Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.24819

174 (2020) 116–122
January

Fiber and carbon materials for wastewater purification from petroleum products

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Received 3 March 2019; Accepted 23 August 2019

ABSTRACT

This article considers sorbents from waste-based materials that can be used for the absorption of petroleum products (PP). The articles considering sorbents based on hydrophobic expanded perlite, carbonized coal, carbonate sludge from chemical water treatment water are discussed. The work on the use of multicomponent adsorption filters and sorption materials based on modified bentonite is presented. Some types of fibrous sorbents used for wastewater treatment are given. In the experimental part of the work, the possibility of using thermally expanded graphite (TEG) and materials based on it (TEG initial, TEG granulated; coarse-cut foil; finely cut foil) for purification of wastewater from PP was studied. Investigation of their sorption properties showed that the maximum efficiency of wastewater purification from PP is achieved when using TEG. A filter based on TEG and polyacrylonitrile fibers was developed, which has high efficiency of wastewater purification from PP (E = 99.5%). For the developed sorbents, the sorption capacity for the dissolved oil product was calculated, which decreases in the following order: filter based on TEG and PANV (95 g/g) > TEG (86 g/g) > TEG foil (fine-cut) (68 g/g) > TEG foil (coarse-cut) (60 g/g) > granulated TEG (40 g/g).

Keywords: Wastewater; Adsorption of petroleum products; Sorbents; TEG; Perlite

1. Introduction

Currently, due to the widespread tightening of requirements for the quality of household water, many classic methods for water purification have become unable to provide the necessary depth of purification of natural and wastewater from petroleum products (PP) or are unprofitable from an economic point of view [1–4]. Therefore, much attention is paid to the search and development of new, non-traditional ways to remove toxic substances [5–11]. A sorption method of purification that successfully combines a high, practically not achievable by other methods, degree of extraction of dissolved impurities and high efficiency of the cleaning process with relatively small material and energy costs is quite promising and is already used in practice. Inexpensive, biologically safe sorbent substances that can be further processed can become promising sorbents.

The authors [12] propose to use inexpensive materials based on waste as sorbents, and present data on the sorption capacity of American sorbents and some Russian materials that can be used to absorb PP. Foam rubber, crushed cardboard, filter paper, writing paper, and other waste were investigated as Russian sorbents that have almost the same characteristics as the American sorbents.

A special place among adsorbents is occupied by fibrous sorbents, namely:

- Cellulose, the main component of most plant materials. Due to the presence of free space inside the cellulose macromolecules bounded by micelles or polymer

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chain nodes, they can hold oil and oil products more firmly [13];
- Fibrous materials obtained from waste of 21030-16 – 21060-16 polypropylene and disinfected disposable syringes. (Patent 2179600 of the Russian Federation);
- Activated carbon fiber "AQUALEN" (US Patent N 5,521,008);

Great attention is paid to sorbents based on carbon materials [14–19]:

- Activated carbons of various grades;
- Hydrophobic expanded perlite (perlite is a natural silicate rock of volcanic origin, 70% of its composition is silicon dioxide, the remaining part consists of oxides of aluminum, calcium, sodium, and iron) [14];
- Carbon adsorbents obtained during the process of oxidation by semi-coking of coals in fluidized bed generators, and carbonized coal obtained at the Research Institute of the Technological Institute of Carbon Sorbents in Perm (Russia);
- Fluxed graphite, widely used in St. Petersburg (Russia);
- Thermally expanded graphite (TEG) produced by the electrochemical introduction of substances which independently transform into a gaseous state during thermal heating [15–17];

In works [20–24] it was proposed to use carbonate sludge of chemical water treatment as one of the most available materials, which is a large-tonnage waste of energy for wastewater purification from oil products. The authors selected the optimal conditions for manufacture of granules based on carbonate sludge for wastewater treatment of oil products (thermally treated at 700°C for 60 min granules having diameters from 0.5 to 2.5 mm, with a ratio of 1:2 with a binder, soaked with 5% aqueous emulsion "NGL-94 M", and dried to constant weight).

In [25–29], the possibilities of wastewater treatment from organic pollutants using multi-component adsorption filters and sorption materials based on modified bentonite were studied. Various bentonite modifications were considered, as well as adsorption filters based on modified bentonite, anion exchange resin, and silica gel for water purification. The authors determined the physicochemical characteristics of bentonite clay, such as specific surface area $S = 54.4$ m^2/g, total pore volume $V_{pore} = 0.079$ cm^3/g, bulk density $\rho_b = 1.32$ g/cm^3 [26].

In [30], it was shown that TEG is very efficient for water purification from soluble and insoluble organic pollutants. For it, oil absorption reaches 60 g/g. Comparative analysis of the absorption of PP and wastewater using TEG and powder activated carbons of the OUA brand showed that the rate of absorption for TEG is significantly higher due to its highly developed surface. The authors [31] developed a sorbent based on the fruit shell of sunflower seeds, produced from cheap and readily available raw materials – the large-tonnage waste oil industry. It is non-toxic, improves the structural characteristics of the soil, and is completely decomposed by soil microorganisms. To increase the efficiency of the process of cleaning soils from oil pollution oil-oxidizing microorganisms were immobilized in the form of the bacterial agent Devoroil on the surface of the sorbent. The agent includes several types of bacteria-oil destructors, mainly of the Pseudomonas genus, as well as yeast fungi.

Many works are devoted to the development of composites based on graphene and chitosan. Due to the large active surface, hardness, and geometric shape, graphene provides the necessary connection between the components of the nanocomposite. The use of graphene oxide significantly improves the sorption of heavy metal ions in aqueous solutions [32]. Aerogel from graphene oxide and chitosan turned out to be an extremely efficient sorbent of tetracycline (1.13×103 mg/g) [33].

In [34] it is proposed to extract phosphates and organic compounds using a sorbent based on sawdust and dolomite. The sorption material was made by the joint pyrolysis of dolomite and sawdust at various temperatures. The increase of the pyrolysis temperature to 900°C leads to the formation of a composite rich in carbon particles, as well as CaO and MgO. Sorption occurs at pH 3.0–11.0. The maximum adsorption capacity was quantitatively determined using the Langmuir isotherm model and amounted to 207 mg of phosphorus (or 621 mg of phosphate) and 469 mg of organic substances per gram of composite used. The resulting composite has great potential for extracting phosphorus from wastewater. The spent composite can be used as a promising phosphate fertilizer to improve plant growth.

In [35] it is proposed to use the new hybrid magnetic biochar CeO_2-MoS_2 (CMMB) for the adsorption removal of Pb(II) and humate from an aqueous solution. The material was assessed to magnetic biochar (MB). The results showed that CMMB demonstrated strong magnetic separation capability. CMMB hybridization significantly improved the removal of Pb(II) and humate compared to MB, with >99% Pb(II) and removal of humate within 6 h. The CMMB sorption capacity for the extraction of lead (II) and humate was 263.6 and 218.0 mg/g. The removal mechanism for Pb(II) is mainly associated with electrostatic attraction, the interaction of Cπ-Pb(II) bonds and surface processes adsorption and complexation. The sorption mechanism for humate is the filling of the pores, the separation effect, and the π-π interaction.

A review [36] describes biochar, which is a promising low-cost sorbent for the removal of oxidizing agents from wastewater. The material has a very wide range of pore size, surface area, and chemical properties, which depend on the initial composition of the biomass and the conditions under which it turns into coal. The paper summarizes recent studies of biochar modification for the production of metal-biochar composites, which demonstrate the high ability to remove pollutants and provides an overview of several syntheses used to obtain metal biochar composites. The selection of chemical activation and addition of individual metals allows one to obtain a material with high sorption properties.

This work aimed to study the possibility of using various materials based on TEG and polyacrylonitrile fibers (PANF) as sorbents for the purification of wastewater from PP.

2. Materials and methods

The determination of petroleum product concentration in wastewater was carried out using the PP concentrator KN-2M. For this, the analyzed water sample was acidified with sulfuric acid solution and a further 30 cm^3 of carbon tetrachloride was added for extraction. The sample was extracted using an extractor, first in the full volume of water, and then the major portion of water was poured into the cylinder and extraction was continued in a small separating funnel. The obtained extract was filtered through cotton wool into a container with a ground stopper. When a stable emulsion of the aqueous-organic phase was formed, it was dried with anhydrous sodium sulfate in the amount of 5 g of reagent per 30 cm^3 of extract. The extract was passed through a chromatographic column filled with aluminum oxide. The resulting eluate was investigated for the content of PP using the PP concentrator KN-2M at a wavelength of 3.42 μm in the infrared region.

Microstructural studies were performed using the SteREO Lumar V12 fluorescent stereo microscope of the German company "Carl Zeiss" with a smooth change of zoom 1:12. The control of the optical head movement and magnification is performed from the displays. The minimum magnification is ×12, the maximum magnification is ×50.

Determination of materials specific surface area according to the Brunauer–Emmett–Teller (BET) technique was performed using the automated sorption unit TriStar II 3020 from Micromeritics (USA). The bulk version of the sorption method was used. The measurements were carried out simultaneously for three parallel samples. The sample-specific surface was determined by the method of low-temperature nitrogen adsorption (–196°C).

To determine the bulk density, the adsorbent, dried at 110°C, was poured in 20 ml portions into a 100 ml cylinder (height is 240 mm). The cylinder bottom was tapped on a wooden disc for 0.5 min in an inclined position of 70°–80°. Further, the cylinder was weighed with an accuracy of ±0.5 mg.

To determine the treatment efficiency, real wastewater from the refinery was used, without prior treatment.

3. Results and discussion

TEG are carbon foam structures (Fig. 1), obtained during quick heating of graphite intercalations (GIC) or products of its hydrolysis. This material is described by the chemical formulae $C^{+}_{24n}\cdot HSO_4^{-}\cdot 2H_2SO_4$ (n = 1, 2, 3).

In this research, TEG was used, obtained by electrochemical oxidation of graphite of the UHP GT (C > 99.5) with nitric acid, followed by hydrolysis and heat treatment at a temperature of 900°C. In general, the processing of graphite into TEG is displayed by the scheme shown in Fig. 2.

Microstructural studies of the TEG surface showed the presence of worm-like structures that are hollow inside (Fig. 1). The porous structure of the material allows for predicting its high adsorption properties. In [15,16], the possibility of using TEG as a sorbent for purification of wastewater from oil products as described. The main technical difficulty of using TEG as a load for a bulk filter is because the resulting product is very light, fluffy and, when water is passed through the filter, the TEG material is partially entrained with water.

To solve this problem the following sorbents made of TEG were prepared and investigated (Fig. 3):

- TEG (for comparison);
- Granulated TEG, which was prepared from GIC, which was foamed at a temperature of 900°C in a special form for granules with a 0.5 mm diameter (100 mg–8 granules);
- TEG pressed into foil, with subsequent cutting into large (5 mm × 7 mm) and small (2 mm × 3 mm) fractions.

The bulk density of the prepared TEG sorbents was determined. Using the BET technique, the specific surface area of the samples was determined (Table 1).

The sorbents made of TEG in the amount of 100 mg were poured into wastewater V = 1 L), with an initial concentration of PP C_{in} = 342 mg/L. Sorption was carried out in static conditions with mixing for 10 min, which corresponds to the sorption equilibrium time, the mixing rate was 200–250 rpm. The mixing speed was maintained using a magnetic mixer.

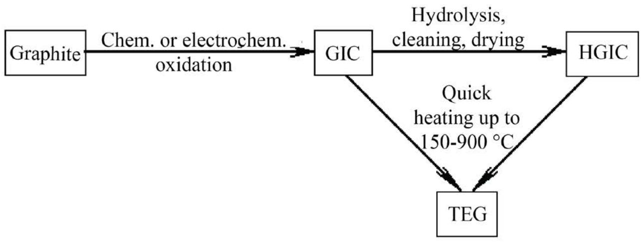

Fig. 2. General technological scheme for TEG obtaining.

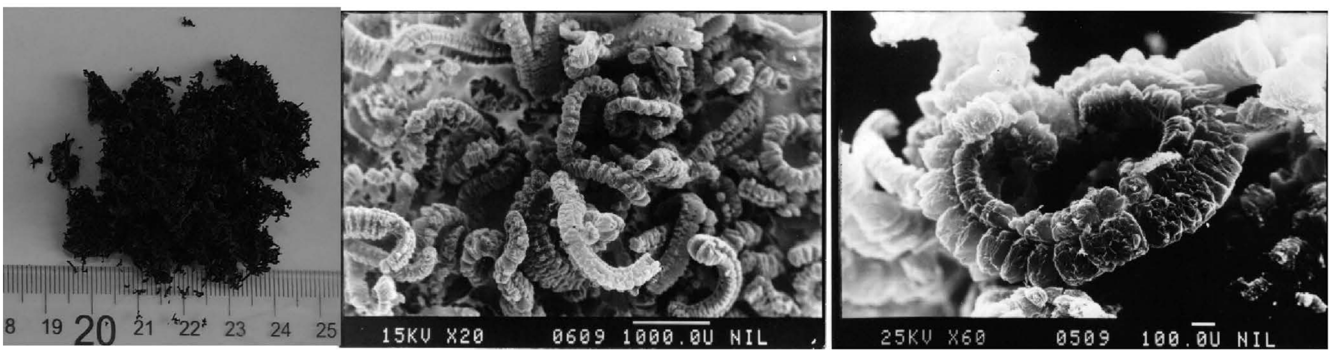

Fig. 1. Photo of thermally expanded graphite: (a) ×0, (b) ×20, and (c) ×60.

Fig. 3. Carbon materials based on TEG: 1 – granulated TEG; 2 – large-cut foil; 3 – small-cut foil; 4 – TEG.

Table 1
Efficiency of wastewater purification from petroleum products (*E*, %) using sorbents made from TEG, and its specific surface

Sorbent type	Initial concentration mg/L	Final concentration mg/L	*E*, %	Specific surface S_s, m²/g	Bulk density g/cm³
TEG	102.6	7.316	92.8	88 ± 5	1.2 ± 0.1
Granulated TEG	102.6	42.153	58.9	15 ± 2	2.8 ± 0.2
Foil from TEG (small-cut)	102.6	11.037	89.0	25 + 3	4.1 ± 0.4
Foil from TEG (large-cut)	102.6	13.406	88.0	21 ± 2	3.9 ± 0.3

The experiment was carried out at room temperature (22°C ± 2°C). After purification, wastewater was filtered and PP concentration was analyzed. The initial and final concentrations were determined using PP concentrator KN-2M, as an average value from 3 independent experiments, Table 1.

It is seen from Table 1 that the maximum efficiency of PP extraction from wastewater occurs when using foamed TEG. The lowest purification efficiency is observed when using TEG granules. This is because bulk density is significantly reduced during granulation. The weight of one granule ranges from 10 to 13 mg. The bulk TEG density is 1.2 g/cm³, and the bulk density of granules is 2.8 g/cm³. TEG in a granule becomes more dense, which is confirmed by microstructural studies (Fig. 4).

The use of TEG in the form of chopped foil and granules allows one to increase the mechanical strength and technically facilitate TEG usage for water treatment, but this reduces its cleaning efficiency.

At the next stage, composite filters were made based on TEG and polyacrylonitrile fiber waste (PANF). It is known

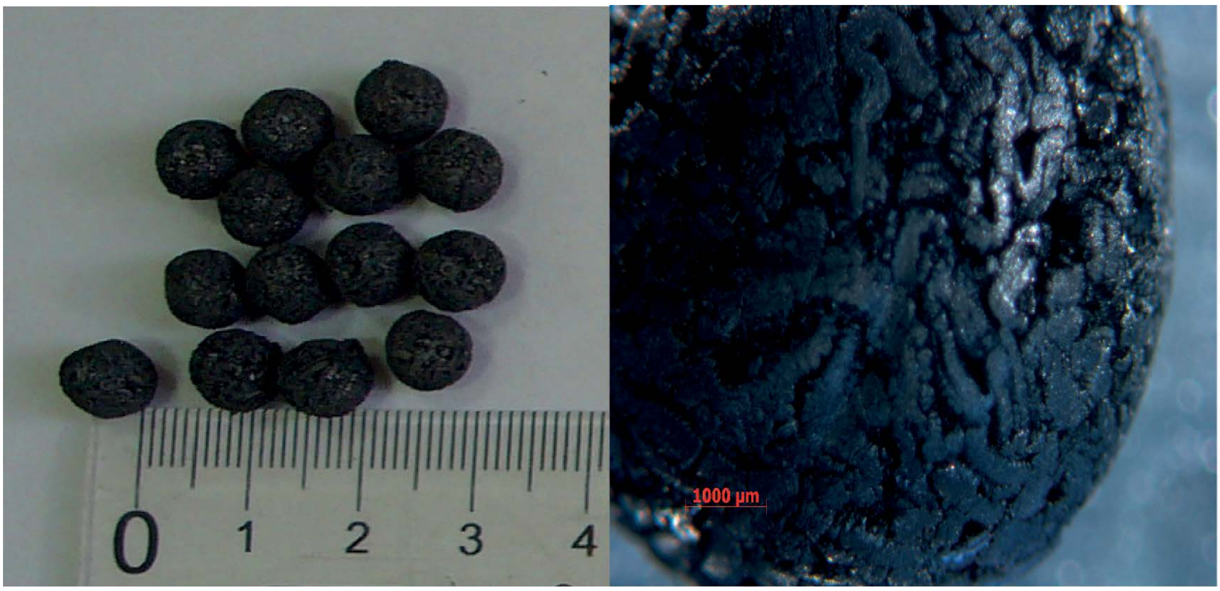

Fig. 4. Photo of granulated TEG: (a) ×1 and (b) ×10.

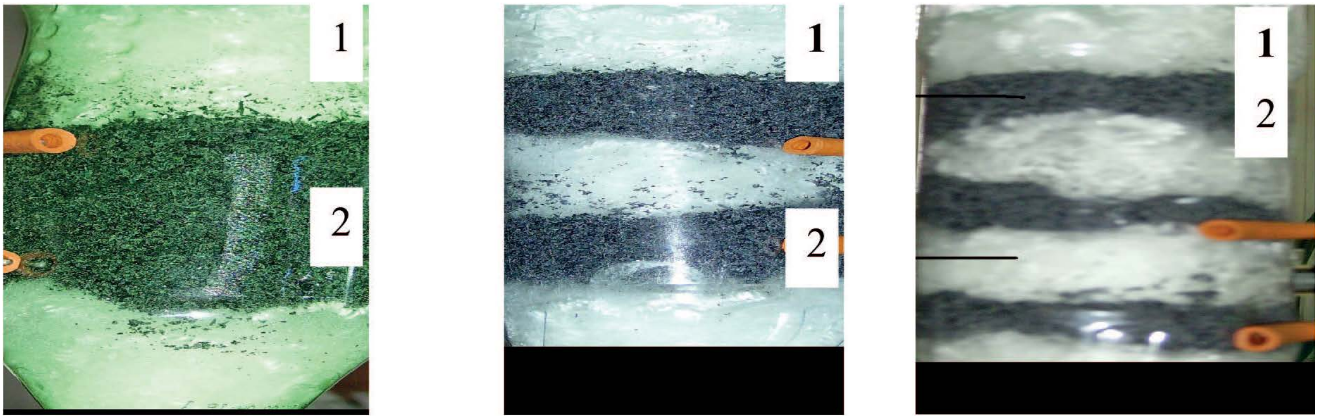

Fig. 5. Multilayer composite filters (MCF) based on 1 – polyacrylonitrile fiber and 2 – TEG.

from the literature that fibrous materials are good sorbents of organic pollutants and heavy metals [37–39]. PANF are synthetic fibers obtained from polyacrylonitrile or copolymers containing more than 85% (by weight) acrylonitrile [38]. Composite filters were made, where PANF waste from Orgsintez OJSC (Saratov) was used as a "frame" for TEG, which was cuttings from production PANF with a fiber length of 5–30 cm. Filters were made as several alternating layers of TEG and PANF. They were laid in such a way that PANF layers of the same thickness created an external rigid mechanical filter frame in the filter volume and ensured good fixation of the TEG layers (Fig. 5). The ratio of the mass of components and the number of layers was varied. The total mass of TEG and mass of PANF was the same in all filters. Model wastewater "SarNPZ" in the amount of 1 L was passed through manufactured filters of 5 g masses. Initial concentration was $C_{\text{in pp}}$ = 244 mg/L, filtration rate was 20 ml/min, T = 295 ± 2 K. The final concentration of PP in purified waters was determined using the PP concentrator KN-2M. The results are shown in Table 2.

It was found that the optimal mass of PANF is 65%–70% of the total mass of the sorption-filtering material, and the

Table 2
Influence of TEG and PANF mass relations in the filter on wastewater purification efficiency from petroleum products (E)

Relation, mass %		Initial concentration, C_{in}, mg/L	Final concentration, C_{fin}, mg/L	E, %
TEG	PANF			
35	65	244	2.4	99.0
30	70	244	1.2	99.5
25	75	244	2.6	98.9
20	80	244	4.8	98.0

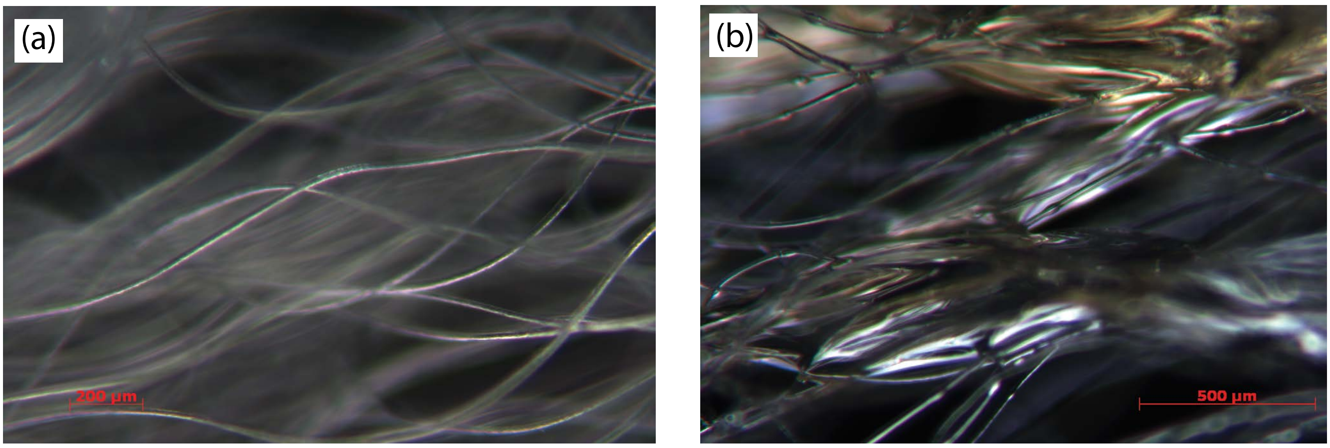

Fig. 6. Microstructure of PAN fiber: (a) initial and (b) after petroleum products removal: ×36.

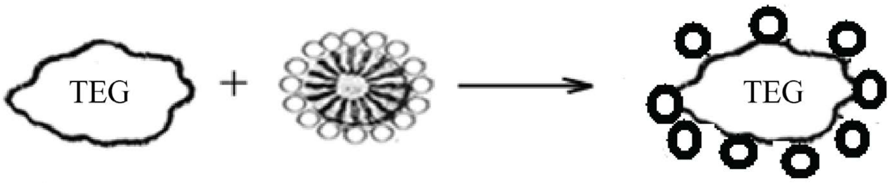

Fig. 7. Scheme for globules formation when TEG is interacting with PP.

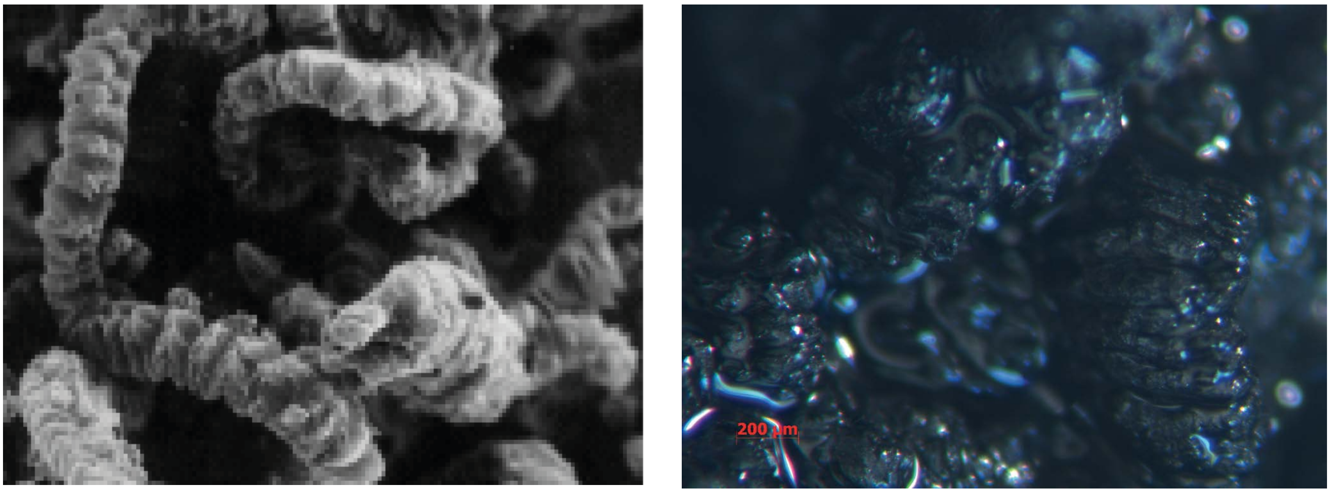

Fig. 8. TEG: (a) Initial and (b) with absorbed PP, ×36.

amount of TEG is 25%–30%, and each PANF layer was evenly covered with a TEG layer, the height of which was 20 ± 2 mm, this value is optimal.

It was established that purification efficiency when passing through a combined TEG and PANF filter is higher than for the initial TEG. High purification efficiency by the combined filter is achieved because two sorbents (TEG and PANF) work.

The main characteristic of sorption materials is sorption capacity. For the developed sorbents, the sorption capacity for the dissolved oil product was calculated, which decreases in the following order: filter based on TEG and PANV (95 g/g) > TEG (86 g/g) > TEG foil (fine-cut) (68 g/g) > TEG foil (coarse-cut) (60 g/g) > granulated TEG (40 g/g).

Microscopic photographs of the PANF surface before and after sewage treatment (Fig. 6) show that PP extraction by fiber occurs due to adhesion, that is, the effect of "sticking" of PP between fibers.

Since saturated hydrocarbons are almost electrically neutral, the mechanism of their adsorption can be represented as a hydrophobic interaction of petroleum particles and TEG. TEG and PP possess hydrophobic properties, and since the affinity of hydrophobic particles to water is less than among themselves, they stick together and join into globules (Fig. 7), as a result of which the effective removal of PP from wastewater occurs.

Fig. 8 shows the TEG microstructure after wastewater treatment from a petroleum product. The photographs of the TEG surface show that PP removal with the use of TEG occurs not only due to adhesion, but also due to the physical adsorption of PP into the TEG pores.

After wastewater purification from oil products, used sorbents are proposed to utilize as a burnable additive during ceramics production or as a filler for chipboard, highly filled polymeric materials, asphalt concrete and paving slabs.

4. Conclusions

The sorption properties of various carbon materials based on TEG (TEG initial, TEG granulated; large-cut foil; small-cut foil) were studied. A filter based on TEG and PANV has been developed, which solves the technical complexity of using downy TEG and has high efficiency (E = 99.5%) of wastewater purification from PP. The microstructural studies of the developed materials were carried out. After wastewater purification from oil products, the used sorbents are proposed to utilize as a burnable additive in the production of ceramics and as a filler for chipboard, highly filled polymeric materials, asphalt concrete and paving slabs.

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