

Sustainable process for the preparation of potassium sulfate by electro dialysis and its concentration and purification by nanofiltration process

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Preparation of the PE-PSt and PE/P4-MS inter-polymer film

The PE/PSt and PE/P4-MS inter-polymer films are prepared by two steps processes. First one is the preparation of PE/PSt and PE/P4-MS inter-polymer pellets and the second step is the blow film extrusion of these pellets in an extruder to respective films. The inter-polymer is prepared by free radical polymerization of Styrene (St)/4-methyl styrene (4-MS), divinyl benzene (DVB) and benzoyl peroxide (BPO) in presence of xylene as solvent at temperature 90 °C, by melt-process method. The PE (mixture of high density polyethylene and linear low density polyethylene (80:20 w/w for PE/PSt interpolymer preparation and 90:10 w/w for PE/P4-MS interpolymer preparation) was added into the reactor under stirring condition along with the slow addition of xylene (500 mL). Once the PE is observed to be melted in the reactor forming homogeneous dough, the additional ~1.5 L xylene was added. The monomer mixture (St/4-MS + DVB + BPO) was added into the molten mixture of PE. 1wt% DVB and BPO with respect to monomer (St/4-MS) was used. After the addition, polymerization was carried out for 3 h at ~90 °C. At the end of the reaction, the reactor temperature was increased to 140 °C and the interpolymer strands was extruded and pelletized with the help of pelletizer. The pellets were thoroughly washed with methanol to remove unreacted monomer and dried in oven at 70 °C for 72 h. The inter-polymer composition in terms of PSt/P4-MS loading is determined by gravimetric method. For the production of the inter-polymer film, a blow-film extruder was used. The extrusion was carried out at 220 °C. Final thickness of inter-polymer film was 150 µm.

Preparation of PE/PSt interpolymer based CEM (CEM_{Inter})

The PE/PSt Interpolymer film of thickness 0.15 mm was treated with 85:10 (v/v) dichloroethane (EDC) and chlorosulfonic acid mixture for 3.5 h at room temperature. the film was washed with water, methanol and stored in 0.1 M NaCl solution.

Preparation of PE/P4-MS interpolymer based AEM (AEM_{Inter})

The PE/P4-MS Interpolymer film of thickness 0.15 mm was kept with 20% dichloroethane (EDC). Next 5 times N-bromo succinimide (NBS) was added in the solution. 1wt% benzoyl peroxide with respect to NBS was added. The solution was refluxed for 48 h. After that the film was kept in 30% trimethyl amine solution for 24 h. Next the film was thoroughly washed with water to remove traces of amine and stored in 0.1 M NaCl solution. The whole process for the preparation of CEM_{Inter} and AEM_{Inter} has been presented in Fig. S1.

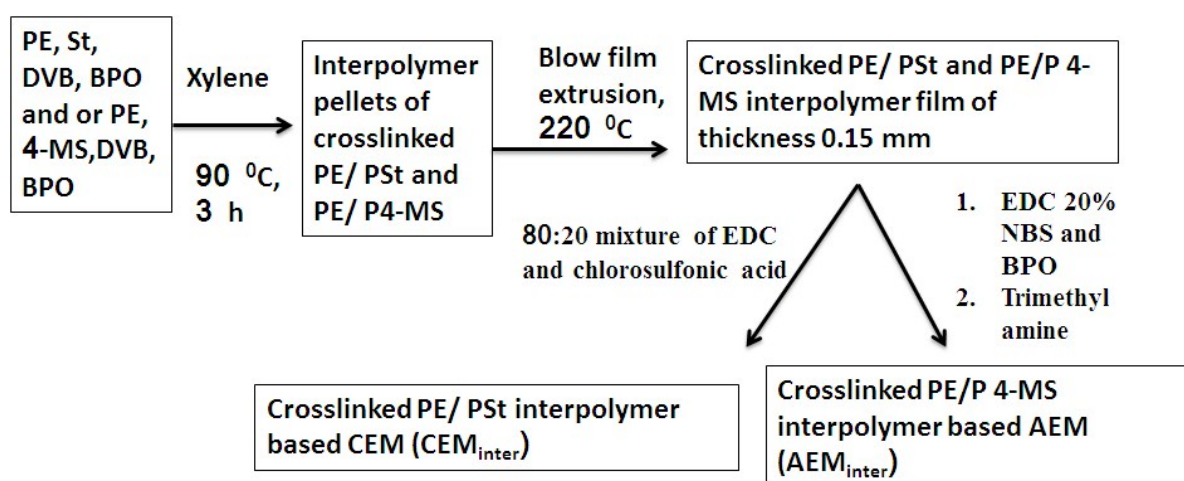


Fig S1: Flow chart for the preparation of CEM_{Inter} and AEM_{Inter} .

Characterization of Ion-Exchange Membranes.

FT-IR spectra of CEM_{Inter} and AEM_{Inter}

FT-IR spectra of the CEM_{Inter} , AEM_{Inter} were recorded in a Perkin Elmer FT-IR Instrument at room temperature. Before analysis the pellets were made by mixing samples with KBr. Fig. S2 shows the FT-IR spectra of CEM_{Inter} and AEM_{Inter} respectively. In the spectrum of CEM_{Inter} the absorption bands appeared at 3406 cm^{-1} and 2964 cm^{-1} to due isstretching vibrations of OH of SO_3H , C-H bonds due to aromatic protons of $PStSO_3H$ part. The bands appeared at $1244\text{--}1177\text{ cm}^{-1}$ and 1043 cm^{-1} were assigned to the stretching vibrations for S=O and O=S=O, respectively. In the spectrum of AEM_{Inter} absorption bands appeared at 1642 cm^{-1} and 1458 cm^{-1} to due isaromatic ring stretching vibration. The absorption band appeared at 3385 cm^{-1} was due to quaternary ammonium moiety.

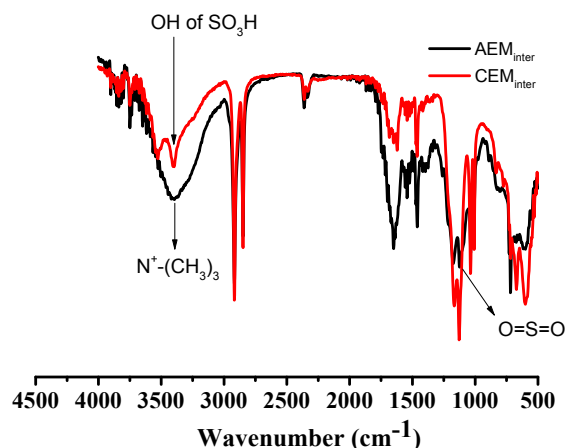


Fig S2: FT-IR spectra of CEM_{Inter} and AEM_{Inter}.

Physicochemical and electrochemical properties of different membranes:

The physicochemical properties such as water uptake (%), the electrochemical properties such as ion-exchange capacity (IEC), ionic conductivity (K^m), transport number (t) of all the membranes used in this work has been measured.

For the determination of water uptake (%), known weight of dry membrane samples (m_d) previously kept in a vacuum oven at 60 °C for 48 h were immersed in distilled water for 24 h at 30 °C to ensure equilibrium water uptake by the membrane and weight (m_w) was recorded after the removal of surface water by blotting paper. The swelling of membranes in water was determined by the following equation:

$$S (\%) = \frac{(m_w - m_d)}{m_d} \times 100 \quad (1)$$

Averages of at least four were taken.

The IEC, defined as the ratio between number of exchangeable ionic groups (equivalents) and the weight of dry membrane, was determined by the classical titration method. For example known weight of dry of membrane pieces were thoroughly washed with double distilled water and equilibrated in 50 mL of 0.10 M KNO₃ solution for 24 h. Equilibrated solution was titrated against 0.10 M silver nitrate solution using di-iododimethyl fluorescein solution in ethanol as indicator. The end point was detected by visualizing the colour change from orange to blue. At least three cycles of ion exchanging and regeneration was used to obtain steady value. Averages of 4-5 were recorded.

The ionic conductivity of the membranes (K^m) were determined in a manually set up clip-on cell, composed of two black graphite electrodes fixed on acrylic plates. The active area of electrodes as well as of the membrane was 1.0 cm². Before determination of ionic resistance and conductivity, membranes were equilibrated with NaCl solutions (400 to 4000

mg/L) for 24 h. During the experiments, the wet membrane was tightly sandwiched between the electrodes and secured in place by means of set of screws. The membrane resistance (R^m) was measured with the help of digital conductivity meter (Model CC 601, Century, India) at ambient temperature. The thickness of the membrane was measured by a digital calibre, and membrane conductivity (K^m) was estimated by the following equation:

$$K^m = \Delta x / AR^m \quad (2)$$

where Δx is the thickness of the wet membrane and A is the effective membrane area.

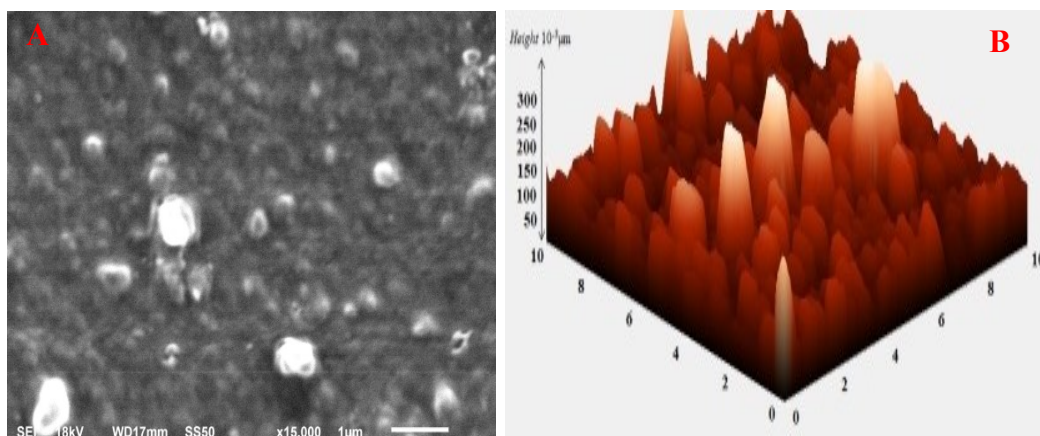
For the determination of transport number (t^+ or t^-) of the membranes used for this work, membrane sample of 9.0 cm^2 effective area was separated by electrolyte solutions (NaCl) of concentration 0.1 mol dm^{-3} and 0.01 mol dm^{-3} respectively in a acrylic made cell. The potential difference across the membrane was measured using a multimeter (MECO, 81K-TRMS) which was connected to calomel reference electrodes. The transport number, t was calculated by the following equation

$$E_m = \frac{RT(2t-1)}{F} \ln \frac{C_1}{C_2} \quad (3)$$

where R is the gas constant, F is the Faraday constant, T is the absolute temperature ($298 \text{ }^\circ\text{K}$), C_1 and C_2 are the concentration of electrolyte solutions in the testing cell. Same procedure was followed for the measurement of transport number using KCl, K_2SO_4 and Na_2SO_4 as electrolyte.

SEM, AFM and ATR-IR analyses of polypiperazine based thin film composite nanofiltration membrane:

Fig S3 shows the SEM (A), AFM (B) and ATR-IR spectra of polypiperazine based TFC NF membrane used in the present study.



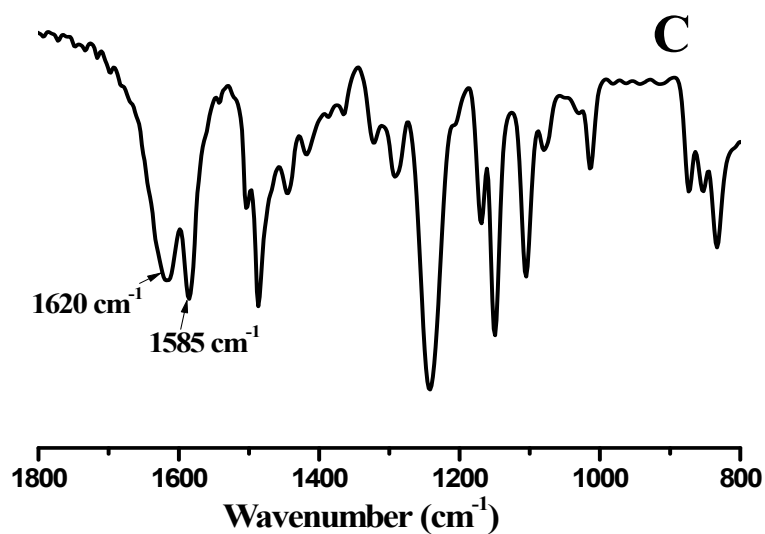


Fig S3: SEM (image A) image, AFM (image B) image and ATR-IR (spectrum C) of poly(PIP) membrane prepared by interfacial polymerization between PIP (2%, w/v in water) and TMC (0.125%, w/v in hexane) on top of PSf support membrane.

XRD pattern of commercial grade Na₂SO₄ and NaCl:

XRD pattern of commercial grade Na₂SO₄ and NaCl powder has been determined and presented in Fig S4.

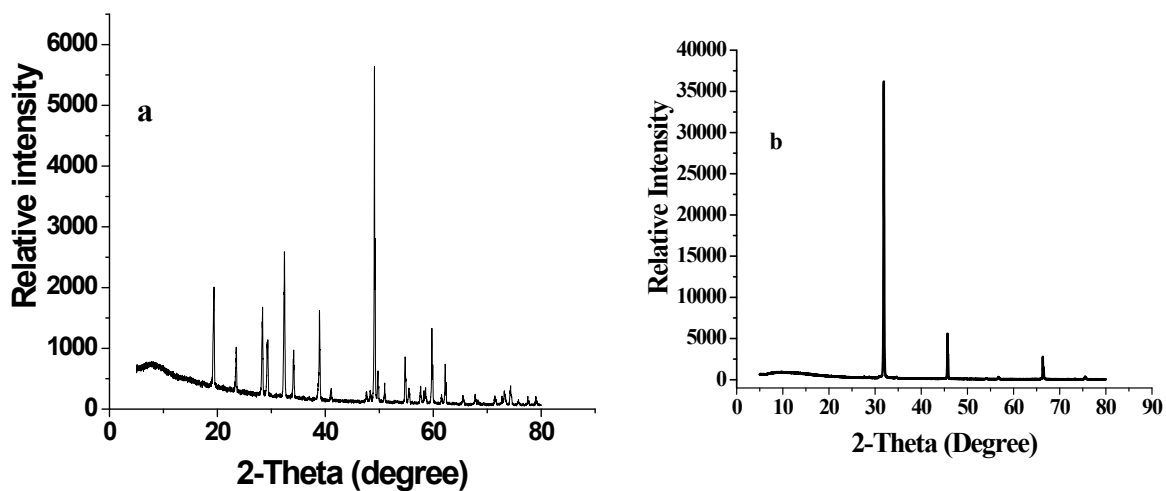


Fig S4: XRD pattern of commercial grade (a) Na₂SO₄ and (b) NaCl crystal.