Purification of water sources from oil contamination by hydrophobic carbonate sludge

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Abstract. The paper presents laboratory and experimental studies on the purification of surface water sources from oil contamination by sorption material on the basis of production waste. Energy waste is a slurry of chemical water treatment, which is formed during liming and coagulation at the stage of preliminary purification of natural water. Based on the sludge, the hydrophobic sorption material "MGSM" was developed. The following requirements are imposed on the sorption materials that allow, at low costs, the most effective cleaning of the water surface from petroleum products: hydrophobicity, oil capacity, buoyancy, ease of utilization from the water surface, efficient work in a different temperature range, resistance to water disruption, non-toxicity, optimal price. The material obtained has these requirements. The technical characteristics of the developed sorption material were determined: oil capacity, wetting contact angle, an express analysis of the quality of the aqueous extract of the hydrophobic sorbent developed for the acute lethal toxicity of fish of the Poeciliareticulata Pet. and crustaceans Daphniamagna Str. A technological scheme for utilization of oil-contaminated hydrophobic sorption material as a secondary energy resource in industrial enterprises is proposed, a calculation of the volume of air and combustion products during its combustion, calculation of harmful emissions, thermal calculation, and prevented environmental damage.

Ecological situation in the country is determined by the enterprises of the heat and energy complex and the oil industry, chemical, petrochemical and machine-building industries, the construction complex and agriculture. The existing structure of industry, obsolete technologies form a wide range of environmental problems and sharply exacerbate the ecological situation. Oil pollution is a particular danger to the environment. Increasingly, accidents occur in the extraction, transportation and refining of oil. In this case, the method of localization of oil contamination by booms and liquidation of oil and oil products by sorption materials, developed on the basis of production wastes, is less resource and energy-consuming.

For the purification of oil and petroleum products use mechanical, physicochemical, chemical and biological methods. One effective method is adsorption - this method allows the purification of natural and waste water from oil and petroleum products to the required value without secondary water pollution. The efficiency of purification depends on the correspondence of the parameters of the porous structure of the sorbent to the size of the impurity molecules.

In the literature [1], waste from the wood processing and cellulose industry - from 88 to 94%, from sunflower to 79%, wheat husk - up to 82%, etc., has been proposed as a sorbent. Previously, [2] a hydrophobic sorption material for aqueous media from oil contamination, a modified hydrophobic sorption material ("MGSM"), was developed on the basis of chemical water treatment sludge. The sorbent is obtained by modifying the powdered chemical water treatment sludge (wetness of the sludge W = 3%, size of the particle fraction r = 0.09-0.5 mm) with a 100% silicon organic liquid "Silor" [3] at a volume ratio of liquid and solid phases of 1: 5. "Silor" is a waste product of chemical destruction: silicone rubber compounds, sealants, compounds formed in the process of manufacturing...
rubber products based on silicone rubbers. Heat treatment is carried out at 150 °C for one hour to establish a constant mass. The developed material is called the modified hydrophobic sorption material "MGSM" [4]. The technological characteristics of "MGSM", which are presented in Table. 1.

| Characteristic                              | Value       |
|--------------------------------------------|-------------|
| Particle size, mm                          | 0.09-0.5    |
| Bulk density, kg / m³                       | 790         |
| Oil intensity (relative to the Shiyskoye field oil), y/y | 0.95        |
| Humidity, %                                | 3           |
| Specific surface, m² / g                   | 65.8        |
| Total pore volume, cm³ / g                 | 0.8         |
| Water absorption, %                        | 1.3         |
| Buoyancy, mass% (96 hours)                 | 98-99       |
| Adsorption capacity by iodine, mg / g       | 14          |
| Adsorption capacity by methylene blue, mg / g | 40          |

To determine the degree of hydrophobicity of "MGSM", the contact angle of wetting the surface of "MGSM" was determined, which was 115 °. A laboratory experiment on the use of "MGSM" for cleaning the aquatic environment from oil contamination was carried out. 0.06 g "MGSM" is placed in a container with water of 1 liter, which is artificially contaminated with oil. The time of contact of "MGSM" with oil is 24 hours, while the value of the total initial concentration of oil products is 100 mg / dm³, the area of the oil slick is 39.5 cm². After 24 hours "MGSM", which is saturated with NP, is collected from the water surface by means of a special device, which is a grid with a cell size of 0.5 x 0.5 mm fixed on a metal frame. The water after the treatment is analyzed for the residual content of the NP. The residual concentration of petroleum products was 0.008 (± 0.03) mg / dm³.

Express - control of water quality for acute lethal toxicity of the guppy culture of *Poeciliareticulata Pet.* and crustaceans *Daphniamaena Str.* for carrying out ecological examination of the technology of surface water purification from oil contamination with a new hydrophobic sorption material [5].

In Table. 2 shows water quality indicators, the analysis of which revealed that "MGCM" does not create secondary pollution of the aquatic environment. At the same time, the efficiency of cleaning oil contamination "MGCM" was more than 90%.

To determine the effectiveness of cleaning water environment from NP in full-scale conditions, an experiment was carried out to remove oil contamination 5 mm thick on the pond-settler of JSC "Mari Pulp and Paper Mill" [6]. The studies were carried out using a frame made of expanded polystyrene with a size of 40x20 cm, which was covered with a polymer cloth and impregnated with silicone liquid "Silor". The quantity of "MGSM" necessary
for purification is calculated - 343.7 g. "MGSM" completely remains on the surface and is collected by special devices. The efficiency of purification from NP "MGSM" was more than 99%.

After carrying out the laboratory and full-scale experiment, a basic scheme for cleaning the pond-settler from oil and oil products "MGSM", which is shown in Fig. 1.

![Diagram](image)

Figure 1. Scheme of cleaning from oil pollution of the pond-settler "MGSM":
1 - concentration of oil pollution, 2 - spraying of "MGSM", 3 - collection of saturated "MGSM", 4 - utilization of spent "MGSM".

For the localization of oil pollution, boom bins of constant buoyancy are used, the brand of booms is selected depending on the size of the oil pollution. For the application of "MGSM" to the region of localized NP, an autonomous sprayer PC-1. In real conditions, it is difficult to determine the amount of "MGSM", which is necessary for the complete absorption of NP, so "MGSM" is sprayed with excess. According to the laboratory experiment, the time of contact of "MGSM" with the oil product to its full saturation is 30 minutes. Silicone-organic liquid "Silor" gives the waterproofing effect of "MGSM" and reduces the risks of drowning saturated "MGSM" to a minimum. The saturated "MGSM" remains completely on the surface and is easily assembled by the NP-2 oil skimmer.

After oil contamination is cleaned, the sorbed material produced by "sorbent material" is formed "MGSM", which is proposed to be used as a fuel resource in the same enterprise.

Based on the biotesting conducted, it was established that the water extract of the lubricated material "MGSM" does not have an acute toxic effect on fish of the Poecilliareticulate Pet. and crustaceans Daphniamagna Str. The obtained results confirm that the lubricated "MGSM" is practically non-hazardous and refers to V hazard class for the environment.

Damage caused to the settling pond due to the spill of the NP, which amounted to 2674.82 thousand rubles, was calculated, while the enlarged ecological and economic assessment of the damage prevented as a result of a spill of 1 tonne of oil will amount to 723.4 thousand rubles. The principal scheme of the solid waste incineration line for the utilization of the lubricated "MGSM" was modernized. The thermal calculation of the boiler was carried out during the combustion of the lubricated "MGSM": the efficiency of the boiler was 85.2%; the total fuel consumption is 0.336 kg/s.

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