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Research paper

Modification of Membranes from Nylon by Microwave Radiation in Argon, Nitrogen and Atmospheric Air

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Abstract

Microfiltration thin-film membranes of nylon were treated with microwave radiation within the decimeter wavelength range in air, nitrogen and argon to increase the specific productivity and the degree of the resistant oil emulsion separation due to structural transformations in the surfaces and membrane pores. After the processing of nylon membrane in air, argon and nitrogen, the specific performance of the membranes increases during the filtration of distilled water by 1.3 times. This circumstance is connected, probably with the increase of membrane pore size. And when the oil emulsion is separated, the specific productivity is increased after the treatment in air and oxygen up to 2.3 times, and after the treatment in argon it is decreased by 2 times. The decrease in performance occurs apparently due to the crosslinking of the pores and the surface layer of the membrane. It has been established that the treatment of nylon membranes with microwave radiation in air, nitrogen and argon leads to the decrease of oil emulsion separation degree, which is explained by the membrane surface etching. The worst degree of purification makes 83% and it is observed after the separation of the emulsion with the membrane treated by microwave radiation in a nitrogen atmosphere, when the loss of membrane mass after the microwave treatment was 0.69%. The purification degree from oil is reduced in the least after the treatment in argon medium - 93, and the loss of membrane mass after treatment makes 0.26%.

Keywords: *Oil-in-water emulsion, oil products, microfiltration, nylon, particle size, microwave radiation, nitrogen, argon.*

1. Introduction

During the process of transportation, storage and oil processing at oil-producing and oil-refining enterprises large volumes of oil-containing wastewater are generated, which are not only the source of pollution of the surrounding natural environment, but also valuable hydrocarbon raw materials [1]. A prolonged storage of oil with water, the contact with atmospheric oxygen, the presence of solid particles, hydrophobized by asphalt-resin and paraffin substances, contributes to the development of such effluents as “intermediate layers”, which are very stable oil emulsions [2].

Standard purification methods such as settling, flotation, filtration do not lead to the complete removal of petroleum products from the aqueous phase and can be used only during the pre-treatment stage. And membrane methods are often used for an effective removal of oil products; in particular, microfiltration and ultrafiltration are used to separate emulsions [3-7]. The advantages of membrane separation are a high degree of separation, a low energy consumption, the absence of need for aggressive reagents and the simplicity of equipment. However, membrane separation methods have certain disadvantages. The main disadvantage is low specific productivity and the phenomenon of concentration polarization, resulting in membrane performance decrease and in operating pressure increase, the clogging of membrane pores, which can further lead to the destruction of the membrane surface layer. The problem is solved by the periodical washing of the membrane surface with cleaning solutions and the pre-cleaning of the emulsion from larger particles by standard methods.

Also, in order to increase the degree of emulsion separation and the specific performance of the membranes, they perform chemical or physical modification of the membranes. Chemical modification [8-10] is the treatment of surface membranes with various aggressive media, the application of a new working layer to the substrate, the provision of hydrophilicity or hydrophobic properties to the membrane surface, the change of membrane surface charge and the production of composite membranes.

Physical modification of membranes provides for the impact on surface by electromagnetic waves and plasma; ultrasonic, thermal and radiation processing [11-13].

2. Methods

In this work, in order to increase the specific performance of the membranes during the separation of oil emulsions, we modified thin-film microfiltration membranes from nylon by ultrahigh-frequency radiation in the decimeter wavelength range without heat exposure using MC-6 laboratory device of microwave preparation system in atmospheric air, nitrogen and argon. During the processing, the following parameters of the MC-6 device were established: power - 750–1500 W, operating frequency - 2450 MHz, temperature - 25 °C, processing time - from 10 to 60 min.

The methods to study the etching of polymer membranes by microwave radiation: weight reduction rate measuring (weight and piezoquartz methods) [14]. They characterize the speed of the etching process. The influence of microwave radiation on the weight of membranes was determined by membrane weight change before and after the treatment with microwave radiation using an analytical balance with the accuracy of 0.00001 g.

For the process of membrane separation, they used the oil emulsion model, which was obtained by carbonic oil dispersion in distilled water with the addition of sodium dodecyl sulfate. The model oil emulsion was obtained from the concentrate prepared as follows: 30 g of sodium dodecyl sulfate was dissolved in 100 cm^3 of distilled water and 1 g of oil was added. After that the emulsion concentrate was stirred at 3000 rpm for 15 minutes. The concentration of oil products in the resulting emulsion was 212 mg/dm^3.

A microfiltration polymer membrane of nylon with an average pore size of 0.45 μm and the diameter of 47 mm was used as the initial membrane for modification.

The particle size of the dispersed phase of oil-in-water emulsions was determined by dynamic light scattering using "Nano Brook Omni" particle size analyzer. To study the properties of the dispersed phase, the following instrument parameters have been established: solvent - water; viscosity - 0.89; scattering angle - 90°; the duration of measurements - 3 minutes, the number of measurements - 3.

The main indicators of emulsion membrane separation were the specific productivity and the degree of the model oil emulsion separation, which was calculated as the ratio of the oil product content in the emulsion before and after separation, determined by KN-3 concentrator meter. During the separation of distilled water, the operating pressure made 0.1 MPa, and the temperature of the liquid was 25 °C.

3. Results and discussion

The results of the membrane weight change after the treatment with microwave radiation, depending on the processing time and gaseous medium, are presented in table 1.

Table 1: Weight reduction of nylon membranes after microwave treatment in air, nitrogen and argon.

Membrane name	Microwave treatment period, min	Membrane weight decrease Δ, %		
		In air	In nitrogen	In argon
Nylon	10	0,12	0,62	0,10
	30	0,25	0,66	0,20
	60	0,33	0,69	0,26

According to Table 1, it follows that the result of the membrane treatment with microwave radiation in a nitrogen, the weight of the membranes decreases most of all. With the increase of membrane processing time in nitrogen, they observe the decrease of membrane weight to 0.69%. The membrane weight is reduced least of all as a result of treatment in argon, to 0.26% only. The processing of membrane in air leads to membrane weight decrease down to 0.33%.

The surface of the original nylon membrane is hydrophilic. To detect the changes of surface wettability as the result of exposure to microwave radiation, the moisture content of the original and modified membranes was determined using "A & MD" moisture analyzer. The results of moisture capacity are presented in table 2.

Table 2: The change of membrane moisture capacity of after microwave treatment in gaseous media

Membrane name	Microwave processing time, min.	Moisture capacity, %		
		In air	In nitrogen	In argon
Nylon	-	79,0		
	10	76,5	72,3	72,3
	30	73,7	71,7	71,4
	60	70,4	70,5	71,2

The study results show that the increase of the processing time by microwave radiation reduces the moisture capacity of the nylon membrane from the initial 79% to 70.4% during the processing in air. After the processing of the membrane in the nitrogen atmosphere, the capacity of the membrane decreases to 70.5%, and to 71.2% in argon. Consequently, microwave radiation affects the wettability of the nylon membrane surface in favor of hydrophobicity.

The initial and modified by microwave radiation membranes made of nylon were used to determine the specific productivity by distilled water (Fig. 1) and by the model oil emulsion with the oil product content of 212 mg/dm^3 (Fig. 2).

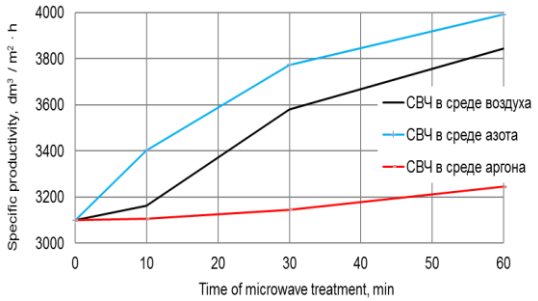

Figure 1: The specific performance of the original and modified nylon membranes by distilled water, depending on the time of microwave processing in various environments.

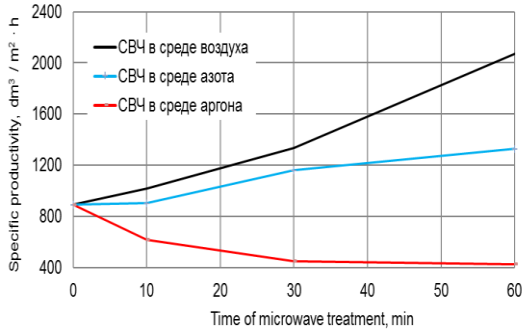

Figure 2: The specific performance of the original and modified nylon membranes by oil emulsion, depending on the time of microwave processing in different environments.

The specific performance of the membranes during the separation of oil emulsion is reduced by about 3.5 times than during distilled water filtration. The processing of nylon membrane by microwave radiation in atmospheric air, argon and nitrogen leads to the increase of membrane specific productivity during distilled water filtration. This circumstance is connected, apparently with membrane pore size increase. Productivity increases with the processing time increase. When the oil emulsion is separated, the specific productivity is increased after the treatment in air and oxygen, and after the treatment in argon it is decreased by 2 times.

To restore the initial performance of the membranes after the emulsion filtering with the volume of 500 cm3, the membranes were washed by backwashing with a 5% sodium dodecyl sulfate solution and then they were washed with distilled water.

Next, they determined the degree of petroleum product removal from the model emulsion with modified membranes. The results of the model emulsion separation by the original membranes and the membranes processed by microwave radiation from NP are presented in Table. 3.

Table 3: The degree of model oil emulsion separation by original and modified nylon membranes

Membrane name	Microwave processing time, min.	Oil product removal rate, %		
		In air	In nitrogen	In argon
Nylon	-	96,5		
	10	95,6	91,2	92,9
	30	94,4	89,0	95,3
	60	91,9	83,1	95,7

The degree of oil product removal from the emulsion with the concentration of 212 mg/dm^3 and with the original nylon membrane is 96.5%. After the treatment membrane with microwave radiation in the decimeter wavelength range, the degree of model oil emulsion separation decreases, and with the membrane treatment time increase, the degree of purification decreases more strongly. They revealed the dependence of oil particle removal degree on gas medium composition in which the membrane is processed. So, after the membrane processing in air, the degree of emulsion separation decreases to 91.9%, to 83.1% in nitrogen, and to 92.3% in argon. Thus, the treatment of nylon membranes with microwave radiation in air, nitrogen and argon leads to the oil emulsion separation degree reduction.

Then they presented the results of the particle size dependence from the dispersed phase of the emulsion on time and the gaseous medium of the membrane microwave processing.

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

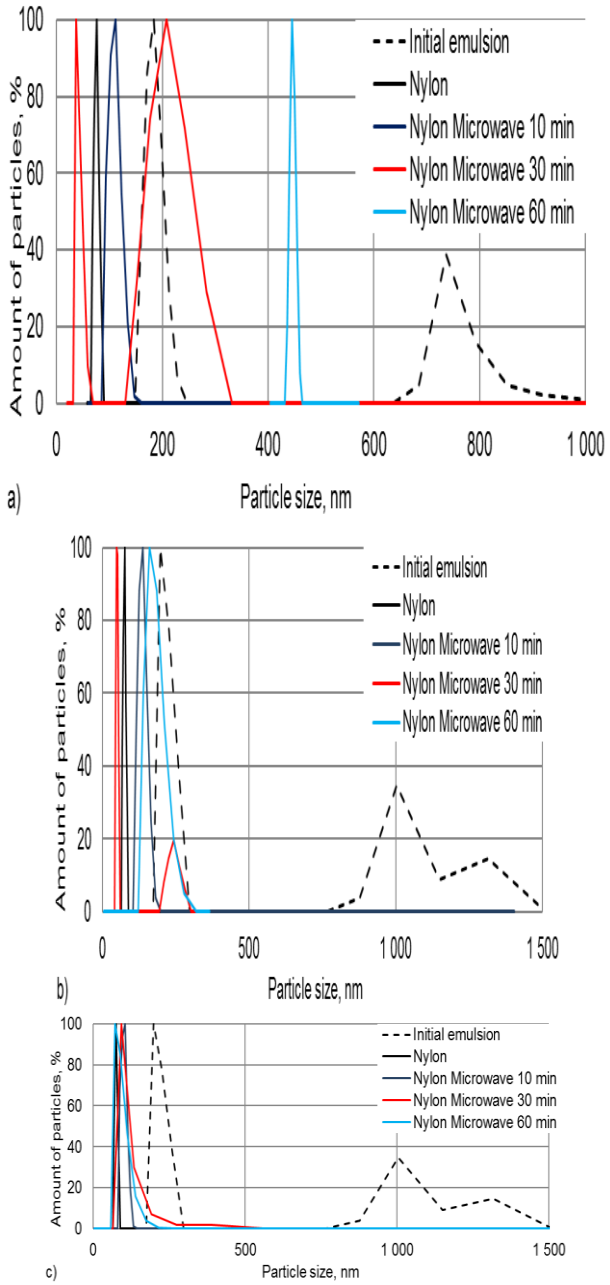

Figure 3: Particle size distribution graph of the dispersed emulsion phase and its filtrates by original and processed by microwave radiation nylon membranes: a) in air b) in nitrogen; c) in argon.

According to Figure 3, after the emulsion filtering through the membranes treated with microwave radiation, the decrease of oil particle size in the emulsion filtrates is observed. At that with the increase of membrane processing time, the size of oil particles increases during the processing in air and nitrogen. And when they are processed in argon, they observe the decrease of particle size with the processing time increase. The maximum size of oil particles, which is cut off by the initial membrane, makes 68 nm, and 93 nm by the membrane treated in air, 114 nm - in nitrogen and 71 nm - in argon. Oil particles are best removed by the original nylon membrane.

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

Emulsion	ζ-potential, mW		
	In air	In nitrogen	In argon
Model Oil Emulsion	-95,7		
Nylon Filtrate	-11		
Microwave Nylon Filtrate (10 min)	-18,5	-21,6	-17,5
Microwave Nylon Filtrate (30 min)	-21,1	-30,4	-15,0
Microwave Nylon Filtrate (60 min)	-40,5	-37,9	-11,6

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

4. Summary

After the processing of nylon microfiltration membranes by microwave radiation, the decrease of membrane weight is observed to 0.66% during the processing in nitrogen, to 0.33 in an air, and to 0.26% in argon. During the etching of polymers by microwave radiation, the etching of the surface layer occurs, therefore the membrane weight is decreased. The etching rate depends on gas type in the atmosphere in which it is carried out, and on the polymer structure and properties. The highest etching rate is observed for oxygen, and the lowest one for inert gases [15].

The moisture content is decreased after the microwave treatment of the nylon membrane surface, which indicates the membrane surface wettability decrease. The moisture capacity is decreased most of all after the membrane treatment in atmospheric air (by 8.6%) and in nitrogen (by 8.5%), less of all after the treatment in argon (by 7.8%). The effect of microwave radiation on the membrane leads to its crystallinity increase [16], thus the strength of the polymer film is increased and the porosity is decreased, which leads to the membrane moisture capacity decrease.

The increase of membrane specific productivity during the treatment in air and nitrogen is explained by the strong etching of the surface layer and the surface of pores. The decrease of specific productivity during the processing in inert argon gas medium occurs apparently due to the crosslinking of the surface layer [17–19].

The treatment of nylon membranes with microwave radiation in air, nitrogen and argon leads to the oil emulsion separation degree decrease. This is due to the etching of the membrane and pore surface. The worst purification degree is 83% with the membrane treated by microwave radiation in nitrogen, when the loss of membrane weight made 0.69% after microwave processing. The degree of purification from oil is reduced least of all after the treatment in argon - 93, and the loss of membrane weight after treatment makes 0.26%.

Oil particles are removed more efficiently from the original nylon membrane. The maximum size of oil particles, cut off by the initial membrane makes 68 nm, and 93 nm with the membrane treated by microwave radiation in an air environment, 114 nm in nitrogen and 71 nm in argon.

5. Conclusions

Thus, it has been proved experimentally that microwave radiation can be used to carry out a targeted change of polymer membrane surface structure, which changes the surface wettability, improves the physicomechanical properties and changes the membrane specific performance and the degree of emulsion separation depending on time and gaseous microwave processing environment.

The processing of thin-film membranes from nylon by microwave radiation within the decimeter wavelength range in air, nitrogen and argon leads to membrane specific productivity increase in distilled water up to 1.3 times, in oil emulsions up to 2.3 times, but leads to emulsion separation degree decrease by 0.8-13%.

Acknowledgements

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References

[1] Yu.V. Antipin, M.D. Valeev, A.Sh. Syrtlanov. The prevention of complications during the production of watered oil. Ufa, Bash. publishing house 1987. - 168 p.

[2] G.N. Pozdnyshev. Stabilization and destruction of emulsions. M., Nedra, 1982. 222 p.

[3] D.D. Fazullin, G.V. Mavrin, I.G. Shaikhiev. Modified PTFE–PANI Membranes for the Recovery of Oil Products from Aqueous Oil Emulsions./ Petroleum Chemistry, 2017, Vol. 57, No. 2, pp. 165–171.

[4] D.D. Fazullin, G.V. Mavrin, I.G. Shaikhiev. Separation of oil products from aqueous emulsion sewage using a modified nylon–polyaniline membrane / Petroleum Chemistry. 2016. Volume 56, Issue 5, pp 454-458.

[5] L.E. Kopylova, A.O. Kashirin, A.A. Sweatsov. The hybrid technology of water-oil emulsion separation, combining the coalescence filtration and microfiltration. Membranes and membrane technologies. 2013. Vol. 3. No. 4. p. 277.

[6] D.D. Fazullin, G.V. Mavrin, I.G. Shaikhiev. Separation of oil water emulsions using microfiltration membranes with a surface layer of polyaniline. Research Journal of Pharmaceutical, Biological and Chemical Sciences. 2016. № 7(5). P. 1751-1757.

[7] M.A. Yablokova, V.V. Bugrov, R.A. Khasaev. Modern technologies and equipment for technology and for the disposal of used coolant fluids. Proceedings of the St. Petersburg State Institute of Technology (Technical University). 2014. No. 25. pp. 62-67.

[8] A.B. Shipovskaya, N.V. Evseeva, G.N. Timofeev. Physico-chemical modification of cellulose acetate for the production of films, membranes and biofilters. The Journal of Applied Chemistry. V. 76. № 9. pp. 1553-1557. (2003)

[9] D.D. Fazullin, G.V. Mavrin, I.G. Shaikhiev, E.A. Haritonova. Separation of oil products from aqueous emulsion sewage using a modified nylon–polyaniline membrane. Petroleum Chemistry. 2016. Vol. 56. Issue 5. pp. 454-458.

[10] K.A. Timakova, A.V. Tarasov, Yu.A. Fedotov, S.A. Lepeshin, Yu.T. Panov. Modification of polymer films, coatings and membranes. Membranes and membrane technologies. 2012. V. 2. № 2. p. 74.

[11] L.I. Kravets, S.N. Dmitriev, A.B. Gilman. Modification of polymer membrane properties under the influence of low-temperature plasma. High Energy Chemistry. 2009. V. 43. No. 3. pp. 227-234.

[12] G.Sh. Safina, V.O. Dryakhlov, M.F. Galikhanov, T.I. Shaikhiev, S.V. Friedland. The separation of waste emulsions containing petroleum products using corona-treated membranes. 2015. Bulletin of Kazan Technological University. Vol. 18. No. 14. pp. 229-231.

[13] V.O. Dryakhlov, I.G. Shaikhiev, I.Sh. Abdullin, B.S. Bonev, A.V. Fedotov. The influence of low-pressure plasma parameters on the efficiency of water-oil emulsion membrane separation. Water: chemistry and ecology. 2015. No. 2. pp. 25-30.Ricard. Reactive plasmas. Paris: SFV. 1996. 180p.

[14] T. Hirotsu, S. Ohnishi // J. of Adhesion. 1980. V.11. P.57.

[15] Dariusz Bogdal, Aleksander Prociak, Microwave synthesis of polymeric materials. Scale up and commercial aspects. Chemistry Today. 2007. Vol. 25. № 3. 2007. P. 30–33.

[16] Sh. Wu, J. Xing, C. Zheng, G. Xu, G. Zheng, J. Xu. J. Appl. Polym. Sci. 1997. V. 64. № 10. P. 1923.

[17] M. Ulbricht, G. Belfort. J. Appl. Polym. Sci. 1995. V. 56. № 3. P. 325.

[18] T.D. Tran, Mori Sh., M. Suzuki // Thin Solid Films. 2007. V. 515. № 9. P. 4148.