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Preparation of TFC-PES Reverse Osmosis Hollow Fibre Membrane for Brackish Water Desalination

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ABSTRACT

High-performance composite reverse osmosis hollow fibre membranes have been recently produced. These membranes have maximum salt recovery 98,1% and permeability 1.2 l/m2*h*bar. The newly developed membranes consist of two layers: active and support. An active layer has been synthesized by interfacial polymerization of the mixture of MPD and aliphatic amine and TMC. PES hollow fibre membranes with an outer selective layer made with a wet-spinning method have been used as the support one. The production of the selective layer of the reverse osmosis membranes has been carried out in two stages through keeping the membrane in isopropyl alcohol. It has been shown that two-stage application through a soaking procedure in isopropyl alcohol allows to achieve a defect-free layer of polyamide. It was also noted that the addition of aliphatic amines to the mPDA solution made it possible to achieve high values of perm selectivity compared to a solution that contained only mPDA.

1. Introduction

Water scarcity is one of the main problems modern societies is faced with. Water consumption has increased six times over last 100 years, and the demand for fresh water is only expected to increase due to population growth, economic and industrial development [1]. Reverse osmosis is currently the leading technology widely used for desalination of sea and brackish water. These facts make up a significant part of desalination plants, since plants based on them consume less energy compared to their counterparts. A sharp increase in demand for reverse osmosis membranes for water treatment is especially observed in the developing economies of the Asia-Pacific region and the Middle East and Africa. This is primarily due to the growing quest for clean drinking water, agriculture and other industries [2].

Most of the reverse osmosis membrane market is occupied by thin film composite (TFC) membranes. The selective layer of such membranes usually consists of polyamide (PA) but the

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support is made of polyethersulfone (PES), polyacrylonitrile (PAN) or polyvinylidene fluoride (PVDF). In most cases, a thin selective layer of such membranes is received as a result of interfacial polycondensation reaction of trimesoyl chloride and/or isophthalic acid chloride in the organic phase and meta phenylenediamine and/or piperazine in the aqueous phase. Such chemistry has been firstly reported by Cadotte *et al.,* [3] in the early 1980's and has become the preferred method with all the major manufacturers for fabricating spiral wound membrane elements for brackish water desalination. A very thin selective layer is formed due to the high rate of the polycondensation reaction even at room temperature, as well as very low solubility of the diamines in the organic phase. Interfacial polycondensation takes place as a result of partial diamine diffusion into the organic phase. A very thin film on the substrate surface is usually formed and as a rule, it is rough, a bit inhomogeneous and highly selective [4].

Hollow fibre membranes are the preferred form in the manufacture of membranes in all separation areas. This allows developing a large area in the membrane element, reducing the adverse effects of concentration polymerization on the membrane surface, and improving the quality of backwashes while membrane module cleaning. Using a hollow fibre membrane compared to a spiral wound allows to increase at least in one and a half times the active surface area in the same volume of membrane element. The effects of concentration polymerization on the membrane surface leads to low recovery in the single stage operation process for brackish water desalination (about 15-25%). But for hollow fibre membrane recovery could be more than 50% cause the improvements in membrane surface area reduce the effects of concentration polymerization at the membrane surface [5].

Polyethersulfone (PES) is one of the most widely used polymers in membrane formulation. Due to its temperature tolerance, high dimensional stability, good strength and porous nature the PES hollow fibre membranes is still commonly applied in modern industry [6].

Nevertheless, in the field of reverse osmosis membranes spiral wound membrane elements are still leading due to the fact that the concentric shape of hollow fibres complicates the homogeneous application of the two monomers, the removal of excess solutions and the drying process, especially while using the traditional TFC preparation procedure. Also, an equally important hampering factor is the formation of drops on the membrane surface when it is immersed in a diamine aqueous solution, which leads to the formation of drop like defects in the polyamide layer, reducing the selectivity of the membrane [7].

Recently many attempts have been made to obtain a hollow fibre TFC membrane. Thus, Türkan Ormanci-Acar *et al.,* has proposed a combination of electrolyte layering and interfacial polycondensation methods on a hollow fibre substrate of polyethersulfone [8]. The layer of polyelectrolytes made it possible to increase the adhesion of the polyamide thin layer and obtain a reverse osmosis membrane with a high selectivity. Yu Zhang *et al.,* has synthesized a zwitterionic polymer that formed pores during its application, remaining on a selective surface and resulting in highly permeable and fouling resistant reverse osmosis membranes for brackish water desalination [9].

Another way to improve the performance of reverse osmosis membranes is solvent activation. Most commonly this is the treatment with aliphatic alcohols, ketones or a mixture of water with aprotic organic solvents such as DMFA and DMSO. W.N. Gill *et al.,* has proposed this method for the first time [10]. In 1996, commercial membranes with aliphatic alcohol/water post-treatment were already produced using this method. However, this method has found its application only in spiral wound membranes.

Another common problem with TFC membranes is the presence of free amino and carboxyl groups in the selective polyamide layer forming nano defects [11]. This can potentially lead to mobility of the polyamide and increase it, especially when the temperature changes with the decreasing selectivity of the membrane. V. G. Dzyubenko *et al.,* proposed a method for post-treatment of a carbodiimides membrane for subsequent cross-linking of polyamide [12].

The main goal of this study is to obtain a hollow fibre reverse osmosis membrane with satisfactory properties from commercially available materials suitable for use in brackish water treatment (with maximum operating pressure up to 20 bar). For this purpose, in this work, we propose a two-layer application of a polyamide layer through soaking in isopropyl alcohol. However, so that the permeability of the membrane does not decrease dramatically after two-layer application, we suggest adding an aliphatic amine to the mPDA solution.

2. Methodology

2.1 Materials

The following materials used for ultrafiltration hollow fibre (RO support): Polyethersulfone (PES) Ultrason E6020P natural (Mw = 75 kDa, BASF, Germany), polyvinylpyrrolidone (PVP) K90 WIRUD (Mw = 1400 kDa, WIRUD GmbH, Germany), glycerol (≥ 99.5, AKRIHIM, Russia), Dimethylformamide (DMFA ≥ 99.0 %, SHANDONG HUALU-HENGSHENG CHEMICAL CO., LTD, China), polyethylene glycol 400 (PEG-400, Forward Group, Russia).

The following materials used for fibres top skin (selective layer): anhydrous cyclohexane (≥99.0%) and isopropyl alcohol (CHIMMED, Russia), M-phenylenediamine (MPD) flakes, 99%, 1,3,5 - Benzenetricarbonyl trichloride (TMC) 98%, Sulfocamphoric acid, triethylammonium bromide and sodium dodecyl sulphate (SDS) were obtained from Shandong Deshang Chemical Co., (China), Triethylamine (TEA) was obtained from RUSHIM, Russia, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMO-T) was obtained from Evonik (Germany), Polyetheramine (jeffamine t-403) was obtained from Huntsman (USA), hexamethylphosphoric triamide (≥98%, HMPA) was obtained from VECTON, Russia. All chemicals were used without further purification. Reverse osmosis water with a specific conductivity of no more than 30 S/cm was produced on-site.

Hollow fibre was characterized with SEM, bubble point, full porometry liquid-liquid pore size distribution, and tested for permeability and cutoff for some organic molecules. A standard sodium chloride rejection test was also provided.

2.2 Methods

2.2.1 Scanning electron microscopy method

Scanning probe microscope Horiba Smart SPM (France) was used. Scanning of the samples was conducted in the tapping mode. Wet membrane samples were flash-frozen in liquid nitrogen and then cracked to obtain the cross-section. The samples were dried overnight. An Emitech SC7620 sputtering machine was used to coat surface samples for 30 s and cross-section samples for 45 s with gold–platinum. ImageJ 1.41 software (National Institutes of Health, Bethesda, Maryland, USA) was used to determine the average pore A mean and a standard deviation were calculated for each size distribution. Average membrane thickness was measured at 5 different locations for each membrane sample using a Mitutoyo digital micrometre (Mississauga, Ontario Canada).

2.2.2 Pore size distribution

The pore size distribution was made based on the methodology used by previous researchers. The POROLUX™500 instrument was used to determine the pore size of the hollow fibre membrane [13].

2.2.3 Bubble point measure

The principle of its operation is based on capillary porosimetry, determination of pore size distribution and gas permeability. Capillary porosimetry makes it possible to determine open pores in the tested material by the pressure method: testing the material with a gradual increase in pressure and ejection of the test liquid from the pores with compressed air. On this device we have measured maximum pore size. To do this, a sample of the membrane was immersed in a wetting liquid, Porefil™ (surface tension γ=16 dyne/cm). Next, the sample was placed in a special holder and subjected to increasing pressure. When the gas pressure became greater than the capillary force holding the liquid in the largest pores, the wetting liquid was pushed out. The pressure of the supplied gas and the resulting gas flow, when the liquid was displaced, were measured.

2.2.4 Liquid-liquid porometry (LLP) test

Since POROLUX™ showed very low flow rate for the hollow fibre samples, we used the alternative liquid-liquid porosimetry (LLP) method. The principle was to impregnate the sample with a wetting liquid. So that this wetting fluid does not mix with the supply fluid (displacement fluid) under increasing pressure. On this device limiting pore size was measured. Water saturated with isobutanol was used as a displacement fluid. Samples for measurements were prepared by the following method: membrane samples after being in water were placed in pure isobutanol to force it out of the pores. Samples in isobutanol were subjected to heating to 35°C for about 3 hours. The samples were then measured on POROLIQ™.

2.2.5 Sodium chloride rejection test

The measurements were carried out on the basis of a technique you can see elsewhere [14,15]. A laboratory-scale experimental setup was used to measure the performance of the TFC membrane during RO (Figure 1).

The test module consisted of a steel tube with an outer diameter (OD) of 15 mm and an inner diameter (ID) of 12 mm and with 10 hollow fibre membranes, each with an effective length of 40 cm. The experiments were performed using wet hollow fibre membranes. An aqueous solution of NaCl was used (2000 ppm). It was fed into the interfibre space at a pressure of 15 bar. C_F and C_t denote the concentration of salt in the original and passed solution, respectively. They were obtained using a device measuring electrical conductivity. Rejection of sodium chloride Rs was measured by the following formula

$$R_S = \left(1 - \frac{C_t}{C_F}\right) \times 100 \tag{1}$$

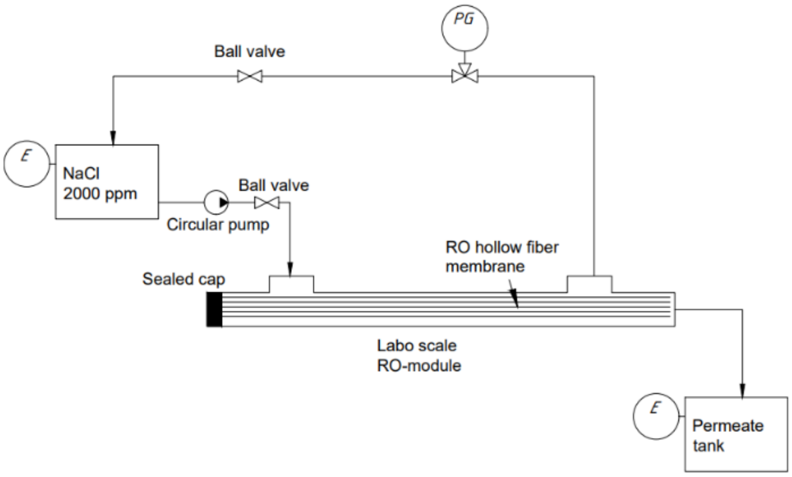

Fig. 1. Sodium chloride rejection test system

2.2.6 Organic molecules cut-off and permeability test

A laboratory-scale experimental setup was used in current study Figure 2. The permeability test was carried out on reverse osmosis water at a transmembrane pressure of 10 bar as it was described in the literature [16]. The cut-off was carried out at a transmembrane pressure of 8 bar with dead-end filtration for the following organic molecules: albumin, myoglobin and cyanocobalamin in case of hollow fibre supports and for creatinine, glucose, carbamide and folic acid in case of reverse osmosis hollow fibres according to the repeatedly mentioned method [17].

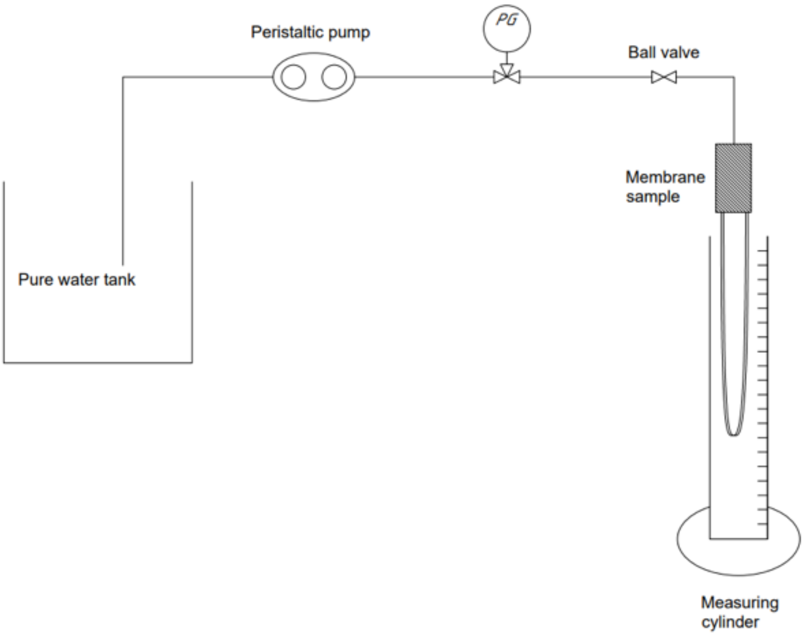

Fig. 2. Permeability and cut-off test system

The initial concentrations of organic molecules in solutions can be seen in the Table 1. 15 membrane samples were cast into a ¾ inch 100mm length PU tube with two-component polyurethane compound on one side. After it had cured, the tube was shaped with a blade so that the holes in the fibres were completely open. The opposite end of the fibre bundle was sealed with hot glue. The test solution was fed into the fibres through a polyurethane tube and collected from the side into the permeate into a graduated cylinder.

Table 1
The content of the components in initial cut-off solution

№	Component	Concentration, g/l
1	glucose	3
2	creatinine	0.1
3	carbamide	2
4	Glycerol	8.7
5	Folic acid	$3*10^{-4}$
6	myoglobin	$2*10^{-5}$
7	albumin	20
8	cyanocobalamin	$40*10^{-7}$

Samples for determining the concentration of organic molecules were determined on a Roche Cobas analyser Table 2.

Table 2
Methods to determine organic molecules

Assay	Equipment	Description
Glucose	Roche Cobas 8000 automated modular platform with c702 biochemistry module	Enzymatic hexokinase method. The required quantity of specimen is added to the reagents per the assay protocol provided by the diagnostic kit manufacturer. After the incubation period, the absorbance at 340 nm is taken, and concentration is calculated using sample blank, reagent blank, and calibration data.
Albumin		Bromocresol method. The method is based on the specific binding of bromocresol green (BCG), an anionic dye, and the protein at acid pH produce a colour change of the indicator from yellow –green to green –blue with the resulting shift in the absorption wavelength of the complex. The intensity of the colour formed is proportional to the concentration of albumin in the sample.
Creatinine		Colorimetric – kinetic method. The assay is based on the reaction of creatinine with sodium picrate as described by Jaffe. Creatinine reacts with alkaline picrate forming a red complex. The time interval chosen for measurements avoids interferences from other serum constituents. The intensity of the colour formed is proportional to the creatinine concentration in the sample.
Urea		As the previous one.
K^+, Na^+, Cl^-	Roche Cobas 8000 automated modular platform with ISE 900, Roche Diagnostics, Switzerland	Ion-Selective electrodes potentiometry. The ion-selective membrane situated between the two aqueous phases, i.e., between the sample and inner solution that contain an analyte ion forms an essential part of the ISEs. It can be made of glass, a crystalline solid, or a liquid. The potential difference across the membrane is measured between the two reference electrodes positioned in the respective aqueous phases.
Vitamin B12	Roche Cobas 8000 automated modular platform with e801, Roche Diagnostics, Switzerland	Immunochemiluminescent method. Chemiluminescence (CL) analysis based on the enhancive effect of cobalt liberated during acidification was shown to be ultrasensitive and to have a wide linear range for the detection of vitamin B12. CL is a simple, sensitive, and selective analytical method, offering an attractive alternative for determination of organic and inorganic species
Folic acid		As the previous one.
Myoglobin		As the previous one.

3. Results

Membrane fabrication can be divided into the following main steps

i. PES hollow fibre support spinning
ii. Dope solution preparation
iii. Hollow fibre support manufacture by wet spinning method
iv. Soaking in sodium chloride solution
v. Impregnation of pores in 15% glycerol
vi. Polyamide selective layer formation
vii. Applying of amine solution
viii. TMC solution applying
ix. Soaking in isopropyl alcohol
x. Re-applying of amine solution
xi. Re-applying of TMC solution
xii. Impregnation in 15% glycerol
xiii. Mini modules manufacturing

3.1 Hollow Fibre Support Preparation

The polymer solution was prepared in a flask using an anchor type stirrer. PES and PVP k-90 were dissolved in ¾ part of dimethyl sulfoxide with constant stirring for 3 hours at 90°C. After complete dissolution of PES and PVP in DMSO the temperature was reduced to 55 °C. The remaining solvent DMSO (¼ part) was mixed with glycerol. This solution was divided in 5 parts to add in the polymer solution. After adding each part, the solution was mixed for at least 40 minutes. Mixing of glycerol with the part of DMSO solvent was necessary so that the local coagulation of the polymer solution, when glycerol was added, was not so drastic. Then the solution was evacuated overnight. The composition of the solution is in the Table 3.

Table 3
The content of the support dope solution

No	Component	W, %
1	PES Ultrason E6020P	22
2	PVP K90	1.5
3	DMSO	67.8
4	Glycerol	8.7

Polyethersulfone (Figure 3) was chosen as the support material, because it is a commercially available polymer with excellent stability over a wide pH range.

To increase the hydrophilicity of the membrane and the degree of porosity of its surface, PVP K90 was introduced into the polymer solution [18]. DMSO was chosen as the solvent for the PES/PVP system. Glycerol was used to shift the casting solution system closer to the binodal line (Table 1).

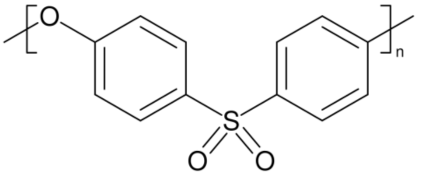

Fig. 3. The polyethersulfone structure formula

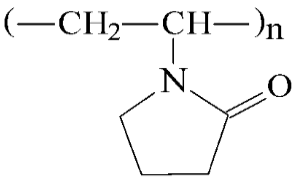

Fig. 4. The polyvinylpyrrolidone structure formula

The hollow fibre membrane was prepared using the lab-scale manufactory line described previously [19,20]. The main goal was to obtain a substrate with an outer selective layer to facilitate the synthesis of polyamide on its surface, with a spongy wall structure without macrovoids and a ratio of wall thickness to fibre inner diameter of 1 to 2 to ensure the resistance of the membrane to high pressures. Main parameters of the hollow fibre support spinning are in Table 4.

Table 4
Hollow fibre support spinning parameters

External / internal diameter of the membrane, mm	0.9/0.5
Air gap cm	0
Temperature of the polymer solution, °C	Room
Coagulation bath temperature, °C	55
Coagulation bath composition	20% PEG-400 in deionized water
Temperature of internal coagulant, °C	room
Composition of the internal coagulant	85% DMSO in deionized water
Take-up speed, m/min	7

The absence of macrovoids is the main criterion to achieve the mechanical strength of the membrane. In case of its appearance under pressure, nonselective flow may occur due to formed macrovoids.

The outer selective layer was needed to facilitate the removal of excess amounts of monomers used to form the thin film layer (TFC). In case of using standard ultra- or nanofiltration membranes made of polyethersulfone with an internal selective layer, the entire membrane substrate will be impregnated with these same monomers.

Another goal was to obtain pores on the outer surface of no more than 12 nm in order to ensure the most uniform application of the selective polyamide layer.

The membrane was prepared by wet spinning method without any air gap directly into the coagulation bath. The composition of the coagulation bath was 20% PEG-400/80 water. The composition of the internal coagulant was 85% DMSO/15% water. The addition of PEG-400 to the coagulation bath was necessary to suppress the formation of macrovoids closer to the outer selective layer of the fibre [21]. A high concentration of DMSO in the composition of the internal precipitant provided a high porosity of the inner surface of the membrane substrate not to create additional resistance to the water flow.

The manufactured hollow fibre support had an outer diameter of 1 mm and an inner diameter of 0.5 mm. After the spinning, the resulting membrane was stored for 24 hours in a 0.5% (wt.) sodium hypochlorite solution at room temperature to remove excess PVP from the fibre structure. Further the support was kept in a 15% aqueous glycerol solution for 48 hours and dried at 50°C to prevent collapse of the pores.

The samples used in this work (Figure 5) had visible external pores with a diameter of 8–11 nm, and internal pores with a diameter of 600–900 nm.

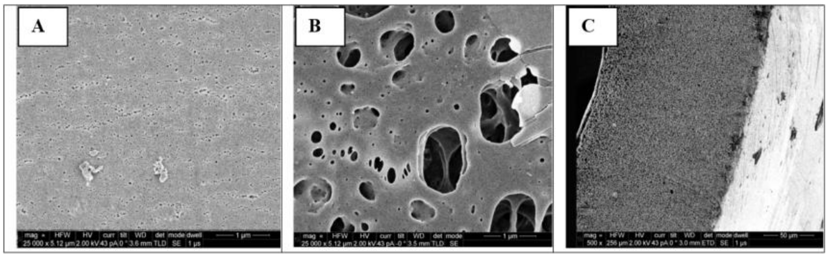

Fig. 5. SEM support surface images: A - outer selective layer, B – inner layer, C – cross-section

3.2 Hollow Fibre Support Characteristics

The hollow fibre membrane support was characterized with SEM, bubble point, full porometry liquid-liquid pore size distribution, and tested for permeability and cutoff for some organic molecules. The results are in Table 5 and Table 6.

Table 5
The support cut-off results

No	Component	M_w, kDa	Rejection, %
1	Bovine serum albumin	66.5	>99.9
2	Myoglobin	18	>99.9
3	Cyanocobalamin	1.36	24.6

The obtained cut-off results correlate with the data on the limiting pore of the membrane support. Large molecules such as albumin and myoglobin do not penetrate into the permeate space, while the cyanocobalamin molecule’s cut off is only partial. The values obtained can be correlated with the characteristics of dialysis membrane from low-flux dialysis to mid-high flux class II and III membranes according to the Japanese classification of dialyzers [22]. This fact confirms that the limiting pore of the hollow fibre membrane is in the range from 4 to 7 nm.

Table 6
The support characteristics

No	Support parameter	Value
1	Permeability, l/m^2*h*bar	22
2	Bubble-point pressure, bar	25
3	Limiting pore size, nm	4.5
4	Selective layer pore size, nm	9.8
5	Inner layer pore size, nm	720

3.3 Polyamide Active Layer Preparation

To apply the polyamide layer, five different aqueous solutions of diamines were prepared (Table 7). Also, TMC 0.11% solution in cyclohexane was produced. According to Hyosung An's *et al.,* recommendations, the weight ratio of TMC and mPDA should be between 1:15 and 1:20 to obtain an optimal polyamide layer [23]. Density of crumples in active polyamide layer is connected with the concentrations of either MPD or TMC. An increase in the concentrations of these components can affect the hollow fibre structure. It can be explained by the MPD diffusion into non-polar solvent and the way it reacts with TMC molecules. To be more specific TMC molecules show low solubility in the water phase and quickly react with MPD into a polyamide film. Thus, the MPD and TMC concentrations were chosen as experimental. However, to increase the permeability of the membrane and make the structure of the selective layer less dense, we proposed adding aliphatic amines. In order not to lose much in selectivity, the concentrations of amines were much lower than mPDA. Increasing the concentration of aliphatic amine above 1% introduced a strong loss of membrane selectivity.

Table 7
The aqueous solution composition

No	Component	Value				
		Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
1	M-phenylenediamine	1.5	1.5	1.5	1.5	2
2	Damo-t	-	-	0.2	0.4	-
3	Jeffamine t-403	0.2	0.4	-	-	-
4	Triethylammonium bromide	0.15	0.15	0.15	0.15	0.15
5	Triethylamine	2.2	2.2	2.2	2.2	2.2
6	Hexamethylphosphoric triamide	1.8	1.8	1.8	1.8	1.8
7	Sulfocamphoric acid	4.2	4.2	4.2	4.2	4.2
8	Sodium dodecyl sulphate	0.15	0.15	0.15	0.15	0.15
9	H20	89.8	89.6	89.8	89.6	89.5

The interfacial polycondensation reaction was carried out on the outer surface of the hollow fibre. Triethylamine is the standard catalyst for the polycondensation reaction of polyamides. The use of tetraethylammonium bromide as a phase transfer catalyst makes it possible to improve the conditions for the formation of an ultrathin polymer selective layer, which additionally contributes to an increase in productivity and selectivity. The common surfactant sodium dodecyl sulphate helps to avoid the collapse of the pores during the drying of the membrane. Hexamethylphosphoric triamide was used as an additional solvent providing a thin continuous polyamide layer [24]. Organic acids such as camphor sulfonic acid (CSA) can improve absorption of the amine solution in the support [25].

Interfacial polycondensation of mPDA (solution 5) with TMC (solution in cyclohexane) yields a cross-linked polyamide.

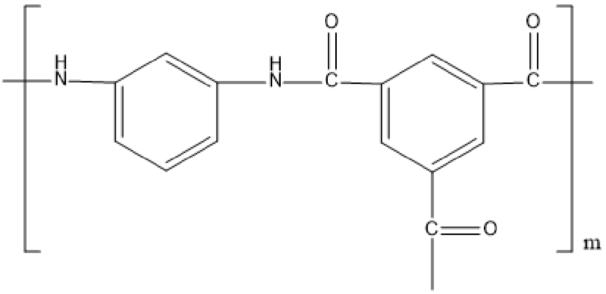

Fig. 6. Polyamide structural formula

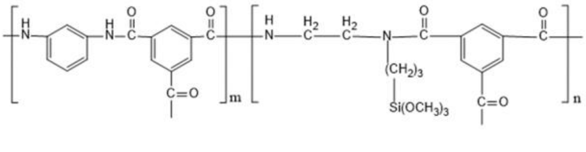

Fig. 7. Copolymer 1 structural formula

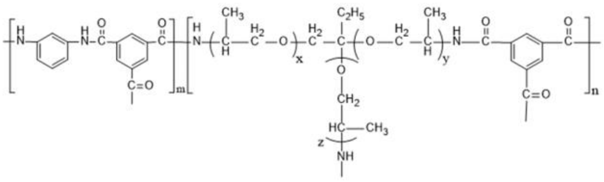

Fig. 8. Copolymer 2 structural formula

Cross-linked copolyamides formed by the interaction of a mixture of mPDA with Damo-T (aqueous solutions 3 and 4) with TMC.

During the reaction of a mixture of mPDA with "Jeffamine T-403" (aqueous solutions 1 and 2) with TMC (solution in cyclohexane), cross-linked copolyimides are formed.

Hollow fibres test samples in the amount of ten, sealed on both sides to prevent the penetration of solutions onto its inner surface, were placed in a diamine solution for 180 seconds. The samples were blown off to remove the excess solution. After that, the samples were placed in the TMC solution for 60 sec. The samples were blown off again and dried for 30 minutes at 70°C. Furthermore, the samples were placed in isopropyl alcohol for 60 minutes. They were dried for 15 minutes at 70°C. Subsequently proceeded to apply the second layer of polyamide. To do it the procedures described above were repeated.

Ramanuja *et al.,* built a mathematical model to describe the buoyancy-driven boundary layer problem which takes place because of the hollow fibre geometry. It considers the fluid flow of a nanofluid past an isothermal horizontal cylinder in the existence of a chemical reaction effect [26].

A control sample 5* was also made based on solution 5. But in this case, the fibre samples were not soaked in alcohol. And the polyamide layer was not reapplied. Both sides of this sample were also sealed to prevent the penetration of solutions onto its inner surface, were placed in a diamine solution for 180 seconds. The samples were blown off to remove the excess solution. After that, the samples were placed in the TMC solution for 60 sec. The samples were blown off again and dried for 30 minutes at 70°C.

All the samples were stored in 15% glycerol solution.

3.4 TFC Membrane Characterization

Prepared samples of the reverse osmosis membrane were characterized by SEM and furthermore water permeability and cutoff were measured. Reverse osmosis water and some organic molecules were used respectively. The membranes were also characterized with a standard sodium chloride rejection test by conductometry.

The permeability of the membrane samples was measured at 25°C and a transmembrane pressure of 10 bar. The cutoff for organic molecules was carried at a transmembrane pressure of 5 bar and a temperature of 25°. RO figures-of-merit of the composite polyamide hollow fibres for the removal of 2,000 ppm dissolved organics at 15 bars after 1 hour of measurement.

The main characteristics of the membrane are shown in Table 8. It’s divided according to the diamine solution used in its manufacturing.

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Table 8
Obtained membrane parameters

No	Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 5*
1	Permeability, l/m^2*h*bar	1.3	1.2	1.5	1.5	0.3	2
2	Rejection, %						
3	Folic acid	>99	>99	>99	>99	>99	>99
4	Glucose	63	70	65	71	75	52,5
5	Creatinine	53	56	55	57	59	35
6	Carbamide	8	10	9	7	9	2
7	NaCl	97.2	98.1	97.1	97.8	98.8	91.5

As shown in Figure 9, the polyamide membranes had a classic irregular structure with heterogeneous “crumples”. The largest size “crumples” is measured in membrane sample 5, which didn’t contain aliphatic diamines. It seemed to happen because more reactive aliphatic diamines prevent active diffusion of mPDA into the organic phase. From the other side the introduction of aliphatic diamines potentially reduces the free volume of the polymer, therefore, the observed decrease in selectivity is not so dramatic [27]. It is obvious that a single layer application of a polyamide layer on a hollow fibre support is not sufficient and leads to defects on its surface. This is indicated by the cut-off values for the control sample 5*. Whereas the two-layer application of polyamide from a composition containing only mPDA without an aliphatic amine led to a sharp drop in membrane permeability. This makes it unattractive for use in water treatment processes.

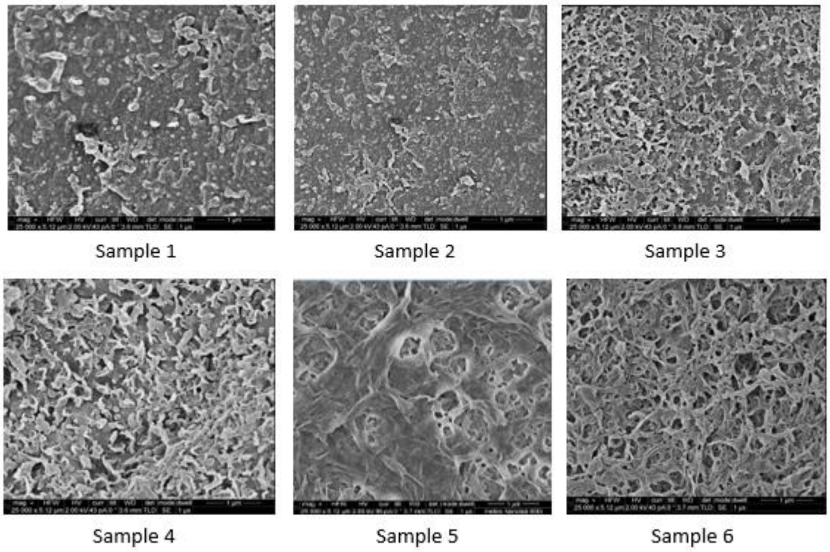
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6

Fig. 9. Selective layer SEM images

It has been noticed from Table 8 that the organic molecules selectivity of reverse osmosis membranes decreases from 99% up to 2% in order of decreasing their molecular weights. While NaCl selectivity of such membranes remains at a fairly high level (91,5 - 98,1) in case of molecular weight of 58,4 Da. This effect occurred because ionized NaCl molecules have a strong hydrate shell of water molecules, the size of which significantly exceeds the size of the salt molecules themselves

Among the samples (1-4) in the selective layer of which an aliphatic diamine was included, the densest structure was observed while using the tertiary amine Jeffamine t-403 (1 and 2), due its high reaction rate with TMC . The use of aliphatic polyamine "Jeffamine T-403" in solutions led to the formation of a selective layer with a uniform curd structure. These membranes performed highest perm selectivity values.

According to the data, polyamide layer obtained from solutions 3 and 4 can be characterized with the most regular alternation of “crumples”. The main component of these solutions is the aminosilane “DAMO-T“ that has surface-active properties and the ability to control pore sizes.

As mentioned earlier control sample 5* had the lowest selectivity values due to the impossibility of defect-free deposition of polyamide in one layer on the hollow fibre. To achieve high values of selectivity, a denser structure of the selective layer is necessary because of the concentric shape of the fibre. In Table 9 comparison with other reverse osmosis membranes is given.

Table 9
Comparison of NaCl retention and permeability

Membrane	NaCl retention, %	Permeability, L/m^2*h*bar	Conditions	References
1.5 mPDA + 0.4 Jeffamine t-403	98.1	1.2	2000 ppm, 15 bar	This work
3.5 PDADMAC/PSS	97.6	0.6	295.5 ppm, 5 bar	8
FilmTech XLE	96.8	2.7	2000 ppm, 25 bar	28
TFC	98.1	8.9	1000 ppm, 10 bar	29
mHKUST-1@PA	97.6	6.94	2000 ppm, 4 bar	30
TFC HF	99.1	0.8	2.000 ppm, 15.5 bar	5
DuPont Permasep BW-L hollow fibre	97.3	0.1	2.000 ppm, 15.5 bar	31

4. Conclusions

Two-layer deposition of polyamide through an isopropyl alcohol soak procedure allowed a defect-free selective layer to be achieved. At the same time, the use of an aliphatic diamine in mPDA did not result in a strong drop in membrane permeability in the case of repeated application, as in the case when the aliphatic diamine was not included in the composition. A breakaway from the standard high "crumpled" reverse osmosis membrane seems to be necessary in the case of hollow fibres. Manufactured membranes had maximum salt recovery 98.1% and permeability 1.2 l/m^2*h*bar. However, the fibre with the selective layer structure achieved in this work showed lower permeability value compared to spiral wound membranes. Nevertheless, the high active surface of the hollow fibre membrane can make it possible to level this factor. Using a hollow fibre membrane module allows to increase the active surface compared to a spiral wound membrane element. Backwashing the hollow fibre membrane elements also gives a huge potential for commercial use of the membranes prepared in this work for brackish water purification.

The approach itself, described in this work, involves the production of a finished composite membrane on a continuous spinning line, without intermediate stages. Forming asymmetric substrate, washing it off excess solvent, drying this fibre, carrying out interfacial polycondensation in order to obtain a selective polyamide layer - all these stages can be organized within a single production line.

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