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# Conversion of microfiltration membrane into nanofiltration membrane by vapour phase deposition of aluminium for desalination application

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ABSTRACT

Preparation and modification of NF membrane are challenging aspects in research. In the present work, we have synthesised Polysulfone (PSf) microfiltration membrane and reduced the pore size to nano level by physical vapour deposition (PVD) of aluminium metal. Membrane pore size was reduced from micro pore to nano pore, which rejected 42.22% of NaCl from the solution with 164 L/m$^2$h. And also water permeation decreases from $1.10324{\cdot}10^{-10}$ to the $9.141{\cdot}10^{-12}$. The SEM and AFM pictures showed the surface modification and metal deposition in the pores. The performance of the membrane was studied by dead end flow cell using 3.5% of NaCl solution, in which PVD membrane showed 42.22% of rejection with 16.4 L/m$^2$h flux. Thermal analysis from DSC showed Tg of 265 °C. Contact angle measurement, and water uptake were also reported.



## 1. Introduction

Membrane technology has been used in many separation techniques extensively in water treatment field [1–4]. The hydrophilicity of the membrane and its porous structure plays an important role in membrane separation process. A suitable porous membrane must have high permeability, good hydrophilicity and excellent chemical resistant to the feed solution [5]. Surface modification of the membrane is one of the best techniques, which is being applied to increase the efficiency of the membrane filtration. It changes the properties like hydrophilicity and chemical resistivity [6,7]. It also affects the pore distribution which is helpful to increase the selectivity of the membrane. Some of the surface modification techniques are Plasma etching, cleaning cross-linking, grafting, addition, substitution, and formation of functional groups. Depending on the presence of active species, surface modified membranes by plasma method can be obtained [8]. Plasma etched membrane increases the productivity (flux) as well as the selectivity of the membrane filtration [9]. In our previous research [10], we presented the effect of argon and nitrogen treatment on the membrane surface.

Physical vapour deposition (PVD) on the membrane is one of the surface engineering techniques. This process is used to form optical interference coatings [11], mirror coatings [12], decorative coatings [13], permeation barrier films on flexible packaging materials [14], electrically conducting films [15], wear resistant coatings [16], and corrosion protective coatings [17]. It involves changing the properties of the surface and near-surface region in a desirable way. In this process a material is added to the surface and the underlying material (substrate) is covered and not detectable on the surface. An atomistic film deposition process is one in which the overlay material is deposited atom-by-atom. Deposition can range from single crystal to amorphous, fully dense to less dense, pure to impure, and thin to thick. Generally the term "PVD" is applied to layers which have thickness of the order of several microns or less and may be as thin as a few atomic layers, and to the membranes it can be restricted to the nano level thickness on the treated membrane. Often the properties of the deposited membrane are affected by the properties of the underlying material (substrate) and can vary through the thickness of the deposition.

Recent studies of membrane modifications have focused on blending with inorganic materials, addition of inorganic fillers has led to increased membrane permeability and improved control of membrane surface properties [18,19]. Inorganic materials that can be blended with polymer include silica [19], zirconium oxide [20], silver nanoparticles [21], aluminium oxide [22] and small inorganic salts, such as lithium [23]. There is no any specific report of metal deposition on the membrane using PVD hence in our work we are introducing the PVD process to decrease the pore size.

In our present work, we are newly introducing the PVD process to the membrane which helps to decrease the pore size. Here we have carried out aluminium coating on the microporous polysulfone membrane by PVD method. Polysulfone is a remarkable membrane material that has been known for a long time because of its flexible nature. Aluminium coating on membrane decreases the pore size which is highly effective on membrane performance.

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## 2. Experimental

### 2.1. Membrane preparation

Polysulfone (PSf) with molecular weight 35,000 Da was obtained from Sigma-Aldrich Co, Germany. 1-Methyl-2- pyrrolidone (NMP) was procured from Merck India, Ltd. These were used without any further purification. Solution containing 100 wt.% of PSf (2 g) in 8 mL of NMP was prepared by mild stirring for 24 h at a constant temperature of 65 °C. The so obtained viscous solution was casted over glass plate using K-Control coater purchased from United Kingdom. Further, this casted membrane was kept in oven at 180 °C for about 2 min to evaporate the excess of solvent and finally membrane (MI) was separated by spraying water at the sides and stored in double distilled water [24–27].

### 2.2. Vapour phase deposition of aluminium

The deposition of Aluminium was done by evaporating Al (Merck, 99.99%) in a I HVP box coater model-IVP 12A4BC. In order to get a very thin coating, time of deposition was restricted by adjusting the time. The thickness of the deposited film was found to be 45 nm as indicated by online thickness monitoring system which includes a crystal oscillator. The deposition carried out in a vacuum less than $10^{-5}$ m bar inside a custom made vacuum chamber equipped with rotary and a diffusion pump and deposition time is 3 min. Membrane was mounted at a distance of 20 cm from the source to avoid possible heating and was rotated using a substrate rotation assembly to ensure better thickness uniformity. The membrane was then washed with water to remove the aluminium present on the surface.

### 2.3. Characterization of the membrane

#### 2.3.1. Performance study of the membrane

The performance of the NF membrane was studied using in-house made dead end cell with 3.5% of NaCl solution at different pressures (2–8 bar). The procedure used for the study of rejection and flux has been taken from the literature [26]. The cell, which had an effective membrane area of 5 $cm^2$, was used in dead-end filtration mode. The salt concentration in permeate was determined by conductivity measurement. The observed rejection coefficient (R) was determined as usual from the permeate ($C_P$) and the feed ($C_R$) molar concentrations:

$$R = \frac{C_P - C_R}{C_P} \times 100$$

Using the same cell, water permeate was also studied for both membranes hence it is an evidence for the decreasing pore size.

#### 2.3.2. Water swelling study, contact angle measurement and DSC of the membrane

Water swelling study was done as mentioned in the literature [10]. Thermal analysis was carried out using a differential scanning calorimeter using a Perkin Elmer Pyris 1 instrument, in order to observe the effect of aluminium particles on the thermal property of polymer membrane. The contact angle between water and the membrane surface was measured with a contact angle measurement apparatus FTA-200 Dynamic contact angle measurement according to the sessile droplet method.

#### 2.3.3. Surface modification study by SEM and AFM

The surface and cross sectional structures of the membrane were studied in scanning electron microscopy. Cross sections were prepared by fracturing the membrane at the temperature of the liquid nitrogen. All the specimens were coated with a thin layer of gold before being observed using SEM. EDAX of the membrane was also measured to find out the presence of aluminium.

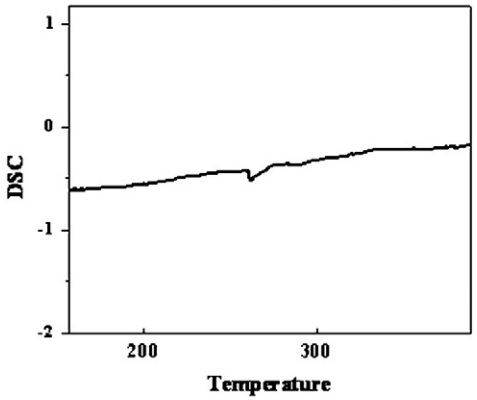


**Fig. 1.** DSC curve of the PVD membrane.

## 3. Results and discussion

### 3.1. Thermal study, water swelling and contact angle measurement of the membrane

Thermal analysis was performed to the PVD membrane in order to investigate the interaction between the polymer and the metal particles. Thermograms were recorded during the heating at a controlled rate to evaluate their thermodynamic properties. Sample was heated from 35 °C to 600 °C at the rate of 10 °C/min. Fig. 1 shows that, the deposition of aluminium has increased the Tg of the membrane. Whereas, Tg of the polysulfone was 195 °C and PVD membrane showed 265 °C (Table 1).

Contact angle is an important parameter for measuring the surface hydrophilicity. In general, more hydrophilic membrane shows low contact angle. As can be seen in Table 1, PVD membrane showed more contact angle i.e. 89.45 °C whereas, polysulfone membrane showed 66.84 °C. Deposition process increases roughness on the membrane which increases the contact angle.

Water swelling study is very important to the water filtration membranes. Polysulfone membrane showed more water uptake than the PVD membrane (Table 1). In polysulfone membrane, pores are in micro size so, water can easily enter into the pores. Whereas, in PVD membrane pores are reduced to the nano size and more surface roughness has resulted in the decrease in the water uptake.

### 3.2. Surface morphology of the membrane

On the surface morphology, AFM pictures showed more roughness (Figs. 2–5) on the PVD membranes than the polysulfone membrane. The comparison of Figs. 2 and 3 showed the deposition of the aluminium on the membrane pores. In Fig. 2, pores are clearly noticeable whereas, in Fig. 3 those pores are not observable and Figs. 4 and 5 show the roughness of the membranes. These morphologies still further proved the result of unevenness obtained from the SEM photographs (Figs. 6–10). SEM pictures clearly showed that, micro pores are filled with the aluminium which has reduced the pore size. Before deposition of metal, the pore size was above 100 nm but after the deposition the pores are filled with aluminium increasing the

**Table 1**
Membrane water uptake, contact angle and Tg.

| | Water uptake in % | Contact angle | Tg |
|---|---|---|---|
| Before PVD | 54% | 66.84 | 195 °C |
| After PVD | 33% | 89.49 | 265 °C |

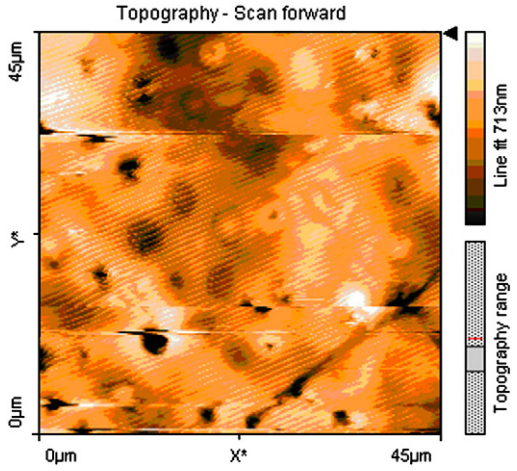


**Fig. 2.** AFM picture showing surface profile of PSf membrane.

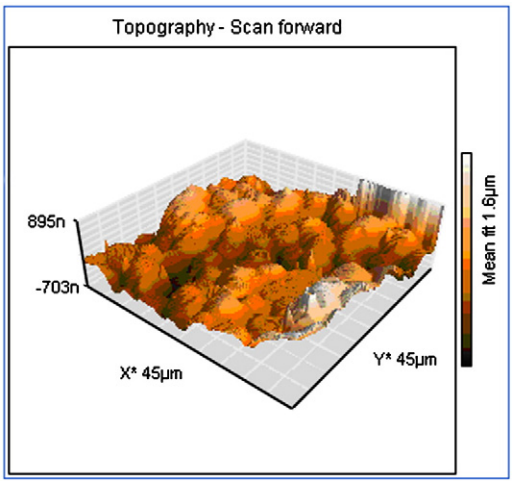


**Fig. 5.** 3D AFM of PSf membrane after PVD.

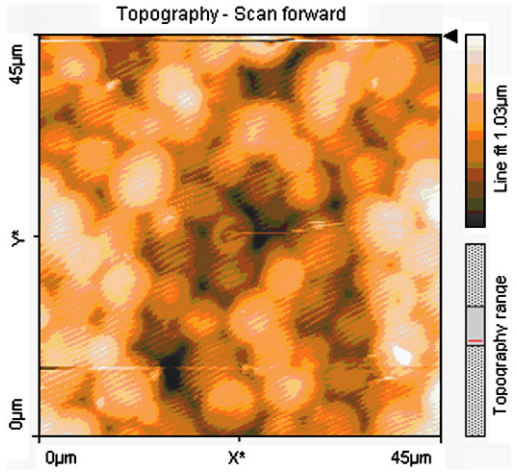


**Fig. 3.** AFM picture showing surface profile of PSf membrane after PVD.

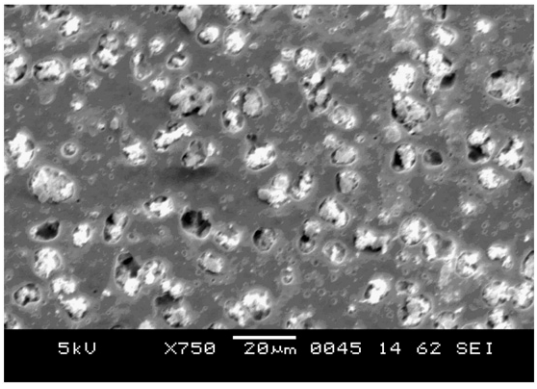


**Fig. 6.** Surface picture of membrane after PVD.

mechanical strength and reducing the pore size. This also changed the shape of the microvoids along with changes in the thickness of the membrane. Average thickness of the membrane was approximately $(107 \pm 20)$ µm whereas, after the deposition it was increased to $(125 \pm 20)$ µm so, i.e. up to 15–19% of thickness increases. Cross section of the membrane clearly showed distribution of aluminium particles in the microvoids. EDAX of the cross sections showed the presence of 3.5% of aluminium in the 1 µm area.

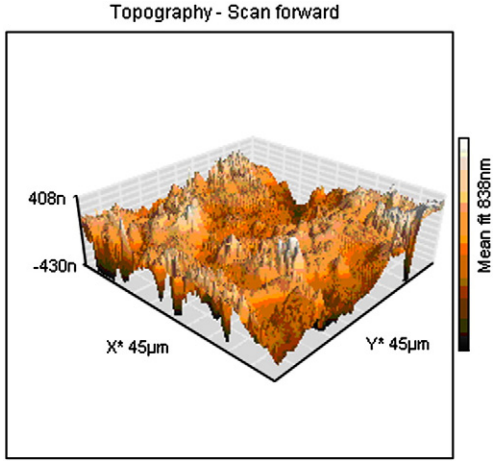


**Fig. 4.** 3D AFM of PSf membrane.

### 3.3. Performance study of the membrane

Pure water flux was obtained by measuring the flux for pure water against operating pressure. As shown in Fig. 11, the flux increases linearly with the operating pressure. The details of water flux study for PSf and PVD membrane has been presented in Table 2. This linear behaviour is described by a slope, close to pure water permeability, according to the Spiegler–Kedem model [28]. The hydraulics permeability coefficient of

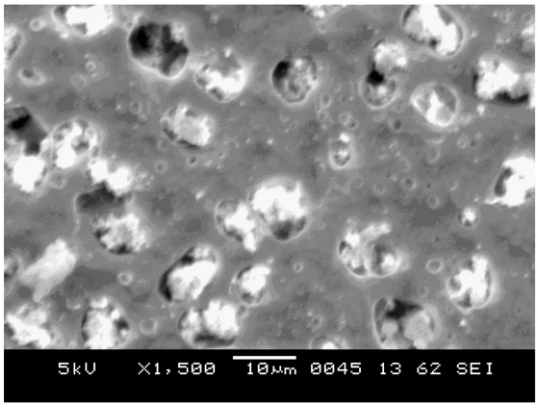


**Fig. 7.** Surface picture of membrane after PVD.

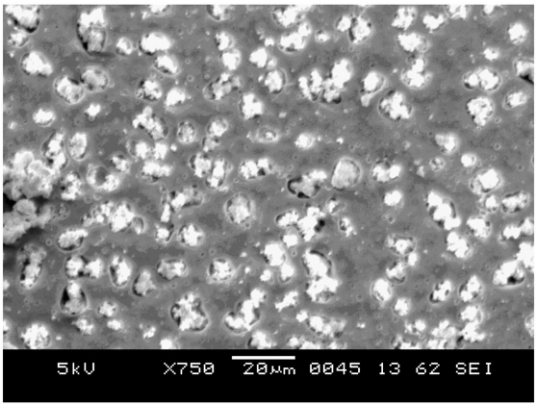


**Fig. 8.** Surface picture of membrane after PVD.

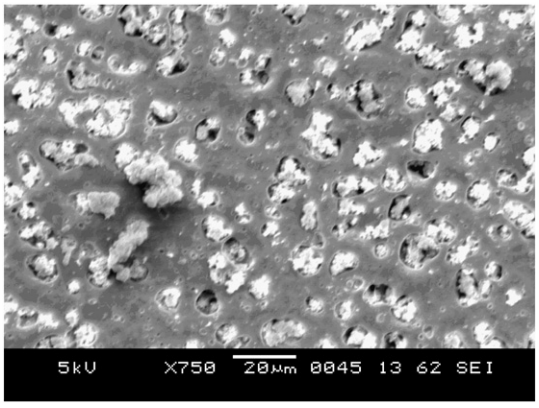


**Fig. 9.** Surface picture of membrane after PVD.

the Polysulfone membrane is $1.10324 \cdot 10^{-10}$ m/sPa. After the PVD, and decreases to the $9.141 \cdot 10^{-12}$ m/sPa. Hence exhibit nanofiltration membrane's permeation.

Performance study of the membrane was carried out by dead end flow cell, with 3500 ppm of NaCl solution at different pressures ranging from 2 to 8 bars. All the experiments were carried out three times, the difference was negligible so the mean values of the results were reported. The rejection and flux for NaCl (Fig. 12, Table 3) is worth to mention that the rejection of membrane is 42.22% with 16.4 L/m$^2$h flux at 2 bar pressure. PVD is one of the process in which the aluminium particles are inserted into the micro pores of the membrane to reduce pore size. SEM pictures of membrane clearly showed insertion of aluminium into the pores reduced pore size, as a result there is more rejection because of size exclusion principle and less flux. Due to the size exclusion principle smaller sized water molecule permeates into the membrane and NaCl particles were rejected. Surface roughness is a major factor which decides the performance of the membrane. If roughness is more, rejection is also more and flux is low, as it is evident from AFM pictures and rejection results. Increasing the pressure decreases the salt rejection with increasing flux. Results clarified that, increase in the flux decreases the salt rejection.

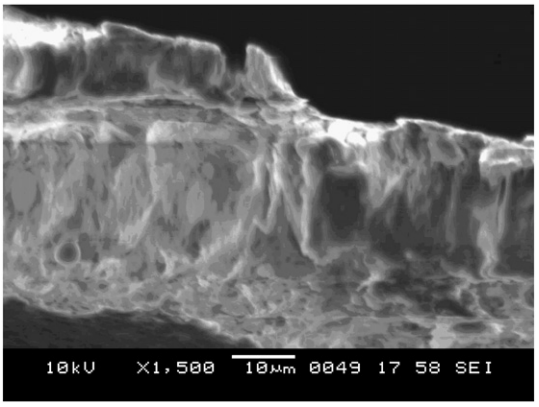


**Fig. 10.** Cross section picture of the membrane after PVD.

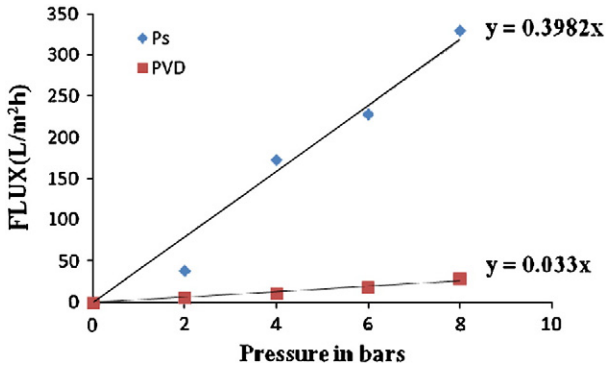


**Fig. 11.** Water flux study of the Polysulfone and PVD membrane.

**Table 2**
Water flux study of the PSf and after PVD membrane.

| Pressure in bars | PSf membrane water flux in L/m$^2$h | After PVD membrane water flux in L/m$^2$h |
|---|---|---|
| 2 | 38.41 | 6 |
| 4 | 173.05 | 11 |
| 6 | 228.6 | 18 |
| 8 | 329.68 | 29 |

## 4. Conclusion

The prepared polysulfone microporous membrane was converted into nanoporous membrane by depositing an aluminium metal. The PVD method changed the hydrophobicity of the PSf membrane by the means of contact angle 66.84 to 89.49. This was confirmed by the SEM images, AFM study and also by the DSC measurements. Aluminium coated membrane possessed higher Tg value, indicating the elevated thermal stability of the treated membrane. Moreover there is a significant

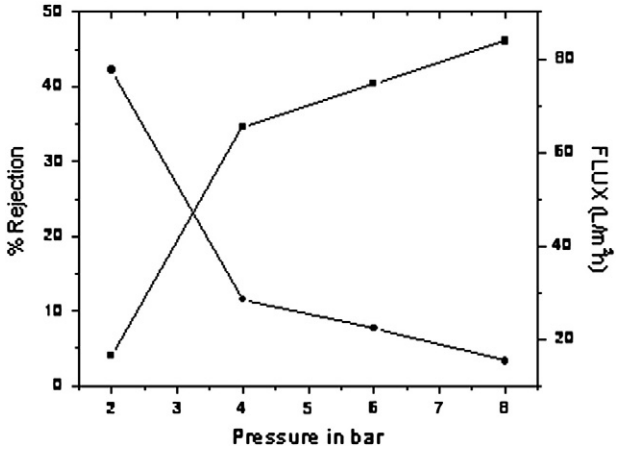


**Fig. 12.** Flux and % rejection of NaCl of the PVD membrane.

**Table 3**
Flux and % rejection of the membrane at different pressure.

| Sl no | Pressure in bar | % Rejection | Flux (L/m$^2$h) |
|---|---|---|---|
| 1 | 2 bar | 42.22% | 16.4 |
| 2 | 4 bar | 11.55% | 65.5 |
| 3 | 6 bar | 7.7% | 74.68 |
| 4 | 8 bar | 3.3% | 83.82 |

increase in the selectivity of the salt ions. This is one of the best methods for the preparation of NF membranes and surface modification. Further research on this may lead to a revolution in membrane surface modification.

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