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New CPS-PPEES blend membranes for $CaCl_2$ and NaCl rejection

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Abstract. Carboxylated polysulfone (CPS), poly (1,4-phenylene ether ethersulfone) (PPEES), membranes were prepared and used for the separation of NaCl and $CaCl_{2,}$ in efficient way with less energy consumption. In this work, nanofiltration and reverse osmosis membranes were employed to the salt rejection behavior of the different salt solutions. The influence of applied pressure (1-12 bar), on the membrane performance was assessed. In CM series of membranes, CM_1 showed maximum of 97% water uptake and 36% water swelling, whereas, CM_4 showed 75% water uptake and 28% water swelling. In RCM series, RCM_1 showed 85% water uptake and 32% water swelling whereas, in RCM_4 it was 68% for water uptake and 20% for water swelling. Conclusively reverse osmosis membranes gave better rejection whereas nanofiltration membrane showed enhanced flux. CM1 showed 58% of rejection with 12 L/(m^2 h) flux and RCM_1 showed 55% of rejection with 15 L/(m^2 h) flux for 0.1 wt.% NaCl solution. Whereas, in 0.1 wt.% $CaCl_2$ solution, membrane CM_1 showed 78% of rejection with 12 L/(m^2 h) flux and RCM_1 showed 63% rejection with flux of 9 L/(m^2 h).

Keywords: carboxylated polysulfone; NF; RO; synthesis; rejection

1. Introduction

Membranes play vital role in the separation/recovery and permeation applications. Broadly membranes are categorized into four types, namely reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) (Mulder 1996). As one of the most important advances in membrane technology, nanofiltration (NF) membranes have been developed and widely used in removal of salts in water treatment and the fractionation of salts and small molecules in a number of industries, such as drinking water production, dairy industry and the paper industry. NF membranes have properties between ultrafiltration (UF) and reverse osmosis membranes, the solute separation mechanisms of which have been studied intensively (Lina *et al.* 2008). NF is not as fine as RO filtration; however it does not require the same energy to perform the separation. NF also uses a membrane, that is partially permeable to perform the separation, but the membrane's pores are normally much larger than those used in reverse osmosis. NF is capable of concentrating sugars,

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divalent salts, bacteria, proteins, particles, dyes, and other constituents that have a molecular weight greater than 1000 daltons (Kim *et al.* 2005, Kimura *et al.* 2003). NF, like RO, is affected by the charge of the particles being rejected. Thus, particles with larger charges are more likely to be rejected than others. RO membranes require operating pressure in the range of 30-70 bar pressure; however, NF membranes can be operated 2-12 bar pressure.

Several materials are employed for the preparation of membranes, to name few, materials like polysulfone, polyimide, polycarbonate and cellulose acetate. Polysulfone membrane possesses excellent mechanical, biological, and chemical stability, as well as having an extensive operating range at temperature (>80°C), unfortunately due to its hydrophobic nature, which results in low water flux. Hydrophilicity of polysulfone has already been improved in several investigations by chemical modification. It has been studied that, hydrophilicity of polysulfone can be enhanced by introducing charged and polar groups like -SO_3H and -COOH onto polysulfone and these charged as well as hydrophilic polysulfones were used to prepare membranes by blending with other commercial polymers (Latha *et al.* 2005). Our present work involves preparation of NF, RO membranes, study of water uptake, swelling and rejection performance of the membranes in terms of NaCl and $CaCl_2$ (Thanuttamavong *et al.* 2002).

2. Experimental

2.1 Synthesis of carboxylated polysulfone (CPS)

All the required reagents were obtained from Sigma-Aldrich and were used without any further purification. The carboxylation of polysulfone was done as mentioned in Guiver *et al.* (1990) and

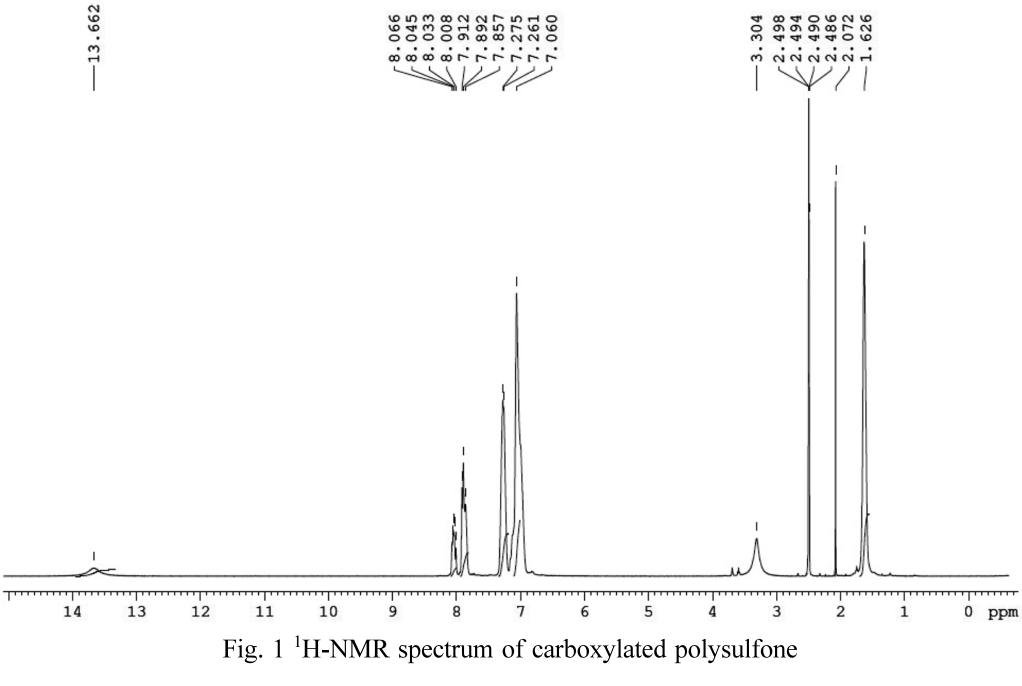


Fig. 1 ^{1}H-NMR spectrum of carboxylated polysulfone

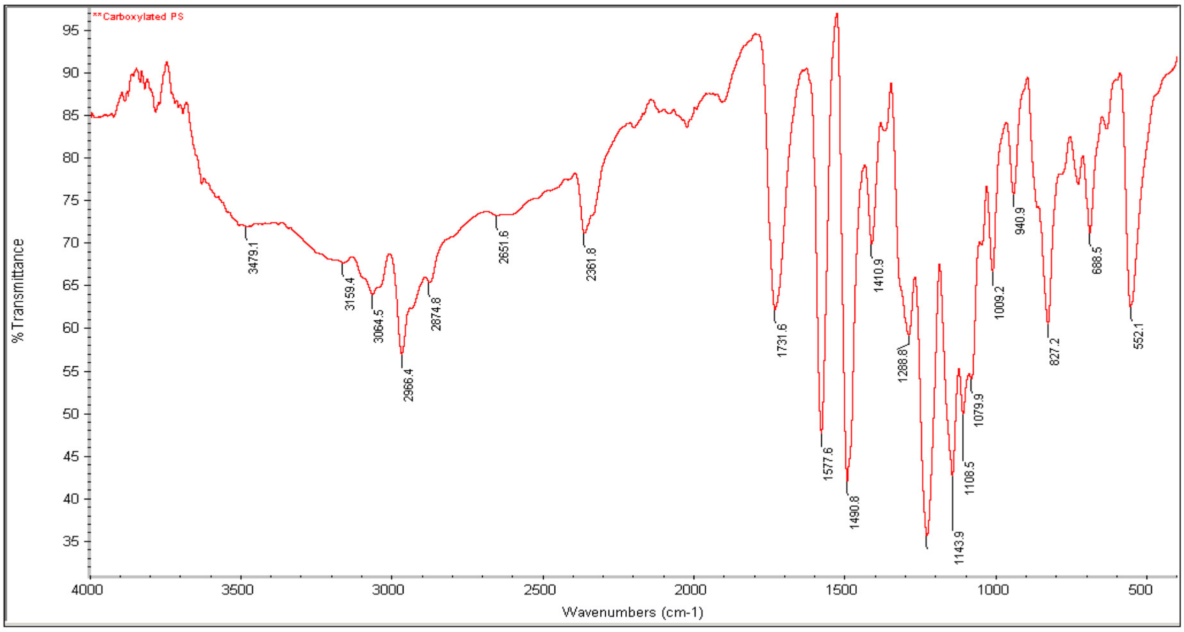


Fig. 2 IR spectrum of the carboxylated polysulfone

Sajith *et al.* (2002). The dried udel polysulfone (Mw = 35000 Da) was placed into a 100 mL three neck Schlenk equipped with a dropping funnel, a thermometer, N_2 inlet and a magnetic stirrer. 2 g (0.0045 mol) polysulfone was dissolved in THF anhydrous (75 mL) and the solution temperature was reduced to 50ºC. *n*-Butyllithium (2.5 mol equiv., 0.0112 mol, 7.03 mL of 1.6 M in hexane) diluted with THF (10 mL) was added dropwise over 12 minutes, during which time the mixture turned a red-brown color. The polymer was quenched after 30 minutes by the slow addition (10 g) of $CO_{2(S)}$ during 30 min, and then warmed slowly to room temperature THF was evaporated on a Schlenk line to afford the white slurry. The polymer was precipitated into dilute aqueous HCl (10%) solution, washed with distilled water and finally dried at 50ºC in vacuum oven to obtain a white solid (2 g, yield 98%).

The ^{1}H-NMR spectrum (Fig. 1) of carboxylated polysulfone was recorded on a Varian Unity Inova 400 NMR Spectrometer. ^{1}H NMR (500 MHz, DMSO):8.03 (D, ^{3}J-9 Hz, 2H, H_5), 7.31 (d, ^{3}J=8 Hz, 4H, H2), 7.16 (dd, ^{3}J=8 Hz, 4H, H2) 7.16 (dd, ^{3}J Hz, ^{5}J=Hz, 2H, H_4), 7.09 (D, ^{4}J=3 Hz, 2H, H_3), 7.07 (D, ^{3}J=8 Hz, 4H, H1), 1.61 (s, 6H, CH_3), 13.9 (br, 2H, OH) ppm.

The IR spectrum of the carboxylated polysulfone sample was recorded by exposing thin films in Nicolet Avatar 5700 FTIR spectrophotometer. From the IR spectrum, the substitution of carboxyl group in polysulfone was identified by the presence of carboxyl group in 1577-1731 cm^{-1}. Fig. 2 represents IR spectrum of the carboxylated polysulfone.

2.2 Preparation of CPS - PPEES NF/ RO membrane

Solutions containing different wt.% of CPS and PPEES (Table 1) in 5.5 mL of 1-methyl-2-pyrrolidone (NMP) were prepared by mild stirring for one day at constant temperature of 65ºC. Obtained viscous solution was casted over glass plate using K-Control coater 202, UK. Casted

Table 1 Solutions containing different wt.% of CPS and PPEES

Membrane code	wt% composition (CPS)	wt% composition (PPEES)
CM1/RCM1	90	10
CM2/RCM2	80	20
CM3/RCM3	70	30
CM4/RCM4	60	40

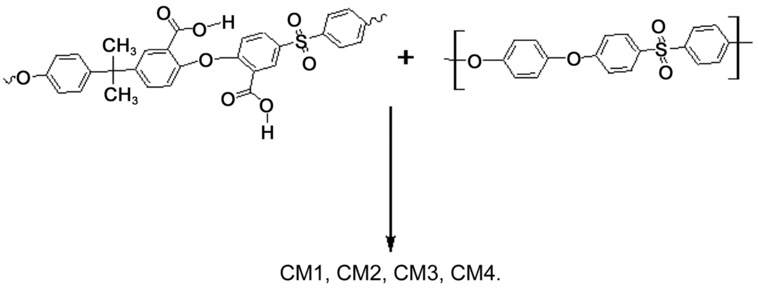


Fig. 3 Schematic route for the synthesis of CPS-PPEES membranes

membrane was again heat-treated at 220ºC, then washed thoroughly with deionized water and immersed in deionized water for 24 h to give NF (nanofiltration) CM1, CM2, CM3 and CM4 membranes. In case of RO (reverse osmosis), RCM1, RCM1, RCM1 and RCM1 membranes, casted membranes were allowed to cool to room temperature without any heat treatment. Fig. 2, shows the schematic route for the synthesis of CPS- PPEES membranes (Chitrakara *et al.* 2011).

2.3 Structural characterization

For the confirmation of the blend membranes, IR spectra were recorded using Nicolet Avatar 5700 FTIR (Thermo Corporation) spectrometer. Scanning electron microscope (SEM) (Jeol JSM-84) was used to observe the microstructures of the dried membranes. In order to get morphology, membranes were cryogenically fractured in liquid nitrogen and after carrying out sputtering it is observed under SEM.

2.4 Water uptake

The water uptake of the membrane was determined by measuring the change in the weight after the hydration. The membrane was first immersed in deionized water for 24 h. Then the membrane was weighed quickly after removing the surface attached water using botling paper to determine the weight of wetted membrane (W_{wet}). The weight of the dry membrane (W_{dry}) was determined after drying. The percentage of water uptake was calculated by using the following equation (Ren *et al.* 2000)

$$\text{Water uptake } (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

2.5 Swelling

The surface swelling characteristics were determined by measuring the change of the membrane geometrical area upon equilibrating the membranes in water at room temperature for 24 h. The swelling ratio was calculated by the following equation (Ren *et al.* 2000)

$$\text{Swelling } (\%) = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100$$

where, A_{dry} and A_{wet} are the area of dry and wet samples, respectively.

2.6 Permeation experiment

Salts with different valence distribution are used for NF membrane experiments to investigate membrane properties. The permeability of pure water through this NF membrane was also measured. Flux, F (L/m^2 h*)*, was calculated as Eq. (1)

$$F = W/(A\ t) \tag{1}$$

Where W (L) is the total volume of the water or solution permeated during the experiment, A(m^2) is the membrane area, and t (h) is the operation time. Rejection, *R*, is calculated as Eq. (2)

$$R = (1\text{-concentrate permeates/concentrate feed}) \tag{2}$$

Schematic diagram of the filtration set up has been presented in Fig. 3. The feed was taken from the feed tank and was pumped into the module. The pressure difference between the feed inlet and the outlet during operation was adjusted from 1 to 12 bar. The rate of the permeate stream was measured by a rotameter and a gauged cylinder where as rejection (%) was studied by conductivity measurements (Toshinori *et al.* 2010).

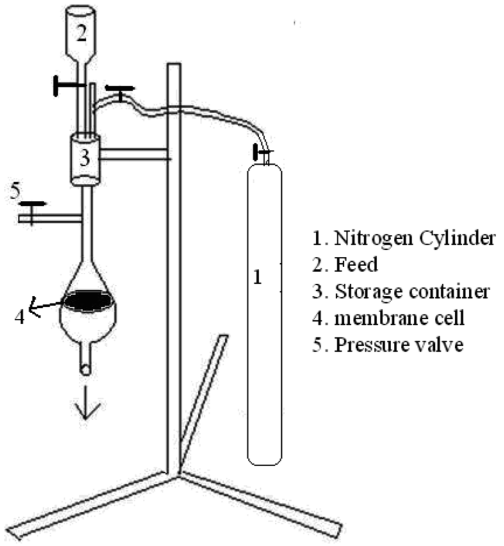


Fig. 4 Schematic representation of the salinity checking unit

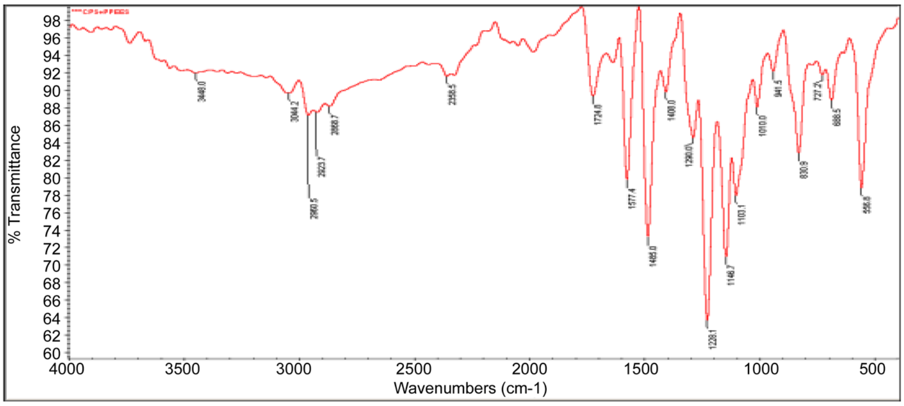


Fig. 5 IR spectrum of the CPS-PPEES membrane

Table 2 Water uptake and swelling values for different membranes

Membrane code	Water uptake (%)	Swelling (%)
CM1	97	36
CM2	85	34
CM3	77	30
CM4	75	28
RCM1	85	32
RCM2	76	28
RCM3	71	23
RCM4	68	20

3. Results and discussion

3.1 Spectral characterization

Fig. 5 shows IR spectrum of the CPS-PPEES membrane. CPS-PPEES, gave following stretching frequencies; carboxyl group was identified in 1577-1731 cm^{-1}, 3600-3200 cm^{-1} for O-H stretching vibrations along with characteristic group frequencies as mentioned in PS-PPEES membrane.

3.2 Water uptake, swelling

The water uptake and swelling play important roles in membrane performance. The water uptake of the CPS-PPEES membranes was increases with carboxylation concentration. This is due to the fact that the carboxylate groups are hydrophilic in nature and hence the membranes with higher carboxylation absorb more water (Wayne *et al.* 1994). From the study, it was observed that, the rejection of different salts increases with higher carboxylated polysulfone concentration.

3.3 Morphology of the membranes

The morphology of CPS-PPEES membranes were studied by scanning electron microscopy

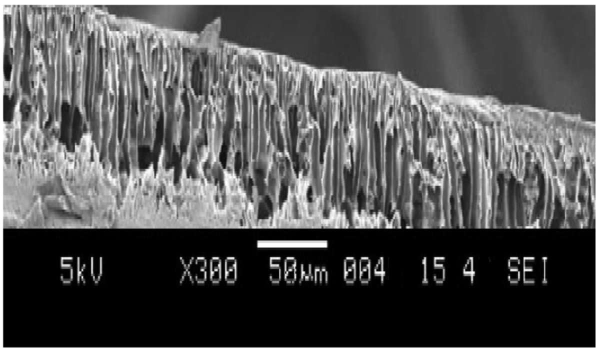


Fig. 6 Cross section image of the CM1 membrane

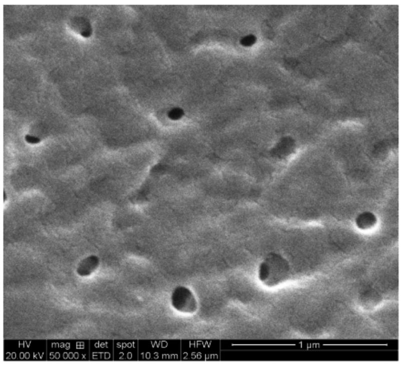


Fig. 7 Surface image of the membrane RCM1

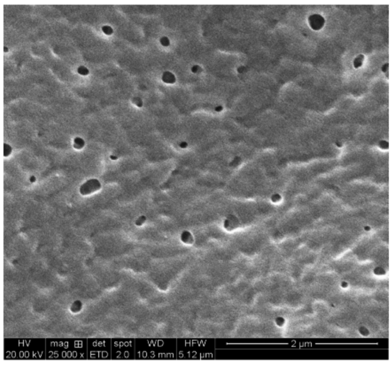


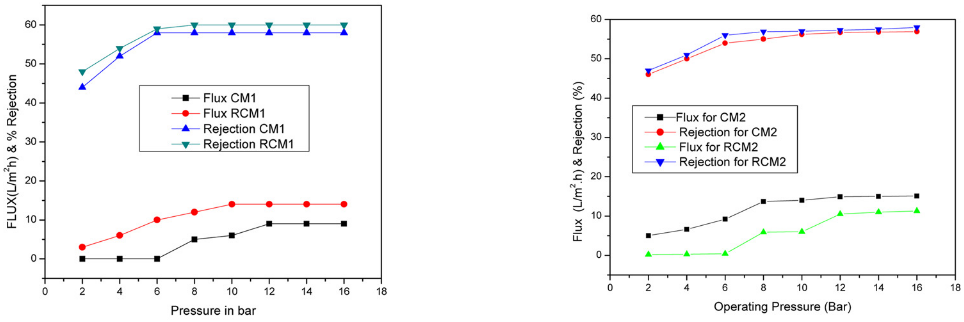
Fig. 8. Surface image of the membrane RCM2

(SEM). Figs. 6 and 7 show surface image of the CPS-PPEES membrane. Fig. 5 represents cross section image of the CPS-PPEES membrane. Cross section image of the membranes shows dense and channel-like microvoids which eases the flow within the membrane matrix. It can be concluded that SEM study of the membranes however does not clearly signify the effects of carboxylation on the membrane structure (Han and Bhattacharyya 1994).

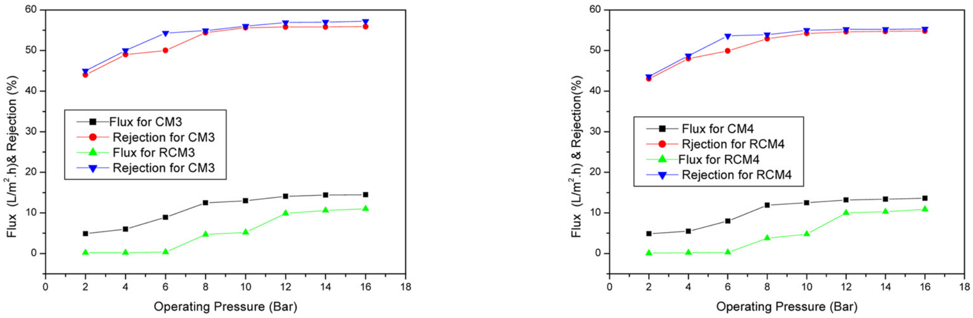
3.4 Comparison between NaCl and $CaCl_2$ salts rejection (R)/flux by different CPS-PPEES NF/RO membranes

Regardless the NF or RO membrane, all carboxylated membranes showed enhanced performance in terms of sodium chloride and calcium chloride rejection (Bowen *et al*. 1997). This fact can be attributed by the reason of dissociated –COOH groups, which is responsible for the enhanced negative charge density on membrane surface, hence membranes can easily trap positively charged cations. Fig. 9(a) to Fig. 9(c), describes rejection rate of NaCl and Fig. 9(d) to Fig. 9(h), illustrates rejection rate of $CaCl_2$ respectively by the different membranes (Andriy *et al*. 2002, Jiraratananon *et al*. 2000). Relatively RO membranes show better rejection than NF membranes. It is also understood that membranes showed increased $CaCl_2$ rejection than NaCl. This is due to the fact that $CaCl_2$ have smaller ionic size but have larger size of aquation.

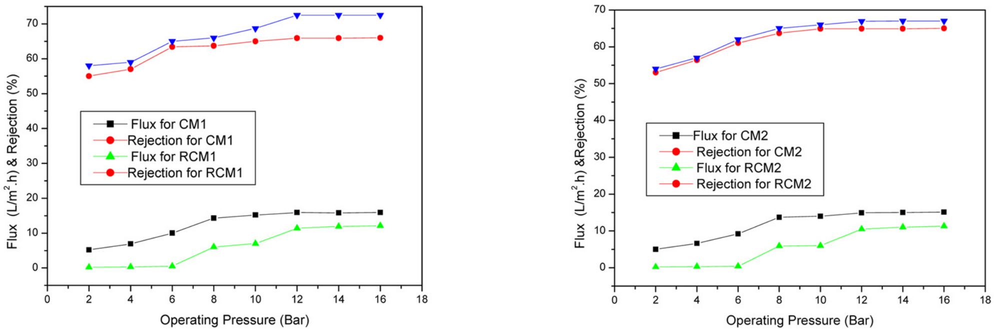
(a) CM1 &RCM1 (b) CM2 &RCM2



(c) CM3 &RCM3 (d) CM4 &RCM4



(e) CM1 &RCM1 (f) CM2 &RCM2



(g) CM3 &RCM3 (h) CM4 &RCM4

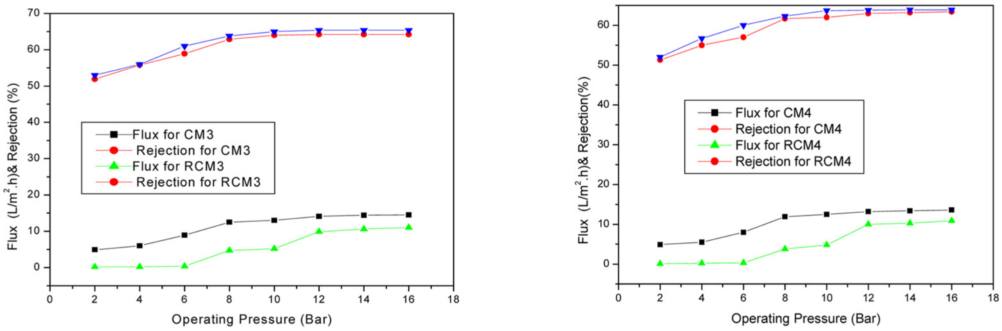


Fig. 9 Flux and rejection performance of the membranes with 0.1% NaCl (a-d) and 0.1% $CaCl_2$ (e-h)

4. Conclusions

In the present work, we have successfully carried out the preparation of CPS-PPEES composite NF and RO membranes by DIPS method. It is observed that both NF and RO membranes gives reasonably good water uptake, swelling rate. SEM pictures of the membranes were used to identify pore size and presence of channel like microvoids on membranes. Dimensions of the pore size also confirmed the formation of NF and RO membranes. Both NF and RO membranes, showed better $CaCl_2$ rejection than NaCl with much energy efficiency. In case of NF membranes Donnan exclusion plays vital role in rejection of the salt, where as in RO membranes diffusion and convection transport play major role in rejection of the salt.

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