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HYDROPHOBIZATION OF PET TRACK-ETCHED MEMBRANES FOR DIRECT CONTACT MEMBRANE DISTILLATION OF LIQUID RADIOACTIVE WASTES

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This article provides the results of liquid low-level radioactive wastes treatment by direct contact membrane distillation using polyethylene terephthalate hydrophobic track-etched membranes. The hydrophobization of track-etched membranes was carried out by UV-induced graft polymerization of triethoxyvinylsilane with styrene and coating with fluorine-containing silanes. Hydrophobic membranes were investigated by scanning electron microscope, Fourier-transform infrared spectroscopy, contact anglemeasurements, and liquid entry pressure analysis. Prepared membranes were tested in treatment of liquid low-level radioactive wastes by membrane distillation. The influence of pore sizes on water flux and rejection degree was studied. Rejection degree was evaluated by conductometry and atomic emission method. Decontamination factors evaluated by gamma-ray spectroscopy for ^{60}Co, ^{137}Cs, and ^{241}Am are 85.4, 1900 and 5.4 for membranes modified with polystyrene and triethoxyvinylsilanewith pore diameters of 142 nm; 85.0, 1462 and 4 for membranes modified with perfluorododecyltrichlorosilanewith pore diameters of 150 nm respectively.

Keywords: UV-induced graft polymerization, track-etched membranes, direct contact membrane distillation, hydrophobization, fluorine-containing silanes, radioactive waste treatment

Introduction

One of the main problems determining the existence and further development of nuclear energy is the solution of the problem of collecting and concentrating radioactive waste [1]. Environmental disasters at the Chernobyl nuclear power plant, Fukushima Daiichi and the problems of former nuclear test sites have led to the focus of attention all over the world on the treatment and concentration of low-level liquid radioactive waste (LLLRW). LLLRW canbe concentrated and solidified with cement, glass and bitumen [2]. Various methods for the separation of liquid radioactive solutions are known, such as plasma processesand sorption [3]. One of the most promising method are also membrane separation. Among membrane methods, ultrafiltration, reverse osmosis and electrodialysis [4] have found their application. Currently, a promising method of direct contact membrane distillation (MD) has been used for the separation and purification of low-level liquid radioactive waste. The advantages of MD are low energy consumption, low operating temperature, over-pressure is not required. Drawback of this process is the short lifetime of the membranes due to gradual surface fouling and poor performance. Despite this, MD is widely used for the desalination of seawater and groundwater, wastewater and natural water treatment from heavy metals [5–7].

The membranes used for the MD process are imposed following requirements: hydrophobicity, high porosity, water impermeability, chemical and mechanical stability, uniform pore size distribution. Hydrophobicity of the membrane surface prevents wetting and provides good separation characteristics. The wetting contact angle allows estimating the hydrophobicity and hydrophilicity of membrane surface. A water contact angle above 90° is required for the treatment of salty aqueous solutions with MD [8].

Various types of polymers for example, polytetrafluoroethylene (PTFE), polyamide (PA), polypropylene (PP) are used in MD due to their hydrophobic nature and thermal stability [9–11]. However, these types of membranes also have their drawbacks such as poor productivity, high cost, fouling of the hydrophobic surface, which led to reducing water purification. Thus, searching for new type membranes for MD is an important task. Recently, track-etched membranes (TeMs) are started to use in the process of MD [12–14]. Regular geometry of the pores with the ability to control their amount per unit area and excellent distribution of pore sizes together with low thickness and tortuosity make track-etched membranes (TeMs)

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attractive for application in precise separation methods. The most frequently used track-etched membranes are based on poly(ethylene terephthalate) (PET). A unique feature of TeMs is the control of the number of pores per unit area, which significantly expands fields of applicationin sensing [15], catalysis, lithium-ion batteries, template synthesis of nanostructures [16–20]. As mentioned above, for membrane distillation it is important that the membrane has hydrophobic properties. However, PET TeMs has medium-hydrophobic properties, and for application in MD process, the membranes should have the water-repellent properties. The most common method of hydrophobization is to cover the surface by hydrophobic layer. Previously obtained hydrophobic PET TeMs by covalent bonding of silicon monomers such as dichlorodimethylsilane [21] and UV-induced graft polymerization of TEVS in presents of acrylic acid and N-vinylimidazole [22] were used for concentration of juices desalination by DCMD.

In this paper, UV-graft polymerization of styrene and triethoxyvinylsilane (TEVS) on the surface of PET TeMsand covalent binding of perfluorododecyltrichlorosilane (PFDTS) in an *o*-xylene solution.TeMs with a narrow pores size distribution and not tortuous channels will be tested in MD of LLLRW solutions. These properties of TeMs led to high salt and radioactive isotopes rejection degree.

1. Experimental part

Sodium hydroxide, N,N-dimethylformamide, benzophenone, sodium chloride, trichloromethane, TEVS, styrene, PFDTS were purchased from Sigma-Aldrich. Deionized water (18.2MΩ) obtained by water purification system Akvilon D-301 used in all experiments. Purification of monomers from inhibitors was carried out by passing through a column filled with alumina oxide.Samples of TeMsin size 10 x 15 were prepared by irradiation with $^{84}Kr^{15+}$ ions with an energy of 1.75 MeV/nucleon and ion fluence of $1 \cdot 10^8$ ion/cm^2, using the DC-60 accelerator in Astana branch of Nuclear Physics Institute. Then membranes were photosensitized for 30 min from each side and were chemically treated in 2.2 M NaOH at certain time to obtain membranes with different pores. Prepared membranes were dried and kept between paper sheets.

In order to increase hydrophobic properties of PET TeMs, two methods of surface modification were considered in comparison. First, modification of PET TeMs was carried out by UV-induced grafting of styrene and TEVS. PET samples were immersed in N,N-dimethylformamide 5% benzophenone solution. After that, samples were put into chloroform solutions of the 10-20% styrene and TEVS concentration with various ratios. The UV-irradiation was carried out for 60 min under UV lamp OSRAM Ultra Vitalux E27. After irradiation, samples were washed first in chloroform, and then in hot water to remove ungraftedhomopolymers, dried and weighed to calculate the grafting degree.

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

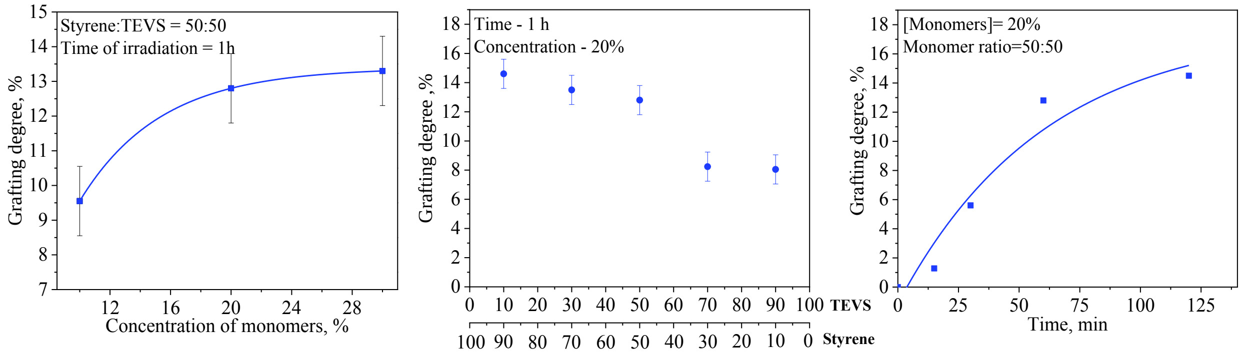
The surface morphology of pristine and modified PET TeMs was examined using JSM-7500F scanning electron microscope (SEM) (JEOL, Japan).Agilent Cary 600 Series FTIR Spectrometer with ATR accessory was used to record FTIR spectra to study different chemical groups appeared after modification. Scan range: 400 to 4000 cm^{-1}, resolution 4.0 cm^{-1}. Spectral analysis was conducted by using Agilent Resolution Pro. Each sample was measured 32 scans at the room temperature. The gas flow rate was measured at a pressure drop of 20kPa. The contact angle (CA) of the pristine and modified PET TeMs was measured goniometrically using the static drop method using Digital Microscope with 1000x magnification. Measurements were taken from different points of the polymer and the average result was calculated.

Liquid Entry Pressure (LEP) was determined by using deionized water flow measurements according to recommendations described in [23,24]. A round sample with the radius of 1.25 cm was compressed inside the hermetically-sealed chamber, and a test was run with air at gradually increasing pressure. The LEP was recorded as the pressure corresponding to the point of initial passage of flow through the membrane using capillary with the diameter of 0.7 mm. According to the recommendation, the LEP should be >2.5 bar for a successful application in MD [23].

The mechanism of the process and DCMD rig was described earlier in the papers. The permeate flux was measured by weighing. LLLRW samples obtained from WWR-K research nuclear reactor (Almaty, Kazakhstan) were tested. The degree of salt rejection was calculated by the change in conductivity that was measured using Hanna Instruments HI2030-01. OPTIMA-8000 ICP-Optical Emission Spectroscopy (the spectral range is 165-900 nm with resolution of < 0.009 nm at 200 nm) was used to estimate elemental content of solutions before and after MD. Gamma-ray spectroscopy Canberra GM1520 with semiconductor Ge detector and the energy range (25 - 3000) keV was used to estimate activity of radioisotopes.

2. Results and Discussion

First, hydrophobization of PET TeMswas carried out by UV-induced graft polymerization two monomers – styrene and TEVS. Chloroform was used as a solvent for UV photo-induced graft polymerization due to its high ability to dissolve monomers and transparency in the UV region. Effect of hydrophobization of different parameters such as concentration of monomers in solvent (10-30%), percentage ratio of monomers (50:50; 10:90; 90:10; 30:70; 70:30) and grafting time was studied (Figure 1).



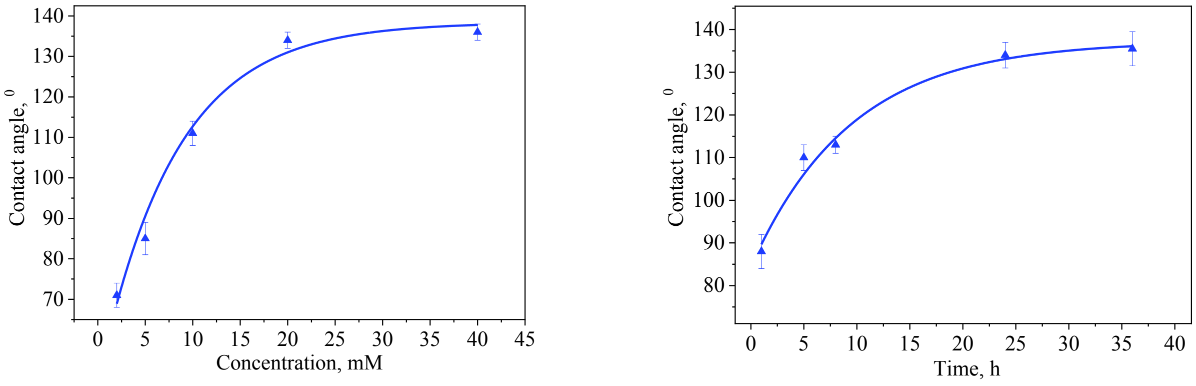
a b c

Fig.1. The degree of grafting of styrene and TEVS to the surface of PET TeMs with various concentration (a) and monomer ratios (b) and time (c)

Due to the high ability of styrene for polymerization in comparison to TEVS, it can be noted that with an increase in the concentration of styrene leads to an increase in the degree of grafting, while an increase in the concentration of TEVS leads to a decrease in the concentration.The effect of the degree of grafting on different ratios of monomers is shown in Figure 1b.A significant increase in the concentration of the monomer mixture from 10% to 20% leads to a significant increase in the grafting degree, however, a further concentration increase only slightly with increases in the grafting degree.Thus, as can be seen from Figure 1a, an increase in the concentration of monomers above 20% is not effective.

Figure 1c shows exponential relationship of grafting degree with time at constant concentration of monomer 20% and monomer ratio 50:50. Grafting degree reaches 12.8% after 60 min and 14.5% after 120 min of grafting. An increase in the time of grafting from 60 to 120 minutes lead to an insignificant increase in the degree of grafting, thus, the optimal time is 1 hour.

The second method of hydrophobization 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 2a shows the dependence of the concentration of PFDTS on the value of the CA. As can be seen, at an optimal monomer concentration of 20 mM the CA reaches a maximum value.



a b

Fig.2. Contact angle of modified PET TeMs at various concentration of PFDTS (a) and reaction time (b) (pore diameter of initial PET TeMs is 200 nm)

A further increase in concentration does not lead to a significant change in the CA. The dependence of the holding time in the reaction on the CA was considered. The results are shown in Figure 2b. The largest CA (134°) was reached after 24 hours. A further increase in time did not significantly affect the value of the CA. Characteristics of hydrophobized PET TeMs by PFDTS are presented in Table 1.

Table 1 - Characteristics of hydrophobized PET TeMs by PFDTS

Sample	Contact angle, °	Effective pore size, nm	Pore size (from SEM analysis), nm	LEP, MPa
Initial PET TeMs	56	198±5	220±8	0.12
PET TeMs – PFDTS	134	148±6	174±4	>0.43

To evaluate the hydrophobic properties of prepared samples, the method of contact angle measurements was used. 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 3.

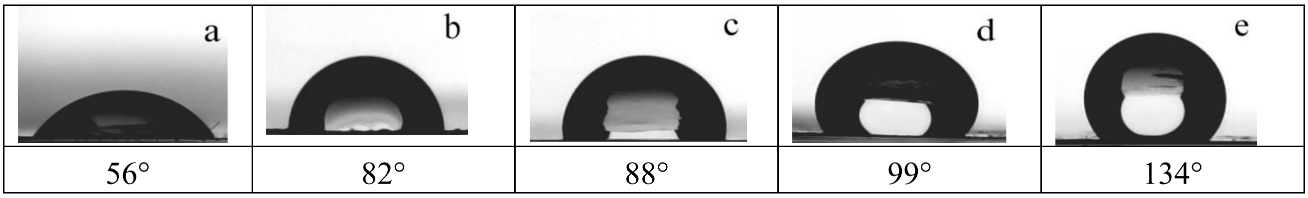


Fig.3. CA for initial PET TeMs (a), PET TeMs-g-Styrene-TEVS (70:30) (b), PET TeMs-g-Styrene-TEVS (90:10) (c), PET TeMs-g-Styrene-TEVS (50:50) (d), PET TeMs – PFDTS (e)

It can be seen, the contact wetting angle of the initial PET TeMs increases significantly from 56 to 99° for PET TeMs-g-Styrene-TEVS with monomer ratio (70:30), (90:10), (50:50) and to 134° for PET TeMs – PFDTS respectively.As it can be seen from Table 2, contact angle is dependent on the degree of grafting and on the concentration of monomer and their ratio. Along with that, the pore diameter of the membrane also significantly affects contact angle and LEP. With an increase in the pore diameter from 142 to 287 nm, the value of the capillary effect exceeds the surface tension force of a water droplet. It is also confirmed a decrease in LEP with an increase in pore diameter. However, according to the recommendation, the LEP should be >2.5 bar for a successful application in MD. The use of a membrane with a pore diameter of 287 nm may lead to liquid slipping. Thus, according to the above given results, the optimal conditions for the modification of PET TeMs with pore sizes 150-250 nm by UV-induced graft polymerization of styrene and TEVS leading to maximum hydrophobization of membranes (99°) with preservation of the pore structure are: grafting time 60 min, total monomer concentration 20% and monomer ratio of 50:50.

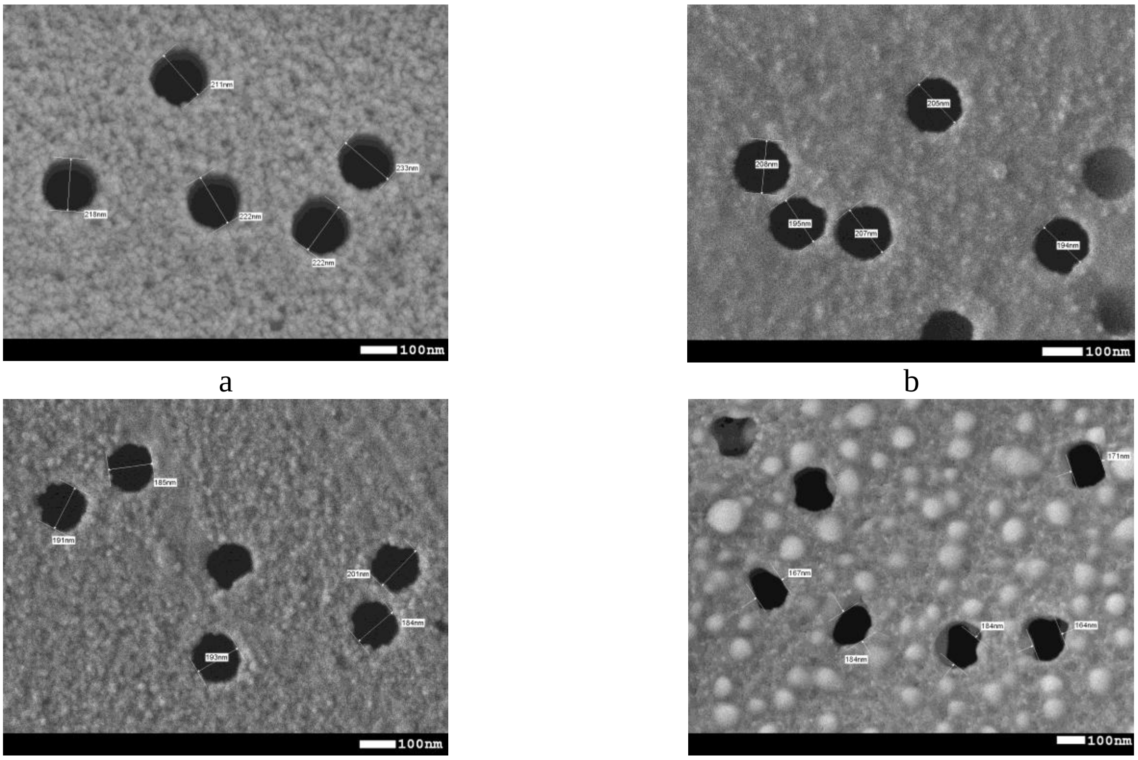
Table 2 - Contact angle and pore sizes of PET TeMs-g-PS-TEVS in various concentration and ratios (time is constant – 1h)

Sample and monomer ratio	Concentration of monomer, %	Contact angle, °	Pore size (SEM analysis), nm	Effective pore size, nm	Liquid Entry Pressure (LEP), MPa	Grafting degree, %
PET TeMs	-	56	220±20	208±6	-	-
PS-TEVS (50:50)	20	99	206±21	200±6	0.34	13
PS-TEVS (90:10)	20	82	211±21	203±7	0.13	8
PS-TEVS (70:30)	20	85	200±21	193±7	0.14	14
PS-TEVS (50:50)*	20	87	287±25	283±6	0.13	14
PS-TEVS(50:50)**	20	92	242±27	235±6	0.25	13
PS-TEVS (50:50)***	20	99	142±12	131±6	0.39	12

** - PET TeMs with pore size of 300 nm; **- PET TeMs with pore size of 250 nm, *** - PET TeMs with pore size of 150nm*

According to Table 2, the liquid entry pressure (LEP) decreases significantly with increasing in pore diameters. When membranes with a large pore diameter (~ 300 nm) are used, concentrate breakthrough occurs, i.e., the filtration process is observed instead ofmembrane distillation. As a result, the value of conductivity and productivity increases significantly. Thus, the developed method of hydrophobization can be applied to PET TeMs with pore sizes up to 200 nm, at which optimal values on the degree of salt rejection and productivity are observed.

The characterization of pore sizes before and after modification, as well as the morphology of PET TeMs surfaces was carried out by SEM analysis.Microphotographs of the pristine PET TeMs surface and modified at different ratios are shown in Figure 4.From Figure 4 it is noticeable that there is a slight narrowing of the pore diameter of PET TeMs, while the pore structure remains unchanged.



a b

c d

Fig.4. SEM images of PET TeMs surfaces before (a) and after grafting at different ratios of monomers styreneand TEVS 50:50 (b), 70:30 (c), and PET TeMs – PFDTS (d)

Table 3 - Average pore diameter of pristine and modified PET TeMs

Sample and monomer ratio	Average pore diameter, nm
Pristine PET TeMs	221±8
PS-TEVS (50:50)	202±7
PS-TEVS (70:30)	191±7
PET TeMs – PFDTS	174±8

To confirm graft polymerization and detect the presence of chemical group vibrations come from TEVS and PS in modified PET TeMs, FTIR-ATR analysis was performed. FTIR-ATR spectra of initial and grafted PET TeMs are shown in Figure 5. Typical FTIR-ATR spectrum of initial PET TeMs consist of main absorption peaks at 2972 cm^{-1} (aromatic C-H), 2910 cm^{-1} (aliphatic C-H), 1715 cm^{-1} (C=O), 1471 cm^{-1} (CH_2 bending), 1410 cm^{-1} (ring CH in plane bending), 1341 cm^{-1} (CH_2 wagging), 1238 cm^{-1} (C(=O)-O stretching), 1018 cm^{-1} (ring CCC bending), 970 cm^{-1} (O-CH_2 stretching), 847 cm^{-1} (ring CC stretching). The presence of grafted TEVS is established by Si-O-Si and Si-CH_3 vibrations at 1180-1110, 761 cm^{-1}, respectively.

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Moreover, peak at 3300-3600 cm^{-1} was detected with low intensity that is corresponding to OH. OH-groups can come from hydrolysis of Si-OC_2H_5 groups.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.

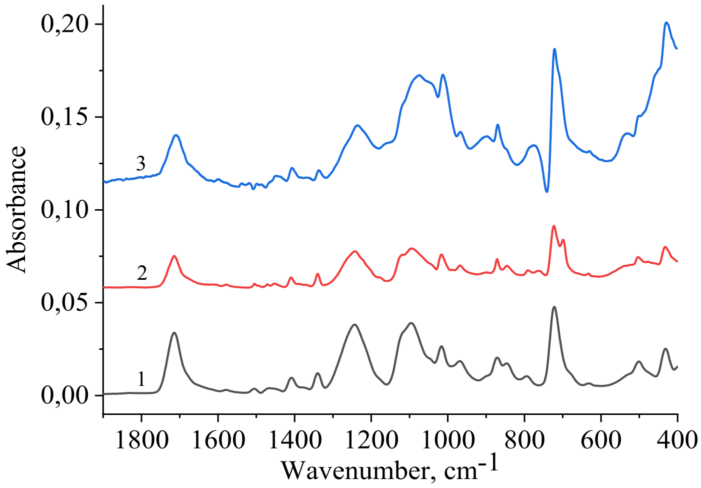


Fig.5. FTIR-ATR spectra of 1–PET TeMs, 2 – PET TeMs-g-PS-TEVS (50:50), 3– PET TeMs – PFDTS

Thus, optimal parameters to obtain membranes with the highest CA and maintaining pore structure for PET TeMs-g-PS-TEVS are 20% monomer concentration at monomer ratio 50:50 during 1h and for PET TeMs – PFDTS are 20mM monomer concentration in *o*-xylene solution during 24h.

Membrane distillation of liquid low-level radioactive wastes

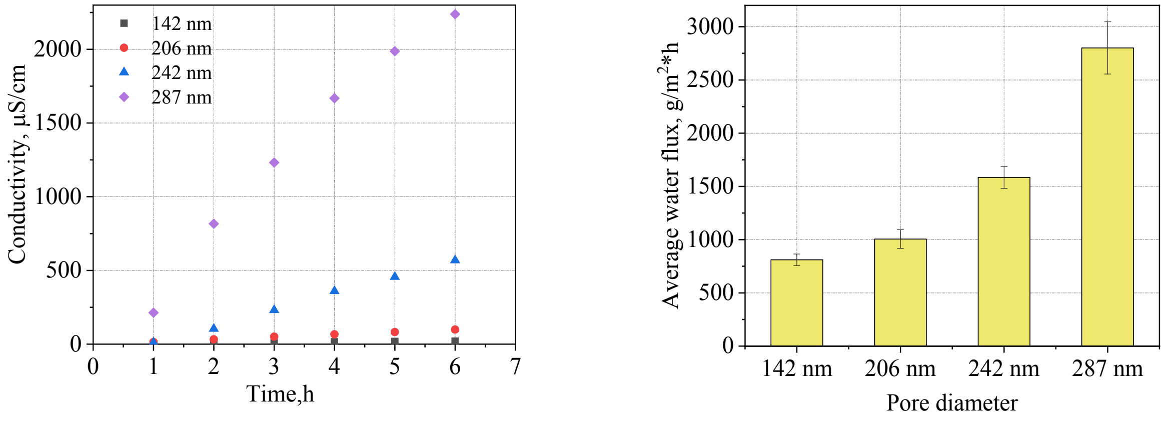
Membrane distillation of LLLRW with hydrophobic PET TeMs-g-PS-TEVS with different pore sizes (142, 206, 242 and 287 nm) and hydrophobic PET TeMs – PFDTS with pore sizes (150, 200 and 250 nm)obtained at optimal parameters was performed in direct contact mode with temperature control. LLLRW was purchased from Research Nuclear Reactor WWR-K (Almaty, Kazakhstan). LLLRW consist of different ions such as Na, Mg, K, Fe, Ca, Al, Sb, Sr, Mo, Cs measured by atomic emission method (Table 3) and consist of radioisotopes ^{60}Co, ^{137}Cs and ^{241}Am with different activity measured using Gamma Ray Spectrometer. In DCMD experiment, hydrophobic PET TeMs were used to evaluate water fluxes and decontamination factor (D) efficiency of LLLRW depends on pore diameter. Decontamination factor (D) was calculated according by the equation:

$$D = \frac{a_f}{a_p}, \tag{1}$$

where a_f and a_p are specific activities of the feed and the permeate respectively.

Removal efficiency of wastes was primarily evaluated by electrical conductivity, which can be also used for overall efficiency of DCMD for metal ions rejections since the main component of the waste sample is Na and K which are highly sensitive to changes in conductivity with changing concentration. Results are presented in Figure 6a. PET TeMS-g-PS-TEVS with pore diameters of 142, 206 and 242 nm showed minor changes in conductivity during MD, whereas using membranes with a pore diameter of 287 nm leads to a significant increase in conductivity from 214 to 2238 µS/cm. Degrees of salt rejection for the hydrophobized PET TeMs-g-PS-TEVS with pore diameter of 142, 206 and 242 nm are 99.2 %, 96.8% and 86.9% respectively.

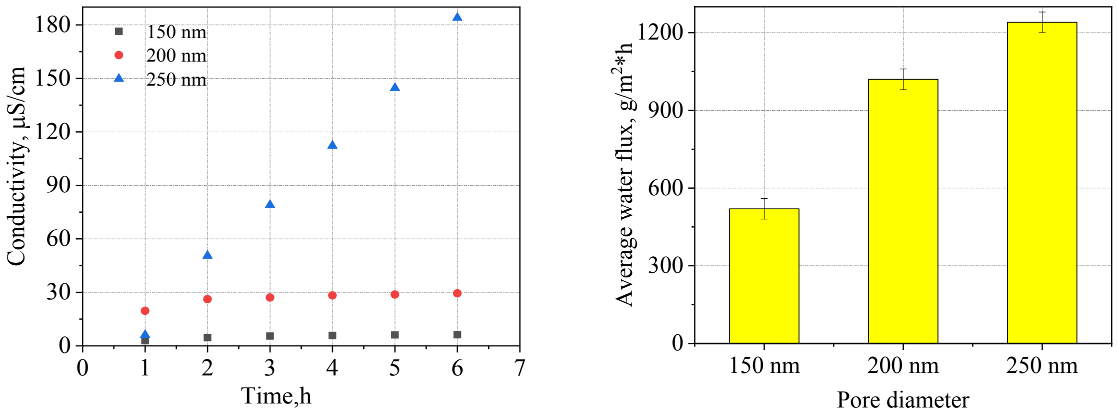
Figure 6b shows us increasing average water fluxes from 810 g/m^{2}h for the PET TeMs-g-PS-TEVS with 142 nm pore diameter to 1584 g/m^{2}h for the membrane with 242 nm pore diameter. It should be noted that according to analysis of conductivity (degree of salt rejection is around 5%), high flux of membranes with pore sizes of 287 nm is due to wetting the channels and filtration through occurs.



a b

Fig.6. Electrical conductivity (a) and MD water flux (b) during continuous DCMD tests using hydrophobized PET TeMs-g-PS-TEVS with different pores for radioactive waste solution

Electrical conductivity and water flux results of PET TeMs – PFDTS after DCMD are showed in Figure 7a, b. For hydrophobic PET TeMs – PFDTSwith pore sizes of 150, 200 nm is a slight increase in conductivity, however, with pore sizes of 250 nm, the conductivity sharply increases from 6 to 184 µS/cm. Degrees of salt rejection for the PET TeMs – PFDTS with pore diameter of 150, 200 and 250 nm are 98.7%, 97.3% and 79.2% respectively. Figure 6b shows us increasing average water fluxes from 520g/m^{2}h for the PET TeMs – PFDTS with pore diameter 150 nm to 1240g/m^{2}h for the membrane with 250 nm pore diameter.



a b

Fig.7. Electrical conductivity (a) and MD water flux (b) during continuous DCMD tests using hydrophobized PET TeMs– PFDTS with different pores for radioactive waste solution

Chemical composition of the waste sample and degree of rejection after DCMD process using hydrophobic PET TeMs are presented in Table 3,4. According to Table 3,4all degree of rejection were more than 94%, most of them are close to 100%. For comparison, hydrophobic PET TeMS – PFDTS with different pore diameter was used. Variations in ion concentration are caused by different salt concentration in feed solution. Decrease in the degree of salt rejection with an increase in the pore radius is associated with a decrease in the LEP (as it seen in Table 1,2). The higher the LEP, the lower the probability of liquid passing through the pores of the membranes.

Results on decontamination factors of radioisotopes are presented in Table 5,6. PET TeMs-g-PS-TEVS with pore diameters of 142 and 242 nm showed decontamination factor for ^{60}Co of >85.4, for ^{137}Cs of >1900 and 42, for ^{241}Am of 5 and >7 respectively. PET TeMs – PFDTS with pore size of 150 and 250 nm showed decontamination factor ^{60}Co >85.4 and 34.2, for ^{137}Cs of 1462 and 815.5, for ^{241}Am of 4 and > 2.6 respectively. It should be noted that in most cases data received was below detection limit. The decrease in the decontamination factor with an increase in the pore diameter is associated with a decrease in the LEP and the contact angle.

Table 4 - Chemical composition of the waste sample and the effluent after DCMD process using hydrophobic PET TeMs-g-PS-TEVS with different pore diameter

Element	Concentration in the feed, µg/l	Concentration in the permeate (PET TeMs-g-PS-TEVS, d=242 nm), µg/l, (degree of rejection, %)	Concentration in the permeate (PET TeMs-g-PS-TEVS, d=206 nm), µg/l, (degree of rejection, %)	Concentration in the permeate (PET TeMs-g-PS-TEVS, d=142 nm), µg/l, (degree of rejection, %)
Cs (σ=±26%)	304	7.13 (97.7%)	1.18 (99.6%)	0.34 (99.9%)
Mo (σ=±15%)	458	4.14 (99.1%)	<0.3 (99.9%)	<0.3 (99.9%)
Sr (σ=±15%)	136	<0,5 (99.6%)	<0.5 (99.6%)	<0.5 (99.6%)
Sb (σ=±15%)	46.3	0.68 (98.5%)	<0.3 (99.4%)	<0.3 (99.4%)
Al (σ=±16%)	660	<12 (98.1%)	<3 (99.5%)	<3 (99.5%)
Ca (σ=±16%)	1780	96.1 (94.6%)	84.2 (95.2%)	18.6 (99.0%)
Fe (σ=±10%)	383	<2.4(99.4%)	<0.6 (99.8%)	<0.6 (99.8%)
K (σ=±15%)	249 200	1523 (99.4%)	236 (99.9%)	54.6 (99.9%)
Mg (σ=±15%)	1046	<4 (99.6%)	2.36 (99.8%)	<1 (99.9%)
Na (σ=±15%)	4 710 000	103 (99.9%)	17.6 (99.9%)	1.87 (99.9%)

Table 5 - Chemical composition of the waste solution and the effluent after DCMD process using hydrophobic PET TeMs – PFDTS with different pore diameter

Element	Concentration in the feed, µg/l	Concentration in the permeate (PET TeMs-PFDTS, d=250 nm), µg/l	Concentration in the permeate (PET TeMs-PFDTS, d=200 nm), µg/l	Concentration in the permeate (PET TeMs-PFDTS, d=150 nm), µg/l
Cs (σ=±26%)	304	6.82 (98.2%)	3.26 (98.9%)	0.85 (99.8%)
Mo (σ=±15%)	458	3.90 (99.1%)	1.82 (99.6%)	<0.3 (99.9%)
Sr (σ=±15%)	136	1.08 (99.2%)	<0.5 (99.6%)	<0.5 (99.6%)
Sb (σ=±15%)	46.3	0.73 (98.4%)	<0.3 (99.3%)	<0.3 (99.3%)
Al (σ=±16%)	660	<12 (98.1%)	<6 (99.1%)	<3 (99.5%)
Ca (σ=±16%)	1780	89.1 (95.0%)	55.6 (96.8%)	33.3 (98.1%)
Fe (σ=±10%)	383	<2.4 (99.3%)	<1.2 (99.7%)	<0.6(99.8%)
K (σ=±15%)	249 200	1 568(99.3%)	838 (99.7%)	215 (99.9%)
Mg (σ=±15%)	1046	<4 (99.6%)	<2 (99.8%)	<2 (99.8%)
Na (σ=±15%)	4 710 000	56 100 (98.8%)	31 800 (99.3%)	7 770 (99.8%)

Table 6 - Radioisotope composition of feed waste solution and permeate solution after DCMD process using hydrophobic PET TeMs-g-PS-TEVS with different pore diameter

Radioisotope	Activity of the feed (Bq/kg)	Activity of the permeate (PET TeMs-g-PS-TEVS, d=142 nm), (Bq/kg)	Decontamination factor (D)	Activity of the permeate (PET TeMs-g-PS-TEVS, d=242 nm) (Bq/kg)	Decontamination factor (D)
^{60}Co	85.4±6.1	<1.0	>85	<1.0	>85
^{137}Cs	1900±27	<1.0	>1900	45.8±1.8	42
^{241}Am	<2.2	<0.41	5	<0.32	>7

Table7 - Radioisotope composition of feed waste solution and permeate solution after DCMD process using hydrophobic PET TeMs – PFDTS with different pore diameter

Radioisotope	Activity of the feed (Bq/kg)	Activity of the permeate (PET TeMs– PFDTS, d=150 nm) (Bq/kg)	Decontamination factor (D)	Activity in the permeate (PET TeMs– PFDTS, d=250 nm) (Bq/kg)	Decontamination factor D
^{60}Co	85.4±6.1	<1.0	>85	2.5±1.1	34.2
^{137}Cs	1900±27	<1.3	>1462	2.33	815.5
^{241}Am	<2.2	<0.55	>4	<0.86	>2.6

The results obtained in terms of the factor of decontamination of radionuclides, the degree of purification from salt and productivity exceed previously published works in some parameters. The authors [25]used commercial polypropylene membranes, which showed a lower water flux about 700 g/m^2·h. However, the salt rejection of radioactive waste of such elements as ^{60}Co, ^{90}Sr, ^{137}Cswas achieved more than 98%. The value of the decontamination factor of radionuclides varied within 10^5-10^6.FeiJia and others [26,27] have conducted research on the purification of ^{60}Co and ^{137}Sr by vacuum membrane distillation with hollow fiber polypropylene membrane. The salt rejection was over 99%, and the permeate water flux reached about 6200 g/m^2·h.However, in these works there are some disadvantages associated with the need for a reduced pressure of approximately (0.1-1 atm), as well as the high cost of hollow fiber membranes.

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-g-PS-TEVS, due to high performance and efficiency in treatment of LLLRW. Using of TeMs with a narrow pores size distribution allows us to achieve better purification from radioactive wastes.

Conclusion

In this research,two simple and effective methods of hydrophobization of PET track-etched membranes by UV-graft polymerization of styrene with TEVS (at optimal conditions of 20% monomer concentration at monomer ratio 50:50 during 60 min) and covalent binding of PFDTS were considered and applied in treatment of liquid low-level radioactive wastes. Prepared membranes were characterized by FTIR, SEM, LEP and goniometric analysis to evaluate hydrophobic properties of the membranes. DCMD was controlled by gravimetric and conductometricanalysis. The effect of membrane pore diameter on water flux and rejection degree was studied. Elemental content of the solutions were evaluatedby gamma-ray spectroscopy and atomic emission method. Modified in two different ways PET TeMs showed an excellent degree of salt rejection of main elements of LLLRW such as Cs, Mo, Sr, Sb, Al, Ca, Fe, K, Mg and Na, decontamination factor for ^{60}Co, ^{137}Cs, and ^{241}Am – >85, >1900 and 5 respectively when using modified membrane with average pore diameters of 142 nm (average water flux for this membrane is 810 g/m^{2}h).

Maximum average permeate flux of 2800 g/m^2·hwere achieved using PET TeMs-g-PS-TEVS, however degree of salt rejection and decontamination factor are not sufficient due to the fact that modified membranes with large pore diameters have lower LEP and contact angle. The optimum ratio between water flux and efficiency of salt rejection is achieved using 142 nm pore radius of the membranes. For the first time track-etched membranes were studied in membrane distillation of liquid low-level radioactive wastes. The use of track-etched membranes with a narrow pores size distribution and not tortuous channels allows us to achieve better purification from radioactive wastes in comparison with hollow-fiber membranes.

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