CHAPTER 3
Chapter 3

Polymer modifications for fabrication of blend membranes for heavy metal removal application

3.1 Introduction

The concept of water salvage is gaining tremendous boost in recent times due to the rise of contaminates being discharged into water resources (Vijayalakshmi 2008: 32–38). Among the various pollutants, heavy metals are abundantly present in polluted waters and are highly toxic. Hence, in present era an effective removal method for such heavy metals is necessary (Mansourpanah 2011: 169–177). There are several methods such as chemical precipitation, ion-exchange, membrane filtration, membrane filtration technique and adsorption (Ferrero 2014: 367–373) for heavy metal removal.

The membrane filtration technique has shown great promise towards water purification (Jayalakshmi 2012: 120–132). The feasible operating condition, energy saving and high efficiency has created new interest in heavy metal removal from membrane technology (Daraei 2012: 250–259). One can see continued efforts from researchers towards betterment of membrane separation with respect to better productivity, maximum selectivity, ease of operational conditions and the ability to be scaled up at low costs (Kumar 2014: 102–108). Especially, NF and RO are found to be very effective in achieving near complete rejection (US EPA 2000). Conversely, these techniques operate at high operating pressure and have low water recovery (Gopal 2013: 243–246) unlike UF and MF, which operate at low pressures and are capable of giving superior flux and water recovery (Amy 1998). However, UF membranes are not suitable for metal ion rejection due to its larger pore size compared to the size of metal ions (Liu 2013: 131–136). But this setback can be resolved by modifying the polymer chemically by incorporating functional groups which in turn induces a charge on the membrane surface (Yu 2015: 10235–10242). The charge on the membrane can considerably mitigate fouling and can append to improve the efficiency and life span of the membrane (Mbareck 2009: 93–101).

PVC is one of the most versatile polymer with good flexibility, chemical resistance, film forming property, being economical and easy to modify (Rabiee 2014:...
PVC has been extensively used in industrial applications namely as packing material, cable insulation, and pipes. However, its use as membrane for water filtration is limited due to its hydrophobicity and membrane fouling property (Mei 2011: 378–383). Its properties can be changed by chemical modifications. In this regard, chemical modification of PVC promises to render the essential properties like membrane charge and hydrophilicity. The surface charge and hydrophilicity are the necessary tools to improve the selectivity of ions and productivity in membrane separations. There are reports already available in the literature on PVC modification, where M. A. Tooma has modified PVC with ethyl acrylate monomer for vacuum membrane distillation (VMD) application (Tooma 2015: 58–70). Methylimidazolium group – modified PVC doped with phosphoric acid membrane used for proton exchange by Q. Che (Che 2015: 1047–1055). On the other hand, there are a few reports on PVC blend and composite membranes for salt rejection by Y. Cui using blend PVC/P(DMA-co-MMA) precursors (Cui 2015: 187–196), PVC–silica mixed-matrix membrane as membrane bioreactor by M.R. Bilad (Bilad 2015: 19–27) and CO₂ gas separation using PVC/Pebax composite membrane by E. Ahmadpour (Ahmadpour 2014: 518–523). But none studied the removal of metal ions. Hence, aim of this study is to prepare novel polymeric membranes by a novel approach to obtain a synergistic effect of optimum antifouling, selectivity and productivity. PVC was chosen and the effect of different organic molecules namely sulfanilic acid (SA), 4-amino benzoic acid (ABA) and L-cysteine (Cys) was studied for removal of Cd, Cr, Pb and As metal ions. The results were then analyzed by comparison with commercially available membrane NF 270. NF 270 commercial membrane is chosen as it is the widely used membrane for heavy metal removal.

3.2 Experimental

3.2.1 Materials and methods

Udel PSf with a molecular weight 35,000 Da, PVC with high molecular weight (62,000 Da), 1-sulfanilic acid, 4-aminobenzoic acid and L-cysteine hydrochloride monohydrate were obtained from Sigma-Aldrich Co, India. Lead nitrate, cadmium nitrate and potassium dichromate were used as the source for Pb (II), Cd (II) and Cr (VI)
respectively. 10 ppm As (V) solution was prepared as the stock solution from Na₂HAsO₄·7H₂O (Sigma-Aldrich) and diluted further as per feed solution requirement. Chemicals like dimethyl sulfoxide (DMSO), triethylamine and methyl-2-pyrrolidone (NMP), ethanol, potassium hydroxide (KOH), tetra hydro furan (THF), per chloric acid (HClO₄), sodium hydroxide (NaOH), sodium chloride (NaCl), calcium chloride (CaCl₂), ferric chloride (FeCl₃), methanol and hydrochloric acid (HCl) were purchased from Merck Chemicals, India of AR grade and were used without any further purification. Poly ethylene glycol of different molecular weights i.e. 6 kDa, 10 kDa and 20 kDa were purchased from sigma-Aldrich. NF 270 commercial membrane was purchased from Sterlitech, USA. The NF 270 membrane was dipped in distilled water for 24 hours prior to its use.

3.2.2 PVC modification

3.2.2.1 Synthesis of PVC-SA

The reaction was carried out using a 2 neck round bottom flask mounted on a magnetic stirrer, equipped with hot plate. 1 g of SA was dissolved in 50 ml of DMSO, together with 10 ml of triethylamine to abstract the proton from SO₃H group of SA. Subsequently, 1 g of PVC was added to the same solution and the reaction mixture was stirred for 24 hours at 60-65 °C at a constant rate of heating in nitrogen atmosphere. The reaction is as proposed in Fig. 3.1. The reaction was quenched by precipitating out in a mixture of cold water/ methanol (1:2) after 24 hours. The precipitate was then washed with distilled water for several times to remove excess of solvent and dried overnight in an oven.

![Figure 3.1 Schematic representation for PVC modification with SA.](image-url)
3.2.2.2 Synthesis of PVC-ABA

In this approach, the reaction was carried out in three different reaction steps as depicted in the Fig. 3.2. Acid group was protected so that it does not hinder in the reaction and the reaction is favored in a single path to give maximum yield.

**STEP 1:** Protection of acid group

4-amino benzoic acid (1 g, 7.29 mm) was dissolved in 25 ml of ethanol and 1ml of H$_2$SO$_4$ was added as the catalyst. The mixture was refluxed continuously for 6 hours until completion of the reaction, which was confirmed via thin layer chromatography (TLC). The obtained mixture of compound was heated in rotamantal and separated by ether extraction process. A pleasant fruity odor was obtained from the end product.

![Figure 3.2 Schematic representation of PVC modification with ABA.](image)
**STEP 2: Modification of PVC**

The reaction was carried out exactly as described in section 3.2.2.1 and the product obtained from the first step was used as the starting material.

**STEP 3: De-protection**

The modified PVC (1 g) obtained from the second step was dissolved in 20 ml of THF solvent. Simultaneously 0.1 g of KOH dissolved in 4 ml of ethanol was added to the polymer solution. The reaction mixture was stirred continuously for 2 hours at room temperature until reaction proceeds to completion.

**3.2.2.3 Synthesis of PVC-Cys**

PVC and L-cysteine were taken in equal ratios and the reaction protocol was as per the method followed in section 3.2.2.1. Triethylamine is added, as L-cysteine in its hydrochloride state will be more prone to be acidic pH. Now the cysteine will be in its zwitterionic form with COO⁻ and NH₃⁺. Since the –SH group is free it reacts with PVC chain and release of HCl (depicted in Fig. 3.3) gives the desired product.

![Figure 3.3 Schematic representation of PVC modification with Cys.](image)

The % extent of modification (% M) of modified PVC with different organic molecules were calculated by the following equation (Nazri 2014: 594):

\[
% M = \frac{\text{weight of modified copolymer} - \text{weight of PVC}}{\text{weight of PVC}} \times 100
\]  

(1)
3.3. Results and discussion

3.3.1 Characterization of modified PVC

3.3.1.1 ATR-IR

The modification of PVC with SA, ABA and Cys was substantiated by IR analysis. The IR spectrum showed the occurrence of some extra stretching peaks in all the modified PVC compounds due to the presence of functional groups like N-H, COOH, SO$_3$H, etc.

(a) In PVC-SA: a new broad peak obtained between 3000 to 3600 cm$^{-1}$ is due to the stretching frequency of O-H bond of –SO$_3$H group and N-H stretching respectively. Further the N-H bending was observed at 1393 cm$^{-1}$, and C-N stretching was observed at 1086 cm$^{-1}$ (Donald 2008). A sharp peak observed at 1629 cm$^{-1}$ resembles the C=C stretching for aromatic groups. All these peaks were absent in the PVC spectrum, and the peaks arising at 1240 and 1084 cm$^{-1}$ may be attributed to C-C and C-H deformation and stretch respectively as shown in the spectra. The C-H stretching was observed at 2934 and 2930 cm$^{-1}$ in both the cases of PVC-SA and PVC respectively.

(b) PVC-ABA: the fresh broad peak obtained between 3000 to 3600 cm$^{-1}$ is due the stretching frequency of O-H bond of –COOH group and N-H stretching which have merged to give a broadened peak, further the N-H bending was observed at 1375 cm$^{-1}$ and C-N stretching was observed at 1069 cm$^{-1}$. The C-H stretching frequencies were observed between 2850 and 2961 cm$^{-1}$. A sharp peak at 1642 cm$^{-1}$ was observed due to the C=O stretching of the acid group which is the characteristic peak for acid containing compounds and it also demonstrates the completion of deprotection step of ester to acid group. The intensity of C-Cl peak at 948 cm$^{-1}$ in PVC-ABA spectra has decreased by considerable extent, which denotes the replacement of Cl with ABA.
Figure 3.4 ATR-IR spectrum of a) PVC b) PVC-SA c) PVC-ABA and d) Cys-PVC.

(c) PVC-Cys: The broad peak obtained at 3386 cm\(^{-1}\) is due to the N-H stretching of the amine group giving a broad peak. C-H stretching of PVC chain is observed at 2961 cm\(^{-1}\). The peaks observed in the range of 1242 cm\(^{-1}\) are the C-C deformation peaks of the PVC polymer chain. The sharp and weak peak at 1364 cm\(^{-1}\) depicts N-H bending of the cysteine moiety. The characteristic peak for carbonyl group of the acid group is observed at 1645 cm\(^{-1}\). Also, a new peak is observed at 760 cm\(^{-1}\) due to the formation of a bond between the carbon and sulphur atom of PVC and cysteine group respectively. All these spectra confirm PVC modification with different organic molecules.
3.3.1.2 $^1$H NMR

For (a) PVC-SA (Fig. 5 (a)) : in the $^1$H NMR spectra it can be clearly observed that, the peak at $\delta$ 6.4 and $\delta$ 7.2 represents the aromatic proton peaks giving a doublet. A singlet observed at $\delta$ 5.1 is due to the NH proton. The $-\text{CH}$ and $-\text{CH}_2$ protons show multiplet at $\delta$ 1.75 and $\delta$ 2.35 due to the presence of long alkane chain present in its vicinity. It has merged with the intense peaks of DMSO at $\delta$ 3.3 and $\delta$ 2.5 (Mahesh 2013: 489–497) giving broadened peaks. The expected peak for O-H appears to have been merged with peak at $\delta$ 2 hence not visible. The spectrum is in accordance to the peaks of expected product.

(b) PVC-ABA: The peaks at $\delta$ 6.0 and $\delta$ 6.5 represents the aromatic proton peaks giving doublet, the peaks have undergone shielding effect hence the values obtained at lower intensity. A singlet is observed for NH proton at $\delta$ 4.1. The $-\text{CH}_2$ and $-\text{CH}$ protons show multiplet at $\delta$ 1.35 and $\delta$ 2.45 due to the long alkane backbone of PVC. The peaks appears to have merged with solvent peaks. Also, the expected peak for O-H of the acid group has undergone shielding effect and the peak value is shifted from higher $\delta$ value (10-12) to lower $\delta$ value of $\delta$ 7.7 giving a singlet.

(c) PVC-Cys: The characteristic peak for amine group is observed at 4.5 $\delta$ in combination with the triplet peak for the neighboring carbon atom. It can be seen that there is no peak observed for the O-H stretch of the acid group and this can be due to the existence of the cysteine molecule in its zwitterionic phase and the acid group will be in COO$^-$ form. The stretching peaks for CH and CH$_2$ groups of PVC backbone are observed at 1.5 and 2.3 $\delta$ due to the presence of long alkane chain in its vicinity. It has merged with the intense peaks of DMSO at $\delta$ 3.3 and 2.5 ppm giving broadened peaks. No peak is observed for SH group owing to its reaction with the carbon of PVC chain.
Figure 3.5 $^1$H NMR spectrum of PVC modified with a) sulfanilic acid b) 4-amino benzoic acid and c) L-cysteine.
From equation (1) the percent of modification was calculated for different molecules and is depicted in Table 3.1.

Table 3.1 Details of % PVC modification.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Weight ratio</th>
<th>% modification (% M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC/ PVC-SA</td>
<td>1:1</td>
<td>31.2</td>
</tr>
<tr>
<td>PVC/ PVC-ABA</td>
<td>1:1</td>
<td>60.1</td>
</tr>
<tr>
<td>PVC/ PVC-Cys</td>
<td>1:1</td>
<td>52.6</td>
</tr>
</tbody>
</table>

3.3.1.3 Differential scanning calorimetry

The thermal behavior of PVC polymer and the modified PVC was studied from the DSC plots. The DSC plots (Fig. 3.6) where, \( T_g \) and \( T_m \) represents glass transition temperature and melting temperature respectively.

(a) PVC-SA: The PVC polymer showed \( T_g \) at 85.27 °C and \( T_m \) at 276.79 °C and it is in accordance with the \( T_g \) temperature reported for neat PVC (Aouachria 2006: 1101–1108). However PVC-SA showed \( T_g \) at 58.58 °C and \( T_m \) at 233.04 °C. The \( T_g \) and \( T_m \) values of PVC-SA is less as compared to neat PVC. This is because during the chemical modification of the polymer, the polymer chain is shortened which show remarkable impact on physical properties of the polymer. This indicates the better heat tolerance of PVC over PVC-SA. During the course of heat treatment the polymer undergoes changes in physical state into three different phases. The state below the \( T_g \) point represents the glassy state of the polymers and the area between \( T_g \) and \( T_m \) represents the rubbery state. Once the temperature crosses the \( T_m \), the polymers get converted into a liquid state.
(b) PVC-ABA: PVC–ABA showed $T_g$ at 69.87 °C and $T_m$ at 270.43 °C (Fig. 3.6.c) respectively. The decrease in the $T_g$ and $T_m$ values for PVC-ABA can be compelled due to the shorting of PVC chain as mentioned above which leads to hampering of physical properties of the polymer owing to the chemical modification. This indicates the better heat tolerance of PVC over PVC–ABA. In addition, it can be observed that the peaks observed (for $T_g$ and $T_m$) in PVC-ABA are not very sharp as that observed for neat PVC polymer. This can be reasoned out to be due to the increased amorphous nature of the polymer due to the incorporation of bulky ABA group.

(c) PVC-Cys: Fig. 3.6.d depicts the DSC plot for PVC–Cys showing reduced $T_g$ at 66.56 °C and $T_m$ at 277.1 °C as observed in other modifications in comparison to PVC polymer. In addition, due to the increased amorphous nature of the polymer after L-cysteine
incorporation in PVC chain T_g and T_m points were not very sharp. From all the DSC plots it is noticed that PVC modification leads to reduced thermal stability of the polymer.

3.4 Studies of PVC-SA blend membrane

The long aliphatic chain in PVC gives the strength to the polymer backbone and is widely used in various applications. However, in water purification technology changing the chemical properties of PVC is essential to get good productivity as it is hydrophobic in nature. This can be accomplished by incorporating hydrophilic groups into the polymer chain. Also, the presence of chlorine site along the polymer chain makes it easy for chemical modification as it is a good leaving group. Modification, thus improves the membrane performance in terms of flux and rejection, but may lead to severe loss of mechanical strength of the membrane which is not appropriate for its use. Hence, the blending of modified PVC with a much stronger polymer such as PSf regains its lost strength. The blend membrane will have the optimum properties like improved mechanical strength, surface charge and hydrophilicity for heavy metal ion rejection.

3.4.1 Preparation of blend membrane

The blend membrane was prepared by DIPS method. DIPS process is based on the phenomenon of precipitation of the polymer in a controlled manner, when it comes in contact with water to form solid porous film. 4 g of PVC was dissolved in 16 g (15.54 ml) of NMP and stirred for 24 hours at 60 °C to obtain a viscous solution. The obtained viscous solution was then casted on a glass plate using a glass rod. The thickness of the membrane was maintained using double sided tape. The glass plate was dipped in a coagulation bath containing distilled water at room temperature (Jyothi 2014: 1537–1545). The membrane was peeled off by phase inversion method and the obtained membrane was washed and stored in distilled water for 24 hours to remove any excess of NMP and also to gain mechanical strength. Similarly, neat PSf membrane was prepared by the same method by adding PSf instead of PVC. The same procedure was extended to prepare blend membranes; in this case both the polymers were added in different concentration. Series of blends were prepared with different compositions as depicted in Table 3.2.
Table 3.2 Composition of concentrations of the polymers for membrane preparation.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Membrane</th>
<th>Composition (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PSf</td>
<td>PVC/SA-PVC</td>
<td>NMP</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>PSf</td>
<td>20</td>
<td>-</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PVC</td>
<td>-</td>
<td>20</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3% PVC-SA/PSf</td>
<td>19.4</td>
<td>0.6</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5% PVC-SA/PSf</td>
<td>19.0</td>
<td>1.0</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8% PVC-SA/PSf</td>
<td>18.4</td>
<td>1.6</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10% PVC-SA/PSf</td>
<td>18.0</td>
<td>2.0</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

3.4.2 Membrane characterization

3.4.2.1 Ion-exchange capacity

Table 3.3 represents the ion-exchange capacity of the blend membranes of different compositions of PVC-SA in PSf matrix.

Table 3.3 Ion-exchange capacity of the blend membranes.

<table>
<thead>
<tr>
<th>Membranes PSf: PVC-SA</th>
<th>IEC = AB/ m_{dry}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(90:10)</td>
<td>0.1673 ± 0.006</td>
</tr>
<tr>
<td>(92:8)</td>
<td>0.1348 ± 0.022</td>
</tr>
<tr>
<td>(95:5)</td>
<td>0.1146 ± 0.020</td>
</tr>
<tr>
<td>(97:3)</td>
<td>0.09421 ± 0.009</td>
</tr>
</tbody>
</table>

From the table it can be clearly seen that as the composition of PVC-SA increases from 3 to 10 %, the ion-exchange capacity of the blend membrane also increases. This substantiates the presence of –SO₃H and –NH functional groups in the polymer matrix of the membrane. An increase in the ion-exchange capacity of the membranes implies that
the density of the functional groups is more in the membranes containing more concentration of PVC-SA.

**3.4.2.2 Water uptake capacity**

The SO\(_3\)H group enhances the hydrophilicity of the prepared blend membranes due to the ability to form hydrogen bonds (Mahesh 2012b: 42–48). From Fig. 3.7 it can be noticed that neat PSf shows the lowest water uptake capacity followed by PVC membrane and this is because of highly hydrophobic nature of the PSf and PVC membrane, which resists the water to get absorbed. This is also supported by the contact angle measurement values obtained as 76.7 and 78.8 for PSf and PVC membranes respectively.

![Figure 3.7 Water uptake capacity and contact angles of the blend membranes.](image)

PVC membrane shows slightly higher water uptake due to the macro porous nature of the membrane as can be seen from the SEM image (Fig. 3.9). The water uptake capacity of the blend membrane is much higher and increases proportionately with increase in concentration of functional groups to enhance the hydrophilicity of the membranes. The contact angle decreases from 73.6 to 64.8 while water uptake increases from 22.5 % to 82 %, proportionately for the corresponding increase in PVC-SA concentration in the blends. The sulfanilic group being hydrophilic facilitates absorption of water and hence increase in functional groups proportionately enhances affinity.
towards water. This is because, the presence of hydrophilic groups make it easy for the water to get absorbed in the membrane and more the number of functional groups present more will be the affinity towards water and more will be the absorption.

3.4.2.3 AFM analysis

To investigate the surface topology of the membranes, AFM analysis was carried out and the hydrophilicity was correlated to the surface roughness of the membranes. Fig. 3.8 gives the 3D surface images of all the membranes with its corresponding $R_a$ values.

![AFM Images](image)

**Figure 3.8 3D images of AFM (a) neat PVC (b) 3 % PVC-SA/PSf (c) 5 % PVC-SA/PSf (d) 8 % PVC-SA/PSf and (e) 10 % PVC-SA/PSf membranes.**

Increase in content of PVC-SA, increases the number of valleys (can be differentiated by light and dark areas) leading to an increased surface roughness from 6.9 nm to 48.4 nm. The trend observed is due to the increase in hydrophilic groups which enhances the rate of phase inversion process, due to its mobility towards water.
surroundings. This observed phenomenon is well in agreement with the results obtained by N. A. M. Nazri et al. (Nazri 2014: 594) and Liu et al. (Liu 2013: 66–75).

3.4.2.4 SEM analysis

SEM analysis is another very essential tool to study the cross section morphology of the prepared membranes. It gives vital information of the micro pore structure of the membranes; which is the prime source responsible for the selectivity and productivity of the membranes. Fig. 3.9 reveals the SEM images neat PSF, PVC and PVC-SA/PSf blend membranes.

Figure 3.9 Represents cross section SEM images of (a) PSf membrane (b) PVC membrane (c) 3 % PVC-SA/PSf (d) 5 % PVC-SA/PSf membrane (e) 8 % PVC-SA/PSf and (f) 10 % PVC-SA/PSf, the scale represents 100 µm in all the images.
As it can be seen, neat PVC membrane has long and more finger like structures without much differentiation in layers, whereas neat PSf membrane depicts three distinct layers. Upper dense layer (skin layer), middle layer (finger like projections) and bottom layer (sponge like with big pores) is responsible for the selectivity, productivity and strength (Mahesh 2012a: 35–42). In PSf membrane, the bottom layer is very thick as compared to other membranes. Addition of PVC-SA to PSf separates the three different structural layers with a substantial density of the skin layer being visible in comparison to neat PSf. Increase in concentration of PVC-SA diminishes the appearance of sub layers. Skin layer becomes less dense and they appear a merge of middle and bottom layers in 5% PVC-SA/PSf. The selective layer has completely merged with middle layer to give one single layer with broad finger like structure in 8% PVC-SA/PSf membrane. Whereas, big hollow finger like projection (marked in red for better understanding) are randomly observed in 10% PVC-SA/PSf membrane running from top to bottom of the membrane, where all the three layers have merged to give one single layer. During phase inversion process, the non-solvent penetrates at a faster rate and the solvent (NMP)-non solvent (water) inter change occurs much quickly to give big pores (Vatanpour 2011: 284–294, Zinadini 2014: 145–154). This observation is well in concurrence with the roughness values obtained in AFM analysis. Similarly as the composition of PVC-SA is lowered the interchange of solvent and non-solvent takes place at slow rate giving it the dense pore network.

3.4.3 Performance study

3.4.3.1 Pure water flux

In order to find the rate of permeation of water, flux study was carried out at different pressures from 100 to 500 kPa, and it was depicted in Fig. 3.10 that increase in pressure increases the flux in all the cases owing to the stress on the membrane pores at higher pressure. Increase in the content of PVC-SA increases the flux favorably due to enhanced hydrophilicity. Nevertheless, the flux of plane PVC is near to the flux of 5% PVC-SA/PSf membrane and much more than 3% PVC-SA/PSf membrane, even though PVC is highly hydrophobic in nature. The macro porous nature of the PVC membrane having big long pores (as explained by SEM image) gives it a reasonably good flux rate. PSf
being an ultrafiltration membrane and highly hydrophobic with a very low flux or zero flux (Jyothi 2014: 189–199) adversely affects the flux of the blend. However the PSf membrane showed thick bottom layer in SEM analysis. It may be also one of the reasons for low flux rate. But beyond the addition of 5 % PVC-SA to PSf, the flux enhances considerably owing to the increase in hydrophilicity and bigger pore structure in the membrane, which lets the water pass through the membrane with ease.

![Figure 3.10 Pure water flux of NF 270, neat PVC and the blend membranes.](image)

Whereas, if we compare the flux of commercially available membrane NF 270 it is considerably high as to that of the PVC-SA/PSf blend membranes and may be attributed to its hydrophilicity.

The flux graph is a model fit, trend line was drawn to study the hydraulic permeability. Table 3.4 depicts the $L_p$ value of the membranes. From the table it is clear that the $L_p$ of the membrane decreases with decrease in concentration of functional groups present in the blend membrane. However, the $L_p$ of neat PVC is near to 5 % PVC-SA/PSf membrane due to its high flux owing to its macro size pores. Also the $L_p$ of NF 270 membrane is the highest owing to its pretty high flux compared to the other membranes.
Table 3.4 Represents the Hydraulic permeability coefficient ($L_p$) of the membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Hydraulic permeability coefficient ($L_p$) (m/s Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf: PVC- SA</td>
<td></td>
</tr>
<tr>
<td>Neat PVC</td>
<td>$2.70 \times 10^{-12}$</td>
</tr>
<tr>
<td>(90:10)</td>
<td>$12.44 \times 10^{-12}$</td>
</tr>
<tr>
<td>(92:8)</td>
<td>$6.89 \times 10^{-12}$</td>
</tr>
<tr>
<td>(95:5)</td>
<td>$3.12 \times 10^{-12}$</td>
</tr>
<tr>
<td>(97:3)</td>
<td>$0.26 \times 10^{-12}$</td>
</tr>
<tr>
<td>NF 270</td>
<td>$32.02 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

### 3.4.3.2 Rejection of metal ions

To check the workability of the prepared membranes they were applied in rejection experiments, for the removal of toxic heavy metals like Pb (II), Cd (II) and Cr (VI). 10 ppm of Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$ and K$_2$Cr$_2$O$_7$ was batch filtered at various pressures (in neutral conditions). The rejection of all the metal ions showed interestingly 90-95% rejection of all the metal ions at 100 kPa pressure (Fig. 3.11). The behavior of the membranes for metal retention can be explained as follows: in neutral pH the functional group SO$_3$H will be in its ionized form as SO$_3^-$ gives it a negative charge. The metal ions exist as M$^+$ (M = Cd and Pb) in its free ionic state, leading to an attraction of metal ions towards membrane functional groups, either forming metal-ion complexation or ionic interactions ("O…M$^{n+}$…O") (Mbareck 2009: 93-101). Whereas, Cr (VI) exists in its two ionic form, such as Cr$_2$O$_7^{2-}$ and CrO$_4^{2-}$ species in the neutral pH. Hence, instead of attraction repulsion takes place between the negatively charged Cr species and SO$_3^-$ groups which leads to its rejection (Wang 2006: 307–315). However in the case of Cd (II) and Pb (II), both the ions are positively charged leading to attraction. So, the interaction (repulsion and attraction) between membrane surface and ions leads to the rejection of metal ions.
Figure 3.11 Rejection of metal ions (a) Cd (b) Cr and (c) Pb using blend membranes and (d) represents the rejection of all three metal ions by NF 270 membrane.

However, 10 % PVC-SA/PSf membrane showed the lowest rejection compared to all the other membranes even though it had the maximum density of functional groups in its vicinity. This can be because of the larger pore size (Fig. 3.9 (f)) and flux of the membrane (Fig. 3.10). This indicates that even though the rejection depends on charge, porosity plays very important role. If the pores are large and more, than the ions can easily pass through the pores of the membranes due to the applied pressure. Hence, there is no chance for the charge interaction. Instead 3 % PVC-SA/PSf membrane results in maximum rejection. As explained in the SEM section, the hydrophilic component PVC-SA beyond a particular limit causes the loss of selective skin layer. The same trend is observed in 5 % PVC-SA/PSf and 8 % PVC-SA/PSf membranes. It was also confirmed
by AFM images, where the surface roughness increased with increasing concentration of PVC-SA. This is because of hydrophilic functional group moving towards water molecule of the coagulation bath, which causes the more membrane surface roughness. Further the rejection performance was decreased with respect to the pressure increases from 100 to 500 kPa. The metal ions are forced out from the membrane decreasing the rejection at high pressures. This suggests the importance of morphology of membranes in metal ion retention.

Still, the metal ion rejection was almost similar because of the near similar size of 0.43 nm, 0.426 nm and 1.34 nm for Pb (II), Cd (II) and Cr (VI) metal ions respectively in their hydrated states (Mbareck 2009: 93-101, Habibi 2015: 306–316). The trend of rejection follows the order 10 % < 8 % < 5 % < 3 % PVC-SA/PSf membrane. In 10 % PVC-SA/PSf membrane, the rejection was very less owing to more charge and porosity. Hence, it is necessary to attain optimum size and charge of the membrane to obtain good results. The obtained result is consistent with the reported value of 99.44 % of lead removal (at pH 5.7) by C.V. Gherasim (Gherasim 2014: 67–74) and 98 % retention of iron (III) ions by X. Bernat et al. (Bernat 2009: 129–137) (at pH 2).

It is observed (in Fig. 3.11 (d)) that the rejection pattern for all the three 3 metal ions by NF 270 membrane shows a maximum of 78 % rejection for Cd (II) ions followed by Pb (II) (76 %) and Cr (VI) (60 %). Also there is variability in the rejection pattern over the increasing pressure range which is due to the fouling of the membrane over time. However the selectivity of commercial membrane towards metal ion is not acceptable. The lack of flux in the blend membrane is overcome by its enhanced rejection, thus making it compatible with the existing membranes.

3.4.3.3 Antifouling study

Fouling is one of the major drawbacks of the membrane as it decreases the life span and flux of the membrane. The adsorption of proteins on the membrane surface causes membrane fouling. Generally the adsorption takes place because of hydrophobic and electrostatic interaction between protein and membrane. In order to validate the antifouling capacity of the prepared membranes the rejection of BSA protein solution was
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experimented in room temperature at 500 kPa pressure (Kumar 2013: 140–147, Kumar 7855–7861). The water flux of the membranes was studied before and after the BSA rejection. Fig. 3.12 indicates the drastic decreases in the flux during BSA filtration because of adsorption or deposition of protein on membrane surface.

Figure 3.12 Antifouling study of the membranes at constant interval of time.

The flux recovery ratio (FRR) of the prepared membrane is shown in Fig 3.13. 59.2 % of FRR and 74 % of total fouling (Fig. 3.14) was observed in the PVC membrane. The modification of the PVC increases the FRR up to 79.65 and decreases the total fouling up to 40 %. Increasing the composition of PVC-SA in the membrane, tend to increase the FRR and lower the fouling. This is because of increasing hydrophilicity and membrane surface charge.

Fig. 3.13 presents the percent of BSA rejection from the membranes. The result obtained is similar to that of metal ion rejection with the highest of 98.5 % of BSA being rejected by 3 % PVC-SA/PSf membrane. However, the rejection of BSA is more in comparison to metal ions due to the larger size of proteins, unlike the small sized metal ions.
In studying complete fouling, the reversible and irreversible fouling parameters are very important. In reversible fouling, the foulant can be removed by washing because those are loosely bonded on membrane surface. Whereas, in irreversible fouling, the foulant cannot be removed because those are stuck inside the membrane pores. The total fouling, reversible and irreversible fouling ratios were calculated and are presented in Fig. 3.14. Reversible fouling decreases from 3% to 10% PVC-SA/PSf membrane. However, irreversible fouling increases from 3% to 10% PVC-SA/PSf membrane. It is the effect of hydrophilic membrane surface and pore size. BSA is hydrophobic in nature, which loosely adheres on the hydrophilic membrane surface (Hebbar 2016: 764–774). Hence, increasing hydrophilicity of the membrane decreases the reversible fouling. The foulant can be easily removed from such membrane surfaces by washing. On the other hand, the pore size of the membrane goes on increasing with respect to concentration of PVC-SA, which allows the BSA particles to go inside the membrane matrix and block the pores, which causes more irreversible fouling.

![Figure 3.13 Flux recovery ratio and BSA rejection of the membranes.](image)

Figure 3.13 Flux recovery ratio and BSA rejection of the membranes.
3.4.3.4 Recyclability test

In order to estimate the reproducibility of the membrane performance, a two cycle water and BSA flux were performed in a similar fashion as mentioned above for 3 % PVC-SA/PSf membrane as it showed the highest rejection capability. It is observed that there was a slight decline of the water flux in the second cycle after the BSA rejection; however the FRR was not very much affected. It decreased from 69 % to 62 % indicating high efficiency of the membranes towards foultants. But the cycle was not able to extend further as the flux had increased drastically; this is due the rupturing of the pores during cleaning process with warm water. Hence, it was clear that the incorporation of functional groups not only increased the hydrophilicity but also the efficiency of the blend membranes. Also as the experiment was carried out in dead end filtration unit there is a possibility to produce better recyclability in crossflow filtration mode.
3.4.3.5 Effect of interfering ions on rejection

The study of interfering ions on rejection is very essential to assess the efficiency of the membrane to reject a particular metal in presence of other competing metal ions. Thus rejection was experimented with mixture of all the ions namely Pb (II), Cd (II) and Cr (VI) studied individually earlier. The efficient 3 % PVC-SA/PSf membrane was selected as it showed the highest rejection for individual metal ions. All the remaining parameters were maintained constant.

The effect of counter ions on rejection of specific ion can be observed. The mixture concentration in the feed is the sum of 10 ppm of each metal ion, which is overall 30 ppm concentration of the feed. One more intention of this study is to know the performance of the membranes in high concentrated feed sample. The results reveal that, there is considerable decrease in the metal ion rejection. The rejection of Cr (VI) is about 68 %, Cd (II) and Pb (II) is about 62 %. It can be pointed out that the amount of Cr (VI) rejected is more compared to the other two ions present. This is accounted due to the difference in rejection mechanism of Cr (VI) ions (repulsion) whereas, attraction for Pb (II) and Cd (II) ions cause the difference. The rejection was decreased in mixed ion rejection up to 10 % in Cr (VI), 18 % in Cd (II) and 13 % of Pb (II) as compared to single
ion rejection. In higher concentration of feed solution, accumulation of ions near the surface causes saturation of functional groups and allows some of the ions to pass through the membrane. Also mobility of ions decrease with increase in concentration leading to reduced overall rejection, which is observed by Jyothi et al. (Jyothi 2014: 189–199). However, characteristic feature of charged membranes is less rejection at high feed concentration and vice versa (Ortega 2008: 204–216). Unexpectedly high rejection was observed at high pressure. This is because high concentration of ions can lead to the deposition of metal ions on membrane surface, which causes membrane fouling with time. While, decreasing in water flux rate (Fig. 3.16) as compared to pure water flux, which are evidences for the membrane fouling. Similar observation was found for NF 270 membrane, where the rejection of metal ions varies with pressure unlike that of blend membrane, the rejection remains constant throughout the experiment. Besides, the NF membrane shows more affinity towards Pb (II) ion rejection over the Cr (VI) ions distinct from blend membrane. Also the flux of the membrane has reduced to half than its initial pure water flux, which owes to the large amount of fouling that takes place on the membrane surface and also which leads to the constant amount of rejection over the complete set of experiment.

![Figure 3.16 Rejection of Cd, Cr and Pb metal ions together at different pressure by (a) 3 % PVC-SA/PSf membrane and (b) NF 270 membrane.](image)

The present study demonstrates an improved membrane for removal of heavy metal ions as compared to the existing NF 270 membrane but with lack of flux; however
the study opens a lot of scope for improvement in the area of productivity in the near future.

### 3.5 Conclusion

A blend of modified PVC with PSf membrane matrix showed high impact on heavy metal removal. The modification was carried out by a newly developed method using sulfanilic acid. \(^{1}\)H NMR, ATR-IR spectroscopy and DSC confirmed the modification of PVC with sulfanilic acid. The blend membrane showed enhanced hydrophilicity and surface charge, which was confirmed by water uptake, water flux and IEC respectively. AFM and SEM analysis substantiated an improved surface roughness and porosity, due to modified PVC. A good rejection of 90 – 95 % was observed for 3 % PVC-SA/PSf membrane for Cd, Cr and Pb metal ions. The blend membranes show enhanced flux and antifouling property compared to the neat PVC and PSf membranes. Antifouling study demonstrated a good FRR value of 75.6 % for 10 % PVC-SA/PSf membrane. The study gains significance in synthesizing an optimized and functionalized PVC-SA blend for a good metal ion rejection and good antifouling property.
3.6 Studies of PVC-ABA blend membranes

As studied in the previous study modification of PVC with sulfanilic acid gave PVC the necessary charge, which improved the rejection efficiency of the blend membranes. However, it was observed that the flux was not greatly enhanced. Since, flux is one of the most important features for a membrane it is necessary to get sufficient flux to meet the global demand of water.

In this effort, a novel chemical modification of PVC polymer is carried out. PVC is functionalized with 4-amino benzoic acid to induce hydrophilicity and charge, which tends to overcome the said drawbacks above. As per the studies reported, carboxylic acid groups were considered to be stronger and have higher water affinity then the sulfonic acid groups (Xu 2016: 63–71). The charge on the membrane shall also facilitate attraction and hence removal of metal ions in aqueous solution.

3.6.1 Preparation of blend membrane

Blend membranes with different compositions were prepared following DIPS method, as described in previous section. The different compositions of blends is illustrated in Table 3.5.

Table 3.5 Composition of concentrations of the polymers in membrane preparation.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Membrane</th>
<th>PSf</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PSf</td>
<td>20</td>
<td>PVC/ABA-PVC</td>
</tr>
<tr>
<td>2</td>
<td>PVC</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.25 % PVC-ABA/PSf</td>
<td>19.95</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>0.5 % PVC-ABA/PSf</td>
<td>19.9</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0.75 % PVC-ABA/PSf</td>
<td>19.85</td>
<td>0.15</td>
</tr>
</tbody>
</table>

3.6.2 Ion-exchange capacity

Table 3.6, represents the ion-exchange capacity of the blend membrane having different compositions of modified PVC in PSf. Clearly, IEC values imply that the density of the functional groups has increased for the blends with increase in composition of PVC-ABA
in the order $0.25 < 0.5 < 0.75 \%$. This demonstrates the presence of $\text{–COOH}$ and $\text{–NH}$ functional groups in the polymer matrix of the membrane, which are capable of exchanging protons when present in appropriate surrounding conditions.

Table 3.6 Ion-exchange capacity of the blend membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Ion exchange capacity (mequiv/g), $\text{IEC} = \frac{\text{AB}}{d_{\text{dry}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf: PVC-ABA</td>
<td></td>
</tr>
<tr>
<td>(99.75:0.25)</td>
<td>0.5702</td>
</tr>
<tr>
<td>(99.5:0.5)</td>
<td>1.5850</td>
</tr>
<tr>
<td>(99.25:0.75)</td>
<td>2.6650</td>
</tr>
</tbody>
</table>

3.6.3 AFM

To investigate the effect of PVC-ABA concentration on the surface characteristics, AFM analysis was employed. Fig. 3.17, illustrates the surface AFM images of the prepared membranes and it can be visualized that the uppermost point is represented by the brightest area and the dark regions are the valleys on the membrane surface. It’s clear that the surface roughness increases with increase in ABA-PVC content. This change occurs due to the presence of hydrophilic groups in the membrane matrix, which leads to faster rate of phase inversion owing to its attraction towards water. Similar, observation is noticed in our previous modification of PVC with sulfanilic acid (Vignesh 2016: 25492–25502); where a strong change was observed in the roughness values. However, in this case the increase is small. This may be attributed to smaller amount of hydrophilic content incorporated. However, higher surface roughness has more tendency of getting fouled by accumulation of additive on the membrane surface, leading to blocking of pores (Vatanpour 2016: 300–309). Hence, hydrophilic membranes with less surface roughness are preferred. Neat PVC shows minimum $R_a$ value. But, it is observed that 0.5 \% PVC-ABA/PSf membrane has maximum $R_a$ value and again the $R_a$ value decreases for 0.75 \% PVC-ABA/PSf membrane; the $R_a$ value of 0.75 \% PVC-ABA/PSf is more than 0.25 \% PVC-ABA/PSf membrane. This may be attributed to the increase in the viscosity of the solution with the increase in content of PVC-ABA in the casting solution. This
increase hinders the phase separation process at the surface interface of the membrane leading to lesser dense upper layer as seen in SEM image (Fig. 3.18 (e)) thus leads to the decrease of surface roughness. This observation is well in agreement with the results obtained by A. Rahimpour and S.S. Madaeni (Rahimpour 2007: 299–312). Who observed a similar phenomenon for their blend membranes with the increased composition of the filler CAP in the PES matrix. Hence, 0.5 % composition is considered as optimum.

Figure 3.17 Represents the 3D AFM image of (a) neat PVC (b) 0.25 % PVC-ABA/PSf (c) 0.5 % PVC-ABA/PSf and (d) 0.75 % PVC-ABA/PSf membrane.

3.6.4 SEM

Fig. 3.18, represents the SEM cross section images of the prepared membranes which give essential information on the pore distribution of the membrane. Pore distribution in membranes play a key role in the rejection experiments. The thickness of the membranes was found to be in the range of 120 -140 µm.

As the concentration of PVC-ABA increases in the casting solution, it is noticed that the upper layer density increases for 0.25 % PVC-ABA/PSf membrane and for 0.5 % PVC-ABA/PSf membrane larger pores in the sub layer is observed with good selective
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It is observed that blending of PSf enhances pore distribution throughout the membrane matrix. Whereas, as the concentration of PVC-ABA further increases to 0.75% the pores club together to give broad finger like projections running from nearly top most part of the sub layer to the bottom layer of the membrane with diminished selective layer. The membrane pores seem to revert back to the initial pore distribution as in neat PVC membrane. Such behavior is likewise noticed when sulfanilic acid modified PVC was incorporated into PSf matrix (Vignesh 2016: 25492–25502), however in this case it is observed that much bigger pores are obtained, which is due to the stronger nature of acid groups.

Figure 3.18 Represents cross section SEM images of (a) PVC membrane (b) PSf membrane (c) 0.25 % PVC-ABA/PSf (d) 0.5 % PVC-ABA/PSf membrane and (e) 0.75 % PVC-ABA/PSf, the scale represents 50 µm in all the images.
In addition, many other works are reported earlier (Zheng 2006: 230–237, Han 2002: 55–61), where they have studied the morphological changes for poly ethylene glycol and Polyvinylpyrrolidone hydrophilic fillers in PSf. This behavior is attributed to the increased hydrophilic content resulting in faster rate of phase inversion process between the non-solvent (water) and the solvent (NMP) (Vatanpour 2011: 284-294, Zinadini 2014: 145-154). Hence, it is observed that increase in the hydrophilic content increases the density of membranes selective top layer increases to a certain limit and decreases again with further increase of hydrophilic filler.

### 3.6.5 Water uptake capacity

From Fig. 3.19, it can be noticed that neat PSf and PVC membrane show least water uptake capacity due to their hydrophobic character as evident from the high contact angle values of 76.7 and 78.8 respectively, which inhibits water to enter the membrane pore easily. Neat PVC showed better water absorption in comparison to neat PSf owing to its larger pore network as seen from SEM (Fig. 3.18 (a)). Increase in content of PVC-ABA in the membrane matrix from 0.25 to 0.75 increases the water uptake capacity of the membranes and correspondingly decrease the contact angle values from 69.8 to 61.8 respectively. This confirms that the hydrophilicity has increased linearly with increased concentration of PVC-ABA, due to the presence of hydrophilic functional groups (-COOH and -NH) which increase the affinity of the membrane material towards water. As they can form hydrogen bonds with water, they allow water to diffuse easily into the membrane matrix, and in turn increase the water uptake capacity of blend membranes.
3.6.6 Pure water flux

In order to assess the membrane hydraulic permeability, flux study was carried out with respect to pressure from 100 to 500 kPa. Fig. 3.20, represents the evaluation of water flux with pressure for various membranes, where it is observed that the flux increased almost linearly when pressure increases. Neat PSf showed negligible or nil flux followed by neat PVC owing to their hydrophobicity and is in agreement with water uptake capacity. Flux increases with increase in PVC-ABA content in the casting solution from 0.25 to 0.75 %. This is because of the increase in hydrophilic nature of the blends as explained in above section, which in turn leads to better pore structure formation during the phase separation process. Letting the water pass through the membrane without difficulty. The water permeability of the membranes is consistent with the water uptake and membrane morphology parameters described above.
Moreover, NF 270 membrane shows high water permeability, 4 times higher than the least permeable blend membrane. This can be ascribed to the highly hydrophilic nature of the commercial membrane having COOH groups.

Table 3.7 Represents the Hydraulic permeability coefficient ($L_p$) of the membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Hydraulic permeability coefficient ($L_p$) (m/s Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf: PVC- ABA</td>
<td></td>
</tr>
<tr>
<td>Neat PVC</td>
<td>$2.70 \times 10^{-12}$</td>
</tr>
<tr>
<td>(99.75:0.25)</td>
<td>$3.34 \times 10^{-12}$</td>
</tr>
<tr>
<td>(99.5:0.5)</td>
<td>$3.92 \times 10^{-12}$</td>
</tr>
<tr>
<td>(99.25:0.75)</td>
<td>$5.06 \times 10^{-12}$</td>
</tr>
<tr>
<td>NF 270</td>
<td>$32.02 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

As expected the hydraulic permeability coefficient increase with the increase in flux rate as it is directly associated to flux which in turn is correlated to the hydrophilicity of the membrane. NF 270 shows highest $L_p$ and is similar to other reported works.

3.6.7 Rejection of metal ions

3.6.7.1 Rejection at neutral pH

In order to evaluate the efficiency of the membranes for field water treatment, the prepared membranes were tested for rejection of toxic heavy metals namely Pb, Cd and Cr. Fig. 3.21 represents the rejection of all the metal ions for different membranes at various pressure. A rejection of about 60 to 85 % at 100 kPa pressure was observed for all the metal ions. Maximum efficiency is shown by 0.5 % PVC-ABA/PSf membrane to an extent of 80 % rejection for all the metal ions.

Figure 3.21 Rejection of metal ions (a) Cd (b) Cr and (c) Pb in neutral condition.
In the present study, the rejection predominantly depends on the charge developed on the membrane and as the concentration of PVC-ABA increases from 0.25 to 0.5 %, the rejection also increases, but any further increase in the concentration to 0.75 % decreases the rejection. This behavior can probably be explained by a more important hydrophilic component PVC-ABA, which enhances the pores to a greater extent than 0.25 and 0.5 %. It can be observed that for 0.25 % PVC-ABA/PSf membrane shows lower rejection, probably because of the less number of functional groups, corresponding to the less charge reported in ion-exchange study. Indeed, it is well known that ions are strongly rejected by electrostatic interactions between ions and the membrane charge (Déon 2012: 24-31) and therefore the presence of charged functional groups at the membrane surface tends to repel the metal ions, leading to lower rejection (Rether 2003: 13-21).

Also, even though 0.25% PVC-ABA/PSf membrane has lower flux and less porous structure the rejection was less as the charge on the membrane was also lesser as obtained by ion-exchange capacity. In addition as the pressure increases from 100 to 500 kPa the rejection decreases, as the metal ions are forced out from the membrane at high pressure decreasing the rejection. Thus, 0.5 % is the optimum concentration and the trend observed for rejection is 0.25 < 0.50 > 0.75. This substantiates that optimum charge and hydrophilicity is required for maximum efficiency. The phenomenon behind the performance of the membranes for metal retention can be explained as follows. In neutral pH the functional group COOH will be in its ionized form as (COO⁻) giving a negative charge. The metal ions exist as Mⁿ⁺ (M = Cd and Pb) in its free ionic state, leading to an attraction of metal ions towards membrane functional groups, either forming metal-ion complexation or ionic interactions ("O⋯Mⁿ⁺⋯O⁻"). Comparable study is noticed by C. Mbareck et al. for the removal of Cr⁺³, Pb⁺² and Cd⁺² using polyacrylic acid and polysulfone blend membranes (Mbareck 2009: 93-101). Whereas in the present case, Cr⁺⁶ exists in its ionic form as Cr₂O₇²⁻ and CrO₄²⁻ species in the neutral pH. Hence, instead of attraction repulsion takes place between the negatively charged Cr species and COO⁻ groups which leads to its rejection (Wang 2006: 307-315).
In addition, it can be observed that the optimum blend (0.5 %) showed maximum removal efficiency for Cr\(^{6+}\) ions with 85 % rejection followed by 82 % for Cd\(^{2+}\) and 82.1 for Pb\(^{2+}\). Cd\(^{2+}\) and Pb\(^{2+}\) ions show same extent of removal. But, Cr\(^{6+}\) ions are better retained. This behavior of the blend may be attributed to the repulsive interaction between Cr\(_2\)O\(_7^{2-}\) ions and the negatively charged functional groups.

### 3.6.7.2 Rejection in acidic pH

As only 80 to 85 % rejection was maximum possible, the experiments were tried out at acidic pH, since feed pH is able to change the charge on the membrane surface, its pore size and also the nature of the dissolved species, which can affect the separation performances (Ballet 2004: 369-376). The pH was maintained at 4 with the aid of 0.1 M HClO\(_4\) solution. This value was chosen since the metal ion solutions are stable below 6 and not very low pH due to environmental factors (Gherasim 2014: 67-74). It is already well established that at higher pH the functional groups such as acids will be in their ionic form, which is responsible for the retention of the metal ions in the neutral condition, as explained above. At pH = 4, the same functional groups will be in the protonated form at lower pH (Mbareck 2009: 93-101). Thus, the pH of feed solution becomes a major factor in the removal of heavy metals from waste water. Fig. 3.22 depicts the rejection of all the metal ions in acidic medium.
Interestingly, it was observed that 100% rejection is obtained for all the metal ions at 1 bar pressure. This can be attributed to the effect of the feed pH which makes the functional groups positively charged and since the metal ions (Pb$^{+2}$ and Cd$^{+2}$) are also in the positive state, repulsions lead to high rejection of the metal ions. Unlike in the neutral condition where the retention was due to the complexation of the metal ions with the functional groups, here repulsion takes the lead role. Indeed, it is possible that the –NH group may also get protonated and aid in the repulsion of metal ions. Leading to high rejection. Whereas, Cr exists HCrO$_4^-$ species (Wang 2006: 307-315) in the acidic condition, leading to the complexation of the negatively charged ions with the positively charged functional groups.
charged functional groups. Hence, it is observed that the Cr ions behave differently with respect to Pb and Cd ions towards rejection mechanism.

The results were compared with that of NF 270 membrane maintaining the same condition. From Fig. 3.22 (d), it is evident that the rejection for blend membranes is higher with 100 % retention compared to NF 270 membranes that exhibits 70 -85 % of retention. These values are different than those reported by B.A.M. Al. Rashdi et al. (Rashdi 2013: 2-17) for Cd\(^{+2}\) (99 % rejection), whereas they were similar for Pb\(^{+2}\) (74 % rejection). However the experiments were conducted in crossflow filtration cell whereas in dead end unit in present work (Rashdi 2013: 2-17).

Hence, it can be said that the blend membranes showed higher retention capacity compared to NF 270 membrane and it can be owed to the presence of two functional groups (-COOH and -NH) and the hydrophilic nature of NF 270 membrane as depicted by the flux results and mentioned elsewhere (Rashdi 2013: 2-17). In addition, the present work demonstrates 4-amino benzoic acid group modification for PVC is proven beneficial over the sulfanilic acid modification studied in our previous report (Vignesh 2016: 25492–25502). The blend membranes deliberated in this work have flux more than 5 times higher than the previous study and without sacrificing heavy metal ion rejection. Thus, introducing a competitive alternative to improve the productivity and selectively of membranes for metal ion rejection.

3.6.7.3 Competitive ion study

The competitive ion study was performed in order to investigate the efficiency of the membrane to selectively reject ions in mixture and especially the affinity of the metal ions towards membrane. All the conditions were maintained constant and the rejection was carried out at acidic pH as the maximum efficiency of the membrane was observed at lower pH. The total concentration increased to 30 ppm as each metal ion constituted 10 ppm each. From the figure, it can be seen that the rejection did not suffer much even when the concentration was high and almost similar rejection pattern is observed. On the contrary, the retention in NF 270 has increased from 70 to 85 % rejection for individual
ions to 80 to 95 % rejection in mixed ion solution and show more affinity towards Pb ion rejection over the Cr ions distinct from blend membrane.

Figure 3.23 Rejection of Cd, Cr and Pb metal ions together at different pressure by (a) 0.5 % PVC-ABA/PSf membrane and (b) NF 270 membrane in acidic medium.

Also, it can be observed that the rejection for NF 270 membrane was nearly constant even at higher pressure throughout the experiment and it was noticed that the flux had declined considerably during the process. This may be explained by the potential fouling of the membrane with time, which can block the pores of the membrane and increase rejection contrary to blend membranes for which rejection decreases due to low fouling tendency. This was visually confirmed since a strong deposition of metal ions was observable on the surface of NF 270 membrane. Whereas, the surface of blend membrane was only slightly fouled, as it can be seen in Fig. 3.24. Besides, the blend membranes showed better performances than NF 270 membrane.

Figure 3.24 0.5 % PVC-ABA/PSf blend and NF 270 membrane (a) before and (b) after filtration experiment.
The results show that retention of metal ions during separation process depends on the pH of the feed, membrane properties, nature of the permeating species and the interactions between membrane surface and permeating species (whether complexation or repulsion plays the important role). However, it’s not easy to quantify the role of each factor. Herein, the rejection obtained for the prepared blends suggests that complexation process in neutral pH and repulsion phenomenon in acidic pH for Pb$^{+2}$ and Cd$^{+2}$, whereas repulsion and complexation phenomenon for Cr ions in neutral and acidic pH respectively to play a key role in separation. Due to the presence of acid groups which play a major role on separation and a theoretical investigation of each phenomenon could be useful.

3.7 Conclusion

The modified PVC using 4-amino benzoic acid, was blended with PSf in different compositions to prepare blend membranes. Maximum of 70 to 85 % rejection of heavy metals namely Cr, Cd and Pb was observed for the optimum 0.5 % PVC-ABA/PSf membrane at low pressure and neutral pH. The rejection was enhanced in acidic pH showing 100 % efficiency in comparison to the rejection of 70 – 85 % shown by NF 270 membrane. Competitive ion study revealed that there was no much effect on the rejection and flux of the blend membrane, reveal the high performance efficiency for the blends. The rejection obtained followed complexation and repulsion phenomenon for Cd, Pb and Cr ions respectively in neutral pH and followed reverse trend at acidic pH. The study demonstrates a synthesis of highly efficient membrane with good reproducibility for heavy metal ion rejection.
3.8 Studies of PVC-Cys blend membranes

Arsenic is currently considered as one of the most potent environmental metal and is being used from centuries by mankind as a drug and poison. Studies have shown the risk of arsenic causing skin cancer (Alfred 2005: 631-641). In fact several other lethal effects of arsenic are well documented such as arsenic poisoning, black foot, cardiovascular pathologies and alterations in reproductive, immunological and neurological functions (Jesus 2016: 428-437). Several countries namely Bangladesh, India, Vietnam, Mexico, Argentina, Chile, Hungary, Romania, and the United States (Zhang 2015: 1-11) are under serious alarm to safeguard water from As contamination. It is important to adhere to the permissible limit of 10 µg/L) in drinking water as set by the World Health Organization (WHO) (Daniel 2016: 210–221). Arsenic typically exists in + 3 and + 5 oxidation state, of which arsenate (As (V)) form is thermodynamically stable and mostly present in surface water bodies (Anup 2016: 2683-2691). Arsenic is mainly introduced in the environment by natural process like volcanic eruptions and arsenic minerals. Human activities like mining, pharmaceutical industry, pesticides, herbicides, dyes, woodworking enterprises, oil refineries and metal smelting further contribute to the accumulation of arsenic in surface water bodies (María 2015: 1-8).

Herein, an attempt is being made to fabricate a novel UF membrane by blending PSf and functionalized PVC. For PVC modification, selection of functional groups is very crucial as they tend to influence many fundamental phenomena like formation of micro-emulsions, polymer mechanical relaxation, selectivity and permeability of membranes which directly governs the membrane efficiency (Bey 1998: 3335–3340). Chemical modification gives an upper hand in introducing the functional groups specifically desired for rejection application on the basis of donnan exclusion principle (Philip 2001: 1-14). Few recent work on exploitation of zwitterionic effect such as, the introduction of zwitterionic polymer namely poly(sulfo betaine methacrylate) (PSBMA), poly(sodium methacrylate) (PNaMAA) and poly(sodium p-styrene sulfonate) (PNaSS) into PSf to improve its antifouling property (Tao 2016: 162-171) and also in use of zwitterionic polymer for surface-modification of polyamide reverse osmosis membrane for reduced biofouling (Miguel 2016: 490-498) can be found. Hence, PVC was
chemically modified with L-cysteine to induce hydrophilicity and provide the necessary charge. L-cysteine being an amino acid has 3 different functional groups namely sulphur (-SH), amine (-NH$_2$) and acid (-COOH) group. Hence, it can give sufficient charge to the membrane with two free functional groups available for rejection process. The aim is to allow the reaction of -SH group with PVC chain, such that the acid and amine groups are freely available and can assist in rejection of arsenic by its zwitterionic effect.

3.8.1 Membrane preparation

Maximum possible content of Cys-PVC was blended with PSf, so as to obtain maximum flux. The ratio of modified PVC and PSf was selected based on the miscibility and membrane forming ability of the blend solution and was optimized to be 10% (0.8 g) of modified PVC with 90% (3.2 g) PSf in 16 ml NMP. Lower concentrations of PVC-Cys was not preferred owing to low productivity.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cys-PVC  PSf  NMP</td>
</tr>
<tr>
<td>Cys-PVC/PSf</td>
<td>4    16   80</td>
</tr>
</tbody>
</table>

3.8.2 SEM analysis

Fig. 3.25, represents the SEM images of the membrane surface. It can be observed that both the membranes (neat PSf and blend) have asymmetric surface pore structure. Surprisingly, irregular spherical domains are observed in the blend whereas no such observation can be made in neat PSf membrane. These spherical domains can be attributed as a result of the interaction between the polar groups of Cys-PVC and the non-polar PSf during the phase inversion process (Surya 2014: 1-18).
Cross sectional morphology gives an idea of the membrane core structure, which can be divided into 3 sections namely a) upper selective layer-responsible for the membrane selectivity b) middle finger like layer responsible for membrane productivity and the broad bottom layer responsible for the strength. Fig. 3.26 shows the cross section images of the neat PSf and blend membrane. Neat PSf membrane (Fig. 3.26 (a)) can be divided into the three layers as described above. On blending the three layer structure of PSf gets enhanced with the sub layer showing long finger like structure. This is due to the faster rate of diffusion between the non-solvent (water) and the solvent (NMP) during the phase inversion process resulting in porous membrane structure. And such behavior is observed in hydrophilic membrane.
3.8.3 Ion-exchange and hydrophilicity studies

The extent of ion-exchange capacity gives a rational idea about the number of functional groups in the membrane matrix. From Table 3.9, it can be observed that the ion exchange capacity of the blend membrane has increased with the blending of PVC-Cys with PSf. Also, the water uptake capacity and contact angle measurements indicate the hydrophilicity of the blend membrane has increased drastically indicating the enhanced bulk and surface hydrophilic nature of the blend.

Table 3.9 Ion-exchange capacity and hydrophilicity study of the prepared membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ion-exchange capacity (mequiv/g)</th>
<th>Water uptake capacity (%)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf</td>
<td>-</td>
<td>6.83 ± 5</td>
<td>76.79 ± 2</td>
</tr>
<tr>
<td>PVC-Cys</td>
<td>4.0702 ± 0.5</td>
<td>80.1 ± 5</td>
<td>63.86 ± 2</td>
</tr>
</tbody>
</table>

3.8.4 Membrane performance studies

3.8.4.1 Pure water Flux

Neat PSf is having negligible or nil flux as observed from experimentation, hence is not included in the table.

Table 3.10 Water flux and rejection study results.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water flux (1 bar)</th>
<th>Hydraulic permeability coefficient (Lp) (m/s Pa)</th>
<th>% rejection (effect of pH)</th>
<th>% rejection (effect of feed concentration (ppm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC-Cys</td>
<td>17.99</td>
<td>2.19 × 10^{-11}</td>
<td>4 7 9</td>
<td>1 3 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>67.5 73.27 83.5 73.27 41.4 35.08</td>
<td></td>
</tr>
</tbody>
</table>
From Table 3.10, it can be seen that the flux is greatly enhanced for the blend membrane, this is owed to the increased hydrophilic nature of the membrane as confirmed from water uptake and contact angle results. Also, due to the enlarged pore structure of the membrane matrix as explained in SEM section (Fig. 3.26 (b)) the flow of water is eased out giving high flux.

### 3.8.4.2 Rejection in neutral pH

From Table 3.10, it can be observed that the blend membrane has shown a rejection of nearly 73%. This suggest that the charge provided by the zwitterionic effect of cysteine plays a significant role in rejecting As (V) species. Cysteine which is attached to the PVC chain, will be at its peak of zwitterionic form on reaching isoelectric point (pH =5.1) (Shu 1985: 442-446). At neutral pH, As (V) will predominantly be present in its divalent (HAsO$_4^{2-}$) form and the membrane close to its isoelectric point will have most of its functional groups as NH$_3^+$ and COO$^-$. Now, these HAsO$_4^{2-}$ anions tend to interact differently with each of these specific functional groups. The positively charged amine groups attract HAsO$_4^{2-}$ ions and form complexes whereas, the negatively charged acid groups will repel the As (V) anions. This dual phenomenon leads to the retention of As (V) ions.

### 3.8.4.3 Effect of feed concentration

To study the membrane capacity in holding the As (V) ions, different feed concentrations were rejected (Table 3.10). It can be observed that as the concentration of feed solution increases from 1 to 3 to 5 ppm the rejection decreases proportionately. This is due to the fixed charge which exists on the given membrane surface. As the concentration of As (V) ions increases, the charge on membrane remains fixed thus decreasing the rejection. Thus, as the maximum rejection is obtained for 1 ppm, same was maintained in feed pH study.
3.8.4.4 Effect of feed pH

From the above table the major observation can be made that the blend membrane have performed better in basic pH. The control membrane has positive and negative charges provided by functionalized PVC and the rejection is dependent on these charges.

However, based on the pH, the mode of rejection will vary due to the changed behavior of the membrane as well as As (V) species. When the pH is altered to 9, the rejection increases and this is because, the dissociation of As (V) is to a higher extent to give divalent anions (HAsO$_4^{2-}$) (Sergio 2009: 458–465) and simultaneously the zwitterionic form of the membrane shifts more towards negative charge (the change in charge at various pH is depicted in Fig. 3.27) due to the presence of excess –OH ions (Sara 2013: 79–86). The divalent form of anions is known to get rejected preferably by the negative charge of the membrane owing to Donnan exclusion principle. Whereas, in acidic form As (V) dissociates to lesser extent giving monovalent species (H$_2$AsO$_4^-$) and the negative charge becomes less effective. Hence, the rejection efficiency suffers. However, rejection is not completely compromised in acidic pH as the membrane also contains positively charged NH$_3^+$ groups (Sergio 2009: 458–465) and the rejection follows adsorption phenomenon (Fig. 3.27). Similar results are previously reported (Philip 2011: 1-14) where, the rejection predominantly depends on the negative nature of the membranes. And the Donnan exclusion surpasses the attraction phenomenon.

![Figure 3.27 Schematic representation of membrane behavior at different pH.](image-url)
3.9 Conclusion

The present study involves the successful fabrication of Cys-PVC/PSf membrane for efficient removal of As (V). PVC polymer was modified with amino acid L-cysteine to get zwitterionic effect. IR and H\textsuperscript{1}NMR spectra confirmed PVC functionalization, WUT and CA studies revealed the increase in hydrophilicity of the membrane with PVC-Cys blending. SEM analysis illustrates the enhancement in membrane internal pore structure owing to the blending, thus overall the flux is enhanced. The zwitterionic effect from cysteine plays the major role in rejection at neutral pH whereas, the negative charge in basic (owed to COO\textsuperscript{-}) and positive charge in acid (owed to NH\textsubscript{3}\textsuperscript{+}) pH. As a result, making it possible to work in all the pH, but basic pH was preferred due the tendency of the As (V) to get rejected by negative charge is high.