

Sorption of Petroleum Products from Aqueous Solutions and Emulsions Using Disperse and Fibrous Materials

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Abstract

Water-soluble and emulsified petroleum products were removed from water using ultrafine aluminium oxyhydroxide (AOH) and fibrous materials (polypropylene, carbon fibre and basalt) in static and dynamic modes. The adsorption values of water-soluble petroleum products with AOH decrease in the series: diesel fuel – crude oil – gasoline. The efficiency of water purification from dissolved hydrocarbons amounts to 98% for diesel fuel in static modes. Sorption of petroleum products from emulsions is significantly greater and amounts to 15 mg/g of adsorbent under static conditions. The purification efficiency of water containing up to 100 mg/L of petroleum products amounts to 90%. Increasing AOH/emulsion ratio we shorten time of water-oil emulsion destruction and decrease residual concentration of oil in water. The efficiency of the removal of dissolved hydrocarbons and gasoline is about 80% in the dynamic purification process and that of an emulsion – about 90%. At the thickness of a filtering layer of only 1 cm AOH effectively removes both dissolved and emulsified petroleum products. One can use fibrous filtering materials to filter water-oil emulsions. It is shown that filtration of emulsions through the filters filled with carbon fibre and compressed basalt fibre with clay-cellulose binder increases purification efficiency up to 70-80%. Carbon fibre and compressed basalt fibre sorbents proved to be the most effective materials; the purification degree at their application amounts to 70-80%. Compressed basalt fibre is effective in a wide range of linear filtration rates (3-6 m/h) and a minimal thickness of filtering layer is 1 cm without any noticeable loss of purification quality. Combining of ultrafine AOH and fibrous filtering materials in a multilayered adsorbing filter allows one to purify water from petroleum products with various dispersion degrees in a wide concentration range. The filter is regenerated with live steam.

Introduction

At present pollution of natural water basins has become catastrophic. Crude oil and the products of its refining occupy a particular place among a great diversity of contaminants. Oil fields, oil-refining and oil-transporting enterprises, a huge network of petroleum storage depots and filling stations, inevitable disposal of process waste into water basins and onto the soil, as well as industrial emergency situations cause negative effects on the environment.

Crude oil and petroleum products in aqueous medium may be present both as large disperse inclusions (drops and surface films) and in emulsified and dissolved states. Coarse-disperse admixtures may be

comparatively easily removed from water using mechanical methods, whereas the destruction of fine emulsions and especially the removal of water-soluble petroleum products remains a sufficiently complicated technical issue to the present day. By this reason an integrated purification of sewage from oily contaminants is generally carried out in several stages. At the first stage the sewage is subjected to a primary treatment: settling, filtration through mechanical filters, coagulation, flotation *etc.* Adsorption, membrane filtration, and other technologies are applied in fine sewage polishing.

Among the existing techniques, the sorption methods are the most adequate and allow the admixtures to be almost completely removed from aqueous medium. The sorption treatment is efficient within the entire range of oily admixtures, nevertheless, its advantages, in comparison with other methods of treat-

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ment, are seen at low admixture concentrations. That is why the sorption processes using a wide range of natural and synthetic adsorbents are already applied in technologies of preparation of super pure water for new high-tech technologies, in technical means of fine treatment of drinking water and in treatment of industrial sewage [1].

The filtration method is widely used in the sewage purification from emulsified inclusions of crude oil and petroleum products. Filtering beds may include quartz sand, expanded clay, anthracite, perlite. Hydrophobisation of such materials increases their sorptive capacity. Thus, hydrophobised perlite provides for decrease in the concentration of dissolved petroleum products from 1-3 to 0.2-0.3 mg/L [2-5]. Granulated and fibrous polymer materials (polypropylene, polyethylene terephthalate, polystyrene, foamed polyurethane *etc.*) possess a high mechanical strength, chemical resistance, hydrophobic surface properties and high capacity towards the petroleum products [1,6,7]. Mineral fibres – ultrafine quartz fibrous material, basalt fibre *etc.* are efficient filtering materials in the processes of sewage purification from emulsified petroleum products [8-10]. The efficiency of emulsion separation depends on the fibre diameter and their stacking density. The smaller are the fibre diameter and size of interfibrillar pores, the better is the effect of emulsion separation.

Nevertheless, above filtering materials do not solve the problem of removal of dissolved pollutants, including hydrocarbons. Ultrafine adsorbents for integrated sewage purification from petroleum products and a wide range of cocontaminants were developed at the Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia (IPC SB RAS) [11-13]. These sorbents were produced via oxidation of nanosized aluminium by water and represent a mixture of aluminium oxyhydroxides of variable composition. The phase composition of reaction products depends on the reaction temperature and time, pH of the reaction medium, and properties of the initial aluminium powder. Structural and texture AOH parameters may be widely varied through thermal treatment of the initial sample [14]. The research work performed has shown that the materials treated in the temperature range 300-600°C possess the maximal adsorption ability.

To carry out an integrated water treatment, it is appropriate and more economically feasible to use disperse adsorbents and fibrous sorbents placed layerwise. We have developed a filtering and adsorp-

tion technology of oily sewage treatment that is successfully applied in the filtration station at the Tomsk petroleum storage depot (Russia) since 1995 [15]. Multilayered adsorbents used in the installation possess a high sorptive capacity towards the petroleum products and efficiently remove a wide range of contaminants. In addition to dissolved and emulsified petroleum products, removed are heavy metal ions, organic contaminants, surfactants *etc.* [16]. The efficiency of the installation consisting of 6 units is 1-5 m³/h at the initial concentration of petroleum products 10-300 mg/L. The filtration station is monitored during all the period of its operation.

Our work presents the kinetic relationships of removal of dissolved and emulsified crude oil and petroleum products from water using the ultrafine aluminium oxyhydroxide and fibrous filtering materials: basalt fibre, compressed basalt fibre with clay-cellulose binder, carbon and polypropylene fibres.

Experimental

Characteristics of the subjects of investigation

We studied the commercial crude oil of the Sovetskoye oil field (West Siberia), density of 0.866 g/cm³ and viscosity of 5.33 g/cm³ (crude oil), winter diesel fuel according to GOST 305-82 (diesel fuel) and AI-92 grade gasoline according to GOST P 51105-97 (gasoline).

The initial AOH sample was produced by hydrolysis of electroexplosion nanosized aluminium at 55°C for 5-7 hours, and then it was kept in mother solution (pH 10-11) for 24 hrs to complete the oxidation process of large aluminium particles [11]. The product obtained was dried on air at 130°C followed by the calcination in isothermal mode at 400°C for 2 hrs. AOH synthesised has the composition Al₂O₃·0.7 H₂O, specific surface area 356 m²/g and specific pore volume 0.835 cm³/g. The maximum of pore distribution by size is at 5 nm (Fig. 1). The sample consists mainly of γ -Al₂O₃ and residual pseudoboehmite.

Carbon fibrous material (CF) is a product of carbonisation of a polymer mixture with petroleum or coal-tar pitch and has a porous fibrillar structure. The fibril diameter is 0.1-3 μ m, total pore volume is 2-3 cm³/g. The presence of fibrillar structure ensures high sorptive properties of the material [17]. CF is made in the form of non-woven fabric, which enables its application as a filtering material.

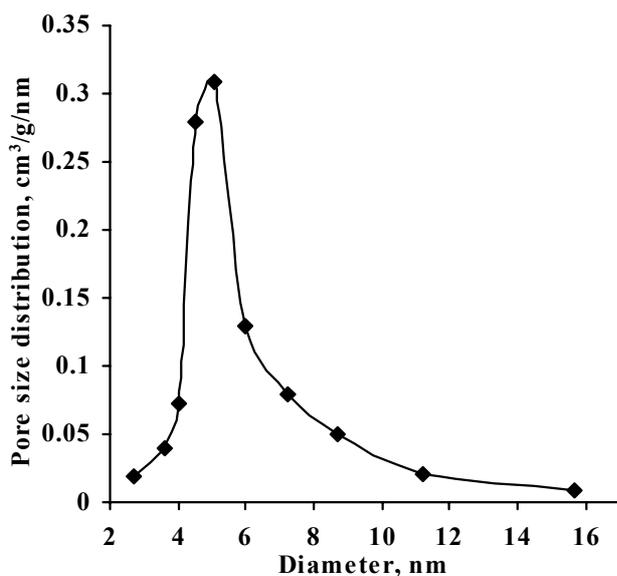


Fig. 1. Pore size distribution in ultrafine AOH.

Superfine basalt fibre (BF) was produced from a melt of basalt rocks. Chemical composition of basalts used for fibre production may be represented as follows (wt.%): SiO₂ – 49.06; TiO₂ – 1.36; Al₂O₃ – 15.70; Fe₂O₃ – 5.38; FeO – 6.37; MgO – 6.17; CaO – 8.95; Na₂O – 3.11; K₂O – 1.52; MnO – 0.31; P₂O₅ – 0.45; H₂O – 1.62. SiO₂ content in basalt rocks ranges from 44 to 53.5%. Basalt density is 2520-2970 kg/m³, melting temperature is 1100-1250 to 1450°C [18]. Compressed basalt fibre with clay-cellulose binder (BFC) produced by compression of BF preliminary treated by white clay and cellulose was obtained from the "Altai" Federal Scientific and Production Centre (Biysk, Russia) [19].

Polypropylene fibre (PP) produced from a melt of recycled thermoplastics was obtained from the Research Institute of Construction Materials (Tomsk, Russia) [20].

Specific surface ($a_s(BET)$) and pore size distribution of the samples were determined by the method of nitrogen thermal desorption using an specific surface analyser (Sorbometr M, "Katakon" Ltd., Novosibirsk, Russia) [21]. Thermal analysis of AOH was carried out on a Q-1500 derivatograph of the Paulik-Paulik-Erdey type in the temperature range 20-1000°C and heating rate 10 °C/min on air; the sample weight was 0.2 g. The curves of X-ray scattering were recorded on a DRON-3 diffractometer in the range of middle and large angles ($2\theta = 3-60^\circ$, Mo K α irradiation) with continuous scanning 1 °/min.

Interfibrillar or intergranular porosity of fibrous materials was calculated using the formula $1 - (\rho_a/\rho_r) \times$

100%, where ρ_a is apparent density (the ratio of fibrous material mass to its volume in the filter); ρ_r is real density of fibrous materials: 0.91, 2.2 and 1.9 g/cm³ for PP, BF and CF, respectively (tabulated values).

Stacking density was calculated on a MBI-15 optical microscope.

The properties of fibrous materials are shown in Table 1.

Table 1
Properties of fibrous materials

Properties	CF	BF	BFC	PP
Porosity, %	96	88	94	84
Specific surface, m ² /g	600	1.67	0.9	0.8
Stacking density, g/cm ³	0.078	0.221	0.128	0.148
Fibre diameter, μm	0.1-3.0	0.5-3.0	0.5-3.0	3-10

Preparation of solutions and emulsions of crude oil (or petroleum products) in water

Solutions of crude oil (or petroleum products) in water were prepared as follows. 100 mL of crude oil (petroleum products) were mixed with 5 g of distilled water and kept for 7-10 days at room temperature with periodical mixing. Water containing dissolved hydrocarbons was poured out through the lower discharge cock without stirring the sediment up.

Water-oil emulsions were prepared by mixing water and crude oil (petroleum products) using a high-speed (2500 rpm) mechanical mixer. 10 mL of crude oil or petroleum products were poured into 1 L of distilled water and mixed for 10 min. Suspended petroleum products were separated. Initial concentrations of crude oil (petroleum products) in water were 200-500 mg/L.

Petroleum products adsorption using AOH under static conditions

One litre of water-oil emulsion or petroleum product solution was placed into a conical flask, then 10 g of ultrafine AOH was added. The mixture was stirred in a magnetic mixer for 5-120 min. The adsorbent was filtered and the concentration of petroleum products in the filtrate was determined.

Petroleum products adsorption under dynamic conditions

A defined weight or volume of sorbent was placed into a model filter 80 mm high, with cross-section area 16 cm² and volume 128 cm³. Hydrocarbon emulsion or solution were fed through the filtering layer downwards using a BVP-Z (Ismatec) peristaltic pump at a linear speed 3-16 m/h. The thickness of the fibrous sorbent layer was from 1 to 5 cm. The concentration of dissolved or emulsified crude oil (petroleum products) was determined in the filtrate obtained. The analysis of complex action of AOH – fibrous materials was made on a filter where two AOH layers were separated by three layers of fibrous material 2 g each (Fig. 2).

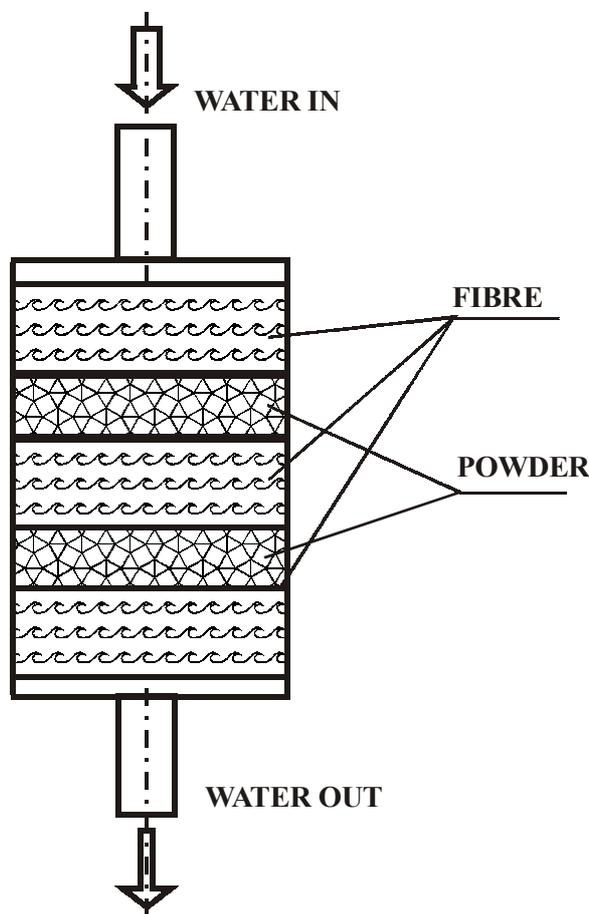


Fig. 2. Diagram of the model multilayered filter.

Analysis of solutions and emulsions of crude oil and petroleum products in water

Dissolved product concentration was determined using IR spectrophotometry [22]. Petroleum products were extracted from water by CCl₄ and separated from

other classes of organic compounds on column packed with chromatographic alumina. IR spectra of the solutions obtained were recorded using a SPECORD-M80 spectrophotometer (Karl Zeiss) in a quartz cell in the wave number range 2500-3500 cm⁻¹ corresponding to valency vibrations of C–H groups of different classes of hydrocarbons. Cell thickness was 1 cm. The content of petroleum products was determined using a calibration curve. A state standard sample for petroleum products was used to plot the calibration curve.

The concentration of emulsified products was determined using colorimetry [23]. Sudan-III dye that is insoluble in water was added to water containing emulsified petroleum products. The content of petroleum products in water was assessed by coloration intensity. The optical density of the sample was measured by the FEK-60 photoelectrocolorimeter equipped with a blue filter at $\lambda = 450$ nm. The concentration of petroleum products was calculated using the calibration curve. The initial concentration of crude oil (petroleum products) in water was 200-500 mg/L.

The purification degree was determined using the formula $[(C_0 - C)/C_0] \times 100\%$, where C_0 is initial concentration, C is actual concentration.

Results

Removal of petroleum products using ultrafine aluminium oxyhydroxide

The contact of crude oil or petroleum product with water results in the formation of a multi-component mixture whose composition depends on many factors, including the composition of crude oil and commercial petroleum products, temperature, solubility of individual components *etc.* Aromatic hydrocarbons, predominating by toluene and xylene (10 and 63 wt. %, respectively), possess the highest solubility in water. Figure 3 shows the results of adsorption of water-soluble crude oil components under static conditions.

The hydrocarbons of diesel fuel boiling off within 125-340°C and characterised by low solubility in water are best adsorbed from aqueous solutions. The lowest adsorption value is observed for gasoline hydrocarbons. As seen from Figure 3a, the adsorption value decreases with increasing hydrocarbon solubility in water. The adsorption values decrease in the series: diesel fuel – crude oil – gasoline and are 0.61, 0.46 and 0.3 mg/g, respectively. Efficiency of water purification from dissolved hydrocarbons increases and reaches 98% for diesel fuel (Fig. 3b).

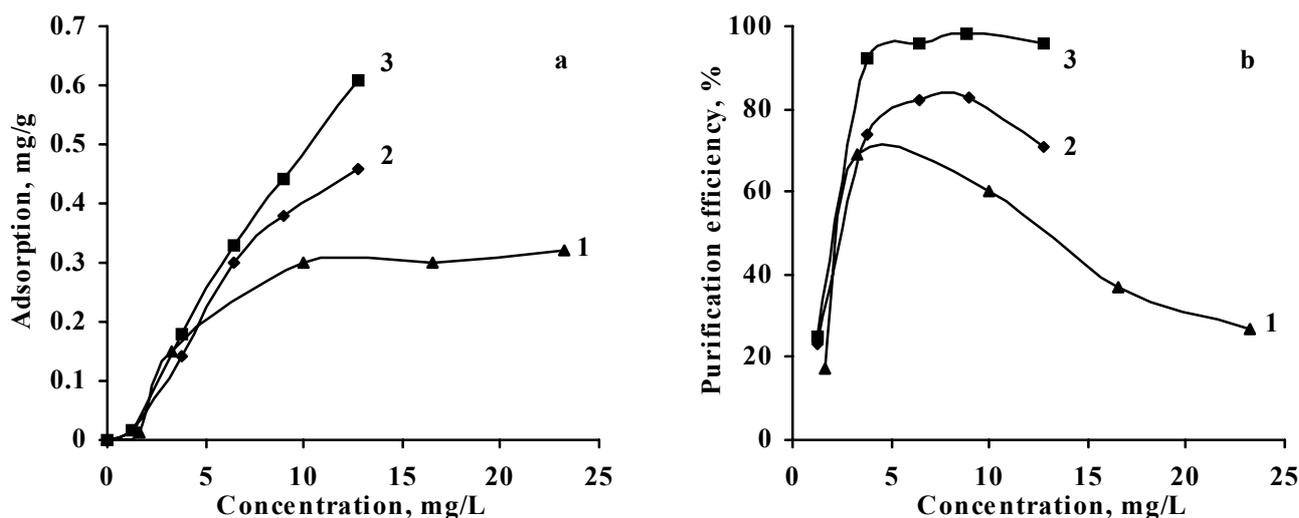


Fig. 3. Isotherms of adsorption of dissolved petroleum products (a) and efficiency of water purification from dissolved hydrocarbons (b) using the ultrafine AOH under static conditions: 1 – gasoline, 2 – crude oil, 3 – diesel fuel.

Sorption of petroleum products from emulsions is significantly higher and reaches 15 mg/g of adsorbent under static conditions (Fig. 4a). The sorption isotherm has a linear behaviour, the straight lines practically coinciding for all the petroleum products, *i.e.* crude oil, diesel fuel, gasoline. The introduction of an ultrafine adsorbent into a water-oil emulsion breaks the stability of the system, the coagulation of petroleum product drops takes place and large aggregates with the particles of ultrafine AOH are formed. A high total degree of purification is reached because only the finest disperse part of emulsion and some dissolved hydrocarbons remain in water.

The relationship between the efficiency of water

purification from emulsified products and initial concentration of disperse phase is ambiguous. The purification degree of water containing to 100 mg/L of petroleum products reaches 90% for all petroleum products studied. An increase in the initial concentration to 400 mg/L results in the decrease in purification degree to 70%. With gasoline, even at the concentration of 30 mg/L, water is purified only by 75% (Fig. 4b). It is obvious that the decrease in petroleum product solubility in water enables a higher removal degree.

Figure 5 shows the data on adsorption kinetics of dissolved and emulsified petroleum products ($C_0 \sim 200$ mg/L) using an ultrafine AOH in the static mode.

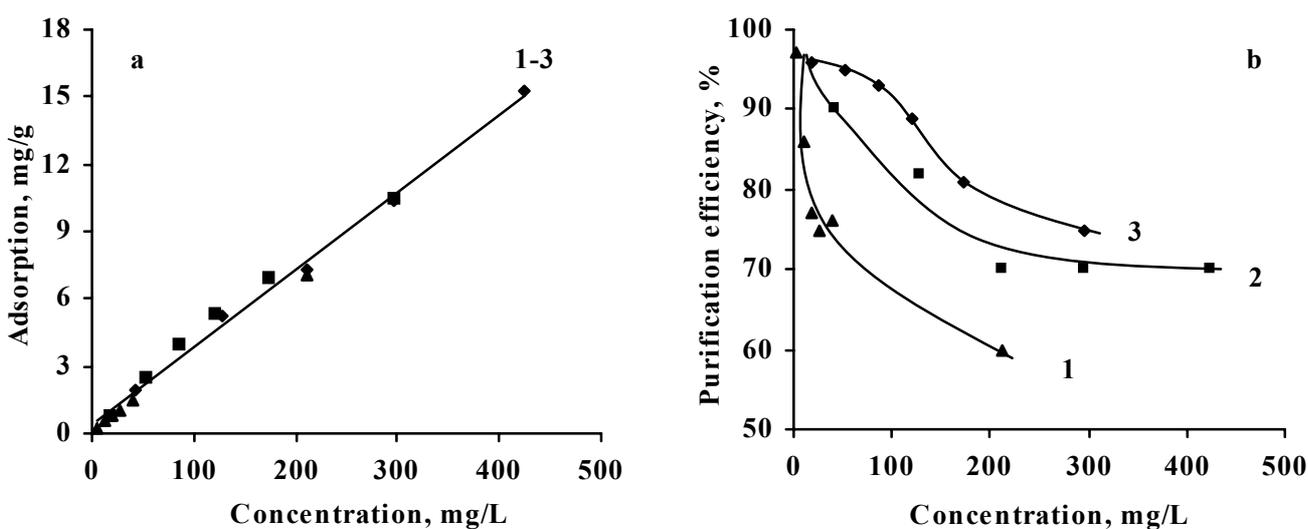


Fig. 4. Isotherms of adsorption (a) and efficiency of water purification (b) from emulsified petroleum products using the ultrafine AOH under static conditions: 1 – gasoline, ($C_0 = 23.2$ mg/L); 2 – crude oil ($C_0 = 12.8$ mg/L); 3 – diesel fuel ($C_0 = 12.7$ mg/L).

The system equilibrium is reached in 40 min both for petroleum product solutions and crude oil emulsions. The highest efficiency of water purification from dissolved hydrocarbons was 28%, 68% and 93% for gasoline, crude oil and diesel fuel, respectively. Purification efficiency from emulsified petroleum products is higher and is within 76-99%.

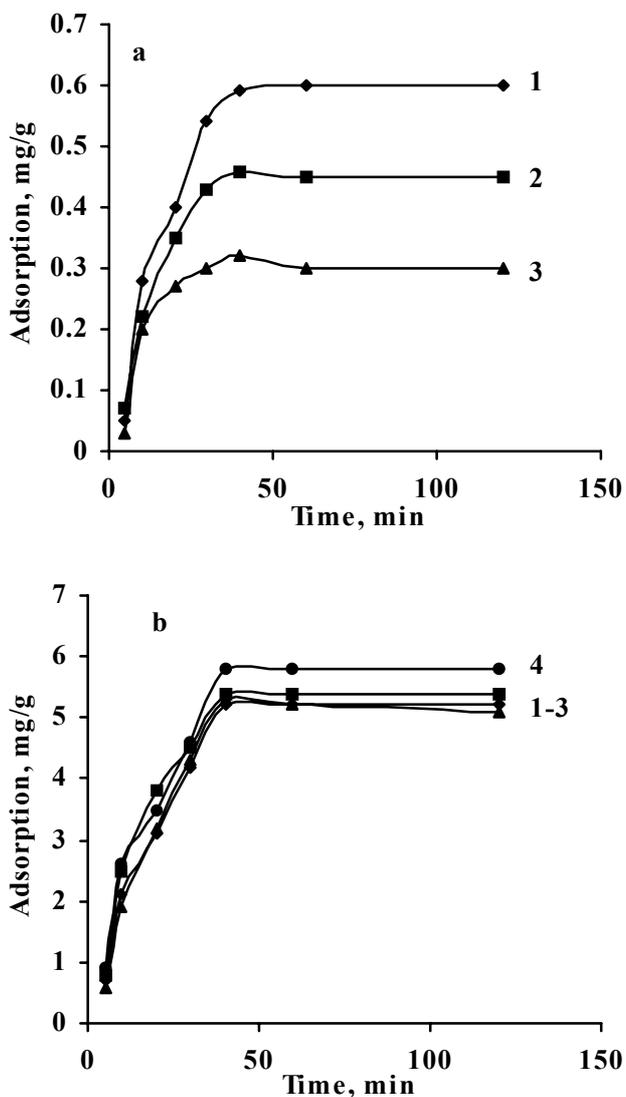


Fig. 5. Kinetic curves of the sorption of dissolved (a) and emulsified ($C_0 = 200$ mg/L) (b) petroleum products using the ultrafine AOH: 1–diesel fuel, 2–crude oil, 3–gasoline.

We studied the effect of adsorbent concentration on the process of water-oil emulsion destruction. The time of emulsion destruction is the period of time when the sorption of emulsified petroleum products by an adsorbent takes place. It is seen from Figure 6 that the destruction time of water-oil emulsion and residual concentration of oil in water decrease with

increasing AOH/emulsion ratio. An optimal AOH/emulsion ratio is about 10 g of sorbent per 1 litre of emulsion, the decomposition time being 30-50 min.

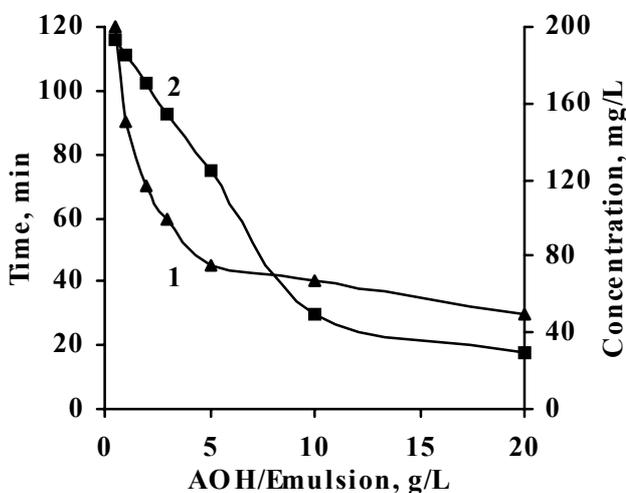


Fig. 6. Effect of AOH/emulsion ratio on the time required for water-oil emulsion destruction (1) and residual concentration of petroleum products (2); oil content was 250 mg/L.

Figures 7 and 8 shows the results of the tests of AOH sorption activity in the dynamic purification process. During the filtration of sewage polluted by dissolved oil components through an AOH layer (1 cm thick and weighing 10 g) their concentration reduces to 1 mg/L, residual concentration of more soluble gasoline hydrocarbons – to 5 mg/L, the purification degree from dissolved hydrocarbons of oil and gasoline being about 80% (Fig. 7b).

Purification degree of water-oil emulsions under dynamic conditions, similarly to static ones, decreases with increasing initial hydrocarbon concentration in water (Fig. 8a). Purification degree of an emulsion is about 90% for sewage containing 200 mg of oil per litre, and 70% at the concentration 500 mg/L (Fig. 8a). In this case the residual concentration of petroleum products increases from 10 to 150 mg/L (Fig. 8b).

Thus, AOH demonstrate a high efficiency in the processes of removal both of dissolved and emulsified petroleum products at the thickness of the filtering layer of 1 cm already. Increased initial concentration and solubility of petroleum products resulted in reduced water purification efficiency.

AOH layer 1 cm thick does not provide for complete removal of petroleum products from water. It becomes necessary to increase the thickness of the filtering layer, which will result in the increase in filter resistance and pressure drop at the filter out-

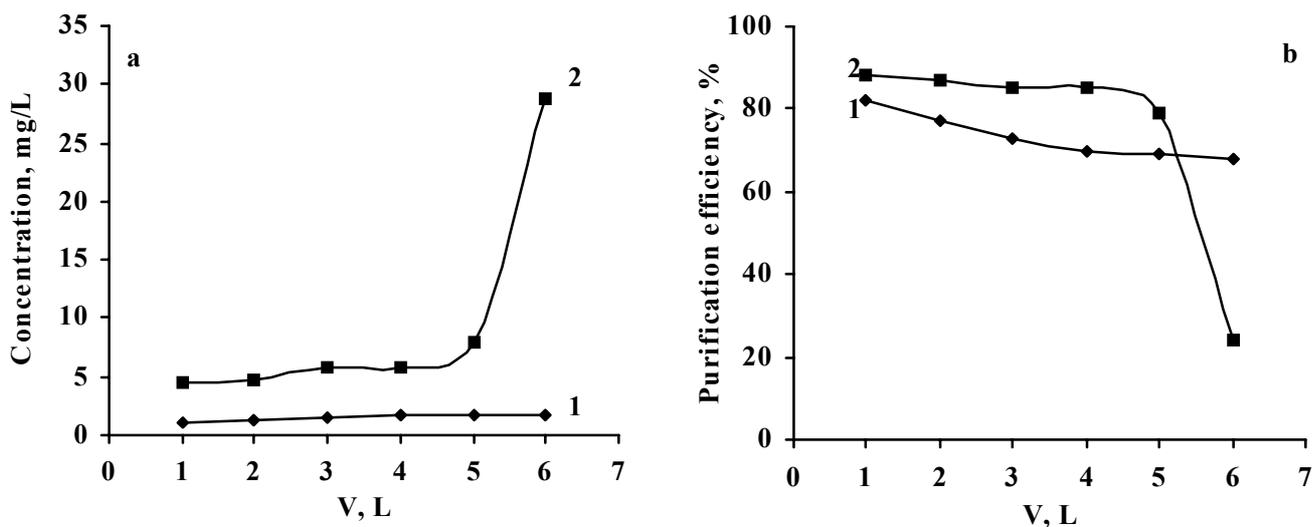


Fig. 7. Changes in the residual concentration of dissolved hydrocarbons (a) and purification degree (b) in the process of water filtration: 1 – crude oil ($C_0 = 5.7$ mg/L), 2 – gasoline ($C_0 = 37.9$ mg/L).

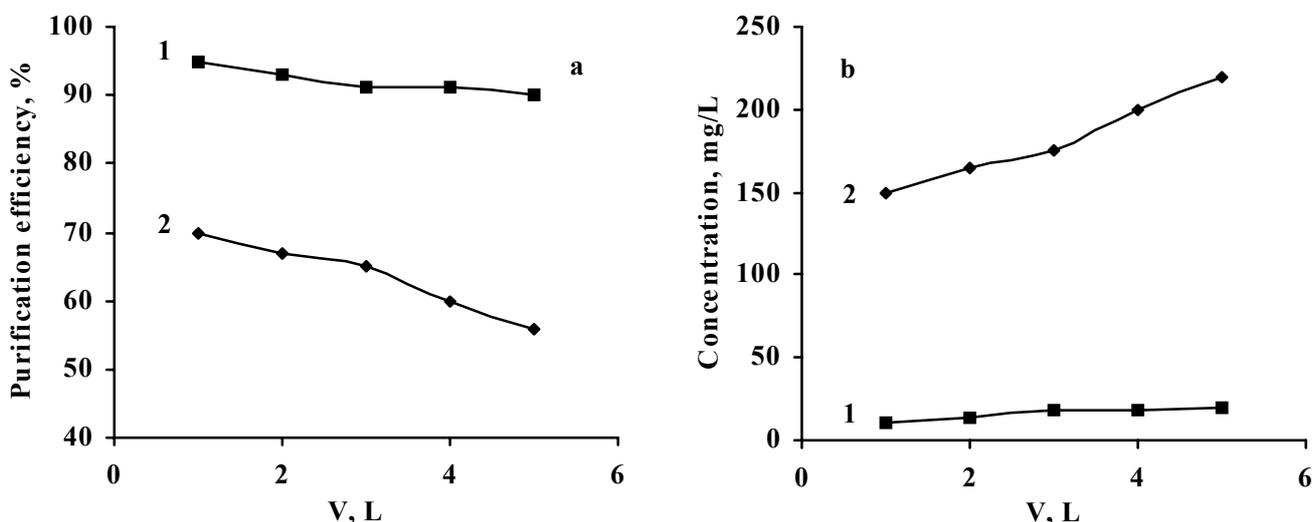


Fig. 8. Changes in the purification degree (a) and residual concentration (b) of emulsified petroleum products in the process of water filtration: 1 – $C_0 = 200$ mg/L, 2 – $C_0 = 500$ mg/L.

flow. AOH sectioning allows this problem to be avoided. It is advisable to put fibrous filtering materials between the AOH layers. In addition, isolation of AOH layers by fibrous materials allows the charge of the petroleum pollutant on the AOH that is an artificial and rather expensive sorbents to be reduced.

Separation of water-oil emulsions by fibrous materials

Fibrous filtering materials are cheap and environmentally safe. They may be used for filtration of water-oil emulsions. Figure 9 shows the relationships between the purification degree (Fig. 9a) and oil

adsorption (Fig. 9b) during filtration of water-oil emulsions through the filters filled with BFC, CF, BF and PP. As seen, the most efficient are fibrous BFC and CF sorbents; the purification degree at their application reaches 70-80%. The operating efficiency of filters filled with BF and PP 1 cm thick is not high due to a small stacking density of fibres and, therefore, a short period of protective filter action.

The effect of adsorbent layer thickness on water purification efficiency is shown using BFC as an example. The increase in the thickness of BFC layer from 1.0 to 5.3 cm results in the improvement of water purification efficiency from 30 to 98% (Fig. 10a). The optimal layer thickness is within 2-3 cm, the pu-

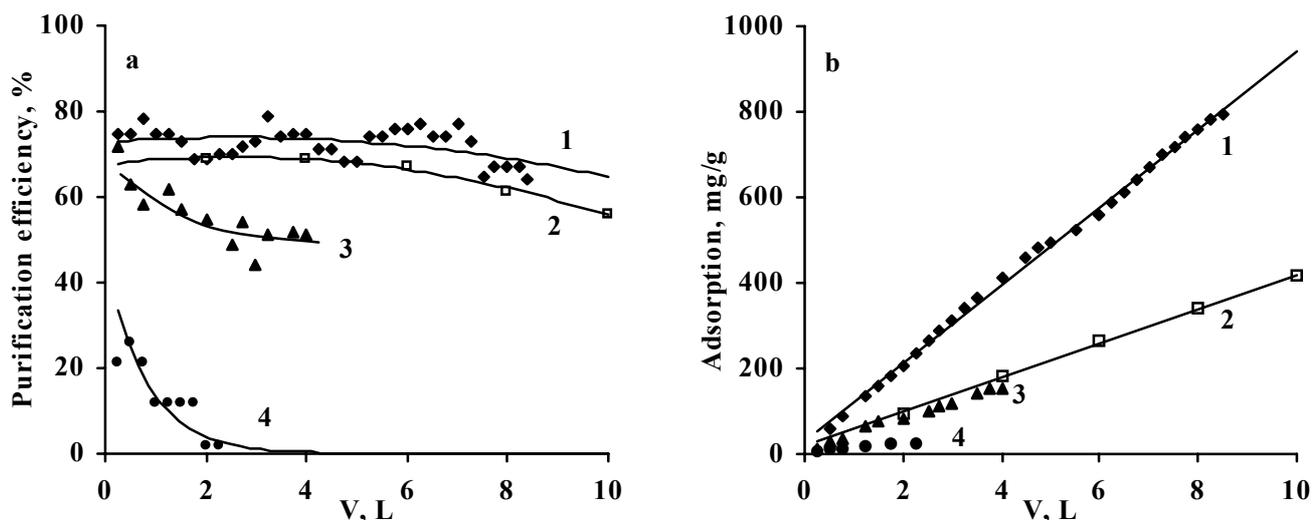


Fig. 9. Effect of the nature of filtering materials on the water purification efficiency (a) and adsorption value (b) during filtration of water-oil emulsions: 1 – BFC, 2 – CF, 3 – BF, 4 – PP, $C_0 = 500$ mg/L.

purification efficiency reaching 70-80%. The application of the sorbent with filtering layer thickness 5.3 cm allows the maximal purification efficiency of 99% to be reached, nevertheless, the lower sorbent layers are not used efficiently.

BFC efficiently operates in a wide range of linear rates of water feed up to 16 m/h (Fig. 10b).

In accordance with existing conceptions [8] and data obtained, the filtering materials, such as CF and BFC with the porosity of 90-98% possess the high-

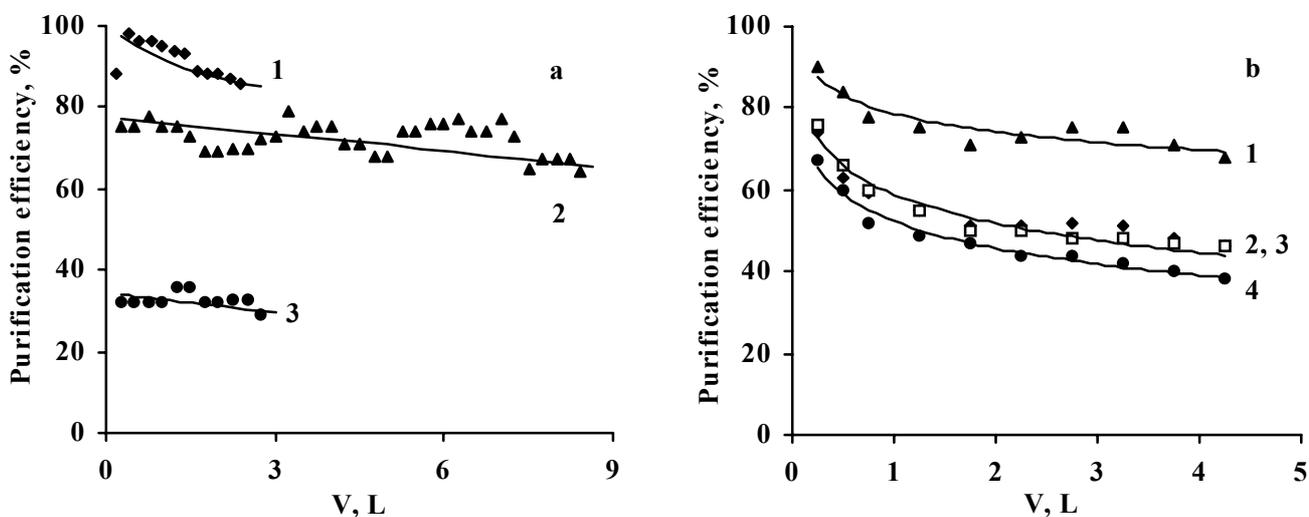


Fig. 10. The influence of the process parameters on the efficiency of water purification using the compressed basalt fibre: a – thickness of the filtering layer, cm, b – filtration rate, m/h.

est capacity towards petroleum products. Adsorption capacity of CF to the dissolved petroleum products may reach 300 mg/g. Nevertheless, a wide CF application, especially for commercial use, is limited by its high cost. Fire-polished basalt and polypropylene fibres are characterised by a low value of specific surface. Therefore, these fibrous materials are not

efficient in the removal of dissolved hydrocarbons, although they may be used to decompose the coarse emulsions. Fibrous materials produced from basalt and polypropylene recyclable waste are chemically inert, cheap and environmentally safe. Material regeneration may be made by live steam. The materials withstand several regeneration cycles, and then

they may be used in road building, fired in boiler furnaces or disposed in the solid waste dump.

Water purification from petroleum products by multilayered filters

To enhance the quality of water purification, it is purposeful to apply the multilayered filters that allow the petroleum products of a high dispersion range to be removed [24].

We studied the application of the combinations AOH + BFC and AOH + PP (Fig. 2) as multilayered filters. The results given in Table 2 show that even the application of one multilayered filter filled with AOH and BFC provides for purification of water containing 200-300 mg/L of petroleum products up to the level of ecological regulations adopted in Russia. AOH + PP filter, as compared to AOH + BFC is less efficient. At all conditions being equal, the filtrates contain ten times more crude oil and diesel fuel, and two times more gasoline.

Table 2
Results of petroleum product removal using multilayered AOH + BFC filter

Concentration of emulsified petroleum products, mg/L					
Crude oil		Diesel fuel		Gasoline	
initial	final	initial	final	initial	final
29	0.05	77	0.05	60	2.92
58	0.05	154	0.05	119	4.21
116	0.05	308	0.05	238	4.93
231	0.05	616	0.08	474	12.44
374	1.01	925	0.73	715	16.11
463	7.30	1233	6.29	953	20.96
694	9.24	1850	18.5	1430	23.45

During filtration of water-oil emulsion through multilayered filters the large emulsion drops are retained by fibrous materials. Dissolved petroleum products and drops whose diameter is less than 1-4 μm are sorpted by the developed AOH surface and fill the intergranular pore space of ultrafine adsorbent. When PP possessing a lower oil capacity as compared to BFC is used the load to AOH increases, which leads to decreased water purification efficiency and reduced service cycle of the filter.

Thus, the combination of ultrafine aluminium oxyhydroxides and fibrous filtering materials in a multilayered adsorbing filter may be efficiently used to purify water from petroleum products with various dispersion degrees in a wide concentration range. The filter is regenerated by live steam.

Conclusions

The features of removal of dissolved and emulsified crude oil and petroleum products from water by ultrafine AOH and fibrous sorbents have been studied.

The removal degree of dissolved hydrocarbons by AOH is 70-80%, of emulsified products – 60-90%. Dissolved hydrocarbons are adsorbed on AOH pores, emulsified products are retained in the intergranular pore volume.

BFC efficiently operates in a wide range of linear filtration rates (3-6 m/h) and minimal thickness of filtering layer (1 cm) without marked reduction of purification quality.

The combination of ultrafine AOH and fibrous filtering materials in a multilayered adsorbing filter allows both emulsified and dissolved petroleum products to be removed from water, thus providing for a water purification degree from petroleum products of 95-99%.

Ultrafine aluminium oxyhydroxide and fibrous materials are chemically resistant and are not hazardous to the environment.

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