Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2578

27 (2011) 231–236
March

Outside skin tubular ultrafiltration membranes for separation of proteins and polysaccharides and removal of turbidity from seawater[1]

S. Prabhakar, A.K. Ghosh*, R.C. Bindal, P.K. Tewari

Desalination Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400 085, India
Tel. +91 22 25594738/25595602; email: akghosh@barc.gov.in

Received 28 April 2010; Accepted 7 July 2010

ABSTRACT

In this study, ultrafiltration (UF) membranes were prepared in outside skin tubular configuration using polysulfone and sulfonated polysulfone polymers in order to study the effect of chemical nature of membrane surface on separation performance as well as surface fouling. Separation of polysaccharide and protein with its fouling tendency, removal efficiency of turbidity from seawater with flux recovery after fouling were evaluated. Tubular configuration was chosen, as the membrane surface is most exposed for cleaning after fouling than any other configurations. Bovine serum albumin (BSA) and sodium salt of alginic acid were used as model protein and polysaccharide, respectively, to probe the rejection behavior of these tubular membranes. Sulfonated polymeric membranes were compared with pure polymer membranes for resistance to fouling by the model protein and polysaccharide solutions. Pure water flux recovery on water flushing for polysaccharide fouled membrane was comparatively more (6–8%) than protein fouled membrane, particularly in case of polysulfone membrane. In general, the pure water flux recovery after fouling, i.e., reversibility of fouling was more (up to 10%) for sulfonated polysulfone membranes than that of pure polysulfone membranes. Finally, these membranes in tubular configurations were used for removal of turbidity from seawater as periodic washing by flow reversal recovers flux after fouling.

Keywords: Tubular module; Ultrafiltration; Separation; Fouling; Proteins and polysaccharides; Turbidity removal

1. Introduction

Ultrafiltration (UF)/microfiltration (MF) membranes are used for removal of colloidal and particulate matters and hence it is widely used in applications like seawater reverse osmosis pretreatment and separations in the food, dairy, paper, textile, chemical industries [1]. In seawater reverse osmosis pretreatment, UF membranes are used to remove colloidal and particulate matters composed of proteins, polysaccharides, suspended silica, clay materials, etc. [2]. However, membrane fouling is one of the biggest challenges faced in UF membrane operations till date. UF elements could not operate at high flux rates without severe fouling of membrane surfaces and plugging of feed channels [3]. Extent of surface fouling depends mainly on membranes morphology, its chemical nature, membrane assembling configuration and operating conditions [4].

---

*Corresponding author.

[1] Most of the work in this paper was presented in Indian Desalination Association (InDA)—Asia-Pacific Desalination Association (APDA) conference on Desalination and Water Purification (INDACON-2010) (2010) from 10–12th March 2010, Chennai, India and it was selected for best poster paper award.

Synthetic membranes are prepared mainly in flat sheet and cylindrical geometries [5]. Flat sheet membranes are used in disc, spirally wound, plate and frame modules whereas cylindrical geometry utilized in tubular, capillary and hollow fiber modules. The choice of the module is generally determined by the type of application and economic considerations. Despite being the most expensive configuration (as not compact, more cost per unit membrane area), the tubular module is well suited for applications with a high fouling tendency [6]. The particle plugging is much less in tubular due to higher Reynolds numbers and turbulent flow. For same velocity, more turbulent flow will be encountered in tubular system which minimizes particle plugging and hence preferred for its good process control and ease of membrane cleaning. In tubular modules, the membrane elements design configuration is both 'outside-in' and 'inside-out' with respect to the feed–permeate flow direction. Outside-in flow is considered as it provides a greater filtering surface and thus for a given mass of particles deposited, the cake layer formed is thinner that introduces a lower additional resistance [7]. So the pressure rise in the module is slower. Outside-in operation also offers the advantage of facilitating backwashing and as the purified water flows through the capillary bore, capillary diameter can be reduced to any appropriate value without posing the threat of capillary blockage by the feed water. Tubular configuration is chosen in our study as the membrane surface is most exposed for cleaning after fouling than any other configurations.

Membrane surface hydrophilicity/hydrophobicity, i.e., chemical nature of the membrane surface is an important factor which influences membrane fouling. In general, membrane fouling is expected to be more with hydrophobic than hydrophilic surfaces [8–10]. However, in a recent study, it is shown that membrane hydrophilicity does not appear to be advantageous from the fouling propensity except from the perspective of cake resistance reversibility, which is significantly higher than hydrophobic membranes. Actually pore plugging is more serious for the hydrophobic membrane but polysaccharide and protein removal is much higher by the hydrophobic membrane [11]. From the studies of membrane fouling in terms of surface energy changes involved, it is shown that most hydrophobic polyvinylidene fluoride membrane shows the lowest fouling tendency out of cellulosics, polysulfone, and polyvinylidene fluoride polymeric membranes [12]. So, hydrophobic polysulfone (PSf) and relatively more hydrophilic sulfonated polysulfone (SPSf) are chosen as membrane materials in order to study the effect of chemical nature of membrane surface on separation performance as well as surface fouling. Polysulfone and modified polysulfone based UF membranes are commonly used for protein separation [13,14].

Polysaccharides, proteins, humic and fulvic acid or their derivatives and different classes of biopolymers are contributed to natural organic matter (NOM) commonly present in natural water sources including seawater. It is reported in a study that biopolymers are the major cause of UF fouling [15] in NOM separation. In another study, on fractionation of NOM in surface water by ultrafiltration membranes, it is shown that the fouling rates are in the order—hydrophilic NOM > transphilic NOM > hydrophobic NOM and polysaccharides (Mol. Wt. >20,000) is identified as being the main cause of UF fouling [16]. Among others, non-humic components of NOM (proteins and saccharides) [17] are some of the potential membrane foulants in water treatment by membranes. So, sodium salt of alginic acid and bovine serum albumin (BSA) were used as model polysaccharide and protein, respectively, in the present study as foulants. Finally, fouling of membranes on filtration of actual seawater was studied.

So, the goal of the study was to elucidate the extent of fouling occurs when protein, polysaccharide and seawater (contains different class of polysaccharides, proteins, and different classes of biopolymers) were filtered through UF membranes for outside skin tubular configuration and flux recovery thereafter on water flushing. We evaluated the separation performance of UF membranes prepared in outside skin tubular configuration over porous polypropylene tubes using polysulfone (PSf) and sulfonated polysulfone (SPSf) polymers using polyvinyl pyrrolidone (PVP) as pore-forming agent. The membranes were characterized in terms of pure water flux and separation of sodium salt of alginic acid and BSA. The pure water flux recovery after protein, polysaccharide fouling was evaluated for PSf and SPSf UF membranes. These membranes were also tested for turbidity removal from seawater and thereafter periodic flux recovery on deionized (DI) water flushing.

2. Experimental

2.1. Preparation of tubular membranes

Polysulfone (PSf) polymer (molecular weight, Mw – 90 kDa) in bead form was obtained from M/s. Solvay Specialities India Pvt. Ltd. *N*-methyl-2-pyrrolidone (NMP) of analytical grade and PVP (molecular weight – 40 kDa) were received from Sisco Research Lab. Pvt. Ltd., India and used as such without further purification. BSA (molecular weight – 69 kDa) was purchased from Himedia Laboratories Pvt. Ltd., India. Alginic acid sodium salt from brown algae (Sigma–Aldrich, India) (with reported viscosity ~250 cP for 2% solution in water at 25 °C) in powder form was employed in all the experiments.

Stock solutions for BSA and alginic acid sodium salt (2 g/l) were prepared by dissolving the foulant in deionized (DI) water under vigorous stirring for 6–8 h.

Sulfonated polysulfone (SPSf) synthesis from polysulfone and determination of ion exchange capacity (IEC) were carried out according to the procedure described by Manea and Mulder [18]. By adjusting the polysulfone to chlorosulfonic acid ratio, SPSf with 0.58 meqv./g IEC was prepared.

In a airtight glass bottle, 20 g of polymer (PSf and SPSf independently) and 10 g of PVP were taken with 65 ml of NMP solvent and kept agitated for several hours for complete dissolution to form casting solution. Central hole of the polypropylene tubes (internal diameter of 20.0 mm, an outer diameter of 30 mm, and a length of 50 cm, supplied by M/s. Sonadka, Mumbai, India) were blocked by putting rubber cork on both the sides. Inside blocked polypropylene tubes were dipped in the casting solution for predetermined time. Then outside polymer coated tube was taken out from the polymer casting solution, positioned vertically to drain the excess casting solution till it stop dipping freely and subsequently it was immersed in demineralized water to induce phase inversion. It was kept in water for 10 min and then tube supported polysulfone membrane was removed from the water bath. The membrane was washed thoroughly with demineralized water and stored in 0.5% sodium metabisulfite solution. Before testing, the tubular membrane was assembled in a pressure vessel.

2.2. Performance evaluation and fouling studies on tubular membranes

Tubular UF membranes were assembled properly in a pressure vessel (internal diameter of 66.0 mm). As soon as feed entered inside the pressure vessel, it got pressurized and part of it pass through outside skin tubular membrane to form permeate which was collected from centre tube and unfiltered concentrated part passed in the same direction to feed flow and collected as reject. The performances of these membranes were evaluated operating at recirculation mode, i.e., both permeate and reject is taken back to the feed tank. The sequence of the filtration experiments were as follows:

1. Pressurized a membrane coupon at 450 kPa (100 kPa more than operating pressure was used for experiment) using pure water till it gives constant pure water flux.
2. Then pressure reduces to 350 kPa and continues to check pure water flux till it shows constant value over 30 min time. At this point, reported pure water permeability of the tubular membranes was evaluated.
3. Model protein or polysaccharide or seawater was changed as feed in place of pure water and permeation experiment continued at 350 kPa. When the product water flux remained constant over 45 min, the reported solute rejection was determined.

Feed concentration was 1000 mg/l for both BSA and sodium salt of alginic acid. The pH of the BSA solution was 6.9–6.8. The separation of both BSA and alginate concentrations were determined by measuring total organic carbon (TOC) (Instrument—TOC Analyser, Model No. TOC-1200 of M/s. Thermo Electron Corporation make and it works on combustion method) of feed and permeate samples for both the membranes. It was also cross checked by measuring UV absorbance (Instrument—at 280 nm for BSA and at 220 nm for alginic acid sodium salt followed by estimation of concentrations from calibration graph) [19]. These membranes in tubular configurations were also used for removal of turbidity from seawater. Turbidity removal values were obtained by measuring the turbidity of feed and permeate samples using standard turbiditimeter.

For fouling experiments, DI water was first passed through the membrane at 350 kPa pressure until the flux remained constant over at least 30 min (it took 3–4 h time). The end of the stabilization period was taken as the zero time point in the filtration plots. Then the model foulant solution was passed at constant flux for both membranes. Fouling studies were carried out at constant initial flux (50 $lm^{-2}h^{-1}$) for proper comparison of fouling tendency on change in membrane material with respect to change in nature of foulants. Accordingly, applied feed pressures were 350 kPa and 324 kPa for PSf and SPSf membranes, respectively. A sample of permeate was collected after every 1 h of filtration. After 8–10 h of operation when the flux remained constant, DI water was used as a feed to determine the reversibility of fouling.

3. Results and discussion

3.1. Membrane performances

The pure water permeability along with the protein and polysaccharide rejection data for both PSf and SPSf tubular membranes are given in Fig. 1. The pure water permeability of the SPSf tubular membrane is more (12.5% in $lm^{-2}h^{-1}$) with marginally less protein (2.2% less) and polysaccharide (3.1% less) rejection than that of pure polysulfone tubular membrane. BSA with molecular weight of 69 kDa is rejected more than 90% by both the membranes but the rejection of sodium salt of alginic acid is in the range of 80%. The more water permeability

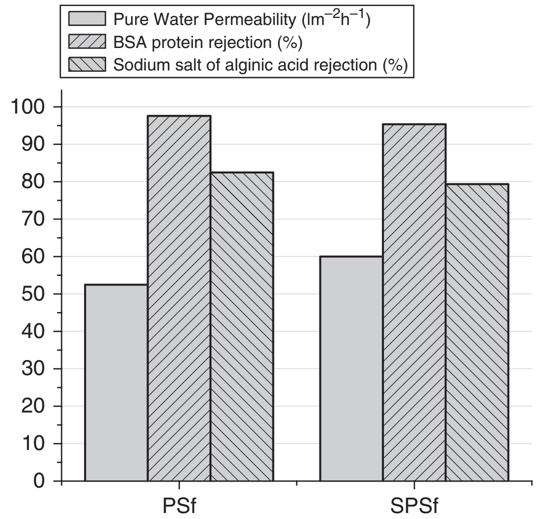

Fig. 1. Performances of PSf and SPSf membranes in tubular configuration.

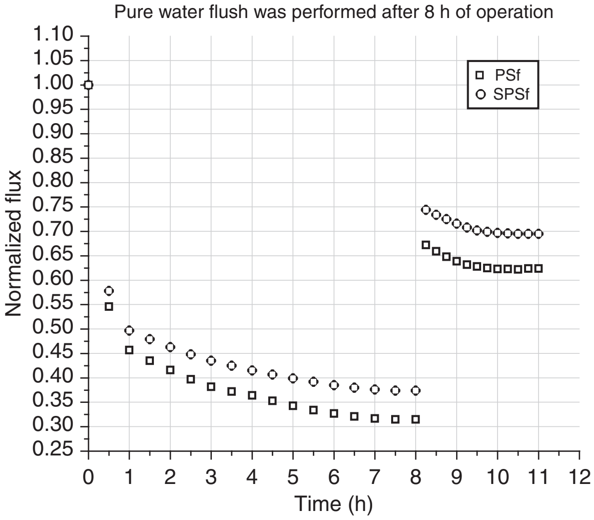

Fig. 2. BSA flux decline and recovery for PSf and SPSf membranes in tubular configuration.

in SPSf membranes could be due to the combined effects of slightly bigger pore size (as evident from lower solute rejection) and more hydrophilic (contact angle of PSf and SPSf membranes are 71.0 ± 1° and 64.2 ± 2°, respectively) membrane surface than PSf membranes. Other than the pore size, the rejection of both BSA and sodium salt of alginic acid (both charged) could be enhanced for SPSf membranes due to charged interactions.

3.2. Protein (BSA) fouling studies

The BSA fouling studies were carried out at initial flux of 50 $lm^{-2}h^{-1}$ (at zero time in the plot) for both PSf and SPSf membranes using 1000 mg/l solution of BSA. Though average concentration of proteins in surface or seawater are much less than 1000 mg/l, this concentration was chosen to perform rapid fouling tests. The constant initial flux was maintained by adjusting the applied pressure. The plot of normalized flux (defined as ratio of instant flux to pure water flux at the end of the compaction, i.e., 50 $lm^{-2}h^{-1}$) as a function of time of operation is shown in Fig. 2. During the filtration of the BSA solution, both the membranes showed flux decline but the decline is more for PSf membranes. In a previous study also it is reported that with increasing level of sulfonation and carboxylation in PSf membranes, static BSA adsorption decreased, ultrafiltration flux reduction decreased and cleanability increased [20]. The flux decrease was about 40–45% within the first half an hour of filtration. As the rejection of BSA was more than 90% for both the membranes, the flux decline could be mainly due to the formation of an adsorption layer on the membrane surface. As the BSA is charged species, the total protein adsorption in more hydrophilic SPSf membrane surface could be less than the relatively more hydrophobic pure PSf membrane. The SPSf membrane recovered 70% of its initial flux but PSf membranes recovered 63% of initial pure water flux after flushing with pure water. So, membrane surface hydrophilicity enhances fouling resistance in membrane at certain extent. It is reported by Nabe et al. [21] that sheet polysulfone membrane modified by direct sulfonation had the lowest surface energy and exhibited the highest volumetric flux with BSA solution (feed: 80 mg/l) when tested in stirred dead-end ultrafiltration test cell. It was also easy to clean and exhibited the higher initial flux recovery. But as the testing condition of reported study was different than the present study, the extent of fouling and flux recovery is different.

3.3. Polysaccharide (sodium salt of alginic acid) fouling studies

The sodium salt of alginic acid fouling studies were also carried out at initial flux of 50 $lm^{-2}h^{-1}$ for both PSf and SPSf membranes using 1000 mg/l solution of foulant. Though average concentration of polysaccharides in surface or seawater are much less than 1000 mg/l, this concentration was chosen to perform rapid fouling tests. The plot of normalized flux as a function of time of operation is shown in Fig. 3. During the filtration of the polysaccharide solution, both the membranes show almost similar flux decline. But the overall flux decline is less for polysaccharide solution than that for protein (BSA) solution. The flux decrease is the maximum within the first half an hour of filtration. As the rejection of sodium salt of alginic acid is around 80% for both the

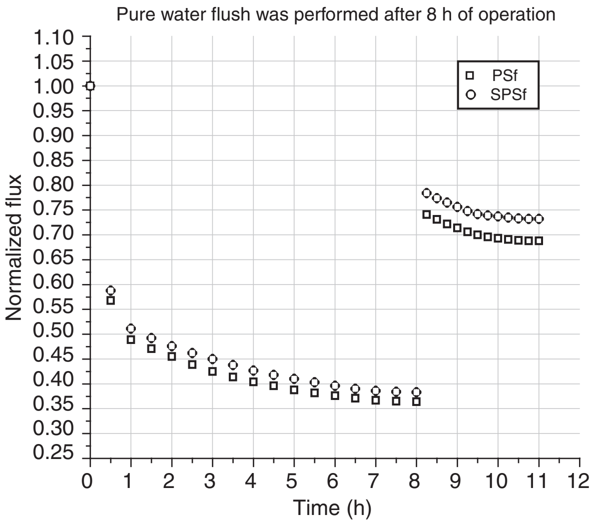

Fig. 3. Sodium salt of alginic acid flux decline and recovery for PSf and SPSf membranes in tubular configuration.

membranes, the flux decline could be due to the formation of an adsorption layer on the membrane surface as well as some pore plugging. But as the flux decrease in polysaccharide filtration is less than the protein filtration, the adsorption layer is thinner than that formed by proteins. Similar observation is reported for polyethersulfone (PES) membrane in which the surface coverage by protein is found much greater than membrane surface coverage by polysaccharides and hence fouling caused by protein is also more severe [22]. The SPSf membrane recovered ~74% of its initial flux but PSf membranes recovered ~70% of initial pure water flux after flushing with pure water. So, flux recovery after polysaccharide fouling is slightly more than protein fouling and it is more prominent in hydrophobic PSf membrane.

3.4. Turbidity removal from seawater and flux recovery on water flushing

After testing the separation performance of model protein and polysaccharide, experiments were carried out for removal of turbidity from seawater (Source: Trombay creek, Arabian Sea) with turbidity of around 60 in Nephelometric Turbidity Units (NTU) and total dissolved solid (TDS) of 22,000 ppm. The membrane performance is given in Table 1. It can be seen that both the membranes remove more than 99% turbidity from quite turbid seawater but flux is low. In seawater treatment, as both colloidal and particulate matters get deposited on membrane surface, it gives lower flux than deposition only by colloidal matters like proteins and polysaccharides solution.

Table 1
Membrane performance on turbidity removal from seawater

Membrane	Product permeability (L m^{-2} h^{-1})	Turbidity of the permeate (NTU)
PSf	20.5	0.35
SPSf	23.8	0.43

Turbidity of the diluted seawater : 60 NTU.

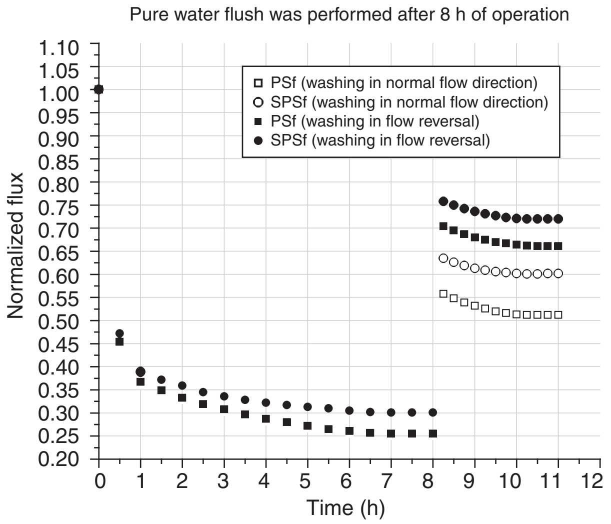

Fig. 4. Flux decline and recovery for PSf and SPSf membranes on removal of turbidity from seawater in tubular configuration.

The seawater fouling studies were carried out at initial flux of 30 lm^{-2}h^{-1} for both PSf and SPSf membranes. The plot of normalized flux as a function of time of operation is shown in Fig. 4. In this case, the reversibility of fouling was determined for both in normal flow direction (feed to reject side) and in flow reversal (reject to feed side) using DI water as a feed. In case of seawater also, both the membranes show almost similar flux decline like protein and polysaccharide cases. But the overall flux decline is more than that for both protein and polysaccharide solution. As the rejection of materials caused turbidity in seawater is more than 99% with high flux decline for both the membranes, the flux decline is mainly due to deposition of particulate matter as well the formation of an adsorption layer. The SPSf membrane recovered 60% of its initial flux but PSf membranes recovered only 50% of initial pure water flux after flushing with pure water in normal flow direction. However, SPSf membrane recovered 72% of its initial flux and PSf membranes recovered 66% of initial pure water flux after flushing with pure water in flow reversal. So for seawater pretreatment applications, SPSf membrane has enhanced fouling resistance than pure PSf membrane.

4. Conclusions

It is found that both protein and polysaccharides are caused significant fouling in both PSf and SPSf membranes. However, PSf membranes are more fouled than SPSf membranes from both the foulants solutions. The extent of fouling by protein is greater than by polysaccharides in both the UF membranes. The pure water flux recovery after fouling, i.e., reversibility of fouling is more for SPSf UF membranes than that of pure PSf membranes. These membranes in tubular configurations can be used for removal of turbidity from seawater though the flux is less. Periodic washing by flow reversal is more effective to restore the productivity in tubular membrane for seawater pretreatment.

References

[1] W. Eykamp, Microfiltration and ultrafiltration, in: R.D. Noble, S.A. Stern (Eds.), Membrane Separation Technology: Principles and Applications, Elsevier Science, Amsterdam, 1995, pp.1–40.

[2] M. Busch, R. Chu, U. Kolbe, Q. Meng and S. Li, Ultrafiltraion pretreatment to reverse osmosis for seawater desalination—three years field experience in the Wangtan Datang power plant, Desalinat. Water Treat., 10 (2009) 1–20.

[3] M. Wilf and K. Klinko, Effective new pretreatment for seawaer reverse osmosis systems, Desalination, 117 (1998) 323–331.

[4] M.F.A. Goosen, S.S. Sablani, H. Ai-Hinai, S. Ai-Obeidani, R. Al-Belushi and D. Jackson, Fouling of reverse osmosis and ultrafiltration membranes: a critical review, Separat. Sci. Technol., 39 (2004) 2261–2297.

[5] K.C. Khulbe, C.Y. Feng and T. Matsuura, Synthetic Polymeric Membranes—Characterization by Atomic Force Microscopy, Springer, Berlin Heidelberg, 2008, p. 6.

[6] M. Mulder, Basic Principles of Membrane Technology—Chapter-VIII, Springer, 2003, p. 473.

[7] C. Serra, M.J. Clifton, P. Moulin, J.-C. Rouch and P. Aptel, Dead-end ultrafiltration in hollow fiber modules: Module design and process simulation, J. Membr. Sci., 145 (1998) 159–172.

[8] L. Fan and L. John, Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes, Water Res., 35 (2001) 4455–4463.

[9] D.S. Kim, J.S. Kang and Y.M. Lee, The influence of membrane surface properties on fouling in a membrane bioreactor for wastewater treatment, Separat. Sci. Technol., 39 (2005) 833–854.

[10] H.-Y. Yu, M.-X. Hu, Z.K. Xu, J.-L. Wang and S.-Y. Wang, Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH_3 plasma treatment, Separat. Purificat. Technol., 45 (2005) 8–15.

[11] N. Maximous, G. Nakhla and W. Wan, Comparative assessment of hydrophobic and hydrophilic membrane fouling in wastewater applications, J. Membr. Sci., 339 (2009) 93–99.

[12] K.-H. Choo and C.-H. Lee, Understanding membrane fouling in terms of surface free energy changes, J. Colloid Interface Sci., 226 (2000) 367–370.

[13] S. Nakao, H. Osada, H. Kurata, T. Tsuru and S. Kimura, Separation of proteins by charged ultrafiltration membranes, Desalination, 70 (1988) 191–205.

[14] L.E.S. Brink and D.J. Romijin, Reducing the protein fouling of polysulfone surfaces and polysulfone ultrafiltration membranes: optimization of the type of presorbed layer, Desalination, 78 (1990) 209–233.

[15] M.D. Kennedy, J. Kamanyi, B.G.J. Heijman and G. Amya, Colloidal organic matter fouling of UF membranes: role of NOM composition & size, Desalination, 220 (2008) 200–213.

[16] M.D. Kennedy, H.K. Chun, V.A.Q. Yangali, B.G.J. Heijman and J.C. Schippers, Natural organic matter (NOM) fouling of ultrafiltration membranes: fractionation of NOM in surface water and characterisation by LC-OCD, Desalination, 178 (2005) 73–83.

[17] G. Amy and N. Her, Size exclusion chromatography (SEC) with multiple detectors: a powerful tool in treatment process selection, Water Sci. Technol.: Water Supply, 4 (2004) 19–24.

[18] C. Manea and M. Mulder, Characterization of polymer blends of polyethersulfone/sulfonated polysulfone and polyethersulfone/sulfonated polyetheretherketone for direct methanol fuel cell applications, J. Membr. Sci., 206 (2002) 443–453.

[19] A. Asatekin, S. Kang, M. Elimelech and A.M. Mayes, Anti-fouling ultrafiltration membranes containing polyacrylonitrile-*graft*-poly(ethylene oxide) comb copolymer additives, J. Membr. Sci., 298 (2007) 136–146.

[20] D. Möckel, E. Staude and M.D. Guiver, Static protein adsorption, ultrafiltration behavior and cleanability of hydrophilized polysulfone membranes, J. Membr. Sci., 158 (1999) 63–75.

[21] A. Nabe, E. Staude and G. Belfort, Surface modification of polysulfone ultrafiltration membranes and fouling by BSA solutions, J. Membr. Sci., 133 (1) (1997) 57–72.

[22] H. Susanto, S. Franzka and M. Ulbricht, Dextran fouling of polyethersulfone ultrafiltration membranes—Causes, extent and consequences, J. Membr. Sci., 296 (2007) 147–155.