High-performance cellulose acetate/polysulfone blend ultrafiltration membranes for removal of heavy metals from water
Pourya Moradihamedani and Abdul Halim Abdullah

ABSTRACT
Neat cellulose acetate (CA) and CA/polysulfone (PSf) blend ultrafiltration membranes in the presence of polyvinylpyrrolidone as a pore former were prepared via a phase inversion technique. The prepared membranes were characterized by Fourier transform infrared, scanning electron microscopy, mechanical strength, water content, porosity, permeate flux and heavy metals (Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$) rejection to comprehend the impact of polymer blend composition and additive on the properties of the modified membranes. The water flux expanded by increasing of PSf content in the polymer composition. CA/PSf (60/40) had the highest flux among prepared membranes. Prepared blend membranes were able to remove heavy metals from water in the following order: Pb$^{2+}$ > Cd$^{2+}$ > Zn$^{2+}$ > Ni$^{2+}$. The CA/PSf (80/20) blend membrane had great performance among prepared membranes due to the high heavy metals removal and permeate flux.

Key words | blend membrane, cellulose acetate, metal ions, polysulfone, ultrafiltration

INTRODUCTION
Nowadays, membrane separation technique has become one of the most developing technologies that have been generally operated in different industries such as pharmaceutical, food and chemical companies (Eren et al. 2005). Ultrafiltration (UF) process, which is employed to separate micro-solutes from macromolecules and to treat wastewater, has been applied to different industries such as metallurgical, pharmaceuticals, beverages, potable water, dairy, and electrocoating paint mixtures (Han et al. 2013). Cellulose acetate (CA) is one of the primary polymer membranes that have been utilized for aqueous based separation, i.e. UF techniques and reverse osmosis (Qin et al. 2005). An important point of preference of UF is its capacity to perform two tasks in one stage, i.e. concentration and separation. Similar size molecules cannot be separated by UF; however, it can separate molecules that differ by at least an order of magnitude in size. The hydrophilicity, porosity and surface roughness as well as mechanical strength of UF membrane play an important role in membrane separation process (Padaki et al. 2012a). Being hydrophilic, CA offers a good fouling resistance (Idris & Yet 2006). However, CA is not appropriate for aggressive cleaning due to its low oxidation and chemical resistances and poor mechanical strength, and thus the modification of CA becomes important for such a situation (Arthanareeswaran et al. 2008). In contrast, polysulfone (PSf) has high strength, rigidity, creep resistance and dimensional stability due to its replicating phenylene rings and is broadly utilized in membrane applications (Padaki et al. 2012b). However, the utilization of PSf in the aqueous phase is limited because of its hydrophobicity, but can be improved by modification through blending (Sajitha & Mohan 2005; Arthanareeswaran et al. 2007; Kalaiselvi et al. 2013; Kumar et al. 2013).

The polymer blending is a proven way to acquire new materials with widely differing qualities of properties intermediate between those of pure components along with economic advantages (Arthanareeswaran et al. 2007; Kalaiselvi et al. 2013; Kumar et al. 2013). The blend membranes have better permeability and selectivity over those of the membrane prepared from the individual polymers. Synthesis of a polymer blend membrane is motivated by the necessity to superimpose requisite properties upon the basic transport properties of the base polymer. Thus, the hydrophilic–hydrophobic balance, as well as properties of a membrane system, can be effectively changed if the membrane is prepared from multicomponent polymer blends. Polyacrylonitrile with
polyvinyl chloride (PVC), CA and PSf miscible pairs exemplify the use of polymer blend membrane comprising hydrophobic and hydrophilic polymers. Hence, an attempt has been made to blend PSf with a hydrophilic polymer in order to incorporate the hydrophilicity and to increase the performance of PSf membrane (Arthanareeswaran et al. 2008).

It is shown in several kinds of literature that CA/PSf and polyethersulfone (PES) blend membranes have been prepared and applied for heavy metals removal from water (Mahendran et al. 2004; Sivakumar et al. 2006). They utilized the CA as the basic polymer. Since CA is not suitable for aggressive cleaning, PSf and PES with higher chemical and mechanical strength were added to CA casting solution, separately, to improve the final properties of membranes. The separation of Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ from aqueous solutions, containing one metal ion at a time, by complexing them with 1 wt.% concentration of polyethylenimine (PEI) through UF using CA and CA/PSf blend membranes was attempted by Sivakumar et al. (2006). According to their results, the percent rejection of metal ions diminished from 98.5 to 94 in the case of Cu$^{2+}$ for pure CA membrane when polyvinylpyrrolidone (PVP) concentration was expanded from 0 to 7.5 wt.%. Similar trends were observed for other metal ions and for blend membranes as expected. Moreover, Cu$^{2+}$ has higher separation than other metal ions due to stronger ligand formation with polymer chelating agent, PEI. In another study, the permeability and mechanical properties of CA membranes blended with polyethylene glycol 600 (PEG) for the treatment of municipal sewage were studied by Haolong et al. (Bai et al. 2012). According to their results, the properties of the membranes were improved due to the addition of PEG 600. The pure water flux of membranes went up with increasing of PEG 600 concentration in the casting solution. Both the porosity and the mean pore size of the membranes blended with PEG 600 were increased compared with those of the pure CA membranes.

In this study, we prepared CA/PSf blend membrane with different blend compositions via phase inversion method in presence of PVP as a pore former. The main aim of this study is to investigate the effect of PSf and PVP concentrations on the morphology of the membranes and evaluate their performance in removing Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ from aqueous solution. The novelty of the present study is high rejection of Pb$^{2+}$ from water (98%) as well as high Pb$^{2+}$ permeate flux (49 L.m$^{-2}$.h$^{-1}$) at 3 bar feed pressure by CA/PSf (80/20) membrane. Moreover, Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ percent rejections of CA/PSf (80/20) membrane were 71, 65 and 65 respectively at 3 bar feed pressure, which were slightly lower than that of membranes produced in other works. In contrast, the Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ permeate fluxes of CA/PSf (80/20) in lower feed pressures were significantly higher than that of prepared membranes in other studies.

**EXPERIMENTAL**

**Materials**

The CA with average molecular weight of 100,000 was purchased from ACROS Organics, New Jersey, US. PSf resin with the average $M_n=22,000$ was purchased from Sigma-Aldrich. N-methyl-2-pyrrrolidone (NMP), utilized as a solvent for casting solution preparation, and PVP with a molecular weight of 25,000 g mol$^{-1}$ were supplied from Merck, Germany. Pb(NO$_3$)$_2$ from Bendosen, NiCl$_2$.6H$_2$O from HmbG Chemicals, ZnSO$_4$.7H$_2$O from SYSTERM and Cd(NO$_3$)$_2$.4H$_2$O from R&M Chemicals were utilized separately as salts for preparing single aqueous solutions.

**Preparation of membranes**

The casting solutions (18 wt.%) were prepared by blending of CA and PSf polymers with different compositions in presence of PVP as a pore former in NMP under constant stirring for 24 h at room temperature. Phase inversion technique was applied for membrane preparation. Based on this method, the solution was cast on a glass plate by a Doctor blade with a thickness of 80 μm. The wet film was immersed into a coagulation bath containing distilled water for 24 h at room temperature. At the final stage, the membranes were dried at room temperature for a day. The composition of prepared membranes and their designations are listed in Table 1.

**Removal of heavy metal ions**

Heavy metals removal was carried out with 50 mg/L single aqueous solution of Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ at solution pH of 5.0. All experiments were carried out three times at room temperature (25 ± 2°C) in a batch type and dead-end UF cell (Merck) with an effective membrane filtration area of 13.8 cm$^2$. In this work, the collection time was recorded for 50 cm$^3$ of the permeate solution and then the permeate flux, heavy metals rejection and morphology of each membrane were analyzed.
schematic diagram of the dead-end UF system used in this experiment (Moradihamedani & Abdullah 2016).

The performance of the membrane in the removal process was evaluated based on the flux measurement and the rejection percentage. The flux of feed solution was measured at feed pressure range of 1 to 3 bar. The following equation was used for calculation of the feed flux:

$$J_w = \frac{Q}{A \Delta t}$$

(1)

where \(J_w\) is the flux (L/m\(^2\).h), \(Q\) is the amount of collected permeate (L), \(A\) is the effective membrane area in cm\(^2\) and \(\Delta t\) is the sampling time (h).

The metal ion rejection of prepared membranes was calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

(2)

where \(C_p\) and \(C_f\) are the heavy metal concentrations in permeate and the feed, respectively (Moradihamedani & Abdullah 2016).

**Characterization of the membrane**

The surface functional groups of the neat CA and CA/PSf blend membranes were analyzed by Fourier transform infrared spectroscopy (Series 100 PerkinElmer FT-IR 1650) in the scanning range of 280–4,000 cm\(^{-1}\), while the morphology of the membranes was observed using the scanning electron microscope (Philips XL-30).

The membrane water content was measured by soaking the membrane in water for 24 h and weighing it after wiping off the excess water with tissue paper. The membranes were dried in an oven at 40 °C for 24 h and weighted. Based on wet and dry weights of the membranes, the water content was calculated using the following equation:

$$\% \text{ Water content} = \frac{W_w - W_d}{W_w} \times 100$$

(3)

where \(W_w\) and \(W_d\) are the weights of wet and dry membranes, respectively.

### Table 1 | Compositions of CA/PSf blend membranes

<table>
<thead>
<tr>
<th>Composition (18 wt.%)</th>
<th>Additive (wt.%)</th>
<th>Solvent NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA 100</td>
<td>PSf 0</td>
<td>PVP 2</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>2</td>
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<tr>
<td>100</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>8</td>
</tr>
</tbody>
</table>

Total mass for casting solution; CA + PSf + PVP + NMP = 10g.

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![Schematic diagram of the dead-end UF system for removal of heavy metals from water.](https://iwaponline.com/wst/article-pdf/75/10/2422/452638/wst075102422.pdf)
The porosity of prepared membranes was calculated using the following formula:

\[
\text{% Porosity} = \frac{W_w - W_d}{dAL} \times 100
\]

where \(W_w\) is the weight of wet membrane, \(W_d\) is the weight of dry membrane, \(d\) is the density of water (g/cm\(^3\)), \(A\) is the membrane effective area (cm\(^2\)) and \(L\) is the thickness of membrane (cm) (Moradihamedani & Abdullah 2016).

Tensile strength and elongation at break were measured using an Instron 4301 universal testing machine at a cross-head speed of 5 mm/min, according to the ASTM Standard Method D638-5. The dumbbell-shaped samples were cut utilizing a pressure driven cutter. The average was calculated from five measurements of tensile strength.

## RESULTS AND DISCUSSION

The permeability of the prepared membranes at a pressure range of 1–3 bar was evaluated in term of flux. The variation

### Table 2 | The heavy metal ion aqueous solutions flux in different feed pressures

<table>
<thead>
<tr>
<th>Membrane (18 wt.%)</th>
<th>PVP (wt.%)</th>
<th>Pb(^{2+}) solution flux (L.m(^{-2}).h(^{-1})) at Pressure (bar)</th>
<th>Cd(^{2+}) solution flux (L.m(^{-2}).h(^{-1})) at Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Neat CA</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CA/PSf (90/10)</td>
<td>2</td>
<td>0</td>
<td>12 (0.6)</td>
</tr>
<tr>
<td>CA/PSf (80/20)</td>
<td>2</td>
<td>10 (0.4)</td>
<td>28 (1.2)</td>
</tr>
<tr>
<td>CA/PSf (70/30)</td>
<td>2</td>
<td>280 (11.0)</td>
<td>590 (26.0)</td>
</tr>
<tr>
<td>CA/PSf (60/40)</td>
<td>2</td>
<td>450 (18.3)</td>
<td>940 (38.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn(^{2+}) solution flux (L.m(^{-2}).h(^{-1})) at Pressure (bar)</td>
<td>Ni(^{2+}) solution flux (L.m(^{-2}).h(^{-1})) at Pressure (bar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Neat CA</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CA/PSf (90/10)</td>
<td>2</td>
<td>0</td>
<td>25 (1.0)</td>
</tr>
<tr>
<td>CA/PSf (80/20)</td>
<td>2</td>
<td>29 (1.1)</td>
<td>60 (2.3)</td>
</tr>
<tr>
<td>CA/PSf (70/30)</td>
<td>2</td>
<td>304 (14.0)</td>
<td>644 (30.0)</td>
</tr>
<tr>
<td>CA/PSf (60/40)</td>
<td>2</td>
<td>515 (23.3)</td>
<td>990 (40.7)</td>
</tr>
</tbody>
</table>

The values in brackets are variance of three experimental determinations.

### Table 3 | The rejection of heavy metal ions by the prepared membranes at different feed pressures

<table>
<thead>
<tr>
<th>Membrane (18 wt.%)</th>
<th>PVP (wt.%)</th>
<th>Pb(^{2+}) rejection (%) at Pressure (bar)</th>
<th>Cd(^{2+}) rejection (%) at Pressure (bar)</th>
<th>Zn(^{2+}) rejection (%) at Pressure (bar)</th>
<th>Ni(^{2+}) rejection (%) at Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Neat CA</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CA/PSf (90/10)</td>
<td>2</td>
<td>0</td>
<td>99</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>CA/PSf (80/20)</td>
<td>2</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>77</td>
</tr>
<tr>
<td>CA/PSf (70/30)</td>
<td>2</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>76</td>
</tr>
<tr>
<td>CA/PSf (60/40)</td>
<td>2</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>73</td>
</tr>
</tbody>
</table>

The values in brackets are variance of three experimental determinations.

### Table 4 | Water content and porosity of prepared membranes at different casting solution compositions

<table>
<thead>
<tr>
<th>Membrane (18 wt.%)</th>
<th>Water content %</th>
<th>Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat CA</td>
<td>51.2 (2.5)</td>
<td>53.2 (1.9)</td>
</tr>
<tr>
<td>CA/PSf (90/10)</td>
<td>53.4 (2.9)</td>
<td>55.8 (2.0)</td>
</tr>
<tr>
<td>CA/PSf (80/20)</td>
<td>58.1 (1.3)</td>
<td>57.6 (2.3)</td>
</tr>
<tr>
<td>CA/PSf (70/30)</td>
<td>72.7 (5.8)</td>
<td>69.4 (3.2)</td>
</tr>
<tr>
<td>CA/PSf (60/40)</td>
<td>80.5 (8.3)</td>
<td>78.3 (4.5)</td>
</tr>
</tbody>
</table>
of permeate flux passing through the membranes with different CA and PSf concentrations is shown in Table 2. Neat CA membrane did not have any permeability until 3 bar feed pressure. The impermeability can be due to the formation of the thick surface layer as well as the dense substructure of the membrane. The membrane permeability in all tested heavy metals aqueous solutions increased with further loadings of PSf in the casting solution. The enhancement of membrane flux in the presence of PSf may be due to the fact that PSf, as well as PVP, contributes to the formation of larger pores and cavities in membrane morphology (Qin et al. 2003). The CA/PSf (60/40) blend membrane had the highest permeate flux of 1,631 L.m⁻².h⁻¹ (Ni²⁺ solution), 1,540 L.m⁻².h⁻¹ (Zn²⁺ solution), 1,339 L.m⁻².h⁻¹ (Cd²⁺ solution), and 1,320 L.m⁻².h⁻¹ (Pb²⁺ solution) at 3 bar feed pressure. The difference between permeate fluxes of metal solutions might be due to the different fouling behaviors of metal ions. The ionic sizes for the tested heavy metals are in the following order: Pb²⁺ (1.32 Å) > Cd²⁺ (0.97 Å) > Zn²⁺ (0.74 Å) > Ni²⁺ (0.69 Å). Accordingly, lower diffusivity of larger metal ions might cause fouling on the surface of the membranes and reduce the permeate flux (Mbareck et al. 2009).

The effectiveness of prepared membranes for heavy metals rejection (Pb²⁺, Cd²⁺, Zn²⁺, and Ni²⁺) at different feed pressures is shown in Table 3. The results revealed that the highest Ni²⁺ rejection was achieved by CA/PSf (90/10) in 2 bar feed pressure, which was 72%. At the same condition, the rejection percentage increased to 76% and 83% for Zn²⁺ and Cd²⁺, respectively. Interestingly, all prepared CA/PSf blend membranes were able to remove Pb²⁺ from water by 98% and higher. The rejection difference of heavy metals could be justified through the differences in the size of the ions. The ionic sizes for the tested heavy metals are in the following order: Pb²⁺ (1.32 Å) > Cd²⁺ (0.97 Å) > Zn²⁺ (0.74 Å) > Ni²⁺ (0.69 Å). Accordingly, nickel ions are more likely to pass through the pores of the membrane structure due to their smallest size, while lead, being the biggest ion, cannot pass the membrane pores easily; hence the prepared membranes are able to reject it from water significantly (Kalantari et al. 2014; Moradihamedani et al. 2016).

The water content and porosity of the prepared membranes are reported in Table 4. The membrane water content and porosity increased as the PSf concentration in blend compositions was increased, with CA/PSf (60/40) exhibiting the highest water content (80.5) and porosity (78.3%). Since the development of pores is due to the PSf coagulation with water, membranes with higher PSf content
will have bigger pore size, resulting in higher water content and porosity in membrane structure (Sivakumar et al. 2006).

The mechanical properties of the prepared UF membranes were another important concern toward the functional application. The mechanical stability of the prepared membrane, which includes tensile strength and elongation at break, was evaluated and the results are recorded in Table 5. The tensile strength and the elongation at break of the prepared membrane diminished gradually with increasing PSf content in the casting solution up to 20%. A crucial reduction of mechanical property was observed for CA/PSf (70/30) and CA/PSf (60/40). This may be attributed to the arrangement of macrovoids and cavities in the membrane structure at PSf contents of 30% and above.

Fourier transform infrared (FTIR) was utilized to determine specific functional groups and chemical bonds that exist in a material. The FTIR spectrums of neat CA, CA/PSf (80/20) and CA/PSf (60/40) are shown in Figure 2. A broad transmittance band around 3,500 cm$^{-1}$ and 2,700–2,900 cm$^{-1}$ was assigned to OH and CH$_2$ groups (CH stretching) in CA, respectively (Pielesz & Binias 2010; Kamal et al. 2014). The characteristic bands at 1,065 cm$^{-1}$ were noted for C-O-C (ether linkage) from the glycosidic units in CA (Pielesz & Binias 2010). The asymmetric and symmetric stretching mode of sulfonate group (–SO$_2$–) in PSf caused two small peaks in CA/PSf spectrums at approximately 1,290 and 1,320 cm$^{-1}$ (Moradihamedani et al. 2013a, 2013b).

The impact of CA/PSf blend on the membrane morphology was evaluated via cross-sectional scanning electron microscopy (SEM) images of the membranes as displayed in Figure 3. The neat CA membrane (Figure 3(a)) exhibits a typical asymmetric structure, which comprises a thick top layer and a dense sub-layer. The dense sublayer consists of sponge pores and shallow tear-like pores within the...
Figure 4 | The SEM-EDX images of CA/PSf (80/20) after UF of (a) lead ion, (b) zinc ion and (c) nickel ion.
polymer matrix. The prepared membranes containing PSf (Figure 3(b)–3(d)) demonstrate significant changes in the top layer and sub-layer morphology. These membranes have thin top layer and finger-like pores in the support layer. The porosity of walls and the size of finger-like pores increased in higher PSf concentrations. The SEM image of the CA/PSf (70/30) and CA/PSf (60/40) (Figure 3(c) and 3(d)) showed the presence of long and deep finger-like pores starting from the top to the bottom layer. This phenomenon clearly reveals that higher PSf loadings in the casting solution will not only increase the number of pores but the size of the pore as well. Muthusamy et al. (Sivakumar et al. 2006) have also reported a similar observation on the morphology variation.

SEM with an energy dispersive X-ray (SEM-EDX) can provide spatial and composition distribution of elements in solid materials. Heavy elements (high atomic number) backscatter electrons more strongly than light elements, and thus appear brighter in SEM-EDX images (Casuccio et al. 2004; Mbareck et al. 2009). SEM-EDX topographic photographs of the surface layer of CA/PSf (80/20) membrane after the UF of Pb (II), Zn (II) and Ni (II) ions are shown in Figure 4. Bright zones on the top layer of the membrane after removal of heavy metals correspond to the presence of lead, zinc and nickel ions (Figure 4(a)–4(c)). This phenomenon reveals that the metal ions rejection in membrane UF process happened through the sieving mechanism, which is related to the pore size and solute size (Sivakumar et al. 2006).

The effect of PVP concentration enhancement in the casting solution, from 2 to 8 wt.%, on the permeate flux of the neat CA and CA/PSf (80/20) blend membranes at 3 bar feed pressure is shown in Figure 5. The permeate flux increased gradually with increasing PVP concentration in the casting solution. Since PVP acts as a pore former, higher PVP concentration in the blend may lead to the formation of larger pores in the membranes. Moreover, the coagulation of PSf with water also develops the pore size of the membrane. By increasing both PSf and PVP concentrations simultaneously, the repulsive forces between polymer segments along with the leachability of PVP are increased. This phenomenon boosts the formation of large size pores (macrovoids) resulting in higher permeate flux and water content of the CA/PSf membrane (Sivakumar et al. 2006). The variation in CA/PSf (80/20) membrane morphology containing 2 and 8 wt.% of PVP is illustrated in Figure 6. As provided in these SEM micrographs, the membrane containing 2 wt.% of PVP (Figure 6(a)) has smaller pores compared with that prepared.
in presence of 8 wt.% of PVP (Figure 6(b)). Thus, a higher PVP concentration in blend polymer incorporates a higher number of pores as well as the bigger pore size in CA/PSf membrane.

The effects of PVP concentration on water content, porosity and mechanical properties of CA/PSf (80/20) membrane are provided in Table 6. By increasing the PVP concentration from 2 to 8 wt.%, the water content and porosity were increased from 58.1 to 76.5 and 57.6 to 73.5%, respectively. The tensile strength and elongation at break of CA/PSf (80/20) with 2 wt.% of PVP in casting solution were 3.60 and 12.80%, respectively. These numbers diminished significantly in higher PVP concentrations in casting solution. These phenomena might be attributed to the
formation of macrovoids and cavities in the membrane structure at PVP content of 4 wt.% and above.

Table 7 shows the rejection of heavy metals as a function of different concentrations of PVP in CA/PSf (80/20) blend membrane. It is evident that rejection of Pb$^{2+}$ decreased from 98% to 54% with increase in PVP content in casting solution from 2 to 8 wt.%. Other heavy metals also exhibited a similar trend and their percent rejections decreased significantly in higher pore former (PVP) loadings. This may be due to the fact that the rejection mechanism in the UF of heavy metals is based on sieving mechanism, which is related to the pore size and solute size.

In Table 8, we have summarized previous studies relevant to this research. Based on the obtained results, CA/PSf (80/20) membrane had excellent performance for Pb$^{2+}$ removal at 3 bar feed pressure compared with blend membranes prepared in other studies. The Pb$^{2+}$ percent rejection of this membrane was 98 with 49 L.m$^{-2}$.h$^{-1}$ permeate flux at 3 bar feed pressure. Table 8 shows that Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ percent rejections of CA/PSf (80/20) membrane decreased from 98% to 54% with increase in PVP content in casting solution from 2 to 8 wt.%. Other heavy metals also exhibited a similar trend and their percent rejections decreased significantly in higher pore former (PVP) loadings. This may be due to the fact that the rejection mechanism in the UF of heavy metals is based on sieving mechanism, which is related to the pore size and solute size.

### Table 7 | The effect of PVP concentration on CA/PSf (80/20) heavy metal rejection

<table>
<thead>
<tr>
<th>PVP wt.%</th>
<th>Pb$^{2+}$ rejection (%) at Pressure (bar)</th>
<th>Cd$^{2+}$ rejection (%) at Pressure (bar)</th>
<th>Zn$^{2+}$ rejection (%) at Pressure (bar)</th>
<th>Ni$^{2+}$ rejection (%) at Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
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</tr>
<tr>
<td>2</td>
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<tr>
<td>8</td>
<td>69</td>
<td>61</td>
<td>54</td>
<td>38</td>
</tr>
</tbody>
</table>

### Table 8 | Comparison of membrane separation performance in current work with the literature

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Heavy metal rejection</th>
<th>Permeate flux (L.m$^{-2}$.h$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA/PSf (80/20) + PVP 2 wt.%</td>
<td>Pb$^{2+}$ = 98 (1 bar) Cd$^{2+}$ = 77 (1 bar) Zn$^{2+}$ = 73 (1 bar) Ni$^{2+}$ = 70 (1 bar)</td>
<td>Pb$^{2+}$ = 10 (1 bar) Cd$^{2+}$ = 15 (1 bar) Zn$^{2+}$ = 29 (1 bar) Ni$^{2+}$ = 35 (1 bar)</td>
<td>This study</td>
</tr>
<tr>
<td>CA/PSf (80/20) + PVP 2 wt.%</td>
<td>Pb$^{2+}$ = 98 (3 bar) Cd$^{2+}$ = 71 (3 bar) Zn$^{2+}$ = 65 (3 bar) Ni$^{2+}$ = 65 (3 bar)</td>
<td>Pb$^{2+}$ = 49 (3 bar) Cd$^{2+}$ = 55 (3 bar) Zn$^{2+}$ = 110 (3 bar) Ni$^{2+}$ = 217 (3 bar)</td>
<td>This study</td>
</tr>
<tr>
<td>PVC/CA (90/10) + Fe$_3$O$_4$ 0.1 wt.%</td>
<td>Pb$^{2+}$ = 45 (5 bar)</td>
<td>Pb$^{2+}$ = 76 (5 bar)</td>
<td>Gholami et al. (2014)</td>
</tr>
<tr>
<td>PSf/GO 0.2 wt.%</td>
<td>Pb$^{2+}$ = 93 (4.14 bar) Cd$^{2+}$ = 92 (4.14 bar)</td>
<td>Pb$^{2+}$ = 60 (4.14 bar) Cd$^{2+}$ = 62 (4.14 bar)</td>
<td>Mukherjee et al. (2016)</td>
</tr>
<tr>
<td>DS = 0.43</td>
<td>Cd$^{2+}$ = 95 (4.14 bar)</td>
<td>Cd$^{2+}$ = 16 (4.14 bar)</td>
<td></td>
</tr>
<tr>
<td>CA/PSf (85/15) + PVP 2.5 wt.%</td>
<td>Ni$^{2+}$ = 82 (3.45 bar) Zn$^{2+}$ = 80 (3.45 bar) Cd$^{2+}$ = 72 (3.45 bar)</td>
<td>Ni$^{2+}$ = 12.7 (3.45 bar) Zn$^{2+}$ = 17.5 (3.45 bar) Cd$^{2+}$ = 22.5 (3.45 bar)</td>
<td>Sivakumar et al. (2006)</td>
</tr>
<tr>
<td>CA/PES (75/25) + PEG 2.5 wt.%</td>
<td>Ni$^{2+}$ = 85.01 (3.45 bar) Cd$^{2+}$ = 79.65 (3.45 bar)</td>
<td>Ni$^{2+}$ = 55 (3.45 bar) Cd$^{2+}$ = 55 (3.45 bar)</td>
<td>Mahendran et al. (2004)</td>
</tr>
</tbody>
</table>

CPSU: Carboxylate polysulfone, DS: Degree of carboxylation, PES: Polyethersulfone, GO: Graphene oxide.
were 71, 65 and 65, respectively, at 3 bar feed pressure, which was lower than that of membranes produced in other works. In contrast, the Cd\(^{2+}\), Zn\(^{2+}\) and Ni\(^{2+}\) permeate flux of CA/PSf (80/20) membrane was significantly higher than for other membranes used in other studies.

**CONCLUSIONS**

Neat CA and CA/PSf blend UF membranes were successfully prepared using phase inversion method. The higher amount of PSf in casting solution enhanced the membrane hydrophilicity and porosity, resulting in the increase in permeate flux. The mechanical properties of CA/PSf membranes are decreased in higher PSf loading, and this reduction was intense for PSf content of 30\% and above. The efficiency of the membrane in rejection of heavy metals is influenced by the porosity of the membrane. The rejection percentage declined at higher PSf concentrations due to the presence of large size pores within the polymer matrix. The CA/PSf (80/20) had high performance in terms of water flux and heavy metals rejection. The CA/PSf (80/20) exhibits excellent performance in terms of Pb\(^{2+}\) removal with the percent rejection of 98\% and permeate flux of 49 L.m\(^{-2}\).h\(^{-1}\) at 3 bar feed pressure. Moreover, the CA/PSf (80/20) was able to have acceptable percent rejection and higher permeate flux for Cd\(^{2+}\), Zn\(^{2+}\) and Ni\(^{2+}\) in comparison with other literature.

**REFERENCES**


Moradhamedani, P., Ibrahim, N. A., Yunus, W. Z. W. & Yusof, N. A. 2013b Separation of CO\(_2\) from CH\(_4\) by pure PSf and PSf/PVP blend membranes: Effects of type of nonsolvent, solvent,


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