Materials for Adsorption Purification of Water from Petroleum and Oil Products

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Abstract

The most interesting results among those described in literature on the development and application of the materials for adsorption purification of water from petroleum and oil products are considered and generalized. Sorbents used both for elimination of oil outflow and for purification of oil-containing waste water are considered. Natural (plant- and mineral based), artificial and synthetic sorbents are described. Fibrous (non-woven, in the form of chaotically positions fibres, wool, pressed, *etc*.) materials are considered along with those used in the dispersed or granulated form. It is stressed that combination of materials differing both in origin and in the state of aggregation, with additional modifications if necessary (for the purpose of enhancing the actual properties or imparting new characteristics) leads to a multiple increase in the efficiency of purification process.

Contents

1. INTRODUCTION

At present, a global problem of preventing environmental degradation during the development of natural resources and transformation of natural systems is urgent. Pollution is deterioration of the quality of environment, both due to admission of extrinsic chemical or biological agents and due to the physical action. With reasonable nature management, environmental pollution is not heavy; it recovers its quality due to natural self-regulation and self-purification (passive purification). In the case of non-reasonable management, the environment itself is unable to cope with pollution; active purification is required.

As we have already noted above, physical (mechanical, radioactive, light, noise, electromagnetic, and thermal), biological (biotic, micro- and macrobiological) and chemical kinds of pollution of the biosphere can be distinguished. Classification of chemical pollutants of water depending on the degree and features of the action of chemicals on the living environments looks as follows:

– biologically unstable organic compounds;
– low-toxic inorganic salts;
– biogenic compounds;
– substances with specific toxic properties, including heavy metals, biologically strict (indecomposable) organic synthetic compounds;

– oil products, *etc.* [1–5].

Petroleum and oil products (OP) comprise a special group of pollutants of the hydrosphere. Water gets polluted with OP during petroleum production, transportation and processing, when OP are used as a fuel for marine engines, when tanks pf oil-tankers are washed, when water flows from OP-polluted lands, *etc.* [3, 6–10, 73]. Among the total amount of OP getting into seas and oceans annually, losses from oil transportation account for about 35 %, about 32 % is brought out by rivers, urban and industrial wastes account for 10 %, and the same amount comes from the atmosphere and from natural sources [2, p. 19].

The solubility of oil in water is insignificant, so OP get accumulated first of all on the surface and at the bottom of water reservoirs [1–5, 11]. In the case when the oil film is more than 0.1 mm thick, both oxygen penetration into the water and removal of carbon dioxide from water slow down. The effect of OP on living organisms is exhibited as disorders of physiological activity, diseases caused by penetration of hydrocarbons into organisms, changes in the biological features of environment, *etc.* Water microorganisms gradually destroy oil products but this process is slow. Accumulation of oil sediments on the bottom of water bodies may bring about anaerobic conditions and become the source of secondary pollution of the hydrosphere.

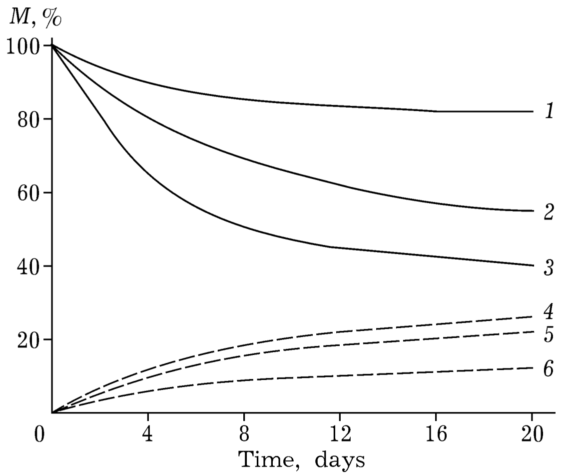

Fig. 1. Changes in the mass of the oil film (*M*) on water surface (*1–3*) and at the bottom (*4–6*) depending on water temperature [13], °C: 2–5 (*1*, *6*), 10–15 (*2*, *5*), 22–27 (*3*, *4*).

A decrease in the concentration of petroleum and OP in water due to self-purification occurs as a result of their natural decomposition, chemical oxidation, evaporation of low-boiling fractions and biological destruction by microorganisms living in water. As we have already stressed, these processes are characterized by low rate, which depends mainly on environmental temperature. For instance, a decrease in oil mass in a film within the first days after its formation occurs mainly due to evaporation: within the first three days, the loss reaches about 25 % for water temperature 22–27 °C and 12 % for 2–5 °C (Fig. 1) [13].

At present, various methods are used to purify water from petroleum and oil products: mechanical, physicochemical, chemical, biochemical. Among physicochemical methods, absorption is the most interesting procedure; it is very efficient and can ensure purification to any required level in the case of multi-step arrangement of the process. Sorbents may be either natural, based on plants or minerals (cotton, turf, peat-moss, sawdust, wood shavings, wood flour, hemp, straw, clay, pearlite, *etc.*), or artificial or synthetic materials based on viscose, hydrated cellulose, synthetic fibres, thermoplastic materials, polyurethane foam, etc. In order to render hydrophobic properties to sorbents, many substances are used: paraffin, silicon or petroleum oil, monoalkyl ethers of polyethylene glycol, high-molecular compounds, *etc.* The materials are treated with hydrophobizing agents by immersing the former into the solutions or melt of the latter, by spraying over the surface followed by hardening, *etc.* A hydrophobizing agent itself should possess good adhesion to the material, get uniformly distributed coating the material completely, be non-washable during performance and insoluble in OP. The maximal effect may be achieved by choosing such a hydrophobizing agent, which would allow one to exclude the addition of an active substance providing an increase in oil capacity of the resulting material.

An adsorbent based on straw treated with polymers (polyethylene, polypropylene, polystyrene, polyvinyl chloride, *etc.*) was proposed for purification of water surface from petroleum about 25 years ago. The sorbent was manufactured in the form of a mattress; treatment was carried out either by immersing straw into the solution of a polymer or by spraying it over the material [14]. However, this sorbent could not be recovered, possessed rather low adsorption capacity, and was rather difficult to manufacture.

Modern materials are more up-to-date and technologically reasonable. For example, a method was proposed to purify water from OP by introducing adsorbents into a layer of OP [15]. Porous materials based on schungite, tripoli, pearlite, diatomite, calf (with particle size not more than 500 μm) and a thermoplastic hydrophobic polymer (with particle size not more than 300 μm) with the mineral : polymer mass ratio of 100 : (25–130) are used as adsorbents. The mixture is subjected to thermal treatment at a temperature of the melt off the thermoplastic polymer for 5–40 min. Low- or high-pressure polyethylene, wastes of polyethylene, polystyrene, and polyvinyl chloride in the form of powder. After thermal treatment, a sorbent is formed into different shapes: discs 5–15 mm thick with the diameter of 150–1000 mm; cylinders with the external diameter of 150–1000 mm, length of 250–1000 mm and wall thickness of 5–15 mm; a continuous ribbon 50–1000 mm wide and 1.5–2.0 mm thick. The sorbent ribbon is duplicated on one side with a non-woven fabric of the same width not more than 1 mm thick at a temperature equal to the melting temperature of the polymer of non-woven fabric. A disc, a cylinder or a ribbon is placed into water polluted with OP and rotated at a frequency of 1–120 rpm. Adsorbed products are continuously taken off with knives, brushes or by suction. This method also involves shaping of the sorbent as plates of various configuration which are immersed into water to be purified and kept there for a time interval necessary for OP removal to the level of MPC equal to 0.05 mg/l. Recovery is carried out by centrifuging [15].

In the present work we have made an attempt to generalize and analyze some data reported in literature on the development and application of materials for adsorption purification of water from petroleum and oil products. We consider sorbents that can be used both for oil outflow elimination and for purification of petroleum-containing waste water (PCW) from oil-mining and oil-processing plants, petroleum storage depots, refueling stations, car wash, *etc*.

2. ADSORBENTS FOR ELIMINATION OF THE ACCIDENTAL OUTFLOW OF PETROLEUM AND OIL PRODUCTS

Outflow in oil mining (oil blowout at the Bravo drilling platform in the North Sea, at the underwater well Istok-1 in Mexico, *etc.*) and during transportation of petroleum and OP with the help of oil-pipe lines, means of river, sea and trucking delivery services, *etc.* (pipeline breaking in the Persian Gulf, in Louisiana, at the Usinskoye oil field; tanker wreck near the shores of France in 1999 when more than 10 000 t of crude oil and the products of its processing got into the sea [11], *etc.*) causes large-scale losses of the valuable raw material (from several tons to tens thousand tons) and at the same time very dangerous environmental pollution [16].

The strategy of measures against oil outflow events includes localization of the oil patch, collection of the major part of oil spoiled over the water surface, and elimination of the residual film [16, 17].

In order to localize an oil patch on water surface and at the same time to absorb spoiled OP, and in order to remove continuous layers of OP up to several millimeters thick in small water areas, sorbents encapsulated in permeable shells are often used in the form of harbour booms of different design and kinds [18, 19].

Adsorbents are used in different arrangements to collect spoiled oil and OP. In the disperse or granulated form in thin layer, adsorbents are mainly used to eliminate separate spots of products on water surface. In order to remove continuous layers of spoiled OP up to several centimeters thick from a small water area, sorbents made in the form of mats are most frequently used. The use of sorbents in the form of napkins excludes some densification of the material, which sometimes occurs with mat formation and causes a slight decrease in capacity. In mechanical oil-spill boats, sorbents are used in the form of multilayer units, absorbing shells, *etc*.; this provides collection of OP from water surface, removal of OP from the absorbing material, followed by their export into a collector. The above-listed materials for elimination of oil outflow (mats, napkins, booms, absorbing shells, *etc*.) are manufactured on the basis of disperse, granulated and fibrous sorbents considered in detail below.

2.1. Materials used in the disperse and granulated form

As we have already mentioned, among natural sorbents, most frequently used ones are turf, bog moss, sawdust, wood chippings, *etc*. For instance, 1 kg of bog moss absorbs 8.5 kg of transformer oil, 9.8 kg of crude oil and 12.9 kg of petrol [13].

Artificial sorbents based on natural pearlites, vermiculite, zeolites, aleurite, silica, silicates, scoria and so on are widely used. Thus, an adsorbent of interest to collect oil from water is that based on circulite; the specialists from the Kiev Polytechnical Institute and Institute of Colloid Chemistry and Water Chemistry, National Academy of Sciences of the Ukraine, developed the technology of obtaining this sorbent. The sorption capacity of this kind of pearlite is mote than 800 % of its own mass and is maximal for the fraction size of 0.2–0.4 mm [13].

Modification of circulite by organosilicon compounds (OSC) causes its hydrophobization and an increase in the efficiency of collecting the floating oil (oil capacity increases by a factor of 3–4). Another advantage of pearlite modified by OSC in comparison with circulite is the possibility to use the former both to purify open water areas from OP and to treat oil-containing water. The material is cheap, technologically favourable (filters have a simple design, it is easy to deposit the sorbent onto water surface and to collect it after sorption) and exhibits increased sorption capacity, which is about 8 g/g. In addition, pearlite modified by OSC, after working in a filter in the dynamic mode, can be used to collect floating oil.

Some synthetic materials, for example polyurethane foam, absorb petroleum and OP in the amount 20 times as large as their own mass. Such foam plastic can absorb a layer of petroleum up to 10 mm thick from water surface and decrease the oil content of water from 4000–6000 to 10–14 mg/l [13].

In addition, sorbents based on polyurethane foam allow one to solve the problem of oil collection with simultaneous prevention of its spread over water. For this purpose, the foam plastic is obtained directly on water surface by mixing the components preliminarily. For example, after mixing polyester, carbamide solution and toluylenediisocyanate at a bank or on board the ship, followed by discharge of the resulting mixture to an oil spot on water surface, foam plastic is formed which prevents oil from spreading and at the same time absorbs it. Such a foam plastic may be recovered by mechanical streak or by washing with solvent and used many times as usual petroleum sorbent [16].

It was also proposed to use plastic plamilon micro-containers developed at BashNIPIneftr as the sorbing material. Plamilons are obtained by spraying a mixture of synthetic thermoreactive resin, gas forming agent and a solidifying agent in drying chambers. These materials are recommended for use when it is necessary to

TABLE 1

Parameters of the purification of water surface from petroleum with the help of microballoons with a size of 1 10^{-5}–4 10^{-4} m [13]

Resin for microballoons	Sorbent density, g/cm^3	Thickness of petroleum film, mm	Specific consumption of microballoons, g/g	Purification degree, %
Bakelite "V"	0.15–0.25	1.5	0.770	92
	0.15–0.25	1.0	0.052	97
	0.15–0.25	0.5	0.040	97
FRV-1A	0.12–0.20	1.5	0.128	86
	0.12–0.20	1.0	0.095	90
	0.12–0.20	0.5	0.056	91

TABLE 2

Parameters of the purification of water surface from petroleum with the help of various materials

Material	Oil capacity, g/g
Bog moss	9.8
Circulite	8.0
Polyurethane foam	20.0
Microballoons:	
a) based on Bakelite "V"	
for film thickness, mm:	
1.0	19.2
0.5	25.0
b) based on FRV-1A	
for film thickness, mm:	
1.5	7.8
1.0	10.5
0.5	17.9

remove petroleum film 0.5–1.5 mm thick from water surface (Table 1) [13].

Comparison of the characteristics of above-listed sorbents shows that the highest capacity with respect to petroleum is exhibited by polyurethane foam and micro-containers based on Bakelite B (Table 2). However, as we have already mentioned, the latter are efficient in removing oil films not thicker than 1.5 mm. In addition, similarly to the majority of synthetic materials, both materials are toxic (especially in the case of fire), which limits their application. The main advantages of natural adsorbents are availability, cheapness, sufficient raw resources, non-toxic character, *etc.*; for practical application, these advantages compensate somewhat lower oil capacity.

2.2. Fibrous materials

Fibrous materials (FM) are highly efficient against oil outflow when they are used to collect oil and OP from water surface. It is most promising to use various FM (hydrophobized, additionally treated with an active substance) in the form of mats, multilayer units, *etc.* [16–18, 27–30]. These sorbents may be used many times; they may be recovered at the site by mechanical streak, by treating with solvelnts, live stream, *etc.*

These adsorbents are often based on natural FB, either plant-based (cotton, flax, hemp) or mineral ones (asbestos, *etc.*) [18, 20, 21, 24–28].

There are sorbents composed of a fibrous cellulose material in the form of technological wool or wastes of textile works (93–97 mass %) treated with the oxidized ataxic polypropylene (OAPP) (3–7 mass %) [20] or a block copolymer of butadiene and 10–50 % styrene (2–10 mass %) [21]. The advantages of these materials are high sorption capacity with respect to oil (up to 30 g/g) and the ability to survive many recovery cycles, which ensures multiple use of these materials. A shortcoming is the trend to be prone to microbiolgocial decomposition when stored and used in filters.

A sorbent has been proposed which incorporates a fibrous support (93.0–99.5 mass %), an active organic susbtance (0.4–5.0 mass %) and a hydrophobic component, in particular polybutadiene (0.1–2.0 %) [22, 23]. The active substance is a mixture of fractions of alkyl carboxylic compounds C_{10}–C_{16}, C_{17}–C_{20}, C_{20}–C_{25} taken in the ratio of 1 : 3 : 3. Disadvantages of this material are rather low capacity and the presence of such an expensive and scarce component as alkyl carboxylic acids.

A sorbent has been developed which is obtained by modifying natural cellulose fibrous materials with 1,2-polydienes based on the monomers with 4–5 carbon atoms in the molecular chain, in syndiotactic form (molecular mass: 100 000–300 000) taken in the amount of 0.5–1.0 mass % [24]. This material is characterized by highly hydrophobic character, high sorption capacity, floatation, and admits more than 10 recovery cycles (Table 3).

Cellulose was treated with a 33 % aqueous emulsion of polybutadienes at room temperature and dried to the constant mass. It was established that when the amount of polybutadienes used for modification is less than 0.5 %, the sorbent is characterized by negative floatation, while for this amount larger than 1.0 % the sorbent requires elevated expenses for production and exhibits lower oil-sorbing capacity. The sorption capacity of the proposed material (with respect to the commercial mixture of West Siberian petroleum) is 20.0 g/g [24].

Cellulose may be hydrophobized also with the help of insoluble aluminium soap by

TABLE 3

Results of test of sorbent [24]

Concentration of polydienes, mass %	Sorption capacity with respect to petroleum, g/g	Time of full sorption, s	Floatation
0.4	23	150	–
0.5	23	150	+
0.8	20	150	+
1.0	16	120	+
1.3	2	120	+

precipitating it form the aqueous solution in the amount of 1–15 % of cellulose mass using a water-soluble aluminium salt in equimolar amount with the sodium soap [25].

In order to reduce the cost of production of highly efficient fibrous adsorbents for petroleum and OP collection from water surface and at the same time to solve the problem of efficient utilization of large-scale wastes formed in flax raw processing, the authors of [26] developed adsorbents based on the wastes of flax production. Preliminary cottonizing followed by hydrophobization with OAPP allowed obtaining sorbents with the capacity with respect to petroleum 11–14 g/g, while the initial material itself possessed oil capacity of 4–5 g/g.

Purification of water surface from petroleum and OP is possible also with the help of a cotton-containing sorbent (cotton wastes of spinning are used to manufacture this sorbent) shaped as mats with a thin layer of machine or transformer oil sprayed onto their outer surface [27]. A layer of cotton-containing sorbent is fixed in a mat between the layers of cotton or synthetic sparse cloth or a cotton net. The distance between threads in the cloth or mesh size in the net fixing the sorbent in a mat is less than the particle size of cotton-containing sorbent. The length and width of the mat are 0.5–1.0 m, the ratio of its thickness to the thickness of spoiled petroleum or OP layer is (0.5 : 1.0)–(1 : 1).

On the basis of one of the waste products of cotton-processing plants, SINTAPEKS sorbent was developed. It is close to sheet wadding and sintepon in its oil absorbing capacity but it is cheaper [18]. The absorbing capacity of this material towards a broad range of OP (from petrol to various kinds of oil) is

TABLE 4

Oil capacity of some materials based on cellulose, treated with various hydrophobizing agents

Material	Hydrophobizing agent	Oil capacity, g/g	Ref.
Cellulose material*	OAPP	30	[20]
	Block copolymer of butadiene and styrene	–	[21]
	1,2-Polydienes	23	[24]
	Insoluble aluminium soap	–	[25]
	Machine or transformer oil	–	[27]
	–	10–15	[18]
Flax	OAPP	4–5	[26]
Flax**	OAPP	11–14	[26]

*In the form of sheet wadding, technical wool or wastes from textile plant.

**Preliminary cottonizing of the material.

5–20 g/g. After collecting OP, the sorbent can easily be squeezed and can be used many times. The SINTAPEKS sorbent can be used to remove oil outflow not only in the form of mats but also in the disperse form in a thin layer, as cylindrical booms, as well as in mechanized oil-spill boats providing sorption, extraction and petroleum withdrawal into a collector.

Analysis of the data shown in Table 4 indicates that all the materials based on cellulose exhibit high oil capacity. In this row, a minimal (4–5 g/g) capacity of flax-based sorbent is likely to be due to an increased size of flax fibres as the roughest material. An increase in the capacity of the flax sorbent can be achieved by preliminary cottonizing of the raw material [26].

An increase in the ability of a sorbing material to be used repeatedly in cycles (especially for collecting stiff petroleum) is ensured when a multilayer sorbent is used [28], which is a material composed of basaltic fibres impregnated with an active substance and with a hydrophobizing agent; it is equipped with reinforcing, feltproofing, thermo- and steam-resistant elements made of basalt cloth. The application of this material ensures many cycles of purification process (the number of cycles reaches 2000–4000 for one sample), high sorption rate (the characteristic sorption time is 10–20 s), high oil capacity and mechanical strength of the sorbent (the limit may be due to a decrease in the strength of basaltic fibres due to fatigue processes).

The sorbent is composed of alternating layers of the fibrous basis made of basaltic fibres 0.2–2 μm in diameter with the specific surface of 700–1400 m^2/kg (70–93 mass %). These layers are impregnated with the active substance belonging to the class of alkyl carboxylic acids (1–5 %) and a hydrophobizing agent which is an aliphatic ester if alkyl carboxylic acids (1–5 %), then feltproofing elements made of basalt cloth with the specific surface of 200–300 m^2/kg (3–5 %) are imposed; finally, thermo- and steam-proof elements are placed at the outer side of the sorbent.

The procedure of sorbent obtaining includes several stages. The basaltic fibre with the specific surface of 700–1400 m^2/g) is merged for 1.0–1.5 h into a solution containing a mixture of alkyl carboxylic acids C_9–C_{27} in organic solvent and an aliphatic ester of carboxylic acids; then it is dried. Feltproofing elements made of basalt cloth are set onto the dried layer, then again a layer of impregnated basaltic cloth and finally a layer of reinforcing elements made of basaltic cloth. For strength, the layers are stitched. Plaits or ribbons made of basalt cloth with the specific surface of 500–700 m^2/g are imposed on the resulting multilayer cloth (the number of layers depends on the required characteristics). The multilayer sorbent is cut into charts or stripes. Purification of surfaces from petroleum and OP within one working cycle sorption – desorption includes contacting with the sorbent (preferably in a separator), sorbent recovery with live steam, additional introduction of the active substance and hydrophobizing agent (about 0.7–1.4 mass %) [28]. Disadvantages of this method include complicated obtaining technology and increased consumption of the modifying agents (the hydrophobizing agent and active substance) due to partial washout during operation.

At present, increasingly wide application for adsorption purification of water from petroleum and OP has been won by synthetic fibrous materials [30–35].

For instance, a material based on thermoplastic polymer [31] with chaotically positioned fibres 5–20 μm in diameter with the density of 0.01–0.20 g/cm^3 is known. Liquids are soaked and retained in this sorbent due to capillaries formed by the fibres twisted in balls and plaits; the content of these capillaries in the material reaches 60 %.

A sorbent composed of nonwoven fabric was proposed; the sorbent is impregnated with a mixture of alkyl carboxylic acid fractions from C_9 to C_{27} and with aliphatic esters of alkyl carboxylic acids, reinforced with the elements made of polyethylene threads in epoxy resin or thermofibre in thermoplastic polymers; the sorbent is equipped with feltproofing elements made of glass fibre [29]. The capacity of this sorbent is about 42–46 kg/kg, number of operation cycles is 23–36, and a decrease in capacity per cycle is 2–5 %.

A material for petroleum and OP sorption was developed which is a nonmoven fabric made of hydrophobic and/or hydrophobized polymeric fibres attached to each other (the bulk density 0.01–0.06 g/cm^3) [30]. The sites of attachment are coated with the fastening hydrophobizing polymeric film made of synthetic latex. The content of the polymeric film counted for the dry residue is about 3 to 15 % of the fibre mass. The ratio of hydrophobic to hydrophobized fibres in the material varies depending on operation conditions (negative or positive temperature range). The polymeric cloth may also have crimped structure and reinforcing net. Disadvantages of this material include complicated manufacture method and not very high capacity.

Fibrous sorbents obtained from waste thermoplastics (polyethylene–polypropylene single-use syringes and plastic bottles made of polyethylene terephthalate) [32–34] were tested with petroleum from the Grushevoe deposit of West Siberian region, industrial oil I-20A, summer diesel oil and AI-92 petrol [35]. In the dynamic mode of determination of the sorption capacity, the performance of filtering load of steady waste disposal plant was modeled, and in the static mode sorbent performance in the form of mats or booms on water surface was modeled for petroleum and op outflow (Table 5).

The data obtained were compared with the characteristics of other sorbents known on the world market. For example, the static sorption capacity V_g of Pitsorb (Canada) is 6–7 g/g, Turbosorbjet (France) about 4, Sibsorbent (France) 8–9, BTI-1 (Russia) 12–15 g/g. It should be noted that the listed materials (Pitsorb, Turbosorbjet, *etc.*) are single-use sorbents, while the fibrous products developed on the basis of thermoplastic wastes can be used many times. The dependencies of sorption capacity of the samples of polymeric fibrous materials on the number of recovery cycles are shown in Fig. 2. One can see that even after 15 performance cycles the capacity of the proposed sorbents is conserved at a level of 50–70 % of the initial value.

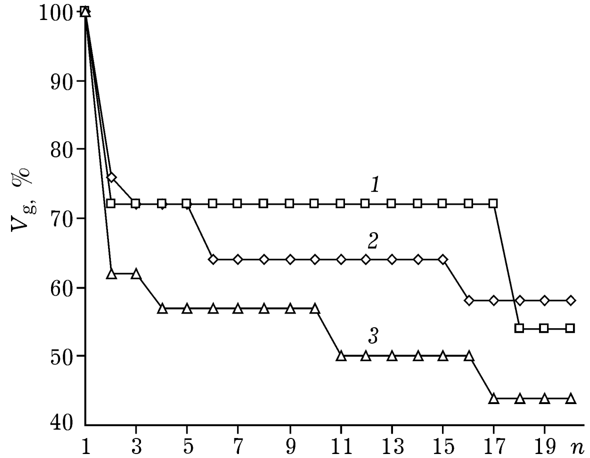

Fig. 2. Sorption capacity (V_g) of polymeric fibre made of thermoplastic wastes, with respect to petroleum in the blotting regime for multiple cycles (n) of saturation (sorption–recovery) [35]: *1* – fibre made of the worked out medical single-use syringes (polypropylene); *2* – made of the used bottles (polyethylene terephthalate); *3* – hybrid fibre made of polyethylene and polypropylene wastes (worked out bodies and rods of single-use medical syringes).

TABLE 5

Sorption capacity (V_g) of the samples of polymeric fibre with respect to hydrocarbon liquids, g/g [35]

Sorbent,	Dynamic regime				Static regime			
material	Petroleum	Diesel fuel	AI-92	I-20A	Petroleum	Diesel fuel	AI-92	I-20A
FN from the single-use syringes, PP	6.1	6.9	5.6	6.9	15.6	15.7	10.0	22.3
The same, PE : PP = 1 : 1	5.9	8.5	5.2	8.5	15.0	17.9	10.3	17.0
FM based on the used plastic bottles, PETP	3.9	5.3	3.7	5.3	12.9	13.2	10.6	17.3
Paursorb (France), PP*								

Note. FM – fibrous material, PP – polypropylene, PE – polyethylene, PETP – polyethylene terephthalate.

*No data for the dynamic regime; for static regime, sorption capacity is 13–25 g/g.

As a result of investigations, the authors of [35] concluded that the fibrous sorbents based on thermoplastic wastes could be competitive with the foreign analogues.

3. MATERIALS FOR PURIFICATION OF OIL-CONTAINING WASTE WATER

As we have already mentioned, in case of unpractical maintenance, the environment is unable to cope with pollution; active purification is required, including purification of industrial solutions and gases, waste water (WW), *etc.* Purification of WW to the level of industrial water supply with utilization of recovery solutions (for example, distribution as the commercial product, *etc.*) is characterized by high economic efficiency and allows not only to prevent waste water discharge into water bodies but also to solve the problem of supplying the national economy with additional water resources [2–5, 73].

In the general case, in order to choose and optimally combine purification methods [9, 53–56, 59–72], it is necessary to analyze the structural chemical and phase disperse composition of water to be purified meeting the requirements to the quality of purified water. In doing this, one should take into account changes in the character and phase-disperse state of impurities during purification. After choosing the purification chart, either for groups or for separate impurities within a group, it is necessary to choose materials for the process.

In the present work we will focus on the problems of OWW (oil-containing waste water) – water from oil-mining and oil-processing plants, petroleum storage depots, filling stations, car wash stations, *etc.* Pollutants most characteristic of OWW include first of all petroleum and OP, surface-active substances, heavy metals, *etc.* However, the subject of investigation chosen for the present study is OWW purification from petroleum and OP.

3.1. Purification of OWW with filters made of natural and artificial materials

In view of the complicated character of the process pf WW purification, as a rule, multilayer combined filters are used (materials, devices, installations in which various processes are carried out starting with filtration, coalescence and finishing with adsorption itself) in combination with multistage purification technologies. However, many works report on the data dealing with the investigation of separate materials for efficient purification of WW from OP. It is clear that one should investigate in detail the characteristics of all the constituents for the purpose of studying the operation of multicomponent systems. The authors are likely to expect further use of these sorbents either separately (let us call them filters in this case) and in various combinations with other materials (combined filters).

Materials used in dispersed and granulated forms. The most of authors discussing this subject pay attention not only to the efficiency but also on the availability (therefore, low cost) of sorbents involved. The requirement of low cost is best of all met by the natural materials and the materials based on various wastes (industrial, technological, domestic, *etc.*). As far as the degree of purification is concerned, as a rule, the best sorbents are artificial and synthetic ones.

Let us consider in more detail the application of natural and artificial materials used in the disperse and granulated forms for purification of OWW [36–38, 42, 46–53, 55–58].

Thus, it was proposed to use fine dispersed clays from the deposits of Bashkortostan to purify WW of various works. The use of these clays in purification units of some oil-processing plants allowed achieving a decrease in OP content by a factor of 5.4–7.3 [36, 37]. In addition, investigations aimed at utilization of the worked out clays showed the possibility to add them into mixtures for the production of construction materials, which allows us to consider the mentioned technologies as ecologically safe and waste-free [38].

It is known that such natural sorbents as zeolites can be successfully used to purify various aqueous media from the pollutants of various kinds [39–41]. The authors of [42] investigated the extraction of OP from water polluted with petroleum, petrol and oil, with the help of natural zeolites represented by the minerals of heulandclinoptilolite group from the Sakhaptinskoye (the Krasnoyarsk Territory) and

Kholinskoye deposits. It was shown that the application of zeolites allows one to purify polluted water from emulsified oil products (EOP) by 100 % and from dissolved oil products (DOP) by 86 %. The highest OP capacity is exhibited by the zeolite from the Kholinskoye deposit for which the Si : Al ratio is 5.5, unlike the zeolite from the Sakhaptinskoye deposit for which Si : Al = 5.0. The latter fact confirmed the assumption that the adsorption activity of zeolites increases with an increase in Si : Al ratio. Special attention was paid to the mechanisms of pollutant retention by zeolites; in the opinion of the authors, these mechanisms involve either the formation of surface compounds and complexes with the participation of active surface groups (including hydroxyl ones) or absorption of pollutant particles the size of which is smaller than the entrance "windows" of crystal channels [42–45].

Investigation of the possibilities to use natural and modified zeolites in the processes of water purification from OP was continued with the zeolites from the Khonguruu deposit (Yakutia) [46]. Maximal sorption of the hydrocarbons of the Talakan oil on khongurine under static conditions was 12 10^{-3} mg/g, the dynamic sorption capacity of this material reached 1.7 mg/g. The results of extraction of the dissolved hydrocarbons in the dynamic regime are presented in Fig. 3.

Activation of the zeolite by calcination at 350 °C for 2 h resulted in an increase in the specific surface of the material followed by an increase in its sorption capacity from 30 to 50 % as a mean.

Treating it with solvents, life steam, and centrifugal separation can perform recovery of the worked out zeolite. It is also possible to utilize it by adding into mixtures for the production of construction materials, for example as an additive for brick production to improve the structure and increase the porosity of the resulting material. Zeolites saturated with OP can be used as an active reducing flux in ore electrofusion and so on. In the cases when both recovery and utilization of the worked out materials are hindered till economical unsuitableness, their single use is possible.

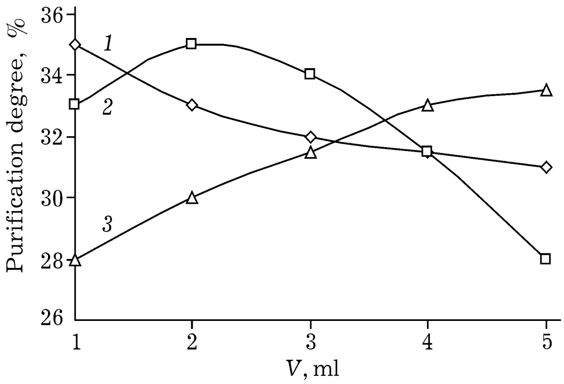

Fig. 3. Curves of filtering for the aqueous solutions of the Talakan petroleum (*1*) and its fractions through the initial khongurine [46]: *2* – petrol fraction; *3* – diesel fraction.

Carbon-containing sorbents are often used to purify WW from petroleum and OP at oil-mining and oil-processing plants, petroleum storage depots, filling stations [47, 48, 100].

For example, it is possible to purify water systems from OP by adsorption with a carbon-containing sorbent [47]. The sorbing material is recovered after use by washing with a solvent at a temperature from 0 to 149 °C.

Intercalated graphite obtained from its oxidized forms and containing 0.1–0.5 mass % of fine dispersed chemically modified amorphous silicon dioxide is used as a sorbent [48]. After saturation, the sorbent is recovered by washing with a solvent, followed by drying at 120–140 °C. The saturation threshold is conventionally assigned at a level when the oil to sorbent mass ratio M_o/M_s reaches 20.

The authors of [49] proposed to sorb oil with aluminosilicates (hollow microspheres isolated form the ash of coal thermal stations) and then burn oil out with the free access of the air till combustion finishes.

Such conventional sorbents as different kinds of coal (with preliminary activation and without it) are frequently used to purify OWW. Granulated and powdered, decalcified and low-ash microporous activated coal (AC) is used, as well as the coal of heat contact coking (CHCC), brown coal sorbents like BKZ, ABD, *etc.* are applied [50–53, 55]. The initial raw material to obtain AC can be any carbon-containing materials: coal, turf, wood, *etc.* [54, 55]. Manufacture of high-quality AC is rather complicated and time-consuming, which causes the high cost of the material and the necessity of its multiple use. The kinds of coal most suitable for water purification are considered to be KAD-iodine, AG-3, BAU, DAK, AGM. The coal of KAD-iodine, AG-3 and BAU types possesses high capacity towards the compounds with small molecules; BAU and DAK are efficient for OP adsorption, KAD-iodine, AGM and AG-3 are used for additional purification of biochemically purified WW [56].

To ensure efficient use of porous carbon materials as sorbents, it is also necessary to know the main characteristics of adsorbent particles and the parameters of larger aggregates of particles, for example adsorbent layers. For example, the authors of [52] carried out densitometric measurements and estimations with the help of complexation theory and nomographs to determine porosity of the layers of polydisperse materials. Carbon materials of two kinds were studied: those made of AC and of the materials obtained by activation of coal tar pitch by carbon dioxide, and those made of intercalation compounds of ferric trichloride with graphite.

The authors of [74] studied WW purification processes with aluminium compounds as adsorbents. It is known that aluminium oxide is an efficient sorbing material: it is widely used in chromatography as filler, in the production of catalysts, in purification processes, *etc.* At present, ultrafine materials attract much attention. It was established [75, 76, 78, 87–89, 91, 92] that synthetic sorbents based on ultrafine powder materials (UFP), in particular oxide-hydroxide phases of aluminium (OHA) can be used to collect petroleum and oil products from aqueous solutions and emulsions. It was shown [75] that for adsorption of the dissolved and emulsified petroleum, diesel fuel and petrol, the highest water purification degree is observed for diesel fuel (98 %). An increase in the adsorbent to solution ratio under static conditions leads to an increase in purification degree; however, the efficiency of adsorp\bent use decreases.

The UFP of aluminium oxide obtained under different conditions and possessing different specific surface was used to purify water from mineral oil [76]. The initial oil content of water was 109 mg/l. Purification was carried out in two stages. After the first one, the oil content of water was about 20 mg/l, after the second one (with the fresh portion of sorbent) only the trace amount of oil was detected in water. Water to be purified was in contact with the sorbent for about 30 min, the concentration of the sorbent was 5 g/l. As a result of investigations, the authors of [76] concluded that the amount of mineral oil sorbed is only slightly dependent on the specific surface of sorbents, while purification itself is a layer-by-layer filling of the surface pores of disperse materials.

The possibilities to use such synthetic and natural microporous materials as the UFP of aluminium oxide, mineral adsorbent ADM-2F (aluminosilicates polyfunctional adsorbent based on natural opal-cristobalite rocks, with total pore volume 0.7 cm^3/g [77]) and natural zeolite khongurine were studied by the authors of [78]. The concentration of dissolved OP was monitored by means of IR spectroscopy, that of emulsified OP – by means of photocolorimetry with Sudan dye [79, 80].

One can see in the data presented in Table 6 and Fig. 4 that the most efficient material among those listed above is the adsorbent based on OHA. In the opinion of the authors, high sorption capacity of this UFP is due to the nanometer-sized nature of the particles of this

TABLE 6

Comparison of the efficiency of purification of model petroleum-containing water with microporous adsorbents [78]

Adsorbent	Purification degree, %	
	Dissolved hydrocarbons	Emulsified hydrocarbons
UFP of aluminium oxide	70–80	60–70
ODM-2F	20–40	25–40
Khongurine	10–15	5–10

Note. Initial content of oil products in the dissolved and emulsified hydrocarbons is 5.7 and 500 mg/l, respectively.

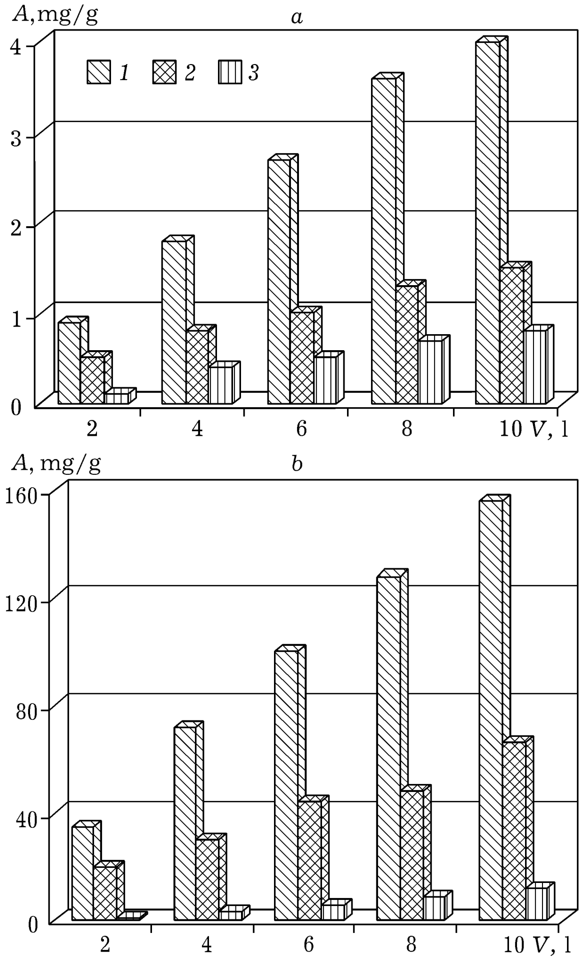

Fig. 4. Sorption of the dissolved (*a*) and emulsified (*b*) oil products with microporous sorbents [78]: *1* – aluminium oxide; *2* – ODM-2F; *3* – khongurine.

material, which provides an increase in the molar surface free energy accompanied by a sharp increase in the capacity of the material [78, 81]. The main advantages of natural mineral adsorbents include their availability, cheapness and the presence of sufficient raw material resources [78].

Fibrous sorbents for waste water purification. The data on the application of fibrous materials in the pure form to OWW purification are almost completely absent from literature. It is clear that, in spite of cheapness, availability and other advantages of these sorbents, the latter have also some shortcomings preventing their use for this purpose. These shortcomings include low mechanical and thermal stability, low stability to long-term action of humidity and chemical reagents (corrosive media). At the same time, artificial and synthetic FM for OWW purification are used very widely and efficiently [32–35, 66, 82–86].

For instance, good adsorbents are carbon-containing FM obtained from different kinds of raw materials under different conditions [83, 84]. The possibility to use carbon fibrous sorbents based on hydrated cellulose fibre modified with the compounds of transition metals was shown [83]. This material was manufactured by the research-and-production association "Neorganika" (Elektrostal' city) in the form of nonwoven cloth of ANM trademark. Investigation of water purification with this sorbent was carried out with the help of imitate solutions of organic compounds. The filter contained 29 g of ANM material, filtration rate was 14 m/h, and contact time was 8 s. The results of experiments showed that this carbon fibrous material demonstrates high efficiency in extracting oil hydrocarbons from the aqueous solutions of kerosene-gas-oil fraction, both for their high and low content (180 and 5 mg/l). The final content of hydrocarbons in the imitate solutions purified with ANM sorbent was about 6 mg/l (for the initial concentration of 180 mg/l) and 0.29 mg/l (for initial 5 mg/l).

In order to elevate the selective sorption capacity with respect to higher hydrocarbons, a sorption material based on hydrophobic basalt fibre was proposed [85]. It was obtained by breaking the hydrated mass of basalt fibre and the hydrophobizing agent (which was composed of 160–170 mass parts of water and 0.025–0.03 mass parts of an organosilicon compound per 1 mass part of the fibre) followed by molding and drying. The basalt fibrous material had the density of 70–150 kg/m^3, fibre diameter 0.5–2.0 μm, the length to diameter ratio 100 to 1000. A decrease in the amount of hydrophobizing agent resulted in the formation of hydrophilic regions in the material and subsequent decrease in its sorption capacity. An increase in the amount of hydrophobizing agent above the optimal value decreased the lifetime of organosilicon emulsions; an increase in its concentration resulted in coagulation of the compositions and hindered uniformity of fibre treatment. The resulting hydrophobic compacted material was used as adsorbent for higher hydrocarbons from aqueous solutions of alkanolamines. Under intense operation, the sorbent did not lose its properties, and the degree of hydrocarbon recovery even after operation of the material for a long time was 90 % [85].

An investigation described in [86] deals with the studies of physicochemical and filtration characteristics of a number of FM manufactured at plants in Russia. The subjects of investigation were basalt wool, pressed basalt fibre with the clay-cellulose binder (manufactured by the Federal Research and Production Centre "Altay"), nonwoven carbon FM VM [84], and polypropylene fibrous nonwoven material. It should be noted that the nonwoven carbon FM is based on a carbonized composition of polycaproamide and pitch and possesses porous fibrillar structure with the following characteristics: fibre diameter 0.1–3.0 μm, total pore volume 2–3 cm^3/g. Investigation showed that the most efficient sorbents are pressed basalt fibre and nonwoven carbon material; the use of these materials allows one to achieve 70–80 % purification of water from OP. High cost of the fibrous carbon material limits its application on the industrial scale. Filters based on basalt wool and nonwoven PP material demonstrated lower efficiency (50–70 % purification degree), possibly due to low porosity of these materials (88 and 84 %, respectively). So, it was established that the most promising sorbent among the proposed number of sorbents is the pressed basalt fibre which possesses high adsorption ability with respect to petroleum and OP, strength, thermal stability, availability and low cost. In addition, it was demonstrated that the basalt fibre does not become caked and consolidated by water flow thus increasing filter restriction, does not require any additional fixing partitions, *etc.* [86].

We have already mentioned above (see Section 2.2) the investigations of synthetic fibrous sorbents made of the wastes of thermoplastics (polyethylene-polypropylene single-use medical syringes and plastic bottles made of polyethyleneterephthalate) [32–35]. It should be reminded that the operation of the filtering charge of steady purification constructions was modeled in the dynamic mode of determination of sorption capacity of these materials with respect to petroleum, industrial oil, summer diesel fuel and AI-92 petrol (see Table 5) [35]. So, the possibilities to use the indicated materials as fibrous sorbents for OWW purification in the dynamic mode were studied.

3.2. OWW purification with combined filters

Combined adsorbing filters involve various combinations of materials differing both in the origin (natural, artificial and synthetic) and in the aggregate state (powdered, granulated, ground, *etc.*; fibrous – nonwoven in the form of chaotically positions fibres, wool, pressed ones, *etc.*). In addition, the materials can be additionally subjected to modification (chemical and/or physical, *etc.*) for the purpose of enhancing the existing properties or rendering new ones. Such an approach allows one to develop new purification technologies including a large number of materials, and purification flowcharts admitting flexible rearrangement and characterized by high efficiency [88, 89, 93, 94].

Synthetic sorbents based on UFP, in particular OHA, are actively proposed in various efficient combinations with other materials [78, 87–89, 91–93].

For example, it was shown in [87–89] that the combination of the adsorbents of different types in one filter results in a multiple increase in the capacity characteristics of such a filter. Combinations of some FM were tested: hydrophobized cellulose, carbon FM (Viskumak, Mytishchi city, Moscow Region; carbon cloth, Perm) and basalt fibre of various modifications (BSTV-1, Kemerovo), with fine aluminium-containing powders [87]. Comparative estimation of the efficiency of fibrous sorbents showed that the best results are demonstrated by carbon cloth; however, its high cost allows us to recommend it only for application in domestic filters to purify drinking water. Cellulose is distinguished by instability to putrefaction under humid conditions. So, hydrophobized basalt fibre is recommended for use in industrial fibres [[89].

Investigations of the processes of water purification from EDOP and DOP with miltilayer filters containing both UFP based on OHA and fibrous polypropylene and basalt sorbents were described in detail in [87]. Some data obtained in these investigations are shown in Fig. 5.

It was established that the use of hydrophilic and hydrophobic adsorbents at the same time in one filter broadens the range of problems that can be solved with such a filter. Separation of an ultrafine oxide adsorbent possessing high bulk density into the layers with the help of FM results in a decrease in filter restriction. In addition, fibrous hydrophobic adsorbents operate satisfactorily with high concentrations of OP in coalescence regime. With the OP content not higher than 10 mg/l, FM are inefficient as the collectors of OP [87]. However, it was noted that the application of polypropylene FM allowed the authors of [90] to achieve the maximal OP capacity. It seems likely that the polypropylene FM obtained on the basis of PP wastes (which was studied by the authors of [87]) does not provide high purification degree due to its characteristic smooth surface. Either further improvement of the technology of obtaining this sorbent or its special modification is necessary.

One of the problems arising with the use of multilayer filters based on ultrafine UFP of aluminium oxide, basalt ultrathin fibre, polyamide FM, *etc.*) is due to high resistance of adsorbent layers, which hinders filtration

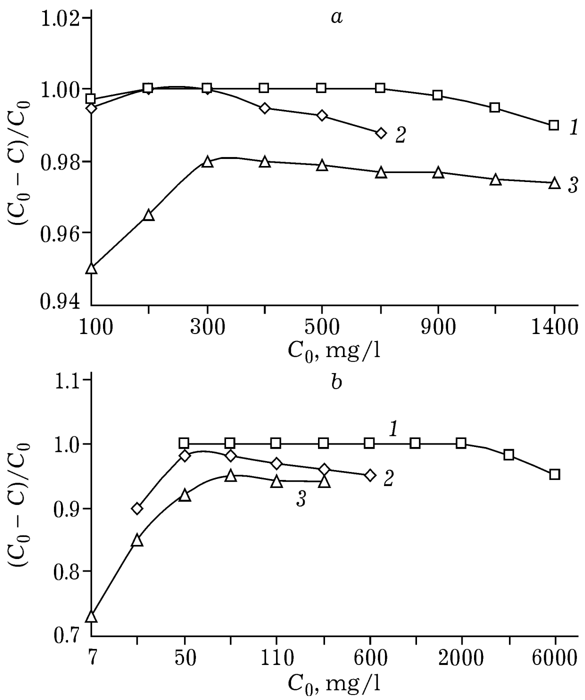

Fig. 5. Effect of the initial concentration of emulsified oil products on the degree of purification with the filters: oxide + basalt fibre (*a*) and oxide + polypropylene fibre (*b*) [87]: *1* – diesel fuel, *2* – petroleum, *3* – petrol.

and decreases the flow-through capacity of the devices. Maximal resistance is observed in a thin layer at the boundary between FM and the powder; to decrease this resistance, it is desirable to separate the fibrous and powdered materials with a layer of a porous material: a ceramic membrane, nonwoven cloth, *etc.* As a result, it is expected to achieve a substantial increase in the filter cycle [91].

On the basis of a new original adsorption technology, the filtration station for WW purification from OP was developed at the Institute of Petroleum Chemistry, SB RAS, and launched into experimental operation since 1995 at the Tomsk Petroleum Storage Depot of the Tomsknefteprodukt JSC [92]. The filtration-adsorption set-up Sever-3 based on multilayer adsorbents (firstly oxide ones) is able to purify water efficiently if the initial content of OP is 25–30 to 300 mg/l and more. The degree of purification from suspended and emulsified OP reaches 100 %, as a rule (with efficient removal of DOP). The OP content of the purified water is 0.2 to 0.8 mg/l; even after the resource of filter operation is exceeded 2–3 times, this value reaches 1.6–2 mg/l.

A multilayer filter for water purification both from DOP and EOP includes an adsorbent based on pressed basalt fibre and the layers of adsorbent based on OHA [78]. The major part of petroleum emulsion is filtered through the basalt fibre, while DOP and their drops with a size less than 1 μm are sorbed with UFP of OHA. As a result, the purification degree increases from 77 (for a single-layer filter made of pressed basalt fibre) to 97 % (for the multilayer filter described above).

As we have mentioned above several times, the combinations of materials for OWW can be diverse. Let us consider the use of natural sorbents in these combined filters [95–97].

A set-up for the purification of WW from car wash units was developed and recommended for application at the Tomsk State University of architecture and construction; the set-up is equipped with the cassette-type filters with the combined charge including granulated turf and FM from PP wastes. The use of this set-up allows one to pass to the recycling zero-discharge water supply of the "dirty cycle" with the purification of waste water from car wash. The use of cassette filters provides a decrease in the content of suspensions from 500 to 3–5 mg/l, OP from 900 to 0.5–5 mg/l. The fibrous filling of the filters is recovered by centrifuging and used repeatedly, while the worked out turf is utilized as fuel briquettes [95].

At the first stage of a two-stage purification procedure for OWW (and also for natural one), the initial water is passed through a two-layer filter composed of a layer of coal (fossil coal with the specific surface of 25–150 m^2/g) and a layer of sand, at the second stage it passes through a one-layer filter made of the same coal. After saturation, the filter is recovered by washing at first with water, then with an alkaline solution during bubbling. The method is characterized by the following efficiency: OP content of the initial water is 3–7 mg/l, in the purified water 0.1–0.2 mg/l [96].

An increase in the efficiency and a decrease in net cost of the process of purification of petroleum-containing water was achieved due to the use of a natural adsorbent (burnt rock) and cotton-containing wastes of spinning works [97]. Burnt rock (BR) is a metamorphized coal-bearing material composed of carbonaceous and weakly carbonaceous argillites, siltstones or sandstone subjected to burning in underground fire. These materials accompany coal and are present in all the coal basins [98]. At the first stage [97], water to be purified is passed through a BR adsorbent, at the second stage – through a cotton-containing sorbent until the amount of OP in water ensures the ratio of oil to the sorbent mass $M_o : M_s$ = 5 for BR and $M_o : M_s$ = 24 for the cotton-containing sorbent.

TABLE 7

Purification of waste water from oil products with the help of burnt rock [97]. The content of oil products: 100 mg/l

Thickness of adsorbent layer, mm	Filtration rate, cm/s	Residual content of oil products, mg/l
45	1.3	4.5
75	1.3	1.0
100	1.3	0.7
125	1.3	0.6
150	1.3	0.5
100	1.5	0.8
100	2.1	1.5

TABLE 8

Purification of waste water from petroleum and oil products with the help of cotton-containing sorbent [97]. Thickness of sorbent layer: 100 mm, filtration rate: 1.5 cm/s, filtration time: 3.5 s

Content of oil products, mg/l	Residual content of oil products, mg/l
1	Not detected
3	Not detected
5	Not detected
10	0.01

The regime of water passing through the sorbent layers during purification is important in achieving the highest purification degree. For instance, the following conditions were chosen (or calculated using the known procedures [99]): the diameter of BR granules, 0.12–0.5 mm; thickness of sorption layer, 150 mm; height and diameter of columns: 1m and 10 mm, respectively; excess pressure, 0.15 atm; filtration time, 32 s; filtration rate, 1.30 cm/s (Table 7).

For the second stage (additional purification from petroleum and OP till the maximum permissible concentration which is 0.01 mg/l), the following conditions are most suitable: the thickness of sorption layer, 100 mm; height and diameter of columns, 1 m; excess pressure, 0.15 atm; filtration time, 3.5 s; filtration rate, 1.50 cm/s (Table 8).

With the indicated filtration conditions, water with the initial OP content of 100 mg/l is purified to 0.5–0.9 mg/l (at the first stage – through a layer of BR), with the initial OP content of 1–10 mg/l to 0.01 mg/l (at the second stage – through a layer of cotton-containing sorbent). After 10 cycles of BR sorbent recovery, the residual amount of petroleum in water under purification was 8.1 mg/l. Five cycles of recovery of the cotton-containing sorbent allowed one to purify water to the OP content not more than 0.05 mg/l [97].

CONCLUSIONS

So, in the present work we made an attempt to generalize and analyze some reported data on the development and application of materials for adsorption purification of water from petroleum and oil products, either to eliminate the consequences of oil outflow or to purify petroleum-containing waste water from oil-mining and oil-processing plants, petroleum storage depots, car filling stations, car wash units, *etc*. Natural (plant-based or mineral), artificial and synthetic sorbents are described. Fibrous (nonwoven in the form of chaotically positioned fibres, wool, pressed, *etc*.) materials and the materials used in disperse and granulated forms are considered.

On the basis of analysis of literature data, the following conclusions can be made. In order to eliminate continuous layers of spoiled oil products, the most efficient sorbents are fibrous ones encapsulated in permeable shells in the form of mats; the main method of their application is the so-called blotting. The oil capacity of the materials is characterized in this case by oil sorption in the static regime. It is most reasonable to use the disperse or granulated sorbents to eliminate separate spots of oil products on water surface.

Purification of oil-containing waste water is most efficient with multilayer combined filters containing sorbents differing from each other both in origin (natural and synthetic) and in the aggregate state. The oil capacity of the materials in this case is characterized by oil sorption in the dynamic regime. In addition, it should be noted that there is the possibility to modify the materials additionally in order to enhance the existing properties of to render new ones. Such an approach in general allows one to develop new purification technologies in which a large number of materials and purification flowcharts is used, admitting flexible adjustment and characterized by high efficiency.

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