MJFAS MALAYSIAN JOURNAL OF FUNDAMENTAL AND APPLIED SCIENCES
PRINT ISSN: 2289-5981 | ONLINE ISSN: 2289-599X

RESEARCH ARTICLE

Study on the effect of PVP additive on the performance of PSf/PVP ultrafiltration hollow fiber membrane

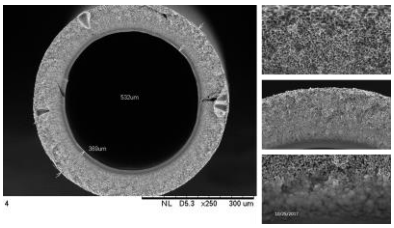
Sumarni Mansur [a], Mohd Hafiz Dzarfan Othman [a,*], Ahmad Fauzi Ismail [a], Muhammad Nidzhom Zainol Abidin [a], Noresah Said [a], Pei Sean Goh [a], Hasrinah Hasbullah [a], Siti Hamimah Sheikh Abdul Kadir [b], Fatmawati Kamal [b]

[a] *Advanced Membrane Technology Research Centre (AMTEC), Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia,81310 UTM, Skudai Johor, Malaysia*
[b] *Institute of Molecular Medicine and Biotechnology, Faculty of Medicine, Universiti Teknologi Mara Sungai Buloh Campus, Jalan Hospital, 47000 Sungai Buloh, Selangor, Malaysia*

* *Corresponding author: hafiz@petroleum.utm.my*

Article history
Received 29 Mac 2018
Revised 1 June 2018
Accepted 2 July 2018
Published Online 3 September 2018

Graphical abstract



Abstract

Asymmetric, porous ultrafiltration polysulfone (PSf) hollow fiber membranes were fabricated based on different compositions of polyvinylpyrrolidone (PVP) additive concentration. The physical structure or morphology of a fabricated membrane is a major concern in determining the efficiency of a dialysis membrane. Different types of membrane morphology will give a different result in terms of membrane permeability and clearance efficiency. The phase inversion spinning technique is suitable in producing ultrafiltation (UF) membrane where the average pore size of the fabricated membrane is in the range of 0.001 – 0.1 µm. However, there are many factors need to be controlled and manipulated during the phase inversion technique. In this study, the effect of the PVP on membrane pore size and performances were analysed. The contact angle was measured to determine the hydrophilicity of the membranes. The hydrophilic polymer is favorable to avoid fouling and to increase membrane biocompatibility. Furthermore, the diameter of the membrane fibers was determined using a scanning electron microscopy (SEM). The effects of different morphologies of the hollow fibers on the performance of the membranes were evaluated by pure water flux and BSA rejection. Both experiments were conducted using permeation flux system. It was found that the finger-like macrovoids in PSf hollow fiber membranes were suppressed by the addition of 8% PVP (Mw of 360 kDa) as the result of a drastic increase in dope solution viscosity. On top of that, the fibers spun with 8% PVP showed a more porous structure which contributes to higher membrane permeability.

Keywords: Polysulfone, hollow fiber membrane, ultrafiltration membrane, spinning parameter, non-induced phase inversion technique

INTRODUCTION

In haemodialysis, membrane is considered as the heart of the treatment. The membrane will determine the amount of uremic toxins to be filtered and protein to be retented [1]. Blood flows into the lumen of the hollow fibers while dialysate is counter-currently flowing at the side of the hollow fiber simultaneously [2]. Uremic toxins diffuse out from the blood to dialysate due to the difference in concentration gradient during the convection and ultrafiltration (UF) processes [2]. According to Barzin *et al.* [3], uremic toxins such as urea and creatinine, ranged from the size of 10,000-55,000 Da need to be excreted out from the blood. Whilst, proteins such as albumin (66,000 Da) need to be retained. Thus, a desirable hollow fiber membrane with suitable pore size distribution need to be achieved [4].

There are few selection factors need to be considered when designing and fabricating hemodialysis ultrafiltration hollow fiber membrane. The membrane selection is totally based on patient's need. If the amount of toxins within the patient's blood is high, nephrologist normally will prefer high flux dialyser due to it's ability to have better middle size molecule removal. Asymmetric, porous ultrafiltration hollow fiber membrane is preferable for haemodialysis application [4–6]. To increase the total surface area to volume of the membrane, the membrane needs to have a very thin skin and small size diameter. Small and thin membranes will increase the surface area of the membrane which will allow more blood to be exposed to dialysate [7]. Consequently, more solutes can be removed from the blood. From the study conducted by Hayama *et al.*, the commercial hollow fiber membrane of APS- 150 (Asahi-medical, Japan) has an internal diameter (ID) of 210 µm and a wall thickness of 45 µm [8].

Thin selective skin is highly favored to reduce blood cell damage and to enhance the membrane separation performance during the removal of toxins from the blood stream [9]. Meanwhile, an outer loose

supporting layer helps in reducing the flow of cytokine-inducing materials from dialysate to blood while retaining the proteins movement from blood to dialysate at the same time [9]. A sponge-like asymmetric structure can provide higher mechanical strength to the membrane and prevent any leakage of unwanted substances in or out of the membrane. Thus, the property of both inner selective skin and outer supporting layer may influence the diffusive permeability and selectivity of the membrane [9].

Polysulfone (PSf) is one of the most common synthetic polymers used in clinical dialyzers due to its excellent physical and chemical properties which include high thermal stability, good hydrolytic stability and good mechanical strength [10].

In this work, PSf haemodialysis hollow fiber membranes were fabricated using non-solvent induced phase separation (NIPS) technique via dual-bath coagulation. Phase inversion is a technique involved in demixing process whereby the homogenously prepared dope solution is transformed to a solid state in a controlled manner. This fabrication technique is suitable in producing UF membrane where the average pore size of the fabricated membrane is in the range of 0.001 – 0.1 µm. In NIPS process, the dope solution is immersed in a non-solvent coagulation bath. Here, demixing and precipitation occur due to the solvent and non-solvent exchange. In addition, PVP loading is manipulated to tailor the structure of the membrane.

EXPERIMENTAL

Materials

Polysulfone (PSf, Udel-P1700) was purchased from Solvay Advanced Polymers (average molecular weight = 69 500 g mol^{-1}). Polyvinylpyrrolidone (PVP, K90) with average molecular weight = 360,000 g mol^{-1} was obtained from Fluka analytical, Sigma-aldrich, USA. Both *N*-methyl-2-pyrrolidone (NMP, purity = 99.5%) and bovine serum albumin (BSA, purity = 98%) were obtained from Sigma-aldrich, USA.

Dope solution preparation

Prior to dope solution preparation, PSf pellet was dried in oven at 50°C for 24 h to remove moisture content. Polymeric dope solutions comprising PSf, PVP and NMP were prepared as shown in Table 1. Cole-Parmer® viscometer was used to measure the viscosity of the dope solution in order to determine the rheological behavior of the dope solution. Prior to spinning, the dope solution was degassed for 2 h and left at room temperature overnight.

Table 1 Compostion of PSf/PVP dope solution.

Dope composition	PSf (wt%)	PVP (wt%)	NMP	Viscosity (mPa.s)
A	18	3	79	1301.0
B	18	8	74	3001.0

Fabrication of PSf/PVP hollow fiber membrane

The dry-wet phase inversion technique was used for the formation of the hollow fiber in this study. The set-up of the spinning system is shown in Fig. 1. The dope solution extruded out from the dope reservoir and passed through a spinneret with a dimension of 0.3 mm and 0.6 mm for inner and outer dimension, respectively. The dope extrusion rate (DER) was regulated by a gear pump controller. Bore fluid is needed for the formation of hollow fiber lumen. The bore fluid was channelled into the spinneret using a constant-flow syringe pump once the dope solution extruded out from the spinneret. As stated by Mansur *et al.* [4], there are two types of phase inversion during the membrane formation process using NIPS technique. The spinning parameters for the hollow fiber membrane are shown in Table 2.

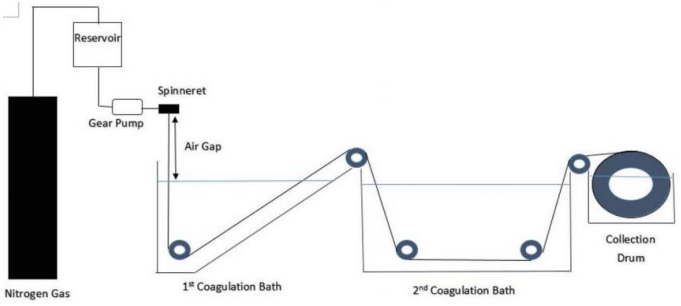


Fig. 1 Schematic diagram of dry/wet spinning system [4].

Table 2 Spinning parameter for hollow fiber membranes fabrication.

Air gap (cm)	50
Dope extrusion rate, DER (cm^3/min)	1
Bore fluid flow rate, BFFR (cm^3/min)	1
Collection drum speed (m/min)	1.5
Coagulation bath	Water
Coagulation bath temperature	Room temperature (25 °C)
Bore fluid	Distilled water

Membrane characterisation

The morphology of PSf/PVP hollow fiber membrane was examined using scanning electron microscopy (SEM) (Model: TM3000, Hitachi) to obtain the micrographs of the cross section and surface of membrane at different magnifications. The pore size of the membrane was also obtained during SEM analysis. For cross section analysis, the fiber was immersed and snapped under liquid nitrogen to produce a clean-cut surface. The fiber was attached to a stub and was sputter-coated with gold using an ion-sputtering SC7620 sputter coater (Quorum Technologies, UK) to have a clearer image during the analysis.

The hydrophobicity/hydrophilicity of the hollow fiber membrane was determined using contact angle system OCA (Dataphysics, USA). Sessile drop method was used to measure the static contact angle of the membrane surface, whereby a constant dosing volume of 0.2µL of pure water with 1.0 µL/s of dosing rate was dropped on the membrane surface and the contact angle was recorded. The average contact angle was recorded from 10 measurements made for each fibre.

Performance test of PSf/PVP hollow fiber membrane

For water permeation and BSA rejection tests, the ultrafiltration system used was in the cross-flow filtration mode by pumping the feed across the shell side of the membrane and allowing water to completely fill the module. 10 fibers were potted into each membrane module. Prior to any measurement, the steady state flux should be done by compacting the membrane at the pressure of 1 bar for 30 min. All filtrations were conducted using the membrane with length of approximately 15 cm with module area of 10 cm^2. The pure water flux was calculated from the eq. (1),

$$\text{Flux } (\text{L/m}^2\text{h}) = \frac{\Delta V}{A_m \Delta t} \quad (1)$$

where V is the volume of permeation (L), A is the total area of the hollow fiber (A), and t is the time taken (h).

Tap water was used as the feed for the pure water flux experiment. The permeation was collected and measured at 10 min interval at 0.5 bar pressure. The pure water flux and permeability analysis (eq. (2)) were repeated three times for each sample to get a reliable value.

$$\text{Permeability} = \frac{\text{Flux}}{\text{Pressure}} \quad (2)$$

For BSA rejection analysis, 500 ppm BSA (67 kDa) solution was used. All modules were operated under the pressure of 0.5 bar and 10 mL of permeate was collected. The feed and permeate were determined at the wavelength of 280 nm by a UV-spectrophotometer (DR-

5000TM, Canada). The test was repeated three times for each sample to get a reliable value. The rejection (R) was obtained by from eq. (3),

$$R = \left[1 - \frac{C_p}{C_F}\right] \times 100\% \quad (3)$$

Where R is the rejection of BSA (%), C_P and C_F are permeate and feed concentrations, respectively (ppm).

RESULTS AND DISCUSSION

Morphology of PSf/PVP hollow fiber membrane spun at different spinning conditions

The cross sectional image of the fabricated hollow fiber membrane was observed and summarised as in Fig. 2. Longer dry phase inversion (50 cm air gap) prolonged the solvent and non-solvent demixing process, thus, resulted in the fast phase separation at outer skin layer and slow phase separation at inner layer [3]. Therefore, dense skin layer at the inner lumen and long pore structure near the edge of the membrane were produced in both membrane A and B as shown in Fig. 2. Membrane A that was spun with 3 wt% of PVP concentration formed a finger-like pore structure at its outer layer. Meanwhile, membrane B that was spun with 8 wt% of PVP concentration showed a denser spongy-like structure at its outer layer. The different outer layers formed on both membranes were due to the effect of the differences in viscosity of the dope solution during the solvent/non-solvent exchange. Addition of higher PVP concentration caused the dope solution to become more viscous. When dope solution viscosity is high, the membrane outer layer becomes denser. This is because the viscous solution will hinder the movement of the pore former and solvent during the phase inversion, slow down the liquid-liquid demixing process and thus, increase the density of the membrane.

Fig. 3 shows the surface region of both PSf/PVP membrane A and B. Membrane A pore size ranged from 0.7 µm to 1.60 µm, where the pore size of membrane B ranged from 2.53 µm to 4.9 3µm. PVP acts as the pore former for the membrane. The increasing PVP concentration enhanced the formation of larger pores at the outer surfaces, whereby the hydrophilic nature of PVP allowed it to migrate from one point to another point. The migration of the PVP during the phase inversion helped to form membrane pores. Due to the high concentration of PVP, two or more pores converged to form one bigger pore.

Based on the results in Fig. 4, both membranes formed an asymmetric membrane with dense area at the innermost side and long pore structure near the end of the outer membrane. Long pore structure (Fig. 4 A2 and B2) near the edge of the outer membrane eased the movement of solutes from blood into dialysate during cross-flow and prevented the backflow of the solutes to occur. Furthermore, this long pore structure would provide mechanical strength to the whole structure and prevent the hollow fibre membrane from collapse. The membrane became denser near the inner surface and this particular area, which is called 'skin layer' (Fig. 4 A3 and B3) acted as selective layer in retaining or releasing protein and waste substances for blood purification purpose. Furthermore, the outer layer of membrane A (Fig. 4 A2) is less spongy as compared to membrane B (Fig. 4 B2). This could be explained based on the concentration of the PVP during the phase inversion process. The hydrophilic nature of PVP causes the additive to leach out from the the membrane during the phase inversion process and influence the formation of the outer layer of asymmetric PSf membrane. Low concentration of PVP causes the phase inversion process became faster. When the outer skin of the membrane started to solidify, the inner skin was still in precipitating process. Bore fluid flows into the membrane and contributes to the formation of the finger-like structure. High concentration of PVP increased the viscosity of the dope solution and further slowing down the phase inversion process. During the solidification process of the membrane, high viscosity hindered the movement of PVP and solvent out from the dope solution into the bore fluid during dry phase inversion. Membrane started to solidify, PVP and solvent leached out from the membrane at slower rate, thus forming spongy structure.

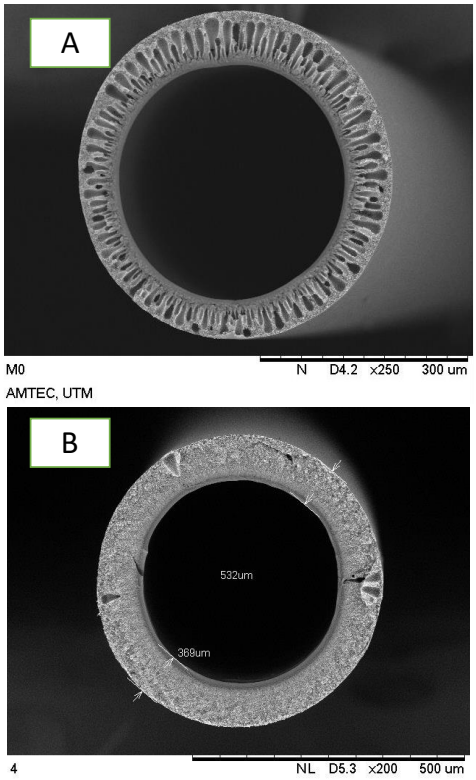


Fig. 2 SEM images of asymmetric PSf/PVP membranes spun with different PVP compostions.

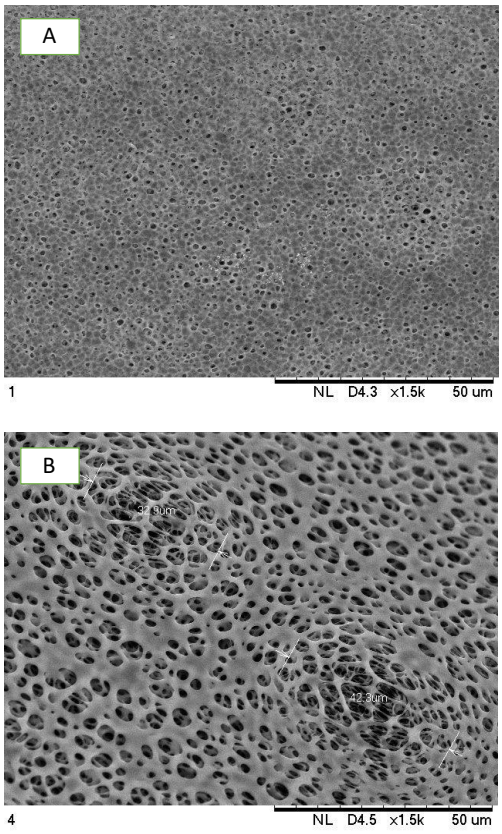


Fig. 3 SEM images of PSf/PVP membranes at outer surface region.

Hydrophobicity/hydrophilicity of PSf/PVP hollow fiber membrane spun with different PVP concemtrations

The hydrophobicity/hydrophilicity of the fabricated hollow fiber membrane was determined by measuring the contact angle of water droplet on the surface of the membrane. Lower contact angle

Meanwhile, high contact angle measurement indicates that the membrane is more hydrophobic. Table 4 shows the contact angle measurement for each of the fabricated PSf/PVP hollow fiber membrane. Based on the results, membrane A, which contained 3% of PVP concentration had a higher reading compared to membrane B, which contained 8% of PVP concentration. This indicated that membrane B is more hydrophilic compared to membrane A. This results is in agreement with the pure water flux of the membranes. Membrane B had the highest pure water flux (98.32 L/m^{2}h). Thus, the higher the hydrophilicity of the membrane, the higher the pure water flux of the membrane. In addition, these results can also be explained based on the morphological characteristics of the membranes, as shown in Fig. 4. The spongy structure that was formed at the outer layer of membrane, the increased pore distribution and pore size produced high membrane permeability.

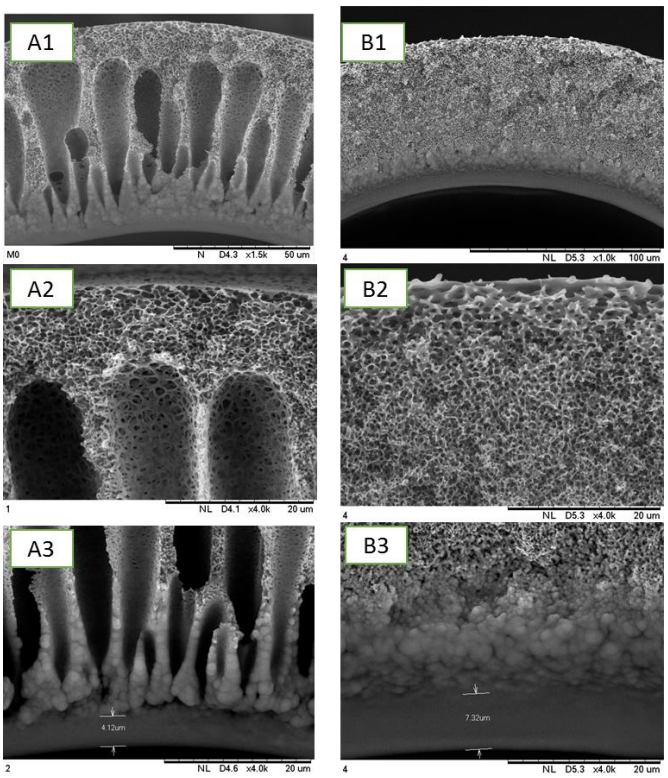


Fig. 4 SEM images of skin layer near the inner surface (A3 and B3) of the membrane and near the edge of the membrane (A2 and B2). Magnification 1500 x.

Table 3 Comparison of PSf/PVP hollow fiber membranes spun at different conditions in terms of contact angle measurement and pure water flux.

PSf/PVP spun at different conditions	Contact angle measurement (°C)	Pure water flux (L/m^{2}h)
A	66.62 (± 4.29)	29.32 (± 0.76)
B	12.40 (± 0.36)	98.32 (± 2.33)

Performance of PSf/PVP hollow fiber membranes in terms of water permeation and BSA rejection

The comparison of both PSf/PVP hollow fiber membranes based on the permeation and BSA rejection analysis are shown in Table 4. In order to evaluate the effect of different dope compositions on the performance of PSf/PVP hollow fiber membrane, water permeation and BSA rejection tests were conducted. Bovine serum albumin (BSA) was chosen as the marker to determine the percentage of solute rejection due to its size. The normal size of the protein that needs to be retained during haemodialysis is in the range of 64-66 kDa, whereby the BSA molecular weight is 67 kDa. Thus, higher percentage value of BSA rejection will indicate that the membrane can retain more proteins.The results of ultrafiltration experiments and protein rejection are summarised in Table 4. Based on the results in Table 4, hollow fiber with 8 wt% PVP concentration (membrane B) exhibited the higher reading of water flux (98.32 L/m^{2}h) with lower protein rejection (17.31%). This is the common trade off phenomena in membrane fabrication and these results were in correlation to the morphology of the membranes produced. Membrane B has larger pore size that helps in increasing the flux of the membrane. However, the large pore formation decreased the rejection performance of the membrane. Higher flux produced convective force which is able to drag the large protein that needs to be retained during the clearance of the uremic toxins. This phenomenon is called permeation drag. Membrane B showed a better result in terms of the flux, however, its ability to sieve protein was low. Thus, some modification on membrane B needs to be done to counter this problem.

Table 4 Comparison of PSf/PVP hollow fiber membranes with different dope compositions on membrane performances.

PSf/PVP spun at different conditions	Pure water flux (L/m^{2}h)	BSA rejection (%)
A	29.32	91
B	98.32	17.31

CONCLUSION

In this study, PSf hollow fiber membranes with different PVP concentrations were prepared, characterised and tested in an ultrafiltration system setup. This research aims to study the effect of different concentrations of PVP as the pore former on the membrane morphology and performances. It was found that the morphology, porosity, flux and rejection are depending on the pore former loading. Membrane A and B have different morphological structure and pore size. The porous spongy-like structure of membrane B possessed larger pore size at the surface region of the membrane. The large pore size in membrane B caused the membrane to become more hydrophilic and thus increased the flux and permeability of the membrane. However, the solute rejection of membrane B was poor (17.31%). A further study needs to be done to eliminate this trade off effect by decreasing the pore size of membrane B and increasing the number of pores of the membrane. This is to ensure more water molecules can be channelled through the membrane and enhance the rejection performance at the same time. Surface modification at the surface of the membrane may solve the low rejection problem.

ACKNOWLEDGEMENT

This work is financially supported by Universiti Teknologi Malaysia under Flagship Program (Project number: Q.J130000.2409.01G46). The authors would also like to thank Research Management Centre, Universiti Teknologi Malaysia for the technical support.

REFERENCES

[1] Gao, A. Liu, F., Xue, L. Preparation and evaluation of heparin-immobilized poly (lactic acid) (PLA) membrane for hemodialysis. *J. Memb. Sci.* 2014; 452:390–9. doi:10.1016/j.memsci.2013.10.016.

[2] Kerr, P. G., Kerr, P. G. Review : Membranes for haemodialysis Correspondence. *Nephrology* 2010; 15:381–5. doi:10.1111/j.1440-1797.2010.01331.x.

[3] Barzin, J., Feng, C., Khulbe, K. C., Matsuura, T., Madaeni, S. S., Mirzadeh, H. Characterization of polyethersulfone hemodialysis membrane by ultrafiltration and atomic force microscopy. *J. Memb. Sci* 2004; 237:77–85. doi:10.1016/j.memsci.2004.02.029.

[4] Mansur, S., Othman, M. H. D., Ismail, A. F., Kadir, S. H. S. A., Kamal, F., Goh, P. S., *et al*. Investigation on the effect of spinning conditions on the properties of hollow fiber membrane for hemodialysis application. *J. Appl. Polym. Sci.* 2016; 133:1–10. doi:10.1002/app.43633.

[5] Vanholder, R., De Smet, R., Glorieux, G., Argilés, A., Baurmeister, U., Brunet, P., *et al*. Review on uremic toxins: Classification, concentration, and interindividual variability. *Kidney Int.* 2003; 63:1934–43. doi:10.1046/j.1523-1755.2003.00924.x.

[6] Krieter, D. H., Wanner, C. Membranes for dialysis and hemofiltration. *JAMA J Am Med Assoc* 2010; 304:1497. doi:10.1001/jama.2010.1431.

[7] Sakai, K. Determination of pore size and pore size distribution: 2. dialysis membranes. *J. Memb. Sci.* 1994; 96:91–130. doi:10.1016/0376-

7388(94)00127-8.
[8] Bowry, S. K., Gatti, E., Vienken, J. Contribution of polysulfone membranes to the success of convective dialysis therapies. *High-Performance Membr. Dialyzers* 2011; 173: 110–18. doi:10.1002/9783805598132.ch14.
[9] Yang, Q., Chung, T. S., Santoso, Y. E. Tailoring pore size and pore size distribution of kidney dialysis hollow fiber membranes via dual-bath coagulation approach. *J. Memb. Sci.* 2007; 290:153–63. doi:10.1016/j.memsci.2006.12.036.
[10] Said, N., Hasbullah, H., Ismail, A. F., Othman, M. H. D., Goh, P. S., Zainol, M. N. A., *et al*. Enhanced hydrophilic polysulfone hollow fiber membranes with addition of iron oxide nanoparticles. *Polym. Int.* 2017. doi:10.1002/pi.5401.