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# Biodestruction of lubricated motor oils in sewage water with the use of pilot biological installation

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## Abstract
This article presents the results of an experiment on the choice of technology for purification and final purification of wastewater of small sewage enterprises and large-scale productions from waste lubricating oils of mineral origin with a wide change in the pH of the medium, providing dissolved oxygen and biogenic elements. It is proved that a high degree of biodegradation of oil-contaminated effluents is achieved by the wide use of the newly created consortium of hydrocarbon-oxidizing microorganisms (HOM), which includes nine strains belonging to the genera: *Alcaligenes*(1 species), *Bacillus* (1 species), *Brevibacterium* (2 species), *Clostridium* (1 species), *Flavobacterium* (1 species), *Micrococcus* (1 species) and *Pseudomonas* (2 species). The association of this microorganismsis able to oxidize various fractions of oil ranging from n-alkalis, to asphaltenes, including mineral, semi-synthetic and synthetic oils of various origin. It has been established that the load change from 25 to 100 mg/dm$^3$ (COD from 450 to 650 mg/dm$^3$) when using lubricating oil in stock ROB almost does not affect the degree of biodegradation of the original pollution. During the contacting of the ON-NOVO consortium with the oil-containing waste liquid in the bioreactor and further in the secondary settling tank, with a total duration of 1.5 to 4.5 hours, the degree of effluent purification reaches up to 77.4%. With the addition of a normalized amount of nutrients in the amount of 20 mg/dm$^3$ (optimal zone), the degree of neutralization of waste water exceeds 86%. In terms of residual content of oxidized mineral oil, the cleaning intensity exceeds 94%.

## 1. Introduction
Currently, environmental protection from polluted wastewater is one of the main tasks. Actions for water purification from pollution will help to keep air and water clean. There is a lot of water on the globe, but there is very little pure fresh water. The water cycle in nature creates the necessary conditions for the existence of mankind on earth.

In recent years, the question of the purity of water and air has been raised in many world forums. To reduce the harmful effects of industrial and agricultural water use on the ecology of the globe, a deeper sewage treatment is necessary. The growth of cities, the rapid development of industry, the intensification of agriculture, a significant expansion of irrigated land, improvement of cultural and living conditions, and a number of other factors increasingly complicate the problem of water supply [1]. In connection with the annual increase in industrial potential and the growth in the output of industrial equipment, it is necessary to steadily increase the production of lubricants. With the growth of production and operation, inevitably increases the volume of wastewater due to ingestion of waste lubricant motor materials [2].

Lubricating motor oils get into the reservoirs in various ways: with storm and melt waters, discharge of industrial wastewater, etc. According to experts, approximately 10 million tons of lubricating oils enter the world ocean annually [3]. Lubricating oils, getting into the reservoirs, impede the gas exchange between the atmosphere and water. The national economy is utilized only 15-20% of the total volume of waste oils produced in our country and the rest of the oil (20%) is composed of industrial waste water and 40% is located in the objects of urbanization in the form of liquid waste, and the remaining percentage of waste oil enters the surrounding (water, soil) environment [4, 5].According to foreign researchers, oil-polluted drains exceed the volume of accidental emissions and oil losses during production, transportation and processing [6]. In this regard, the use of promising technologies for water purification from lubricants is very important.

Selection and application of the purification method of cleaning device generally depends on the physico-chemical properties of the contaminants, the requirements for the degree of fluid cleaning, the installation location and operating conditions of the equipment used.

Currently, there are many methods and techniques for purifying wastewater from oil contamination: mechanical method using oil separators; hydrocyclones and filters; physical and chemical method with coagulation and with the help of flotation method; chemical method using oxidation (ozonation and chlorination) and a biological method using the metabolic potential of hydrocarbon-oxidizing microorganisms (HOM) [7-10].

Recently, the biological method of purification of hydrocarbon contaminants, based on the use of microorganisms in the biodegradation of oils, has become a priority for virtually any quantities and concentrations of contaminants. This method is characterized as the most economical, efficient and harmless cleaning method.

The purpose of this study was to identify the ability of microorganisms to biodegrade mineral motor oils using a spray-settling bioreactor (SSB) and to study the biotechnological foundations of this process. From this it follows that we face the following tasks:

1. selection of the most environmentally friendly, resource-saving method of cleaning and additional treatment of oily wastewater;
2. development of technological schemes for the treatment and purification of various categories of oily wastewater in an industrial enterprise and agricultural facilities using the biological method;
3. testing on a semi-production installation of a spray-settling bioreactor (SSB) in laboratory and production conditions.

## 2. Material and Methods

A study on the treatment of industrial wastewater polluted with spent solar oil was carried out on a semi-production facility - a spray-settling bioreactor (SSB), created by Biotechnology Research and Production Company together with NPO Neftepromkhim LLC, Kazan. Model water was prepared with a volume of 700 liters with additions of solar oil in quantities of 25, 50, 75, 100 and 200 ml.

Solar oil is a mixture of hydrocarbons obtained by direct distillation of petroleum fractions, with a temperature range from 270 to 360 °C. This oil has a density of 830-860 $kg/m^3$, and the viscosity index is 5 - 9 $mm^2/s$ [11].

Strains of heterotrophic hydrocarbon-oxidizing microorganisms (UOM) isolated from industrial wastewater from operating treatment facilities of Kazanorgsintez OJSC and united in the ON-NOVO consortium and consisting of nine bacteria belonging to the genera: *Alcaligenes* (1 species),*Bacillus* (1 species), *Brevibacterium* (2 species), *Clostridium* (1 species), *Flavobacterium* (1 species), *Micrococcus* (1 species) and *Pseudomonas* (2 species)were used as a biological agent. The association was called "ON-NOVO" (the original oil-oxidizing new oxidation possibilities).The association called "ON-NOVO" (the original oil-oxidizing new oxidation possibilities). The originality of the consortium is “in operation” of the association in a wide range of pH (from 2.5 to 9.0), medium temperature (from 10 to 30 ºC), the ability to oxidize various fractions of oil from n-alkalis to asphaltenes, including mineral, semi-synthetic and synthetic oils ofvarious origin.It has been established that in order to intensify the process of purifying water from lubricating oils, it is necessary to ration the nutrients. As the latter, in production experiments, nitroammophos (nitrogen, phosphorus, potassium at 16% each) was used with its content from 20 to 30 $mg/dm^3$ in the purified water.

Culture for suspension hydrocarbon-oxidizing microorganisms (HOM) was obtained from pure isolates stored in the laboratory on the electoral mineral medium of Müntz with the addition of vaseline oil 0.5% by volume. At the initial stage, each strain was seeded on a slanting meat-peptone agar (MPA), grown in a thermostat for 2 days at a temperature of 25 ºC. Passaging was carried out at 25 ºC for 7-10 days. Having ascertained the purity of the grown cultures of the strains on MPA, they washed off with saline (0.44% NaCl solution), mixed in a single

association on Müntz medium with petroleum jelly in 1000 $cm^3$ storage flasks. Grown strains under statistical conditions on rocking for 4 days. The growth of the HOM was estimated by the optical density at KFK-3 to a value of 0.45, which corresponded to the population of $104•10^{-6}$-$108•10^{-6}$ cells/$dm^3$.
The following parameters were the norm on the biological oxidation of waste lubricating oils in wastewater: optical density on a photometric calorimeter KFK-3-01 ZOMZ, concentration meter KN-2M, residual oil analyzer; biological oxygen consumption ($BOC_5$), dissolved oxygen ($O_2$), chemical oxygen consumption (COC), $NO_2$, $NO_3$, $NH_4$, $Cl^-$, Fe, $SO_4$ by common chemical and biological GOST-approved PND F methods [6,12-19]. The content of residual hydrocarbons was also determined by the gravimetric method, using carbon tetrachloride as the extractant [20, 21].

## 3. Results and discussion

Biological purification method dominates compared with other methods (mechanical, physical, chemical, etc.) In modern purification technology. A modern achievement in the development of biological treatment is the creation of a microbiological method of waste processing, and its basis is the use of hydrocarbon-oxidizing microorganisms (PCR). In addition, the advantages of this method include a significant reduction in the financial cost of cleaning, due to hydrocarbon-oxidizing microorganisms [22].
The modular principle of purification of oil-containing (waste mineral) wastewater based on the use of a formed consortium of hydrocarbon-oxidizing microorganisms in a spray-settling bioreactor (SSB) of continuous action and operating in changing environmental conditions was developed for the first time. SSB column type with built-spray element - a nozzle providing atomization of waste liquid to form a dispersed state with a large contact surface contaminants entering the drain contact on the received technological purification scheme (Figure 1).

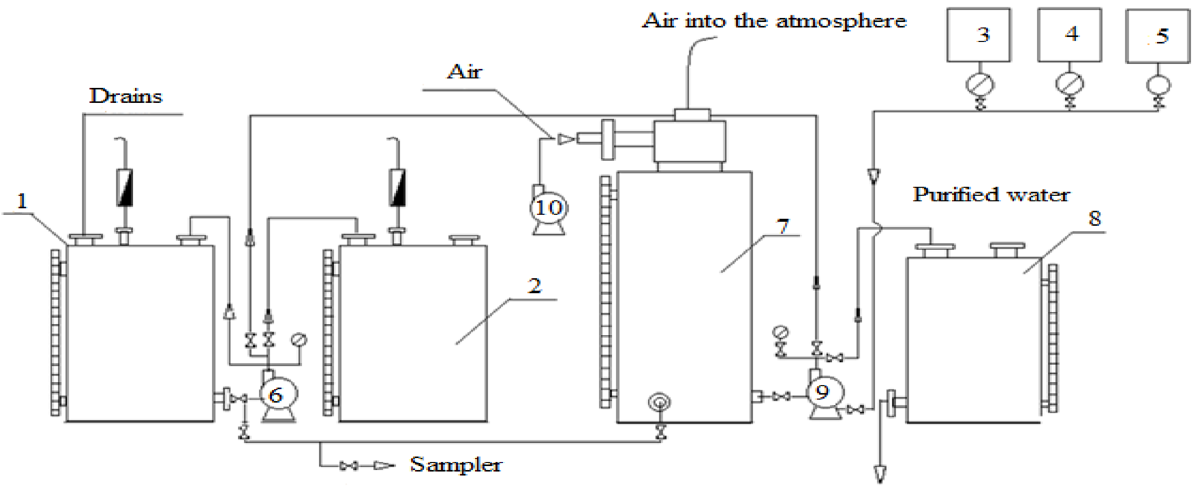


**Figure 1.**Technological scheme for the purification of industrial wastewater from waste lubricating oils: 1) the receiver is the primary clarifier; 2) averager - mixer; 3,4,5) dispensers - hydrocarbon-oxidizing microorganisms, biogenic elements and inducing compounds, respectively; 6) pumping - to supply wastewater from the receiver and averaged to the bioreactor; 7) bioreactor with a spray; 8) secondary settling tank; 9, 10) pumping - for circulating water supply and pumping of the grown biomass of microorganisms into the dosing unit and purified water into the averager to optimize the load.

According to the adopted technological scheme (Figure 1), waste liquid produced by Limited Liability Company Scientific and Production Association "Neftepromhim" (Kazan) polluted with used solar oil of the following composition: COC 500-1200 mg/$dm^3$, including dissolved in $O_2$ water within 6.7-9.8 mg/$dm^3$, the sum of inorganic forms of nitrogen ($NH^{-4}$, $NO^{-3}$, $NO^{-2}$) up to 30 mg/$dm^3$, diesel oil 25, 50, 75, 100, 150 and 200 mg/$dm^3$. The average number of HOM adopted for the experiments ranged from $104•10^{-6}$ to $108•10^{-6}$ cells/$cm^3$. The cleaning mode is adopted as continuous, with a bio-oxidation time of 1.5, 3.0 and 4.5 hours.

Purification of polluted water was carried out as follows: mechanically purified water freed from coarse, coarse-grained and finely dispersed substances after 1-1.5 hours of sludge in the primary sedimentation tank enters the averaging mixer (pos. 3). Further, the balanced flow of organic substances is fed into the SSB centrifugal pump and through a pipe mounted at the top of the entrance, enters the flow element - nozzle.
Simultaneously in the same stream as a result of vacuum created in the main line supplying the liquid waste from the feeder is discharged slurry hydrocarbon consortium of microorganisms with the number $104 \bullet 10^{-6}$–$108 \bullet 10^{-6}$ cells/ml, nutrients (N, P, K) with a total concentration of up to 30 mg/dm$^3$In the zone of outflow of water from the inlet nozzle, where the maximum velocity gradients and shear stresses occur, caused by spraying waste liquid with biogenic elements and microorganisms through the nozzle (pressure up to 3 atm and flow rate 0.5- 0.8 l/s), fog is formed droplet size up to 30 microns, the gap of micellar membranes on droplets of emulsified petroleum products and crushing droplets. As a result, an intensive mixing zone is formed along the entire length of the cylinder 0.5 m in length, which ensures the occurrence of a huge developed contact surface of the components of the waste liquid and microorganisms with pollutants sprayed in the stream. Thus, due to the creation of an optimal environment for HOM (oils, biogens, etc.), active mixing in the nozzle zone, a high intensity of destruction of the original pollutant and other related substances is achieved.
After exiting the first zone - the spraying zone, the finely dispersed mist of fine droplets is condensed and enters into the second zone of the bioreactor loaded to a height of 0.35-0.4 mm Raschig rings. Gradually accumulating in this zone, the water being purified irrigates the rings and spreads throughout its area. At the same time, the speed of the flow is reduced, and the resulting contact with the additional surface creates conditions for the immobilization of hydrocarbon-oxidizing microorganisms associated with waste, both on the surface and in the structure of the rings. Filtering water through the Raschig rings and contacting with microorganisms, there is an additional microbiological purification of water from oils and other related components.
Next, the flow passes to the 3rd zone of the bioreactor - the zone of accumulation, where the partial oxidation of residual oils occurs. Having reached the completion rate of cleaning oily wastewater from the main load of pollution, determined by the residence time of the waste liquid in the bioreactor, the purified runoff with a centrifugal pump is pumped into the secondary settling tank - 8 and subjected to additional treatment by 2-hour settling. Upon completion of treatment, purified water is returned to the circulating water supply or discharged into a water body to replenish water resources without detriment to their ecological condition.
Analysis of the dynamics of changes in biochemical and biological indicators in the process of water purification according to the adopted scheme revealed that the intensity of biodegradation of solar oil in stock depends on the magnitude of the initial load and the contact time of the waste liquid. The initial load (pollution) at the entrance to the bioreactor by COC was from 500 to 650 mg/dm$^3$, which corresponded to the concentration of oil in runoff 57.7; 86.5 and 115.4 mg/dm$^3$.
At 1.5 hours of contact with the HOM in the bioreactor, the COC value decreased on average: in the first experiment, 1.45, in the second, 1.25 and in the third, 1.10 times. An increase in the contact time of runoff by a factor of 2 (by recirculation of previously purified water) was accompanied by a significant change in the COC index. On average, the increase in the variants of the experiment was 3.3, 3.2 and 2.1 times, respectively (Tab. 1). The observed phenomenon seems to be related to the continuation of the “work” of the HOM strains contained in the waste liquid for the neutralization of residual amounts of solar oil in the stream. This once again confirms that even with the creation of optimal environmental conditions it is necessary to ensure the time of contamination with the microflora involved in the oxidation.
Further, the value of 1.5 hour sludge in the secondary clarifier, which performed a certain function of reducing the residual amount of pollution, is still high. Depending on the test options, it ranges from 150 to 270 mg/dm$^3$.
In general, as can be seen from the data presented in Table 1, the adopted technological scheme provides good wastewater treatment not only from organic pollutants (diesel oil), but also from individual nutrients and mineral salts. For example, in the ammonium, nitrate, and nitride forms of nitrogen, the decline was more than doubled. The content of total iron decreased from 5.2 to 1.6, chlorine ion from 30.6 to 17.8, and sulphate ion from 1160 to 398-531 mg/dm$^3$.

**Table 1:** Purification of waste liquid from solar oil according to the accepted neutralization technological scheme by the consortium "ON-NOVA"

| Indica-tors, $mg/dm^3$ | Content, $ml/dm^3$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 50 | | | | 75 | | | | 100 | | | |
| Time, hour | 0 h | 1.5 h | 3 h | 4.5 h | 0 h | 1.5 h | 3 h | 4.5 h | 0 h | 1.5 h | 3 h | 4.5 h |
| COC | 500 | 350 | 160 | 140 | 560 | 400 | 240 | 200 | 650 | 550 | 300 | 270 |
| Contains $O_2$ | 9.80 | 9.6 | 9.4 | 9.2 | 9.2 | 9.0 | 8.8 | 8.7 | 8.7 | 8.6 | 8.3 | 8.0 |
| pH | 7.23 | 7.52 | 7.50 | 7.41 | 7.43 | 7.45 | 7.54 | 7.52 | 7.33 | 7.58 | 7.51 | 7.50 |
| $NH_4^-$ | - | 165 | 87 | 79 | - | 209 | 195 | 69 | - | 194 | 150 | 59 |
| $NO_2^-$ | - | 8.40 | 5.00 | 4.66 | - | 7.65 | 3.60 | 3.14 | - | 9.80 | 3.40 | 3.00 |
| $NO_3^-$ | - | 32.00 | 17.40 | 13.40 | - | 30.00 | 17.20 | 14.80 | - | 29.00 | 17.10 | 13.40 |
| $Cl^-$ | 30.60 | 21.90 | 20.00 | 17.80 | 29.90 | 24.50 | 22.50 | 22.50 | 30.50 | 26.70 | 24.80 | 24.50 |
| $SO_4^{2-}$ | 1160 | 659 | 558 | 531 | 1050 | 625 | 412 | 412 | 1112 | 605 | 411 | 398 |
| $Fe^{3+}$ | 5.20 | 3.41 | 2.71 | 2.07 | 4.34 | 3.86 | 2.01 | 1.81 | 4.00 | 3.76 | 2.50 | 1.60 |
| Oilproducts | 57.70 | - | - | 2.40 | 86.50 | - | - | 4.08 | 115.40 | - | - | 5.76 |

As for the intensity of oxidation of diesel oil in stock, its content at the outlet of the secondary clarifier fell, according to a series of experiments, in the first experiment - by 95.84%; in the second experiment - by 95.3% and in the third experiment - by 95.0%.

In the subsequent stage of the work, we found that the optimal time for the ROB effluent stays to be 4.5 hours.

The testing of the technological scheme of sewage purification from solar oil in different concentrations (25; 50; 75; 100; 150 and 200 $mg/dm^3$) by the above-mentioned associations of bacteria at the initial stage has the same dynamics of pollution neutralization. Subsequently, as the load increases, at a concentration of diesel oil to 200 $mg/dm^3$, the intensity of the cleaning water falling slightly, but it remained high.

The latter is connected with the participation of polycultures in the process of neutralization, the mixed associations of HOM presented in our consortium and possessing different enzyme systems and capable of purifying highly concentrated oil-polluted drains. We noted this in our experiment, it was stated repeatedly in previous studies, and it was also noted by other authors [19, 23].

With the residence time of the waste liquid in the scheme of 4.5 hours at an ambient temperature of 20 ºC, it is freed from initial contamination (200 $ml/dm^3$), more than 70%, nitrate nitrogen 71.7, total iron 87.6, chlorine and ion sulfate up to 40% (Table 2).

A similar result was achieved in the process of wastewater treatment with an ambient temperature of 10 ºC. At the same time, COC decreased from 720 to 320, nitrogen content of nitrates from 12.2 to 3.84, chlorine ion from 36.9 to 25.5, total iron from 3.04 to 0.2, and sulphate ion from 666 to 427 $mg/dm^3$.

**Table 2:** Changes in the chemical parameters of the waste liquid in the process of cleaning it from spent solar oil with HOM (200 $mg/dm^3$)

| Indicators of runoff cleaning, $ml/dm^3$ | COC | pH | Dissolved $O_2$ | Nitrates ($NO_3$) | Nitrites ($NO_2$) | Chloride ($Cl^-$) | Iron (Fe) | Sulfates ($SO_4$) |
|---|---|---|---|---|---|---|---|---|
| Stockstock | 1200 | - | - | - | - | - | - | - |
| Stockafteraveraging | 720 | 7.5 | 9.4 | - | - | 38.85 | 4.04 | 752 |
| Bioreactor, 1.5 hours | 580 | 7.5 | 9.2 | 4.45 | 10.6 | 26.20 | 2.06 | 515 |
| Circulation in a bio-reactor, 1.5 hours | 350 | 7.5 | 9.8 | 2.45 | 3.2 | 23.50 | 0.90 | 461 |
| Settling, 1.5 hours | 310 | 7.5 | 9.6 | 2.00 | 3.0 | 23.50 | 0.50 | 455 |

In general, as the test results, the technological purification scheme comprising averager, bioreactor and secondary settling tank in a continuous mode for 3.0-4.5 hours provides local neutralization of wastewater concentration with high diesel oil in the effluent discharge standards to a biological sewage treatment plant.

In the waste liquid with a dose of mineral oils (diesel, compressor, transmission and industrial) up to 25 mg/dm$^3$, the ON-NOVA consortium neutralized the flow to sanitary norms (0.16 mg/dm$^3$). This is achieved in the technological scheme with a jet-settling reactor while maintaining the same cleaning regimes (flow rate, oxygen provision and abundance of HOM up to 108•10$^{-6}$ cells/dm$^3$) [24-27].

## Conclusion

The vital signs of HOM are tested and improved by bioactive components, which ensure the processes of biotransformation of pollution. The use of the HOM for purification and tertiary treatment of wastewater in various industries, agricultural facilities and households, including production for the disposal of waste and commercial oils of various nature and composition, can be recommended for import substitution by biotechnical systems and technologies supplied from abroad.

The studies performed convincingly showed that the technological purification scheme, with the inclusion of the newly created bioreactor, where the purified wastewater is mixed in the stream with a specified amount of HOM, the required amount of biogenic elements (sprayed in the form of mist), provides a high degree of phase contact - contamination with the participating microflora and accelerated biodegradation of oil pollution. It is noted that even when the initial pollution varies - solar oil in a drain of 50, 75, 100 ml/dm$^3$ under the influence of the ON-NOVO consortium in 4.5 hours of contact, a 95-96% purification effect is achieved. When the concentration of pollution in the treated drain is up to 25 ml/dm$^3$, the proposed scheme allows preparing the purified wastewater to sanitary standards. This opens the way for the widespread use of the original purification scheme in the disposal of oil-contaminated industrial wastewater from small sewage enterprises and large-scale production facilities in many industries, including agricultural and household facilities.

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