complex” must have directed high adsorption capability and must meet the requirements to be biocompatible, must significantly reduce the period of adaptation of introduced microorganisms, and contributes to more complete localization and destruction of oil pollutants.

Therefore, the main task of research is to found a dependence between the structural features and sorption properties of the different raw cellulosic materials - pine, oak, and corncobs after pyrolysis that can justify their use as a carrier material for oil destructive bacterias.

METHODS OF RESEARCH

The surface properties of the carbon material were evaluated according to indicators measured in accordance with standard methods: specific surface; the content of acid and carbonyl groups and the capability to regenerate. The concentration of the absorbed substance was determined by weighing, colorimetry, and UV spectrometry. The specific surface of the sorbent was determined by the argon thermal desorption method. The sorption volume of pores was determined by the desiccator method of benzene vapor sorption, X-ray phase analysis. Changes in the concentration and composition of oil on the surface of the biosorbent were determined by the methods of IR spectroscopy and photocolorimetry.

RESULTS AND DISCUSSION

The study of the organic chemical composition (Table 1) showed the same concentration of cellulose and lignin as the chemical components responsible for the sorption capacity and immobilization of bacteria. But the level of hectosan is low 4.06 % in oak and the level of pentosan is high (2 times greater) in corncob. Thus, a sufficiently high content of key chemical components in the structure of corncobs makes it possible to obtain an effective carbon plant material for pyrolysis that is cheaper and fast recovering than wood materials.

Table 1. Chemical content of natural raw materials, %

Components	pine	oak	corncob
cellulose	41.93	44.17	30-34
lignin	29.52	23.93	15-17
hectosan	12.78	4.06	12-15
pentosan	10.80	24.60	17-20
resin and wax	3.17	0.68	-
protein	1.27	1.62	1.58
ash	0.53	0.94	0.96

The main requirement in the sorption capacity of the carbon matrix is the interaction of its hydrophobic surface with oil. The branched natural porosity micro- and mesopores in pine and corncob biochar form its wide internal specific surface, which is an important factor for absorption properties of searched optimal material for sorbent. The pore distribution of carbon material obtained from pine and corncob is almost the same on poregram (Fig. 1). Minor changes in the surface ratio of mesopores (2–50 nm) and macropores (> 50 nm) in the corncob particles were revealed.

Obtaining carbon sorbent from corncobs has a number of features. The sorption capacity of biochar in relation to oil depends on the parameters of the corncob pyrolysis process and the raw material preparation conditions. Thermal treatment (pyrolysis) of raw materials containing cellulose allows one to form and stabilize the porous structure of the obtained carbon material, as well as to obtain a large volume and a large total share of meso- and marcopores responsible for oil absorption. The temperature and duration of pyrolysis affect the sorption properties of the pyrolyzate. Pyrolysis of corncobs in a strictly functional mode allows obtaining a carbon sorbent with specific properties in relation to oil it self and oil products.

A complex of oil-destroying microorganisms of natural origin was used for bioactivation of the sorbent. For the selection of strains of oil-destroying microorganisms, samples were taken from oil-contaminated objects and pure cultures of destructive microorganisms were obtained, which were grown on a nutrient medium (Fig. 1). Pyrolysis of cellulose-containing raw materials is the decomposition of the source material (wood, plant residues) when heated to a certain temperature without access to air with the formation of gaseous (liquid) products, as well as solid residues - coal.

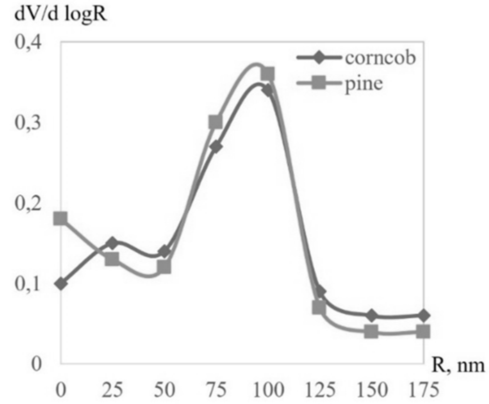


Fig. 1. Poregram of biochar (*R* – pore radii)

The final product of complete pyrolysis of raw materials is practically pure carbon, containing little potassium, sodium, calcium, magnesium and iron oxides in the form of impurities. The free-radical reaction of the thermal destruction of hemicelluloses, cellulose and lignin, which takes place at 200–260, 240–350 and 250–400 °C, is the basis of pyrolysis. Heat treatment at a temperature below 250 °C does not allow obtaining a stable porous structure. For such a material, heating during subsequent use can lead to changes in the parameters of the porous structure. Heat treatment at a temperature above 400 °C leads to a certain decrease in the total volume and a change in the part of meso- and macropores from the total volume of pores. Structural and chemical transformations in the process of pyrolysis of cellulose, which contains the raw material, determine the properties of the obtained carbon material. During the thermal oxidation of the primary material in an oxygen-free atmosphere, amorphous carbon is formed. Amorphous modification of carbon in coal from such raw materials was proven earlier. If the pyrolysis time is not enough, then the X-ray image (Fig. 2) reveals two wide halos, typical for cellulose with a maximum of 5.52 and 3.97 Å. An increase in the time and temperature of pyrolysis above 400 °C leads to the destruction of the structure of amorphous coal, crystallization of inorganic compounds.

The optimal pyrolysis process and the conditions for the synthesis of biochar were determined - at a temperature of 300-350°C for half an hour (Fig. 3). Under such conditions, an exothermic reaction occurs with the formation of an important property - the hydrophobicity of the sorbent surface and a high level of adsorption: 5–7.5 g of oil per 1 g of sorbent.

Oil-absorbing properties of the carbon material of corncobs under different pyrolysis conditions are shown in Fig. 4. In laboratory, the optimal conditions of pyrolysis of raw materials for obtaining high-quality oil-absorbing carbon material, which is used as a matrix for immobilization of oil-oxidizing microorganisms, have been found. The optimal pyrolysis temperature is 300–350 °C, pyrolysis time is 25–30 min. The oil content strongly depends on the time and temperature of pyrolysis and reaches values of 5–7.5 g/g.

The quality criterion of the sorbent material is the sorption properties, which were evaluated by oil capacity (the number of grams of oil absorbed by one gram of sorbent) and the retention of sorbed oil on the surface. The porous structure and chemical nature of the surface of the carbon sorption matrix based on pyrolyzate of corncob determine its sorption properties in relation to oil hydrocarbons. But the dominant factor in the carbon material - oil interaction is the hydrophobic interaction.

The concentration of functional (carboxyl and phenolic) groups on the surface of the carbon material determines the capability to retain biological molecules on the surface.

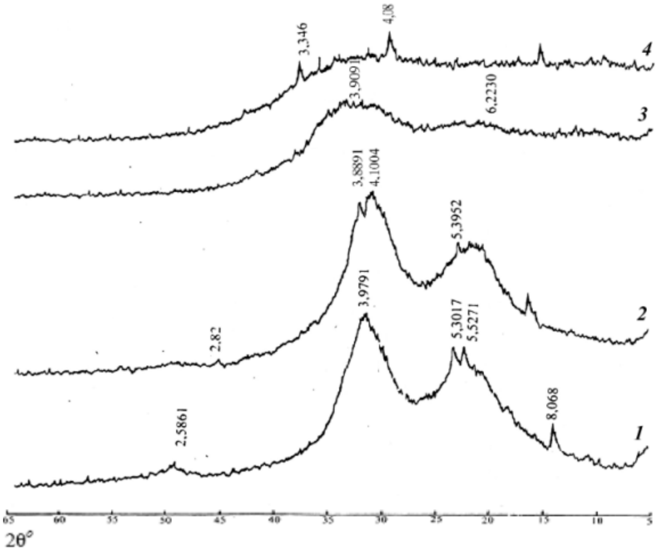


Fig. 2. Diffractograms of pyrolyzate from corncobs: *1* – raw material, *2* – 250 °C, 30 min, *3* – 350 °C, 30 min, *4* – 400 °C, 30 min

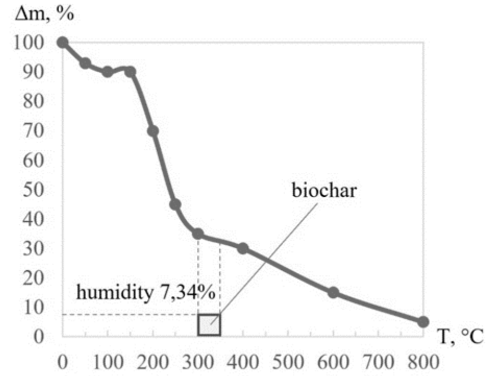


Fig. 3. Conditions for the synthesis of biochar

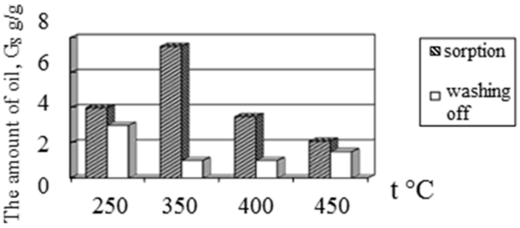


Fig. 4. Influence of pyrolysis temperature on the sorption properties of carbon sorbent from corncobs

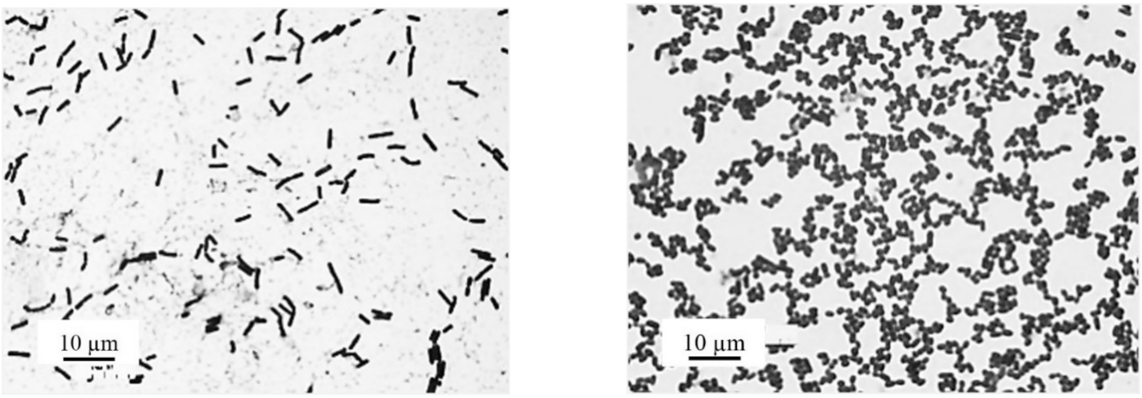
The capability to use hydrocarbons as the only source of energy allows destructive microorganisms attached to the surface to biodegrade directly oil and oil products localized on the biosorbent. A complex of oil-oxidizing microorganisms of natural origin was used for bioactivation of the sorbent. For the selection of strains of oil-degrading microorganisms, samples were taken from oil-polluted objects and pure cultures of destructive microorganisms were obtained, which were grown on a nutrient medium (Fig. 5).

The adaptation of a complex of microorganisms to the destruction of oil hydrocarbons and oil products of various genesis allows them to be used for various objects. Under natural conditions, there is an accumulation of positive properties of combined microorganisms. The development of microorganisms and the intensity of their vital activity are determined by environmental conditions. Cultivation and adaptation of NOM was carried out in a nutrient medium with oil composition (g/cm^3): Na_2CO_3 – 0.1, $CaCl_2$ – 0.01, $MnSO_4$ – 0.02, NaCl – 3.0, Na_2HPO_4 – 1.5, KH_2PO_4 – 1.0, K_2HPO_4 – 1.0, nutrient agar for cultivation of MO – 20.0 g, oil – 1 cm^3, distilled water up to 1 dm^3.

The most active oil-oxidizing microorganisms that were isolated are classified as: *Pseudomonas, Arthrobacter, Rhodococcus, Acinetobacter, Flavobacterium, Corynebacterium, Nocardia, Candida, Mycobacterium, Bacillus, Enterobacteriaceae, Micrococcus*.

After cultivation of the bacteria-destructors, the culture fluid was separated to a concentration of 10^9–10^{10} cells in 1 cm^3 to obtain a concentrate of isolated cultures of microorganisms. In our experiment, we abandoned the stage of separation of the culture fluid and cells of oil-destroying microorganisms and immobilized the obtained substrate, firstly, to obtain nutrients, to maintain the life of microorganisms during storage, and, secondly, to provide better sorption on the surface of the carbon carrier.

The rate of microbial decomposition of oil localized on the surface of the sorbent was much higher than that of the biodegradation of a continuous layer of oil on the water surface (Fig. 6) with the same amount of oil-oxidizing cultures of microorganisms and oil.



a *b*

Fig. 5. Growth of oil destructive bacteria in nutrient medium without oil (*a*) and on nutrient medium with oil (*b*)

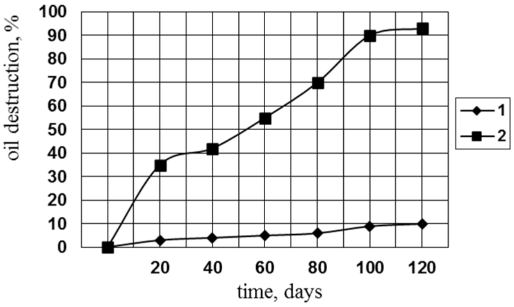


Fig. 6. Kinetics of destruction of oil on the surface of water (*1*) and adsorbed on a biosorbent (*2*)

The rate of destructive action depends on the total surface area of hydrocarbons decomposed by microorganisms. The greatest activity is manifested in the dispersion of hydrocarbons, when the largest plane of the contact surface per unit mass is provided. Dispersion or emulsification of hydrocarbons contributes to the active development of biogenesis.

For further bioactivation of the carbon carrier, the most active aerobic 779×10^{13} and anaerobic

736×10^{13} microbial cultures per 1 g of biosorbent were selected (Table 2).

Immobilization of microorganisms on the surface of the sorbent provides selective conditions for the biodestruction of oil in the sorbed state. The use of cultures of microorganisms from the environment has a number of advantages: first, the original natural population is well adapted to environmental conditions; secondly, high stability and synergism can ensure more complete use of the target substance as the only source of power; thirdly, the return of the microorganism to the original environment provides a selective advantage.

Table 2. The total number of aerobic and anaerobic microorganisms as dependent on the presence of oil in a nutrient medium

Sample	Total amount of MO in 1 g of sample	
	aerobes	**anaerobes**
carrier (carbon sorbent)	no growth	no growth
biosorbent (nutrient medium without oil)	448×10^{2}	736×10^{2}
biosorbent (nutrient medium with oil)	779×10^{13}	614×10^{13}

An oil sorbent based on corncobs pyrolyzate and oil-destroying microorganisms immobilized (fixed) on its surface, isolated from natural objects, ensures the ecological safety of the use of such a biosorption complex. A comprehensive approach to solving the problem of liquidation of oil pollution - sorption + microbial destruction - allows to increase the efficiency and environmental friendliness of works.

CONCLUSIONS

The possibility of obtaining carbon oil-absorbing material from corncob for the immobilization of oil-oxidizing microorganisms during the creation of a biocarbon sorbent with a high capability to break down oil is substantiated.

It has been found that the pyrolyzed raw material (corn cobs) has significant indicators of surface oleophilic and sorption properties in relation to oil. The porous structure and chemical nature of the surface of the carbon sorption matrix based on corncob pyrolyzate determines its sorption properties for oil hydrocarbons. But the dominant factor in the carbon material is oil interaction is the hydrophobic interaction.

According to the research results, the carbon sorbent from corncob is biocompatible with fluorine-degrading microorganisms, which is explained by the presence of centers of different chemical nature on its surface: polar and non-polar. Bioactivation makes it possible to obtain an effective ecological carbon material of a destructive type for the neutralization of oil pollution in the environment.

Хіміко-фізичні особливості нафтодеструктувального сорбента на основі біовугілля

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Основним завданням і актуальністю даної роботи є розробка найбільш ефективних сорбентів для очищення нафтових забруднень або аварійних розливів нафти. Узагальненим критерієм оцінки ефективності сорбента є локальна доступність і швидка відновлюваність сировини для біовугілля. Описано особливості отримання біовугілля з целюлозовмісної рослинної сировини качанів кукурудзи. Досліджено вплив умов піролізу відібраної рослинної сировини на фізико-хімічні властивості біовугілля, які відповідають за міжмолекулярну взаємодію сорбента з адсорбованою речовиною та за іммобілізацію та життєздатність бактерій, які розкладають нафтопродукти, що вказує на можливість контролювати властивості нафторуйнівного сорбента на етапі виробництва. Розроблено оптимальний режим карбонізації такої сировини для отримання *сорбента з пористістю та хімічною сумісністю з нафтодеструкторами. Проводили культивування для іммобілізації маслорозкладних бактерій на живильному середовищі та готували концентрат. Показано, що біовугілля із закріпленими на його поверхні мікроорганізмами-нафтоокиснювачами має значні сорбційні та деструктивні властивості.*

***Ключові слова**: нафтозабруднення, деструкція нафти, біоактивний сорбент, абсорбція, бактерії біодеградації, піроліз*

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