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## Biotechnical Systems and Technology for Hydrocarbon-Containing Waste Water Purifying In a Controlled Manner.

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### ABSTRACT

Biotechnical systems and technologies are aimed at deep cleaning and purification of oil-contaminated natural and waste waters to comply with regulations for water recycling. The solution to this problem is possible using selected carbohydrate-containing microorganisms (SCM) with a wide range of various fractions of oil oxidation and oil products in a specially designed jet settling device (JSD) and constructed on the biotechnological scheme basis for oily waste water purification. Intensification of hydrocarbons oxidation by microorganisms in the adopted purification scheme is carried out by creating optimal conditions for SCM of the following variations: temperature 15-28°C, pH 5-9, calculated amounts of nutrients (nitrogen of 2.5 – 20 mg/dm<sup>3</sup> and phosphorus of 0.1-0.5 mg/dm<sup>3</sup> ) and composite compounds (alanine, valine, glutamic and succinic acids, glucose, maltose  $15 \cdot 10^{-6}$  -  $35 \cdot 10^{-6}$  M. Also found that in the process of oil biological destruction and oil products in sewage a significant role plays the ratio of strains in the consortium which corresponds to the following amount (%): Alcaligenes -14, Micrococcus – 6, Brevibacterium – 6, Pseudomonas – 25, Bacillus - 6, Flavobacterium – 6, Clostridium – 6, which comprises the titer of viable cells  $5 \cdot 10^{10}$  –  $7 \cdot 10^{10}$  cells /dm<sup>3</sup> in the drain. Managed bioremediation of oil-contaminated wastewater, adopted by the technological purifying system, also is provided by selected technical parameters and modes of neutralisation for each individual production.

**Keywords:** neutralization, biodegradation, biotechnological systems and devices, technology, oil and hydrocarbon-oxidizing microorganisms.

## INTRODUCTION

Water pollution by oil and oil products is one of the main environmental problems. According to the literature data open bodies of water annually receive over 5 million tons of oil and oil products, about 55 million tons of mineral salts, more than 70 million tons of phenols and other related organic and inorganic substances [1, 2]. It is established that the flow of oil spillages is connected with a significant loss of quantities of extracted and processed oil which exceeds 1% [3, 4]. For these and other reasons, the oil content in the water of rivers of oil-producing and oil-refining areas in the low water period is at the level of 0.2-50 mg/l, and in the period of accidents exceeds 2000mg/l [3, 5].

Disposal of the oil industry wastewater and similar facilities is carried out largely by the technology based on the biochemical oxidation of contaminants. Widely used for this purpose traditional (aeration, bio - and aero filters) or advanced systems (large capacity bio-tanks, etc.) occupy a considerable territory, are capital-intensive in construction and expensive in operation.

Their effectiveness on cleaning and disposal of hydrocarbon-containing sewage is not great, as it does not provide wastewater treatment to comply with regulations for water recycling. There is a question whether they are really needed in practice in the field of purification and deep purification of oil-contaminated wastewater, because new systems, devices and technologies that can dispose oil pollution and its persistent connections to sanitary (0.1-0.3 mg/l) and fishery (0.05 mg/l) standards [1-3, 13].

With gained experience in restoring the natural properties of oil-polluted water and sewage becomes clear that their purification and post-treatment it is most appropriate methods based on the use of selected heterotrophic microorganisms, including oil-oxidizing [6-10].

Achieving highly efficient biodegradation of oil and oil products by selected heterotrophic microorganisms, in our experience, lies in a special set up for this purpose unit, and on its basis the scheme of the biotechnological purification of sewage up to the standards of water recycling supply or drainage to surface water sources without compromising their ecological condition.

The objective of this paper was to carry out works on neutralization technology development of oil-containing industrial wastewater associative culture of hydrocarbon-oxidizing microorganisms in a specially constructed for this purpose installation and on its basis the scheme of biotechnological purification and advanced treatment of industrial effluents to the standards of recycling water supply.

## RESULTS AND DISCUSSION

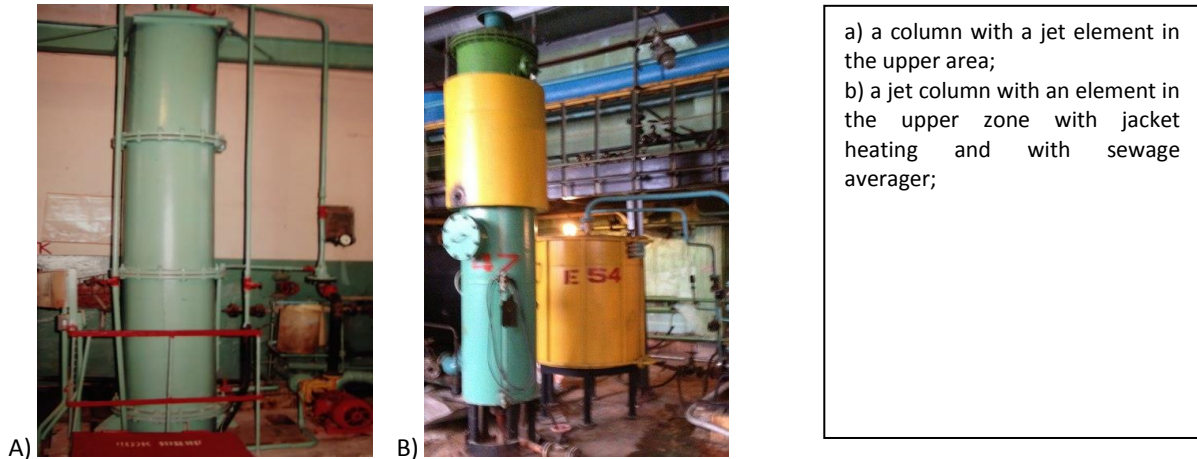
The installation, description of the flow pattern and the principles of oily waste disposal.

For cleaning and advanced treatment of oily waste waters of the enterprises with small sewage systems, large-scale production and equated farms by selected hydrocarbon-oxidizing microorganisms was proposed a jet settling device (JSD) of various modifications.

Settings for this purpose are selected on the modular principle basis, which allows creating basic facilities included in the technological scheme of cleaning and deep purification of chemical plants standard equipment.

JSD is made in the form of cylindrical shape columns with a diameter of 500-1200 mm and a height of 4200 mm (Fig.1, 2).

At the top of the column there is a jet element for supplying a mixture of liquid waste from the hydrocarbon-oxidizing microorganisms and compounds that provide a controlled biodegradation of petroleum and petroleum products to the final product - CO<sub>2</sub> and H<sub>2</sub>O



**Figure 1: Jet settling device (JSD)**

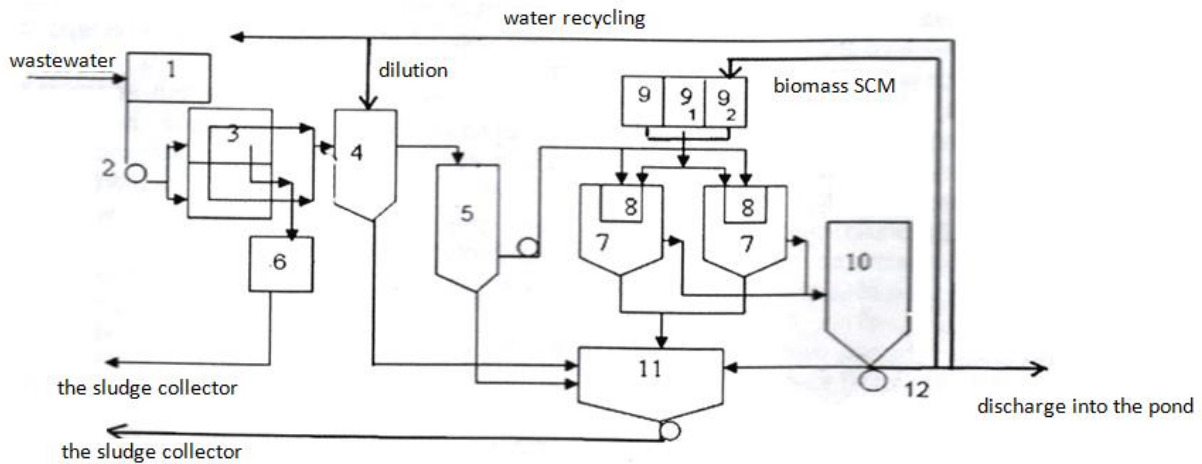
The latter is a node with height from 500 to 800 mm, diameter 150 mm with perforated or smooth surface.

The work of the JSD in the operating mode includes:

1. Spraying of oil-containing waste fluid with a jet element (crushing drops of oil and oil products and transferring them together with flow into their dispersed phase with the formation of a huge contamination contact surface with microorganisms participating in the biodegradation). As a result of achieving a high mixing intensity it is quite acceptable to consider the area of the jet element as a zone of ideal mixing. In this zone, the chemical and microbiological processes of biodegradation, resulting in intensive growth of microorganisms' biomass and intensification of dispersed (crushed) and oil hydrocarbons biodegradation.
2. The circulation of the waste fluid down to the middle of the column and below, i.e. its even transition upwards at the given speed of movement and stable biodegradation increasing of oil spills and other related compounds with the translation from slightly oxygenated to the fully oxidized state. The area is characterized by a slowdown in the growth of hydrocarbon-oxidizing microorganisms and stabilization of process of contaminants bioremediation. In the area of petroleum products biochemical oxidation begins to fade, the speed of microorganisms' biomass increase and the release of effluent from the hydrocarbon minimum.
3. Deposition of adherent biomass and removing it together with purified water from the device into the next stage of the process (means, two subsequent JSD stages) or the discharge of treated water for further clarification.

**Technological scheme and regulation of hydrocarbon cleaning process of wastewater in certain industries.**

We tested the complex bacterial consortium comprising nine strains belonging to the genera: Alcalignes (1 species), Pseudomonas (2 species), Brevibacterium (2 species), Bacillus (1 species), Flavobacterium (1 species), Micrococcus (1 species), Clostridium (1 species) ability to oxidize various fractions of petroleum hydrocarbons using biotechnology circuit cleaning and deep purification of the mixed waste waters of OJSC "Kazanorgsintez" (Figure 3).



**Figure 3: Technological scheme of oil and hydrocarbon-containing production wastewater purification and additional treatment.**

The scheme included: 1 - the sewage receiver with removal of coarse impurities; 2 – pumping station for supplying the flow from the collector to the oil trap; 3 – oil trap; 4 – neutralizer governing the main load of pollutants in wastewater prior to feeding to the next filtration stage; 5 – primary sedimentation tank; 6 – oil collector; 7 – jet settling device (JSD); 8 – jet elements; 9 – biogenic elements’ block-dispenser; 9.1 – block-dispenser of inducing compounds; 9.2 – block-dispenser of oil-oxidizing microorganisms; 10 – a purified water storage with a pump station of hydrocarbon-oxidizing microorganisms’ attached biomass supplying into the dispenser (11) and water recycling.

The cleaning cycle of hydrocarbon wastewater according to adopted scheme provided: a) mechanical filtering – the rough-finely dispersed materials removal, the supply of flow using gravity collector into the oil trap (item 3) and settling it for 1.5 hours. With its ascent the oil skim is moved by the gate to the receiver, and then enters the oil receiver (item 6): a) exempted from floating hydrocarbon drain is then fed into the construction of neutralization and is neutralized to a pH of 6.5-7.0 and pumped to the primary settling horizontal tank and undergoes a two-hour settling; b) the clarified waste water flows by gravity into the neutralizer, then, it is mixed in a ratio of 1:1 with a domestic drain and a brought to the chemical oxygen demand (COD) from 570 to 1680 mg/dm<sup>3</sup> (pos. 4) is further directed by the centrifugal pump to the jet element JSD (pos. 7, 8). Simultaneously, from the dispensers (pos. 9, 9.1, 9.2) there are directed biogenic elements (nitrogen, in the form of ammonium sulfate, phosphorus, in the form of superphosphate), inducing compound (glutamic, succinic acid, valine, alanine, glucose, maltose) in various ratios and the number of suspensions consortium of hydrocarbon-oxidizing bacteria at an average of 130 mln.cells/dm<sup>3</sup> or by biomass within 0.3-0.5 g/dm<sup>3</sup>.

In the jet element (Fig.1, pos.8) the waste liquid with all the added components is blended and forms in it the direct and reverse flows, due to large gradients of velocity and shear stress shattering, it tears the drops of emulsified oil products into small dispersed particles saturated with air bubbles. In the result there forms a large surface area where the microorganisms and the hydrocarbons are in contact at the phase boundaries (environment-air). This creates optimal conditions for bacteria "attacks" on dispersed oil pollution. The amount of JCD in the scheme is determined by the volume of wastewater in local or other production, the productivity and the required degree of wastewater purification from hydrocarbons.

**Production testing of biotechnological block module of hydrocarbon wastewater mixed flow purification.**

With optimal choice of the microorganisms consortium and the concentration of additional stimulating power sources there are able to be accelerated the oil pollution biological oxidation in the tens and hundreds of times to neutralize the waste water up to standards of recycling water supply or drainage into natural water source [2, 12-14].

This has been confirmed by us in a series of the technological scheme tests of wastewater treatment mixed flow JSC "Kazanorgsintez" (Fig. 3) with following indexes (mg/dm<sup>3</sup>): pH - 6.5-9; COD 780.4-1048; O<sub>2</sub> in the range from 1.0 to 5.6; inorganic forms of nitrogen (NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>) – 15.0-35.0; phosphorus (P<sub>2</sub>O<sub>5</sub>) – 1.4-15.3; oil products from 34.0 to 186. The total number of SCP at the entrance to JSD ranged from 104 million cells/cm<sup>3</sup> to 150 million cells/cm<sup>3</sup>.

The duration of the petroleum hydrocarbons in waste liquid bio-oxidation, supplied to the JSD in a continuous mode, was applied: 1) when the concentration of oil products was 20-186 mg/dm<sup>3</sup>, the flow rate of 0.015-0.03 m/sec, the residence time from 0.1 to 1.5 hours; 2) at concentrations exceeding 200 mg/dm<sup>3</sup> or COD load of 1000 mg/l or more, the speed of waste water in a pilot plant was approaching 0.031 inch-0.045 m/sec, with the residence time of 1.3-3.0 hours.

The purification mode was continuous, the exposure time of drain settling in the JSD varied – 0.3; 0.6; 0.8; 1; 1.2; 1.4; 2; 3 and 4 hours. Optimal time was defined as 1.2 hours, which corresponds to the feed rate of waste water into the jet settling device of 8-10 l/min. Purification process intensification was provided by adding to the flow of biogenic elements – nitrogen and phosphorus (nitrogen in the form of ammonium nitrate, phosphorus as calcium superphosphate), which ratio in the main pollution load was accepted BOD<sub>full</sub>:N:R:100:5:1 (determined experimentally from the following variations – 2.5; 0.5; 5; 10; 20; 40). The accepted ratio of nutrients in sewage stimulated the growth of SCP consortium population in 2 times, and the efficiency of oil hydrocarbons degradation at a contact time of 1.2 hours to 75%. In the variant without addition of nutrients the degree of water purification from impurities did not exceed 25-36% (Fig. 4)

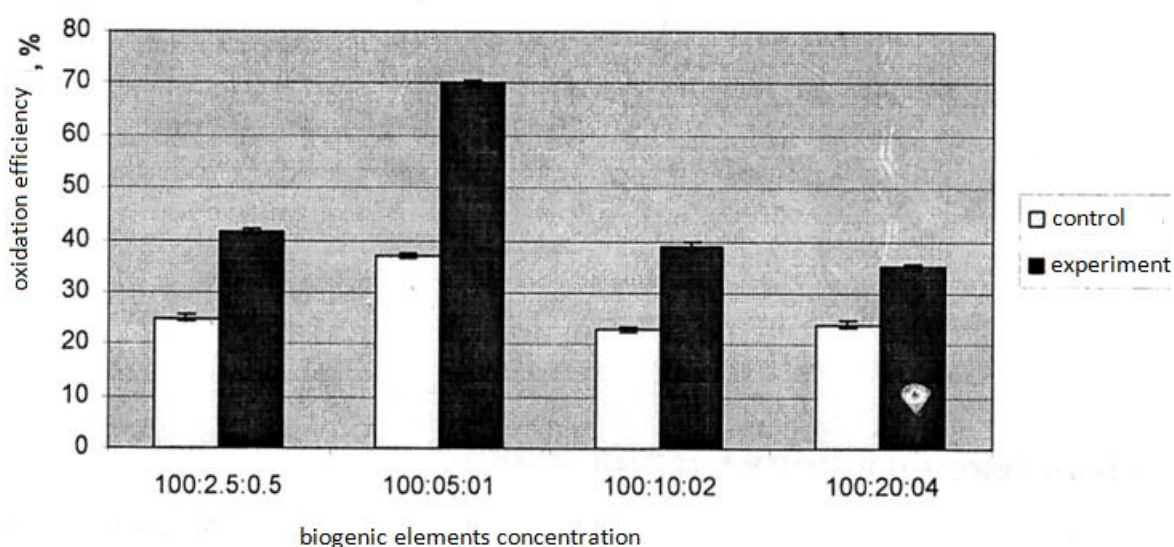


Figure 4: The effectiveness of petroleum products oxidation in the drain consortium with different ratios of nutrients

Adjustment of nutrients (N, P) in the waste liquid at JSD processing there can increase the load on the COD to 1.000 mg/l and higher. The latter fact is positive in the primary hydrocarbon waste water preparation up to the discharge standards for further deep purification and post-treatment [9]. In order to achieve higher efficiency bio-oxidation process intensification into subsequent test series were added purified complexes of inducing substances into the waters (composite compounds). They include: glutamic acid, succinic acid, alanine, valine, glucose and maltose in equal amounts (1:1:1:1:1:1) with a total dose of 35·10<sup>-6</sup>M. The introduction of inducing compounds into the purified water flow in the JSD, under the same conditions and modes of treatment, there increases the amount of hydrocarbon-oxidizing microorganisms more than 2-fold (from 150·10<sup>6</sup> cells/ml to 325·10<sup>6</sup>kl/ml), which increases the efficiency of bio-oxidation up to 75 -78% (Fig. 5), and in the control the oxidation degree remains at 32-40%.



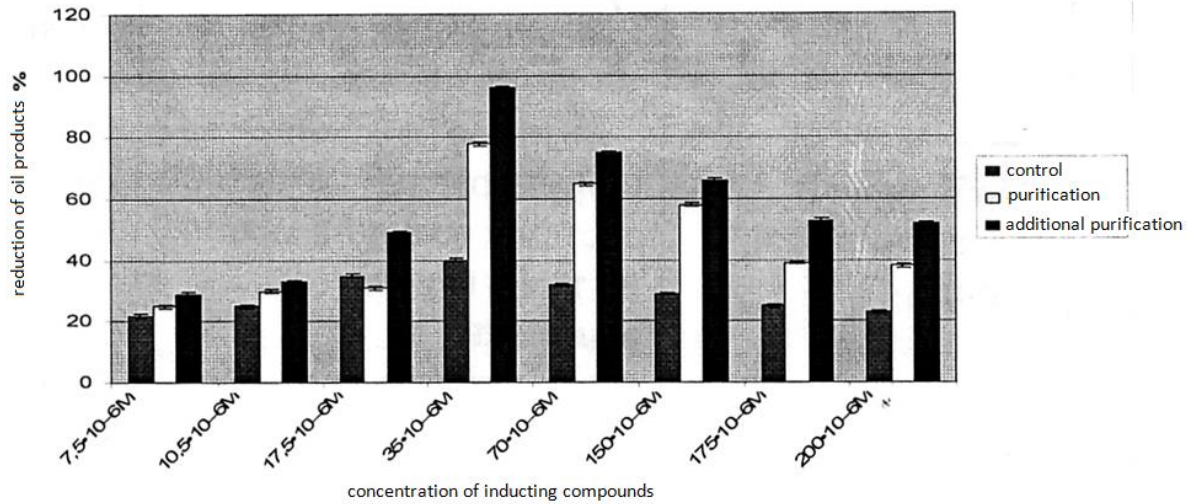


Figure 5: The effectiveness of bio-oxidation oil products by consortium at different ratios of inducing compounds (IC).

In order to stabilize the residual hydrocarbon contamination of additionally purified waste liquid is directed further to the second stage of JSD and is subjected to post-treatment in the duration from 30 minutes to 1.5 hours. At the same time purification efficiency reaches 92-96%, i.e. the concentration of hydrocarbons is reduced to 0.12-0.17 mg/dm<sup>3</sup> (Fig. 6)

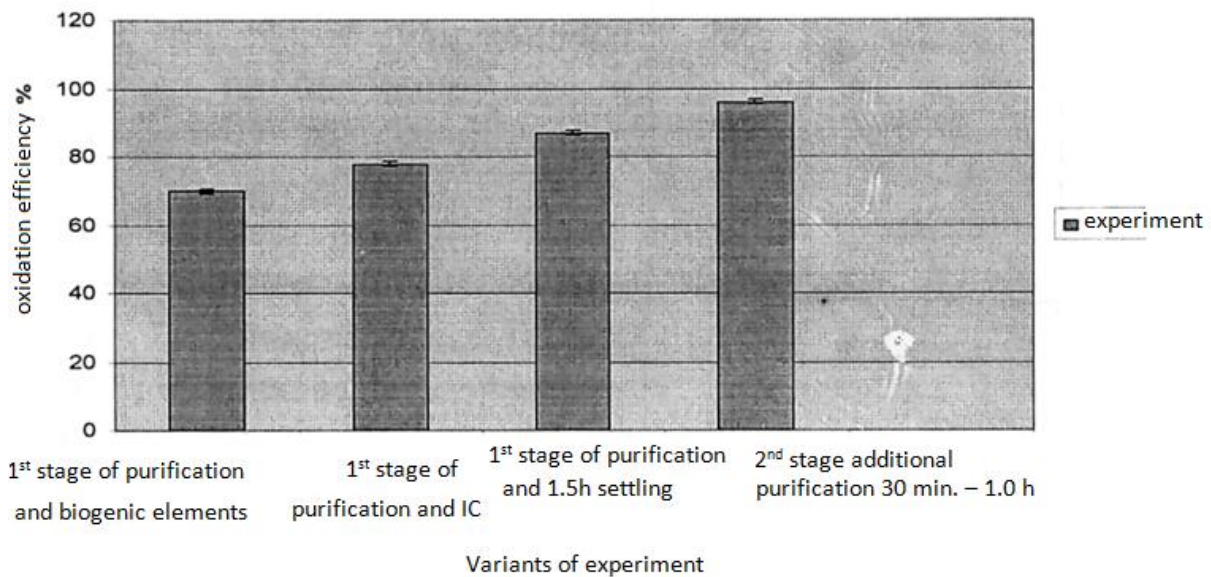


Figure 6: The oxidation of petroleum products in the JSD (stages 1, 2)

The output of the 2-stage JSD the amount of oil products in waste water fits into the sanitary standards of discharge into open water sources or use in recycling water supply. Optimization of the environmental conditions is to regulate the pH, temperature, addition of the calculated amount of nutrients, other inducing substances and compounds.

The experience of studying the influence of all the above conditions in certain defined concentrations, and in the composition of drains on the life of oxidizing microorganisms allows to assume, that at their development conditions optimization in the artificial structures can achieve maximum biochemical activity and management of petroleum hydrocarbons microbiological decomposition process [5-8].

SUMMARY

- Biotechnology of oil and hydrocarbon-containing waste water purification, comprising as the main structure the jet settling device with jet dispersing element, which provides the initial runoff neutralization with a load of over 1600 mg (COD), when the ratio of BOD<sub>5</sub>:N, P:100:5:1 with a content of composite substances  $35 \cdot 10^{-6}$  M and a number of oil-oxidizing bacteria, in average, 130 million cells/dm<sup>3</sup> for 1.2 hours of contact up to 78%.
- Additional waste liquid passing through the second JSD, the duration from 30 minutes to 1.5 hours without addition of hydrocarbon-oxidizing microorganisms' fresh portion and a settling of 1.5 - 2 hours in the secondary clarifier releases the drain from oil pollution up to sanitary standards. This helps to achieve and use treated up to standards of recycling water supply water.

### CONCLUSION

The conducted experiments and tests using SJD pilot plant allow us to conclude that the proposed biological method of oil hydrocarbons destruction in the waste water production of organic synthesis is quite acceptable for the preparation of mixed sewage of JSC "Kazanorgsintez" to the standards of water recycling.

### ACKNOWLEDGEMENTS

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