

OIL SPILLS IN THE OCEANS: MEANING, CAUSES, CONSEQUENCES, CONTROL MEASURES AND METHODS OF ELIMINATION

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Abstract

This paper classifies possible sources of oil and oil products spills, possible risks of oil spills during its production on land and offshore, as well as during storage and transportation of oil and oil products due to accidents. An overview of existing techniques and sorbents for the elimination of hydrocarbons from the water surface is given, their characteristics and the principle of operation of devices that are currently used for elimination of oil spills are studied. An original method for liquidating hydrocarbon spills using a natural sorbent - natural sheep wool - has been proposed. The carried out fluorescent diagnostics of the process of water purification from oil contamination with a sorbent based on sheep wool showed that wool absorbs up to 61% of oil, depending on its initial concentration and the amount of sorbent.

Keywords: oil spills, modeling, response, sorbents

1. INTRODUCTION

Oil is the most valuable raw material, without which modern civilization is impossible. However, the processes of extraction, transportation, storage and processing of oil and oil products very often become sources of environmental pollution, which can become catastrophic.

Environmental disasters occur when oil pipelines break down, when soil and water sources are polluted with oil over large areas. Fires and sabotage at pipelines and oil storages have a serious impact on the ecological situation. As a result, the environment (air, water, soil and vegetation) is polluted with oil products, the animal world suffers, and the ingress of oil products into drinking water directly threatens the health of the population.

Among the numerous harmful substances of anthropogenic origin that enter the environment, oil products occupy one of the first places. The ingress of oil and its components into the environment causes a change in the physical, chemical and biological properties and characteristics of the natural habitat, disrupts the course of natural biochemical processes. During the transformation of oil hydrocarbons, even more toxic compounds than the original ones, which have carcinogenic and mutagenic properties and are resistant to microbiological degradation, can be formed.

Crude oil and its derivatives are an extremely complex mixture of many chemical compounds. It contains around 300 hydrocarbons, with individual concentrations varying by volume from as low as a few per cent. The physical and chemical properties of the oil vary considerably from field to field, and different grades of oil vary in their paraffin, tar and sulphur content. Crude oils vary considerably in density, from very light kg/m^3 to very heavy kg/m^3 . The viscosity of oil depends on its chemical and fractional composition, especially the tar content, and also varies widely [1]. With an annual pollution volume of the World Ocean of 6-12 mln. tons, the pollution sources are distributed as follows: sea transport (wash water, docking, leakages, loading-unloading operations, etc.) - 35 %; industrial discharge - 13 %; sea oil extraction - 1.5 %; river discharge - 32 %; inflows from the atmosphere - 10 %; natural oil sources - about 10 % [2]. The relatively small amount of oil entering the ocean directly from marine production and from natural sources attracts attention, see Table 1.

Analysis of sea surface imagery shows that areas of global oil pollution coincide with shipping routes and the mouths of major rivers. Large-scale pollution zones include not only the shelf, but also some areas of the open part of the sea. Average pollution in such seas as the Barents, Baltic, Black, Caspian

and Mediterranean exceeds the maximum permissible concentration (MPC) several times over. In the course of long evolution, mechanisms of assimilation, self-purification of water bodies from hydrocarbons have developed. However, in recent years there has been a significant excess of anthropogenic inputs of oil to the ocean over the natural volumes.

Source	Contribution, %
1. Urban wastewater	34
2. atmospheric precipitation	14
2. Maritime operations	12
3. Industrial effluent	10
5. Urban flushes	8
6. Tanker operations	7
7. Coastal oil refining	6
8. Tanker accidents	6
9. Oil extraction	2
10. Other	1

Table 1. Relative contribution of anthropogenic sources of marine oil pollution

2. MATERIALS AND METHODS FOR CLEANING THE OCEAN FROM OIL POLLUTION

Currently, there are several methods for cleaning oil pollution in open water and in water areas. One of the most common methods is the mechanical collection of oil products after the containment of the slick by booms, which provide a sufficient thickness of the oil layer for collection. This method has a number of advantages, namely: a spot surrounded by such a fence can be towed to a more convenient, and most importantly, safe place to work [3, 4].

Along with the mechanical method, the thermal liquidation method based on oil burning is widely used. However, this method has a serious disadvantage: its scope is limited to a short period of time immediately after the leak - until the layer has sufficient thickness and an oil-in-water emulsion has not formed.

The third method is the physicochemical method, it is based on the use of dispersants and sorbents. The use of this method assumes that mechanical oil recovery is not possible. For example, when there is an immediate threat to ecologically sensitive areas or the thickness of the oil film is very small.

At the moment, the most accurate method that allows fine cleaning of water areas is the biological method. This method is based on the use of special microorganisms that process oil and oil products [5]. The biological method is often used when the possibilities of other methods (physico-chemical, mechanical and other methods) have been exhausted.

Properties of sorbents for oil recovery from water surfaces

Oil sorbents include a wide variety of organic, inorganic and synthetic products designed to remove oil in preference to water removal. Their composition and characteristics depend on the material used and their intended use in spill response operations.

Although widely used in spill response, sorbents must still be used cautiously to reduce their unnecessary and excessive use, which can pose significant logistical challenges in terms of secondary contamination, waste collection, storage and disposal. All these factors lead to a substantial increase in

the costs of clean-up activities. This is especially true for synthetic sorbents, which should be used in moderation and with maximum efficiency to reduce subsequent waste disposal difficulties.

Sorbents are generally most effective in the final stages of shoreline clean-up, and for removing small puddles of oil that cannot be easily removed by other clean-up methods. Sorbents are not suitable for offshore applications and are generally less effective for more viscous oil products such as heavy fuel oil and oil products that have weathered and emulsified, although special sorbents have also been developed for viscous oil products.

In order to act as a sorbent, the material must attract oil without interacting with water, i.e. it must be oleophilic and at the same time hydrophobic. Sorbents can act on the principle of adsorption (surface absorption) or, less frequently, on the principle of absorption (absorption). In adsorption oil is selectively attracted to the surface of the substance, while absorbents absorb the oil or other liquid to be removed into themselves. Most products offered for oil spill response are adsorbents, and few are true absorbents.

Liquids penetrate the solid absorbent (absorbent) material through a process similar to capillary movement, causing the absorbent to swell. The liquids are connected to the material in such a way that they do not leak out and cannot be pressurised. Absorbents used in pollution removal are made from man-made polymers with a large surface area to facilitate rapid absorption. Because absorbents can reduce the surface area of a liquid, they can be used with volatile products. In theory, absorbents are capable of removing light distillate fuels and some crude oils, but the time required for absorption may be longer than acceptable or required, and they are therefore more suitable for removing low-viscosity liquids and spilled chemicals.

For successful adsorption, the oil must wet the material and therefore spread over its surface in preference to water. A liquid wets a solid if its surface tension coefficient is less than the critical surface tension coefficient (σ_c) of the solid. Therefore, in order for the sorbent to meet the required criteria, it must have a value of σ_c below the σ_c value of water and above the σ_c value of oil. The surface tension coefficient of seawater is about 60-65 mN/m; this characteristic for oil varies with the composition of the oil product, but is usually close to 20 mN/m.

Many natural and synthetic solids have suitable σ_c values. Inorganic solids that do not have the desired characteristic can be modified by applying various surface treatments, including heating, to create the desired condition. An example of such a product is expanded vermiculite. For a number of materials, in particular sorbent foams and loosened fibres, the oleophilic properties can be improved by pre-wetting or pouring in oil.

In some materials adsorption occurs through capillary action. While it depends on the relative surface tension of the solid and liquid, the viscosity of the oil also has a significant influence on the rate of penetration into the sorbent structure. The oil penetration rate can be high (on the order of a few seconds) for low-viscosity oil products, such as light oil, or low (a few hours) to negligible for high viscosity oil products, such as heavy fuel oil or weathered oil products.

Capillary action is particularly important for foam-based sorbents. Fine-cell foams easily collect low viscosity petroleum products, but the pores quickly become clogged with thick petroleum products. Conversely, foams with a large-cell structure are effective against viscous oil products, but are not able to retain low viscosity oil products effectively.

At present about two hundred sorbents are produced and used worldwide for oil and petroleum product spill response. These sorbents can be divided into four main types: inorganic, synthetic, organomineral and natural organic. In their turn, their quality and efficiency are determined by main characteristics such as: capacity in relation to oil, degree of hydrophobicity, buoyancy after oil sorption, degree of hydrophobicity, availability of mechanisms for sorbent regeneration or utilization, possibility of oil desorption.

The data in Table 2 - properties of industrial sorbents for oil recovery - according to manufacturers, show which types of sorbents are available in the Russian market: animal or vegetable products, mineral products, synthetic products and polymers.

Natural organic sorbents are widely covered in scientific studies. In particular, materials based on rice hulls, lignite, wool, walnut shells, peat, straw, graphite have been considered as such [6 - 11].

Here is a description and technical characteristics of the most popular sorbents currently used for the elimination of oil products from the water surface.

Material from	Oil capacity, kg/kg	Water absorption, kg/kg	Spin rate, %	Consumption of sorbent to collect 1 tonne of oil, kg/t
Polypropylene (fibre)	13-25	3-6	70-80	40
Urea Styrofoam	40-60	5-10	60-80	25-30
Urea-formaldehyde resin	30-50	4,6-10,0	70-80	33
Vermiculite	8-12	2-17	-	100-120
Peat	6-7	1,6	0	110
Moss	2-8	2	10-25	213
Graphite	40-60	0,2	-	25-30
Wool	6-9	1-4	65-80	150-270
Cellulose	7-9	5-7	-	100-200
Bacteria	5-10	-	-	200

Table 2. Properties of industrial sorbents for oil recovery

One of the best sorbents is natural sheep wool. The authors of the paper [2] found that untreated sheep wool weighing $m_w = 1$ gram is guaranteed to absorb from 6 gram of oil and other hydrocarbons (diesel fuel, sunflower oil). Studies of the sorption capacity of wool were carried out in a liquid at rest and in rotation, consisting of a mixture of water and various hydrocarbons (sunflower oil, diesel fuel, crude oil). On the surface of a two-component liquid containing $V_o = 50$ ml of an immiscible impurity, various amounts of wool fibers were placed. Depending on the weight of the wool used, the values for the typical surface cleaning rate and the residual surface area covered with the immiscible additive varied. Sequential images of the oil absorption process are presented (Fig. 1), illustrating its dynamics.



Fig. 1. Evolution of the oil distribution pattern over the water surface ($m_w = 1$ gram):

$t = 0, 80, 110$ s

After placing the selected amount of sorbent material on the water surface, the sorption process began, which violates the uniformity of the thickness of the oil spot on the free surface. The introduction of sorbent water onto the surface of a two-layer oil-water system leads to the formation of flows that are visible to the naked eye, under the influence of which the distribution of pollution changes, the shape of the spot on the surface changes.

The characteristic times inherent in the absorption of oil by wool are tens of seconds. For the one shown in Fig. 2 cases, the characteristic time of ϵ times decrease in the surface coverage area with oil, calculated from the approximation of the data obtained on the basis of the photometry method, is 63.4 ± 4.9 s; 1 ± 0.4 s.

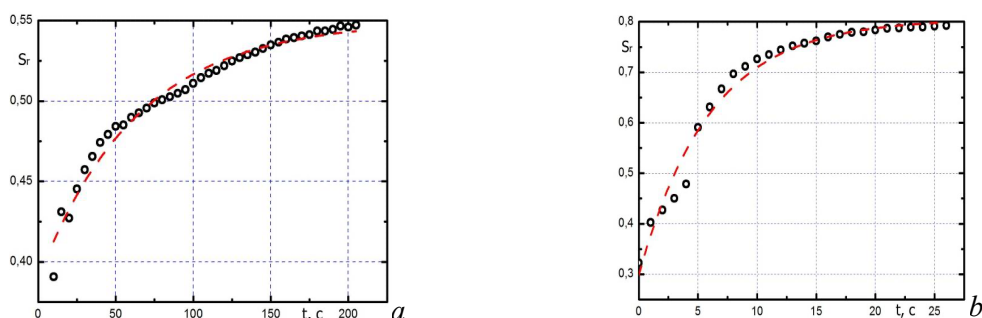


Fig. 2. Time dependence of the area free from surface contamination (in relation to the size of the initial spot, $V_o = 50$ ml): a) $m_w = 2$ g; b) $m_w = 3$ g

The graphs (Fig. 2) show the relative areas of the cleaned water surface: the ratio of the initial area of the hydrocarbon spot to the residual area of contamination is measured, and then the resulting value is subtracted from unity. The captured oil binds to the fibers of sheep's wool quite firmly, and the formed compact volume is easily amenable to mechanical extraction from the cuvette.

Device for collecting liquid hydrocarbons (oil, diesel, etc.) from the water surface under laboratory conditions

As a result of these experiments, a prototype of a device for collecting liquid hydrocarbons from the water surface has been developed and will be used to clean up surface spills of various hydrocarbons in water bodies.

The essence of the claimed utility model is explained by an example of its implementation and a drawing which schematically shows the general view of the device (Fig. 3).

The device for separation from water and collection of liquid hydrocarbons includes a frame made of hollow elements or mesh 1, filled with natural sheep's wool 2 (washed or unwashed). The frame can be made of various geometric shapes - in the form of a mat in the form of a rectangular parallelepiped (as shown in the drawing) or a mat. The wool volume 2 is divided by a watertight partition 3 located perpendicular to the direction of the smallest dimension of the frame.

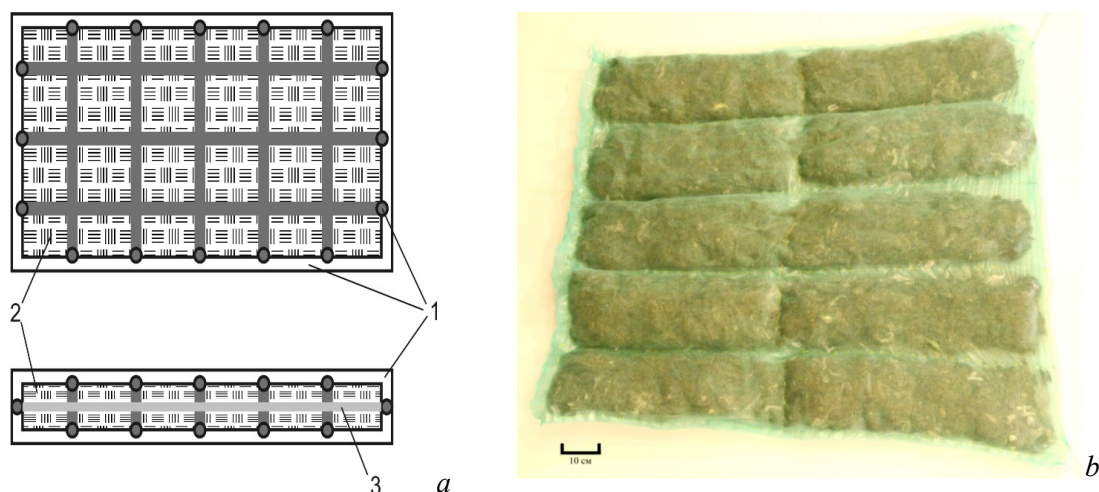


Fig. 3. Sketch model of a device for the collection of liquid hydrocarbons from the water surface: *a*) - scheme, *b*) – photo

The watertight partition is made of polyethylene or fluoroplastic and the frame of the product is made removable. Cellulose fibre in an amount from 10 to 70 % of the wool volume has been added to one part of the unit divided by the partition.

The use of readily available natural sheep's wool, significantly increases the efficiency of the unit. Currently, much of the wool is destroyed due to lack of use (which is a waste product of the meat sheep industry), which significantly reduces the cost of the device. Wool is hydrophobic, almost does not absorb moisture and has a high sorption capacity in relation to hydrocarbons, absorbing them from mixtures with water and even emulsions. Wool has also been found to have the unique ability to catalyse coalescence of liquid hydrocarbons, and a rare coalescence property such as auto-adhesion.

Dividing the wool volume with a watertight partition perpendicular to the direction of the smallest frame size will allow the wool fibres to be used to the fullest extent possible for hydrocarbon adsorption, with both hydrocarbon and water absorption not occurring on the other side of the device, allowing effective use of the other side of the device when flipping, and also increasing the overall buoyancy of the device.

In particular cases of implementation of the device, in order to increase the efficiency of liquid hydrocarbons collection, it is advisable to add cellulose fibre. Adding cellulose fibre to the wool will increase its sorption capacity, as cellulose fibre absorbs hydrocarbons 9-10 times its weight. Also, the addition of cellulose fibre will increase the temperature range of the device, as water penetrating the capillaries of cellulose fibre freezes at temperatures well below 0°C.

The device for collecting liquid hydrocarbons from the water surface can be used repeatedly: extracted after filling the cells with hydrocarbons and returned to continue collecting after removing the collected material (oils, oil products, and other substances), for example by spinning. Experiments have shown that the ability of natural wool to sorb hydrocarbons is retained after the excess material collected has been removed.

Such devices are preferable when cleaning and removing oily liquids, when the use of heavy equipment is ineffective, or in combination with the latter for post-treatment. The developed device can also be used as a preventive means at potentially hazardous facilities: oil depots, motor transport enterprises, air and sea transport enterprises and any enterprises, whose activity is connected with the use of liquid hydrocarbons, accompanied by potential leaks and spills. The device will be capable of operating in two modes: from a surface vessel and from the shore of a body of water. The device's cycle of use includes cleaning of the collected hydrocarbons and reuse (at least three times). In case of

long-term storage of the device (more than 1 month) it must be ensured that there is no contact with the external environment (vacuum packing).

The main advantage of the developed device for the collection of liquid hydrocarbons from the water surface is the relatively low cost and environmental safety of its use, as well as the possibility of multiple (2-3 times) use.

To test the "Liquid Hydrocarbon Collection Device" in laboratory conditions, four pools of different sizes were purchased: three made of glass, measuring 0.4×0.4×0.4 m, 0.6×0.6×0.6 m, 1.2×0.8×0.7 m, respectively, and the fourth, inflatable, measuring 3×4 m, which were filled with tap water. The hydrocarbons used were sunflower and aviation oils, diesel fuel (summer and winter) and oil (Siberian Light grade, density 845 kg/m³(36.5 API), sulphur content 0.57%).

We made samples of "Liquid hydrocarbon collecting device" of three sizes: 0.2×0.4 m, 0.4×0.8 m, 1×2 m several copies of each size, which are net mats, filled with natural sheep wool (Table 3). The wool volume is divided by a waterproof polyethylene partition, with cellulose fibre added to one of the parts in an amount from 20% of the wool volume (Fig. 3). To clarify the terminology, the word 'mats' will be used hereafter when describing the experiments.

Size	№1	№2	№3
Overall dimensions (error), m	0,2×0,4 (0,02)	0,4×0,8 (0,05)	1,0×2,0 (0,05)
Weight of the product, g	195 ± 13	515 ± 36	3300 ± 230
Mass of basic sorbent (sheep's wool), g	125 ± 8	320 ± 21	2010 ± 170
Weight of additional sorbent (cellulose fibre), g	13 ± 2	33 ± 5	200 ± 35

Table 3. Liquid hydrocarbon collecting device characteristics

To test the "Liquid Hydrocarbon Collection Unit" under laboratory conditions, fabricated samples (mats) were placed on the surface of resting water to which oil, diesel fuel (winter and summer) in various concentrations had been previously added. Prior to this, liquid samples were taken to determine the degree of purification (Table 4. Liquid samples).

The samples tested were left on the water surface for 24 hours, after which the mats were removed, weighed, wrung out using a wringer (self-made as a washing machine wringer attachment on a 200 litre drum. As the material passes through the rollers of the machine, the liquid drains by gravity to the bottom of the drum) and is placed in a vacuum pack for further processing or disposal.

It should be noted that after 24 hours none of the test samples had drowned. After the experiments, water samples were taken again to determine the degree of purification from hydrocarbon contaminants. The samples were analysed by fluorescence spectroscopy (fluorimetry) with calibration by Raman scattering of solvent - water or hexane. The spectra were taken on a Horiba Jobin Yvon Fluoromax-4 spectrofluorimeter [12].

No. of Samples	Name	Concentration mg/l, notes
1	Diesel (summer fuel) + water	25.4
2	Diesel fuel (winter) + water	12.8
3	Oil + water	2.02
4	Diesel (summer fuel) + water	41

5	Diesel fuel (winter) + water	20.6
6	Oil + water	3.23

Table 4. Liquid samples

Determination of the effectiveness (degree) of oil or petroleum product treatment of water was carried out at two levels: (a) determination of the degree of purification without determining absolute values of oil or petroleum product (diesel fuel) concentration; (b) determination of absolute values of concentrations and degree of purification as the ratio of oil or diesel fuel concentrations after purification and before purification. In case (a), spectra were measured directly for the original samples - solutions of oil or diesel fuel in water - and after cleaning. The values of parameter F_0 for these samples were determined, and the degree of purification k was determined by the formula (1, a). In the case of (1, b) absolute values of C concentrations were determined by the extract (hexane) method. For this purpose, a calibration curve was preliminarily constructed - dependence of parameter F_0 for solutions of oil or diesel fuel in hexane on concentration C of calibrated prepared solutions. The degree of purification k was determined by the formula (1, b):

$$K = \frac{(F_0^{Before} - F_0^{After})}{F_0^{Before}} - \text{for option (a),} \quad (1, a)$$

$$K = \frac{(F_0^{Before} - F_0^{After})}{F_0^{Before}} - \text{for option (b),} \quad (1, b)$$

C is the concentration of oil or diesel fuel determined by the extractive method; the indices "Before" and "After" indicate samples before and after cleaning, respectively.

Fluorescence spectra taken directly for the aqueous solutions (Figure 4) and formula (1, a) were used to determine the degree of purification without determining the absolute concentration values. Figure 4 shows the fluorescence spectra of aqueous solutions diluted 400 times with respect to the initial solutions.

The excitation wavelength is 280 nm. The 'Background 1' and 'Background 2' spectra are spectra taken for 400 times diluted water without oil/oil product before measuring the spectra of the solutions before and after cleaning; their almost complete overlap indicates good quality sample preparation, in particular the dilution with distillate in the specified proportion.

As tap water was used in the purification experiment, a rather intense natural dissolved organic matter (NOD) fluorescence band was present in the spectrum, interfering with the determination of the oil/oil product fluorescence band intensities and the water CR. All three of these obstacles were eliminated by 400-fold dilution of the original samples with distilled water, for which the PSB band intensity was low (see "background" spectra in Figure 4 - spectra of original water diluted 400-fold with distilled water without oil/oil product). The spectra of the solutions before purification are marked as "Before", after as "After".

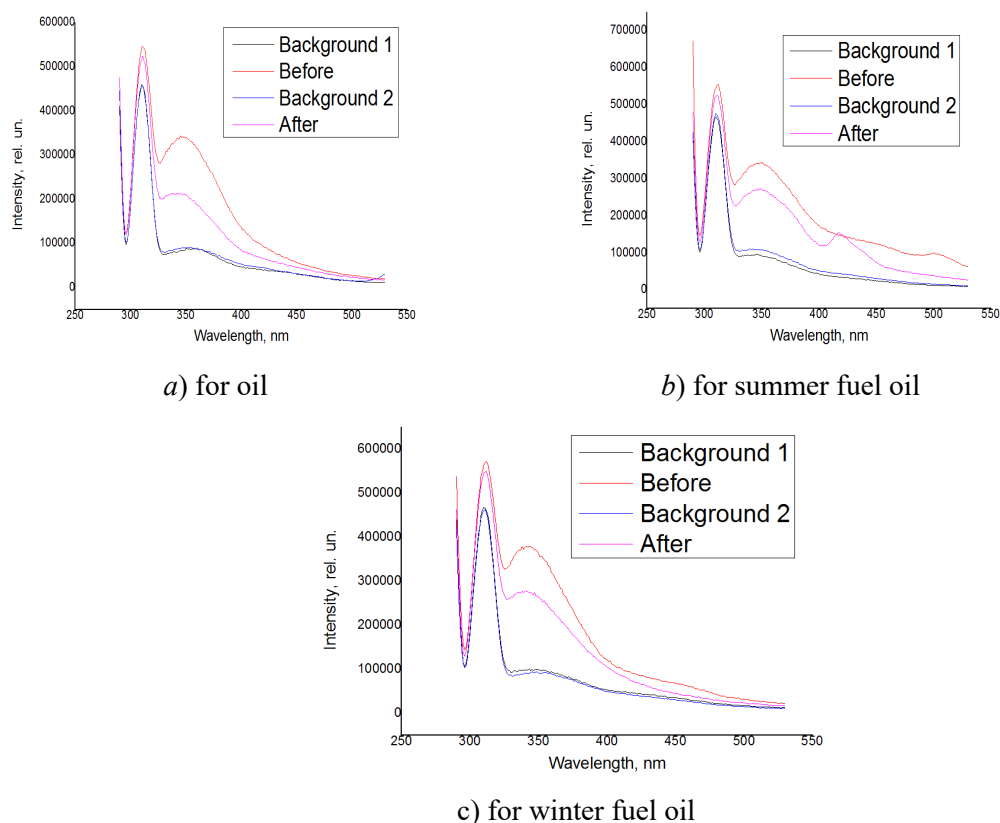


Fig. 4. Fluorescence spectra taken directly for aqueous solutions

The test results are given in Tables 5.

Type of contamination	Parameter $F_0^{\text{After}} / F_0^{\text{Before}}$	Degree of cleaning
Summer fuel oil, concentration 25.4 mg/l	0.66	34%
Winter diesel, concentration 12.8 mg/l	0.67	33%
Siberian Light oil, concentration 2.02 mg/l	0.45	55%
Summer fuel oil, concentration 41 mg/l	0.64	36%
Winter diesel, concentration 20.6 mg/l	0.63	37%
Siberian Light oil, concentration 3.23 mg/l	0.39	61%

Table 5. Water purification results

3. CONCLUSIONS

In the course of tests of a prototype device for collecting liquid hydrocarbons (oil, diesel fuel, etc.) from water surface in laboratory conditions it was shown that the prototype effectively collects hydrocarbon pollution (oil, diesel fuel, etc.) from water surface due to high wool sorption coefficient and its hydrophobicity and can be successfully applied for liquidation of surface spills of different hydrocarbons on water objects.

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