

Investigating the Usability of Alkali Lignin as an Additive in Polysulfone Ultrafiltration Membranes

Gcina D. Vilakati,^a Eric M. V. Hoek,^b and Bhekie B. Mamba^{a,*}

The effects of natural and synthetic polymer additives on the properties of ultrafiltration membranes were studied. The use of NaOH to remove the residual additive remaining in the membranes during coagulation was also investigated, as was the effect of NaOH post-treatment relative to membrane performance. To evaluate the residual additives present, ATR-FTIR was used. Contact-angle analysis and water-absorption experiments were used to examine the hydrophilic properties of the prepared membranes. Membranes modified with lignin (Lig) were found to absorb more water (94% water uptake) than other membranes. In general, the contact angles were found to be low for membranes treated with NaOH. Membrane permeability was greatest in lignin_polysulfone (Lig_PsF), followed by polyvinylpyrrolidone_polysulfone (PVP_PsF), and with polyethylene glycol_polysulfone (PEG_PsF) the least permeable, similar to the trend observed in water uptake. A 'Robeson plot' analogue showed that Lig_PsF membranes had high separation factors regardless of the size of the solute being rejected. This study indicates the feasibility of using cheap, readily available additives to increase the performance of membranes.

Keywords: Additive; Biopolymers; Lignin; Polysulfone; Synthetic polymers

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INTRODUCTION

Ultrafiltration membrane technology has been applied to many types of separation techniques, such as the removal of organics from water. Hydrophilicity and pore size play major roles in the performance of such membranes (Yan *et al.* 2006). However, polysulfone (PSf), a versatile polymer used to fabricate such membranes, is relatively hydrophobic (Zularism *et al.* 2007). To overcome this problem, polysulfone is usually blended with other, more hydrophilic polymers during the casting process (Yeo *et al.* 2000; Chakrabarty *et al.* 2008; Kumar *et al.* 2013). Much effort has been devoted to membrane modification to improve membrane permeability and antifouling properties.

Unmodified polysulfone membranes perform poorly compared to modified membranes (Lafreniere *et al.* 1987). Membrane modification techniques vary from the use of hydrophilic polymers or inorganic nanoparticles as additives to changing certain conditions during membrane fabrication. Polyethylene glycol (PEG), tetra-ethylene glycol (TEG), and polyvinylpyrrolidone (PVP) are examples of polymer additives commonly used to increase the viscosity of the dope solution without adversely affecting the polymer concentration (Aroon *et al.* 2010). These polymers can also be used as pore-forming agents,

hydrophilicity inducers, and macrovoid suppressors. Their incorporation often results in increased permeability (Wienk *et al.* 1995; Machado *et al.* 1999; Ismail and Hassan 2007; Chakrabarty *et al.* 2008). Other additives that have been studied include LiCl and organic acids such as acetic acid and propanoic acid (Shi *et al.* 2008). To determine the effectiveness of an additive, cloud-point determination experiments are typically carried out. These experiments indicate whether or not the additive changes the thermodynamic stability of the dope solution. Some polymer additives increase the viscosity of the casting solution, driving the composition of the solution nearer to the precipitation point (Wang and Teo 1996).

Improving the performance of membranes could lead to lower operating costs because more permeate can be attained using a given membrane. Using relatively cheap, readily available additives to improve membrane flux and reduce fabrication costs has not been studied much in the past. This can be done by substituting well-known additives with the cheaper alternatives. The cost of synthetic additives can be reduced in this way, reducing the overall cost of membrane fabrication. The significance of the cost reduction depends on the overall membrane synthesis process and also depends on the percentage of additive used. Additives have been substituted for up to 20% of the weight of membranes in previous work (Kumar *et al.* 2013). Natural additives are of interest because they are renewable and are often available in abundance.

Although the ideal solution would be to use only renewable additives and solvents when fabricating polymeric membranes *via* phase inversion, the use of a single renewable component (*i.e.*, an additive) is a starting point. Biopolymers such as lignin and cellulose have been used as polymer reinforcements and blenders (Canetti *et al.* 2004; Ciobanu *et al.* 2004). Lignin is an amorphous, phenolic, relatively inert organic polymer and is the second-most abundant natural polymer on earth (Pucciariello *et al.* 2010). It is a by-product of the paper and pulp industry. Although lignin has previously been used as a polymer blender, its complex structure can be disintegrated by treatment with alkali *via* a process called delignification. This process is also used to remove lignin from wood during pulp production.

Lignin derivatives have been used in membrane synthesis because they are readily available and because it is an alternative method of waste removal for the pulp industries. Zhang *et al.* (2005) incorporated lignosulfonates into polysulfone membranes to induce electrolyte transference, reporting that higher concentrations of lignosulfonates facilitated larger surface pores and decreased macrovoid formation. Recently, Nevarez *et al.* (2011) used propionated lignin to fabricate cellulose triacetate membranes for water purification. Propionated lignin was used to improve polymer interaction with cellulose triacetate. In another recent study, Hashim *et al.* (2011) evaluated the use of SiO₂ particles as an additive, focusing on the effects of acid (HF) and alkaline (NaOH) treatments on the performance of the PVDF membranes. Both post-treatments improved membrane permeability because they dissolved SiO₂ particles and washed them out of the membranes.

Polymeric solvent additives (additives that dissolve in the solvent in question) such as PEG tend to adhere to the membrane and leach out over time. Such membranes are not ideal thin-film composite (TFC) membrane supports because leaching removes a considerable amount of the thin film, reducing the half-life of the membrane. The right choice of additive (one that can be easily removed from the membrane) is essential.

Alkali lignin has long been isolated from wood using alkaline treatments (Vilakati *et al.* 2012). It is a natural polymer commercially available in the form of aggregate powders. It can be dissolved in solvents such as N-methylpyrrolidone (NMP), the same

solvent used to dissolve polysulfone, at about 50 °C. One hypothetical lignin structure is shown in Fig.1 and its derivatives have been reported elsewhere (Alder 1977).

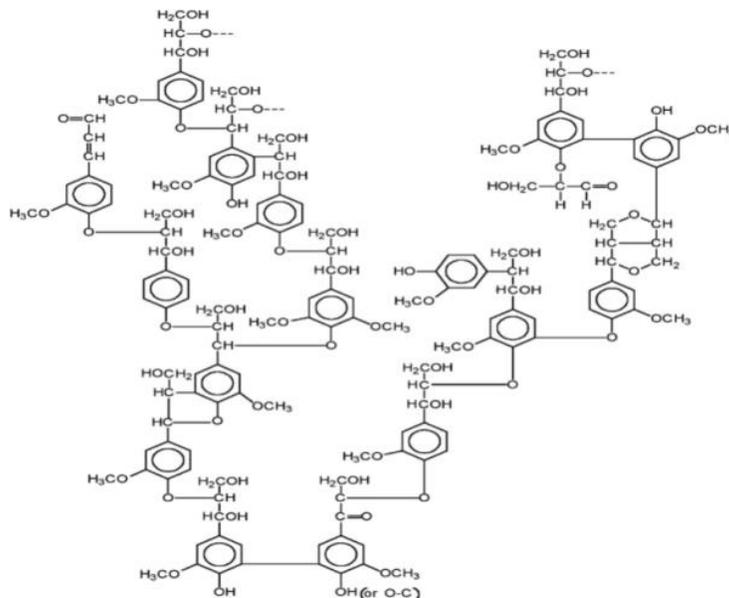


Fig. 1. One hypothetical structure of lignin

Native lignin has not been used as a membrane additive. In the present study, it was used as a novel additive for two reasons. First, it can be removed from the membrane using a modified delignification process and the degree of delignification can be easily confirmed using Fourier transform infrared (FTIR) spectroscopy. Secondly, because of its hydrophilic nature, the surface properties of the membranes can be altered slightly such that good membrane performance and porosity can be achieved with relatively low loadings.

EXPERIMENTAL

Materials

To prepare the polymer solution, polysulfone beads (22 kDa), alkali lignin (28 kDa), and NN-dimethyl formamide (DMF) obtained from Sigma-Aldrich (USA) and NMP obtained from Merck (USA) were used. A commercial fabric was obtained from Hirose Paper Manufacturing Co., Ltd. (Japan). Polyethylene glycol with molecular weights of 10 and 35 kDa and polyvinylpyrrolidone (PVP, 360 kDa) used in rejection experiments were also acquired from Sigma-Aldrich. PEG 10 kDa was also used to modify the membranes (as additive) while PVP 29 kDa, also purchased from Sigma, was only used as additive.

Methods

Fabrication of UF support membranes

The membranes were prepared using a phase inversion process detailed in another study (Vilakati *et al.* 2014). Each additive was dissolved in a mixture of NMP and DMF solvents at 50 °C (a temperature below the flash point of the solvent). After complete dissolution of the additive, small amounts of polysulfone beads (22 kDa) were added, while stirring, to the cold additive-solvent solution in the ratios and amounts shown in Table 1. The solution was then mixed for at least 8 h and allowed to settle overnight. The solutions

were cast onto the non-woven which was attached to a clean glass plate with tape. Using a casting knife with the blade height set at 150 μm , the polymer solution was cast to the fabric and glass plate and the cast solution was immediately immersed in deionized (DI) water for 10 min. The membranes were rinsed in DI water three times for 30 min each. The membranes were soaked in a 5 wt.% aqueous NaOH solution at 50 $^{\circ}\text{C}$ for 30 min and then rinsed with DI water at 80 $^{\circ}\text{C}$ for 5 min. All membranes were stored in a refrigerator (4 $^{\circ}\text{C}$) before performance testing was carried out.

Structure and morphology of membranes

The support membranes were characterised using a JEOL 5000 scanning electron microscope (SEM; Japan) operating at an accelerating voltage of 20 kV. The membranes were gold-coated using a gold sputter coater to make them electrically conductive. The preparation of cross-sectional samples involved soaking the membranes in liquid nitrogen and then quick-freezes fracturing the musing thumb dressing forceps before they were gold-coated.

Contact-angle analysis

The surface tension and capability of the membranes to attract water were assessed using a contact-angle goniometer (DataPhysics Optical Contact Angle SCA20, Germany). The contact angles of the membranes were determined using a sessile drop method. The membranes were pre-dried in an oven at 80 $^{\circ}\text{C}$ overnight and were stored in a desiccator for later analysis. To ensure there reproducibility of the reported data, the contact angle measurements were taken from one membrane at different points and the average of three replicate measurements made on different days was reported.

Water uptake

Membranes were cut into pieces and weighed after oven-drying at 80 $^{\circ}\text{C}$. These pieces were then immersed in distilled water for 10, 20, 30, 60, 120, 240, 480, or 1,440 min. The membrane pieces were then weighed again (wet weight) after the specific time interval had elapsed. It should be noted that once a membrane was removed from the water, it was not immersed again. This was done to avoid error resulting from membrane drying during weighing. The percentage of water uptake was calculated using Eq. 1,

$$\text{Water uptake (\%)} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{wet}}} \quad (1)$$

where M_{dry} and M_{wet} are the dry and wet weights of the membranes, respectively.

FTIR analysis

To determine the presence or absence of lignin in the membranes following treatment, a Perkin-Elmer Spectrum 100 FTIR spectrometer (USA) with an attenuated total reflectance (ATR) component was used.

Cloud-point determination

A phase diagram was plotted using data points obtained *via* titration methods in which the end-point was visually determined according to the formation of a turbid solution. Polysulfone solutions (with concentrations of 1, 2, 4, and 8 wt.%) without additives were titrated with deionized water at 20 $^{\circ}\text{C}$. These results were compared with

those of other similarly concentrated polysulfone solutions containing 0.5 wt.% of each additive. The fractions of coagulant, solvent, and polymer at the end-points of these titrations were used to create a ternary phase diagram.

Pure water permeability and performance analysis

Pure water permeability (L_p) studies were performed after the membranes were compacted using a Sterlitech high-pressure dead-end testing cell (HP4750; USA) with an effective surface area of 12.57 cm² operating at 4 bar. This was done by varying the pressure after the flow rate had stabilised, or when the change in flow rate was less than 6% throughout a 30-minute interval. The gradient of the plot of pressure vs. flux, through zero, yielded the pure water permeability. The same membrane was used for PEG and PVP rejection. This was accomplished by replacing the deionized water in the feed cell with 100 mL of 500 mg/L solute while stirring at 400 rpm. Approximately 3 mL of the first permeate was discarded to account for dilution as a result of the water remaining in the cell. A 5-mL yield was collected, diluted, and analysed using a total organic carbon (TOC) analyser (Teledyne Tekmar, TOC fusion; USA). The rejection parameter was calculated according to Eq. 2,

$$R_o = 1 - \frac{C_p}{C_f} \quad (2)$$

where R_o is the observed rejection and C_p and C_f are the permeate and feed concentrations, respectively.

The ratio of the concentration of the solute in the permeate to that in the bulk solution is defined as the sieving coefficient, S_i . The observed sieving coefficient, S_o , is given by C_p/C_f and $R_o = 1 - S_o$. The actual or intrinsic rejection, R_i , is given by $1 - C_p/C_m = 1 - S_a$, where C_m is the concentration at the membrane surface.

The actual sieving coefficient, S_a , can be estimated with Eq. 3 using a stagnant film model and experimental data (Zeman and Zydney 1996),

$$S_a = \frac{S_o}{(1-S_o) \exp\left(\frac{J_v}{k}\right) + S_o} \quad (3)$$

where J_v and k are the volumetric flux and mass transfer coefficient, respectively.

Mehta and Zydney (2005) defined the separation factor (α) as the ratio of the sieving coefficient of small solutes to that of large solutes, S_{small}/S_{large} . In UF, they observed that small solutes and water (the solvent) passed freely through the membrane, indicating that S_{small} was approximately 1, and that α could be approximated as $1/S_{large}$. Because small solutes were not rejected, S_{small} was assumed to be equal to that of the solvent.

The mass transfer coefficient was calculated by nonlinear least-squares fitting of data using Microsoft Excel and further verified using Libreoffice software. This was done according to Eq. 4, in which the observed rejection and the intrinsic rejection are related to the observed flux (Penga *et al.* 2010):

$$\frac{R_o}{1-R_o} = \frac{R_i}{1-R_i} \exp\left(\frac{J_v}{k}\right) \quad (4)$$

Membrane resistance (R_m) was calculated using deionized water as shown in Eq. 5,

$$R_m = \frac{\Delta P - \beta \Delta \pi}{\eta J_v} \quad (5)$$

where $\beta = \frac{C_m - C_p}{C_f - C_p}$, and η is the viscosity of water. ΔP and $\Delta \pi$ are the transmembrane hydraulic and osmotic pressures. Since $\Delta \beta = \text{zero}$ for deionized water, Eq. 5 reduces to:

$$R_m = \frac{\Delta P}{\eta J_v} \quad (6)$$

Table 1. Specific Conditions for Membrane Fabrication and Post-Treatment using 5% NaOH

Membrane	PSf(wt.%)	Additive (wt.%)	NMP:DMF ratio	Solvent (wt.%)	Coag. bath	Post-treatment
PSf	17	0.000	3:1	83.000	DI	NaOH
0.125%_PEG_PSf	17	0.125	3:1	82.875	DI	NaOH
0.5%_PEG_PSf	17	0.500	3:1	82.500	DI	NaOH
0.125%_PVP_PSf	17	0.150	3:1	82.875	DI	NaOH
0.5%_PVP_PSf	17	0.500	3:1	82.500	DI	NaOH
0.125%_Lig_PSf	17	0.125	3:1	82.875	DI	NaOH
0.5%_Lig_PSf	17	0.500	3:1	82.500	DI	NaOH

Lig_PSf, lignin_polysulfone; PVP_PSf, polyvinylpyrrolidone_polysulfone; PEG_PSf, polyethylene glycol_polysulfone; DI, deionized water

RESULTS AND DISCUSSION

Cloud-Point Determination

The onset of the cloud point was determined by titration methods ultimately leading to liquid-liquid demixing. During demixing, the solution becomes thermodynamically unstable and the system separates into two phases. To determine the effect of additives on the phase separation properties, cloud-point experiments were conducted. The system normally consists of a solvent, a polymer, and the non-solvent. In this case, two systems were used: one with 0.5 wt.% additive (lignin, PEG, or PVP) and another without additive. The polymer concentration was increased in both systems to account for the effect of the introduction of an additive to the system. Table 2 shows that more water was needed to reach the cloud point after lignin was incorporated into the system. Riyasudheen and Sujith (2012) reported that for systems where an additive (PVP) was added, less water was needed to reach the cloud point. It has also been reported that PVP reduces the demixing gap of the ternary system, leading to the formation of a denser structure (Mulder 1996). The same results were obtained (Fig. 2) in this study when using PVP or PEG as the additive. When lignin was added, however, the demixing gap increased and the curve shifted toward the polymer-non-solvent axis. Additives with behaviour like that of PVP or PEG are referred to as solvent additives, unlike lignin, a non-solvent additive that does not dissolve in the solvent (NMP) at room temperature. There are two possible reasons for the shift of the

curve towards the polymer-nonsolvent axis after the addition of lignin. Either lignin increased the water tolerance of the dope solution, or lignin interacted with the polysulfone. Both would delay solvent outflux. It is expected that the membranes would have spongy morphologies if the thermodynamic effect caused by the solvent was not dominant.

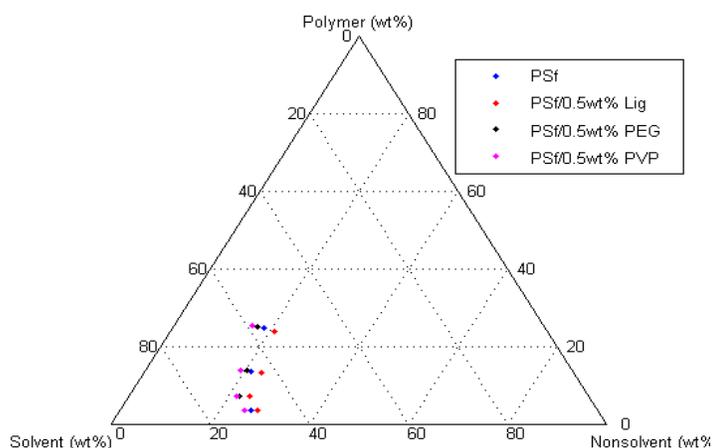


Fig. 2. Phase diagram showing the different concentrations of neat polysulfone and polysulfone with additives (lignin, PEG, PVP) in a 3:1 (NMP:DMF) solvent system. The non-solvent and polymer data have been scaled up five times to enhance visibility.

Although the phase diagram in Fig. 2 indicates that there was delayed liquid-liquid demixing (as the amount of water required to induce precipitation increased after lignin addition), it should be noted that the delayed liquid-liquid demixing was instantaneous at localised points. This means that each water droplet instantly caused precipitation within the polymer solution at the point of contact before dissolving again with vigorous stirring. This was observed following the addition of lignin.

Table 2. Amount of Water Used to Precipitate the Polymer Solution during Cloud-Point Determination

Solvent (wt.%)	Polymer (wt.%)	Water content (mL)	
		Without lignin	With lignin
99	1	7.50	8.00
98	2	7.00	7.00
96	4	6.30	7.25
92	8	6.00	7.00

ATR-FTIR

To confirm that lignin dissolved in the prepared membranes, IR spectra were used to determine the presence or absence of the carbonyl peak characteristic to lignin, as shown in Fig. 3. Lignin from wood, grass, and biomass sources has characteristic peaks at around 1600 cm^{-1} and 1750 cm^{-1} due to aromatic stretching and the vibration of unsaturated carbonyls (C=O), respectively (Hergert 1960; Lisperguer *et al.* 2009; Zhou *et al.* 2011; Vilakati *et al.* 2012). This peak was not present in the spectra before or after post-treatment with sodium hydroxide. The post-treatment was meant to remove trace lignin remaining in the membrane, as lignin solubility in water could not be established. Previous research has shown that lignin dissolution can be achieved with alkaline treatment without adversely

affecting polysulfone, which is known to be resistant to caustic treatment (Vilakati *et al.* 2012). Furthermore, the broad -OH peak present in the spectra of lignin was absent from the membrane spectra. The aromatic peak at 1604 cm^{-1} (characteristic of lignin) was present in both the membranes and the neat lignin because both lignin and polysulfone exhibit aromatic stretching. The IR spectroscopy was inconclusive regarding the total dissolution of lignin because ATR-FTIR was used and the penetration depth into the membrane sample was relatively low. The penetration depth into the sample is typically between 0.5 and $2\text{ }\mu\text{m}$, a function of the wavelength of the incident light (Mirabella 1993). These results, unfortunately, indicate only the removal of lignin from the membrane surface. Membranes modified with PEG and PVP were also characterised by FTIR spectroscopy, as shown in Figs. 4a and 4b. There was no observed difference in the peaks before and after NaOH treatment, except for the appearance of a broad shoulder peak at 1490 cm^{-1} . This peak may be due to the formation of an enolate (an intermediate step in the formation of a methylene group) because of additive derivatives remaining in the membrane.

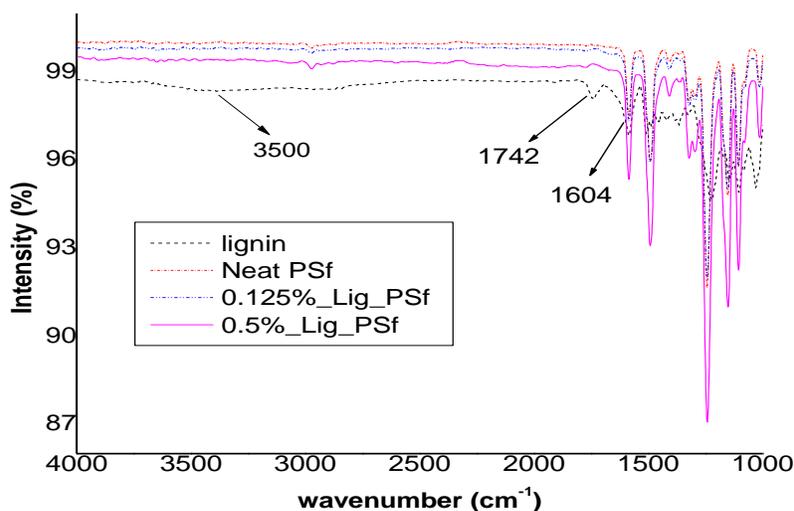


Fig. 3. ATR-FTIR spectra of neat lignin and membranes modified with lignin

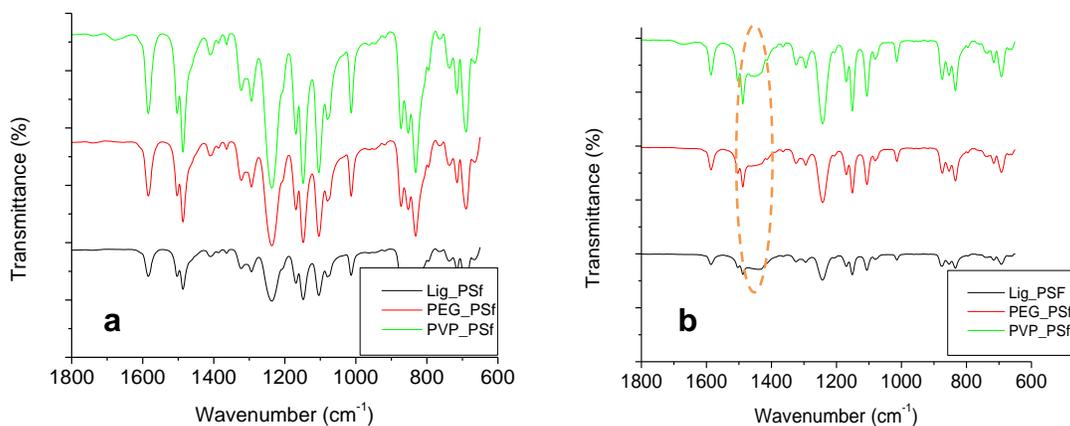


Fig. 4. ATR-FTIR peaks of membranes: (a) before NaOH treatment and (b) after NaOH treatment

Membrane Morphology

An additive to a casting polymer solution either promotes pore formation or suppresses macrovoid formation. Figure 5 shows cross-sections of membranes modified with 0.5 wt.% of each tested additive. The membranes had asymmetrical structures, and there was no visible difference between them. It was expected, however, that the membranes modified with lignin would have a spongy structure because they exhibited delayed liquid-liquid demixing. This was not the case because the thermodynamic effect of the use of a relatively viscous solvent was dominant. Also, the shift towards the polymer-nonsolvent was too small (less than 1%), compared to those of the other membranes, to cause a significant change in the physical structure of the membrane. Ismail and Mansourizadeha (2011) investigated the effect of anon-solvent additive on PVDF hollow-fibre membranes and concluded that two processes were responsible for the appearance of oval-shaped microvoids and the observed variation in the width of the sub-layer macrovoids: the thermodynamic demixing effect and the kinetic effect of viscosity. The thermodynamic effect is characterised by rapid demixing induced by the presence of a viscous solvent, NMP, and overrides the kinetic effect of viscosity increases *via* lignin addition. This is because an inadequate amount of lignin was added to cause a significant change in the overall viscosity (which was not measured) of the polymer solution. Because there was no observed difference in the membrane's morphology, water absorption experiments were conducted to account for the differences in the performance of the membranes.

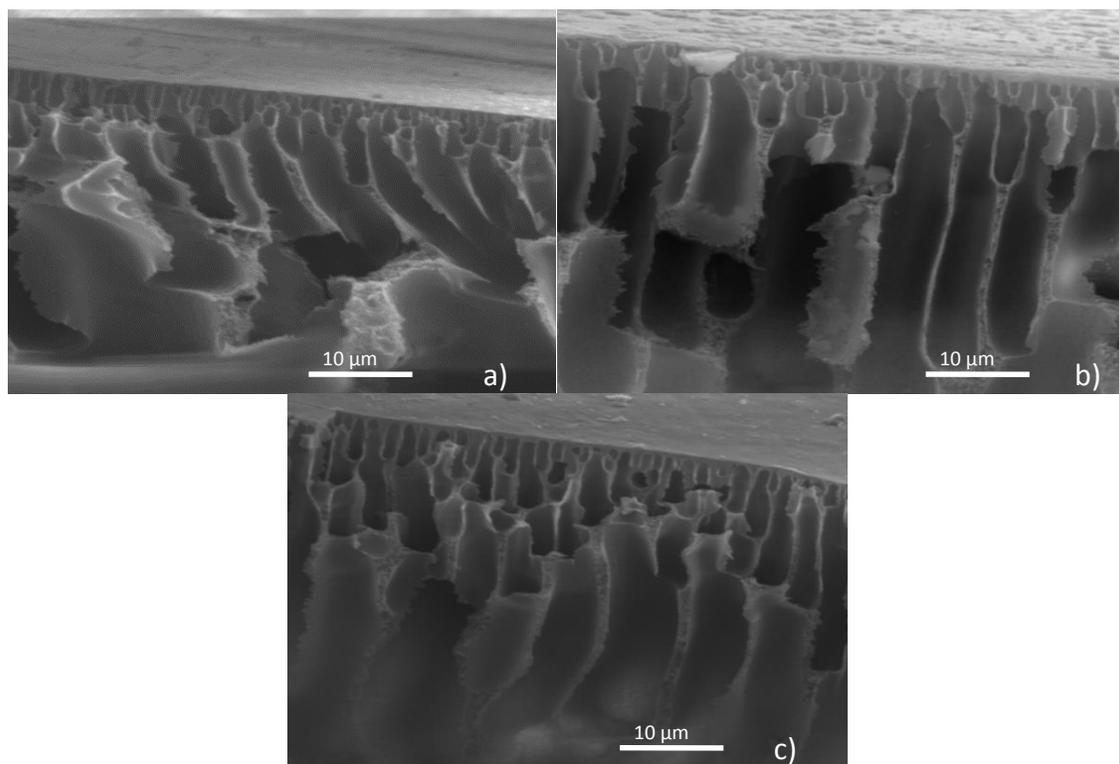


Fig. 5. SEM images showing cross-sections of PSf membranes modified with (a) 0.5wt.% lignin, (b) 0.5wt.% PEG, and (c) 0.5wt.% PVP

Water Absorption and Contact-Angle Analysis

Water uptake is dependent upon the hydrophilicity and porosity of the membrane. More hydrophilic membranes will absorb water faster than relatively hydrophobic ones. The contact angles of membranes also depend on membrane porosity, hydrophilicity, and surface roughness. In essence, the contact angle and water uptake provide indications of the hydrophilicity of a membrane. A membrane with high water content and low contact angle is considered hydrophilic (Sadzadeh and Bhattacharjee 2013). In general (Fig. 6), membranes modified with 0.5 wt.% of each additive had higher water uptake values, with 0.5%_Lig_PSF reaching equilibrium at 94% after 120 min. Most of the membranes attained maximum water uptake after one hour of immersion.

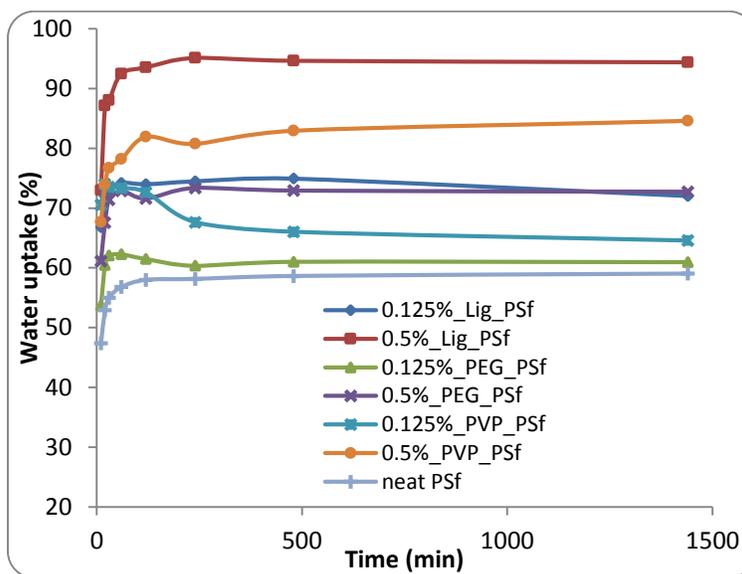


Fig. 6. Water uptake by modified membranes. The standard deviation was between 3 and 7%.

Table 3 shows the contact angles of the membranes before and after NaOH treatment. The purpose of the treatment was to wash away residual additive particles that remained following coagulation. The results did not reveal a relationship between additive content and contact angle before or after treatment. The contact angle decreased following NaOH treatment because the membrane porosity increased as residual additive was removed. Similar results were reported by Simon *et al.* (2013) after the effect of caustic cleaning on nanofiltration membranes was evaluated, although the decrease in hydrophobicity observed in their study was not substantial. A decrease in PSf contact angle was also observed, unexpectedly, because PSf is resistant to alkali treatment. This could be because the residual NaOH on the membrane surface made the membrane relatively hydrophilic. A similar observation was reported by Li and Elimelech (2004) in a study in which membranes were cleaned with SDS and EDTA. Notably, the contact angles of PEG-PSf and PVP-PSf membranes were lower than that of Lig-PSf. From these results, it would have been expected that the permeability of Lig-PSf be lower. To the contrary, Lig-PSf had high permeate flux. These contact angles were decreased by the addition of each additive. Depending on whether each additive dissolves completely during coagulation, the contact angle will remain low if that additive does not come out completely, as was seen for PEG and PVP additives.

Table 3. Effect of NaOH Treatment on the Contact Angle (CA) of Polysulfone Membranes Modified with Lignin, PEG and PVP

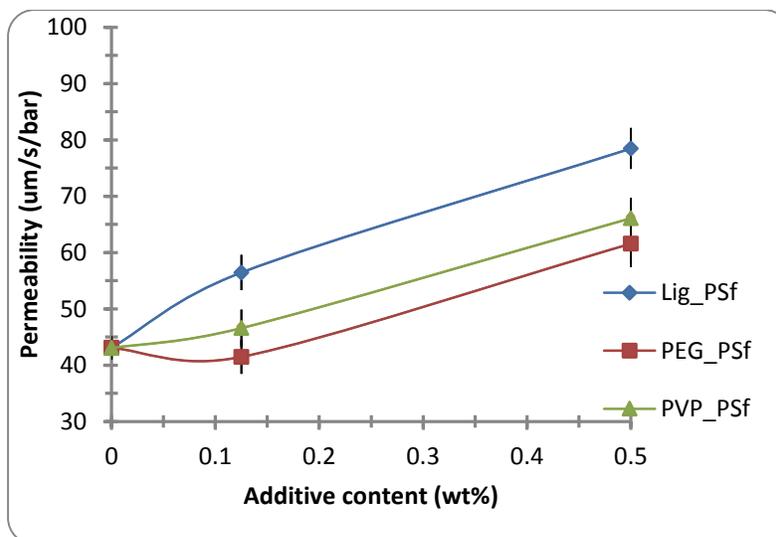
Membrane	Before NaOH Treatment (°)	After NaOH Treatment (°)
PSf	86.5 (0.9)	79.2(2.3)
0.125%_Lig_PSf	72.5 (2.7)	68.5 (1.5)
0.5%_Lig_PSf	73.8 (4.8)	72.6 (2.5)
0.125%_PEG_PSf	67.6 (4.3)	59.0 (1.3)
0.5%_PEG_PSf	67.7 (2.5)	62.7 (1.2)
0.125%_PVP_PSf	67.5 (3.3)	62.9 (4.0)
0.5%_PVP_PSf	70.4 (2.5)	64.8 (1.4)

Lig_PSf, lignin_polysulfone; PVP_PSf, polyvinylpyrrolidone_polysulfone; PEG_PSf, polyethylene glycol_ polysulfone; The standard deviation is in parentheses.

Membrane Performance

Effect of additive concentration on the membrane performance

Using pore-forming agents in membrane synthesis resulted in increased permeate flux. Han *et al.* (2012) assert that the membrane flux increases with the glycol content and observed a decline in the rejection of polyethylene glycol in their study (PEG-10 kDa). Figure 7 shows pure water permeability as a function of additive concentration. As shown in the water absorption section, Lig_PSf had the greatest water uptake, followed by PVP_PSf, and finally, PEG_PSf. The water permeability of the membranes was in the same order. This was expected, since pore-forming agent molecules form pores by occupying spaces in the membrane matrix. These spaces remained empty after coagulation because the additives are soluble in water. This phenomenon is demonstrated in Table 4, where a decrease in the membrane's resistance was observed for membranes modified with PVP and lignin with the latter having a value of $1.37 \times 10^6 \mu\text{m}^{-1}$. This is a reduction of about 2 fold.

**Fig. 7.** Permeability of UF support membranes with different additive contents

Performance analysis

A state-of-the-art ultrafiltration membrane is one that has both good selectivity and high permeability. In a plot of the separation factor ($1/S_a$) against the permeability, such membranes will be represented at the top right corner of the plot. This type of plot has been used to compare the selectivity of different commercial membranes for gas separation. In most cases, these membranes come with a given MWCO that does not necessarily give relevant quantitative analysis when a 99 or 99.9% rejection is desired (Mochizuki and Zydney 1993). In this study, membranes made from different additives were compared using this method of analysis.

Table 4. Membrane Resistance Calculated using Deionised Water and using the Dynamic Viscosity of Water at 23 °C

Membrane	Membrane resistance, R_m (1/m) $\times 10^{12}$
PSf	2.49
0.125%_PEG_PSF	2.58
0.5%_PEG_PSF	1.74
0.125%_PVP_PSF	2.30
0.5%_PVP_PSF	1.62
0.125%_Lig_PSF	1.90
0.5%_Lig_PSF	1.37

Plots of the separation factor *versus* membrane permeability are given for PVP-360 kDa (Fig. 8a) and PEG-35 kDa (Fig. 8b) using the same membranes. One observation from the plot is that the lignin-modified membranes had high selectivity and permeability compared to those of the membranes modified with PEG-10 kDa and PVP-29 kDa additives when PVP-360 kDa was rejected. When PEG-35 kDa was rejected, however, the separation factor was lower, while the permeability remained high. This is because lignin-modified membranes had greater water uptake and porosity characteristics (Fig. 6) than PEG-modified membranes.

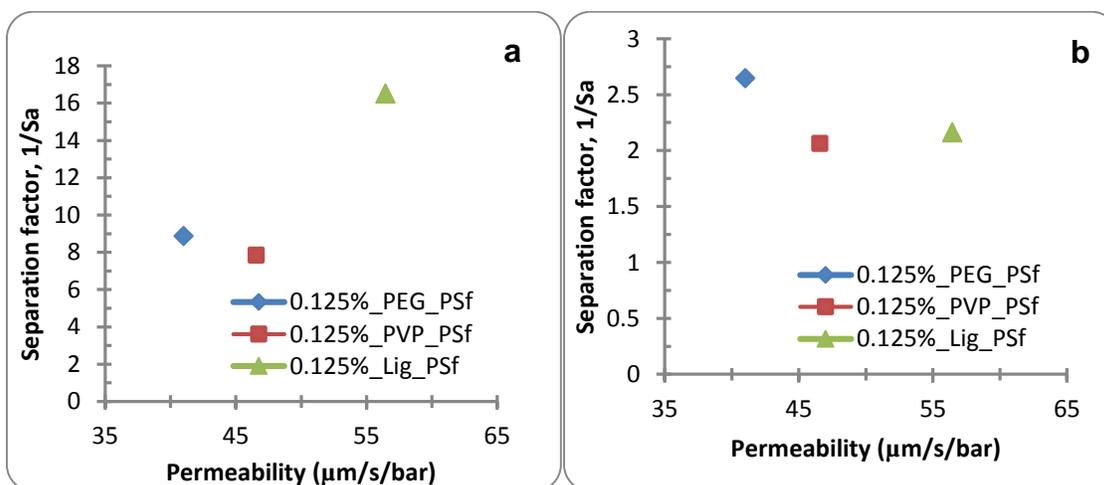


Fig. 8. Separation factors of membranes with different additives: (a) rejection of PVP-360 kDa solute and (b) rejection of PEG-35 kDa solute

When PEG-35 kDa was rejected, the observed rejections were lower for lignin-modified membranes because they had larger pores than the solute rejected, hence the lower separation factors (Mehta and Zydny 2005). This means that the trade-off between selectivity and permeability depends on the size of the molecule being rejected.

Very small molecules exhibit lower rejections if the mechanism of rejection is governed only by size exclusion. The fact that the selectivity of all membranes dropped when rejecting PEG 35-kDa (Fig. 8b) is an indication that the mechanism of rejection is size exclusion.

Table 5. Concentration of PEG-35 kDa at the Membrane Surface Obtained using the Stagnant Film Model

Membrane	$k \text{ (m/s)} \times 10^{-4}$	$C_b \text{ (mg/L)}$	PEG, $C_m \text{ (mg/L)}$	$C_m/C_b \text{ ratio}$
0.125%_PEG_PSF	3.70	500	622	1.24
0.125%_PVP_PSF	3.70	500	608	1.22
0.125%_Lig_PSF	3.70	500	638	1.28

Lig_PSF, lignin polysulfone; PVP_PSF, polyvinylpyrrolidone polysulfone; PEG_PSF, polyethylene glycol polysulfone

A desirable membrane is one that has minimal concentration polarisation (CP) effects, although such effects cannot be entirely eliminated. A membrane has minimal CP when the concentration at the membrane surface is almost the same as that of the bulk solution. To determine if the prepared membranes were affected by CP, C_m was calculated based on the relationship $R_i = 1 - C_p/C_m = 1 - S_a$. Since $S_a = C_p/C_m$ and since S_a can be determined, the concentration at the membrane surface can also be computed, as shown in Table 5. The ratio of C_m and C_b was between 1.3 and 1.2, demonstrating minimal effects of CP. Higher values of this ratio (often called the polarisation index) have been reported in literature. Values obtained by Wijmans *et al.* (1985) were tenor more. For example, when rejecting Dextran T70, C_m and C_b were found to be 0.123 and $1.420 \times 10^{-3} \text{ g/mL}$, respectively. This translates to a ratio of 90. There may be lower or higher values in literature, as this parameter depends on the solutes being rejected and the pressure applied.

Molecular weight cut-off has been regarded as the standard method of describing the solute-retention properties of ultrafiltration membranes. This method is used to estimate the membrane's pore size. It is defined as the molecular weight (dynamic radius) of a solute with which a given membrane has a sieving coefficient (S_o) less than 0.1. Diluted, uncharged solutes of different molecular weights are rejected and a sieving curve plot of retention *versus* the molar mass or solute radius can be created (Platt *et al.* 2002; Hilal *et al.* 2007). As shown in Fig. 9, the MWCO was obtained by rejecting three uncharged solutes of different origins, including PEG-10 kDa, PEG-35 kDa, and PVP-360 kDa, using different membranes.

Although the rejection of the solutes for the two membranes modified with PEG and PVP was below 90%, the membranes' molecular weight cut-offs did not differ by a large margin. The molecular weight cut-off of the 0.125%_Lig_PSF membrane was 33 nm. It should be noted that the MWCO estimated here does not reflect the actual value, since the membrane performance analysis indicates the existence of a concentration polarisation layer. This layer could have been caused by the use of high solute concentration, although

there is no specific minimum value known that can be used to avoid forming the concentration polarisation layer (Platt *et al.* 2002).

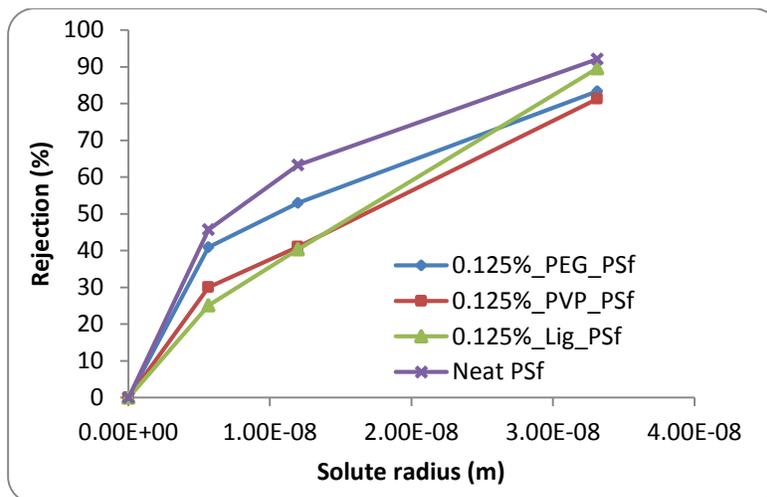


Fig. 9. Molecular weight cut-offs of different membranes. The retention was plotted against the solute diameter.

Effect of NaOH post-treatment on membrane performance

Water-soluble additives are used because they leach out of the membrane during phase inversion. Water-soluble additives like PEG dissolve in the coagulation bath, but it should be noted that some additive remains in the polymer and leaches out with time (Han *et al.* 2012).

Figure 10 shows that there was considerable permeability loss when the lignin content increased. Membranes that were soaked in 5 wt.% NaOH solution experienced appreciable gains in permeability, from 44 to 77 $\mu\text{m/s/bar}$ when 0.5 wt.% lignin was used. Sun *et al.* (2012) researched the extraction of lignin from bamboo wood using aqueous alkaline ethanol, ethanol, and aqueous alkaline solution at different concentrations. Alkali can effectively reduce the molecular size of lignin such that more pores are created when the lignin trapped in the polymer breaks down.

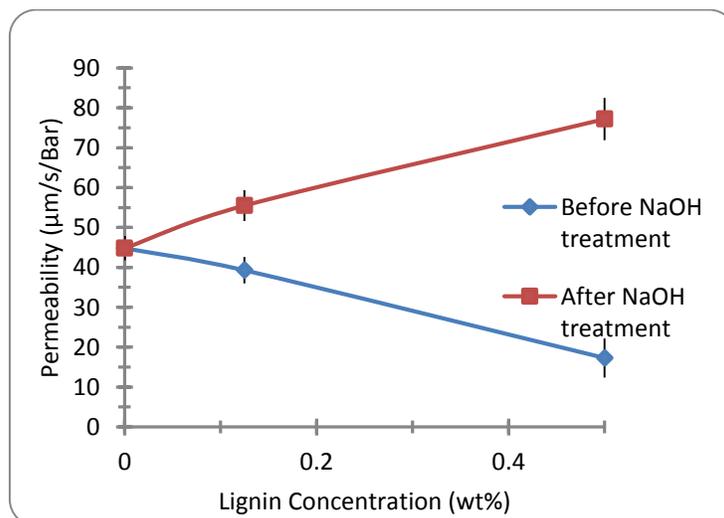


Fig. 10. Permeability results showing the effect of NaOH post-treatment on membranes cast with lignin

CONCLUSIONS

1. Similar to PVP and PEG, the addition of lignin during the preparation of a polysulfone membrane increases the membranes' ability to absorb water.
2. The FTIR results showed that lignin can be removed from within the membrane. This was also confirmed by an increase in membrane permeability after NaOH post-treatment.
3. Contact-angle measurements and water-uptake studies showed that lignin increases the membrane's hydrophilicity.
4. Performance analysis shows that membranes modified with lignin had both high water flux and high solute rejection and were not prone to concentration polarisation.
5. Further studies are needed to investigate the interaction of such membranes with different solutes.

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