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STUDY OF THE EFFECTIVENESS OF THE USE OF BIODESTRUCTORS FOR LIQUIDATION OF OIL SLICKS ON THE WATER SURFACE IN EMERGENCY SITUATIONS

V. Vambol[1*], G. Krusir[2], K. Nuzhna[1], E. Zaitseva[2], A. Kaluzhskykh[1]
[1]National University of Civil Defence of Ukraine, Kharkiv, Ukraine.
[2]Odessa National Academy of Food Technologies, Odessa, Ukraine.
*Corresponding email: violavambol@gmail.com

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Abstract

One of the main factors creating the unfavorable state of the aquatic environment is shipping and the activities of sea trading ports. Special danger is represented by emergency situations with the spreading of a large amount of oil products. Each year, about 10 million tons of oil and petroleum products fall on surface water. This study presents the results of an experiment on the effectiveness of the use of a sorbent-biodestructor for the elimination of oil pollution in emergency situations. Analysis of the main types of biodestructors, which used in Ukraine for the elimination of oil spills from the water surface, carried out analytically using open sources of information. Determination of the effectiveness of the use of biodestructors was carried out in laboratory conditions. Experimentally, a change in the layer thickness of the oil product was observed depending on the time of action of the biodestructor with a different amount of sorbent used. The study of the presence of biological components in the composition of a biodestructor was carried out using a scanning electron microscope with a low-vacuum chamber and with the REM-106 microelectronic microanalysis system. Two samples were examined in a low-vacuum chamber in reflected electrons. Determined that, it is immobilized bacteria-destructors of petroleum hydrocarbons that are widely used in modern environmental biotechnologies. Experimentally installed, that the quality of adsorption does not depend on the time the sorbent stays on the spot. The use of a biodestructor for the elimination of oil pollution from the water surface is advisable as an additional purification stage aimed at the adsorption of thin oil slicks in large-scale man-made disasters. The study using a scanning electron microscope with a low vacuum chamber and with a REM-106 energy dispersive microanalysis system showed that the ecological efficiency of the use of such a sorbent cannot be at a high level, since there is an uneven distribution of microorganisms and it clusters. At the same time, the required number of bacteria (10^7 per 1 g of substance) is not ensured.

Keywords: environmental safety waterbodies; emergency with oil spill; efficiency of biodestructor.

1. Problem statement and Analysis of the recent researches and publications

All components of the environment are under the action of man-made loads. A large number of pollutants [1, 2] enter the air, which then enter the ground and water bodies. The lands are polluted with heavy metals [3, 4], other toxic elements [5] or depleted and are not fertile [6]. Many waterbodies are also contaminated with heavy metals [7] and have an inadequate mineral composition [8, 9]. Problems of environmental protection occupy an important place in developed countries. One of the problems of our time is the effective provision of environmental protection in industrial cities. Its solution largely depends on the improvement and implementation of environmental protection measures, including the protection of natural waters in industrial regions and the effectiveness of their implementation.

Technogenically loaded regions are characterized by a negative impact on the environment. One of the main factors creating the unfavorable state of the aquatic environment is shipping and the activities of sea trading ports. Special danger is represented by emergency situations with the spreading of a large amount of oil products. Each year, about 10 million tons of oil and petroleum products fall on surface water. Currently, almost 30 % of the world's oceans is covered with oil slick. For example, in the first 9 months of 2016, 12 facts of pollution of the water area with oil products that are not spills were registered in the seaports of Ukraine. In the same year, one spill of petroleum products was registered, during which 379 liters of flooded petroleum products were collected [10]. In the Sea of Azov on October 23, 2018, an oil spill was discovered near berth No. 3, namely, a spot with rainbow stripes on the surface of sea water with a total area of 15 m^2 [11]. In the city of Kamenskoye on January 26, 2017, an emergency situation arose with the alleged pollution of the Dnieper’s water area with oil products due to the flooding of the barge and the river crane, which led to the leakage of oil products, probably in the amount of 300 tons [12]. According to the news from October 17, 2018, near the Canadian coast of Newfoundland, due to problems with the underwater pipeline, 250 m^3 of oil leaked into the Atlantic Ocean [13].

Depending on the chemical composition of the oil, its derivatives behave differently: some oil emulsifies with water, some part evaporates from the surface, thereby polluting the atmosphere, some part settles to the bottom. On average, only about 3…15 % of the initial amount of crude oil, it is subject to oxidation processes, biodegradation, as well as photochemical reactions. At the same time as evaporates from 10 to 40 %. The ability of an oil to dissolve in water depends on its chemical composition, air and water temperature, etc. [14].

As shown by the results of experiments with the introduction of crude oil of various concentrations into sea water, the peak of its solubility occurred on the 10th day [14]. This is due to the fact that petroleum hydrocarbons are characterized by their ability to biodegradation, chemical decomposition and transformations in the marine environment. These processes contribute to the emergence of a wide range of substances with different properties. [14].

The thinnest oil slick that remains on the surface of the water reduces evaporation from this area by 60 %. The result of this is the heating of the water surface and the disturbance of gas exchange between the water surface and the atmosphere. This leads to a decrease in the income in the water column of oxygen, so necessary for fish and other marine life. One liter of spilled oil products deprives oxygen of about 40 thousand liters of water, or, in other words, a ton of oil can pollute about 12 km^2 of the ocean surface and destroy all life in it. This is what determines the relevance of this work.

Now physico-chemical and biological methods for the elimination of oil pollution are widely used. These methods are based on the processes of destruction of oil slicks by dispersion, sorption of oil slick and emulsified oil by natural and synthetic sorbents, and the destruction of petroleum hydrocarbons by oil-oxidizing microorganisms. From a scientific point of view, the sorption method of water purification from oil products deserves attention, since its use entails the most rapid and effective elimination of the oil slick with minimal damage to the environment. The main requirements for the sorbents are high flotation and oleophilism, as well as low water absorption.

The advantages of synthetic sorbents include high oil absorption capacity, and disadvantages include the high cost and complexity of utilization of the used sorbent. The most effective of them are polymeric sorbents in the form of fine powders, granules, fabrics and sorbing booms. However, such disadvantages as carcinogenicity of the powder dispersed powders, low absorbing properties of thin oil slicks, difficulties in disposing of used fabrics and sorbent booms limit their use.

Despite the cheapness of natural sorbents, their use is limited due to low oil absorption capacity. Among the organic natural substances that have good sorption properties are sawdust, peat, straw, rice husk and the like. They are recognized as environmentally friendly sorbents in many countries, with peat occupying a leading position as the basis for the production of sorbent. Examples are sorbents produced in Canada – «Pit-sorb», Great Britain – «Fin-sorb», Finland – «Elkosorb», Belarus – «Lesorb», Russia – «Sorboil» and in other countries. A common drawback of these sorbents is the need to collect them, which makes the process time consuming, requires special tools. The practice of oil spill cleaners using sorbents shows that in most cases it is not possible to collect more than 25 % of the sorbent applied to the water surface [15].

2. Statement of the problem and its solution.

Despite the organizational work on the protection of water bodies, emergency situations with pollution of the water area by oil products still occur, as the analysis above shows. Considering the above, it is relevant to determine the effectiveness of the use of modern biodestructive for oil absorption, in the face of emergency situations with oil spills. Therefore, the aim of the work is to determine the effectiveness of the use of modern biodestructors for oil absorption in emergency situations with oil spills. To achieve this goal the following tasks were solved:

– analysis of the main types of sorbents used for the elimination of oil slicks from the water surface, which are used in Ukraine;

– determination of the effectiveness of biodestructor in order to eliminate emergency situations with oil spills.

2.1. Materials and methods.

Analysis of the main types of biodestructors, which used in Ukraine for the elimination of oil spills from the water surface, carried out analytically using open sources of information.

Determination of the effectiveness of the use of biodestructors in order to eliminate emergency situations with oil spills was carried out in laboratory conditions. Experimentally, a change in the layer thickness of the oil product was observed depending on the time of action of the biodestructor with a different amount of sorbent used. For the study, 4 vessels, a volumetric flask, a measuring spoon, a graduated pipette, and diesel fuel – a liquid petroleum product that is used as a fuel for water transport – were taken. 300 g of sea water was poured into each vessel, 10 mg of oil was added to each vessel. Using a measuring spoon was poured biodestructor: 2 g; 4 g; 6 g and 8 g. The experiment was carried out at a temperature of 22…25 °C.

The study of the presence of biological components in the composition of a biodestructor was carried out using a scanning electron microscope with a low-vacuum chamber and with the REM-106 microelectronic microanalysis system. Two samples were examined in a low-vacuum chamber in reflected electrons.

2.2. Results and discussion.

In Ukraine, various types of sorbents are used to clean water from oil products [16–18]. For example, natural mineral glauconite. It is believed that this is a highly effective natural sorbent from environmentally friendly mineral raw materials for physico-chemical cleaning of soil and wastewater. It is used as a sorbent of heavy metals, radionuclides and petroleum products in the treatment of wastewater and wastewater, soils subject to man-made pollution, including roadsides, squares and lawns located near urban highways with heavy traffic; enterprises of oil refining industry, oil pumping stations, gas stations, car repair complexes.

The peat sorbent granulated. It is used for wastewater treatment plants from petroleum products and other pollutants. Available in the form of granules with a diameter of 8...9 mm, a length of 5...15 mm. Used by pouring the sorbent into the filter cassette or treatment plant section. The claimed cleaning efficiency is 99 %, which is confirmed by a test report of a certified laboratory. Simple and easy to use.

The most often used for the elimination of oil pollution is a sorbent-biodestructor, which is brown powder, dispersed, or with fibrous inclusions, floating, hydrophobic. This preparation is based on bacteria-destructives of petroleum hydrocarbons immobilized using a special technology on an organic substrate – peat. This biodestructor is environmentally friendly, non-toxic, odorless. Its sorption capacity is not less than 1 : 4...1 : 8, pH = 7, bulk density is 50...150 g/m^2, the declared cleaning efficiency is 95 %. Under natural conditions, microorganisms are immobilized and attached to solid particles. The attachment of microorganisms to the micro- and macro-aggregate is important primarily for the manifestation of their metabolic activity. Working on the principle of biocatalysts, immobilized cells exhibit high metabolic activity without a significant increase in the biomass of free cells. Therefore, it is immobilized bacteria-destructors of petroleum hydrocarbons that are widely used in modern environmental biotechnologies. Moreover, these bacteria are attached to a solid surface. The properties of the immobilized bacteria ensure their rapid introduction into natural ecosystems and high destructive activity.

According to the results of the experiment, we observe that a clear line of petroleum product formed on the surface of the water after a few seconds. The thickness of the oil slick was 4 mm. The vessels were in a ventilated room and after 16 hours, the remaining layer of biodestructor was removed and the result was observed. For sample No. 1 – the oil product was partially adsorbed, a layer of diesel fuel 2 mm thick remained on the water surface, the rainbow oil slick is clearly visible. For sample No. 2, the oil product is partially sorbed, rainbow circles can be observed on the surface, and there is no clear line of oil product. For sample No. 3, the oil product was completely adsorbed; after removing the sorbent, there are no visible signs of the presence of oil products in the water. For sample 4, the oil product was completely adsorbed; after sorbent removal, there are no visible signs of the presence of oil products in the water; some amount of sorbent precipitated. The dependence of the oil slick thickness of the oil product on the time of action of the sorbent is shown in figure 1.

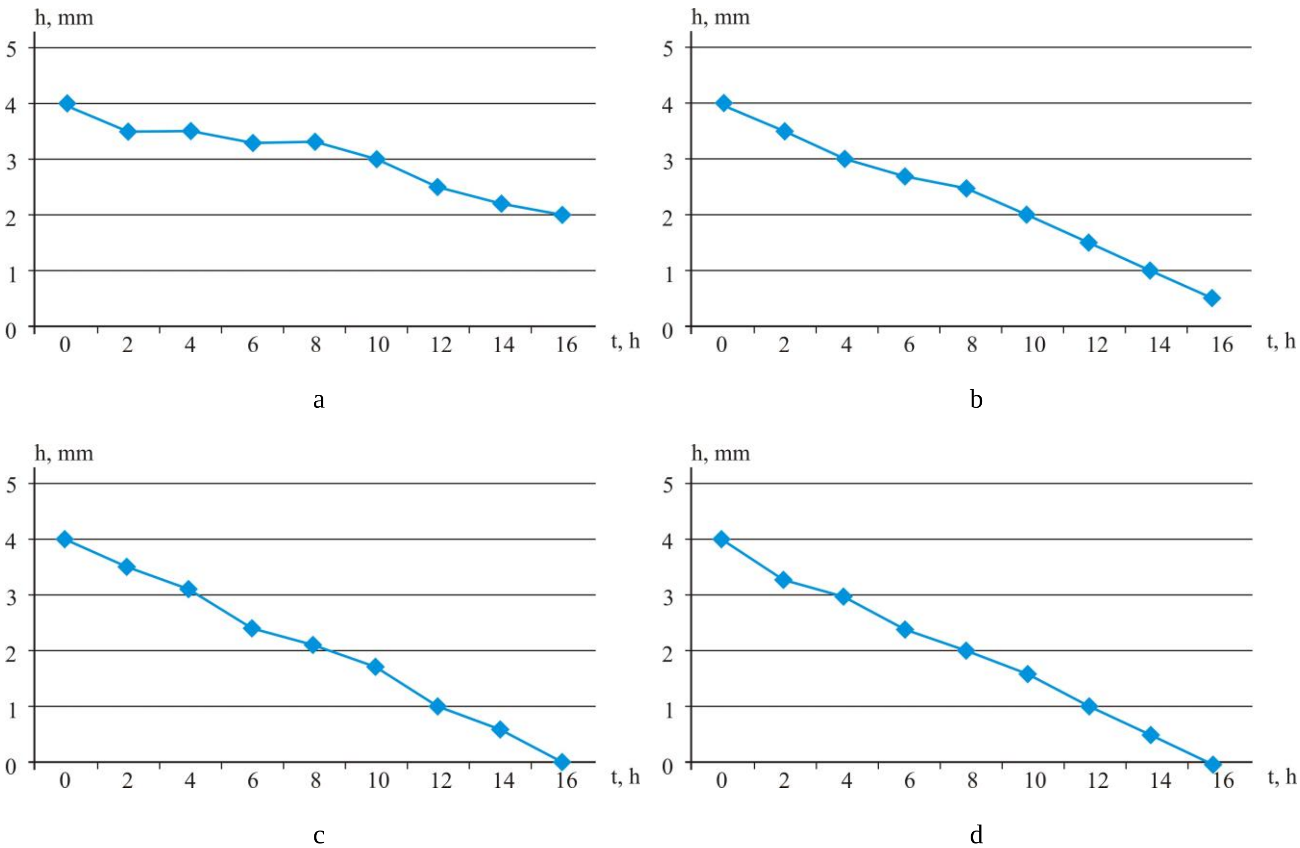

Figure 1 – Graph of thickness (h) of oil product spot from the time of action (t) of biodestructor:
a – sample No. 1; b – sample No. 2; c – sample No. 3; d – sample No. 4

Thus, we see that the quality and time of adsorption of oil products from the surface of water depends on the amount of sorbent.

The plot of oil slick thickness versus sorbent is shown in figure 2.

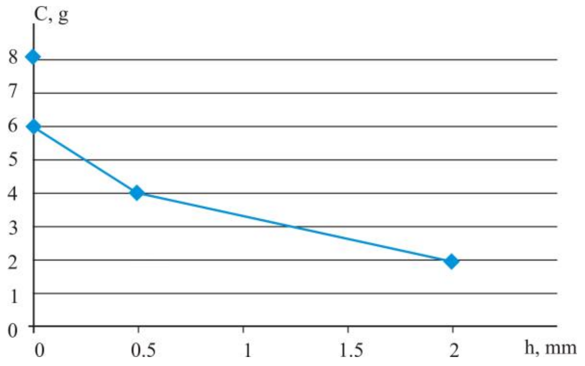

Figure 2 – A graph of the dependence of the oil slick thickness of the oil product from the amount of biodestructor

The elimination of oil pollution is a task of rapid response. The faster the spray sorbent is sprayed over the surface, the more efficient the adsorption of the oil product will be, the smaller the area of the oil slick will be. To effectively solve the problem, it is necessary not only to clean the surface of petroleum products of high quality, but also to reduce cost of events. Therefore, we will conduct an experiment using a small amount of sorbent, while increasing the reaction time. We investigate samples: No. 1 in which 2 g of a biodestructor and No. 2 in which 4 g of a biodestructor.

When observing, you can see how the thickness of the oil slick changes over time. The reaction in sample No. 2 is somewhat faster than in sample No. 1. After five hours, in sample No. 1 and No. 2 an equilibrium of reactions is observed — the slick thickness of the oil product has decreased by 1 mm. Further, the reaction rate decreases markedly. At the end of 24 hours, we observe the following changes:

– in sample No. 2, the slick thickness of the oil product is 1 mm;

– in sample No. 1 – 2 mm.

The graph of the oil product slick thickness change over time in samples No. 1 and No. 2 is shown in figure 3.

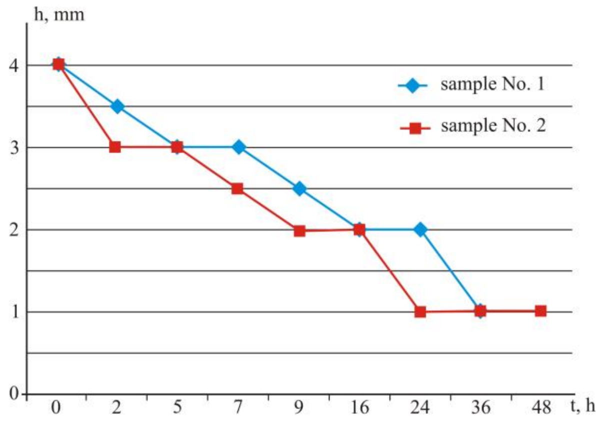

Figure 3 – Graph of changes in the thickness of the oil slick over time

In sample No. 2, the adsorption of petroleum products occurs faster than in sample No. 1, that is, the rate of adsorption depends on the amount of sorbent. At the end of 24 hours, the reaction in sample No. 2 is terminated, while in sample No. 1, the reaction stopped after 36 hours. Thus, the biodestructor has a saturation limit when the process of adsorption of petroleum products is terminated. At the same time, the biodestructor swells due to saturation with oil product.

After removing the sorbent, we have the following results:

– the greater the amount of biodestructor used to eliminate the oil slick, the faster the adsorption occurs;

– the quality of adsorption does not depend on the time the sorbent stays on the spot;

– the use of a biodestructor for the elimination of oil pollution from the water surface is advisable as an additional purification stage, aimed at the adsorption of thin oil slicks in large-scale man-made disasters.

Since the study observed only the sorption properties of the biodestructor, but not the destruction of the petroleum product, an electron microscopy study was conducted on the presence of microorganisms in the biodestructor under study.

It is known that microorganisms attached to a solid base (peat) are in an immobilized state in a biodestructor in a dry form, and when they enter the aquatic environment they must be active. Therefore, two samples were subjected to the study: a dry biodestructor and a waste biodestructor, taken from the water surface after adsorption of petroleum products. The study was conducted using a scanning electron microscope with a low vacuum chamber and with a REM-106 energy dispersive microanalysis system. Two samples were examined in a low-vacuum chamber in reflected electrons. In figures 4 – 9 presents the results.

In figure 4, at a magnification of 100 times, a sorbent pore is clearly visible on a 100 micron size area. In the reflected spectrum, in the center of the picture you can see the bacteria. When considering the spent sorbent, in addition to the pores filled with oil, it was not possible to consider anything in the low vacuum of reflected electrons. A shot of the spent biodestructor at a magnification of 500 times over a 100 micron area is shown in figure 5. Further consideration of the samples with a larger increase was not possible, since the sample began to deform. In order to examine the dry sorbent at high magnification, sample preparation was carried out: a thin layer of copper up to 100 nm thick was sprayed onto the dry biosorbent sample. The sprayed sample was examined under high vacuum in secondary electrons.

Figure 6 shows a shot of a dry biodestructor at a magnification of 2000 times over a 20 micron area. The photo clearly shows the pores, there are small inclusions. The study of another part of the sample with an increase of 1,500 times in the area of 20 microns showed the presence of various kinds of spherical inclusions (figure 7), which indicates the presence in its composition of agricultural waste.

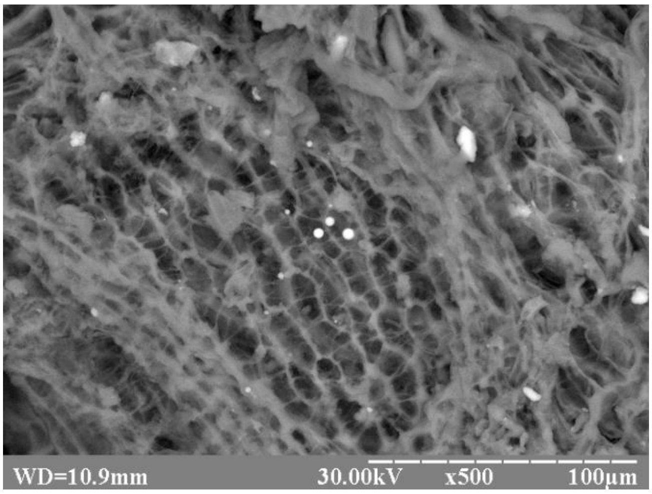

Figure 4 – A shot of the dry biodestructor taken with an electron microscope

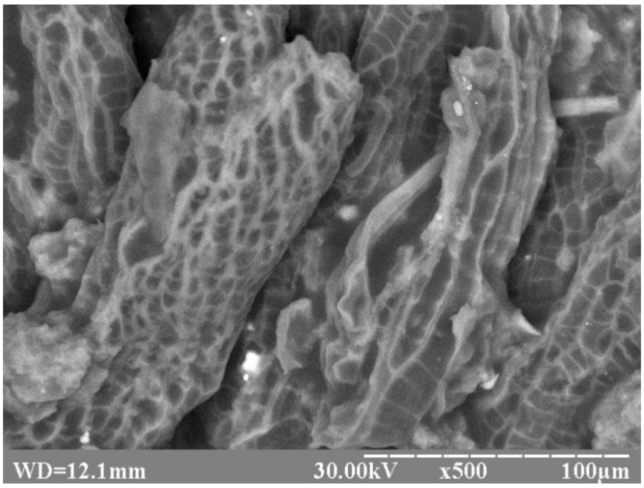

Figure 5 – A shot of the spent biodestructor at a magnification of 500 times

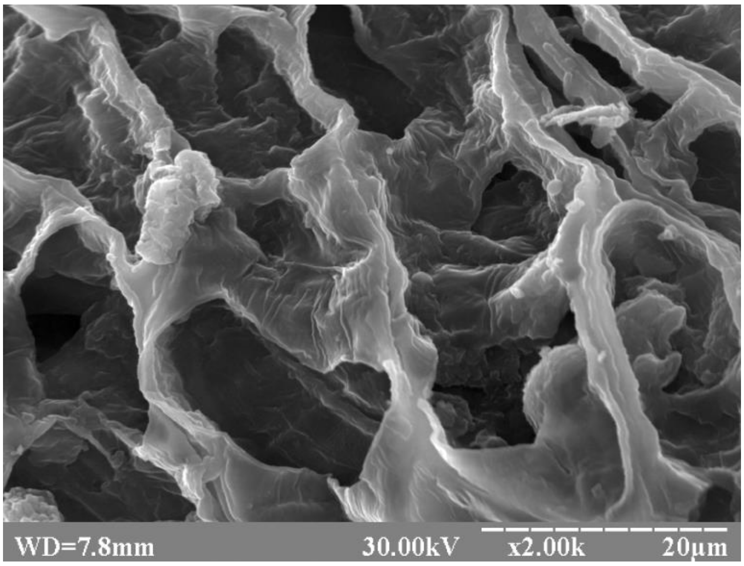

Figure 6 – A shot of the dry biodestructor at a magnification of 2000 times over a 20 micron area

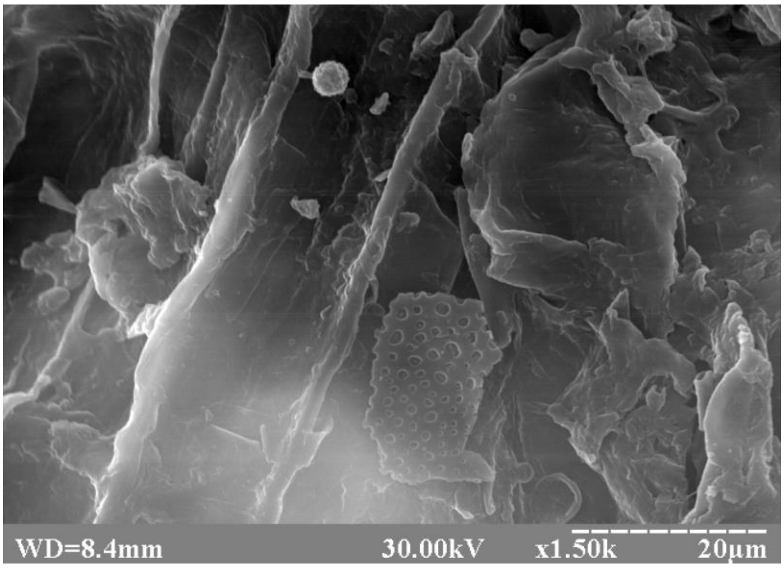

Figure 7 – A shot of another part of the sample dry biodestructor at a magnification 1,500 times in the area of 20 microns

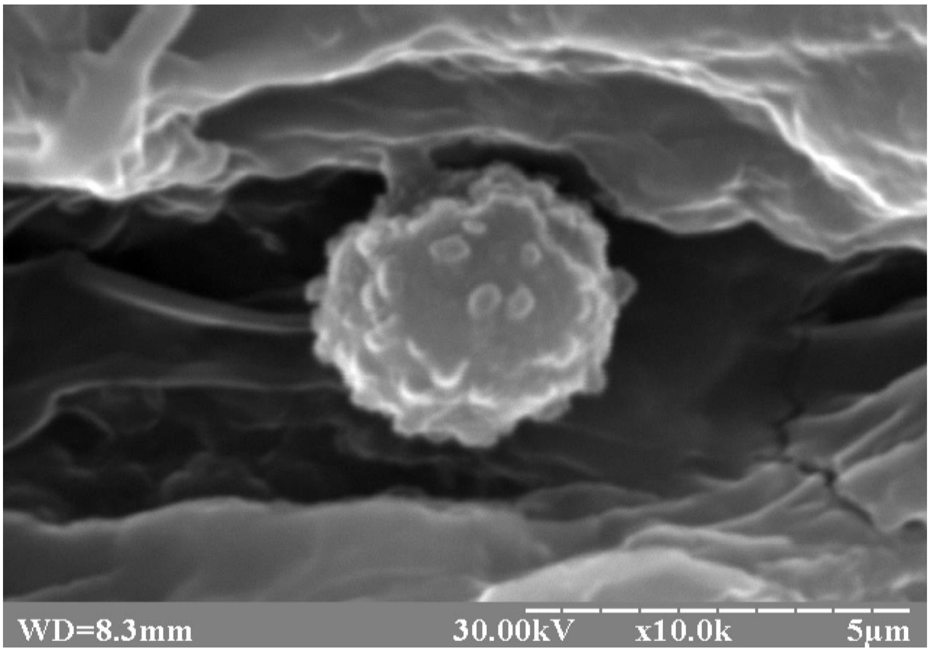

Figure 8 – A bacterium attached to a solid base in the sample of biodestructor
(a shot taken using an electron microscope with a magnification of 10,000 times)

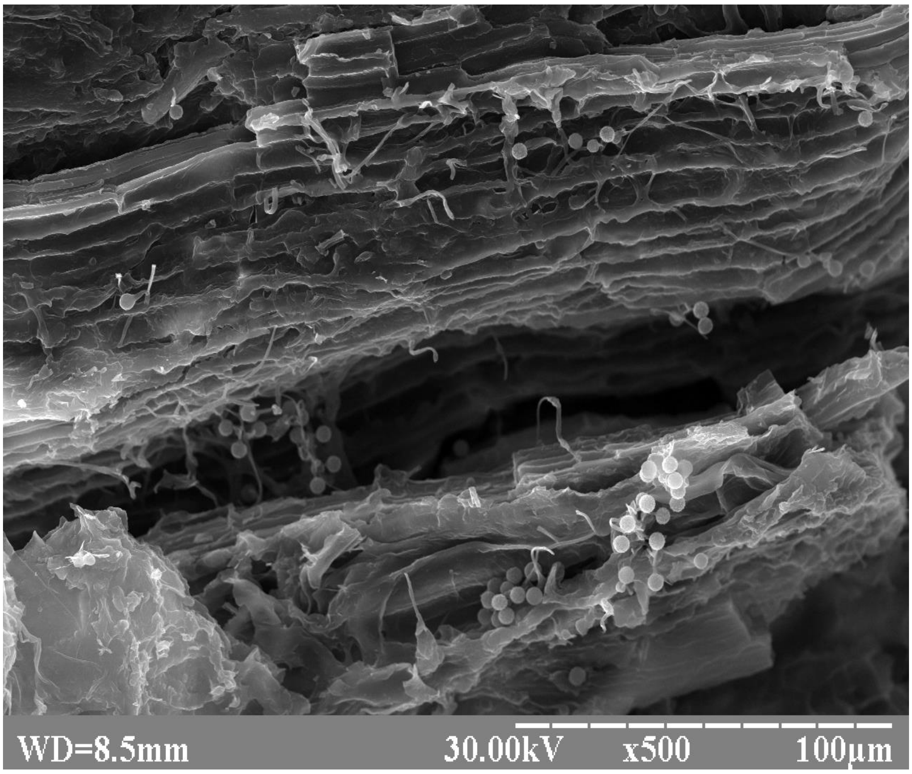

Figure 9 – A cluster of spherical microorganisms in the sample of biodestructor

In figure 8, with a magnification of 10,000 times, a bacterium attached to a solid base is clearly visible in a 5 micron area. At a magnification of 500 times, a cluster of spherical microorganisms can be seen in a 100 micron area (figure 9), but their distribution is uneven in the biodestructor.

The study showed that the ecological efficiency of the use of such a sorbent cannot be at a high level, since there is an uneven distribution of microorganisms and their accumulations. At the same time, the required number of bacteria (10^7 per 1 g of substance) is not ensured. That is, the use of the investigated biodestructor for emergency response with the spill of oil and oil products is not effective.

Conclusion and recommendations.

According to the research we have the following conclusions:

– the greater the amount of biosorbent used to eliminate the oil slick, the faster the adsorption occurs;

– the quality of adsorption does not depend on the time the sorbent stays on the spot;

– the use of biodestructor for the elimination of oil pollution from the water surface is advisable as an additional purification step, aimed at the adsorption of thin oil stains.

This means that it is not efficient to use only biological methods for cleaning water from oil in large-scale man-made emergencies.

It should be noted that in this study, the analysis of the effectiveness of a biodestructor was carried out for use in water, the temperature of which is 22...25 °C. This means that conclusions were obtained for the use of a biodestructor in the warm season. However, emergency situations can occur during the cold season, when the temperature is much lower.

As noted earlier, the reactions of oil with water occur differently, depending on the chemical composition of oil and its derivatives. Moreover, the environmental consequences also depend on the temperature of air and water [14].

This will allow the development of effective technologies that will prevent adverse environmental consequences for the living components of the seas and oceans in case of emergencies.

Another area of research should be the study of the possibility of creating, developing and researching the effectiveness of the use of complex measures to eliminate oil spills. Such measures should first of all ensure the rapid delivery of the biodestructor to the emergency zone, as well as combine mechanical methods of collecting oil and the ability of microorganisms to ensure the destruction of oil.

As mechanical methods for the elimination of oil pollution from the water surface, oil skimmers of various designs are widely used. The highest efficiency of such devices is achieved in the first hour after the spill. This is due to the fact that the thickness of the oil layer remains quite large. The efficiency of mechanical devices reaches 80...90 %. However, they are ineffective in the elimination of oil, which spread out as thin slick on the water surface or passed into the emulsified state. At the same time, when the mechanical collection of spilled oil is not possible, then apply biodestructor effectively. Thus, the acceptable effectiveness of ensuring environmental safety in case of emergency situations with oil spills can be achieved by applying integrated protection measures natural waters (seas, oceans etc.).

As an example, may be recommended a combination of a floating structure on which a skimmer and a device for spraying a biodestructor are installed. At the same time, a skimmer intake [19, 20] collects oil from the sea surface, directing it to a collection tank. Mechanisms of oil drainage from the surface of the water include oleophilic systems based on oil sticking to the moving surface, suction systems, gravity drainage systems and systems that lift oil from the surface. The oleophilic skimmer uses materials that attract oil and repel water. Oil sticks to the surface of the material. After the release of water, the oil is squeezed out of the oleophilic material and pumped into a settling tank, from which it is transferred to a storage tank. Their use provides the maximum ratio of the amount of oil collected and collected separately or together with oil water, known as the coefficient of oil intake. They are most effective. The working body of the oleophilic skimmer are brush rollers. Such brush rollers work effectively with any thickness of the oil layer and provide a minimum percentage of water collection. Also, containers with a biodestructor for spraying are attached to the floating structure from different sides.

In this case, the main cleaning of the water surface will occur during the operation of the skimmer, and after-treatment - with a biodestructor. The quality of cleaning will depend on the speed of decision making on spill response, as over time, oil spreads over the surface, contaminating clean areas, evaporating from the surface, polluting the atmosphere, settles to the bottom and emulsifying with water, making it difficult to eliminate the spill from the sea.

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Conflicts of Interest.

None of the authors have any potential conflicts of interest associated with this present study.

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В. Вамболь, Г. Крусір, К. Нужна, Е. Зайцева, А. Калужських

ДОСЛІДЖЕННЯ ЕФЕКТИВНОСТІ ВИКОРИСТАННЯ БІОДЕСТРУКТОРІВ ДЛЯ ЛІКВІДАЦІЇ НАФТОВИХ ПЛЯМ З ВОДНОЇ ПОВЕРХНІ ПРИ НАДЗВИЧАЙНИХ СИТУАЦІЯХ

Одним з основних факторів, що формують несприятливий стан водного середовища, є судноплавство і діяльність морських торговельних портів. Особливу небезпеку становлять надзвичайні ситуації з розливом великої кількості нафтопродуктів. Щорічно близько 10 мільйонів тонн нафти і нафтопродуктів потрапляють на поверхневі води. В цьому дослідженні подані результати експерименту з ефективності використання сорбенту-біодеструктору для ліквідації нафтових забруднень у надзвичайних ситуаціях. Аналіз основних видів біодеструкторів, які використовують в Україні для ліквідації розливів нафти з поверхні води, проводили аналітично, з використанням відкритих джерел інформації. Визначення ефективності використання біодеструкторів проводили у лабораторних умовах. Експериментально спостерігали зміну товщини шару нафтопродукту залежно від часу дії біодеструктору з різною його кількістю. Дослідження наявності біологічних компонентів у складі біодеструктору проводили на скануючому електронному мікроскопі з нізковакуумною камерою РЕМ-106. Два зразка були досліджені в нізковакуумній камері в відображених електронах. Визначено, що саме іммобілізовані бактерії-деструктори вуглеводнів нафти широко використовуються в сучасних екологічних біотехнологіях. Експериментально встановлено, що кількість адсорбованих нафтопродуктів не залежить від часу перебування сорбенту на забрудненій ділянці. Використання біодеструктору для ліквідації нафтових забруднень з поверхні води при великомасштабних техногенних катастрофах доцільно як додаткова стадія очищення, спрямована на адсорбцію тонких нафтових плям. Дослідження з використанням скануючого електронного мікроскопа з камерою низького вакууму і системою енергодисперсійного микроанализу РЕМ-106 показало, що екологічна ефективність використання сорбенту-біодеструктору не може бути на високому рівні, оскільки існує нерівномірний розподіл мікроорганізмів і їх скупчень. У той же час необхідну кількість бактерій у препараті біодеструкторі (10^7 на 1 г речовини) не забезпечується.

Ключові слова: екологічна безпека водойм; аварійна ситуація з розливом нафти; ефективність біодеструктором.

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В. Вамболь, Г. Крусир, К. Нужная, Е. Зайцева, А. Калужских

ИССЛЕДОВАНИЯ ЭФФЕКТИВНОСТИ ИСПОЛЬЗОВАНИЯ БИОДЕСТРУКТОРОВ ДЛЯ ЛИКВИДАЦИИ НЕФТЯНЫХ ПЯТЕН С ВОДНОЙ ПОВЕРХНОСТИ ПРИ ЧРЕЗВЫЧАЙНЫХ СИТУАЦИЯХ

Одним из основных факторов, формирующих неблагоприятное состояние водной среды, является судоходство и деятельность морских торговых портов. Особую опасность представляют чрезвычайные ситуации с разливом большого количества нефтепродуктов. Ежегодно около 10 миллионов тонн нефти и нефтепродуктов попадают на поверхностные воды. В данном исследовании представлены результаты эксперимента по эффективности использования сорбента-биодеструктора для ликвидации нефтяных загрязнений в чрезвычайных ситуациях. Анализ основных видов биодеструкторов, которые используют в Украине для ликвидации разливов нефти с поверхности воды, проведен аналитически, с использованием открытых источников информации. Определение эффективности использования биодеструкторов проводили в лабораторных условиях. Экспериментально наблюдали изменение толщины слоя нефтепродукта в зависимости от времени действия биодеструктора с различным его количеством. Исследование наличия биологических компонентов в составе биодеструктора проводили на сканирующем электронном микроскопе с низковакуумной камерой РЕМ-106. Два образца были исследованы в низковакуумной камере в отраженных электронах. Определено, что именно иммобилизованные бактерии-деструкторы углеводородов нефти широко используются в современных экологических биотехнологиях. Экспериментально установлено, что количество адсорбируемых нефтепродуктов не зависит от времени пребывания сорбента на загрязненном участке. Использование биодеструктора для ликвидации нефтяных загрязнений с поверхности воды при крупномасштабных техногенных катастрофах целесообразно как дополнительная стадия очистки, направленная на адсорбцию тонких нефтяных пятен. Исследование с использованием сканирующего электронного микроскопа с камерой низкого вакуума и системой энергодисперсионного микроанализа РЕМ-106 показало, что экологическая эффективность использования сорбента-биодеструктора не может быть на высоком уровне, так как существует неравномерное распределение микроорганизмов и их скоплений. В то же время необходимое количество бактерий в препарате биодеструкторе (10^7 на 1 г вещества) не обеспечивается.

Ключевые слова: экологическая безопасность водоемов; аварийная ситуация с разливом нефти; эффективность биодеструктора.