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STUDIES OF THE EFFECTIVENESS OF THE USE OF BIOSORPTION COMPLEXES FOR PURIFICATION OF OIL POLLUTED SANDY SOILS

Об'єктом досліджень є створений біосорбційний комплексний препарат для очищення забруднених нафтою піскових ґрунтів. Очищення ґрунтів, забруднених нафтою і нафтопродуктами, має особливості, так як через велику адсорбуючу здатність грунт накопичує забруднювач. Одним з найбільш проблемних є метод очищення піскових грунтів з бідним біоценозом від застарілих нафозабруднень. Перспективним напрямком в очищенні грунтів від забруднення нафтою є мікробіологічні технології. Застосування спеціальних мікробних препаратів дозволяє прискорити деструкцію нафти. Існуючі препарати мають свої особливості застосування і недоліки. Вони втрачають деструктивну активність з часом і мало ефективні при ліквідації застарілих нафозабруднень з великою концентрацією. Біосорбційний комплекс (біосорбент) на основі екологічного матричного сорбенту світлого кольору і іммобілізованих на його поверхні активних мікроорганізмів-деструкторів нафти природного походження дозволяє очищати світлі піщані ґрунти від застарілих концентрованих забруднень. Введення до складу біосорбенту аеробних і анаеробних мікроорганізмів дозволяє здійснювати біодеструкцію нафти як на поверхні в аеробних умовах, так і в глибині. Іммобілізовані на сорбційному матеріалі мікроорганізми володіють великим потенціалом деструктивної дії. При іммобілізації зберігається життєздатність клітин мікроорганізмів і значно підвищується ефект їх застосування. Встановлено оптимальні параметри отримання олеофільної сорбційної матриці з різних типів сировини та отримання мікробної біомаси з високою деструктивною активністю до вуглеводнів нафти. Вивчено експлуатаційні характеристики отриманих біоактивних сорбентів світлого кольору на основі моху та глауконіту, технологічні особливості і технічні прийоми їх застосування при очищенні піскових грунтів. Проведеними дослідженнями показано зміна концентрації нафтового забруднення піскового ґрунту від 30–40 % до 1–5 % нафти в процесі біодеструкції через 140 діб. Проведені випробування біосорбенту світлого кольору на промисловому об'єкті нафтобази при очищенні піскових ділянок із застарілим нафтозабрудненням показали ефективність очищення до 90 %.

Ключові слова: *очищення забруднених нафтою піскових ґрунтів, мікроорганізми-деструктори нафти природного походження.*

1. Introduction

Oil is a complex and persistent pollutant. Hydrocarbons of oil are available for assimilation only specialized bacteria. Such selectivity in relation to oil formed the basis for bacterial methods of neutralizing oil pollution. Bacteria are highly active microorganisms, which contain enzymes, that is, biological catalysts that can act on a large amount of substrate per unit time. Biosorbents, built based on adsorption material with immobilized oil-oxidizing bacteria, are able to localize and destroy oil products. Oil destruction can be carried out to the final stages, when only the decomposition products of oil remain carbon dioxide, water and asphaltenes, environmentally inert components. The residual part of the biosorbent is the initial base of the sorption material. The process of oil biodegradation takes place both on the surface under aerobic conditions and in depth, that is, under microaerophilic conditions.

This effect is achieved by introducing aerobic and anaerobic oil-oxidizing bacteria into the composition of biosorbents. Biosorbents can often be the only means of dealing with accidental oil pollution. The use of sorbents of this type will quickly and effectively localize emergency spills of oil and oil products and further ensure a complete schedule of the remains of the latter.

Technologies for purification of oil-contaminated soils, as noted in the works of the authors [1, 2], provides for the activation of self-purification processes by inducing microorganisms that destroy pollution. The introduction of microorganisms is advisable in those cases when the activity of the natural biocenosis is low and the oxidation of oil is extremely slow. Therefore, creation and study of bioactive sorption complexes, which absorbed the mobile pollutant (oil) and had a destructive ability for oil, specifically for specific sandy soils, is topical.

2. The object of research and its technological audit

The object of research is biosorption complexes based on natural moss and glauconite, bioactivated by a natural consortium of oil-oxidizing microorganisms.

In this case it is necessary to take into account the requirements for oil absorbents, namely, the sorbent should:

– absorb, if possible, more pollutant per unit mass;
– be non-toxic;
– do not disturb the balance of natural ecosystems;

– have a relatively low cost and sufficient raw material base.

This problem is solved by using natural glauconite as a carrier sorbent. Microorganisms-destructors (of a broad spectrum of action, possessing synergism, stable in natural conditions)) for bioactivation of the sorbent surface are extracted directly from oil-contaminated natural objects.

Investigation of adsorption and destructive properties with respect to oil samples of various origin of oil absorbing biologically active sorption material will determine the directions of practical implementation of the technology for obtaining and applying effective environmentally friendly biosorbents for the localization of oil pollution and its subsequent destruction. The optimum parameters for the synthesis of the oleophilic sorption matrix from various types of raw materials and the production of microbial biomass with high destructive activity to oil hydrocarbons are established. Sorption properties of the matrix carrier relative to petroleum products of various chemical composition and microorganisms-destructors have been studied. Microorganisms-destructors, isolated from oil contaminated natural objects and immobilized on the surface of the sorbent-carrier, have an increased destructive capacity with a wide spectrum of action. This fact determines the performance characteristics of bioactive oil absorbing sorbents.

Purification of sandy soils from oil pollution has certain differences. The mineral composition of the sand is heterogeneous, there are many minerals in it, but several are worth mentioning, the number of which is significant as a percentage: chlorites – 1 %, dolomite – 3 %, calcite – 7 %, feldspars 8 %, quartz (which, by the way, is the most common mineral on Earth) – 70 %, other minerals account for 11 %. This statistics shows that sand consists mainly of quartz and feldspar. It follows that such sands are the most widely distributed. The light color of sandy soils requires the use of only light modifications of bioactive sorbents of destructive type. Secondly, the natural biocenosis. Sandy soils are poor in microorganisms. In such soils, only 1 % of dry biomass is. In addition, there is low moisture content of sandy soil. In moist soils microorganisms reproduce better than in dry form, therefore the microbial component in the biosorption preparation for purification from oil contamination of sandy soils should have increased directed activity.

Among light-colored sorption materials, moss natural and glauconite have the best indicators on sorption activity for both oil and oil-oxidizing microorganisms. Glauconite is widely distributed in sedimentary rocks of shallow-marine origin and in modern marine sediments. Glauconite contains bathyal green ooze, glauconite sandstone, light green glauconite chalk sands and many other species. However, it does not form large monomineral aggregations in nature, but occurs only as a mixture with other minerals of clayey or sandy strata. That is, glauconite is related to sandy soils.

In the existing conditions of oilfield facilities exploitation, an important environmental factor is the cleaning from oil of sandy soils with poor natural biocenosis and low self-cleaning ability. Priority direction is the use in environmental technologies of mineral materials having a natural affinity with the object. One of the most problematic moments is that when creating an oil-oxidizing biosorption complex, a light-colored sorbent-sorbent, sorption-active to oil and microorganisms-destructors, is needed.

3. The aim and objectives of research

The aim of research is development of an efficient technology for cleaning concrete sandy soils from old oil contamination using specialized light-colored biosorption complexes. To achieve this aim, it is necessary to solve the following tasks:

1. To select from the existing natural mineral and vegetable ecological light-colored sorbents the sorbent carrier, which possesses sorption activity, petroleum hydrocarbons and biocompatibility with oil-oxidizing microorganisms.

2. To isolate from the natural oil contaminated sites a consortium of microorganisms-destructors of hydrocarbons of a wide spectrum of action, which has a synergism that is stable when returning to the environment for bioactivation of the surface of the sorbent.

3. To determine the effectiveness of the biosorption complex on samples of model sand contaminated with oil products of different origin and on samples, selected at oil facilities.

4. To test the biosorbent complex (biosorbent) in the field.

4. Research of existing solutions of the problem

Numerous studies have determined the technological features of production and techniques for using materials and methods for cleaning soil from oil pollution for various environmental objects. As shown in [3], the purification of soils contaminated with oil and oil products has features. Due to a large adsorbing surface, the soil accumulates a pollutant. The sorption capacity depends on the properties of the soil, primarily on the capillary forces, which are determined by the granulometric composition of the soil and its moisture content. Dependence of migration – the accumulation of oil and oil products in soils from the level of their moisture content is confirmed experimentally and shown by calculation methods. With increasing soil moisture, there is less likelihood of soil consolidation of oil and high activity of its radial and material displacement. The water-saturated soils bind only the residual amount of oil in the form of a liquid phase. The natural complex (native biocenosis) already exists in the soil, where more bacterial cells are kept on the surface or within the soil aggregate. The authors of [4, 5] show, that the introduction into the soil of adapted microorganisms with high destructive activity accelerates the decomposition of oil. Immobilized on different materials, microorganisms have a greater potential for destructive action. However, when using microbial preparations, as noted by the authors [6, 7], there is a contradiction in the results, technical difficulties in their production and application. Immobilized on different materials, microorganisms have great potential for destructive actions. Immobilization increases the viability of microorganism cells. The choice of optimal adsorbents for the immobilization of microorganisms can significantly increase the effect of their use. A promising direction is the combination in one material of the ability of physical and chemical sorption of oil and its biodegradation in a localized state under the action of microorganisms. The advantages of using immobilized microorganisms-destructors are given in the articles [8, 9].

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from pollution. Of all types of environmental pollution, soil contamination with oil and petroleum products is now widespread. Practice shows that the restoration of such soils represents a particular difficulty and indicates the need for research on the ground. The development of a technology for cleaning oil-contaminated soil should determine the necessary methods based on scientific and experimental research. Assessment of the state of the contaminated area after applying the technology determines the possibility of using a particular technology. In a significant number of biosorbents, the distinguishing feature of which is the variety of carriers (sorbents) used and the cultures of microorganisms immobilized on them. However, the question of their use for cleaning sandy soils remains open because of the specifics. The paper [10] presents the results of studies of cleaning contaminated sandy homogeneous and heterogeneous soils of different granulometric composition by washing them with water. However, the effectiveness, efficiency and relevance of such technology are questionable, although this statement can be controversial.

Thus, the results of the analysis allow to conclude that the development of a light combination of a bioactive sorbent with an increased destructive capacity of immobilized microorganisms is relevant and necessary.

5. Methods of research

Surface and sorption characteristics of various possible carriers for immobilization of oil-oxidizing microorganisms are studied. The sorption capacity of the carrier relative to the microbial culture is very important when creating a light-colored biosorption complex and is determined by the adsorption interaction between the carrier sorbent and the bioculture. The evaluation of this characteristic was carried out according to the index of «specific sorption» and the strength of the culture fixation in the stage of intensive growth under standard conditions. The amount of fixed biomass (dry weight) was calculated from the difference in weight of the sample before and after treatment of the sorbent with biomass (weight in mg per 1 g of sample weight) [5–8]. Research results show that the sorption of biomass on the carrier is from 100 to 400 mg of dry biomass per g of sorbent. It is known that with «monomolecular» adsorption (one layer of cells), specific sorption of the biomass of the culture is 80–120 mg/g of material.

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The sorption capacity of the carrier relative to the microbial culture is very important for the creation of a biosorption complex and is determined by the adsorption interaction between the carrier sorbent and the bioculture. One of the important parameters of the immobilization process, which characterizes the possibility of functioning of immobilized cells under conditions of increased hydrodynamic action, is the binding force on the carrier surface [8]. Therefore, the ability to desorb cells from the surface of carriers is studied. On average 76 % of the cells are immobilized on the surface of the carrier. A quantitative and qualitative assessment of the degradation of petroleum hydrocarbons was determined using IR spectroscopy and GLC. Studies have shown that the potential of oil-oxidizing microorganisms is much higher if they are immobilized on the surface of the sorbent. At the same sorbents are not inert, but sorption active against carbohydrates. Such complex of biosorption allows to clear sandy soil contaminated with oil by 90 %. Microorganisms that are bound to the surface of the sorbent do not change their activity for a sufficiently long time (more than a year). It is possible to use the biosorption complex several times. It is only necessary to restore its activity (the addition of biological elements – phosphates and nitrates).

6. Research results

In the process of destruction, the number of microbial cells increases during the first 100 days of purification, when the maximum decomposition rate of petroleum hydrocarbons takes place. The dynamics of oil destruction was determined from the change in the content of residual oil in the soil (Table 1).

Table 1

Dynamics of soil purification from oil when treated with a biosorption complex

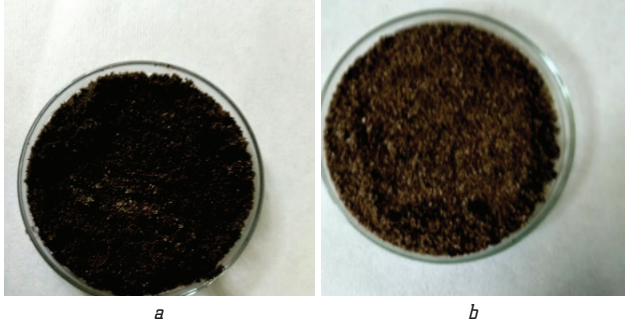
The term from the beginning of purification, the day	Residual oil content (loam), Carbon carriers – carrier glauconite – carrier natural moss, %			Residual oil content (sand), Carbon carriers – carrier glauconite – carrier natural moss, %		
0	40	40	40	40	40	40
10	24	29	31	26	18	14
33	18	20	20,1	21	18	15
42	13	18	19	18	21	22
56	11	14	17	16	14	16
68	10.5	11	12	14	13	15
85	9.8	9	10	10.1	12	11
91	8.4	10	9	9.1	8	6
110	7.6	6	7	8.4	7	6
126	5.2	4	7	6	5	7
130	2.4	3.5	5	4	4	5
140	**0.4**	**2.1**	**1.9**	**2.8**	**2.9**	**1.8**

When a sandy soil contaminated with oil is treated with a biosorption complex, the mechanism of action is not only the biochemical destruction of oil, but also the activation of poor natural microbial biocenosis. The process of oil decomposition in soil has the same character for models and industrial designs. The studies show the change in the oil concentration in the biodegradation process in industrial soil samples (black earth, loam, sand).

After 140 days, the concentration of oil contamination decreased from 30–40 % to 1–5 %.

Taking into account the specificity of sandy soils (light color); it was used in parallel for the treatment of biosorption complexes based on a light carrier (glauconite, sawdust, crushed straw, moss).

The biosorbent has an advantage over other sorbents – the treatment of the oil stain with biosorbent blocks its further spread (the effect of physical and chemical booms), which allows collecting more than 90 % of this pollutant, since petroleum products are a food for microorganisms, while a stain treated with a simple sorbent can spread further after saturation of the sorbent with oil products. Biodegradation is practically solved by the utilization of destructive biosorbents after use, which greatly simplifies their use. Fig. 1 visually states the degree of cleaning sandy soil from oil (a sample of the ground tank farm).



a *b*

Fig. 1. Cleaning of sandy soil from the tank farm Bronchi: *a* – contaminated soil; *b* – after treatment after 3 months

A technical solution for the bioactivation of a sorption vehicle includes two steps:

1 – production of microbial biomass (suspension);

2 – application of biomass to the sorbent carrier.

After grinding the material of the sorbent – glauconite of the necessary fractional composition, the material enters the hopper for further processing.

The microbial suspension is manufactured in an enzyme chamber. Water and components are fed into the chamber (2 m^3 capacity):

– concentrate of the oil-oxidizing microbial complex;

– gel component;

– mineral components (phosphorus, potassium and nitrogen containing salts) and nutrient medium.

Bioactivation of the sorption carrier is carried out in a vertical mixer at a temperature of 40–50 °C and duration (20–30 hours), where there is a process of bioactivation and drying of the sorbent.

7. SWOT analysis of research results

Strengths. Investigation of the processes of biodegradation of oil in sandy soil under the influence of biosorption complexes based on light sorption matrix materials of various types, activated by an identical composition of oil-oxidizing microorganisms of natural origin, shows the possibility of using sorbent-microbial compositions on the basis of glauconite mineral or vegetable carrier (moss). The composition was injected with microelements in the amount necessary for the development and activity of microorganisms, a mixture of compounds to maintain pH = 6–8 and starting HOM concentrate isolated from natural eco-objects.

The production of a biosorption material does not require expensive initial reagents and equipment. At receipt, cheap natural raw materials are used.

Weaknesses. The cost price will be only adjusted in the production process. Calculation of economic parameters for a particular production will help reduce cash costs.

Opportunities. Opportunities for further research can bring additional opportunities in the introduction of the biosorption material being presented not only for Ukraine, but also for near and far abroad objects.

Threats. The use of technology for cleaning oil-contaminated sandy soils on existing oilfield facilities using biosorption complexes of a destructive type will undoubtedly lead to additional production costs. The change in existing practices and the improvement of traditional methods for cleaning oil-contaminated soils, the introduction and use of fundamentally new scientific and practical results entail certain difficulties in the organization of production.

8. Conclusions

1. It has been established that bioactive sorption complexes of light color on the basis of natural glauconite and immobilized microorganism-destructors of oil, which are isolated from natural oil-polluted objects, solve the problem of purification of specific sandy soils from old oil contamination. Glauconite of light color has an affinity with sands, satisfactory oil content (3–4 g of oil/g of sorbent) and is biocompatible with oil-oxidizing microorganisms.

2. The destructive activity of various sorbent-carrier compositions and a microbial component with respect to hardly decomposable petroleum products (fuel oil, aromatic compounds, tar) has been investigated. The microbial component was isolated from industrial samples of sandy soils in oil storage tanks (Ukraine) and Kuwait sands contaminated with oil and mazut. It has been established that the most destructive activity is the mixed composition of microorganisms adapted to oil products of various origins and possessing synergism. It was shown that the culture fluid for bioactivating the sorbent carrier should have a biotite of 10^9–10^{10} CFU, contain mineral and organic (oil) nutrients.

3. It is shown that the bioactivated sorbent has an advantage over other sorbents – the treatment of the oil stain with biosorbent blocks its further spread (the effect of physico-chemical booms), which allows collecting more than 90 % of this contaminant, since oil products are food for microorganisms, while the stain, treated with a simple sorbent can spread further after saturation of the sorbent with oil products. It is established that biodegradation practically solves the problem of utilization of destructive type biosorbents after use, which greatly simplifies their application.

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4. Efficiency of application of light biosorbent of destructive type on the basis of bioactive glauconite, confirmed by the conducted experimental field tests to clean sandy soils from contamination of obsolete petroleum products and petroleum products at the site of the industrial facility (oil base). Chemical analysis of soil samples showed a concentration of oil contamination of 34–41 % (non-volatile hydrocarbons). After 3 months, analysis of samples of sandy soil showed neutralization of oil pollution by 80 %, a change in the color of sandy soil from black to light gray. A year later, analysis of soil samples showed neutralization of oil contamination to 95 %. The positive effect and high efficiency of a light biosorption preparation of a destructive type on the basis of biologically active glauconite were established during the purification of specific sandy soils from obsolete oil-contaminated.

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