Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.934738

56 (2015) 366–378
October

Modification of polyethersulfone using sericin and polyvinylpyrrolidone for cadmium ion removal by polyelectrolyte-enhanced ultrafiltration

Y. Lukka Thuyavan[a], N. Anantharaman[a], G. Arthanareeswaran[a,*], A.F. Ismail[b]

[a]*Department of Chemical Engineering, Membrane Research Laboratory, National Institute of Technology, Tiruchirappalli 620 015, India, Tel. +91 431 2503118; Fax: +91 431 2500133; email: arthanaree10@yahoo.com (G. Arthanareeswaran)*
[b]*Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*

Received 4 March 2014; Accepted 8 June 2014

ABSTRACT

The present study deals with the synthesis of polyethersulfone (PES)-based membrane using a biopolymer sericin and polyvinylpyrrolidone (PVP) by phase inversion process. The synthesized membranes were characterized for hydrophilicity, pure water permeability (PWP), membrane stability, and surface functional group analysis. The synthesized membranes were used to study the effective removal of cadmium ions using poly(diallyldimethylammoniumchloride) and polyethyleneimine (PEI) by polyelectrolyte-enhanced ultrafiltration. PVP-sericin-incorporated PES membrane resulted in the highest average pore radius (22 nm) and PWP ($34.11\,\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$). It also showed that higher antifouling resistance of 10 folds than neat PES membrane retained the higher flux rate. Overall, PES/sericin/PVP membrane has better characteristics, and maximum percentage of cadmium removal was obtained when added with PEI ligand.

Keywords: Membrane modification; Polyvinylpyrrolidone and sericin; Hydrophilicity; Cadmium ion removal; Maximum retention capacity

1. Introduction

Polyethersulfone (PES) is a commercial membrane material which has an extensive application in various industrial processes owing to their excellent chemical, thermal, and mechanical stabilities. The main inherent drawback of PES membrane is its hydrophobic nature, which leads to the adsorption of solute particles resulting in the fouling on the membrane surface [1,2]. This in turn reduces the flux and membrane performance [3]. Membrane modifications have major influence on prerequisite properties for separation processes such as minimize fouling, enhance hydrophilicity, stability, and permeability. The modification in PES membranes is achieved through methods like coating, grafting, physical blending, and interfacial polymerization by modifying the surface [4,5]. Most of the membranes were prepared by blending/mixing with additives for enhancing hydrophilicity and permeability. The additives can easily alter the pore structure in such a way that it is compatible with the polymer [6]. Other methods used to modify the membranes are very expensive and require harsh conditions like acidic/alkaline conditions [7,8]. Hence, the blending method is appropriate to form uniform structure and easy to synthesize.

Polyethyleneglycol and polyvinylpyrrolidone (PVP), the hydrophilic water-soluble additives, are

---

*Corresponding author.

preferred greatly in altering the membrane morphology by physical blending methods. PVP, apart from being an excellent swelling and pore-forming agent, also improves the membrane hydrophilicity. Such properties enhance the flux and antifouling behavior which widely improves water treatment and biomolecule purification [9–13]. Al Malek et al. [14] studied the effect of PVP on PES at different concentrations. An improvement of pure water permeability (PWP) was also observed with increase in PVP concentration from zero to 15 wt.%. Hydrophilic PVP has the characteristics of dissolving in water (non-solvent) under phase inversion process which aids in the formation of micropores on the membrane surface. However, a further increase in concentration of PVP on casting dope solution results in the formation of denser structure which leads ultimately to a reduction of water permeability [11]. Hence, in order to improve the porosity of the membrane surface, trace quantity of PVP can be added in the PES polymer matrix [15].

Of late, sericin, a hydrophilic globular protein, is being used as a modifier for polymers. Sericin improves hydrophilicity, biocompatibility, UV resistance, and antioxidant and antimicrobial properties. For these reasons, they are used in the fields of biomedical engineering and cosmetics industries. Sericin possesses a structure constituted by 18 amino acids. It is rich in serine and aspartic amino acid residues. These amino acids consist of polar groups such as hydroxyl, carboxylic, and amino groups [16,17]. Ahn et al. [18] observed that sericin has good miscibility with polymers like polyacrylic acid (PAA) which forms protein–polymer complexes that are used in drug delivery applications. They are interconnected through the hydrogen bonding between the hydroxyl group of serine and carboxyl group of PAA. Moreover, permeability and hydrophilicity of polyvinyl alcohol membrane can be improved using sericin as a modifier. Sericin, being a good swelling agent, cross-links with dimethylthiourea and the resulting membrane can be used in ethanol and water separation [19]. In earlier work, modification of polymers using PVP was studied widely [11,13,15], however, modification of polymers using of sericin and synergic effects of sericin and PVP on polymers are limited. Hence, an attempt for modification of PES using sericin and sericin/PVP was intended to enhance the performance of PES membrane. Moreover, antifouling efficiency was evaluated in cadmium ion removal using polyelectrolyte-enhanced ultrafiltration (PEUF) process.

Cadmium has profound detrimental effects on human beings. This toxic substance causes cancer, weakening of bones, damages in kidney and liver, etc. Common sources of cadmium pollutants include industrial effluents (zinc smelters, paint sludge), discarded batteries, and increasing e-wastes [20]. The prescribed limit for cadmium in potable water as directed by the World Health Organization is $0.005\,\mathrm{mg\,L^{-1}}$. Existing techniques employed in removal of cadmium includes chemical precipitation, adsorption, electrochemical treatment, ion exchange, and reverse osmosis [21,22].

High-pressure operations like nanofiltration and reverse osmosis are currently used in the removal of metal ions and salts. PEUF promises to be a cheap low-pressure alternative in removing metal ions from aqueous solutions. PEUF is extensively used in the removal of metal ions like Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+}. Polymers used in PEUF should ensure high charge density, high molecular mass, and low toxicity and binding capacity [23–25]. Canizares et al. [23] obtained a cadmium rejection of 98% using PAA as binding agent. Ennigrou et al. [26] reported the removal of cadmium using poly(ammonium acrylate)-enhanced ultrafiltration through polysulfone membrane. It was also observed that an increase in poly(ammonium acrylate) ligand concentration resulted in dominant concentration polarization. Li et al. [27] also investigated PEUF methods for the removal of cadmium using polyethyleneimine (PEI) as coupling agent. In addition, the use of various organic ligands for cadmium ions removal with PEI was also studied. In this study, water-soluble cationic polymers such as PEI and poly(diallyldimethylammoniumchloride) (PDDA) were chosen as macroligand for the removal of cadmium ion through PEUF method. Thus, the obtained enlarged macroligand–metal ion complex aids in separation of cadmium molecule through ultrafiltration by retention on the membrane surface. Cadmium ion retention over the synthesized membranes were compared for the macroligands.

Based on the literature, the present study focuses on effect of sericin and PVP on PES membrane formation by phase inversion process. It also evaluates the synergetic mechanism of sericin and PVP on pore formation of PES membranes. Membrane properties like hydrophilicity, membrane morphology, mechanical and thermal stability of neat PES, PES/sericin, PES/PVP, and PES/sericin/PVP are compared. Also, cadmium ion removal using PEUF was investigated. Further, using enrichment method, maximum retention capacity and antifouling property of modified PES membranes for PDDA–cadmium complex and PEI–cadmium complex were also compared.

2. Materials and methods

2.1. Materials

PES Grade 3000P was purchased in powder form from M/s. Solvay Process India Ltd. Model proteins of bovine serum albumin (BSA) (66.5 kDa) was supplied by M/s. Merck Chemical India Ltd. Egg albumin (44 kDa) and lysozyme (17 kDa) were procured from M/s. Alfa Aesar, USA. PVP (K30) (MW: 40 kDa) and cadmium sulfate were from M/s. CDH Laboratory Reagent, India. Sericin protein was obtained from M/s. Chinese Commercial Manufacturers, Levochem Technologies Co., Ltd. N,N-dimethylformamide (DMF), sodium dihydrogen phosphate, disodium hydrogen phosphate, hydrochloric acid, sodium dodecyl sulfate (SDS), and sodium hydroxide were bought from M/s. Merck Chemical India Ltd. All the experiments were carried out using double-distilled water. PEI (60,000 Da) and PDDA (400–500,000 Da) were procured from M/s. Alfa Aesar, USA and M/s. Aldrich Chemical Co., (Milwaukee, WI), respectively.

2.2. Membrane preparation

2.2.1. Effect of sericin on PES membrane preparation

Sericin is a biopolymer having properties of hydrophilicity, swelling agent, resilent material, and also used as an organic additive. Serine, a functional compound present in the sericin, helps in bonding of sericin with organic polymer such as PES and PVP and the interactions between them are well illustrated in Fig. 1. Such interactions aid for the better performance of the membrane. Hence in this work, sericin is chosen as a modifier to evaluate the performance of PES membrane. Total polymer casting solution constitutes 17.5 wt.% of PES along with varying compositions of sericin and PVP which are dissolved in DMF and membrane was synthesized using phase inversion process. Dope solution is mixed by constant mechanical stirring at 60˚C for a time period of 3–4 h. This homogenized solution is cast on a glass plate using a thin film applicator which is set to a thickness of 400 μm. An idle time of 30 s for the thin film on the glass plate, allows partial solvent evaporation under room temperature. Subsequently, it is immersed in cold water bath maintained at 10˚C for a period of 12 h. The additive compositions of membranes and corresponding membrane labels are provided in Table 1.

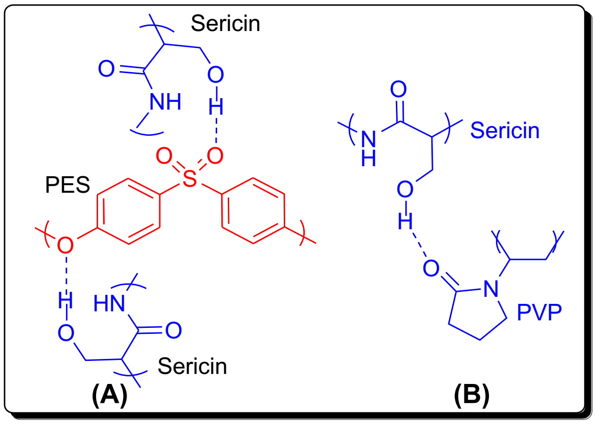

Fig. 1. Schematic illustration of (A) PES/sericin and (B) PVP/sericin binding.

2.3. Membrane characterization

Hydrophilicity is measured using contact angle measurement. Contact angle is determined by sessile drop method using goniometer (model 250-F1 Rame Hart Instruments, Succasunna, NJ). About 5 μL drop of water are injected on a dry membrane surface at five different locations through a microsyringe. The average of contact angle value was measured from the individual droplets in the five regions which determine the hydrophilicity of membrane. Any presence of chemical functional groups over the membrane surface was identified using attenuated-total-reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Thermo Scientific Nicolet iS5 FTIR spectrometer). The spectra for all the dried membrane samples, PVP, and sericin are observed in the wavelength range of 4,000–550 cm^{-1}. Cross-sectional morphology of the membranes are observed using SEM (JEOL JSM-5600 SEM) at 15 kV. Membrane samples are coated with platinum powder on the surface. Thermal stability is observed using thermal analyzer (model SDT 2000, New Castle, DE). Thermal analysis-based membrane characterization is executed under a temperature range of 25–600˚C gradually ramped at a rate of 10˚C per minute in a nitrogen-controlled atmosphere. To test the maximum tensile stress, the membrane under test is cut into two dumb bell-shaped pieces. For performing this analysis, ASTM D412 standard method was followed using uni-axial mechanical testing machine (Instron, Canton, MA).

2.4. Porosity and average pore radius

To measure pore size and porosity, small pieces of membrane are mopped with filter paper. These wet membranes are then dried in an oven at a temperature of 60˚C for 24 h. The porosity (ε) is calculated from the wet and dry weights of the membrane using following Eq. (1) [28].

Table 1
Composition and contact angle, PWP analysis of synthesized membranes

Membrane type	Polymer composition (17.5 wt.%)* PES	PVP	Sericin	Contact angle measurement (°)	Pore radius (nm)	Water permeability ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)
M1	100	–	–	69.05	5.25	1.00
M2	95	5	–	64.70	7.02	3.08
M3	90	10	–	54.00	19.2	24.82
M4	95	–	5	52.50	18.9	17.83
M5	90	–	10	57.70	15.5	13.25
M6	90	5	5	48.75	22.2	34.11

*DMF is used as solvent at 82.5 wt.% for all polymer compositions.

$$\varepsilon = \left(\frac{(\omega_1 - \omega_2)/d_w}{(\omega_1 - \omega_2)/d_w + (\omega_2/d_p)} \right) \quad (1)$$

where ω_1 is the wet weight of membrane (g) and ω_2 is the dry weight of membrane (g). Density of the water (d_w) and polymer (d_p) are 0.998 and 1.37 g/cm^3, respectively.

The average pore radius of the membrane is determined using the Guerout–Elford–Ferry Eq. (2) [28].

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8Ql\eta}{\varepsilon \times A \times \Delta P}} \quad (2)$$

where Q the flow rate of the permeate (m^3/s), A the effective cross-sectional area of the membrane, ΔP the transmembrane pressure (Pa), η the dynamic viscosity of the water (Pa s), and l is the thickness of the membrane (m).

2.5. Water permeability studies

Synthesized membranes are compacted up to reach steady flux at a transmembrane pressure of 400 kPa using dead end stirred cell ultrafiltration membrane module. In this study, a dead end stirred cell ultrafiltration module (Ultrafiltration cell-S76-400-Model, Spectrum USA) with a compressor is used for all the experiment runs. Pure water flux of membranes is measured by varying the transmembrane pressure from 100 to 400 kPa. Water flux (J_w) is calculated using the following Eq. (3):

$$J_w = \frac{Q}{A} \quad (3)$$

Slope of the plot between pure water flux and transmembrane pressure measures the membrane permeability (L_p).

$$L_P = \frac{J_W}{\Delta p} \quad (4)$$

The obtained modified Guerout–Elford–Ferry equation derived from Eqs. (2)–(4) is presented below

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8L_P l\eta}{\varepsilon}} \quad (5)$$

2.6. Ultrafiltration experiments

2.6.1. Protein rejection analysis

Characterization of the membrane is performed using model proteins such as lysozyme, BSA, and egg albumin at a 0.3 g/L concentration. Protein solutions are dissolved in 0.05 M phosphate buffer at pH 7. Ultrafiltration experiments using model proteins such as BSA (66 kDa), egg albumin (44 kDa), and lysozyme (17 kDa) are carried out under a transmembrane pressure of 400 kPa. Stirrer speed is maintained at 500 rpm mainly to avoid build up of solutes on the membrane surface. UV–visible spectrophotometer quantifies the concentration of proteins in permeate (C_p) and retentate (C_r) sample at 280 nm. The percentage rejection is calculated using the following Eq. (6):

$$\text{Rejection } (\%) = \left(1 - \left(\frac{C_p}{C_r}\right)\right) \times 100 \quad (6)$$

2.6.2. Cadmium removal

Characterized ultrafiltration membranes are used in the study of cadmium ions removal using PEUF with water-soluble ligands such as PDDA and PEI at pH 7. Transmembrane pressure was varied from 100 to 400 kPa for a concentration of 50 mg L^{-1} cadmium under different concentrations of 0.5 and 1.0% macroligands (PDDA and PEI). For every experimental run, initial water flux ($J_{\rm iw}$) was measured at the transmembrane pressure of 400 kPa and then the feed solution was tested on to the ultrafiltration unit for 2 h. Again, the water flux ($J_{\rm fw}$) was measured at constant operating conditions. Then, the membrane was cleaned by passing 0.2% SDS solution at the transmembrane pressure of 400 kPa for 45 min. In order to remove the traces of SDS, water was flowed through the membrane. Finally, the ultrafiltration module was dismantled and membrane was stored in container.

2.6.3. Fouling analysis

Flux declines in the membrane separation process is mainly because of fouling and concentration polarization. Fouling is a combination of reversible fouling which occurs due to concentration polarization or gel layer formation whereas irreversible fouling is the pore blocking of solutes through the physical and chemical interactions of solutes in membranes. Cadmium removal by macroligands of different concentrations was analyzed for fouling and concentration polarization studies using the resistance in series model approach by the following Eq. (7) [26,29].

$$J_w = \left[\frac{\Delta P}{\eta(R_m + R_f)}\right] \tag{7}$$

where J_w is the solvent permeate flux, η is the viscosity of the permeate solution, ΔP is the transmembrane pressure, R_m is the intrinsic membrane resistance, and R_f is the fouling resistance. By introducing one more resistance factor, $R_{\rm cp}$ is the polarizable layer resistance, the Eq. (7) can be rewritten as

$$J_w = \left[\frac{\Delta P}{\eta(R_m + R_f + R_{\rm cp})}\right] \tag{8}$$

$$R_m = \frac{\Delta P}{\eta J_{\rm iw}} = \frac{1}{\eta L_p} \tag{9}$$

$$R_m + R_f = \frac{\Delta P}{\eta J_{\rm fw}} \tag{10}$$

$$R_m + R_f + R_{\rm cp} = \frac{\Delta P - \sigma\Delta\Pi}{\eta J_v} \tag{11}$$

where J_v is the feed flux, σ is the reflection coefficient, and $\Delta\Pi$ is the osmotic pressure which is assumed to be negligible. The resistance resulting from fouling can be calculated from the initial water ($J_{\rm iw}$) and final water flux ($J_{\rm fw}$). Similarly, resistance owing to concentration polarization was estimated using the above Eq. (11).

To determine the maximum retention capacity (C) of metal ions macroligand complex on the membranes were calculated for two different concentrations of ligands at the transmembrane pressure of 400 kPa for 2 h. The calculation based on enrichment method can be given by Eq. (12) [30].

$$C = \left(\frac{MV}{P_m}\right) \tag{12}$$

where M is the initial concentration of cadmium (mg L^{-1}), V is the total permeate volume collected in 120 min, and P_m is the amount of macroligands (g).

The enrichment factor binding efficiency (E) of polymer with metal ions can be obtained from the calculated maximum retention capacity. It can be expressed as

$$E = \frac{PC}{M} \tag{13}$$

where P is the concentration of macroligands (g/L). The concentration of cadmium in permeate and retentate were analyzed using atomic absorption spectrometer (Perkin-Elmer precisely, Analyst 4000). Thus, cadmium rejection can be calculated using Eq. (6).

3. Results and discussions

3.1. Membrane characterization

3.1.1. FTIR analysis

FTIR spectra for neat PES and modified PES membranes are shown in Figs. 2 and 3. The spectral bands of neat PES membrane (M1) were observed in 1,151 and 1,238 cm^{-1} which correspond to the sulfone group ($S{=}O_2$) and aromatic ether band. In addition, C=C stretching at 1,485 and 1,577 cm^{-1} of aromatic benzene ring band was also obtained in the ATR spectra. A similar pattern for the PES membranes was also observed by other researchers [8,31,32]. The new spectral wavelength of 1,655 cm^{-1} belonging to primary amide bond was noted in PVP-modified membrane (M3). The higher peak intensity of C–O bond was viewed at 1,105 cm^{-1} in all the additive-modified PES membranes. Addition of 10 wt.% sericin-modified membrane (M5), showed two distinct peaks of one similar primary amide bond and other bands at the

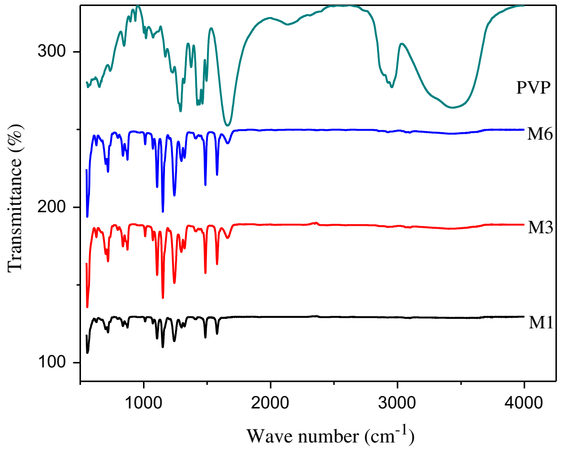

Fig. 2. FTIR-ATR spectra bands for neat PES, PES (90%)/PVP (10%), and PES (90%)/sericin (5%)/PVP (5%) membrane.

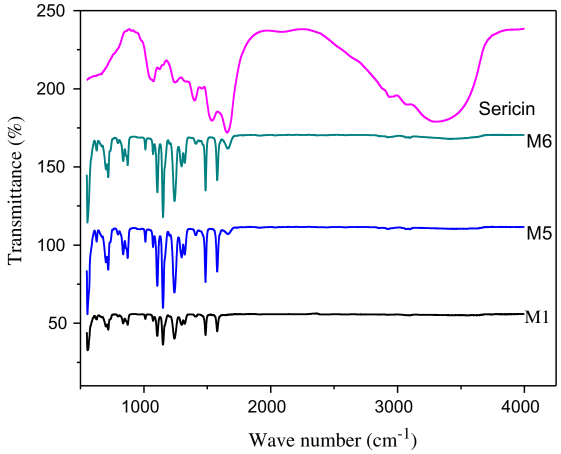

Fig. 3. FTIR-ATR spectra bands for neat PES, PES (90%)/sericin (10%), and PES (90%)/PVP (5%)/sericin (5%) membrane.

intensity of wavelength around 718 cm^{-1} which corresponds to primary amide V group [17]. These spectral band results clearly indicated the presence of PVP and sericin in PES membrane matrix.

3.1.2. *Effect of additives on porosity and average pore radius*

Average pore radius of the membranes are listed in Table 1. Neat PES membrane (M1) has the lowest average pore radius of 5.25 nm. This was mainly due to the dense porous structural arrangement. It was observed that the loading of PVP from 5 to 10 wt.% on a PES dope solution has resulted in the increase of average pore radius from 7.0 to 19.2 nm. PVP in dope solution alters the exchange rate of solvent from the PES polymer into non-solvent water bath during membrane formation. Further, membrane with 5 wt.% sericin, vastly affects porosity and average pore size of 18.9 nm. It is interesting to note that addition of 10 wt.% sericin has decreased the pore radius to 15.5 nm. Highest average pore size of 22.2 of nm was observed for 90/5/5 wt.% of PES/sericin/PVP combinations. It is certain that PVP and sericin addition to the casting dope solution has resulted in the formation of loose membrane matrix enhancing porosity and pore sizes.

3.1.3. *Effect of additives on mechanical properties of the membranes*

The tensile stress of neat PES and modified membranes are shown in Table 2. The maximum tensile stress of neat PES membrane is 8.68 MPa. It decreases to 4.11 and 4.35 MPa, respectively, upon addition of 5 and 10 wt.% of PVP in PES dope solution. The decrease in tensile strength was attributed to the formation of macrovoids in the PES matrix [14]. It was found that sericin-incorporated membranes showed the highest maximum tensile stress. It was mainly because of silk sericin, which has the arrangement of β sheets in its structure. The sericin moiety encompasses amino acids which provide higher mechanical stiffness. As reported by Dash et al. [17] silk sericin improved the tensile strength. Furthermore, tensile stress decreased to 7.54 MPa on addition of PVP (5 wt.%) and sericin (5 wt.%) in PES (90 wt.%) membrane (M6). It clearly indicated that the addition of PVP reduces the mechanical strength on membranes.

3.1.4. *Effect of additives on thermal properties of the membranes*

It is well known that glass transition temperature (T_g) is one of the most important measurements for the miscibility of blend components [33]. PES/PVP membranes had a faster decomposition rate than the neat PES and PES/sericin membranes which are shown in Fig. 4. The glass transition temperatures (T_g) for membranes are presented in Table 2. 10 wt.% of sericin-modified PES membrane (M5), had the higher thermally stability up to a temperature of 460℃ (T_d). It was attributed to the absorption of heat by sericin causing the delay in decomposition of membrane. In the case of 10 wt.% PVP on PES membrane (M3), weight loss percentage was decreased to 403℃ when compared to a neat PES membrane. A marginal shift in T_g value was varied for additive-incorporated PES

Table 2
Effects of mechanical and thermal properties for the additive-modified and unmodified PES UF membranes

Membrane type	Tensile strength (MPa)	Decomposition temperature (T_d, ℃)	Glass transition temperature (T_g, ℃)
M1	8.68	450	231
M2	4.11	410	232
M3	4.35	403	235
M4	10.31	452	239
M5	10.76	460	230
M6	7.54	425	225

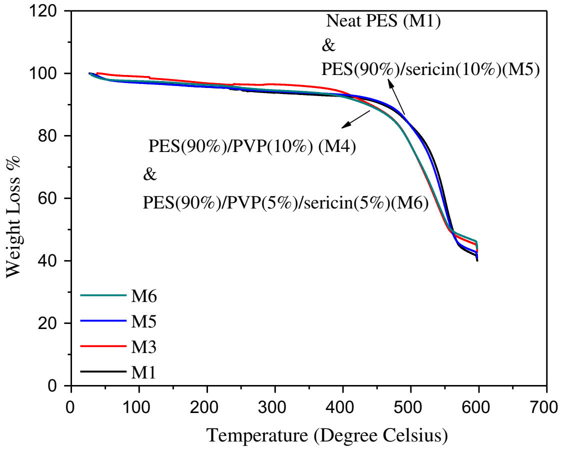

Fig. 4. TGA pattern for the modified and neat PES membrane.

membranes when compared to neat PES membrane. It is due to the effect of interaction of additives with PES. In addition, sericin has enriched amount of serine which has the stronger interaction with the PES through the sulfone and ether linkage. This polymer chain forms porous membrane matrix. However, thermal stability of membrane decreases with the addition of mixed additives (PVP and sericin) in PES membrane (M6). Therefore, thermogravimetric results of membranes ensured that membrane morphology was altered by the addition of additives.

3.1.5. Effect of additives on hydrophilicity and permeability of membranes

Table 1 illustrates the results of PWP, and hydrophilicity of neat PES and modified PES membranes. Neat PES membrane has a maximum contact angle of 69° due to its hydrophobic nature. Contact angle value was decreased to 54° for 10 wt.% PVP-added PES membrane (M3). This suggested that the contact of water molecules on membrane surface was enhanced by the incorporation of PVP on PES membrane matrix through polar amide group. It allows water molecules to flow through the membrane pores owing to capillary forces [34]. In the case of 5 wt.% sericin, contact angle was observed as 52°. The existence of various polar function groups like hydroxyl, amino, and carboxylic groups in sericin makes the hydrogen bonding and attraction to water molecules possible. The highest reduction in contact angle to 48.75° was observed for the PVP- (5 wt.%) and sericin (5 wt.%)-modified PES (90 wt.%) membrane (M6). It is clear that higher hydrophilicity was observed for the combination of both PVP- and sericin-modified membranes.

From Fig. 5, the permeability of membrane increases from 3.08 to 24.82 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ for 5 to 10 wt.% increase in PVP. It confirms that the addition of PVP influences the formation of porous structure on the surface of membrane. The loose porous structure on the membrane matrix helps in enhancing the flow of water inside the PES matrix. A similar trend was observed with the change in PVP concentration from 0 to 15 wt.% on PES ultrafiltration membranes [14]. However, PWP of neat PES membrane is 1.0 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$. In the case of sericin, 5 wt.% loaded membrane (M4) showed 17.83 and 13.25 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ for 10 wt.% membrane (M5). Overall, maximum permeability was obtained for the mixed additives-modified PES membrane (M6) which was 34 folds higher than that of the neat PES membrane. Both PVP and sericin increase the viscosity of PES dope solution which resulted in DMF-exchange rate during phase inversion process. It is mainly due to: (i) PVP increases the thermodynamic instability of the cast film because of non-solvent property and so it causes instantaneous demixing in the coagulation bath [11]; (ii) PVP and sericin increase viscosity of the cast film due to inter and intramolecular entanglements of the polymer chains; and (iii) the presence of both in cast film speeds up the diffusional exchange rate of solvent (DMF) and non-solvent (water) during solidification process and consequently encourages in the formation of pore radius of higher

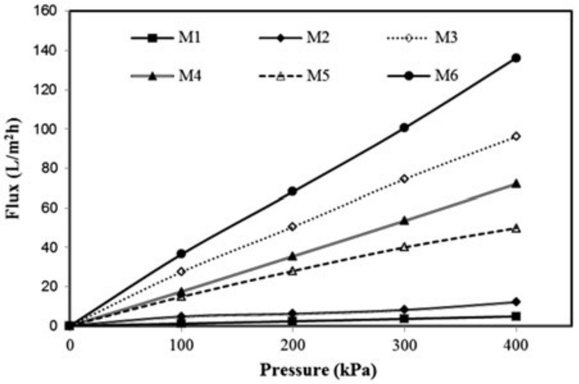

Fig. 5. Effect of transmembrane pressure on pure water flux analysis in neat and modified PES membrane.

magnitude [10]. Hence, adding hydrophilic additives, to the casting solution has a dual effect on the membrane morphology. The average pore radius, FTIR, and contact angle measurement values were also supported with the results of PWP. These result concluded that synergetic effect of both additives favours to increase in hydrophilicity and PWP of PES membranes.

3.2. Membrane morphology

The cross-sectional view of neat and modified PES membrane is shown in Fig. 6(a)–(d). It is well known that the skin layer and porous sublayer in the membrane determine the water permeation rate and separation factor [35]. The thick and dense asymmetric structures were observed on neat PES membrane (Fig. 6(a)). Such morphology was responsible for the lower pore radius and membrane permeability. In case of modified PES membrane, interconnection between skin top layer and substructure (bottom layer) were improved and shown in Fig. 6(b)–(d). The phenomenon mainly occurs due to increase in exchange rate of solvent and non-solvent rates. Finger-like substructures and thin skin layer were clearly observed in Fig. 6(b) with the addition of 10 wt.% of PVP. So, the permeability and pore radius were increased. Macrovoids were decreased with the loading of both PVP and sericin. It is mainly due to synergetic effect of both PVP and sericin which increases the volatility of the casting solution. As the hydrophobic PES has lower affinity in non-solvent (water) than the hydrophilic PVP/sericin, it shows higher tendency for the PES to move towards the solution (water)–air interface during immersion in the coagulation bath [36]. Moreover, extended porous sublayer for permeation was noticed on the mixed additive-modified membranes.

3.3. Protein rejection analysis

As shown in Fig. 7, M1 membrane showed highest rejection compared to modified membranes. Rejection of lysozyme in the neat PES is around 93%. These results clearly revealed that the neat PES membrane had lower porosity and hence, the protein molecules are not able to pass through the pores. BSA holds the highest rejection in all the membranes due to higher molecular weight. Next to that, egg albumin has higher rejection. Low molecular weight lysozyme has lesser rejection of 48% in the 5 wt.% PVP-modified PES membrane (M3) while in M3 and M5, the rejection was 68 and 58%, respectively. Similar effects of protein rejection with the incorporation of PVP on various polymers were also observed [37]. Moreover, additives enhanced the transport of protein molecules in the membrane. These results agreed quite well with the contact angle value of membranes. Finally, PVP- and sericin-incorporated PES membrane (M6) combination showed lowest rejection of 42%. The reason for reduction in the rejection was due to increase in pore size on membrane surface. Rejection data clearly indicate that sericin also acts as a pore former which is similar to the effect of PVP. Thus, water-soluble polymer PVP has a tendency to leach out from the membrane surface in gelation bath during membrane formation [9]. Thereby, it allows the transport of protein molecules through pores. The inferred result showed that all synthesized membranes are of low molecular weight cut-off range. From the above PWP and protein rejection performance, M1, M3, M4, and M6 were chosen for the metal ion removal studies.

3.4. Ultrafiltration performance of PDDA/PEI–cadmium solution

The effect of transmembrane pressure variation from 100 to 400 kPa on membranes using PDDA/PEI–cadmium ions was studied at pH 7 and is shown in Figs. 8 and 9. As observed in the case of neat PES membrane, macroligand of 0.5% PEI–Cd^{2+} complex solution had higher flux of 6.03 L/m^2 h at the transmembrane pressure of 400 kPa. The flux was decreased to 4.57 L/m^2 h for increase in macroligand concentration of PEI from 0.5 to 1.0 wt.%. Other macroligand PDDA–Cd^{2+} complex solution had the maximum flux of 4.33 L/m^2 h at their lower concentration. The similar flux pattern was observed in all the other membranes. With the addition of additives, 5 wt.% incorporated sericin on PES membrane (M4) showed the flux of 9.07 L/m^2 h for the 0.5 wt.% PEI–Cd^{2+} complex solution. On the other hand, PVP of 10 wt.% modified PES membrane had the flux of 15.46 L/m^2 h.

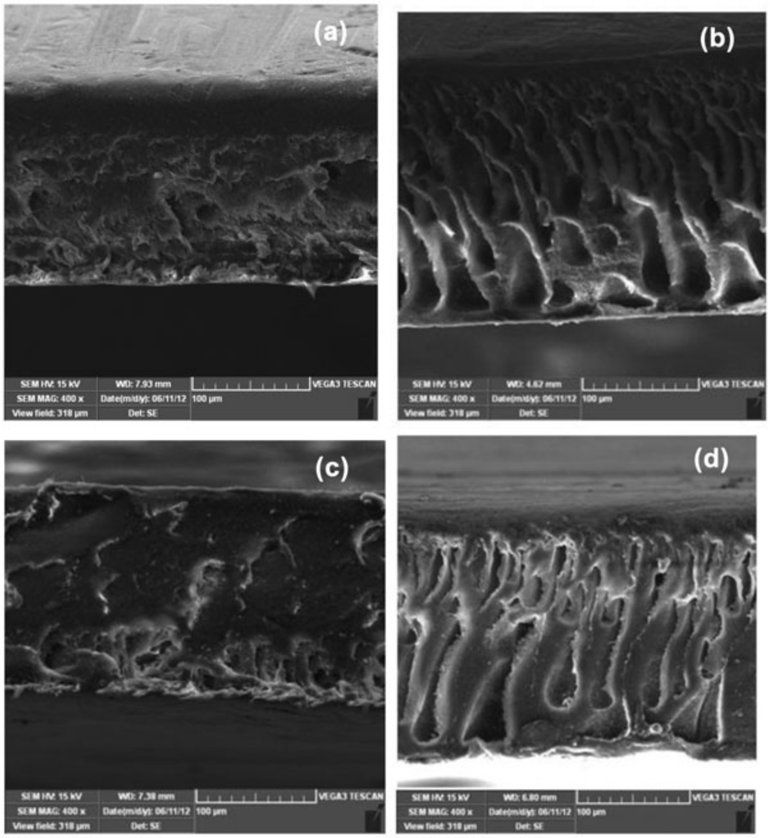

Fig. 6. SEM cross-sectional image for membranes (a) PES (100%), (b) PES (90%)/PVP (10%), (c) PES (95%)/sericin (5%), and (d) PES (90%)/sericin (5%)/PVP (5%).

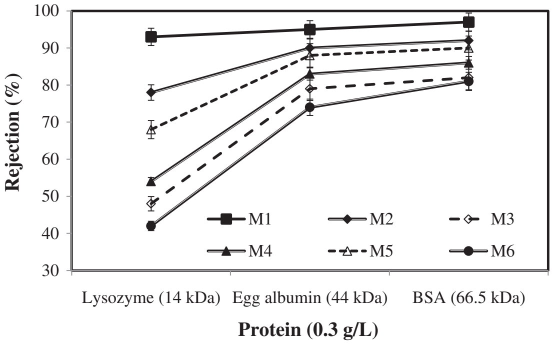

Fig. 7. Effect of additives on protein rejection studies in neat and modified PES membranes.

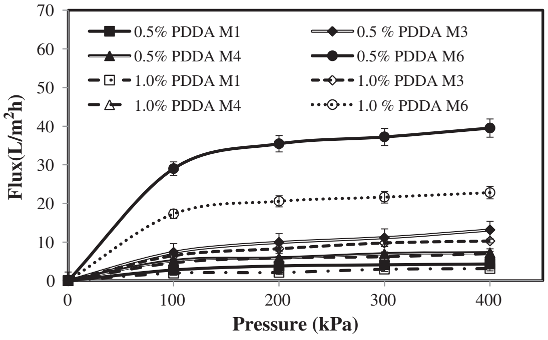

Fig. 8. Effect of additives on flux for different concentrations of PDDA with cadmium concentration of 50 mg L^{-1}.

The flux reduction was due to higher molecular weight of PDDA, PEI, and their concentration. Moreover, the highest permeate flux of 50 L/m^2 h was observed at 400 kPa for PVP and sericin-modified PES membrane. These data prove that PVP and sericin additives had a major role in the enhancement of pore size and hydrophilicity on membrane. Hence, it resulted in reduction of the interaction forces between feed solution and membrane surface [38]. Thus, the flux performance for macroligand PEI–Cd^{2+} complex solution got improved with the addition of additives.

3.4.1. Fouling analysis

Membrane fouling study on the ultrafiltration of PDDA/PEI–Cadmium solution was evaluated at

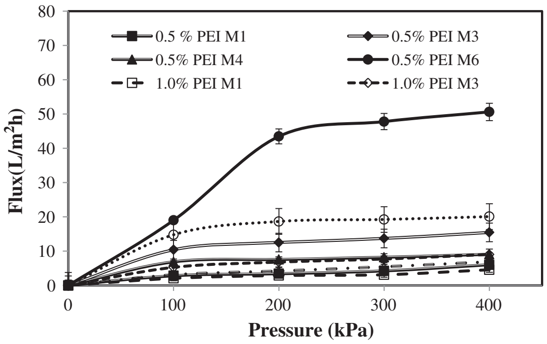

Fig. 9. Effect of additives on flux for different concentrations of PEI with cadmium concentration of 50 mg L^{-1}.

400 kPa using resistance in series model. The experimental observation of resistance tends to fouling, and concentration polarization was calculated from the Eqs. (9)–(11) and listed in Table 3. The another important parameter to assess the membrane performance was made through fouling studies. For the neat PES membrane, highest resistance of fouling was 29.64 × 10^{13} m^{-1} for PDDA–Cd^{2+} complex solution at the macroligand concentration of 1.0 wt.%. It is clearly seen that fouling value got decreased to 10.47 × 10^{13} m^{-1} for the same concentration of PEI. This result also indicated that the resistance due to concentration polarization was higher than fouling for both modified and unmodified PES membranes. This could be due to macroligand characteristics and concentration of the polyelectrolyte (PDDA/PEI) which has led to an increase in viscosity which causes deposition of solutes on the membrane surface. Investigators have also found that concentration polarization was dominant in the removal of metal ions using PEUF process [22,23].

About 10 wt.% PVP incorporated membrane showed 3.6 folds of reduced fouling than a neat PES membrane for 1.0 wt.% macroligand of PDDA–Cd^{2+} complex solution. In sericin-modified PES membrane (M4), resistance due to fouling was 3.0 folds, whereas, in the case of mixed additives resistance value was reduced to maximum of around 10 folds than that of in the neat PES membranes. In general, membranes with hydrophilic and low pore size are preferred for various industrial applications to alleviate the fouling performance. From the present study, it was concluded that PES membrane modified by mixed additive as PVP and sericin (M6) resulted in largest pore size with better fouling resistance. The resistance in series model data also confirms that the modified PES membrane by both additives PVP and sericin show higher flux and lower fouling resistance.

3.4.2. *Cadmium rejection and maximum retention capacity analysis*

Figs. 10 and 11 shows the effect of PDDA and PEI on cadmium rejection with respect to transmembrane pressure at pH 7. The experimental results from PEUF show that PEI is a favourable choice of formation of macromolecular complex with cadmium ions than PDDA. This is mainly due to the mechanism of cationic exchange of PEI with binding of Cd^{2+} ions to form a stronger PEI–Cd^{2+} macromolecular complex by the replacement of H^{+} ions in the PEI at higher pH [27]. PES membrane with addition of both PVP and sericin (M6) shows that the maximum rejection of 96% for the 0.5 wt.% macromolecule ligand concentration of PEI. The rejection of metal ions increased with increase in transmembrane pressure up to 400 kPa on all the membranes. The observed result of transmembrane pressure on membranes indicates that flux as well as rejection was improves with the increase of transmembrane pressure. It is due to that membranes are of lesser in pore size and thus the complex formed by macroligand are rejected on the membrane surface.

In addition, with the increase in macroligand concentration from 0.5 to 1.0 wt.%, rejection got decreased. The fouling results also conclude that resistance due to concentration polarization has increased with increase in the concentration of macroligands. Therefore, formation of macroligand–metal ion layer over the membrane surface and it causes the decrease in flux and rejection. PDDA also has a similar mechanism of replacing chloride in the PDDA moiety to form a PDDA–Cd complex. The mechanism of PDDA

Table 3
Fouling and concentration polarization resistances for PDDA– and PEI–cadmium solution

Membrane type	0.5% PEI		1.0% PEI		0.5% PDDA		1.0% PDDA	
	R_f (×10^{13} m^{-1})	R_{cp} (×10^{13} m^{-1})	R_f (×10^{13} m^{-1})	R_{cp} (×10^{13} m^{-1})	R_f (×10^{13} m^{-1})	R_{cp} (×10^{13} m^{-1})	R_f (×10^{13} m^{-1})	R_{cp} (×10^{13} m^{-1})
M1	6.26	15.37	10.47	25.69	5.90	19.1	29.64	58.86
M3	1.65	2.52	2.95	3.91	5.70	10.18	8.16	16.2
M4	1.70	4.41	3.30	6.62	7.90	4.99	9.86	13.20
M6	1.89	1.95	3.17	6.43	1.10	2.57	2.99	5.60

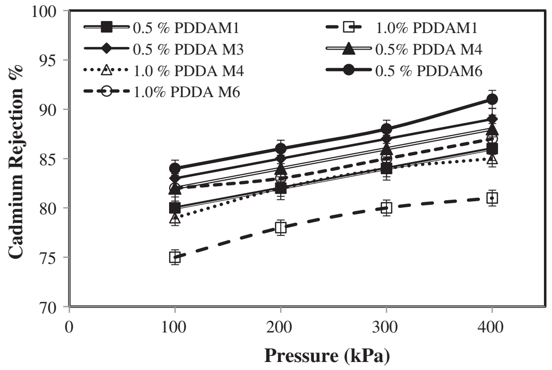

Fig. 10. Cadmium ion rejection for different concentrations of PDDA with respect to transmembrane pressure.

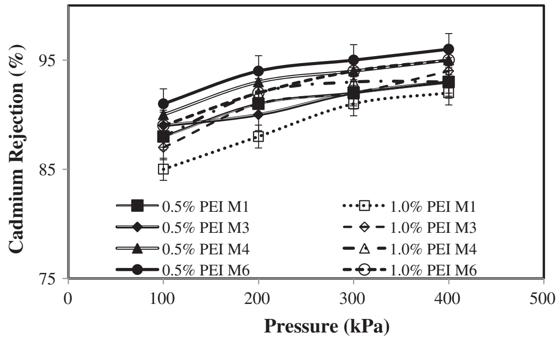

Fig. 11. Cadmium ion rejection for different concentrations of PEI with respect to transmembrane pressure.

and PEI binding with cadmium are illustrated in the Fig. 12. The rejection and flux pattern obtained membranes using PDDA were similar of all membranes, mixed additive of PVP and sericin-incorporated PES membrane has showed better flux performance. Maximum retention capacity and enrichment factor for the PDDA and PEI for the membranes are listed in Table 4. Neat PES membrane has lesser flux rate owing to its hydrophobicity. As a result, retention capacity as well as the enrichment factor of macroligand–Cd^{2+} was not improved while comparing with other modified membranes. In comparison of two macroligand, the higher maximum retention capacity was observed for the PEI. The rejection is higher for the PEI–Cd^{2+} complex due to the effective binding and formation of PEI and Cd^{2+} macromolecular complex. This is due to PEI, which has a stronger binding capacity for primary imine group with the anionic cadmium, whereas, in the case of PDDA, Cd^{2+} has a weaker interaction in the formation of covalent complex due to the presence of tertiary amine structure [39–41]. Thus, the rejection got lowered. Later, the cadmium molecules with macroligand occur in a free state and it may flow through membrane in permeate. Thus, the cadmium ions rejection and retention capacity of the polymers was decreased with an increase in the concentration of macroligand loading of metal. Hence, the enrichment factor of PEI–Cd^{2+} macroligand complex was higher in the membranes at the lower concentrations. Overall, the performance of PES membrane with mixed additives shows a higher enrichment factor and a rejection of 5.83 and 96%, respectively.

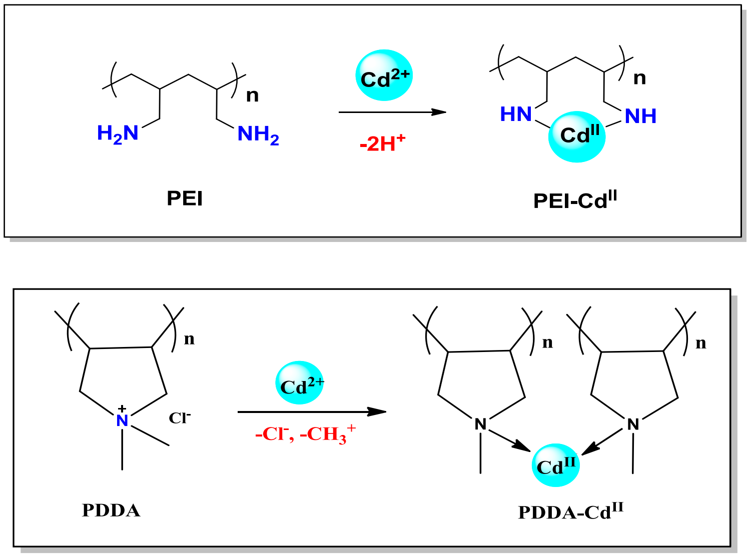

Fig. 12. Schematic representation of PEI and PDDA interaction with cadmium.

Table 4
Maximum retention capacity and enrichment factor for PDDA and PEI–cadmium solution

	0.5% PDDA		1.0% PDDA		0.5% PEI		1.0% PEI	
Membrane type	*C**	*E***	*C**	*E***	*C**	*E***	*C**	*E***
M1	19.23	0.19	6.73	0.13	58.25	0.58	16.83	0.34
M3	140.38	1.40	52.88	1.06	398.06	3.98	144.23	2.88
M4	96.15	0.96	31.73	0.63	296.12	2.96	132.21	2.64
M6	207.69	2.08	72.12	1.44	582.52	5.83	199.52	3.99

*Maximum retention capacity (mg of cadmium/g polymer).

**Enrichment factor.

4. Conclusion

The effects of addition of PVP/sericin combination and PVP/sericin to the PES blend membrane on its characteristics, performance, and stability were analyzed. It is found that PES/sericin membranes improved the mechanical and thermal stability. On the contrary, PES/PVP-modified membranes have poor effects on the same. Both PES/sericin- and PES/PVP-modified membranes improve the hydrophilicity as indicated by the FTIR-ATR spectroscopy and contact angle measurement analysis. In addition, ultrafiltration experiment results of PWP and flux performance of PDDA/PEI–cadmium solution was higher for both PVP and sericin-modified PES membranes. It is evident that the hydrophilicity as well as the pore radius of the membrane increased. PEI enhanced ultrafiltration using PES/sericin/PVP-modified membrane provides efficient cadmium removal (of 96%) when compared to utilizing PDDA (of 85%).

Nomenclature

r_m — average pore radius of the membrane (nm)
Q — flow rate of the permeate (m^3/s)
A — effective cross-sectional area of the membrane (m^2)
ΔP — transmembrane pressure (kPa)
η — the dynamic viscosity of the water (Pa s)
l — the thickness of the membrane (m)
J_w — solvent permeate flux ($L/m^2\,h$)
L_p — permeability of the pure water flux ($L/m^2\,h\,bar$)
C_p — concentration of the permeate (g/L)
C_r — concentration of the retentate (g/L)
R_m — intrinsic resistance of the membrane (m^{-1})
R_f — resistance due to fouling (m^{-1})
R_{cp} — resistance due to concentration polarization (m^{-1})
J_{wi} — initial water flux ($L/m^2\,h$)
J_{wf} — final water flux ($L/m^2\,h$)
J_v — feed flux ($L/m^2\,h$)

Greek letters

ε — porosity of the membrane
σ — reflection coefficient
$\Delta\Pi$ — osmotic pressure of the solution (pa)

References

[1] D. Wang, W. Zou, L. Li, Q. Wei, S. Sun, C. Zhao, Preparation and characterization of functional carboxylic polyethersulfone membrane, J. Membr. Sci. 374 (2011) 93–101.

[2] Y.Q. Wang, Y.L. Su, X.L. Ma, Q. Sun, Z.Y. Jiang, Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance, J. Membr. Sci. 283 (2006) 440–447.

[3] N. Ali, S.S.M. Tari, Surface modification of polyethersulfone ultrafiltration (PES-UF) membrane using myoglobin as modifying agent, Desalin. Water Treat. 47 (2012) 171–181.

[4] Y. Su, C. Li, W. Zhao, Q. Shi, H. Wang, Z. Jiang, S. Zhu, Modification of polyethersulfone ultrafiltration membranes with phosphorylcholine copolymer can remarkably improve the antifouling and permeation properties, J. Membr. Sci. 322 (2008) 171–177.

[5] Q. Shi, Y. Su, W. Zhao, C. Li, Y. Hu, Z. Jiang, S. Zhu, Zwitterionic polyethersulfone ultrafiltration membrane with superior antifouling property, J. Membr. Sci. 319 (2008) 271–278.

[6] B. Van der Bruggen, Chemical modification of polyethersulfone nanofiltration membranes: A review, J. Appl. Polym. Sci. 114 (2009) 630–642.

[7] W. Zhao, J. Huang, B. Fang, S. Nie, N. Yi, B. Su, H. Li, C. Zhao, Modification of polyethersulfone membrane by blending semi-interpenetrating network polymeric nanoparticles, J. Membr. Sci. 369 (2011) 258–266.

[8] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, J. Membr. Sci. 327 (2009) 125–135.

[9] S. Zhao, Z. Wang, X. Wei, B. Zhao, J. Wang, S. Yang, S. Wang, Performance improvement of polysulfone ultrafiltration membrane using well-dispersed polyaniline–poly(vinylpyrrolidone) nanocomposite as the additive, Ind. Eng. Chem. Res. 51 (2012) 4661–4672.

[10] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait, Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive, J. Membr. Sci. 315 (2008) 36–47.

[11] E. Saljoughi, T. Mohammadi, Cellulose acetate (CA)/polyvinylpyrrolidone (PVP) blend asymmetric membranes: Preparation, morphology and performance, Desalination 249 (2009) 850–854.

[12] N. Bolong, A.F. Ismail, M.R. Salim, D. Rana, T. Matsuura, Development and characterization of novel charged surface modification macromolecule to polyethersulfone hollow fiber membrane with polyvinylpyrrolidone and water, J. Membr. Sci. 331 (2009) 40–49.

[13] J. Marchese, M. Ponce, N.A. Ochoa, P. Prádanos, L. Palacio, A. Hernández, Fouling behaviour of polyethersulfone UF membranes made with different PVP, J. Membr. Sci. 211 (2003) 1–11.

[14] S.A. Al Malek, M.N. Abu Seman, D. Johnson, N. Hilal, Formation and characterization of polyethersulfone membranes using different concentrations of polyvinylpyrrolidone, Desalination 288 (2012) 31–39.

[15] A.F. Ismail, A.R. Hassan, Effect of additive contents on the performances and structural properties of asymmetric polyethersulfone (PES) nanofiltration membranes, Sep. Purif. Technol. 55 (2007) 98–109.

[16] Y.Q. Zhang, Applications of natural silk protein sericin in biomaterials, Biotechnol. Adv. 20 (2002) 91–100.

[17] B.C. Dash, B.B. Mandal, S.C. Kundu, Silk gland sericin protein membranes: Fabrication and characterization for potential biotechnological applications, J. Biotechnol. 144 (2009) 321–329.

[18] J.S. Ahn, H.K. Choi, K.H. Lee, J.H. Nahm, C.S. Cho, Novel mucoadhesive polymer prepared by template polymerization of acrylic acid in the presence of silk sericin, J. Appl. Polym. Sci. 80 (2001) 274–280.

[19] M.L. Gimenes, L. Liu, X. Feng, Sericin/poly(vinyl alcohol) blend membranes for pervaporation separation of ethanol/water mixtures, J. Membr. Sci. 295 (2007) 71–79.

[20] S. Vasudevan, J. Lakshmi, Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water—A novel approach, Sep. Purif. Technol. 80 (2011) 643–651.

[21] J. Huang, G. Zeng, Y. Fang, Y. Qu, X. Li, Removal of cadmium ions using micellar-enhanced ultrafiltration with mixed anionic-nonionic surfactants, J. Membr. Sci. 326 (2009) 303–309.

[22] E. Saljoughi, S.M. Mousavi, Preparation and characterization of novel polysulfone nanofiltration membranes for removal of cadmium from contaminated water, Sep. Purif. Technol. 90 (2012) 22–30.

[23] P. Canizares, A. Pérez, R. Camarillo, J.J. Linares, A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents, J. Membr. Sci. 240 (2004) 197–209.

[24] M. Palencia, B.L. Rivas, E. Pereira, A. Hernández, P. Prádanos, Study of polymer–metal ion–membrane interactions in liquid-phase polymer-based retention (LPR) by continuous diafiltration, J. Membr. Sci. 336 (2009) 128–139.

[25] B.L. Rivas, E.D. Pereira, I. Moreno-Villoslada, Water-soluble polymer–metal ion interactions, Prog. Polym. Sci. 28 (2003) 173–208.

[26] D.J. Ennigrou, L. Gzara, M.R.B. Romdhane, M. Dhahbi, Retention of cadmium ions from aqueous solutions by poly(ammonium acrylate) enhanced ultrafiltration, Chem. Eng. J. 155 (2009) 138–143.

[27] C.W. Li, C.H. Cheng, K.H. Choo, W.S. Yen, Polyelectrolyte enhanced ultrafiltration (PEUF) for the removal of Cd(II): Effects of organic ligands and solution pH, Chemosphere 72 (2008) 630–635.

[28] N.A.A. Hamid, A.F. Ismail, T. Matsuura, A.W. Zularisam, W.J. Lau, E. Yuliwati, M.S. Abdullah, Morphological and separation performance study of polysulfone/titanium dioxide (PSF/TiO_2) ultrafiltration membranes for humic acid removal, Desalination 273 (2011) 85–92.

[29] M.K. Purkait, S. DasGupta, S. De, Resistance in series model for micellar enhanced ultrafiltration of eosin dye, J. Colloid Interface Sci. 270 (2004) 496–506.

[30] J. Sánchez, B.L. Rivas, Cationic hydrophilic polymers coupled to ultrafiltration membranes to remove chromium(VI) from aqueous solution, Desalination 279 (2011) 338–343.

[31] N.K. Saha, S.V. Joshi, Performance evaluation of thin film composite polyamide nanofiltration membrane with variation in monomer type, J. Membr. Sci. 342 (2009) 60–69.

[32] A. Ananth, G. Arthanareeswaran, H. Wang, The influence of tetraethylorthosilicate and polyethyleneimine on the performance of polyethersulfone membranes, Desalination 287 (2012) 61–70.

[33] T.Y. Liu, W.C. Lin, M.C. Yang, S.Y. Chen, Miscibility, thermal characterization and crystallization of poly(L-lactide) and poly(tetramethylene adipate-co-terephthalate) blend membranes, Polymer 46 (2005) 12586–12594.

[34] S. Rajesh, A.F. Ismail, D.R. Mohan, Structure-property interplay of poly(amide-imide) and TiO_2 nanoparticles impregnated poly(ether-sulfone) asymmetric nanofiltration membranes, RSC Adv. 2 (2012) 6854–6870.

[35] K. Boussu, B. Van der Bruggen, A. Volodin, C.V. Van Haesendonck, J.A. Delcour, P. Van der Meeren, C. Vandecasteele, Characterization of commercial nanofiltration membranes and comparison with self-made polyethersulfone membranes, Desalination 191 (2006) 245–253.

[36] J. Barzin, S.S. Madaeni, H. Mirzadeh, M. Mehrabzadeh, Effect of polyvinylpyrrolidone on morphology and performance of hemodialysis membranes prepared from polyether sulfone, J. Appl. Polym. Sci. 92 (2004) 3804–3813.

[37] G. Arthanareeswaran, S. Ananda Kumar, Effect of additives concentration on performance of cellulose acetate and polyethersulfone blend membranes, J. Porous Mater. 17 (2010) 515–522.

[38] A. Rahimpour, S.S. Madaeni, Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: Preparation, morphology, performance and antifouling properties, J. Membr. Sci. 305 (2007) 299–312.

[39] G. Marcelo, M.P. Tarazona, E. Saiz, Solution properties of poly(diallyldimethylammonium chloride) (PDDA), Polymer 46 (2005) 2584–2594.

[40] G. Arthanareeswaran, V.M. Starov, Effect of solvents on performance of polyethersulfone ultrafiltration membranes: Investigation of metal ion separations, Desalination 267 (2011) 57–63.

[41] J. Kochan, T. Wintgens, J.E. Wong, T. Melin, Polyelectrolyte-modified polyethersulfone ultrafiltration membranes for wastewater treatment applications, Desalin. Water Treat. 9 (2009) 175–180.