Reactive modification of PVC membranes for the improved performance

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Abstract. Poly vinyl chloride (PVC) was chemically modified, and used for ultrafiltration to analyze the performance. Non-solvent induced phase separation (NIPS) method was used to prepare membranes. The neat PVC membrane was casted and used as a control membrane. Modified membrane was prepared by reacting PVC with ethanolamine (EA) in the casting solution (labeled as CM-PVC). Pure water permeability (PWP) was evaluated by measuring pure water flux. Humic acid was used as model foulant solute to analyze flux and rejection ability of membranes. Flux and rejection data of neat and modified membranes were compared to prove the improvement in the filtration performance. The experimental results showed that for PVC and CM-PVC, PWP was calculated to be ~64 and ~143 L/m²h, respectively, and the rejection of humic acid was found to be 98% and 100%, respectively. TGA was carried out to analyze the effect of chemical modification on the thermal stability of polymer. FT-IR analysis was another characterization technique used for the comparative study.

Keywords: polyvinyl chloride; permeate flux; ultrafiltration; humic acid; rejection

1. Introduction

The non-equilibrium pressure-driven processes, viz. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have received increasing attention for industrial as well as domestic applications, especially, in wastewater treatment and desalination of sea water. Apart from water treatment, various food and pharmaceutical industries also use these membrane-based processes for removal/recovery of salts, acids, organics, etc. Ultrafiltration plays important role among the other membrane-based processes, especially as a pre-treatment step for desalination, industrial effluent treatment, sewage treatment, etc. Ultrafiltration has the capability of removing/rejecting large size particulates, colloids, high molecular weight compounds like proteins, polysaccharides, and other extracellular polymeric substances (EPS), etc. The advantages of this process are low operating pressure, less energy requirement, smaller footprints, modular design and low operating cost.

Synthetic polymers like polyvinylidene fluoride (PVDF), polyethersulfone (PES), polysulfone (PSf), polyvinyl chloride (PVC), polypropylene (PP), poly vinyl alcohol (PAN), etc. are mostly used as membrane materials due to their good mechanical, chemical and thermal stability. Moreover, PES and PSf were extensively used as a suitable material for commercial membranes. There are two main problems with these membrane materials: 1) their inherent hydrophobicity causes bio-fouling, and 2) they are costly materials. There have been some review reported on

modification of PES membranes to improve the performance (Kumar *et al*. 2015, Van der Bruggen 2009, Zhao *et al*. 2013). However, PVC is the cheapest of the above mentioned polymers and also possesses good chemical resistance as well as high mechanical strength; hence it is widely used in making MF and UF membranes (Liu, Chen *et al*. 2012, Fan *et al*. 2014). The structure of PVC porous membranes were studied as early as 1979 (Hirose *et al*. 1979). In 1997 (Kawai *et al*. 1997), phase system of PVC/THF/water was studied as a function of evaporation time of tetrahydrofuran (THF). Xu and Xu (2002) reported PVC hollow fiber ultrafiltration membranes using polyvinyl pyrrolidone (PVP) as additive and N,N-dimethyl acetamide (DMAc) as a solvent, prepared with the well-known, non-solvent induced phase separation (NIPS) method by dry/wet spinning technique. Mei *et al*. (2011) studied the morphologies of various PVC membranes prepared by NIPS method with different additives and the phase system of PVC/DMAc/water.

The main drawback of using PVC as membrane material is its inherent hydrophobicity, which brings in the problem of organic fouling and bio-fouling. When membranes are used for pre-treatment for sea-water desalination or municipal wastewater, they get fouled due to the presence of extra-cellular polymeric substances (EPS) like humic substances, alginates, proteins, polysaccharides, etc. and dissolved organic matter (DOM) like natural organic matters (NOM), synthetic organic compounds (SOC), soluble microbial products (SMP), etc. (Guo 2012). Being organic in nature, they adsorb on to the hydrophobic membrane surfaces as well as block the pores of the membrane, causing fouling, and hence, results in decreasing the permeate flux and depleting the membrane property. Thus, such membranes are required to be modified by improving their hydrophilicity so as to enhance the anti-

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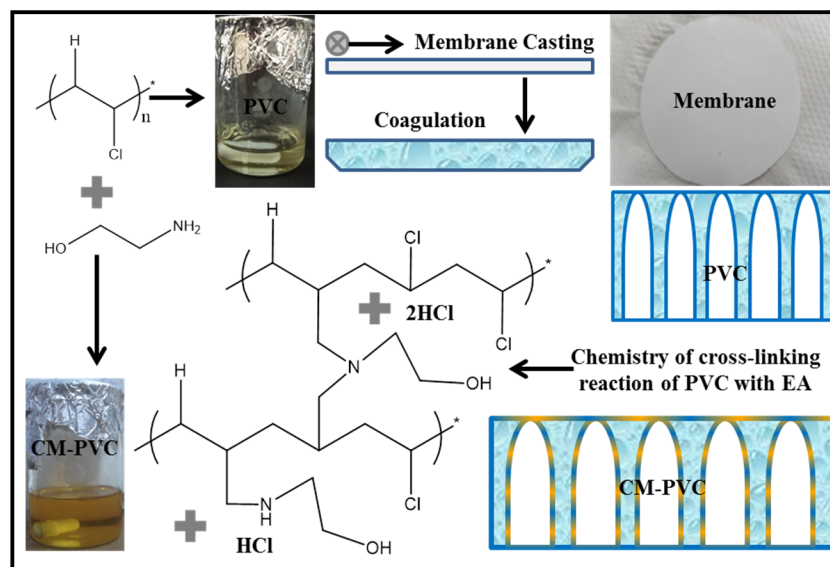 E-mail: zvpm@ched.svnit.ac.in, zvpm2000@yahoo.com

Fig. 1 Schematic diagram showing modification chemistry and mechanism of membrane formation

fouling property. Several reports are available on anti-fouling and low fouling membranes, but the focus here is on the modification of PVC membranes.

For experimental purpose, model foulant solutes like bovine serum albumin (BSA), sodium alginate, humic acid, oil-in-water emulsion, etc. are widely used. The performance of PVC/CPVC blend membranes with different ratios and different concentrations of amphiphilic tri-block co-polymer, Pluronic F127, additive were experimentally studied (Liu, Su *et al*. 2012). Liu, Chen, Zhang, Crittenden and Chen (2012) did similar study by varying Pluronic F127 to PVC ratio, keeping PEG6000 concentration constant. The study of effect of PEG400 concentration in PVC blend membranes on water flux, dextran (model foulant) rejection and flux recovery was also found (Aryanti *et al*. 2015). Su *et al*. (2015) chemically modified CPVC/PVC blend membrane by aminating the surface with ethylene diamine (EDA) and then fluorinating with pentadecafluorooctanoic acid (PFOA). Filtration experiment with oil-in-water emulsion showed enhancement in the flux recovery compared to untreated membrane. In an experimental study done by Zhu *et al*. (2014), PVC was aminated with triethylenetetramine (TETA) in the casting solution, and then aminated PVC membrane was casted via phase inversion method. The different aminated PVC membranes were zwitterionicalized via quaternary amination reaction with sodium chloroacetate for different reaction times, and experimented with 1 g/L of BSA solution for anti-fouling performance. Yu *et al*. (2015) reported the use of silica nanoparticles in the PVC membrane, that contained sodium hexametaphosphate (SHMP) and PVP as additives, and explained that the nano-SiO$_2$ possess good hydrophilicity owing to the presence of –OH group that makes hydrophilic layer with water via hydrogen bonding, causing to repel hydrophobic foulants. Recently, Jhaveri and Murthy (2016a, b) have published comprehensive reviews on nanocomposite and anti-fouling nanocomposite membranes for pressure driven membrane separation processes. Also, a recent review, on engineering nanocomposite membranes, focusing on the use of engineered nanoscale materials, was published (Al Aani *et al*. 2017).

Singh *et al*. (2010) reported the chemical modification of PVC by reaction with various amines, which has brought motivation for the present work. In the present work, an attempt is made to study the performance of chemically modified PVC membranes and compare them with that of the neat, unmodified PVC membrane. The modification of PVC is done by reacting PVC, dissolved in DMAc, with ethanolamine (EA). PVP was used as pore-forming agent.

The cross-linking reaction between PVC and EA occurs by possible elimination of chlorine from PVC in the form of HCl as reported in literature (Singh *et al*. 2010). This may result in change in the thermal stability as well as in the affinity of membrane towards water and solutes present in feed solution. The difference in the mechanism of PVC and CM-PVC membrane formation can be explained hypothetically using the schematic diagram as shown in Fig. 1. Humic acid was used as model foulant solute to simulate the actual fouling conditions for characterizing the anti-fouling effect because most of the fouling occurs due to the presence of humic substances and EPS present in the sea water as well as municipal wastewater.

2. Experimental

2.1 Materials

Poly(vinyl chloride) (PVC, high molecular weight, density ~1.4 g/mL) was purchased from Sigma-Aldrich, Mumbai, India. Polyvinylpyrrolidone (PVP) and N,N-dimethyl acetamide (DMAc) (extra pure) were purchased from Sisco Research Laboratory, Mumbai, India. Humic acid (HA) was supplied by LobaChemie, Mumbai, India. Ethanolamine (EA) was supplied by RFCL Limited, Haryana, India. Deionized (DI) water, used during the preparation and application, was supplied from Millipore

(Elix) system. All the chemicals were used without further purification.

2.2 Membrane preparation

The NIPS method was used to make membranes. Polymer dope solution was prepared by dissolving PVC/PVP in DMAc. Concentration of PVC and PVP was kept at 15 wt% and 2 wt%. The casting solution was kept at 70°C, and magnetically stirred for 24 h to ensure homogeneity. Then, the solution was allowed to degas at room temperature overnight without stirring. Finally, the membrane was casted on the non-woven sheet using Automatic film applicator (Make: Sheen Instruments, Cambridge, UK). The wet thickness was maintained up to 150 μm. The casted membrane was immediately immersed into DI water bath (that acts as non-solvent coagulation bath), and kept under water for at least 24 h to ensure the removal of traces of solvent present in the membrane. Then, the membrane was stored at room temperature. The membrane is labeled as *PVC*. All membranes were kept in DI water for few hours before use.

Chemically modified PVC was also made by NIPS method. The polymer dope solution was prepared with the same composition. After complete dissolution of polymer in the solvent, i.e. after 24 h, EA was added such that weight ratio of PVC to EA is 10:1. The internal cross-linking reaction between PVC and EA was carried out at 60°C for 8 h with continuous stirring. The viscous casting solution, which was initially transparent and colorless, turned yellowish. Membrane casting was done with the same procedure as mentioned above. This membrane is labeled as *CM-PVC*.

We have also attempted to prepare surface modified PVC membrane. The procedure was very simple; neat PVC membrane, prepared previously by NIPS method, was dipped in a 20 vol% ethanolamine aqueous solution. The surface reaction (external cross-linking) of PVC with EA was carried out for 6-8 h at 60-70°C. Then, the membrane was washed with DI water and dried. This membrane is labeled as *SM-PVC*.

2.3 Characterization

2.3.1 Instrumental characterization

Contact Angle (CA) is the measure of degree of hydrophilicity of the surface in contact with water droplet. CA between membrane surface and water droplet was determined by sessile drop method using Optical Contact Angle (OCA) instrument (Make: DataPhysics Instruments GmbH, Germany; Model: OCA15EC). SCA20 Software (provided with OCA instrument) was used to capture the images and extract the profile for contact angle measurement.

Fourier transform infrared spectroscopy (FT-IR, Bruker optics, ALPHA-T, Germany) was carried out in attenuated total reflectance (ATR) mode to compare the modifications done in the virgin material, PVC, especially to know the difference in the peaks corresponding to –OH bond, –Cl bond and –NH bond.

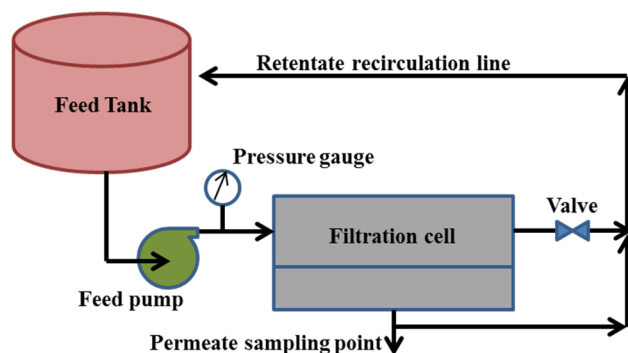To compare the thermal stability, Thermo-Gravimetric

Fig. 2 Block diagram of cross-flow membrane filtration set-up

Analysis (TGA) was carried out for both the membrane types using Thermal analyzer (Perkin Elmer, Pyris-1, TGA, U.S.A.). Temperature was increased from 45°C to 700°C at the rate of 10°C per minute.

The surface and cross-sectional morphologies were analyzed under Field emission gun—scanning electron microscope (FEG-SEM, Model JSM-7600F, U.S.A.). Sample preparation was done by dipping in liquid nitrogen and breaking the sample, followed by gold coating.

2.3.2 Filtration characterization

To study the performance of the prepared membranes, membrane filtration cell in continuous cross-flow configuration is used. Cross-flow filtration set-up was purchased from M/s. Paras Engineering Works, Bhavnagar, India, and was equipped with reciprocating feed pump (Diaphragm type, Model: mROY B-13) and stainless steel membrane cell of effective membrane area 19.6 cm^2. The schematic block diagram of membrane filtration set-up is shown in Fig. 2. Flow rate and pressure were kept constant at 32 L/h and 2.5 kg/cm^2, respectively, during the experiment. A 100 mg/L aqueous solution of humic acid was used to study the anti-fouling performance. Pure water flux was calculated using the formula:

$$J_w = \{\frac{V}{t} \times 60 \div 24\} \times 12.229 \qquad (1)$$

where J_w is the pure water flux (L/m^{2}h), V is the volume (mL) of permeate collected in time t (min). Note that the value 12.229 is the multiplication factor to convert feed flow rate in (mL/h) to flux in (L/m^{2}day) to take into account the effective membrane area (19.6 cm^2).

The concentrations of feed and permeate at the end of each cycle of anti-fouling performance test were determined by analyzing the sample with UV-vis spectrophotometer (DR-6000, Hach, U.S.A.) by getting absorbance at 254 nm wavelength, corresponding to humic acid. It must be noted that the accuracy of measurement of concentration corresponding to the absorbance of feed and permeate samples was up to three decimal places. All the feed and permeate samples were analyzed at least five times, and the average value of concentration was taken for further calculation. Rejection for each experiment was calculated using the formula:

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (2)$$

where C_p and C_f are concentrations of permeate and feed.

3. Results and discussion

Cross-linking reaction between PVC and EA at 60-70°C for 6-8 hours has caused the color of casting solution to change from transparent to yellowish as observed in Fig. 3. The change in color may be considered as the proof of occurrence of reaction, the possible elimination of HCl molecules as reported in the literature (Singh *et al*. 2010). For more insight into the chemical modification, membrane characterization is carried out as discussed in the sub-sections.

3.1 Characterization – Contact Angle measurement, FTIR, TGA, SEM

Contact Angle measurement is one of preliminary analyses to characterize the membrane modification for anti-fouling purpose.

As explained earlier, the degree of anti-fouling depends on thehydrophilicity of the membrane, and CA between membrane surface and water droplet is the measure of hydrophilicity of the membrane surface. The more the spreading of water (i.e. wetting), lesser the contact and more hydrophilic is the surface, and vice-versa. Here, to impart hydrophilic characteristics, hydrophobic PVC is modified. Contact Angle measurement was done using Optical Contact Angle instrument manufactured by DataPhysics Instruments GmbH, Germany. Sessile drop method was used in which a water droplet created by a syringe-needle was received on to the membrane surface and the image was captured as shown in Fig. 4. The drop image shows that CA for PVC was 82.8° while that for CM-PVC was 73.9°, which indicates that hydrophilic modification of PVC has occurred on reaction with EA.

FT-IR analysis of PVC, CM-PVC as well as SM-PVC was done for comparative study. The results shown in Fig. 5, shows that the appearance of broad peak between 3400 cm^{-1} and 3800 cm^{-1} has more absorbance (or less transmittance) for CM-PVC and SM-PVC compared to PVC, which corresponds to the –OH stretching. This denotes the presence of oxygen in the CM-PVC and SM-PVC membrane samples, which is not seen in case of PVC sample. The strong peaks near 2900 cm^{-1} corresponding to –CH stretching, occurs in all the three samples. However, it can be seen that CM-PVC has reduced peak near 2900 cm^{-1} as compared to PVC and SM-PVC, which may be due to replacement of H of –CH bond by amine or hydroxyl groups owing to the reaction with EA. Similar conclusion can be drawn from the –C-Cl stretching peaks lying between 500 and 700 cm^{-1}. Less absorption in this range is found for CM-PVC as compared to PVC and SM-PVC, which indicates the replacement of chloride group during the reaction.
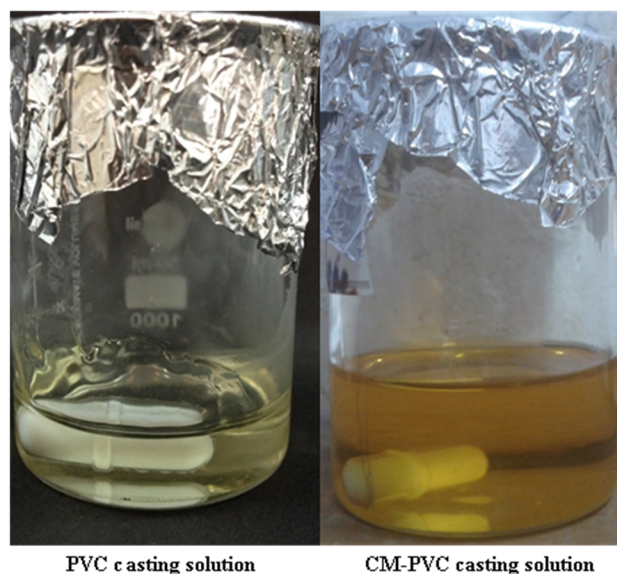

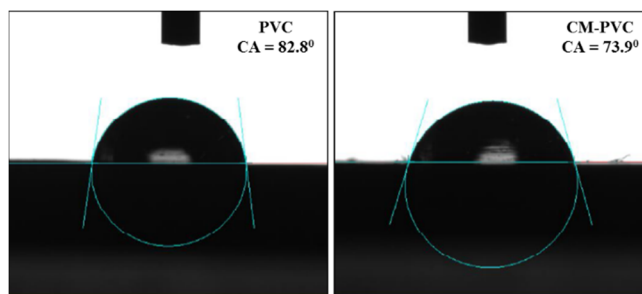Fig. 3 Photographic images of casting solution of PVC and CM-PVC

Fig. 4 Static Contact Angle between water droplet and membrane surface (left: PVC, right: CM-PVC)

Thermo-gravimetric analysis (TGA) of PVC and CM-PVC was done to compare the effect of reaction on thermal stability. The weight percent was measured as a function of temperature by increasing the temperature at the rate of 10°C/min from 45°C to 700°C. Figure 6 shows the TGA curves of PVC and CM-PVC membranes. On comparing the curves, it can be seen that there is no significant effect on the thermal stability when PVC is reacted with EA, the result is similar to that observed elsewhere (Singh *et al*. 2010).

Thermal analysis is important from the point of view of application in industrial effluent treatment plants (ETP), where feed comes at higher temperatures. From Figure 6, it can be observed that loss in mass has occurred at temperature close to 200°C, more for modified membrane as compared to neat membrane; however, our operating condition of filtration is rarely above 100°C, so apparently there is no issue of thermal deterioration.

Surface morphologies of PVC and CM-PVC membrane samples were taken using FEG-SEM at a resolution of 100,000X and cross-sectional images were taken at a resolution of 500X. Figure 7 shows the top surface as well as cross-sectional SEM images of PVC and CM-PVC membranes. The porous finger-like structures can be seen clearly in the cross-section image; visibly, CM-PVC sample has more open porous structure compared to PVC sample.
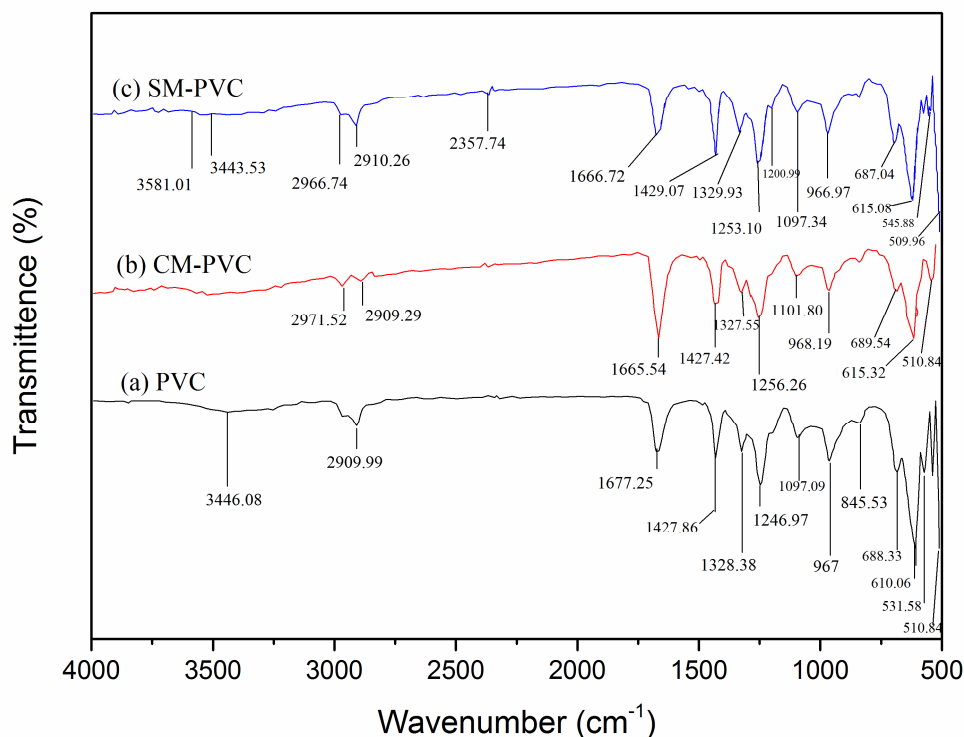
Fig. 5 FT-IR Transmittance versus wavenumber spectra: (a) PVC, (b) CM-PVC and (c) SM-PVC membrane samples
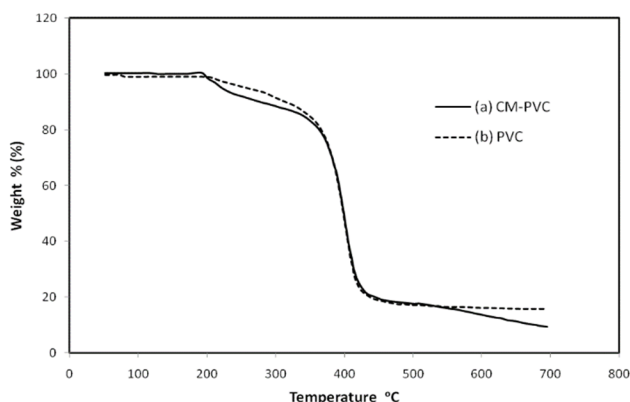

Fig. 6 TGA curves of PVC and CM-PVC membrane samples

Table 1 Standard deviation values for the set of two repeated experiments

Membrane label	For PWP, L m^{-2} h^{-1}	For Rejection, %
PVC	1.3784	0.0003
CM-PVC	1.0954	0.0000
SM-PVC	1.7052	0.0006

Also, it is visible in the cross-section image that top surface (i.e. opposite to membrane support region) of PVC has broader dense layer than that of CM-PVC, which is responsible for resistance to permeate flux. Moreover, it was observed from the filtration experiments that pure water permeate flux of the CM-PVC membrane was higher than PVC membrane, which is in agreement with the SEM images obtained here. The comparison of filtration is discussed in the next section.

3.2. Filtration experiments

Cross-flow filtration set-up was used for ultrafiltration of aqueous feed solution containing 100 mg/L of humic acid as a model feed solution. The term "ultrafiltration" used in the present context is justified in this section. The flow rate and operating pressure were kept constant throughout the experiment at 32 L/h and 2.5 kg/cm^2, respectively. Firstly, the pure water flux was determined. The procedure involves circulation of DI water for 15 min, compaction of membrane at 4 kg/cm^2 pressure, and then, applying the pressure of 2.5 kg/cm^2 to collect the water on the permeate side. The volume of permeate collected was measured at an interval of 15 min using Eq. (1). The calculated values of purewater flux for different membranes whencompared with those found in various literature (Fan *et al.* 2014, Su *et al.* 2015, Peng and Sui 2006) at comparable operating conditions, helped to infer that the membrane prepared lies in the UF range. The next objective is to find the rejection of humic acid, and the procedure involves circulation of feed solution for 30 min and then, filtration by applying 2.5 kg/cm^2 pressure. The volume of permeate collected was measured at an interval of 15 min for almost 1 h. The permeate samples were collected for the rejection analysis.

The concentration of humic acid in feed and permeate corresponding to absorbance at UV$_{254}$ were measured from the calibrated curve. Each sample was taken twice during filtration at an interval of 30 min for the spectroscopy analyses for calculating the average values for the repeated experiments. The percentage rejections were calculated according to the Eq. (2).

Pure water flux for PVC membrane was found to be less by half the magnitude of flux for CM-PVC but was more
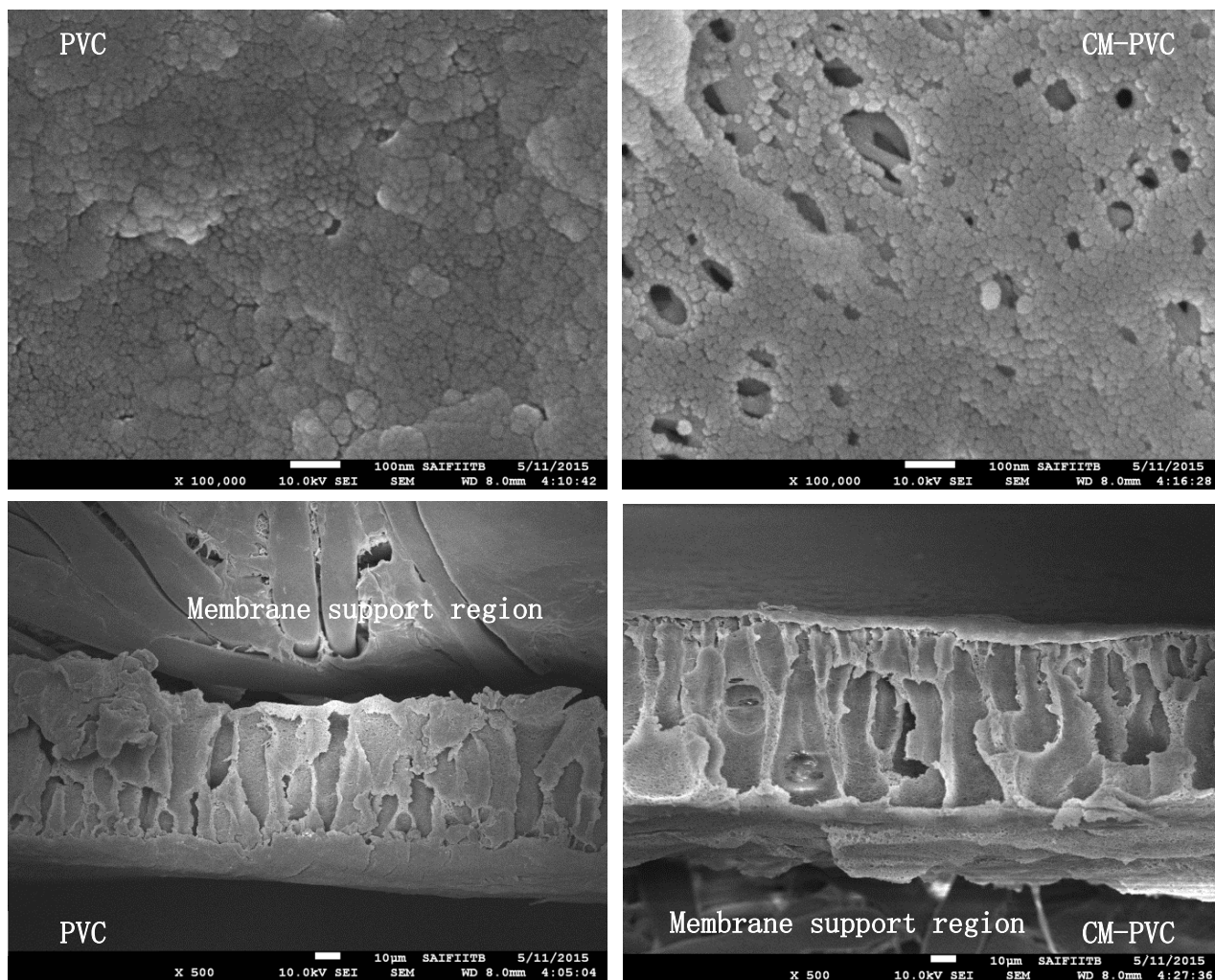
Fig. 7 SEM images of PVC (left) and CM-PVC (right) - top surface (top) & cross-section (bottom)

than SM-PVC that was externally cross-linked by EA. Thus, it can be concluded that internal cross-linking of PVC by EA (as in case of CM-PVC) has improved the flux while external surface cross-linking of PVC membrane (as in case of SM-PVC) has caused the reduction in flux, which might be due to the formation of dense and less porous layer on the surface. Also, it can be observed that CM-PVC gave 100% rejection while rejection for SM-PVC was slightly less than 100% and that for PVC was slightly less than 99%. Figure 8 shows the comparison of pure water flux and solute rejection of PVC, CM-PVC and SM-PVC. Standard deviation of rejection and flux values are tabulated in Table 1.

Figure 9 shows the permeate flux of three membranes as a function of time obtained during the filtration of 100 mg/L humic acid solution. Figure 10 shows the permeate flux obtained during water filtration and aqueous feed filtration as a function of time. The red-colored points indicates the permeate flux obtained during feed cycles while black-colored points are for water permeate flux. It can be seen in Figure 10 that pure water flux as well as permeation of aqueous feed solution is in the order: CM-PVC > PVC > SM-PVC.

It was reported elsewhere (Singh *et al*. 2010) that water
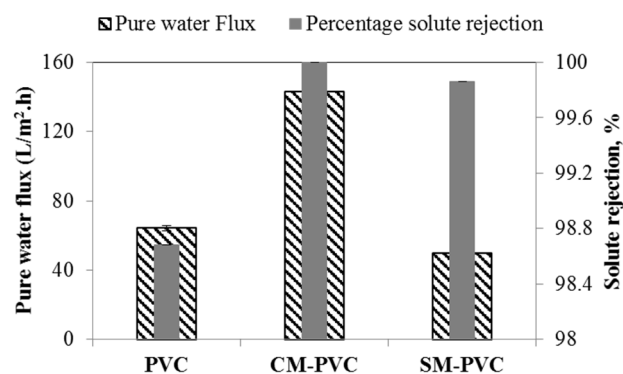

Fig. 8 Comparison of pure water flux and humic acid solute rejection with PVC, CM-PVC and SM-PVC

swelling capacity of PVC cross-linked by EA is more than PVC. Thus, the affinity of CM-PVC for water might be responsible for exceedingly higher flux. Low water flux of PVC is the result of small pores, however, the interaction between humic acid molecules and PVC is responsible for the transfer of solutes while preventing the blockage of pores, leading to decrease in rejection and maintaining the flux.
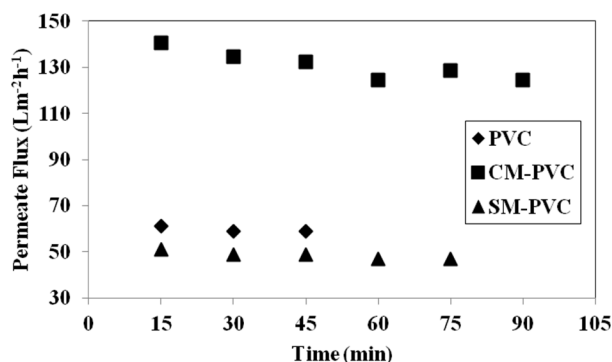
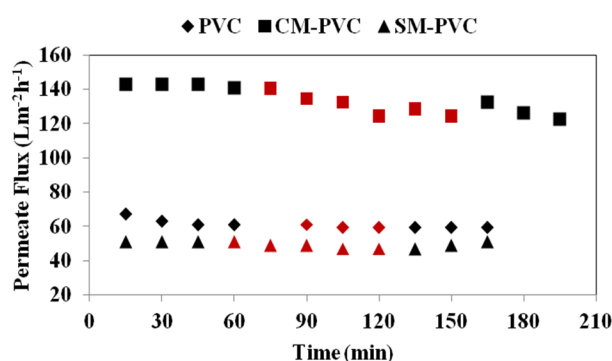Fig. 9 Permeate flux of aqueous feed of humic acid (100 ppm) as a function of time

Fig. 10 Permeate flux of water as well as aqueous feed solution as a function of time (red points - feed flux; black points - water flux)

4. Conclusions

Chemical modification of PVC was done by adding EA into homogeneous casting solution and allowing the reaction to occur at 60°C for 8 h under constant stirring. Surface modified membrane was prepared by dipping PVC membrane in EA and allowing reaction to occur. Following conclusions can be made from the various characterizations and filtration experiments.

• Permeate flux was found to be enhanced by the factor of 2.23 on reaction modification of PVC by internal cross-linking (CM-PVC). While external cross-linking (SM-PVC) has resulted in decrease in flux as compared to neat PVC membrane as the reaction might have caused surface to become dense and less porous. It may be noted that the affinity of CM-PVC for water is responsible for the enhanced flux.

• Cross-sectional SEM shows that thicker top surface of PVC compared to CM-PVC is responsible for more resistance to permeate flux while wider pores in CM-PVC as compared to PVC can be the reason for enhanced permeate flux.

• Rejection of humic acid was near to 100% for all the membranes, but the most efficient was CM-PVC, giving 100% rejection as analyzed by UV-vis spectrophotometer and calculated by formulae. SM-PVC rejected above 99% of humic acid and PVC rejected above 98%.

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