Studying the kinetics mechanism of emulsified petroleum products recovery from waste waters in dynamic conditions

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Abstract. Petroleum products belong to the most common man-made pollutants of surface watercourses, and sometimes even underground drinking water sources. They get to the environment at the extraction and transportation of oil and oil products, as well as at industrial disasters. The oil-contaminated sewage waters produce the general-toxic, embryotoxic and carcinogenic effect, and weaken the immune system. To purify wastewaters from petroleum products the most efficient and environmentally friendly is the sorption method. This paper considers using a carbon-containing material, obtained by thermal modification at 450°C of waste kieselguhr sludge from vegetable oil extraction industry, as petroleum sorbent. The designed sorbent is characterized with mesoporous structure, high hydrophobic properties and the presence of oxygen-containing functional groups – carboxyl, hydroxyl and lactone – on the carbon layer surface. Research has been carried out in purification of test water media from emulsified petroleum products in dynamic conditions with the use of the designed sorbent. The number of passed sorption volumes to the «breakthrough» and the full saturation of the sorbent with oil products were determined. The calculated dynamic exchange capacity of the sorbent for petroleum products is 2.9 mg/g, the total exchange capacity – 8.4 mg/g. The limiting stage of petroleum products sorption process kinetics with the carbon-containing sorption material in the studied conditions is diffusion inside the sorbent grains.

1. Introduction
Environmental pollution with petroleum and petroleum products is one of the global environmental problems of the present-day world. At extraction, storage, transportation, processing and utilization of petroleum and petroleum products the contamination of water, air and soil occurs and petroleum spills produce the adverse effect on plant and animal life. Technological accidents, discharge of untreated or undertreated sewage waters, chaotic organization of storm water runoffs from contaminated industrial territories cause the increase of petroleum products content in surface watercourses, and sometimes even in underground drinking water sources. The total amount of petroleum and petroleum products, getting into the global ocean each year makes up from 6 to 12 mln ton.

Sewage waters, containing petroleum products, produce the general-toxic, embryotoxic and carcinogenic effect and weaken the immune system. The petroleum products content in water bodies within the range 0.3 – 0.5 mg/dm³ inhibits the growth of fish and other aquatic organisms. The influence of such pollutant on the human body causes cardiovascular and nervous systems disorders, can influence the blood values (hemoglobin and erythrocytes decrease), affect liver or skin (dermatitises or eczemas). So, the problem of the efficient purification of oil-contaminated sewage waters is one of the most topical ones.
Getting into water bodies, oil products are mostly contained in them in coarsely-dispersed (drop-wise) state, easily float to the water surface and form a floating film or layer. Another, smaller part of petroleum products is contained in the water in the form of emulsions or solutions. But of all types of petroleum products, which contaminate water bodies, the special attention nowadays is paid to emulsified products, as they are among the most dangerous sources of environment pollution [1, 2]. Emulsified petroleum products are presented with homogeneous disperse systems, consisting of two non-miscible liquids. The dispersed phase of the emulsion is petroleum products (the particle size is over 0.45 nm), and the disperse medium is water. The emulsion stability depends on the emulsified particles' size and concentration, electrokinetic properties of the system, stirring intensity of emulsion’s components, surface tension and the presence of stabilizers.

The sewage waters, containing emulsified petroleum products, include waste cooling-lubricating fluids, used in the modern metalworking technological processes, oily wastes of glass fibers and synthetic fibers production, sewage waters of oil-production enterprises and oil refineries [3, 4]. Heavily polluted are the wastewaters, generated at cleaning and washing liquid cargo vessels’ tanks, which is done in case of accepting the cargo of higher quality than the previously transported cargo. Due to the usage of cleaning agents and other chemical reagents (surface active agents, alkalies, sodas etc.) these wastewaters are presented with very stable emulsions with petroleum products content up to 80-150 g/dm$^3$ [5].

To recover emulsified petroleum products from sewage waters the fine purification is performed, with the usage of physical-chemical (flotation, coagulation, flocculation, sorption, coalescence etc.) [5 - 7] and chemical methods (adding reagents - acids, salts, demulsifiers) [8, 9]. At present the adsorption method has got widespread use, which is conditioned by its high purification efficiency, low cost and availability of the used adsorption materials. The main characteristics of sorbents, used for recovering emulsified oil products from water media, include: oil-binding property and petroleum-binding property, hydrophobicity of its surface, possibility of recovery and the subsequent disposal of the used sorption material [3, 4].

At present the area of using industrial and agricultural waste as sorption materials is rapidly developing [10, 11]. The usage of waste products, as they are, is complicated, which is conditioned by their low sorption properties, high hydrophilic properties, as well as the possibility of washing-out of harmful components and recontamination of water media. So, in order to stabilize their structure and improve their sorption properties, the waste products are subjected to various modification methods – chemical (using acids, alkalies and oxidants solutions), physical (ultrasound treatment, UV and IR radiation) and thermal (carbonization and high-temperature treatment) [12].

Carbonization process is one of the basic methods of obtaining carbon-containing sorption materials. As the raw material source, various mineral and plant materials, as well as garden waste, can be used – moss, brown coal, rice husk, sugar cane bagasse, nutshells, sawdust and leaf litter [13, 14].

The earlier studies have demonstrated [15, 16] that as a source material for obtaining carbon-containing sorption materials to recover petroleum products from water media the sludge waste of vegetable oil extraction industry can be used, for example, waste diatomite (kieselguhr) sludge. Waste kieselguhr sludge (WKS) is an organo-mineral slow pasty mass with organic impurities content up to 70%. These organic impurities contain vegetable oil, low-hydratable phospholipids and unsaponifiables - vegetable waxes, hydrocarbons, sterols, carotenoids, alcohols etc.

According to experimental data, presented in [15, 16], the thermal modification of WKS at temperatures 450-500 °C in conditions of lack of oxygen provides the partial oxidation of organic impurities and the formation of carbonic soot-like layer on the surface of mineral (diatomite) particles. This results in the formation of new carbon-containing sorption material – thermally-modified kieselguhr sludge (TKS).

The purpose of this work is to study the process of emulsified petroleum products recovery from water media in dynamic conditions with the use of the carbon-containing sorption material, obtained from waste kieselguhr sludge of vegetable oil extraction industry.
2. Materials and Methods
As a sorption material, the refined oil extraction industry waste kieselguhr sludge from the AO «EFKO» plant, Alekseevka city, Belgorod region, Russia, was considered, thermally modified at temperature 450ºС and conditionally designated TKS<sub>450</sub>. The main characteristics of TKS<sub>450</sub> are presented in table 1.

Table 1. Characteristics of carbon-containing sorption material TKS<sub>450</sub>.

| Parameter                  | Value       |
|---------------------------|-------------|
| Color                     | black       |
| Carbon content, %         | 10 - 12     |
| Loose density, kg/m<sup>3</sup> | 310        |
| True density, kg/m<sup>3</sup> | 2540      |

As a petroleum product the mineral oil I-20A was taken, the properties of which are presented in table 2.

Table 2. Technological properties of the industrial oil I-20A.

| Parameter name                  | Result                  |
|---------------------------------|-------------------------|
| Kinematic viscosity at 40°C, mm<sup>2</sup>/s | 25-35                   |
| Acid number, mg KOH for 1 g of oil, no more than | 0.03                    |
| Ash content, %, no more than    | 0.005                   |
| Mechanical impurities content   | no                      |
| Water content                   | trace                   |
| Density at 20°C, kg/m<sup>3</sup>, no more than | 890                     |
| Chilling temperature, ºC, no more than | –15                   |
| Color on CNT colorimeter, CNT units, no more than | 3.0                    |
| Open-cup flash point, ºC, not lower than | 180                   |

As a test solution for this research the oil-water emulsion with oil concentration 15 mg/dm<sup>3</sup> was used. The emulsion was prepared by mixing distilled water and oil with a shaker within 6 hours.

As a result of the petroleum product’s contact with water a multicomponent system is formed – which contains both emulsified and dissolved forms of the oil. To describe sorption of a multicomponent mixture, the calculation method of adsorption from two-component solutions was used – a «conventional component» method. As a «conventional component» the total content of oil products in the water – emulsified and dissolved – was considered.

The petroleum products in the test solutions after their purification were analyzed by means of IR-spectrophotometry using a consistency meter KN-3. Petroleum products were extracted with tetrachloride carbon (CCl<sub>4</sub>) c.p., the quantitative determination was performed by studying the intensity of C-H bonds in the infra-red range of spectrum [16, 17].

IR spectra of the sorption material TKS<sub>450</sub> were obtained with a FTIR spectrometer «Bruker Vertex 70». Measuring range is 4000- 400 cm<sup>-1</sup>; reference sample – KBr.

To perform the purification process of the test emulsion from oil products in dynamic conditions a filtration plant was used, the diagram of which is presented in figure 1.

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The sand was preliminarily washed with distilled water and calcinated in a muffle furnace at temperature 500 ºС within 3 hours. The motion of test wastewaters in the plant was performed from top to bottom at a rate of 1.15 cm/min.

The dynamic exchange capacity (DEC), mg/g, was determined by the formula

$$DEC = \frac{V \cdot C_e}{m},$$

where:

$V$ – volume of the purified wastewater, flown out of the column from the start of the experiment to the appearance of oil product in the eluate with a «breakthrough» concentration, dm$^3$;

$C_e$ – equilibrium concentration of the wastewater, mg/dm$^3$;

$m$ – weight of the sorption material, g.

The total exchange capacity (TEC), mg/g, was determined by the formula

$$TEC = \frac{V_k \cdot C_e}{m},$$

where:

$V_k$ – volume of the purified wastewater, flown out of the column from the start of the experiment to the moment, when the concentration of oil products in the filtrate is equal to its initial concentration in the test emulsion, dm$^3$;

$C_e$ – equilibrium concentration of the wastewater, mg/dm$^3$.

3. Results

Obtaining the carbon-containing sorption material TKS$_{450}$ is based on the thermal modification of an organo-mineral material - waste kieselguhr sludge - at 450°C. At this temperature and lack of oxygen the partial oxidation of organic impurities takes place. The generated organic discomposition products and preproducts sedimentate in macropores and large mesopores of kieselguhr particles, «sealing» or blocking them. This is accompanied with the formation of mostly large mesopores over 50 nm and the formation of material with the specific surface 0.9 – 1.5 m$^2$/g.

The qualitative assessment of the sorption material TKS$_{450}$ surface was preformed by IR spectroscopy and electronic microscopy methods.

The findings of IR spectroscopy of TKS$_{450}$ are presented in figure 2.

At the IR-spectrum of TKS$_{450}$ (figure 3) the intensive bands are registered at 2926 and 2853 cm$^{-1}$, which correspond to the range (2850 – 3000 cm$^{-1}$) and belong to the valence vibrations, and the average intensity band at 1470 cm$^{-1}$ - to the deformation vibrations of methylene groups and characterize the presence of C$_{sp3}$-H bond on the carbon surface of TKS$_{450}$. The valence vibrations at 1719 cm$^{-1}$ correspond to the carbonyl group (C=O) of compound ethers or lactone, contained in vegetable waxes and waxlike substances, which provides TKS$_{450}$ with high surface hydrophobicity.
The obtained data correlate well with the research findings, presented in figure 3. A drop of water, placed onto the compacted surface of TKS\textsubscript{450}, forms a sitting drop, the contact wetting angle is 156\textdegree.

So, the considered carbon-containing sorption material TKS\textsubscript{450} is characterized with the mesoporous structure, high hydrophobic properties of the surface and various oxygen-containing functional groups – carboxyl, hydroxyl and lactone – on the carbon layer surface.

The physical and chemical properties of the sorption material TKS450 indicate the promising outlook of its usage in purification of water media from petroleum and petroleum products. The obtained carbon-containing sorption material TKS450 was studied for recovering emulsified petroleum products from test water media in dynamic conditions.

The technological, operational and economic advantages of dynamic conditions in wastewater purification predetermine their wide use at the plant conditions. At developing sewage waters after-purification technologies by the sorption method one of the most important characteristics of sorption materials is their dynamic exchange capacity (DEC).

![Figure 2. IR-spectrum of the carbon-containing sorption material – TKS\textsubscript{450}.

Figure 3. Water drop on the surface of TKS\textsubscript{450}.](image-url)
The dynamic exchange capacity was determined by the «breakthrough» of the absorbed substance at the exit of the purified water from the column. The «breakthrough» concentration is determined with the analytical method’s quantification level, but in the real conditions of technological process it is usually correlated with the maximum allowable concentration (MAC), which depends on the requirements of a certain industry, and thus can have different values. In this experiment as a «breakthrough» concentration of oil products the maximum allowable concentration for cultural and general objects of water use – 0.3 mg/dm$^3$ – was taken. According to the results, presented in figure 4, the volume of the filtrate, flown out of the column from the start of the experiment to the appearance of oil product in the eluate and reaching the concentration 0.3 mg/dm$^3$, amounted to 45 passed volumes or 1125 ml of the emulsion with the initial concentration 15 mg/dm$^3$.

The total exchange capacity (TEC) was determined by saturating the sorption material with the absorbed substance until the concentration of oil products in the filtrate is equal to its initial concentration in the test emulsion.

![Figure 4. Elution curve of recovering petroleum products by using the carbon-containing sorption material TKS$_{450}$](image)

The complete saturation of the TKS$_{450}$ sorption material with petroleum products takes place at 130 passed volumes of the emulsion, which amounts to 3250 ml. The calculation results of DEC and TEC are presented in table 3.

| $C_{\text{init}},$ mg/dm$^3$ | DEC, mg/g | TEC, mg/g |
|---------------------------|------------|----------|
| 15                        | 2.9        | 8.4      |

It should be pointed out that the adsorption efficiency in dynamic conditions depends to a great extent on kinetic factors. Determining the kinetics mechanism of a sorption process is a complex problem, which requires taking into account a number of factors, which influence its rate. These are the sorption material’s particle size, filtration rate, environment temperature etc.

The adsorption process consists of 3 stages: the approach of the absorbed substance molecules to the outer surface of the sorption material (external diffusion), diffusion inside the particles (internal diffusion) and condensation of molecules on the inner surface of the sorption material (sorption act). So, the rate of adsorption process is determined with diffusion. According to the limiting stage, we can single out 3 kinetic modes of the sorption process: external-diffusional, internal-diffusional and combined.
The limiting mechanism of sorption kinetics was determined by sorption process interrupt method or by «kinetic memory» method in dynamic conditions. For this purpose, a test emulsion with petroleum products concentration 15 mg/dm³ was passed through the filtration plant, in fractions by 25 ml. The process interrupt amounted to 24 hours. After 24 hours the test emulsion passing through the filtering unit was resumed, and the adsorption process continued. In the filtrate the residual concentration of hydrocarbons was determined.

In figure 5 the elution curves of petroleum products sorption with the carbon-containing sorption material TKS₄₅₀ in conditions of process interrupt for 24 hours are presented.

As we can see from the curves (figure 5), in all cases with sorption process interrupt the reduction of oil products concentration in the solution, flowing out of the column, was observed. The break of continuity on the elution curves of sorption allows us making a conclusion that the limiting stage of the petroleum products sorption process kinetics with the carbon-containing sorption material TKS₄₅₀ in the conditions under study is diffusion inside the sorbent grains. So, the sorption rate is inhibited with the internal-diffusion processes.

![Elution curves of petroleum products recovery](image)

**Figure 5.** Elution curves of petroleum products recovery by using the carbon-containing sorption material TKS₄₅₀ in conditions of process interrupt for 24 hours, volume of the eluate (filtrate) fraction is 25 ml.

4. **Conclusion**

The carried-out research of petroleum products sorption process in dynamic conditions with the use of carbon-containing sorption material TKS₄₅₀, obtained by the thermal modification of waste kieselguhr sludge from vegetable oil extraction industry, allows us making the following conclusions:

1. The carbon-containing sorption material TKS₄₅₀ has the developed, mostly mesoporous structure, high hydrophobic properties and various oxygen-containing functional groups on the carbon layer surface. The obtained data confirm the supposition, that the considered sorbent would be efficient in purification and after-purification of sewage waters from the pollutants, particularly from the emulsified petroleum products, in dynamic conditions.

2. The obtained carbon-containing sorption material TKS₄₅₀ with particle fraction below 0.315 mm was studied for recovering emulsified petroleum products from test emulsions in dynamic conditions. DEC amounted to 2.9 mg/g, TEC – to 8.4 mg/g.

5. **Acknowledgments**

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