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Formation and properties of a dynamic ultrafiltration membrane

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Annotation. By applying to the surface of the nylon membrane of polystyrene particles, dynamic nylon-polystyrene membranes with a final content of 3.4 % by weight were obtained. The content of polystyrene on the surface of the nylon membrane is indirectly confirmed by IR Fourier spectroscopy methods. An increase in the contact angle of the droplets of distilled water of the membrane as a result of depositing polystyrene particles on the surface of the initial membrane was revealed. According to the results of scanning electron microscopy, it was found that polystyrene particles with sizes from 0.05 to 0.2 microns are located on the surface and in pores of a nylon substrate. After applying a layer of polystyrene on the surface of the membrane, the specific productivity of the membranes decreases by an order of magnitude, due to the intensive accumulation of polystyrene particles in the pores and membrane surface. The maximum productivity of the initial and dynamic membranes is observed when the distilled water is passed through. Dynamic membrane ultrafiltration with a surface layer of polystyrene is designed to separate water-oil emulsions. The degree of separation of water-oil emulsion with a concentration of oil products of 10 g/dm^3 is more than 98 %.

Introduction

Cleaning industrial wastewater from oil products is an important task before discharging into the sewerage system or into natural water bodies. As is known, oily wastewater has a negative impact on the state of natural water: change the physical, chemical properties of water, which as a result leads to the death of hydrobionts, the disturbance of the ecosystem of the water body.

Petroleum products in waste water can be in a free state, dissolved and emulsified. If the removal of free petroleum products does not create special difficulties in the purification by sedimentation, coalescence, a whole complex of technological processes of purification is required to purify sewage from emulsified and dissolved petroleum products. At present, for the separation of emulsions, there are two fundamentally different approaches: reagent and reagent (hardware). To separate emulsions, reagent, acidic decomposition methods, coagulation methods and reagentless methods of filtration, sedimentation, centrifugation, coalescence [1], membrane separation processes are used [2-11]. And for the purification of sewage from dissolved petroleum products, adsorption [12] and membrane separation methods are used. Emulsions occur during extraction extraction of ore components and organic substances from plant raw materials, car washes, during the extraction and processing of petroleum products, and also in mechanical engineering enterprises, stable oil-containing emulsions are formed-spent lubricating and cooling liquids.

Thus, in [13], the authors obtained a superhydrophilic and superolefic membrane of polyvinylidene fluoride on the surface of which polyacrylic acid was grafted. The hierarchical micro / nanoscale structure of the surface of the membrane gives it a super-hydrophilic / superleophobic property. The membrane separates oil-in-water emulsions with a low working pressure (<0.3 bar), and the permeability of the membrane is one or two orders of magnitude higher than that of industrial filter membranes having similar parameters. Also, the resulting membrane has an excellent anti-fouling property.

Of all types of membranes, dynamic membranes have the advantage of separating water-oil emulsions. So, if the permeability of the membranes decreases, you can replace the dynamic layer with a new one, which will restore the initial performance. By using different particle sizes of the applied material or by obtaining several dynamic layers, the required pore size of the membranes can be achieved. Depending on the physico-chemical properties of the applied material, it is possible to obtain different wettability and roughness of the membrane surface.

To separate the oil-in-water emulsion, the authors of [14] obtained membranes with a dynamic layer of titanium dioxide which was formed on a porous substrate of a carbon tube. Dynamic membrane, obtained under optimal conditions, was characterized as homogeneous, dense and hydrophilic. According to the results of the experimental work, the authors found that the oil removal efficiency is 98%, and its concentration in the permeate was less than 8.3 mg / dm^3.

As a dynamic layer, a suspension of magnesium hydroxide was applied in [15], which was applied to a ceramic substrate. The membrane was used to separate the water-oil emulsion. The degree of oil removal was more than 98%, and the filtration rate was more than 100 dm^3/m^2h at an applied pressure of 100 kPa.

The authors [16] obtained a two-layer composite dynamic membrane for the separation of water-oil emulsions. The dynamic layer of the membrane was formed from kaolin and MnO_2. The microstructures of the dynamic membrane were examined with a scanning electron microscope. The results showed that the MnO_2 particles are located on the surface of the dynamic layer of Kaolin, forming a kaolin / MnO_2 two-layer composite dynamic membrane. With increasing oil concentration, the permeate flux has decreased and the oil retention coefficient has increased. In neutral or alkaline environments, the oil retention efficiency was more than 99 %. With an increase in temperature from 283 K to 313 K, the retention efficiency decreased from 99.9 % to 98.2 %, and the filtration rate increased from 120 dm^3/m^2h to 153 dm^3/m^2h.

In [17], a thin-film dynamic membrane of PAN-TFC was obtained. The efficiency of the oil-water emulsion separation was more than 99 %. Also, the authors investigated the process of surface contamination of the membrane with oil and methods of membrane regeneration. The authors decided on the need for more effective anti-fouling TFC membranes.

The main problem of cleaning oily wastewater is the separation of stable emulsified oil particles from the aqueous phase. Therefore, the purpose of this study is to increase the efficiency of the processes of ultrafiltration separation of stable emulsions of the oil-in-water type using a dynamic membrane.

Methods

A microfiltration polymer membrane of nylon with an average pore size of 0.45 μm and a diameter of 47 mm was used as the initial substrate on which the dynamic layer was applied. The dynamic layer was obtained by forming a semipermeable layer on the surface of the porous base of the suspended microparticles of polystyrene present in the filtered aqueous solution of acetone in a dynamic equilibrium with the solution. The content of polystyrene in the membrane was determined by the gravimetric method, by the weight of the membrane before and after the modification.

The particle size of the dispersed phase of emulsions and suspensions was determined by dynamic light scattering (DLS) and the ζ potential by light scattering with phase analysis (PALS) using a NanoBrook Omni analyzer.

Figure 1 shows the distribution of the particle size of the dispersed phase of a polystyrene suspension with a 25% acetone solution.

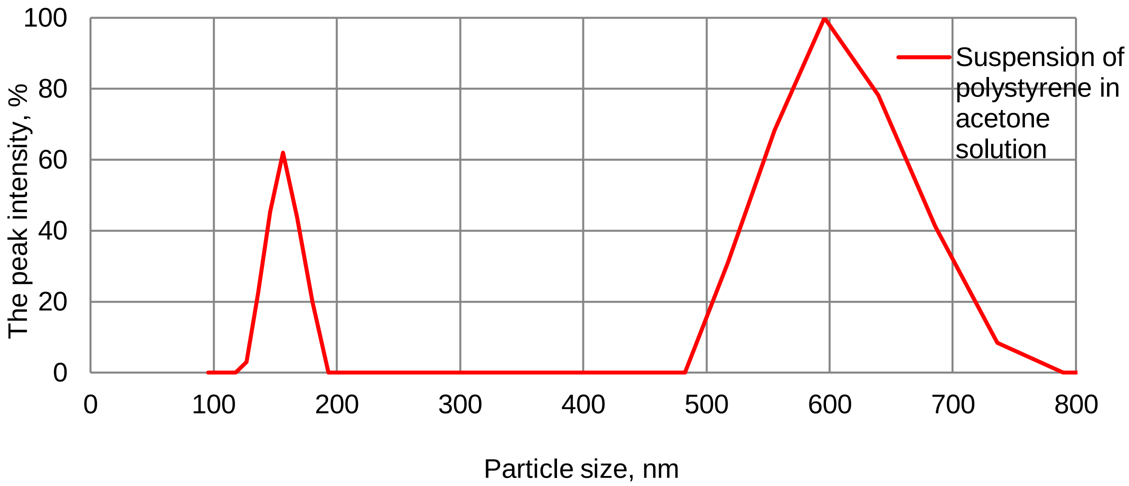

Figure 1. The graph of the distribution of the particle sizes of a dispersed phase of a polystyrene suspension in an aqueous solution of acetone

Table 1. The particle size and the ζ-potential of the dispersed phase of the suspension.

Suspension	Particle size, nm	ζ-potential, mV
Polystyrene 25 % of the p-re acetone	118 – 193, 492-790	- 7,1±0,7

The particle size of the dispersed phase of a polystyrene suspension in a 25 % acetone solution, as shown in Fig. 1 and tab. 1 is from 118 to 790 nm. To obtain a dynamic layer, use this suspension of polystyrene in an acetone-water solution.

The IR spectra of the samples were studied using an infrared FTIR spectrometer of the «Infralum FT-02» brand. IR Fourier spectrometer, allows to obtain high resolution absorption bands.

A change in the surface structure of the membranes was recorded using a scanning electron microscope of the brand «LEO-1430 VP» manufactured by «Carl Zeiss». The samples were glued to aluminum plates, the surface of the membranes was deposited with gold, cathodic deposition in argon, and viewed in high vacuum.

As the main parameters of the membrane separation of the emulsion, the specific productivity was considered, which was defined as the ratio of the amount of the filtrate formed to the product of the membrane area and the process time in terms of dm^3/m^2h, and the degree of separation of the emulsion, which was calculated as the ratio of the content of petroleum products (NP) with the help of a concentrate «KH-3», an emulsion before and after separation.

For membrane separation, a 1 % emulsion of freshly prepared coolant was used as a VME. During the separation of distilled water and emulsions, the working pressure was 0.1 MPa, the liquid temperature was – 25 °C.

Results and discussion

After applying a dynamic layer of polystyrene to the surface of the original nylon membrane, the surface of the membrane becomes hydrophobic, as determined by the increase in the contact angle of the drop of distilled water from 59.6º to 106.2º [4].

The results of investigation of the membrane surface by scanning electron microscopy with an increase of 2000 times are shown in Fig. 2.

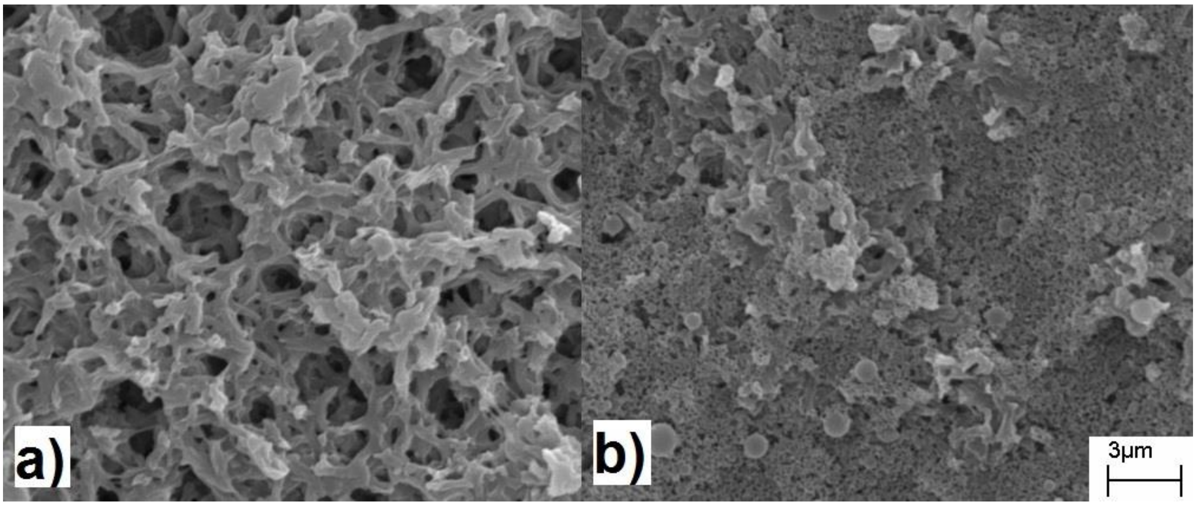

Figure 2. Microphotographs of the membrane surface: a) Initial membrane of nylon; b) the membrane after applying a dynamic layer of polystyrene (an increase of 2000 times).

According to Fig. 2, it can be seen that the polystyrene particles are located on the surface and in the pores of the membrane from nylon. In general, the dimensions of the polystyrene particles are from 0.05 to 0.2 μm.

Spectrums of the investigated membrane samples in the frequency interval 600-4000 cm 1 were obtained using the infrared FTI-08 IR spectrometer. The IR spectra of the initial and modified membranes are shown in Fig. 3.

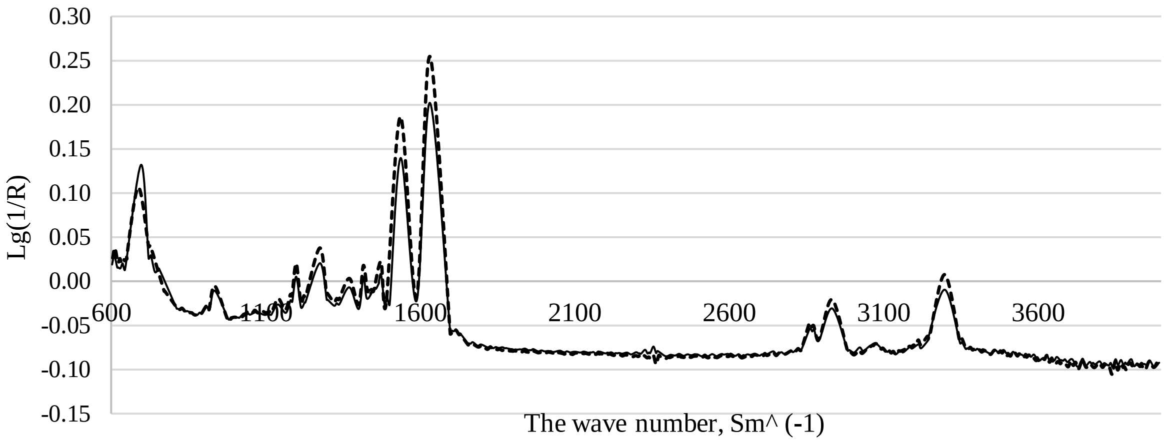

Figure 3. IR absorption spectra of the membrane samples studied: nylon (dashed line) and nylon-PS (solid line).

The characteristic absorption bands for nylon correspond to wavelengths of 1635 cm^{-1} and 1539 cm^{-1} (Fig. 3) [18]. For polystyrene, the absorption bands of 2850 cm^{-1}, 2930 cm^{-1}, 3022 cm^{-1} are characteristic [19]. After the polystyrene nylon membrane is applied to the surface, a decrease in the intensity of absorption of these bands characteristic of the nylon and an increase in the intensity of the absorption bands of 690 cm^{-1} characteristic for non-planar deformation vibrations of C-H are observed. The appearance of a weak absorption band at 753 cm^{-1} corresponds to out-of-plane deformation vibrations of 1,3 substituted C-H, groups of absorption bands of weak intensity at 2330-2370 cm^{-1} correspond to salts of amines $R_2C = NH^+$. Thus, based on the results of IR spectroscopy, in particular, the appearance of changes in the chemical structure resulting from the deposition of polystyrene on the surface of the nylon membrane, the above increase in the hydrophobicity of the nylon-PS membrane occurs.

The results of studies on the specific productivity of membranes are presented in Table. 2.

Table 2. Specific productivity of membranes

Membrane	The content of polystyrene,% (by weight)	Specific capacity of membranes, $dm^3/m^2 \cdot h$	
		for distilled water	by 1% water-oil emulsion
Nylon	-	3845	186
Nylon-PS	3,4	266	23

After applying a layer of polystyrene on the surface of the membrane, the specific productivity of the membranes decreases by an order of magnitude, due to the intensive accumulation of polystyrene particles in the pores and membrane surface. The maximum productivity of the initial and dynamic membranes is observed when the distilled water is passed through.

The results of the separation of a water-oil emulsion from an NP are shown in Table. 3.

Table 3. Degree of separation of water-oil emulsion

Membrane	The content of polystyrene,% (by weight)	Concentration of oil products, mg/dm^3		Степень очистки, %
		initial	after cleaning	
Nylon	-	10120±1012	7020±702	30,6
Nylon-PS	3,4		208±20,8	98,0

According to Table 3, it is obvious that the degree of removal of petroleum products from the water-oil emulsion using the initial nylon membrane is significantly lower than when it is separated using dynamic nylon-PS membranes. It was determined that after the deposition of a dynamic layer of polystyrene on the surface of the nylon membrane, the degree of separation of the emulsion increased to 67 %.

Conclusion

Dynamic membrane ultrafiltration with a surface layer of polystyrene is hydrophobic, designed to separate water-oil emulsions. A layer of polystyrene is formed by filtration on the surface of a nylon substrate from a suspension of polystyrene in acetone. It was determined that after depositing a dynamic layer of polystyrene on the surface of the nylon substrate, the degree of separation of the emulsion with a concentration of oil products of 10 g /dm^3 increased by 67 % and amounted to more than 98 %

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