5.1 A NOVEL METHOD FOR THE PREPARATION OF POLYSULFONE BASED NANOFILTRATION MEMBRANES AND THEIR ROLE IN REMOVAL OF Cr (VI)

A pressure driven membrane separation through which mono and multivalent ions can be separated and the characteristics of which lie between UF and RO is nanofiltration NF (Schafer. 2002). Unlike UF membranes, the separation mechanism for NF membranes is not only size exclusion where the solute particles larger than pores size are rejected but also, the separation is hit by charge on the surface of the membranes which is termed as Donnan exclusion (Bruggen 2004:1349; Korikov 2006:592). The two appealing facts of NF membranes are: a) the molecular weight cut offs (MWCO) which falls between MWCOs of RO and NF membranes i.e., 200 to 2000 Da. b) separation of solute/electrolytes due to the charge on the solutes or charge on the membranes (Schafe. 2005; Fievet. 2002). Hence, NF membranes have an ability to reject the solute particles of lesser size than the pores size of the membranes (Schaep 2001:130). A groups of researchers, Li S. L. et al. (Li. 2003:191), Wang X. L. et al. (Wang. 2002) concluded that, NF membranes as a “dense UF” membranes have an superior selectivity in separations like desalination and purification processes. Other groups of scientists, Wang D. X et al. (Wang 2006:738) and, Jiraratananon et. al. (Jiraratananon. 2000) found that, NF membranes as “loose RO” membranes operate with lower operating parameters and can save energy than RO membranes in water treatment. These kind of uncommon aspects of NF membranes have made them unique and interesting.

Off recently, PSf, polyamides, polyether sulfones, and cellulose acetate membranes along with their composites and modified polymers are used for the membrane preparation. PSf is considered to be a best UF membrane but the utility of that is limited to some extent because of its hydrophobicity. To overcome the above problems and to achieve increased membrane performances, many types of modifications were discovered. Blending of suitable pairs of polymers having required miscibility is one of the best methods to attain enhanced performances. PIAM and its derivatives are the main membrane materials used to develop NF membranes. PIAM possess, repeating units of aliphatic chain with anhydride ring where the ring oxygen can be replaced by other atoms via modifications.
Chapter 5

With a vision on necessity of development of efficient NF membranes for desalination and water treatment, herewith, we propose a new clean and uncomplicated recipe to synthesis a potent NF membrane. Firstly, a chemical modification to PIAM is performed using sulfanilic acid. The obtained product was characterized and was used to prepare blends with PSf with three different weight ratios. The prepared blends were characterized and analyzed for hydrophilicity and performance. Further, the blend membranes were utilized for multiple applications like removal of mono (NaCl rejection) and multivalent (Cr (VI) rejection) ions. A modification to PIAM with sulfanilic acid and employment of blend membranes for the removal of hazardous Cr (VI) as well as salt rejection decides the novelty of the reported effort.

5.1.1 Experimental
5.1.1.1 Modification to PIAM

PIAM was modified using sulfanilic acid and using DMSO as a solvent in the presence of catalytic amount of H₂SO₄ as in Figure 5.1. Firstly, 4 g of PIAM was dissolved in 40 ml of DMSO and upon dissolution; 4 g of sulfanilic acid along with H₂SO₄ was added to the reacting mixture. The reaction mixture was stirred for 15 h at 100 °C. Once the reaction is complete, we were able to make out the changes in color of the reacting mixture. Upon completion of reaction, the mixture was poured in to ice cold water to get yellow precipitate. The obtained product was washed with water, filtered and dried in oven and named as mPIAM.

![Figure 5.1: Schematic representation of modification of PIAM](image)

Figure 5.1: Schematic representation of modification of PIAM
5.1.1.2 Preparation of blend membranes

A plan PSf membrane was referred as control membrane and all the blend membranes along with PSf were prepared by Diffusion Induced Phase Inversion (DIPS) method. mPIAM was dissolved in 3 ml of NMP, and desired amount of PSf was added to it. The reaction mixture was stirred for 24 h at 55 °C to get a viscous casting solution. The solution was casted on glass plate with glass rod and immersed in coagulation water bath to get a flat sheet of membranes. The obtained membranes were washed with distilled water and stored in water for 24 h before proceeding for further studies. The blend membranes were prepared with different weight ratios of PSf and mPIAM, and named as P1, P2 and P3 for the convenience as given in Table 5.1.

<table>
<thead>
<tr>
<th>Name of Membrane</th>
<th>NMP (ml)</th>
<th>mPIAM (wt. %)</th>
<th>PSf (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>12</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>P1</td>
<td>12</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>P2</td>
<td>12</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>P3</td>
<td>12</td>
<td>30</td>
<td>70</td>
</tr>
</tbody>
</table>

5.1.2 Results and Discussions

5.1.2.1 Characterization of mPIAM

The structural analysis of modified polymer was performed with H\textsuperscript{1} NMR and FTIR spectra. Figure 5.2 shows the proton NMR spectra of mPIAM. The peaks from δ 7.1 to 7.9 ppm indicate the presence of aromatic protons. The two methyl groups –CH\textsubscript{2}C(CH\textsubscript{3}) shows peaks from δ 0.7 to 1.2 ppm for 6H, and the same for 2H shows peak at 1.7 ppm. The peaks for CH\textsubscript{CH}, 2H of five membered ring evidence the peaks from 2.7 to 3.1 ppm (Divakara 2013:9389). A solvent DMSO peak was observed at δ 2.501 ppm. Mainly, the presence of aromatic protons indicates the formation of product. The product formation was also confirmed with FTIR signals presented in Figure 5.3. A shift of peaks, 1850 cm\textsuperscript{-1} (C=O, asym. str.) and 1785 cm\textsuperscript{-1} (C=O, sym. str.) of anhydride ring of PIAM to 1767 cm\textsuperscript{-1} (C=O, asym. str.) and 1691 cm\textsuperscript{-1} (C=O, sym. str.), imide ring of mPIAM supports the product
formation. The peaks 1470-1410 cm\(^{-1}\) and 1290-1110 cm\(^{-1}\) illustrate C-C and C-O stretching frequencies respectively. The symmetric and asymmetric stretching’s of sulfone group were accounted by signals, ~1027 and 1098 cm\(^{-1}\) respectively (Lakshmi 2011:16) and hence the NMR and FTIR data collectively substantiate the structure of mPIAM.

![Figure 5.2: H\(^1\) NMR spectrum of mPIAM](image)

The thermal properties of PIAM and mPIAM were analyzed using TGA curves demonstrated in Figure 5.4. A decomposition temperature at 95 °C was due to the moisture content in the modified polymer whereas the same is absent in PIAM. At ~146 °C for PIAM with a % weight loss of 1.83, the decomposition was attributed to the decomposition of main chain of polymer whereas the same is shifted to ~212 °C with a weight loss of 54.8829 % for mPIAM. This concludes that the decomposition temperature has been increased after modification which intern says that the on modification the stability has been increased. An elevated decomposition temperature for mPIAM is owing to the restricted internal rotation of higher molecular chain segments cause due to intramolecular interactions caused by pendent sulfonic acid groups (Lufrano 2008:38).
Figure 5.3: FTIR spectra of PIAM and mPIAM

Figure 5.4: TGA curves for PIAM and mPIAM
5.1.2.2 Morphology and thermal properties of blends

The surface and cross sectional morphologies are the main tools to decide the performance and inner structure of the membranes. Figure 5.5 and 5.6 displays surface and cross sectional SEM images of PSf and PSf/mPIAM blends. Surprisingly, upon blending, we could notice the appearance of spherical domains with uniform dispersion similar to a morphological structure of liquid crystals, whereas, it was not found in plane PSf. The size of the spherical structures has been increased with the increase of mPIAM content, signifying that the changes in morphology is due mPIAM. Surya Subianto et. al. (Surya 2014:14) reported that the formation of these domains is due to the interaction of polar and non polar groups during phase separation process. In present case, the interaction is between polar sulfanilic groups of mPIAM and a non polar PSf groups in blends.

![Surface SEM images of a) P, b) P1, c) P2, d) P3](image)

**Figure 5.5: Surface SEM images of a) P; b) P1; c) P2; d) P3**

Also, the formation of these structures with a uniform size and shape is of more interest since it is not observed frequently. But, with block and grafted PSf/PVDF composites, the spherical phase separation has been observed (Grunzinger 2008:124; Yan 2004:412). On
comparative study between these reports and our work, we could conclude that, the modified mPIAM might have been trapped by PSf segments during phase inversion forming spherical domains. Also, the increase in such visible macroscopic areas with mPIAM content may decrease the stability of the membranes and hence, the membrane forming ability has been decreased at higher mPIAM content which compelled our work not continue further with higher mPIAM composition. The water permeability and performance of the membranes is reliant on inner demonstrates the cross sectional images of blends along with plane PSf membrane. Blending has lead to changes in all the three layers of the membranes, 1) a top skin layer where the selectivity is decided: a keen observation indicates the increase in thickness of the skin layer with increase in mPIAm content; 2) an intermediate layer which resolves the issues of productivity: a prominent changes are observed in productive layer, the spongy like structure of membrane P, is converted into finger like projections in addition with the formation of macro voids which intern increases the flux of the blend membranes. 3) lastly, the lower layer which is awarded for mechanical strength of the membranes: the formation of macro voids has almost reached the lower layer with increment in mPIAM contents, and hence decreasing the mechanical strength. However, the increase in selectivity productivity of the membranes with increase in mPIAM contents is supported by removal of chromium and PWF/permeates flux.

The thermal properties, change in Tg of the membranes was determined by analyzing DSC curves, as shown in Figure 5.7. The DSC curves pronounce the difference in thermal properties as well as Tg of the blends and PSf alone. From literature (Noshay 1976:1890), the Tg of plane PSf was found to be 190 °C (Lufrano. 2001). With a small addition of mPIAM to the PSf, the Tg has been increased to ~225 °C for P1, and it decreased along with the increase in mPIAM content i. e., P2>P3 (~192 and 173 °C) . The changes in thermal properties are due to the different inter/intra molecular van der Waals’ interaction between two polymers. The results reveal that, the thermal property of plane polysulfone was increased initially with lesser amount of mPIAM whereas further decreased with increase in mPIAM content.
Figure 5.6: Cross sectional SEM images of a) P; b) P1; c) P2; d) P3

Figure 5.7: DSC curves indicating Tg values of prepared blend membranes.
5.1.2.3 Hydrophilicity and IEC of the membranes

CA, IEC and WA are the main criterion to predict the wettability/hydrophilicity and performance of the membranes. To minimize the error, the measurements of above three are repeated several times and the average is tabulated in Table 5.2. As expected, the CA values decreased for blends with the addition of mPIAM. The CA of 81.18° of PSf, P has been declined to 74.33° for P, further to 71.96 and 64.53° for P2 and P3 respectively, which clearly indicates the increase in hydrophilicity of the blends with higher mPIAM. In contrast, the IEC (0.275 mmol/g) and WA (7.93 %) increased to 1.091 mmol/g and 36.98 % for P1 membranes and further increased with the mPIAM content. Comprehensively, the order of increasing hydrophilicity of the membranes is concluded as P<P1<P2<P3 due to the increase of hydrophilic -SO_3H groups along with blends.

Table 5.2: Average values of CA, IEC and WA of blend membranes and PSf alone.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CA (°)</th>
<th>IEC (mmol/g)</th>
<th>WA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>81.18</td>
<td>0.275</td>
<td>7.93</td>
</tr>
<tr>
<td>P1</td>
<td>74.33</td>
<td>1.091</td>
<td>36.98</td>
</tr>
<tr>
<td>P2</td>
<td>71.96</td>
<td>1.264</td>
<td>52.81</td>
</tr>
<tr>
<td>P3</td>
<td>64.53</td>
<td>1.339</td>
<td>68.73</td>
</tr>
</tbody>
</table>

5.1.2.4 PWF, salt rejection and flux decline of blends

PWF is one of the best parameter to define the pore size, pore distribution and intern, productivity of the membranes. Figure 5.8 illustrates the PWF of the membranes as a function of applied pressure. The PWF of plane PSf, membrane P was observed to be negligible, whereas, the drastic increment in PWF along with pressure upon blending PSf with mPIAM. For membrane P1, the PWF was ~6.9 L/m²/h at lower pressure and reached ~68.5 L/m²/h at higher pressures.

A linear typical increasing trend of PWF with increase in pressure was observed for all the membranes. PWF varied along with mPIAM content and the maximum PWF for membrane P3 with maximum mPIAM content at higher pressure was ~86.8 L/m²/h. The cause for the increase in productivity (PWF) is supported by SEM cross sectional images.
demonstrated in Figure 5.6. The increase in mass ratio of mPIAM increases the interconnection of finger like projections/pores caused due to the migration of hydrophilic domains of mPIAM forming cavities during phase inversion process, which resulted in improved permeability of the membranes.

![Pure water flux of blends and PSf membrane with respect to applied pressure](image)

**Figure 5.8: Pure water flux of blends and PSf membrane with respect to applied pressure**

The rejection capacity was investigated by accomplishing membrane to NaCl-H$_2$O binary system for salt rejection and by finding FR ratio by flux decline study. Figure 5.9a and 5.9b togetherly reveals the salt rejection as a function of pressure and flux decline as a function of time respectively. The maximum salt rejection for membrane with higher mPIAM content P3 is 59%. The salt rejection decreased with decrease in mPIAM content and also slightly with increased pressure. The lowest salt rejection for P1 at lower pressure was 52.5% and it decreased to a minimum value of 36 % at higher pressure. Hence the % salt rejection was completely dependent on mPIAM content. The rejection is exclusively because of Donnon effect created by fixed charge on the membrane. The sulfonic (SO$_3$H) groups of mPIAM being a negatively charged groups, rejects inorganic groups (Na$^+$) by electronic effect (Reddy 2003:214). The elevated rejection along with mPIAM content is due to the increased charge density on the membranes because of sulfonic groups. As the pressure
increases, the rejection decreases due to more solvent permeate, which concentrate the feed with less available charges on the membranes. Due to Donnon effect, to maintain the charge neutrality towards feed side, the Cl\textsuperscript{-} ions will also gets rejected (Padaki 2011:38).

Flux decline is estimated to be a measure for fouling property of membranes. Figure 9b disclose the flux decline results for neat and blend PSf membranes for permeation of NaCl-H\textsubscript{2}O binary system for about 7 hours at pressure of 50 psi. From figure it is clear that, the drastic decline in the flux is observed initially, for all the membranes whereas, the same will turn to gradual one after 3 to 4 hours and becomes almost same for 6\textsuperscript{th} and 7\textsuperscript{th} hour. Eventually, the deposition of solute particles on the surface of the membranes will blocks the pores of the membrane and intern decrease the permeation of solvent molecules.

![Image: Figure 5.9: a) % salt rejection; b) Flux decline for the blend membranes]

5.1.2.5 Molecular weight Cut off of the membranes

MWCO is a key component to be familiar with pore size of the membranes which can be defined as molecular weight of a component that is retained by 90 % of the membranes. For prepared blend membranes, the rejection experiments for PEG of molecular weights 400, 1000 and 2000 were considered at constant pressure to determine the pore size and type of membranes. The normalized results for % rejection of PEG are presented in Figure 5.10.
A very less % rejection of ~ 56 % for PEG 400 was observed for membrane P1, and ~68 and 72 % were observed for membrane P2 and P3. The % rejection has been increased to 92 to 94 % for all the membranes for a feed of PEG with molecular weight 1000 and the further increased to ~100% for a feed of PEG 2000. According to the report (Ganesh 2012:106), the results indicate that, the pore sizes of the prepared membranes describes the nanofiltration nature for the membranes.

5.1.2.6 Removal of Cr (VI)

All chromium removal experiments were performed at room temperature using dead end cell unit at regular intervals of time and as a function of applied pressure. Along with % rejection of Cr (VI), permeate flux was also measured to compare with PWF. The results of rejection experiments at different pH are presented in Figure 5.11. Membrane P1 showed ~98% for lower, 44% for neutral and 33% for higher feed pH conditions. And the rejection has been decreased with increase in pressure and the same trend was observed for other two membranes, P2 and P3. But, a slight increase in % rejection was observed in P2 and further in P3 on comparison with P1. For membranes P2 and P3, the % rejection increased to ~65% at neutral pH and to ~56% at basic pH.
The transport of metal ions regardless of ionic size of metal ion and pores size of membrane is very complicated. The Cr (VI) ions in the feed are suspected to be caught by SO$_3$H groups on the membrane surface. Also, there is a possibility that, the non solvent water molecules will be attracted by hydrophilic SO$_3$H groups of blends offering an arrangement of hydrophilic groups at the interfaces of the pores. These advantageous packages of groups around the interfaces of the pores may eventually retain the Cr (VI) ions during separation process (Chamekh 2009:98). E. Nordmeier in 1995 (Nordmeier 1995:1321–1374), reported the existence of two types of interactions between charge of counter ions or solute particles or metal ions and charge on the membrane. Firstly, long range interactions where, mobility of counter ions is hindered completely and secondly, short range interactions where the mobility is less.

![Figure 5.11: % rejection of Cr (VI) at different pH, with respect to applied pressure for membranes a) P1; b) P2 and c) P3](image)

Figure 5.11: % rejection of Cr (VI) at different pH, with respect to applied pressure for membranes a) P1; b) P2 and c) P3
hindered. But in both the cases, if the counter ions approach in cogent lane, they might be blocked completely. Hence, from literature it can be forecasted that the metal ions might be engaged in long range and short range interactions on membrane matrix and interface of the pores (Tsuchida 1977:1-87). The participation of metal ions in electrostatic interactions cause heavy metal complexation which sets a retention of counter ions depending on pH and concentration of metal ions in feed, nature of permeating species. In present study, the effect of pH and the concentration of charged groups are discussed. According to results, overall, the % rejection was less at basic and neutral condition but increased to 100% at lower pH. The speciation profile of Cr (VI) varies with pH, at lower pH, K₂Cr₂O₇ will be converted into

![Graphs showing permeate flux for Cr (VI) rejection experiments at different pH, with respect to applied pressure for membranes a) P1; b) P2 and c) P3](image)

**Figure 5.12:** Permeate flux for Cr (VI) rejection experiments at different pH, with respect to applied pressure for membranes a) P1; b) P2 and c) P3
H$_2$Cr$_2$O$_7$, which undergo ionization in aqueous solutions forming monoanion HCr$_2$O$_7^-$ and dianion Cr$_2$O$_7^{2-}$. The free energy of hydration is lesser for monoanions because of lesser pK$_a$ value of 0.74 on comparison with dianions (pK$_a$ of 6.49) (Imam 2013:4472) and thus, the migration of monoions towards membrane matrix will be more which will be repelled by charge on the membranes which acts as electrostatic barrier for the transportation of Cr ions. Since the dissociation of Cr (VI) ions is less in neutral and basic solutions, the retention capacity also decreased. The increased flux with increasing pressure amplifies the concentration of metal ions in feed solution. There might be a competition between higher number of metal ions and the charge density on membrane for the retention of metal ions which intern decreases the rejection at higher pressures.

The permeate flux for the rejection of chromium ions was measured and the results of normalized permeate flux at different pH as a function of applied pressure is shown in Figure 5.12. Like PWF, the permeate flux was also increased with increase in pressure. All the three membranes followed a similar trend of increasing flux with no significant effect of pH. In an average the initial flux for all the membranes were not more than 5 L/m$^2$/h and final flux at higher pressure was not more than 45 L/m$^2$/h.

The results suggest that, at initial stages, the permeate flux and pure water flux were almost same but as the pressure increases, ~ 45 % decrease in permeate flux (comparison between Figure 5.8 and Figure 5.12) was observed suggesting that, the interfering metal ions induce resistance to the flow of solvent molecules. The increase in feed concentration may block the pores of the membranes allowing lesser transport of water molecules to pass through leading to lesser permeate flux.

5.1.2.7 Removal of Chromium in the presence of interfering ions

Recently, removal of chromium ions in the presence of other metal ions using ion exchange membranes has gaining more importance for real time applications since; the waste water from many industries will also contain other heavy metals. A. T. Cherif, in 1998 (Cherif. 1998:1608), made an effort to separate Ag$^+$ from Zn$^{2+}$ and concluded that CMS Neosepta membrane resulted in more permeability of univalent cations than bivalent ones. In present work, the effect of interfering ions of different valences (mono, bi and tri) on rejection of chromium (VI) is investigated. The pH of the feed was maintained lower and composition was varied according to the requirement, tertiary systems of H$_2$O+Cr(VI)+Na$^+$,
H₂O+Cr(VI)+Zn⁺² and H₂O+Cr(VI)+Fe⁺³ were considered as feed. Permeates were tested for the concentration of Cr (VI) and the results are presented in the bar graph Figure 5.13.

![Figure 5.13: % rejection of Cr (VI) in the presence of interfering metal ions](image)

The drastic changes were observed on the rejection of Cr (VI) due to coexisting metal ions. In the presence of monovalent ions, the % rejection decreased to ~82 to 85 % for all three membranes on comparison with Cr (VI) alone. And the rejection was further decreased for a system of bi and trivalent ions feed solution. In the presence of bivalent ions, ~62 to 68 % and with trivalent ions, ~33 to 43 % were observed in an average. Hong-mei Xu et. al. (Hong-mei. 2014:128) suggested that, the presence of metal ions boost the shielding effect for the charge on the membranes, which intern facilitates the permeation of chromium ions due to lack of electrostatic effect between charge on the membranes and an ions of feed. Also, Myoshi et. al. (Myoshi 1999), reported that, the rejection and selectivity of metal ions depends on the mobility and the formation of ion pairs between fixed charge on the membrane and valency of the metal ions. The mobility of ion with lower valency is more towards membrane surface and also their might be a formation of ion pairs which further decreases the rejection.
5.1.3 CONCLUSIONS

An anhydride group of PIAM was modified using sulfanilic acid and characterized. The PSf/mPIAM blend membranes were prepared with different concentration of mPIAM. Surprisingly, the prepared blend membranes showed spherical domains in SEM images and the distribution and size of those varied along with the mPIAM content due to the interaction between polar groups of mPIAM and non polar groups of PSf during phase separation process. Also, the Tg of the blend membranes improved on comparison with plane PSf membrane. The increase in hydrophilicity was observed by contact angle measurements. The blend membranes showed increased performance with respect to water flux, water uptake and ion exchange capacity. The MWCO of the membranes provided information of nature of the membrane pores. Further, the membranes were used for the separation of chromium (VI). The effect of pH and mPIAM content on the separation process was analyzed and it was concluded that, at lower pH for lower pressure 100 % removal of Cr (VI) can be achieved for membrane P3 which is having higher mPIAM content. Also, the pure water flux was compared with permeate flux and results showed the added resistance for the solvent permeation in the presence of metal ions. The company of coexisting metal ions with different valancies affected the separation process by creating a shielding effect around the charge on the membranes. In conclusion, work reported a simple method to prepare PSf based NF membranes for the removal of Cr (VI).