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Research paper



Improvement of Effectiveness of Separation of Emulsion by Processing Ptfe Membrane with Microwave Radiation

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Abstract

In this work, in order to increase the productivity and degree of separation of petroleum emulsions, a modification of thin-film microfiltration membranes from polytetrafluoroethylene (PTFE) by ultrahigh-frequency (microwave) radiation in the decimeter wave band in air, nitrogen and argon was carried out. Treatment of membranes with microwave radiation leads to a reduction in the mass of PTFE membranes depending on the treatment time and the gaseous media. The membrane weight decreases most strongly to 0.17% when treated in atmospheric air, which is apparently due to the aggressive action of oxygen. The least mass of the membrane decreases when treated in argon, only 0.06%. The increase in the specific productivity of membranes during processing in the atmosphere of atmospheric air is explained by the hydrophilization of the surface, due to the formation of polar oxygen-containing groups. A decrease in specific productivity when treated in an argon inert gas environment occurs apparently due to crosslinking of the surface layer. Treatment of the membrane in a nitrogen medium increases the degree of emulsion separation by 6.9%, in air media by 15.3%, in argon media by 21%. An increase in the efficiency of separation of emulsions is also confirmed by a decrease in the size of oil particles in filtrates of emulsions. So the limiting size of the particles of the disperse phase cut off by the initial membrane was 118 nm, and the membrane treated with microwave radiation in the air medium was 39 nm, in the nitrogen medium 68 nm and in argon medium 10 nm.

Keywords: *The oil-in-water emulsion, petroleum products, microfiltration, PTFE, particle size, microwave radiation, nitrogen, argon.*

1. Introduction

Oil-containing wastewater is formed and enters the surface waters as a result of oil production, transportation and processing. Also, oily wastewater is formed as a result of accidents on pipelines, from washing tanks, tanks, machine-building enterprises use detergent solutions for washing parts, which use emulsions of the oil-in-water type. In addition, machine-building enterprises generate waste lubricating and cooling liquids with a high content of oil and surfactants (surfactants), which are highly stable emulsions. The presence of a large number of surfactants (resins, asphaltenes, naphthenic acids) in oil causes the formation of a stable water-oil emulsion during extraction in conditions of high water cut of oil. In petroleum emulsions with a water content of 30.5% and higher, the dispersity of the particles (4.8 μm) increased to 90%) [1]. Some of the petroleum products enter the surface waters in dissolved form or as a result of dissolution after they enter the reservoirs.

It is advisable to organize the purification of oily wastewater at the place of formation, i.e. at the enterprises. Removal of free petroleum products is carried out using sedimentation tanks, various sorts of separators, centrifugation, flotation. Depending on the level of stability of oil-in-water emulsions, coagulation, flocculation, coalescence, reagent decomposition, ozonation, distillation, filtration, membrane separation are used, or several methods of purification are combined [2-9]. When purifying water from dissolved petroleum products, the methods of adsorption and membrane separation are mainly used [10-17]. Membrane separation methods of emulsions have such advantages over the above methods as a high efficiency of emulsion separation, low energy consumption of the separation process, the absence of rotating and moving parts, and the absence of chemical reagents. Membrane methods for the separation of oil-in-water emulsions use microfiltration and ultrafiltration [18-20].

Membrane elements used to separate emulsions must be resistant to high temperatures, acidic and alkaline media, resistant to solvents and high pressures.

Also in the process of membrane separation of emulsions, the phenomenon of concentration polarization is observed, which leads to the formation of a gel layer on the membrane surface and further leads to a reduction in specific productivity. In order to increase the productivity or efficiency of separation of the emulsion, a modification of the membranes is carried out. Modification of membranes is carried out by chemical [11, 21, 22] and physical methods. As a result of the modification, the surface properties of the membranes change: wettability, porosity, roughness, pore size, conductivity.

In recent years, the electromagnetic radiation of the microwave (microwave) range for the treatment of various materials has become widely used [23, 24]. The most interesting is the so-called nonthermal modification of polymers, when the amount of EMR microwave energy absorbed by the substance does not lead to a significant change in the material temperature, but a significant change in the physicomechanical properties is observed. The depth of penetration of microwave radiation into polymeric materials, according to the data given in [24], at the radiation frequency 2.45 GHz for polyvinylchloride ~ 10 cm, polyethylene terephthalate ~ 28 cm, polypropylene ~ 34 cm, polyethylene ~ 41 cm. A large depth of penetration of microwave radiation is sufficient to handle not only flat membranes but also rolled and tubular membrane elements. Improvement of physicomechanical properties of

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polymeric membranes is an actual problem, the solution of which allows to significantly increase the efficiency of emulsion separation and specific productivity.

2. Methods

To improve the productivity and degree of separation of petroleum emulsions, a modification of thin-film microfiltration membranes from PTFE with ultrahigh-frequency radiation in the decimeter wave band without thermal exposure was carried out using a laboratory installation of the microwave sample preparation system MS-6. To determine the effect of microwave radiation on membranes, the change in the mass of membranes after the microwave treatment was determined with the help of analytical weights with an accuracy of 0.00001.

To determine the change in wettability of the surface as a result of microwave radiation, the moisture capacity of the initial and modified membranes was determined with a moisture analyzer of the "A & MD" brand The particle size of the dispersed phase of oil-in-water emulsions was determined using a "Nano Brook Omni" analyzer. To study the characteristics of emulsions, the following parameters are taken from available instrument databases: solvent - water; viscosity: 0.89; the scattering angle is 90°; duration of measurement - 3 min. During the separation of distilled water and emulsions, the working pressure was 0.1 MPa, the temperature of the liquid was 25 °C.

3. Results and Discussion

The reduction in the mass of membranes after microwave treatment in air, nitrogen and argon is presented in Table 1.

Table 1:. Reduction of the mass of membranes after microwave treatment in air, nitrogen and argon.

Name of membrane	Time of microwave treatment, min	Decrease of membrane weight Δ, %		
		in air	in nitrogen	in argon
PTFE	10	0,04	0,04	0,00
	30	0,09	0,06	0,04
	60	0,17	0,13	0,06

According to Table 1, it follows that as a result of the treatment of membranes by microwave radiation in atmospheric air, the mass of the membranes decreases most. With an increase in the processing time of membranes from PTFE in air, a decrease in the membrane mass to 0.17% is observed. The lowest mass of the membrane decreases as a result of processing in argon, up to 0.06%. Treatment of the membrane in a nitrogen medium leads to a reduction in the membrane weight from 0.04 to 0.13%.

The surface of PTFE membrane is hydrophobic. The results on moisture capacity are shown in Table 2.

Table 2:. Change in the moisture capacity of membranes after microwave treatment in air.

Name of membrane	Time of microwave treatment, min	Moisture capacity, %		
		in air	in nitrogen	in argon
PTFE	-	0,6		
	10	2,2	3,9	2,4
	30	4,9	4,0	2,8
	60	5,3	4,7	3,3

From the results of the research it follows that as the processing time of microwave radiation increases, the moisture capacity of the membrane from PTFE increases from the initial 0.6% to 5.3%. After membrane treatment in a nitrogen medium, the moisture capacity of the membrane is increased to 4.7%, regardless of the time of microwave treatment by radiation. The least moisture capacity of the membrane increases after treatment with argon. Consequently, microwave radiation also affects the wettability of the membrane surface towards hydrophilicity.

The initial and modified PTFE membranes determined specific productivity for distilled water (Fig. 1) and model oil emulsion with a content of oil products of 161.5 mg/dm^3 (Fig. 2).

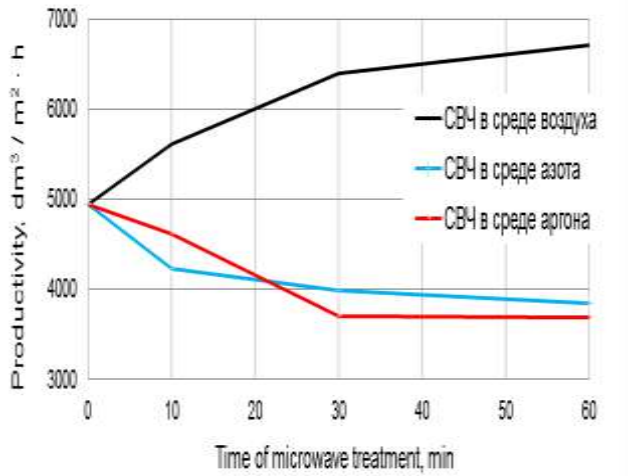


Figure 1:. Specific productivity of PTFE membranes in distilled water as a function of the time of microwave treatment in various media.

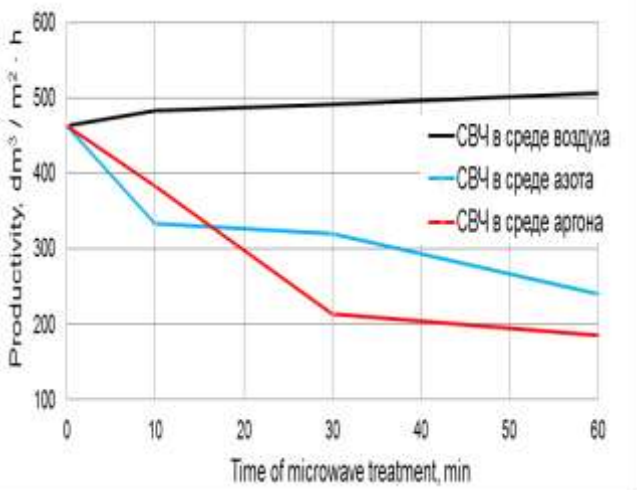


Figure 2:. Specific productivity of PTFE membranes by oil emulsion as a function of the time of microwave treatment in various media.

The specific productivity of membranes in the separation of oil emulsion is reduced approximately 10 times more than when filtering distilled water. Processing of microwave radiation from a PTFE membrane in an atmospheric air environment increases the specific membrane productivity, and as a result of microwave treatment in a nitrogen and argon medium, the productivity is reduced to 1.9 and 2.5 times, respectively. This circumstance is apparently connected with an increase in the pore size of membranes or structural changes in the membrane material take place. Also, these changes are associated with an increase in the wettability of the membrane surface. Specific productivity by distilled water of PTFE membrane during air treatment increased by 26% and by emulsion only by 8%.

The results of separation of the model emulsion from the initial and microwave-treated membranes are presented in Table. 3.

Table 3:. Degree of separation of model oil emulsion

Name of membrane	Time of microwave treatment, min	Degree of oil products removal, %		
		in air	in nitrogen	in argon
PTFE	-	68,0		
	10	81,7	69,4	82,1

	30	83,2	71,5	87,5
	60	83,3	74,9	89,0

The degree of removal of petroleum products from the emulsion at a concentration of 161.5 mg / dm3 with a PTFE membrane is 68%.

After the treatment of the membrane by microwave radiation in the decimeter wavelength range, the degree of separation of the emulsion and the degree of purification with increasing processing time of the membranes increases. The dependence of the degree of removal of oil products on the composition of the gaseous media in which the membrane is processed is determined. Thus, processing of the membrane in a nitrogen media increases the degree of emulsion separation by 6.9%, in air media by 15.3%, in argon media by 21%.

Figure 3 shows the distribution of the particle size of the dispersed phase of the model oil emulsion and its filtrates by the initial and microwave-treated membranes.

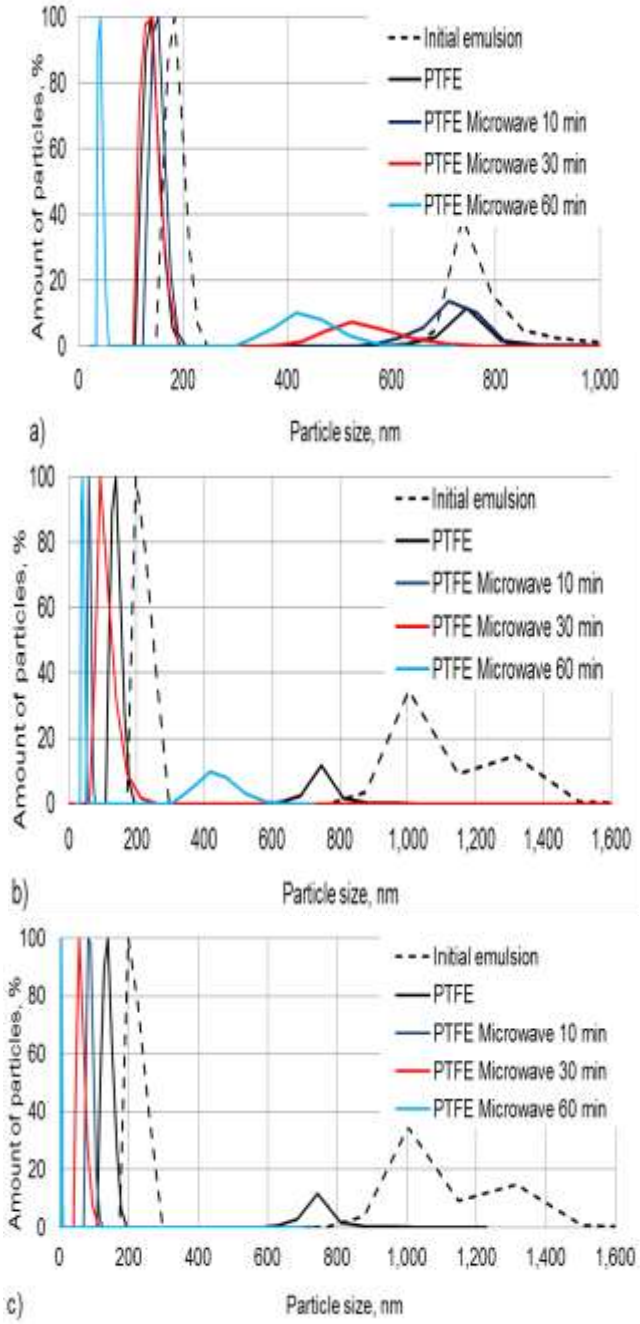


Figure 3:. The graph of the distribution of the particle size of the dispersed phase of the emulsion and its filtrates by the initial and PTFE-treated membranes by microwave radiation: a) in air; b) in nitrogen; c) in argon.

According to Fig. 3, after filtering the emulsion through the membranes treated with microwave radiation, the size of the particles of the dispersed phase of the emulsion decreases, and the particle size of the oil decreases with increasing processing time. The limiting size of the oil particles cut off by the initial membrane was 118 nm, the membrane treated in the air medium was 39 nm, in the nitrogen medium - 68 nm and in the argon medium - 10 nm.

Table 4:. ζ-potential of the dispersed phase of the model oil emulsion and its filtrates.

Emulsion	ζ- potential, mV		
	in air	in nitrogen	in argon
Model oil emulsion	-95,7		
PTFE filtrate	-62,7		
PTFE microwave filtrate (10 min)	-51,8	-51,1	-41,3
PTFE microwave filtrate (30 min)	-32,5	-47,9	-32,6
PTFE microwave filtrate (60 min)	-18,1	-37,4	-27,3

The absolute value of the ζ-potential after separation decreases, which indicates the destruction of the emulsion.

4. Summary

Treatment of membranes with microwave radiation leads to a reduction in the mass of PTFE membranes to 0.17%, depending on the treatment time and the gaseous media.

The membrane weight decreases most strongly to 0.17% when treated in atmospheric air, which is apparently due to the aggressive action of oxygen. The surface layer of the membrane, as a rule, is more defective than its main mass, and is more intensively etched. The etching process is initiated by atomic oxygen, and an activated oxidative destruction of the surface takes place. The lowest mass of the membrane decreases when treated in argon, only 0.06%.

Due to the etching of the surface of the membrane due to microwave radiation treatment, the moisture capacity of the membrane increases, that indicates an increase in the wettability of the membrane surface. The highest moisture capacity increases with the treatment of the membrane in the atmosphere of atmospheric air to 5.7%, least after processing in argon - by 3.3%.

The increase in the specific productivity of membranes during processing in the atmosphere of atmospheric air is explained by hydrophilization of the surface due to the formation of polar oxygen-containing groups. A decrease in the specific productivity when processing in an argon inert gas environment occurs apparently due to crosslinking of the surface layer and a change in its diffusion characteristics.

Treatment of the membrane in a nitrogen medium increases the degree of emulsion separation by 6.9%, in the air media by 15.3%, in argon - by 21%. The efficiency of cleaning is enhanced by the hydrophilization of the surface and the reduction of the pores of the membranes. An increase in the efficiency of separation of emulsions is also confirmed by a decrease in the size of oil particles in filtrates of emulsions. So the limiting size of the particles of the dispersed phase cut off by the initial membrane was 118 nm, and the membrane of the treated microwave was extracted in the air medium - 39 nm, in the nitrogen medium - 68 nm and in the argon medium - 10 nm.

5. Conclusions

As a result of the microwave treatment of PTFE membranes, the surface properties change, which leads to an increase in wettability, a change in the specific membrane productivity, and a degree of emulsions separation.

Treatment of the PTFE membrane in the air environment has a strong oxidative destruction of the surface, which leads to an increase in specific productivity.

The degree of purification is also increased, and treatment in a nitrogen and argon media leads to cross-linking of the surface layer and a change in its diffusion characteristics, which causes a decrease in the specific productivity of the membranes and an increase in the degree of separation of the emulsion.

Acknowledgements

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