Effect of solvents on performance of polyethersulfone ultrafiltration membranes:

investigation of metal ion separations

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ABSTRACT

The new polyethersulfone (PES) based ultrafiltration membranes were formed using two stage process of dry and wet phase inversion in non solvent coagulation bath. The effects of three different solvents such as, N-N dimethylformamide (DMF) , N-methyl-2-pyrrolidone (NMP) and Dimethyl sulphoxide (DMSO) of 82.5% and 85% concentrations on the performance of final membranes were extensively investigated. Experimental results proved that PES ultrafiltration membranes with an asymmetric structure were successfully formed which was confirmed by scanning electron microscopy (SEM). The number of pores formed on the top layer of PES membranes using above-mentioned three solvents was the result of the combined effect of the thermodynamic properties of the system (composition, concentrations, phase behaviour) and membrane formation kinetics, whereas, the formation of the macroporous sub layer of those membranes was controlled by the diffusion rate of solvent–nonsolvent. The flux of pure water, membrane resistance, mechanical stability and separation performance of the PES membranes can be varied using different PES concentrations. Separation of metal ions from aqueous solutions was studied for Ni (II), Cu (II) and Cr (III) using two complexing polymer ligands: Polyvinyl alcohol (PVA) and poly(diallyldimethylammonium chloride) (PDDA).The separation and permeate rate (flux) efficiencies of the new membranes are compared using different solvents and different PES/solvents compositions.

Keywords: Ultrafiltration, Polyethersulfone, Solvents, Liquid-phase polymer-based retention, Removal of metal ions.

1. Introduction

Membranes of a various pore structure were formed by dry and wet phase inversion in non solvent coagulation bath, which is the most common method of two layer membrane (asymmetric) formation [1-3]. A thin film of a homogenous polymer casting solutions was deposited on a glass substrate, then evaporation of the solvent took place for a short period of time and then immersion into a nonsolvent coagulation bath was used. Due to the exchange of a solvent from the polymer solution to a nonsolvent in a coagulation bath, phase separation of polymer solution was induced, which resulted in a formation of a polymer-rich and polymer-lean phases. Polyethersulfone (PES) was selected as a membrane material because of its commercial availability, processing ease, favorable selectivity-permeability characteristics, and good mechanical and thermal properties. PES is an amorphous glassy and hydrophilic polymer containing sulfone groups. PES is used in both the formation of flat sheet and hollow fiber membranes. Hwang et al. [4] formed PES asymmetric membranes using a cosolvent system of dichloromethane and NMP as a volatile and nonvolatile solvents, respectively. Chaturvedi et al. [5] focused on the effects of nature of additives, solvents and ambient humidity on membrane performance of PES ultrafiltration (UF) membranes.

Various solvents have been used for the formation of membranes. A proper selection of a solvent plays a vital role in the characteristics of membranes formed. Chakrabarty et al. [6] formed polysolphone asymmetric membranes using NMP and DMAc solvents separately. Chaturvedi et al. [5] studied the effects of nature of solvents, additives and the humidity during casting of membrane on membrane performance. The competition between liquid–liquid demixing and solid–liquid demixing can be understood through the corresponding

thermodynamic and kinetic (mass transfer) aspects of the immersion-precipitation processes [7]. Khan et al. [8] described the synthesis and characterization of low molecular weight cut-off UF membranes from cellulose propionate polymer using dimethyl acetamide solvent (DMAc). Zhao et al. [9] described the formation of membranes with N,N-dimethylaminoethyl methacrylate (DMEMA) and polyethylene glycol methyl ether methyl acrylate (PEGMEMA) and THF as a solvent. Therefore, one of the purposes of this paper is to examine how solvents of different composition influence the final membrane structure evaporation and immersion of solvent into a nonsolvent bath is used.

Many industries including chemical, electronic, metal plating and refining industries face severe problems in the disposal of their waste streams when highly toxic or valuable constituents such as metal ions are present. From these waste streams heavy metals such as Cr(VI), Cr (III), Cu(II), Zn(II), etc., could be separated and concentrated through binding of the target metal ions to water soluble polyelectrolyte and subsequent ultrafiltration of the bound metals from the unbound components [10,11]. Below we investigate the removal of metal ions from aqueous solutions by complexation- ultrafiltration and PES UF membranes are used for this purpose.

The separation of Cu (II) and Ni(II) from Fe(III) ions by complexation with alginic acid using EC-PEG 4000 alloy membrane has been attempted [12]. Mimoune et al.[13] have studied the removal of metal ions Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+} and Ag^+ from synthetic aqueous solutions using poly(vinyl alcohol) as macromolecular complexing agent through PES UF membranes. PDDA is known to form complexes with negatively charged species and, hence, PDDA can be successfully used for the loading of anionic transition metal precursors by electrostatic interaction [14]. Berna et al [15] studied the effect of various water soluble polymer ligand such as PDDA, PVA for the removal of metal ions. Arthanareeswaran used water soluble polymer

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PVA for the separation of chromium ions [16]. Below PES UF membranes have been selected for their ability to remove the PVA and PDDA. The latter water soluble polymers have been chosen as the macromolecular complexing agents for the removal of Ni (II), Cu (II) and Cr (III) metal ions. Hence, the general purpose of the present study is to provide an understanding of the effect of the solvents on the formation of PES membranes, their mechanical stability, and their ability to separate metal ions using polymer ligands.

2. Materials and methods

2.1. Materials

The PES purchased from Solvay process India Ltd, was used without any further treatment. N,N-Dimethyl formamide (DMF), Dimethyl sulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and Sodium lauryl sulphate (SLS) were purchased from Sisco research laboratories (SRL), India. Proteins such as trypsin M.W= 20 kDa, pepsin M.W= 35 kDa, Egg albumin (EA) M.W= 45 kDa were purchased from central drug house, India. Sodium dihydrogen ortho phosphate and disodium hydrogen ortho phosphate were obtained from CDH Chemicals Ltd., India. Copper (II) sulfate and Nickel (II) sulfate were purchased from Fischer, India. Chromium (III) chloride purchased from CDH, India Ltd. Polyvinylalcohol (PVA) was purchased from CDH, India.

2.2. Membrane formation

The casting solution was prepared by dissolving PES in one of the following solvents DMF, DMSO and NMP in a round bottom flask and subjected to constant stirring for 4 h at room

temperature to obtain a homogenous solution. Membranes were formed using phase inversion technique as explained elsewhere [17]. Different concentrations of solvents were used, 85 % and 87.5 %, were mixed with 15 % or 17.5% of PES, respectively, as shown in Table 1. The ratio of PES/solvents studied is labeled as M1, M2, M3, M4, M5 and M6, respectively. The fabricated membranes were washed with distilled water and stored in the 0.1 wt. % formalin solution to avoid microbial attack.

2.3. Experimental procedures

The UF experiments were carried out in a stirred type, dead end cell fitted with Teflon coated magnetic paddle. This experimental setup was purchased from Millipore Ltd, USA (Millipore-XFUF 076-01-Model, USA). The effective membrane area available for ultrafiltration was 38.5 cm^2. This stirring speed was selected (600 rpm) because it could lead to an effective agitation but prevent the formation of a serious vortex in the dead end cell. All the experiments were carried out at 30°C and 345 kPa transmembrane pressure.

2.4. Membrane characterization

2.4.1. Pure water flux (PWF)

The experiments were carried out at a transmembrane pressure of 345 kPa and permeate was collected. The PWF was calculated as follows:

$$J_{w1} = \frac{Q}{\Delta t \times A},$$

(1)

where J_{w1} is the pure water flux (l m^{-2}h^{-1}); Q is the amount of permeate collected (l); Δt is the sampling time (h) and A is the membrane area (m^2).

2.4.2. Membrane hydraulic resistance

The membrane hydraulic resistance is the resistance of the membrane to the feed flow. It is an indication of the tolerance of the membrane towards hydraulic pressure and it was calculated as below:

$$R_m = \frac{\Delta P}{J_w} \quad , \tag{2}$$

where, J_w is the water flux (l m^{-2} h^{-1}); ΔP is the transmembrane pressure (kPa); R_m is the membrane resistance (kPa. l^{-1} m^2 h^1).

2.4.3. Morphological Studies

The membranes were cut into pieces of various sizes, mopped with a filter paper, immersed in liquid nitrogen for few seconds, and then frozen. The samples were mounted on the sample holders and platinum sputtered to provide electrical conductivity to the membranes. The top surface and cross sectional morphology of the membranes was studied using SEM (JEOL JSM-6360).

2.4.4. Mechanical properties

Tensile stress and elongation at break of the membrane were measured using universal testing machine (Instron 4500 model) at a crosshead speed of 10 mm/min. Cross-sectional area of the

sample of known width and thickness was calculated. The membranes were then placed between the grips of the testing machine. The tensile stress values and elongation at break values of the individual membranes were measured. Stress is defined as the force per unit area, normal to the direction of the applied force, and break elongation as the extension per gauge length at break.

2.5. Metal ion separation

Experiments were carried out to separate metal ions from aqueous solutions in the absence of chelating agent using the UF membranes. It was observed that virtually all the metal ions permeated through the membrane. Hence, poly vinyl alcohol and poly (diallyl diammonium chloride) were used to complex with the metal ions. Solutions of Cu (II), Ni (II) and Cr (III) metal ions were formed at a concentration of 1000 ppm in 1 wt% aqueous solution of the chelating agent. The solutions were then thoroughly mixed and allowed to stand for a day for the completion of binding [18]. The pH of those solutions was adjusted to 6 by adding small amount of either 0.1M HCl or 0.1M NaOH. Metal rejection and permeate flux were determined by analyzing the first 20 ml of permeate. Both metal rejection and permeate flux were integrally averaged because the compositions of the retentate and permeate varied with the filtration time. The reproducibility of all concentration measurements was within 2%. The percentage rejection was calculated using the following equation:

$$\% SR = \left(1 - \frac{C_p}{C_f}\right) \times 100, \tag{3}$$

where %SR is the rejection percentage; C_p and C_f are the concentrations of permeate and feed solutions, respectively. The permeate solutions of corresponding membranes were collected in

graduated tubes for a specified time period and were analyzed for the concentration of the metal ions using an atomic absorption spectrophotometer (Perkin-Elmer 3110).

2.5.1. Maximum retention capacity (MRC)

The liquid-phase polymer-based retention (LPR) procedure by concentration method was used to form polymer–metal complexes. According to this method a solution of a fixed concentration of metal ions is filtrated through a solution of water-soluble ligand (25 ml) at a constant volume flow rate. For that purpose a water-soluble polymer ligand and metal ions are placed into an ultrafiltration cell. When metal ions pass through ultrafiltration cell the macromolecules uptake the metal ions was until saturation. Non-retained metal ion are collected and concentration analyzed by atomic absorption spectrophotometer. A background experiment with metal ions without polymer ligand is required to determine the effect of ultrafiltration membrane and polymer ligand on metal ion retention. The amount of metal ions bound to the water-soluble polymer was calculated as a difference between obtained concentration dependency and the background curve. The MRC was calculated as:

$$MRC = \frac{MV}{P_m},\qquad\qquad(4)$$

where MRC is the milligrams of metal ion retained per gram of polymer ligand, M is metal ion concentration (mg/l), V is the filtrate volume (l) and P_m is the mass of the polymer (g).

3. Results and discussions

3.1. Pure water flux (PWF)

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The pure water flux is an important characteristic if a membranes, which is useful for any industrial process. The pure water flux of all membranes from M1 to M6 is shown in Table 1. The membranes formed from DMSO (M2 and M5) as solvent have higher PWF than the membranes formed from other solvents. M1 has the lowest PWF, which was 9 l l.m^{-2}.h^{-1}, only about 20% of that of M5. The selection of solvents plays a vital role in the PWF all membranes tested. Further, the membrane formed with 15 wt% PES has higher PWF. This may be due to a decrease of the thickness of the polymer reach phase. Reminder: a polymer rich phase forms the thin active layer (of higher resistance) of the membrane whereas the solvent rich phase forms the pores of the support membrane layer. The membrane formed with 15% PES and 85% DMSO (M5) has a PWF of 41 l.m^{-2}.h^{-1} whereas the membrane formed with 17.5% PES and 82.5% DMSO (M2) has PWF of 19.6 l.m^{-2}.h^{-1}. The thinnest wall of porous top active layer (see Fig 3(M6)) makes the membrane formed using DMSO as a solvent shows 15 % higher PWF. Thicker walls of porous top active layer (see Fig 3(M4)) result in lower PWF of the membrane formed using the casting solution with NMP.

3.2. Membrane hydraulic resistance (MHR)

MHR was calculated from the inverse of slopes of the corresponding flux versus pressure linear dependences and are shown in Table 1. It is inversely proportional to the pure water flux of the membrane according to Eq. (2). It is evident from MHR values presented in Table 1 MHR decreases as the concentration of the solvent increases from 85 % to 82.5 %. MHR of the membrane M1 is 34.1 kPa.l^{-1}.m^2.h^1 and of the membrane M4 is 16.6 kPa.l^{-1}.m^2.h^1. The membrane formed with DMSO as solvent has less MHR compared to the membrane formed with other solvents.

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3.3. Morphological studies

Figs. 1, 2 and 3 show that the top surface and cross sectional SEM micro photographs of M1,M4, M5 and M6 membranes, which were formed from NMP, DMSO, DMF as solvents of 82.5% and 85 % weight compositions. Figs. 1 and 2 shows that there are pores visibly distributed in the top surface of M1, M4, M5, and M6 membranes. The M5 and M6 membranes have number of top surface pores and the size of these pores markedly bigger than that of M1 and M2 membranes. The process of formation of top surface pores is affected by the thermodynamic properties of a casting solution and kinetics of membrane formation. In a PES/solvent system during the first stage of membrane formation, solvent evaporates (30s) fast and forms an active top layer. During the second stage, in the immersion process, the PES (polymer rich phase) could be considered practically stable, whereas the solvent and nonsolvent diffuse in the gelation bath [19]. Hence, the mutual diffusion rate of the solvent–nonsolvent has a very significant influence on the sub layer formation. A very good correlation was found between the pure water fluxes of all membranes with solvents and the pore formation on surface. Shen et al [20] reported the significance of the solvent–nonsolvent diffusivity for various systems such as NMP, DMAC and DMF. On the other hand, we found that the rate of the phase separation at a higher polymer concentration (17.5% of PES) determines the formation of denser and less porous top surface structures than those obtained at 15% of PES, that is, at a lower polymer concentration. In the membrane formation, the order of the solvent– nonsolvent (water) diffusivity is DMF>NMP>DMSO.

As shown in Fig. 3, the asymmetric structure with top active porous layer and macrovoid porous sublayer is observed in membranes, which are formed using the casting solutions with all

three NMP, DMSO and DMF. The thickness of the top active porous layer of the membrane formed from DMSO is smaller compared to other two solvents. During the evaporation process, polymer molecules orient in the up direction of the film and the evaporate rate becomes slower; the top porous layer develops within 30s of evaporation. After immersing in water bath, the membrane formation rate is faster; the macrovoid pores grow along the direction of polymer molecule orientation. The shape of macrovoid pores in membranes formed from NMP, DMSO and DMF as a solvent indicates that the formation rate of macrovoids in the sublayer of membranes is the highest for NMP and DMF and almost identical. The top active porous thinner layer and big macrovoid pores build the membrane formed from DMSO as solvent at 85 % have a higher water flux and a lower retention of metal ions, which is consistent with the study of Shen et al. [20]..

3.4. Mechanical properties

The mechanical properties (elongation at break and tensile strength) of the PES membranes formed with different solvents in the casting solution are presented in Table 2. The obtained results show that the mechanical properties of PES membranes decreases at addition of solvents (NMP, DMF and NMP) in PES casting solution at 85% and 87.5 % concentrations. As shown in Table 2, the membrane formed with 17.5% PES and 82.5% NMP (M1) as solvent had tensile stress of 2.39 MPa at the max load. The membrane formed with 17.5% PES and 82.5% DMF (M3) as solvent and the membrane formed with 17.5% PES and 82.5% DMSO (M2) as solvent have tensile stress of 2.04 and 1.4 at the max load, respectively. The latter decrease may be due to the decrease in the thickness of the top active porous layer and fast diffusion rate of solvents in

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the polymer matrix. However, an excessive concentration of PES may cause the increase of the tensile stress and mechanical stability, which confirms the pore formation on the membrane top surface. The elongation at the break of membranes formed from 17.5 % PES in presence of NMP, DMSO, DMF solvents was found 2.39, 1.87, 1.09 and mm, respectively. The percentage strain at max load of same composition membranes was 11.46%, 9.36 and 5.47%, respectively. This result shows decreasing in membrane resistance at adding those three solvents. Similar kind of trend is observed in other membranes. Our results shows that the membrane formed from the casting solution with NMP as a solvent has more tensile strength compared to the membranes formed with DMSO and NMP as solvents.

3.8. Metal ion separation

Water-soluble polymers are commercially available as ligand to bind with metal ions. Among the most important technological requirements are the follows: those polymers are the high solubility in water, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest. The most investigated ligands present in the polychelatogens are amines, amides, alcohols, aminoacids, etc. Among them, polymers containing amino groups have been extensively studied by ultrafiltration [21]. Figs. 4 and 5 illustrate the variation of the rejection of different membranes (M1-M6) for the metal ions aqueous solutions containing respectively Cu (II), Ni (II) and Cr (III) using PVA ligand (Fig. 4) and Cu (II),Ni (II) and Cr (III) using PDDA ligand (Fig. 5). The percentage removal of metal ion with PDDA is higher than the PVA ligand. The percentage removal of metal ions in 17.5% PES and 82.5% DMF membrane is higher as compared to other membranes. The percentage removal of Ni, Cu and Cr with PDDA ligand this membrane is 94.52%, 95.46% and 98.13%, respectively. The same metal

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ion removal with PVA ligand is 77.58%, 80.03% and 86.14%, respectively. The functional allyl chloride with dim ethylamine groups is present in PDDA ligands. Therefore, the interaction of the three metal ions with the ligand groups provides a good binding capacity. In the case of PVA small hydroxyl groups are present. The latter provide weaker electrostatic forces and smaller formation of coordinating bonds. Further, Labanda et al [22] studied removal of chromium (III) with polyvinyl alcohol (PVA), polyacrylic acid-comaleic acid (PACM), polyethylenimine (PEI) and ethoxylated polyethylenimine (EPEI) ligands in dead-end ultrafiltration system. They compared four polymer ligands and used UF processes. They concluded that carboxylic groups formed stable bonds while alcohol groups did not interact with metal ions. Fig. 4 shows that M1 (PES/NMP at 17.5/82.5%) had the highest rejection. The difference of the rejections of the M1–M3 for certain solute is not very high. The effect of solvents performances were comparable to polyimide membranes with DMF, NMP, dimethylacetamide and DMSO as solvents which recently reported by Vanherck et al [23].

3.9. Metal permeation rate

There are two important parameters, which determine the membrane performance, degree of separation (i.e. rejection or selectivity), and permeation rate (flux). The permeate rate of the membranes are given in Figs 6 and 7. The membrane formed from 17.5% PES and 82.5% DMSO showed the permeate rate of the nickel, copper and chromium metal ions 9.98 $l.m^{-2}.h^{-1}$, 7.45 $l.m^{-2}.h^{-1}$ and 6.19 $l.m^{-2}.h^{-1}$, respectively. The permeate rate of the nickel ion is higher as compared to the copper and chromium metal ions. In the case of 15% PES and 85% DMSO membrane, the peremate of the nickel, copper and chromium metal ions were noticeably higher.

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Although even lower polymer concentrations might result in an increased flux, a compromise between a high flux and ease of processibility had to be reached: casting solution intrusion into the polymer material and macrovoid asymmetric structure was evident at lower polymer concentrations. The binding capacity of the chelating agent affects the separation performance. In the present investigation two chelating agents were employed (i.e PVA and PDDA). The metal ion permeate rate is higher in the case of PVA ligand, that is, it is is a more efficient complexing agent. Lower rate was achieved using PDDA. The permeate rate of Ni(II) is higher than that of Cu (II) and Cr (III) due to its higher coordination ability with macroligands. The order of permeate rate is Ni (II) > Cu (II) > Cr (III). The metal ions permeate of the membranes formed with NMP as solvent was higher compared to the metal ion permeate rate of the membranes formed with DMF and DMSO as solvents.

3.10. Maximum retention capacity (MRC)

To determine the MRC for PVA and PDDA, the LPR technique using the concentration method was used and the results are shown in Table 3. According to this method the reservoir contains only metal ions at fixed pH and the UF cell contains only PVA and PDDA respectively at the same pH. MRC was evaluated at pH 6 for Ni (II) and Cu (II)–ligand interaction, although pH 3 was chosen for tri-valent metal ion (Cr (III) to avoid metal ion precipitation. MRC values changed from 38.7 to 18.7 mg metal ion/g of PDDA for Ni (II), and Cu (II), respectively for membrane fabricated from PES/DMSO system at 15/85 % composition. This result could be attributed to the presence of different functional groups participating in PDDA polymer–metal ion interaction or to the polymer structure's dependence in aqueous solution. The MRC value of chromium metal ion is 11.1 mg metal ion/g for the PDDA chelating agent in M1 membrane. All

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MRC values are less for the chromium compared to other metal ions. This may be due to tri-valent metal ions precipitate at low concentration used, where MRC values of chromium should be due to the valency of ion and functional groups that interact quickly forming complexes [24]. Recently, Maureir et al. [25] observed maximum retention capacity of Alginic acid for Ag+, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} at different pH.

4. Conclusion

The effects of three solvents, DMF, DMSO and NMP, on the pure water flux, membrane resistance, mechanical stability and morphology of asymmetric PES membranes was investigated. The applicability of the formed membranes for the metal ions separation using two completing polymer ligands was also explored. The effect of PES composition (15% and 17.5 %) in 85 and 82,5 % solvents were studied. The order of the pure water flux of PES membranes with different solvents was in the following order DMSO>NMP>DMF. The structure of the top active porous layer of PES membranes was the result of the combination of the thermodynamic properties of the mixture and membrane formation kinetics, whereas, the structure of macroporous bottom sublayer of PES membranes was determined by the diffusion rate of solvent–nonsolvent. Membrane resistance and mechanical stability decreased with the decrease in PES concentration while increase with the solvents concentration. When NMP used as a solvent in 82.5 % of PES casting solution, the membrane resistance was 34.1 kPa. $l^{-1}.m^2.h^1$, the rate of the membrane resistance declined sharply if NMP at 85 % is used. Heavy metal ions, Ni(II), Cu(II) and Cr(III), were separated using PDDA and PVA polymer ligand at UF through PES membranes. PDDA and PVA showed a high rejection for tri-valent cations Cr (III) and

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lower rejection of divalent cations Ni (II) and Cu (II), probably due to the steric hindrance. MRC indicate that only Ni (II) - PDDA complex is completely soluble in aqueous solution.

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Table 1

Pure water flux and membrane hydraulic resistance of membranes formed in difference

compositions of NMP, DMSO and DMF as solvents

Membrane NO	PES weight ratio (%)	Solvent weight ratio (%)	Solvents	Pure water flux $(l.m^{-2}.h^{-1})^a$	Membrane Hydraulic resistance $(kPa.\ l^{-1}.m^2.h^1)$
M1	17.5	82.5	NMP	9.0 (±0.2)	34.1
M2	17.5	82.5	DMSO	19.6 (± 0.4)	18.5
M3	17.5	82.5	DMF	12.4 (± 0.2)	24.4
M4	15	85	NMP	19.3 (± 0.3)	16.6
M5	15	85	DMSO	41.0 (± 0.5)	10.0
M6	15	85	DMF	26.4 (±0.2)	12.3

[a] Values in parentheses are standard errors.

Table 2

Mechanical properties of the PES membranes in difference compositions of NMP, DMSO and DMF as solvents

Membrane No	Elongation at break (mm)	Tensile stress (MPa)	% Strain at max load (%)
M1	2.39	2.42	11.46
M2	1.87	1.40	9.36
M3	1.09	2.04	5.47
M4	1.50	0.56	7.52
M5	0.89	0.49	4.49
M6	0.87	0.72	4.36

Table 3

Maximum retention capacity (MRC) of the PDDA and PVA for Ni (II), Cu (II) and Cr (III) metal

ions through PES membranes formed from solvents

Membrane No.	MRC (mg metal ion/g polymer ligand)					
	PDDA			PVA		
	NI (II)	Cu (II)	Cr (III)	Ni (II)	Cu (II)	Cr (III)
M1	34.5	15.2	11.4	10.6	8.5	6.2
M2	24.5	11.3	8.9	11.2	9.1	8.6
M3	30.4	15.2	10	12.9	8.6	6.3
M4	25.0	12.4	7.1	8.9	8.0	6.7
M5	38.0	18.7	12.7	13.5	11.0	4.0
M6	32.0	10.2	11.4	12.4	9.8	8.6

Figure legends

Fig. 1: SEM photographs of the top surface of membranes formed from 82.5 (M1) and 85% (M4) of NMP in 17.5 and 15% of PES respectively, magnification 1,000.

Fig. 2: SEM photographs of the top surface of membranes formed from 85% of DMSO (M5) and DMF (M6) as solvents in 15 % PES polymer, magnification 1,000

Fig. 3: SEM photographs of the cross sectional view of membranes from 85% of NMP (M4), DMSO (M5) and DMF (M6) as solvents in 15% of PES polymer, magnification 500

Fig. 4: Solvents effect and solvents composition in PES membranes on rejection of Cu (II), Ni (II) and Cr (III) metal ions with PVA microligand.

Fig. 5: Solvents effect and solvents composition in PES membranes on rejection of Cu (II), Ni (II) and Cr (III) metal ions with PDDA microligand.

Fig. 6: Solvents effect and solvents composition in PES membranes on permeate rate (flux) of Cu (II), Ni (II) and Cr (III) metal ions with PVA microligand.

Fig. 7: Solvents effect and solvents composition in PES membranes on permeate rate (flux) of Cu (II), Ni (II) and Cr (III) metal ions with PDDA microligand.
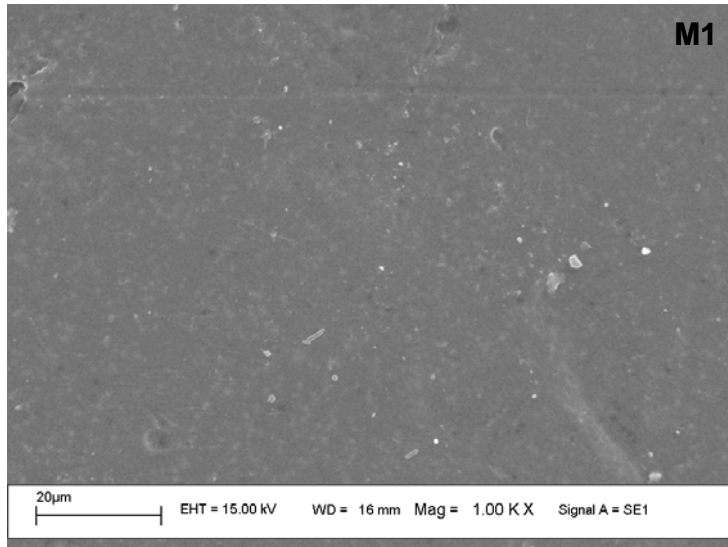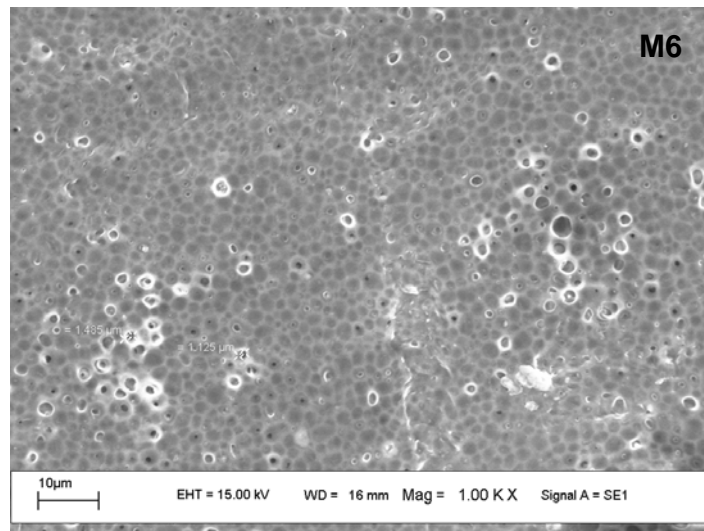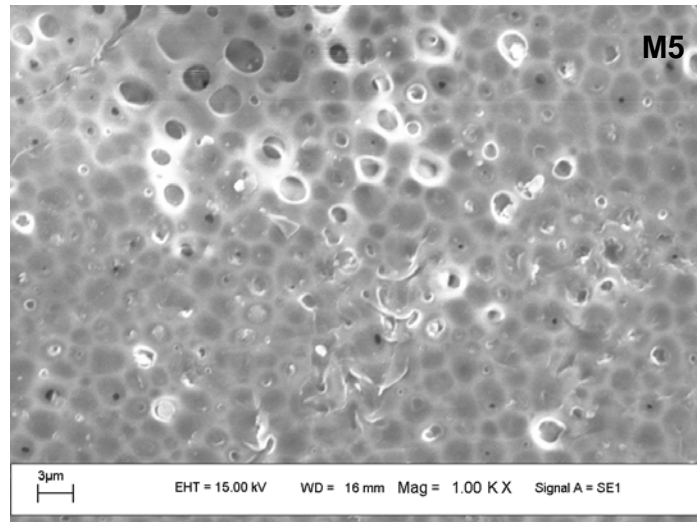
Fig. 1

Fig. 2

Fig. 3

Active layer thickness

active layer thickness **M5**

macrovoid porous sublayer

active layer thickness **M6**

Fig. 4

Fig. 5

Fig. 6

Fig. 7