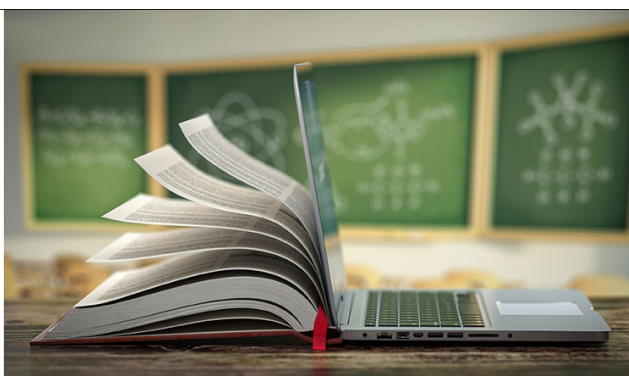


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## Intensification of the biotreatment processes of natural and waste water, contaminated with spent lubricating oils with sorbents of various nature

To cite this article: N V Morozov and I M Ganiev 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **815** 012025

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## Intensification of the biotreatment processes of natural and waste water, contaminated with spent lubricating oils with sorbents of various nature

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**Abstract.** Biodegradation of spent lubricating oils (mineral, semisynthetic, synthetic) was investigated in natural and waste water of consortia of hydrocarbon-oxidizing microorganisms (HOM) under the influence of sorbents of various nature. It was found that the effectiveness of the latter's action on the biotreatment processes of water from oils is determined by the size of particles, concentration, formation of active contact surface of phases by them and their participation in neutralization of contaminants. In direct use of sorbents without HOM, are purified 7 to 19.6 % oils. This is achieved within 10-14 days of contact. The joint use with HOM of inert materials (river sand, coal powder, polyethylene chips, etc.), in the same contact times, water is neutralized from lubricating oils from 44.9 to 63.7 % observed under the influence of HOM only. At the same time, with buckwheat, oats, wheat and barley husks with the same level of pollution, the purification of water from lubricating oils reaches 93.7 %. It is related to the simultaneous participation of these sorbents in the formation of a highly active surface for immobilizing contaminants and microflora, to provide stimulating activity of the latter by involving products associated with these materials in oxidative processes.

Among the many contaminants continuously entering to the environment from industrial enterprises, agricultural facilities and others, spent lubricating oils still remain the most global [1].

With annual world production of them up to 50 million tons. [2] the share of used oils exceeds 30 %. Of these, 20 % is used for production needs [3], part is burned [4], and the bulk is diverted to open water bodies [5].

Multi-annual experience in protecting natural reservoirs from these types of pollution shows that the use of biosorption technologies is the most efficient way to neutralize them. Especially in the first phase of the emergency or other receipt of oil, petroleum products and their derivatives, accompanied by pollution of significant waters and water areas. In the subsequent period, the urgent need for biodegradation of residual amounts of petroleum products, including lubricating oils (film, emulsified and dissolved) in water. To solve the globally, this task of mechanical adsorption, using organic and inorganic porous materials and substances, is economically impractical.

A promising direction is the use of controlled biotechnology, which combines sorption and effective biodegradation of compounds in one material with heterotrophic microflora, which is specifically used for this purpose. We are talking about the joint use of isolated HOM with a wide spectrum of oxidation



of various classes of hydrocarbons and oils of various nature, structure and sorbent substances included in the general metabolism of the cell as additional easily oxidizable organics.

This area of work is in an early stage of development and is not sufficiently studied. Based on this, the aim of the present study was to study the degradation processes of spent mineral, semisynthetic and synthetic motor oils with isolated HOM and to select sorbents that contribute to the intensification of neutralization processes of natural and waste water from these types of pollutants.

Based on the goal, the following objectives are defined:

1. Clarification of degree and intensity of neutralization of natural and wastewater from spent lubricating oils of different composition and properties by a consortium of hydrocarbon oxidizing microorganisms (HOM).

2. Study of influence of organic and inorganic sorbents on biodegradation of lubricating oils with determination of their dimensions, concentrations, as well as types providing intensification of processes of water biodegradation.

As object of researches served mineral oils: transformer (Lukoil VG, Russia), transmission (Mobil ATF 220 Premium Automatic, USA), diesel (Shell Helix Diesel 10W-40, Great Britain, Netherlands), solar (Tatneft, Russia), as well as semi-synthetic (Mobil Super 2000 10W-40, USA) and synthetic oils (Castrol Magnatec A3/B4 5W-40, Great Britain). Their content in the experiments was:  $90 \pm 6$ ,  $400 \pm 6$  and  $1000 \pm 6$  mg/dm<sup>3</sup> per 400 cm<sup>3</sup> of runoff.

Hydrocarbon oxidizing microorganisms (HOM) are united in a consortium consisting of nine species belonging to the genera: *Alcaligenes* (1 species), *Micrococcus* (1 species), *Brevibacterium* (2 species), *Bacillus* (1 species), *Flavobacterium* (1 species), *Clostridium* (1 species) and *Pseudomonas* (2 species) [6].

Suspension culture of HOM to infect water was obtained from pure isolates stored in the laboratory on Münz (composition of medium (g/l): (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> – 2; K<sub>2</sub>HPO<sub>4</sub> – 1.0; KNO<sub>3</sub> – 1.0; MgSO<sub>4</sub>•7H<sub>2</sub>O – 0.2; NaCl – 0.2; FeCl<sub>2</sub> - traces; tap water - 0.1 dm<sup>3</sup>; distilled water - 0.9 dm<sup>3</sup>; pH - 7.2) liquid medium with the addition of vaseline oil. At the initial stage, each strain was sown on oblique meat-peptone broth (MPB), grown in a thermostat for 2 days at a temperature of 28 °C. After verifying the purity of the grown crops on the MPB, they were further washed with physiological saline (0.44 % solution NaCl), mixed in a single association on a fresh medium with vaseline oil (0.5 % by volume). Passaging was carried out at 25 °C for 7-10 days. Having received the number of HOM within the range of  $340 \cdot 10^6$  -  $360 \cdot 10^6$  kl/dm<sup>3</sup>, experimental effluents were further infected.

Sorbent materials were used: river sand, coal powder, polyethylene chips, crushed Tetra paket, sawdust and peat (natural size), buckwheat husks, barley, wheat and oats with a particle size of 0.017, 0.034, 0.07 and 0.1 mm. Their concentration was, depending on the series, of tests, 10, 20, 30, 40, 50 and 100 mg/dm<sup>3</sup>.

Purification of water from spent lubricating oils in laboratory model and full-scale experiments with and without HOM, sorbents of various nature was evaluated by chemical (O<sub>2</sub>, COC (chemical oxygen consumption), oil content) and biological (BOC<sub>5</sub> (biological oxygen consumption), the total number of microorganisms, including hydrocarbon-oxidizing bacteria) unified methods [7; 8].

At the first stage of the studies, transformer, transmission, diesel (solar) oils were subjected to biodegradation. Against the background of the mineral medium (Münz medium) and tap water with a concentration of initial pollution of  $90 \pm 6$  and  $1000 \pm 6$  mg/dm<sup>3</sup>.

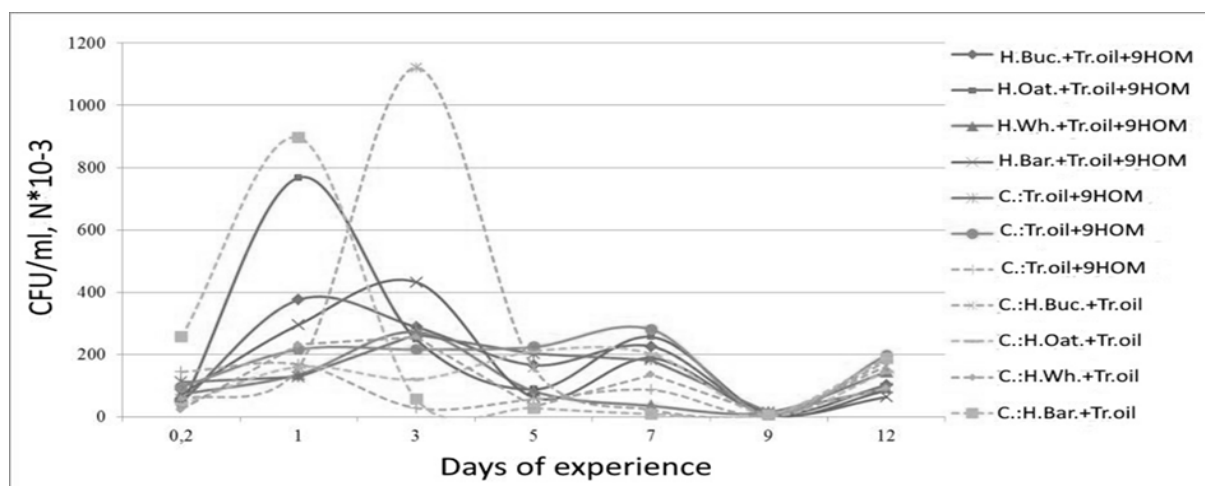
Experiments showed that with an initial number of hydrocarbon-oxidizing microorganisms (HMR) in the range of 24-75 thousand kl/cm<sup>3</sup> on the 2-3rd day, water with oils began to become cloudy, increasing by 5-6 days. At the same time, the oil film formed on the surface began to lose color, turning from light gray to gray (transformer, transmission), and diesel into light pink.

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the initial contamination. In general, water release from the film occurred within 8-14 days, depending on the nature of the oils, and reached up to 80 % of the surface area.

Analysis of residual amounts of lubricating oils in the water column by this date revealed that their content decreased from 56.6 to 72.1 %. The difference between the variants in the number of unoxidized oils was 15-17 %. In the control without infection with HOM in the same period there were no more than 7 %.

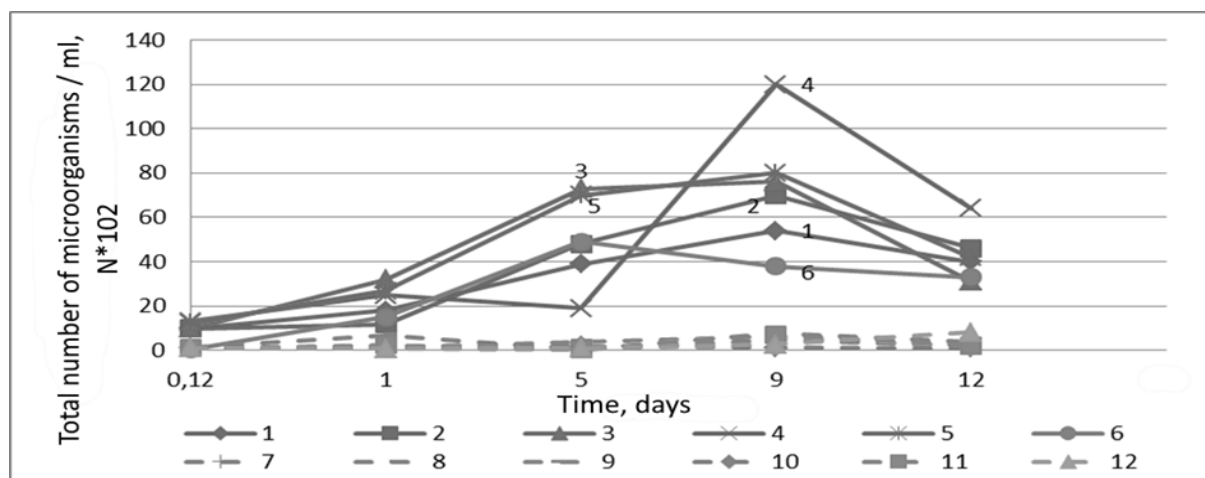
In parallel, with the preservation of the same experimental parameters, on natural (river) water with the introduction of sorbents - river sand, peat, coal powder, film chips, sawdust and grain husks, it was shown that the process of releasing water from suspended, emulsified and dissolved oils (mineral, semi- and synthetic) depends on the activities involved in the oxidation of PDE and the nature of the materials with which they contact. There is a direct connection with the degradation of the above mineral oils from their properties to intensive biooxidation. So, for example, in the presence of sorbents - husks of grain cultures, microorganisms involved in the purification of water from transformer oil obtain a «doping effect» in the interval from 1 to 3 days of contact. This is reflected in their rapid growth in an oil environment. The population of microorganisms increases to 10-12 times in the version with buckwheat and oat husks and increases to 18 times in the presence of barley husks in the water (figure 1).



**Figure 1.** Dynamics of HOM change in the process of water purification from transformer oil under the influence of substrates and without them. Tr.oil. - transformer oil; 9HOM - 9 hydrocarbon oxidizing microorganisms; H.Buc. - buckwheat husks; H.Oat - oats husk; H.Wh. - wheat husks; H.Bar. - barley husks; C - control.

This period coincides with a significant release of the water surface from the oil film and a reduction in suspended and dissolved products in the water column. The number of them varies within 65.0-87.0 %, respectively.

With semisynthetic oil from Mobil Super 2000 10W-40 in the dynamics of HOM in the process of cleaning water from initial pollution, a different picture was obtained (figure 2). Hydrocarbon oxidizing microorganisms introduced into the water slowly adapting to the initial pollution give the largest increase by 6-9 days. By this period, the total reduction of lubricating oil on the surface, as well as in the water column under the influence of mineral sorbents, remains at the level of 44-50 %. In the presence of cereal husks with the same contamination, its reduction in concentration reaches 55.0-63.7 %.



**Figure 2.** Dynamics of the growth of the number of HOM (semisynthetic oil of Mobil Super 2000 10W-40): 1 – coal powder; 2 – peat; 3 – river sand; 4 – polyethylene shaving; 5 – sawdust; 6 – grass dust; 7 and 8 – control.

When considering in detail the change in the main purification indicators (dissolved oxygen content ( $O_2$ ),  $BOC_5$  and  $COC$ ) of water, it was found that their dynamics in versions with buckwheat, oats, wheat, barley husks fully confirm the intensively current process of moderate bioreduction of water quality under the influence of the latter, both from mineral and semisynthetic oils. The proportion of mineral oils subject to biodegradation of HOM, in the same period, exceeds more than 30 %. The total cleaning effect in versions with oat husks reaches 90.6 %, barley 92.2 %, and buckwheat and wheat 93.7-93.8 % (table 1).

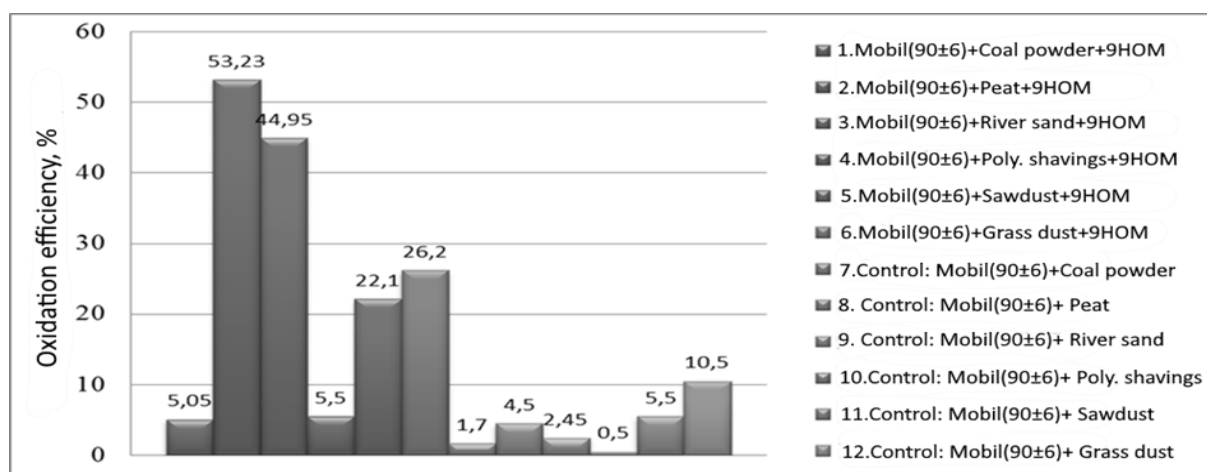
**Table 1.** Biocleaning of water from spent mineral lubricating oils with and without sorbing materials (average of 5 definitions).

Experiment options	Sizes and concentration of sorbents		% water purification from oils
	Dimensions, mm	Concentration, $mg/dm^3$	
River sand + HOM <sup>a</sup>	River fine-grained	up to 50.0	44.9
Coal powder + HOM	-	- // -	40.6
Peat + HOM	Natural	- // -	53.2
Polyethylene shavings + HOM	Various - from shavings to small particles	- // -	67.3
Grass dust + HOM	0.1	- // -	45.0
Husk buckwheat + HOM	0.017-0.034	- // -	93.7
Husk oat + HOM	0.017-0.034	- // -	90.6
Husk wheat + HOM	0.017-0.034	- // -	93.8
Husk barley + HOM	0.017-0.034	- // -	92.2
Water with HOM without sorbents	-	- // -	56.6
Water without HOM and without sorbents	-	- // -	9.0
Inert materials (sand, coal powder, polyethylene shavings, peat, herb dust)	Natural	up to 50.0	11.0
Husks of cereals	0.017-0.034	- // -	22.6

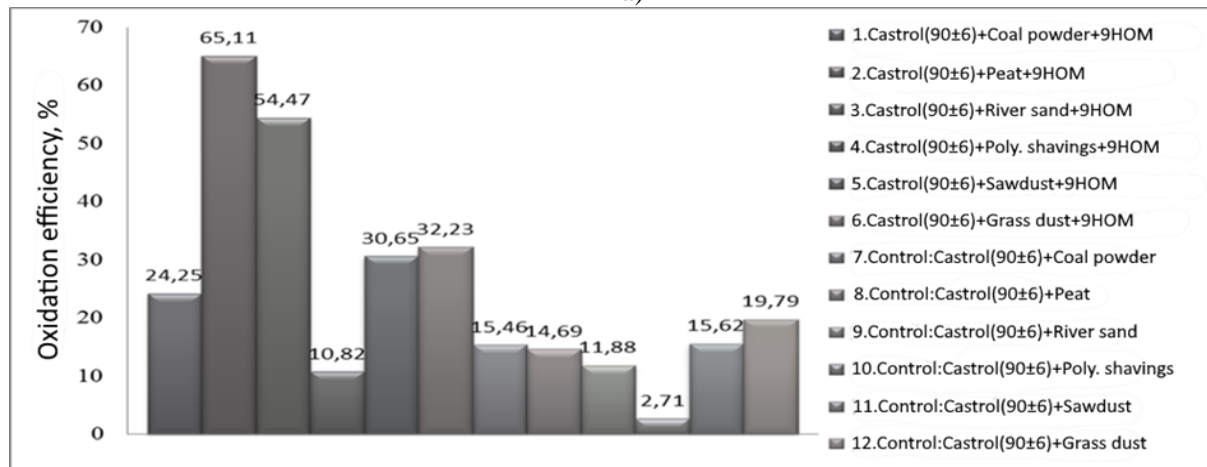
<sup>a</sup> Hydrocarbon oxidizing microorganisms from 24 to 75 cells/ $cm^3$ .

Further studies confirmed this fact. In addition, we have established that the intensity of purification of water from spent lubricating oils is mainly determined by the time of their contact, which is involved in the process of degradation of HOM and the influence of sorbents.

Some sorbent materials and microorganisms have been identified as having a direct link during biodegradation. This is characteristic of the husk of grain crops, in particular buckwheat, barley, oats and wheat. Most likely, the observed is due to the presence of proteins, carbohydrates, amino acids, organic acids and other substances that stimulate the activity of HOM and have an inducing effect on the oxidation of certain hydrocarbons, including lubricating oils. Similar effect of the latter on processes of biodegradation of oil and oil products is proved experimentally [9; 10].



a)



b)

**Figure 3.** Efficiency of biooxidation of semi-synthetic Mobil Super 2000 10W-40 oil (a) and synthetic Castrol Magnatec A3/B4 5W-40 oil (b) with use of sorbents and without them: 1 – Coal powder; 2 – Peat; 3 – River sand; 4 – Polyethylene shavings; 5 – Sawdust; 6 – Grass dust; 7, 8, 9, 10, 11, 12 – Control; 9HOM – 9-th hydrocarbon oxidizing microorganisms.

Whereas in the presence of river sand, polyethylene chips, rubbish, coal powder and even peat, rich in many organic (humus, apocrenic, acids) and inorganic compounds (inorganic nitrogen, phosphorus, potassium, etc.). The efficiency of water purification from spent lubricating oils remained at or below the level observed under the influence of HOM (table 1, figure 3).

Like it is noted also at oxidation of synthetic Castrol Magnatec A3/B4 5W-40 oil. Under the influence of HOM, the maximum reduction in pollution occurred only on the 12-14th day of contact and ranged from

24.2 (coal powder) to 65.1 % (peat). In the control without sorbents and without HOM, the change in the content of Castrol oil ranged from 10.1-11.9 (river sand, coal powder) to 19.4 % (peat).

So, from the results of detailed studies, it follows that inert sorbents of any nature in the fight against oil pollution, including spent lubricating oils supplied to reservoirs by emergency or other, must be considered as a preliminary stage of natural and wastewater treatment.

Increasing the neutralization of water from such contaminants by these sorbents can be achieved by intensifying them together with hydrocarbon-oxidizing microorganisms. (HOM) for maximum purification of water from oil products, used lubricating oils and natural or contaminants (open ponds, production effluents) it is recommended to use controlled sorbents of grain crops - husks of oats, wheat, barley and buckwheat (particle size 0.017-0.034 mm with concentration from 50 mg/dm<sup>3</sup>) together with HOM (up to 350•106 kl/cm<sup>3</sup>). The formed complex – sorbents and microorganisms, being included in oxidative processes, together provide water recovery from these types of contaminants to natural qualities.

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