Purification of natural water and wastewater from petroleum and petroleum products by sorption materials on a basis of industrial waste

E A Tatarintseva¹, I V Dolbnya¹, E A Bukharova¹, L N Olshanskaya¹, N A Politaeva²

¹Yuri Gagarin State Technical University of Saratov, the Russian Federation
²Peter the Great St. Petersburg Polytechnic University
tatarinceva-elen@mail.ru

Abstract. Results of experimental research of sorption purification of wastewater and surface water from petroleum and petroleum products by sorption materials on a basis of industrial waste have been given. Polyethylene terephthalate, ferritized galvanic sludge (FGS), oxidized and thermally expandable graphite have been chosen as the components of the sorption materials (SM). The sorption material on the basis of FGS has magnetic properties and it allows to extract the sorbent from water with the help of a magnetic separation. Physical and chemical properties of SM (buoyancy, water adsorption, petroleum capacity), kinetic regularities of the sorption of petroleum products by the sorption materials have been studied. Specific surface area, porosity, and particles dispersion have been determined. A possibility of using sorbents to collect petroleum products from the water surface has been shown.

Keywords: polyethylene terephthalate, oxidized and thermally expanded graphite, ferritized galvanic sludge, waste utilization, water purification from petroleum products, sorption, sorption materials.

Introduction

Pollution by petroleum and petroleum products is one of the most widespread, dangerous ecological contaminants in the world, which today threatens to water resources. Petroleum leakage has a hugely detrimental impact on marine and freshwater ecology. Petroleum spots slow the flow of oxygen into the water, reduce the passage of sunlight, weakening the process of photosynthesis in plants and plankton. The vital activity is changing for many species of animals and plants with petroleum pollution. The main reasons for petroleum pollution of water are deterioration of petroleum pipelines, safety violation, illegal tie-ins and accidents. In the world, the biggest disasters happen as a result of accidents in the water areas. About 1.5 millions of cubic meters of petroleum and petroleum products get into the water every year. The amount of environmental and economic damage from spills of petroleum and petroleum products depends on many factors, such as a type of spilled petroleum products, a condition of the affected ecosystem, meteorological conditions, marine and river flows, seasons, the condition of local fisheries and tourism etc.

Also, the most acute problem facing humanity is the problem of the accumulation of industrial and domestic waste, which are stored in landfills. Modern scientific and technological progress is associated with a constant acceleration in the rates of consumption of water, land and material
resources. Annually the hundreds of millions of tons of various products of anthropogenic human activity are emitted into the environment. The most dangerous among them are galvanic sludge (GS), polymer waste, petroleum products (PP). The environment pollution by petroleum and petroleum products has the negative impact on the quantitative and qualitative indicators of water and soils. Therefore, the use of industrial waste in the creation of new sorption materials, which have low cost and high efficiency, in cleaning wastewater and surface waters from PP is an urgent task and has scientific and practical value.

The scientific significance of the solution of this problem is substantiated and experimentally confirmed by the possibility of obtaining sorption materials for purification of sewage and surface waters from petroleum products with the use of polyethylene terephthalate, thermally expanded and oxidized graphite, ferritized galvanic sludge, not previously used as composite materials. For the first time, the study of the regularities of adsorption of petroleum and PP has been carried out, possible ways of increasing the sorption capacity and efficiency of water purification by modifying the structure of sorbents, their chemical composition, etc have been proposed. Methods for obtaining sorbents based on industrial wastes for the recovery of pollutants have been developed. Purification of water can include mechanical and physicochemical methods. The choice of the method and technology of spillage of petroleum and petroleum products determines the efficiency of purification. Among a wide variety of methods of water purification from PP, the sorption method is the most appropriate. With the help of SM it is possible to achieve cleaning efficiency up to 80-99 %. An important factor is the possibility of recovery of petroleum products and multiple use of sorbents.

In connection with this, the research tasks were: the development of compositions and technologies for the production of sorption materials based on industrial wastes; the study and assessment of mechanical, physical and chemical and sorption properties of the sorbents obtained, the sorption purification of model solutions and wastewater from industrial products from petroleum products using developed sorption materials in a static mode, the study of the possibility of removing petroleum products from the water surface.

The results of experimental research

It is known [1] that finely dispersed polyolefin powders are used in the liquidation of petroleum spills and petroleum products. They are effective sorbents of these pollutants.

Therefore, the task of creating a fine-dispersed porous polymer sorption material from polyethylene terephthalate (PET) waste (packaging, bottles, tare, etc.) was solved. The method of preparation is based on the phase-inverting transition of the polymer from the liquid state to the solid state [2, 3]. The solvent mixture of benzyl alcohol and dibutyl phthalate plasticizer was heated, then ground PET was added and mixed until complete dissolution of PET to form a homogeneous mixture. Cooling the mixture to room temperature results in the precipitation of a solid product (call it PSM-1 - polymeric sorption material), which was combined with acetone in a ratio 1:2. The pores are formed as a result of leaching molecules of benzyl alcohol and dibutyl phthalate from PSM-1 with acetone. This method makes it possible to obtain a finely dispersed material with mesoporous structure.

![Figure 1](image1.png)  
![Figure 2](image2.png)  

**Figure 1.** Tablets sorption materials TS-1 and TS-2. **Figure 2.** Composite magnetic sorption material (CSM).
The obtained polymeric sorption material PSM-1 can be used for sorption purification of waters from petroleum products, as well as a binder in the production of tablet sorption materials based on thermally expanded graphite (TS-1) and oxidized graphite (TS-2), figure 1 [4, 5], as well as a composite sorption material with magnetic properties based on ferritized galvanic sludge (CSM), figure 2. CSM has magnetic properties, the residual magnetic induction (Br) is equal to 0.05 T. Ferritized galvanic sludge (FGS) presents ferrites of different heavy metals, which included in the composition of the sludge. Ferrites have magnetic properties, and they determine their further useful applying in various spheres [6, 7, 8, 9, 10, 11]. The use of ferritized galvanic sludge as a magnetic constituent makes it possible to utilize industrial waste and to derive on their basis sorbents that can be extracted from the aqueous medium upon the completion of the sorption process by means of magnetic separation without additional capital and energy costs.

The main indicators of sorption materials used to collect petroleum products from the surface of reservoirs are petroleum capacity, buoyancy and water adsorption [12]. The properties of sorption materials are presented in table 1.

### Table 1. Properties of sorbents.

|                        | PSM-1 | TS-1 | TS-2 | CSM |
|------------------------|-------|------|------|-----|
| Water adsorption, g/g  | 0,5   | 0,2  | 0,2  | 0,2 |
| Buoyancy (96 hours), % | 80    | 100  | 100  | 100 |
| Oil capacity, g/g      | 3,0   | 3,5  | 7,5  | 4,0 |
| Petroleum capacity, g/g| 4,5   | 9,0  | 15,0 | 3,5 |

The buoyancy of PSM-1 is determined by the ratio of open and closed pores, which are formed during the course of the formation of the structure. The high buoyancy of TS-1, TS-2 and CSM is related not only to the high hydrophobicity of the surface of these sorption materials, but also to their structure. Depending on the weather conditions, when localizing the petroleum slick, the time reserve should not exceed 24-72 hours from the time of the spill without the danger of causing significant harm to the environment. Thus, the use of developed sorption materials, which retain buoyancy for a long time, allows carrying out measures to collect petroleum from the water surface.

The economic efficiency of sorption technology, including the specific consumption of sorbent, is largely determined by the morphology of the surface and the porous structure of the sorption material [13]. Microstructural studies of sorption materials have shown the presence of an inhomogeneous surface of the sorbent with the presence of a large number of pores and depressions of various shapes and sizes, which are the most important factors ensuring a strong retention of the sorbate on the surface and in the volume of the sorbent.

Such characteristics of sorbents as specific surface area and porosity of the material play an important role in the sorption purification of water. Porosity is described by such characteristics as the determination of the total pores volume and pore size distribution. It was found that the structure of TS-2 has the largest total pore volume compared to PSM-1 and TS-1 (table 2).

Analysis of the distribution of pores by size showed that mesopores prevail in all sorption materials, which are convenient for layerwise penetration of adsorbed molecules of petroleum products. CSM does not have porosity and the specific surface area is provided by the dispersity of the particles. The distribution of the particles of the sorbent CSM by their sizes has the following values: 10 µm – 2 %, from 10 to 100 µm – 15,22 %, from 100 to 1000 µm – 81,02 %.

Sorption properties of the obtained materials in relation to petroleum and petroleum products were studied. It has been experimentally established that the highest rate of sorption of petroleum products in both model systems and in sewage waters of the industrial enterprise «Petroleum refining plant of Saratov» (the Russian Federation) is observed in the first 10 minutes, then the sorption rate decreases. An increase in the sorption time of more than 30 minutes is impractical.
Table 2. Structural characteristics of sorption materials.

| Sorption material | Pores radius, nm | Percentage ratio of total pore volume, % | Specific surface area, m²/g | Total pore volume, cm³/g |
|-------------------|-----------------|----------------------------------------|-----------------------------|-------------------------|
|                   | till 2          | 6,38                                   |                             |                         |
| PSM-1             | 2 till 50       | 89,01                                  | 20,4                        | 0,046                   |
|                   | over 50         | 4,61                                    |                             |                         |
|                   | till 2          | 8,41                                    |                             |                         |
| TS-1              | 2 till 50       | 67,62                                  | 33,9                        | 0,096                   |
|                   | over 50         | 23,97                                  |                             |                         |
|                   | till 2          | 8,83                                    |                             |                         |
| TS-2              | 2 till 50       | 69,61                                  | 42,3                        | 0,126                   |
|                   | over 50         | 21,56                                  |                             |                         |
| CSM               | -               | -                                      | 0,12                        | -                       |

Figure 3 shows the kinetic curves of sorption of petroleum products for TS-1 and TS-2. The weight of the sorbent introduced was 0.5 g per 100 ml of the model system for TS-1 and 0.3 g per 100 ml of the system for TS-2 at t = 25 °C. It has been experimentally established that the greatest recovery of PP for TS-1 is observed in the first 30 minutes and for TS-2 in 20 minutes. A shorter time to achieve sorption equilibrium is characteristic of TS-2, which is explained by a more porous surface, which facilitates the penetration of petroleum products into the depth of the sorption material [14].

Figure 3. Kinetic curves of sorption of industrial oil I-20A by the sorption materials TS-1 and TS-2 (C_initial = 121,7 mg/l), A – sorption capacity, mg/g, C_initial – initial concentration, mg/l.

The analysis of the sorption curves showed that the maximum sorption of industrial oil by the sorption materials PSM-1, TS-1 and TS-2 happens in the first minutes, after which the sorbents are able to retain the sorbate, and it can be due not only to good hydrophobicity and oleophilicity of the obtained sorbents but to their structure [12].

It is known that the size of molecules of petroleum products fluctuates within 5-10 nm, and PSM-1 is mesoporous (the radius of prevailing pores is 2-50 nm) [15]. In addition, when solid oleophilic particles of polymer sorption material PSM-1 come into contact with a thick petroleum film around the sorbent particles, micelles form interacting with each other to form a specific network structure.
This leads to a marked increase in the viscosity of the petroleum-water suspension, and at high concentrations of PSM-1 in water, dense conglomerates of petroleum contamination are observed.

When using TS-1 and TS-2, the placement of petroleum products is also possible in the voids of the sorption material due to capillary forces and oleophilicity. With a large thickness of the petroleum film, an effective introduction of the petroleum pollutant into the porous zone of tableted sorbents occurs. The use of PSM-1 is recommended for the liquidation of petroleum spill in the water bodies as filler for mats or sleeves.

The most promising direction of using magnetic SM is the collection of spilled petroleum products from the surface of water with subsequent extraction by magnetic separation. A series of experiments with the use of CSM for the sorption of petroleum and petroleum products with different film thickness (1-5 mm) was carried out. The contact of the petroleum film with the surface of the sorbents is the largest and prevents contact of SM with water. It is established that the maximum dynamic sorption capacity of the CSM is achieved at a film thickness of ≈ 3 mm and for CSM it is equals to g/g: 0,5 (kerosene); 1,1 (petroleum) and 1,2 (industrial oil). The efficiency of the purification of the water surface when using the sorption materials is determined by the amount of the sorbent used and it can reach values of 99,9 %.

The effective intercalation of petroleum and petroleum products into the porous granular sorbent zone occurs with a greater thickness. Moreover, the formation of micelles around the sorbent particles occurs upon contact of the solid oleophilic particles of CSM with thick petroleum film. These micelles interact with each other with the formation the specific net structure, which leads to a noticeable increase in the viscosity of the petroleum-water suspension, which can be easily removed by a magnet.

Table 3 presents the comparative characteristics of the developed SM with those available on the market.

| Brand of the sorbent | Material | Appearance of the sorbent | Cost per 1 kg, RUB | Petroleum capacity, kg/kg | Water adsorption, kg/kg |
|----------------------|----------|--------------------------|-------------------|---------------------------|-------------------------|
| PSM-1                | PET      | powder                   | 238               | 1,7-4,5                   | 0,5                     |
| TS-2                 | Graphite | tablet                   | 296               | 11-15                     | 0,2                     |
| CSM                  | FGS and PSM-1 | granules              | 153               | 3,0-4,0                   | 0,2                     |
| Turbo-Jet            | Peat     | coarse-grained placer    | 370               | 2-3,6                     | 2,0                     |
| OPUUB                | Polypropylene | granules              | 460               | 1,6-5,0                   | 0,8                     |
| Unipolymer           | Carbamide-formaldehyde resin | crumb           | 420               | 20-40                     | 4,6-10,0                |
| STRG                 | Graphite | powder                   | 560-700           | 20-40                     | 0,2                     |

The adsorbents have the low cost, high sorption capacity, high mechanical strength and they are easily regenerated. The absorbed substances are extracted by the method of centrifugation or vacuum filters after the completion of the sorption process. It allows to reuse petroleum products in the industry as well as to regenerate sorbents with the possibility of their reuse. After the sorption/desorption ability (at least 5 cycles of regeneration), the materials are disposed of utilization by pyrolysis with obtaining the thermal energy or as resinous additives in asphalt mixtures at the production of paving.

**Conclusion**

The conducted research has shown the perspective of the application of the developed sorption materials on the basis of industrial waste for the liquidation of the petroleum products spills from the water surface. It is established that the SM data possess mechanical strength, good sorption capacity
for petroleum products, hydrophobicity, buoyancy, and also the possibility of their regeneration and reuse.

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