CHEMICAL TECHNOLOGY

DOI 10.31489/2020Ch3/99-109

UDC 678.6/7+544.23.057+544.25.057

A.B. Yeszhanov[1, 2*], S.S. Dosmagambetova[2]

[1]*Institute of Nuclear Physic of the Republic of Kazakhstan, Almaty, Kazakhstan;*
[2]*L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan*
(Corresponding author's e-mail: a.yeszhanov@inp.kz)

Phenol solutions treatment by using hydrophobized track-etched membranes

Phenols are one of the most common surface water pollution. The discharge of phenolic waters into water bodies and streams sharply degrade their general sanitary condition, since these compounds have a toxic effect, and phenols can intensively absorb oxygen dissolved in water, which negatively affects the life of organisms in water bodies. Therefore, water treatment of phenols is an important environmental problem. In this study, the hydrophobic polyethylene terephthalate track-etched membranes (PET TeMs) were tested in water treatment from phenol by direct contact membrane distillation (DCMD). Hydrophobic PET TeMs were obtained by UV-graft polymerization of styrene, triethoxyvinylsilane with the addition of vinylimidazole (VIM), as well as by coating with fluorine-containing silanes. Scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy and liquid entry pressure (LEP) analysis were used for membrane characterization. The contact angle after modification of PET TeMs was reached more than 130°. The efficiency of water purification from phenol was evaluated by water-flux measurements and fluorimetric method. The phenols solution was used at a concentration of 0.5, 1 and 2 g/l. The largest permeate flux of hydrophobized membranes was 1.1 kg/ $m^2 \cdot h$.

Keywords: phenol, water treatment, direct contact membrane distillation, UV-induced graft polymerization, styrene, triethoxyvinylsilane, fluorine-containing silanes, track-etched membranes.

Introduction

Nowadays, phenol and its derivatives as by-products of the petrochemical complex, coal and chemical industries, pharmaceuticals are significant pollutants of aquatic ecosystems due to their toxicity, stability, and ability to accumulate in the environment. Sources of phenols in natural water bodies are pharmaceutical effluents, dyes, pesticides, phenol-formaldehyde resins and nonionic surfactants, petrochemical complex enterprises, coal industry, mechanical engineering and chemical industry [1]. The solubility of phenol in water is one of the main causes of wastewater pollution. Moreover, the dangerous effect of phenol on the human body and the environment sets even at very low concentrations [2]. Therefore, water treatment from phenol is an important and urgent problem around the world [3].

Currently various methods for phenol wastewater treatment, such as ozonation [4, 5], wet air oxidation [6], Fenton reaction [7] are known. Also, one of the most effective methods for water treatment from phenol is membrane technology: nano [8] and ultrafiltration [9], as well as reverse osmosis [10]. Recently, DCMD was also used for water treatment from phenols [11, 12].

The essence of MD is based on the separation of the liquid due to the difference in temperature and pressure on both sides. Water evaporates on the hot side, and vapor passes through a hydrophobic membrane and condenses on the cold side. Compared to other membrane processes, MD has high energy efficiency, the process takes place at a relatively low temperature (~50–70 °C on the hot side and ~10 °C on the cold side).

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[*] *Corresponding author*

The movement of vapor from the hot to the cold part is due to convection [13]. However, when vapor passes through the membrane, it partially transfers heat to the material, thereby reducing the temperature gradient. Therefore, it is important that the membrane has low thermal conductivity [14–16]. Various types of polymers, for instance, polytetrafluoroethylene (PTFE), polyamide (PA), polypropylene (PP) are used in MD [17–19]. At the same time, the major disadvantages of these polymers are possible fouling, insufficient water flow and high cost [9]. Thus, the task of finding new types of membranes and materials with good hydrophobic properties and high degrees of purification is relevant.

There has been a significant amount of interest for track-etched membrane (TeMs) in MD. A unique feature of TeMs is the control of the number of pores per unit area [20–25], which significantly expands fields of application in sensing [26], catalysis [27–31], lithium-ion batteries [32, 33], template synthesis of nanostructures [34–38]. At the present time various types of polymers are known, intended as a material for TeMs. The most significant are thin films made of poly(ethylene terephthalate) (PET). PET films have high thermal and chemical resistance, transparency, high-tensile strength. However, for the MD process, this type of membrane requires a significant expansion of its hydrophobic characteristics. PET TeMs were hydrophobized and used for purification of saline solutions [13,39] and liquid low-level radioactive wastes treatment [22, 40] by DCMD.

In this paper, UV-induced graft polymerization of triethoxyvinylsilane (TEVS) and styrene as well as covalent binding of perfluorododecyltrichlorosilane (PFDTS) in an *o*-xylene solution were used to increase hydrophobic properties of PET TeMs. Prepared membranes were tested in DCMD for treatment of phenol solutions.

Experimental

Materials

Benzophenone, dimethylformamide, dichloroethane, carbon tetrachloride, TEVS, VIM, PFDTS, *o*-xylene, styrene were purchased from Sigma-Aldrich. Deionized water (18.2 MΩ) was used in all experiments.

Preparation and improvement of hydrophobic properties of the membranes

Fabrication of PET TeMs was done in the following way. Samples 10×15 cm in size, previously irradiated by DC-60 accelerator (Astana branch of Institute of Nuclear Physics) with an energy of 1.75 MeV/nucleon by $^{84}Kr^{15+}$ ions, were treated in sodium hydroxide to obtain membranes with different pore sizes [26].

In order to increase hydrophobic properties of the membranes, three methods of surface modification were considered in comparison. First, modification of PET TeMs was carried out by UV-photoinduced graft polymerization of TEVS. Membranes with pore sizes of d ~ 200 nm were cleaned in order to remove interfering substances on the membrane surface. Then the samples were placed in a solution of the initiator. Further, the samples were immersed in a solution of dichloroethane and TEVS with a concentration range from 5 to 30 % and VIM (0.3–6.6 %) as an additive to graft polymerization. The resulting solution was irradiated under a UV lamp Ultra Vitalux E27 by OSRAM (UVA — 315–400 nm — W = 13.6 W, UVB — 280–315 nm — W = 3.0 W) within 15–180 minutes on both sides.

The second method was carried out by UV-induced graft polymerization of styrene. Styrene is one of the most accessible and widely used hydrophobic monomer. Samples were placed in a solution of styrene in carbon tetrachloride with concentration of 5–40 %. CCl_4 was chosen as solvent since it is transparent in UV-vis region, it can dissolve the monomer and this solvent has low chain transfer constant. Irradiation was carried out under the same conditions as in the first method.

The third method of hydrophobization was achieved by soaking membranes into *o*-xylene solution of PFDTS at different concentration range and time (1–24 h). After that, membranes were washed and dried.

Membrane characterization

The surface morphology of pristine and modified PET TeMs was examined using JSM-7500F scanning electron microscope (SEM) (JEOL, Japan).

To determine the functional groups before and after modification, FTIR spectra were recorded using FTIR spectrometer Agilent Cary 600. Spectra were recorded in the range from 4000 to 400 cm^{-1} with a resolution of 4.0 cm^{-1}. Each sample was measured 32 scans at the room temperature.

The contact wetting angle (CA) of the pristine and modified PET TeMs was measured goniometrically using the static drop method. Measurements were taken from different points of the polymer and the average result was calculated.

Liquid entry pressure (LEP) was measured to determine the minimum pressure necessary for the liquid to pass through the hydrophobic membrane pores. LEP was evaluated using deionized water on on water flow metering equipment as recommended in Ref. [41].

Water transport in membrane distillation process

Direct contact membrane distillation (DCMD) was used to purify water from phenol dissolved in it using modified PET TeMs. The mechanism of the process was described earlier in [13]. Phenol solutions with concentration of 0.5–2.0 g/l was tested. A personal computer connected to the analytical scale was used to record a data.

The flow rate was calculated by the formula:

$$J = \frac{\Delta m}{A\Delta t}, \tag{1}$$

where J — is the flow rate (kg/m^{2}h); Δm — is the water mass in permeate side (kg) per unit time Δt (h); A — is the effective area of membrane (m^2).

Results and Discussion

Modification of PET TeMs and characterization

Hydrophobization of PET TeMs was carried out in three ways: by UV-induced graft polymerization of TEVS with VIM, styrene and covalent bonding of PFDTS with the membrane surface. The first method can be controlled by time of grafting, concentration of monomer, distance to UV-source and concentration of additives. Effect of these parameters on grafting degree and hydrophobic properties was evaluated and results are presented in Figure 1. VIM in concentration range from 0.3 to 3.3 % (v/v) was used as additive to increase grafting degree of TEVS since TEVS has low tendency to graft polymerization. VIM concentration of 3.3 % is optimal to get the most hydrophobic membrane, a further increase in concentration leads to a decrease in hydrophobic properties, caused by the hydrophilic properties of VIM with higher content.

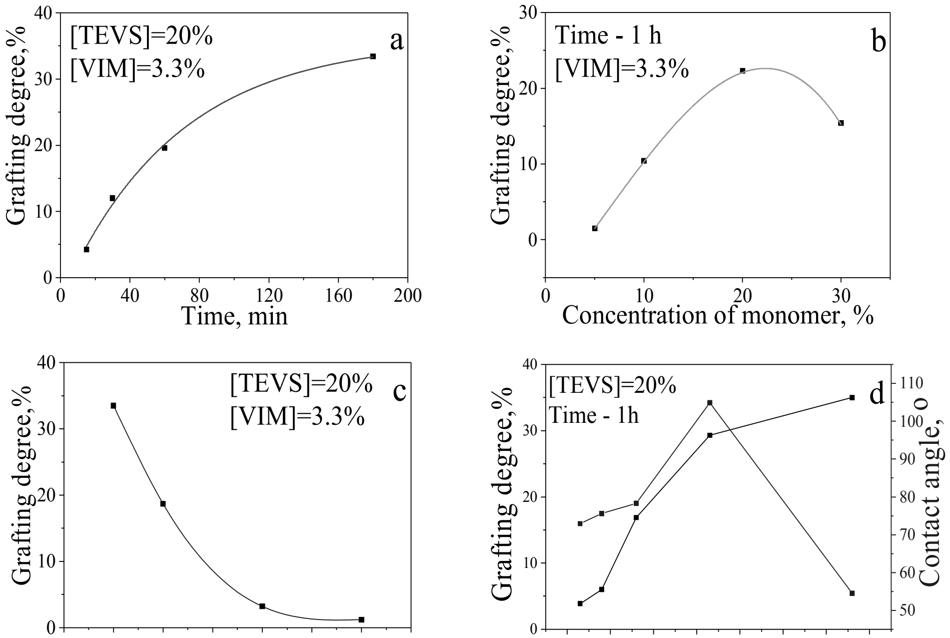

Figure 1. Grafting degree of TEVS onto PET TeMs at variation of time (*a*) and concentration of monomer (*b*), distance to UV-lamp (*c*) and concentration of VIM (*d*)

Figure 1 (*a*) shows a graph of grafting degree versus time of irradiation. With increasing UV-irradiation time, the grafting degree is also gradually grown. An increase in the irradiation time of more than 1h led to the appearance of a gel-like mass, indicating the presence of a homopolymer on the membrane surface. Figure 1 (*b*) represented the dependence of grafting degree on the concentration of the TEVS. The graph clearly demonstrates that the grafting degree reaches maximum value at a concentration of 20 % and a subsequent increase in concentration leads to a decrease of grafting degree. Figure 1 (*c*) shows an effect of the distance to the UV source on the grafting degree (TEVS concentrations of 20 % and VIM 3.3 % at irradiation time 1 h). It should be noted that increasing the distance from the UV source to the sample leads to a rapid decrease in the grafting degree. At the same time, 5 cm led to formation of a gel and membrane contamination.

Thus, the most suitable parameters for the modification of PET TeMs were found: TEVS concentration of 20 % with a VIM concentration of 3.3 %, distance to UV-source — 10 cm, time of irradiation — 60 min.

The second modification method is based on the UV-graft polymerization of styrene. In Figure 2 (*a*, *b*) shows a linear dependence of grafting degree on time at a constant monomer concentration of 10 % and a distance from UV-source (7 cm).

Grafting degree reaches 12 % after 120 min of grafting. An increase in styrene concentration leads to an increase in the grafting degree up to 43 % at 40 % styrene concentration, as shown in Figure 2 (*c*).

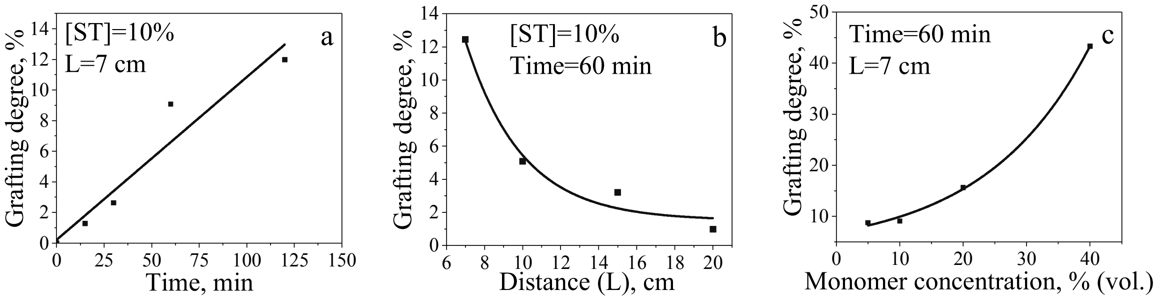

Figure 2. Grafting degree depends on irradiation time (*a*), distance to UV-source (*b*) and monomer concentration (*c*) (pore diameter d ≈200 nm)

The third modification method is based on the soaking of PET TeMs in a solution of *o*-xylene with PFDTS. The principle of the interaction of PFDTS with *o*-xylene is the high hydrolysis ability of the Si–Cl bond, which is able to easily interact with the surface of PET TeMs. Figure 3 (*a*) shows the dependence of the contact angle (CA) on the concentration of PFDTS. As can be seen, the CA reaches a maximum value at an optimal monomer concentration of 20 mM. A further increase in concentration does not lead to a significant change in the CA. The dependence of the CA on the holding time in the reaction was considered. The results are shown in Figure 3 (*b*). The largest CA (134°) was reached after 24 hours. A further increase in time did not significantly affect on the value of the CA.

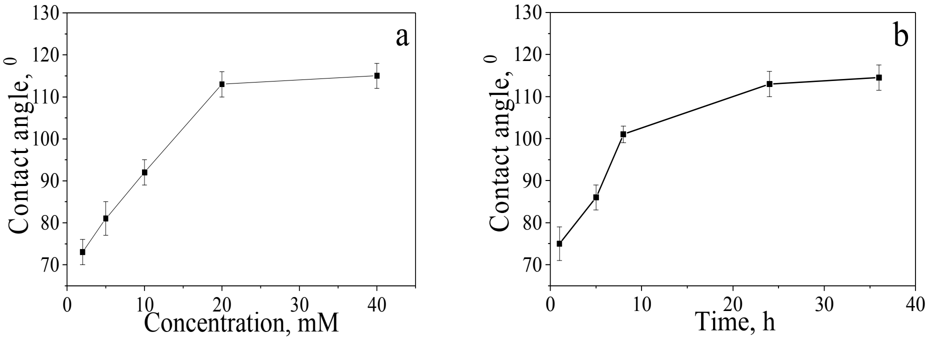

Figure 3. Contact angle (CA) of modified PET TeMs at various concentration of PFDTS (*a*) and reaction time (*b*) (pore diameter of initial PET TeMs is 200 nm)

All hydrophobized PET TeMs were analyzed by methods of contact angle, SEM, FTIR spectroscopy and gas permeability test. Results are presented in Figures 4–6. The measurements of CA were carried out from different places of the sample and the average value was calculated. Images of droplets are shown in Figure 4.

It can be seen, the contact wetting angle of the initial PET TeMs increases significantly from 52 to 83° for PET TeMs-g-TEVS, to 99° for PET TeMs-g-PS and to 134° for PET TeMs–PFDTS.

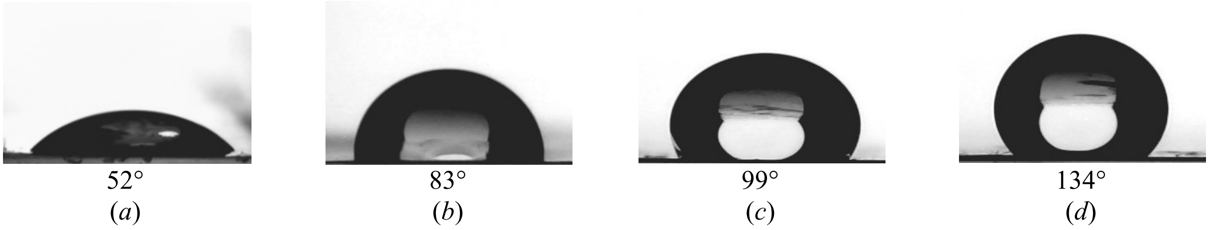

Figure 4. Contact angle (CA) for initial PET TeMs (d ≈ 200 nm) (*a*), PET TeMs-g-TEVS (*b*), PET TeMs-g-PS (*c*), PET TeMs–PFDTS (*d*) (at optimal conditions)

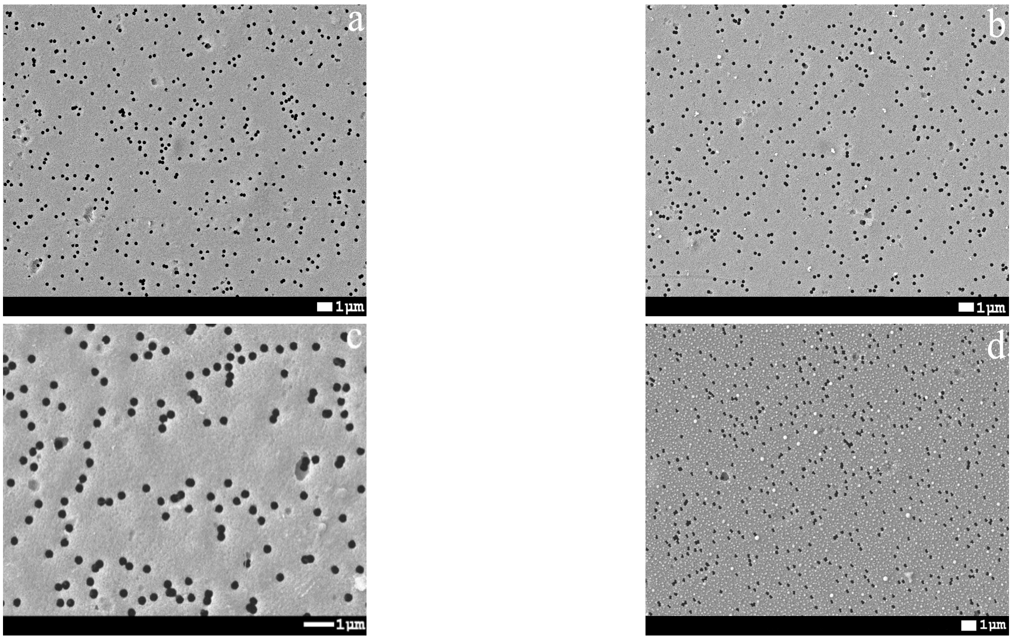

Figure 5. SEM images of initial PET TeMs (*a*), PET TeMs-g-TEVS (*b*), PET TeMs-g-PS (*c*), PET TeMs–PFDTS (*d*)

SEM images of surface initial and modified PET TeMs presented in Figure 5. Modification of PET TeMs has led to a reduction in pore size from 220 ± 15 for initial PET TeMs to 216 ± 4 nm for PET TeMs-g-TEVS, to 215±6 nm for PET TeMs-g-PS and to 174 ± 4 nm for PET TeMs–PFDTS. The decrease in pore size is due to the formation of polymers within the pores.

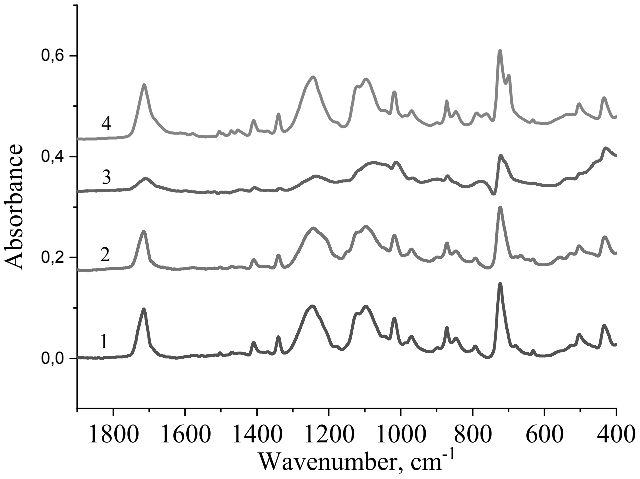

Figure 6. FTIR spectra of PET TeMs (*1*), PET TeMs-g-TEVS (*2*), PET TeMs-PFDTS (*3*), PET TeMs-g-PS (*4*)

To identify the characteristic absorption bands of initial and hydrophobized PET TeMs, FTIR analysis was performed. Typical FTIR spectra are shown in Figure 6. Initial PET TeMs characterized by absorption bands at 3400 cm^{-1}, which corresponds to the absorption of the OH groups, 2900–2980 cm^{-1}are aliphatic and benzene CH_3 rings. The C=O double bond was observed at an absorption of 1720 cm^{-1}. Pulsation vibrations of the carbon skeleton were found at 1420, 1480, 1612 cm^{-1}. The C(O)–O and O–CH_2 bonds were detected at 1220 and 970 cm^{-1}, respectively. Grafting of TEVS led to appearance of new peaks at 1260, 801 cm^{-1} and 1100–1000 cm^{-1} which is related to Si–CH_3 and Si–O–Si vibrations respectively. Moreover, absorbance bands with low intensity and shape of shoulders were found at 1649 cm^{-1} (C=C def.), 1497 and 1085 cm^{-1} (C-N def.) related to VIM. Graft polymerization of polystyrene (40 % concentration) led to appearance of new peaks in FTIR spectra characteristic of polystyrene: 1580, 1450 (CH_2-deformation), 700 (CH_2-rocking mode), 530 cm^{-1} (CH-aromatic), 1480 см$^{-1}$ (C=C aromatic). Covalent bonding of PFDTS led to appearance of new peaks at 1060, 1127 cm^{-1}, as well as peaks of low intensity at 577, 602 and 628 cm^{-1} related to the C-F bond. Characteristics of PET TeMs before and after hydrophobization are presented in Table 1.

Table 1

Characteristics of PET TeMs before and after hydrophobization

Sample	Contact angle, °±4°	Effective pore size, nm	Pore size (from SEM analysis), nm	[Si], % (from EDX analysis)	[F], % (from EDX analysis)	LEP, MPa
Initial PET TeMs	58	198±5	220±8	-	-	0.12
PET TeMs-g-PS	83	215±6	220±15			>0.43
PET TeMs-g-TEVS	89	167±8	216±3	1.5	-	>0.43
PET TeMs–PFDTS	134	148±6	174±4	2.2	11.46	>0.43

Membranes with pore diameters of ≈200nm were hydrophobized at optimal parameters by three methods. LEP analysis (Table 1) showed that hydrophobized membranes with 200 nm can be used in MD in accordance with the recommendations [42]. Hydrophobized PET TeMs have a LEP >0.43 MPa.

Purification of phenol by DCMD

Membrane distillation was carried out using a phenol solution with concentrations of 0.5, 1.0, 2.0 g/l. The process of membrane distillation has already been described earlier in the work. During the experiment, a 50 ml sample was taken every hour to detect traces of phenol.

Figure 7–9 shows water fluxes and electrical conductivity at different concentrations of phenol. PET TeMs-g-TEVS has average water fluxes of 0.71 kg/m^2·h at a phenol concentration of 0.5 g/l, 0.502 kg/m^2·h and 0.546 kg/m^2·h for concentrations of 1.0 g/l and 2.0 g/l respectively. PET TeMs-g-PS has average water fluxes of 0.84 kg/m^2·h at a phenol concentration of 0.5 g/l, 0.770 kg/m^2·h and 0.821 kg/m^2·h for concentrations of 1.0 g/l and 2.0 g/l respectively. PET TeMs — PFDTS has average water fluxes of 1.10 kg/m^2·h at a phenol concentration of 0.5 g/l, 0.92 kg/m^2·h and 1.06 kg/m^2·h for concentrations of 1.0 g/l and 2.0 g/l respectively. Flux changes in concentrations occur with the least differences. It can be associated with temperature instability during DCMD, as well as with more uniform layer of grafted polymer on the surface.

There was a gradual decrease in productivity during the MD process, this is due to the inconsistency of the temperature difference between the cold and hot contours. However, at the same time, the performance of a less concentrated solution is much higher than that of a highly concentrated solution. This is probably due to the fact that there is wetting and contamination of the membrane surface, which reduces productivity.

The efficiency of DCMD was determined by the fluorimetric method and quantitatively performed on a Fluorat-02 analyzer. The selected samples in the process of MD with a volume of 50 ml were diluted to a concentration of 1 mg /dm^3 and measured according to PND F 14.1:2:4.182–02 «The methodology of measuring the mass concentration of phenols in drinking samples, natural and waste water by fluorimetric method on the Fluorat-02 analyzer». The measurement was carried out at least 3 times in the «Measurement» mode and the arithmetic mean was found. As can be seen from Table 2, there is an increase in the concentration in the selected samples with an increase in the concentration of the phenol stock solution.

The increase in concentration in the selected samples is associated with the gradual transfer of phenol from the initial solution to permeate, thereby the permeate becomes more concentrated. Thus, phenols are concentrated in a smaller volume of permeate.

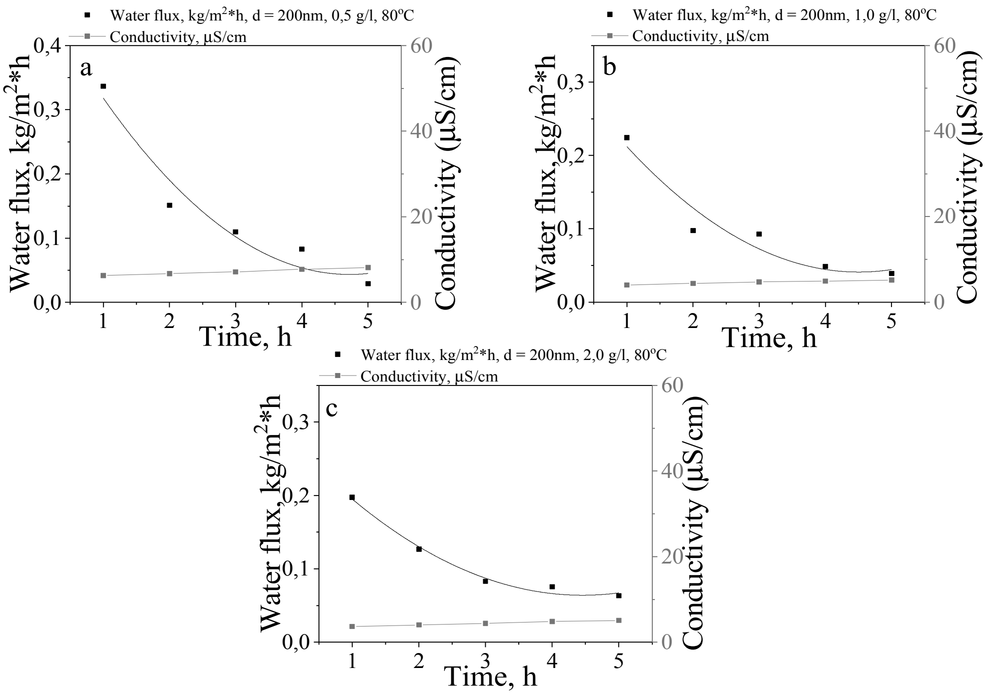

Figure 7. MD water flux and electrical conductivity of PET TeMs-g-TEVS for phenol with concentrations of 0.5 g/l (*a*); 1.0 g/l (*b*); 2.0 g/l (*c*)

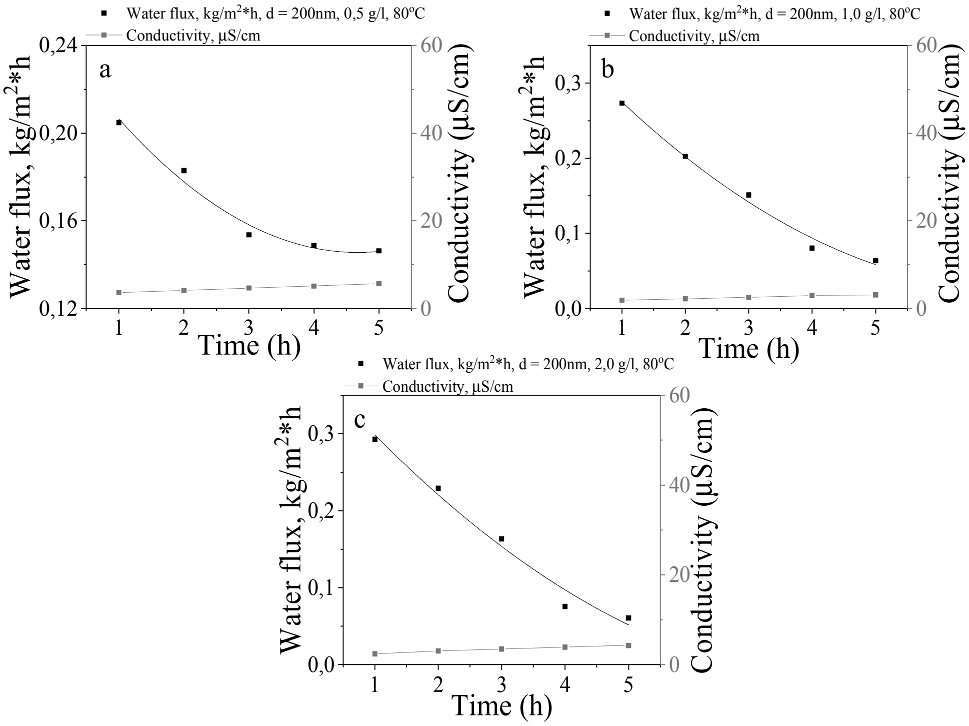

Figure 8. MD water flux and electrical conductivity of PET TeMs-g-PS for phenol with concentrations of 0.5 g/l (*a*); 1.0 g/l (*b*); 2.0 g/l (*c*)

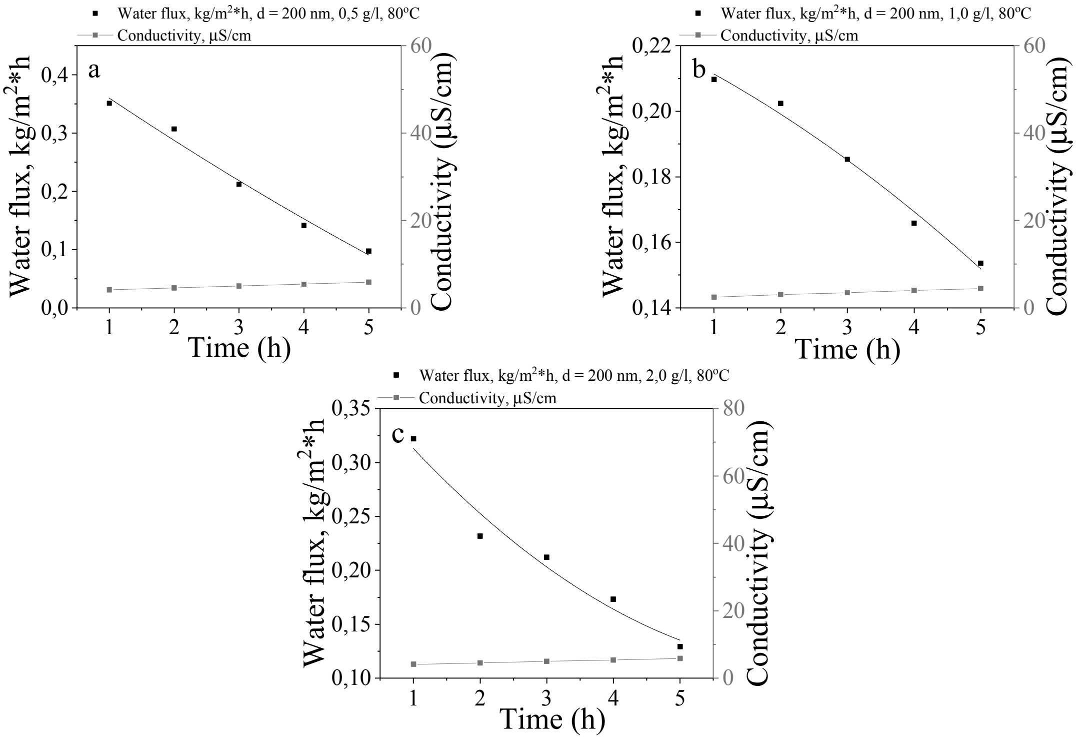

Figure 9. MD water flux and electrical conductivity of PET TeMs–PFDTS for phenol with concentrations of 0.5 g/l (*a*); 1.0 g/l (*b*); 2.0 g/l (*c*)

Table 2

Phenol concentrations in samples at different sampling times

	TEVS			Styrene			PFDTS		
Phenol concentration, g/l	0.5	1	2	0.5	1	2	0.5	1	2
Initial	3.03±0.01	3.65±0.01	7.15±0.01	0.28±0.02	0.76±0.02	0.46±0.01	0.79±0.03	5.49±0.02	5.59±0.02
After 3h	6.30±0.03	7.85±0.01	16.83±0.04	0.32±0.01	1.01±0.01	19.00±0.02	4.03±0.01	10.17±0.03	12.10±0.03
After 5h	8.51±0.03	8.70±0.04	21.24±0.04	0.85±0.01	2.53±0.03	25.80±0.03	4.81±0.02	11.50±0.01	18.82±0.01

Based on the obtained results, methods of hydrophobization of PET TeMs showed good performance. The most preferred type of modification for membrane distillation is PET TeMs — PFDTS, due to its simplicity, high performance and efficiency.

Conclusions

In this research, the ability of modified PET TeMs in water treatment from phenol was studied. Hydrophobized PET TeMs were obtained by graft polymerization of TEVS and VIM, styrene and covalent binding of PFDTS. Various characteristics of modifying agents on the grafting degree and wetting angle values were studied. Membranes with CA of 134°, 99° and 83° were prepared and further used for DCMD of phenol solutions. Maximum permeate flux 1.1 kg/m^2·h were achieved using PET TeMs–PFDTS. Thus, such methods of membrane hydrophobization can be used in MD process for water purification from phenol.

The work was done within the project of the Ministry of Education and Science of the Republic of Kazakhstan titled «Preparation of track-etched membranes with specified properties for membrane distillation and forward osmosis» (grant No AP05132110).

References

1 Hussain A. Kinetic study for aerobic treatment of phenolic wastewater / A. Hussain, S. Dubey, V. Kumar // Water Resources and Industry. — 2015. — Vol. 11. — P. 81–90. DOI: 10.1016/j.wri.2015.05.002.

2 Mohammadi S. Phenol removal from industrial wastewaters: a short review / S. Mohammadi, A. Kargari, H. Sanaeepur, K. Abbassian, A. Najafi, E. Mofarrah // Desalination and Water Treatment. — 2015. — Vol. 53, No. 8. — P. 2215–2234. DOI: 10.1080/19443994.2014.883327.

3 Zhang M. Ultrasound-assisted electrochemical treatment for phenolic wastewater / M. Zhang, Z. Zhang, S. Liu, Y. Peng, J. Chen, S. Yoo Ki // Ultrasonic Sonochemistry. — 2020. — Vol. 65. — P. 105058. DOI: 10.1016/j.ultsonch.2020.105058.

4 Wang J. Catalytic ozonation for water and wastewater treatment: Recent advances and perspective / J. Wang, H. Chen // Science of Total Environment. — 2020. — Vol. 704. — P. 135249. DOI: 10.1016/j.scitotenv.2019.135249.

5 Huang Y. New phenolic halogenated disinfection byproducts in simulated chlorinated drinking water: Identification, decomposition, and control by ozone-activated carbon treatment / Y. Huang, H. Li, Q. Zhou, A. Li, C. Shuang, Q. Xian, B. Xu, Y. Pan // Water Resources. — 2018. — Vol. 146. — P. 298–306. DOI: 10.1016/j.watres.2018.09.031.

6 Yadav A. Removal of phenol from water by catalytic wet air oxidation using carbon bead-Supported iron nanoparticle-Containing carbon nanofibers in an especially configured reactor / A. Yadav, A. Teja, N. Verma // Journal of Environmental Chemical Engineering. — 2016. — Vol. 48, No. 2. — P. 1504–1513. DOI: 10.1016/j.jece.2016.02.021.

7 Gernjak W. Photo-fenton treatment of water containing natural phenolic pollutants / W. Gernjak, T. Krutzler, A. Glaser, S. Malato, J. Caceres, R. Bauer, A. Fernandez-Alba // Chemosphere. — 2003. — Vol. 50, No. 1. — P. 71–78. DOI: 10.1016/S0045–6535(02)00403–4.

8 Ochando-Pulido J. About two-phase olive oil washing wastewater simultaneous phenols recovery and treatment by nanofiltration / J. Ochando-Pulido, J. Corpas-Martinez, A. Martinez-Ferez // Progress Safety and Environmental Protection. — 2018. — Vol. 114. — P. 159–168. DOI: 10.1016/j.psep.2017.12.005.

9 Victor-Ortega M. Recovery of phenolic compounds from wastewaters through micellar enhanced ultrafiltration / M. Víctor-Ortega, R. Martins, L. Gando-Ferreira, R. Quinta-Ferreira // Colloids and Surfaces A: Physicochemical and Engineering Aspects. — 2017. — Vol. 531. — P. 18–24. DOI: 10.1016/j.colsurfa.2017.07.080.

10 Al-Obaidi M. Removal of phenol from wastewater using spiral-wound reverse osmosis process: Model development based on experiment and simulation / M. Al-Obaidi, C. Kara-Zaïtri, I. Mujtaba // Journal of Water Process Engineering. — 2017. — Vol. 18. — P. 20–28. DOI: 10.1016/j.jwpe.2017.05.005.

11 Hamzah N. Membrane distillation of saline with phenolic compound using superhydrophobic PVDF membrane incorporated with TiO_2 nanoparticles: Separation, fouling and self-cleaning evaluation / N. Hamzah, C. Leo // Desalination. — 2017. — Vol. 418. — P. 79–88. DOI: 10.1016/j.desal.2017.05.029.

12 Hamzah N. Fouling prevention in the membrane distillation of phenolic-rich solution using superhydrophobic PVDF membrane incorporated with TiO_2 nanoparticles / N. Hamzah, C. Leo // Separation and Purification Technology. — 2016. — Vol. 167. — P. 79–87. DOI: 10.1016/j.seppur.2016.05.005.

13 Korolkov I. Preparation of PET track-etched membranes for membrane distillation by photo-induced graft polymerization / I. Korolkov, Y. Gorin, A. Yeszhanov, A. Kozlovskiy, M. Zdorovets // Materials Chemistry and Physics. — 2018. — Vol. 205. — P. 55–63. DOI: 10.1016/j.matchemphys.2017.11.006.

14 Yao M. A review of membrane wettability for the treatment of saline water deploying membrane distillation / M. Yao, L. Tijing, G. Naidu, S-H Kim, H. Matsuyama, A. Fane, H. Shon // Desalination. — 2020. — Vol. 479. — P. 114312. DOI: 10.1016/j.desal.2020.114312.

15 Hubadillah S. Hydrophobic ceramic membrane for membrane distillation: A mini review on preparation, characterization, and applications / S. Hubadillah, Z. Tai, M. Othman, Z. Harun, M. Jamalludin, M. Rahman, J. Jaafar, A. Ismail // Separation and Purification Technology. — 2019. — Vol. 217. — P. 71–84. DOI: 10.1016/j.seppur.2019.02.014.

16 Siyal M. A review of membrane development in membrane distillation for emulsified industrial or shale gas wastewater treatments with feed containing hybrid impurities // M. Siyal, C-K. Lee, C. Park, A. Khan, J-O. Kim // Journal of Environmental Management. — 2019. — Vol. 243. — P. 45–66. DOI: 10.1016/j.jenvman.2019.04.105.

17 Tang N. Preparation and morphological characterization of narrow pore size distributed polypropylene hydrophobic membranes for vacuum membrane distillation via thermally induced phase separation / N. Tang, Q. Jia, H. Zhang J. Li, S. Cao // Desalination. — 2010. — Vol. 256, No. 1–3. — P. 27–36. DOI: 10.1016/j.desal.2010.02.024.

18 Zhu H. Preparation and properties of PTFE hollow fiber membranes for desalination through vacuum membrane distillation / H. Zhu, H. Wang, F. Wang, Y. Guo, H. Zhang, J. Chen // Journal of Membrane Science. — 2013. — Vol. 446. — P. 145–153. DOI: 10.1016/j.memsci.2013.06.037.

19 Yang X. Performance improvement of PVDF hollow fiber-based membrane distillation process / X. Yang, R. Wang, L. Shi, A. Fane, M. Debowski // Journal of Membrane Science. — 2011. — Vol. 369, No. 1–2. — P. 437–447. DOI: 10.1016/j.memsci.2010.12.020.

20 Korolkov I. Enhancing hydrophilicity and water permeability of PET track-etched membranes by advanced oxidation process / I. Korolkov, A. Mashentseva, O. Guven, M. Zdorovets, A. Taltenov // Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. — 2015. — Vol. 365. — P. 651–655. DOI: 10.1016/j.nimb.2015.10.031.

21 Korolkov I. The effect of oxidizing agents/systems on the properties of track-etched PET membranes / I. Korolkov, A. Mashentseva, O. Guven, D. Niyazova, M. Barsbay, M. Zdorovets // Polymer Degradation and Stability. — 2014. — Vol. 107. — P. 150–157. DOI: 10.1016/j.polymdegradstab.2014.05.008.

22 Korolkov I. Modification of PET ion track membranes for membrane distillation of low-level liquid radioactive wastes and salt solutions / I. Korolkov, A. Yeszhanov, M. Zdorovets, Y. Gorin, O. Guven, S. Dosmagambetova // Separation and Purification Technology. — 2019. — Vol. 227. — P. 115694. DOI: 10.1016/j.seppur.2019.115694.

23 Korolkov I. UV-induced graft polymerization of acrylic acid in the sub-micronchannels of oxidized PET track-etched membrane / I. Korolkov, A. Mashentseva, O. Guven, A. Taltenov // Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. — 2015. — Vol. 365. — P. 419–423. DOI: 10.1016/j.nimb.2015.07.057.

24 Korolkov I. Protein fouling of modified microporous PET track-etched membranes / I. Korolkov, A. Mashentseva, O. Guven, Y. Gorin, M. Zdorovets // Radiation Physics and Chemistry. — 2018. — Vol. 151. — P. 141–148. DOI: 10.1016/j.radphyschem.2018.06.007.

25 Kutuzau M. Optimization of PET ion-track membranes parameters / M. Kutuzau, A. Kozlovskiy, D. Borgekov, I. Kenzhina, M. Zdorovets, A. Chernik, O. Alisienok, A. Shumskaya, E. Kaniukov // Materials today: proceedings. — 2019. — Vol. 7, No. 3. — P. 866–871. DOI: 10.1016/j.matpr.2018.12.086.

26 Zdorovets M. Functionalization of PET track-etched membranes by UV-induced graft (co)polymerization for detection of heavy metal ions in water / M. Zdorovets, I. Korolkov, A. Yeszhanov, Y. Gorin // Polymers (Basel). — 2019. — Vol. 11, No. 11. — P. 1876. DOI: 10.3390/polym11111876.

27 Korolkov I. Electron/gamma radiation-induced synthesis and catalytic activity of gold nanoparticles supported on track-etched poly(ethylene terephthalate) membranes / I. Korolkov, A. Mashentseva, O. Guven, Y. Gorin, A. Kozlovskiy, M. Zdorovets // Materials Chemistry and Physics. — 2018. — Vol. 217. — P. 31–39. DOI: 10.1016/j.matchemphys.2018.06.039.

28 Korolkov I. Radiation induced deposition of copper nanoparticles inside the nanochannels of poly(acrylic acid)-grafted poly(ethylene terephthalate) track-etched membranes / I. Korolkov, O.Guven, A. Mashentseva, A. Bakar Atici, Y. Gorin, M. Zdorovets // Radiation Physics and Chemistry. — 2017. — Vol. 130. — P. 480–487. DOI: 10.1016/j.radphyschem.2016.10.006

29 Korolkov I. The effect of oxidation pretreatment of polymer template on the formation and catalytic activity of Au/PET membrane composites / I. Korolkov, D. Borgekov, A. Mashentseva, O. Guven, A. Bakar Atici, A. Kozlovskiy, M. Zdorovets // Chemical Papers. — 2017. — Vol. 71, No. 12. — P. 2353–2358. DOI: 10.1007/s11696–017–0229–1.

30 Yeszhanov A. Copper nanotube composite membrane as a catalyst in Mannich reaction / A. Yeszhanov, A. Mashentseva, I. Korolkov, Y. Gorin, A. Kozlovskiy, M. Zdorovets // Chemical Papers. — 2018. — Vol. 72. — P. 3189–3194. DOI: 10.1007/s11696–018–0539-y.

31 Mashentseva A. Electron beam induced enhancement of the catalytic properties of ion-track membranes supported copper nanotubes in the reaction of the P-nitrophenol reduction / A. Mashentseva, D. Shlimas, A. Kozlovskiy, M. Zdorovets, A. Russakova, M. Kassymzhanov, A. Borisenko // Catalysts. — 2019. — Vol. 9, No. 9. — P. 737. DOI: 10.3390/catal9090737.

32 Zdorovets M. Investigation of phase transformations and corrosion resistance in $Co/CoCo_2O_4$ nanowires and their potential use as a basis for lithium-ion batteries / M. Zdorovets, A. Kozlovskiy // Scientific Reports. — 2019. — Vol. 9, No. 1. — P. 1–12. DOI: 10.1038/s41598–019–53368-y.

33 Zdorovets M. Study of phase transformations in $Co/CoCo_2O_4$ nanowires / M. Zdorovets, A. Kozlovskiy // Journal of Alloys and Compounds. — 2020. — Vol. 815. — P. 152450. DOI: 10.1016/j.jallcom.2019.152450.

34 Borgekov D. Temperature dependent catalytic activity of Ag/PET ion-track membranes composites / D. Borgekov, A. Mashentseva, S. Kislitsin, A. Kozlovskiy, A. Russakova, M. Zdorovets // Acta Physica Polonica Series A. — 2015. — Vol. 128, No. 5. — P. 871–875. DOI: 10.12693/aphyspola.128.871.

35 Mashentseva A. Impact of testing temperature on the structure and catalytic properties of au nanotubes composites / A. Mashentseva, M. Zdorovets, D. Borgekov // Bulletin of Chemical Reaction Engineering & Catalysis. — 2018. — Vol. 13, No. 3. — P. 405–411. DOI: 10.9767/bcrec.13.3.2127.405–411.

36 Mashentseva A. Catalytic activity of composite track-etched membranes based on copper nanotubes in flow and static modes / A. Mashentseva, M. Zdorovets // Petroleum Chemistry. — 2019. — Vol. 59, No. 5. — P. 552–557. DOI: 10.1134/ S0965544119050074.

37 Mashentseva A. Influence of deposition temperature on the structure and catalytic properties of the copper nanotubes composite membranes / A. Mashentseva, A. Kozlovskiy, M. Zdorovets // Materials Research Express. — 2018. — Vol. 5, No. 6. DOI: 10.1088/2053–1591/aacb5f.

38 Shumskaya A. Evolution of morphology, structure, and magnetic parameters of Ni nanotubes with growth in pores of a PET template / A. Shumskaya, V. Bundyukova, A. Kozlovskiy, M. Zdorovets, K. Kadyrzhanov, G. Kalkabay, E. Kaniukov // Journal of Magnetism and Magnetic Materials. — 2020. — Vol. 497. — P. 165913. DOI: 10.1016/j.jmmm.2019.165913.

39 Korolkov I. Hydrophobization of PET track-etched membranes for direct contact membrane distillation / I. Korolkov, A. Yeszhanov, Y. Gorin, M. Zdorovets, N. Khlebnikov, K. Serkov // Materials Research Express. — 2018. — Vol. 5, No. 6. — P. 065317. DOI: 10.1088/2053–1591/aacc39.

40 Zdorovets M. Liquid low-level radioactive wastes treatment by using hydrophobized track-etched membranes / M. Zdorovets, A. Yeszhanov, I. Korolkov, O. Guven, S. Dosmagambetova, D. Shlimas, Z. Zhatkanbayeva, I. Zhidkov, P. Kharkin, V. Gluchshenko, D. Zheltov, N. Khlebnikov, I. Kuklin // Progress in Nuclear Energy. — 2020. — Vol. 118. — P. 103128. DOI: 10.1016/j.pnucene.2019.103128.

41 Garcia-Payo M. Wetting study of hydrophobic membranes via liquid entry pressure measurements with aqueous alcohol solutions / M. Garcia-Payo, M. Izquierdo-Gil, C. Fernández-Pineda // Journal of Colloid and Interface Science. — 2000. — Vol. 230, No. 2. — P. 420–431. DOI: 10.1006/jcis.2000.7106.

42 Eykens L. Membrane synthesis for membrane distillation: A review / L. Eykens, K. De Sitter, C. Dotremont, L. Pinoy, B. Van der Bruggen // Separation and Purification Technology. — 2017. — Vol. 182. — P.36–51. DOI: 10.1016/ j.seppur.2017.03.035.

А.Б. Есжанов, С.С. Досмағамбетова

Фенол ерітінділерін гидрофобты тректі мембраналармен тазарту

Жер үсті суларының ең көп таралған ластануының бірі құрамында фенол бар заттар болып табылады. Құрамында фенол бар қосылыстар адамның денсаулығы мен қоршаған ортаға кері әсерін тигізеді, өйткені олар суға түскен кезде оттегіні интенсивті сіңіреді. Сондықтан фенолдарды сумен тазарту — басты экологиялық міндет. Суды фенолдардан тазарту полиэтилентерефталат (ПЭТФ ТМ) негізіндегі гидрофобты тректік мембраналарын қолдану арқылы тікелей жанасатын мембраналық дистилляция әдісімен жүзеге асырылды. Гидрофобты тректік мембраналар егу полимерлеу және фтор бар силандармен жабу арқылы алынды. Сканерлеуші электронды микроскопия (СЭМ), Фурье-трансформалы инфрақызыл (ИҚ) спектроскопия және сұйықтықтың ену қысымын талдау гидрофобты ПЭТФ ТМ сипаттау үшін қолданылды. ПЭТФ ТМ модификациялағаннан кейін ылғалдың жанасу бұрышы 130°-дан жоғары болды. Суды фенолдан тазарту тиімділігі су ағынын өлшеу және флуориметриялық әдіспен бағаланды. Фенол ерітіндісі 0,5, 1 және 2 г/л концентрациясында қолданылды. Гидрофобты мембраналардың ең үлкен пермеат ағыны 1,1 кг/м^2 сағ. құрады.

Кілт сөздер: фенол, суды тазарту, тікелей мембраналық сүзу, УК-егу полимерлеу, стирол, триэтоксивинилсилан, құрамында фтор бар силандар, тректі мембраналар.

А.Б. Есжанов, С.С. Досмагамбетова

Очистка растворов фенола гидрофобными трековыми мембранами

Фенолы являются одним из наиболее распространенных загрязнителей поверхностных вод. Сброс фенольных вод в водоемы и водотоки резко ухудшает их общее санитарное состояние, поскольку, во-первых, эти соединения оказывают токсическое действие, а во-вторых, интенсивно поглощают растворенный в воде кислород, что отрицательно сказывается на жизни организмов в водоеме. Поэтому очистка воды от фенолов является важной экологической задачей. В этом исследовании гидрофобные трековые мембраны на основе полиэтилентерефталата (ПЭТФ ТМ) были испытаны при обработке воды от фенола путем прямой контактной мембранной дистилляции. Гидрофобные ПЭТФ ТМ были получены УФ-прививочной полимеризацией стирола, триэтоксивинилсилана с добавкой винилимидазола, а также покрытием фторсодержащих силанов. Полученные гидрофобные ПЭТФ ТМ были охарактеризованы методами сканирующей электронной микроскопии, ИК-Фурье-спектроскопии, анализом давления проскока жидкости. Разработанный метод гидрофобизации ПЭТФ ТМ привел к повышению угла смачивания до 130°. Эффективность очистки воды от фенола оценивали измерением производительности и флуориметрическим методом. Концентрации растворов фенола составляли 0,5, 1 и 2 г/л. Максимальная производительность гидрофобных мембран достигала 1,1 кг/м^2·ч.

Ключевые слова: фенол, очистка воды, прямая контактная мембранная дистилляция, УФ-прививочная полимеризация, стирол, триэтоксивинилсилан, фторсодержащие силаны, трековые мембраны.