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New polypropylene supported chitosan NF-membrane for desalination application

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ABSTRACT

In the present study, a new NF membrane was prepared by coating chitosan on polypropylene fiber support, by the dissolution of chitosan in 2% acetic acid solution. The resulting membrane was characterized by thermo gravimetric analysis, water absorption, contact angle measurement and scanning electron microscopy. Prepared membrane showed two Tg peaks, one at ~90 °C that was due to chitosan and the other peak at ~170 °C that was corresponding to the supporting polypropylene membrane. The membrane showed a low swelling ratio at pH 7, 9, and 11 as compared with pH 5. The performance of the membrane was assessed out using dead end cell. Water flux was studied at different pressures. The salt rejection study was done using NaCl solution and the effect of pH on performance of the membrane was also examined. Newly prepared membrane showed improved water flux, and % of rejection is highest in acidic pH and lowest in basic pH. Hydrulic permeability coefficient and the dielectric constant confirms that the prepared membrane is nanofiltration membrane.

1. Introduction

Chitosan is a significant biomaterial that has been known from a long time. It is a polysaccharide mainly composed of the b(1–4)-2-amino-2-deoxy-D-lucopyranose (D-glucosamine) repeating unit and includes a small amount (< 20%) of N-acetyl-D-glucosamine (GlcNAc) residues. The material is natural and environmentally safe. Its applications are being found in the fields of health care, food, beverages, cosmetics, toiletries, agriculture, waste and water treatment, product separation, recovery and immobilization and also for cell culture. Membranes prepared from chitosan have been developed for solution filtering, which can improve the qualities of feed solution. Chitosan membranes are being used in separation techniques such as ultrafiltration and reverse osmosis [1,2]. The membrane process is governed by a size exclusion mechanism, solute-solute and solute-membrane interactions that are dependent on membrane surface characteristics such as hydrophilic/hydrophobic balance, electrostatic charges on both membranes, and on the solute [2,3]. Chitosan in the acidic pH range is positively charged due to protonation of $-NH_2$ groups [4]. However the protonation leads to the dissolution of the material in the organic acid at low pH. In ammonia atmosphere, de-protonation of the polymeric chain occurs. Chitosan causes the fine sediment particles to bind together and is subsequently removed with the sediment during sand filtration. Chitosan also removes phosphorus, heavy minerals, and oil from the water. It is an important additive in the filtration process. Sand filtration apparently can remove up to 50 % of the turbidity alone, while the chitosan with sand filtration removes up to 99% turbidity.

Previous researchers [5] have discovered that the lower hydrophilic property of chitosan often leads to problems in performance such as mechanical strength. To further enhance the performance of chitosan membranes, chondroitin sulfate (CS) was utilized to modify the chitosan membranes for preparing composite membranes with better hydrophilicity and biological compatibility [5]. Chemical modification of chitosan is not a easier process because of its insoluble nature in most of the solvents. In membrane technology, membranes with high tolerance to mechanical strain are very desirable. Chitosan membrane with suitable support is much preferred in membrane technology for the filtration applications, instead of chitosan membrane alone due to its high tolerance to mechanical stress.

These findings have prompted us to study more about preparation and properties of polypropylene supported chitosan membrane for better water desalination. We studied the effect of feed solution pH on the performance of membrane. Contact angle measurement, water uptake study (to have an idea about the hydrophilicity of the membrane), morphology, water flux and dielectric characterization of the membrane are discussed.

2. Experimental

2.1. Membrane preparation

Chitosan (degree of Deacytylation75%) from Sigma Aldrich ($M_w = 20000$ Da) and polypropylene support were used for the membrane preparation. Polypropyle support was Cranemat KC, which

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was a gift sample from Dr. Michael Guiver. Membrane was prepared using TIPS (Temperature Induced Phase Separation Technique). Chitosan solution was prepared by dissolving chitosan flakes into 2 wt.% aqueous acetic acid solution at room temperature. After filtering the resultant solution through G3 sand filter, chitosan solution was spread on the surface of the polypropylene support and allowed to dry at 80 °C for 48 h. After drying, the membrane was dipped in 4% of the NaOH solution to neutralize the acetic acid present in the membrane for one hour and then membrane was washed with distilled water until pH of the washed water reaches 7. Membrane was dried in room temperature for 48 h. Before characterization of the membrane, it was immersed in distilled water for 1 h.

2.2. Characterization of the membrane

2.2.1. Morphology study of the membrane

Scanning electron micrographs of membrane were recorded using a Jeol JSM-6380LA scanning electron microscope. Membrane samples dipped and broken in liquid nitrogen before the SEM analysis. Surface was coated with gold by a sputter coating machine.

2.2.2. Thermal properties of the membrane

Differential scanning calorimetry was used to measure glass transition temperatures (Tg). Differential scanning calorimeter thermograms of supported membrane was recorded on a Perkin Elmer Pyris 1 instrument at a heating rate of 10 °C min^{-1}. Scans were carried out from 30 °C to 300 °C in the absence of atmospheric oxygen.

2.2.3. Water swelling and contact angle measurement

To determine the pH-dependent swelling properties of the membranes, pre-weighed 1 cm^2 of dry samples were immersed in buffer solutions with pH values of 5, 7, 9, and 11. After 24 h, swollen membrane was taken out, excess of the water was removed from the surface using blotting paper. After which membrane was weighed. The following equation was used to determine the swelling ratio.

$$\%swelling = \left(\frac{w_w - w_d}{w_d}\right)x100$$

where W_w and W_d are the sample weights after swelling for 24 h and dry state, respectively. In each specimen, five samples were tested and average was reported.

The contact angle between water and the membrane surface was measured with a FTA-200 Dynamic contact angle analyzer according to the sessile droplet method. Contact angle was measured five times at different locations of membrane and an average value was calculated.

2.2.4. Performance study of membrane

To test the rejection properties of the prepared supporting membrane, NaCl solution was employed as inorganic electrolyte. The concentration of inorganic electrolyte was determined conductometrically.

All the permeation experiments were performed at room temperature using self constructed dead end desalination cell [6]. A circular membrane sample with diameter of 60 mm was placed in the test cell with the chitosan surface facing towards incoming feed. Effective membrane diameter was 50 mm. The flux was measured by direct measurement of the permeate flow in terms of liter per meter square per hour (L m^{-2} h^{-1}). The percent salt rejections were determined by comparing the conductivity of feed and permeate solutions. These samples were analyzed for their salt concentration by conductivity measurement. From the results, the percent retention was calculated using

$$\%R = \left(1 - \frac{C_p}{C_f}\right)x100$$

where C_p is the salt concentration in permeate and C_f is the concentration in the feed. NaCl solution (3500 ppm) was used as the feed. The effect of pressure on flux and percent rejection was

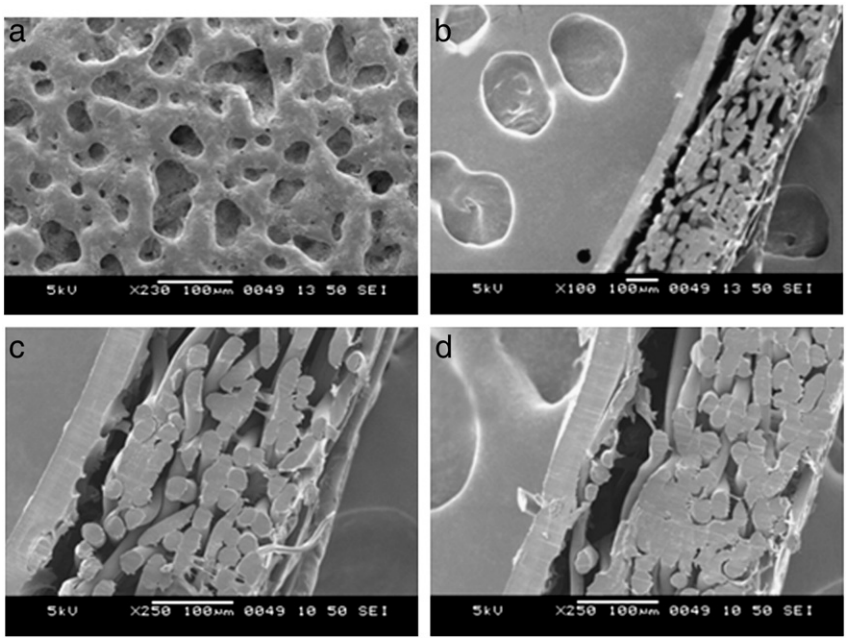

Fig. 1. a. SEM image of the membrane surface of the membrane. b. SEM image cross section of the membrane. c. SEM image cross section of the membrane. d. SEM image cross section of the membrane.

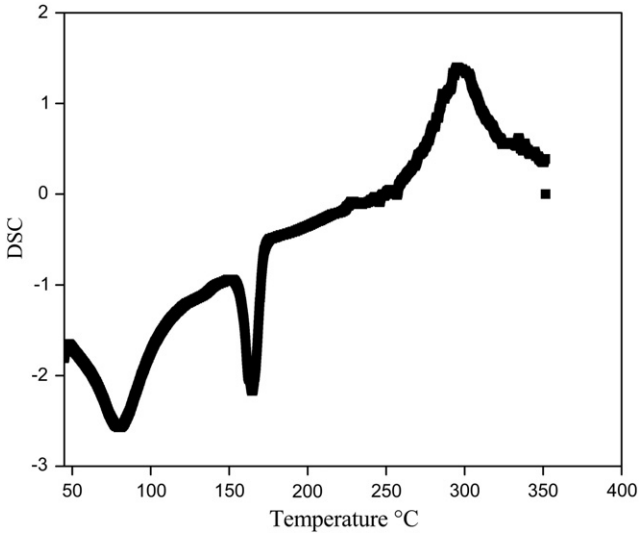

Fig 2. DSC of the membrane.

studied. Performance experiments were carried out using varying pH (5, 7, 9 and 11) of feed sample to study the effect of pH on membrane performance. The pH was adjusted using buffer.

Dielectric constant of the membrane was determined by Precision LRC meter Agilent 4258A with 16451b dielectric test fixture at various frequencies 75 kHz to 30 MHz with 1 MHz steps.

3. Results and discussion

3.1. Morphology of the membrane

Scanning electron micrographs of the typical supported membrane are presented in Fig. 1. It is obvious from the pictures that chitosan thin layer was properly cast on the top of the polypropylene substrate. Fig. 1(a) shows the morphology of membrane prepared by phase inversion technique. Polypropylene substrate shows the microfibers (Fig. 1b,c and d). Chitosan layer thickness was approximately 10 μm from SEM image of Fig. 1(c). Fig. 1a represents the surface of the membrane. As we cast chitosan solution on to polypropylene support membrane, it did not penetrate into voids of support membrane but settled on the surface and thereby forms two separate layers, which is clear from SEM pictures.

3.2. Thermal analysis of the membrane

Fig. 2 represents the DSC curve for chitosan support membrane. It showed two separate Tg values, one ~90 °C is due to chitosan and the other peak at around 170 °C is corresponding to the supporting polypropylene membrane. As there is presence of two different Tg values, it clearly indicates that, two polymers were not blended with each other instead they just stick to one another without any molecular bonding and maintain their individual identity. This is also evident from the SEM image of the membrane.

Table 1
% water uptake, % rejection and flux of the membrane at different pH.

pH	% Water uptake	Flux(L/m^{2}h)	% Rejection
5	88	43.42	44
7	34.67	35	38.42
9	24.36	35	28.5
11	42.00	15	12.63

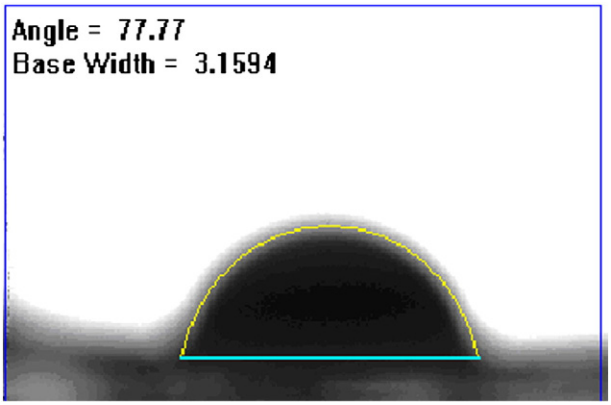

Fig 3. Contact angle measurement of the membrane.

3.3. Water swelling behavior and contact angle measurement

To investigate the swelling behavior with solution having various pH values, the membrane was swollen in buffer solutions of pH values 5, 7, 9, and 11. Membranes were swollen considerably in the selected pH scale. Table 1 shows the pH-dependent swelling behavior of fully swollen membrane. It showed a low swelling ratio at pH 7, 9, and 11 as compared with pH 5. The pH sensitivity of the membrane is from the nature of chitosan itself [7–11]. It exhibits pH-responsive behavior as a weak poly base due to the large quantities of amino groups on its backbone. Acidic media has a pronounced effect on swelling behavior compared to the neutral and basic media. The protonation of the $-NH_2$ group in membranes thus ensures chain relaxation, leading to efficient solvent diffusion. In neutral and basic media, the swelling was mainly driven by solvent diffusion, but the chain relaxation effect due to protonation of amino groups was absent. In addition, the samples with higher porosity had higher extent of swelling, which seemed to preside over the diffusion of solvent in the matrix.

Contact angle is another important parameter for measuring surface hydrophilicity [12,13]. In general, smaller the contact angle higher is the hydrophilicity of the material. Contact angle of the prepared membrane is 77.77° as shown in Fig. 3.

3.4. Performance of the membrane

Water permeability of the membrane was studied using dead end flow cell in different pressure ranging between 200 kPa to 800 kPa. Fig. 4 shows the water permeation results. It is evident from the study that, increase of pressure, increases the water permeation linearly. Water permeability coefficient of the membrane is calculated using the slope and it is found to

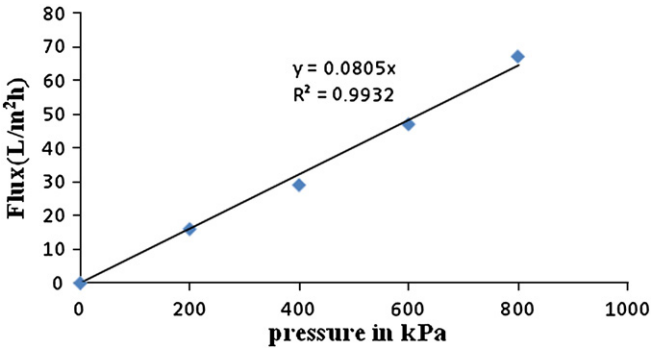

Fig 4. Water flux study of the membrane.

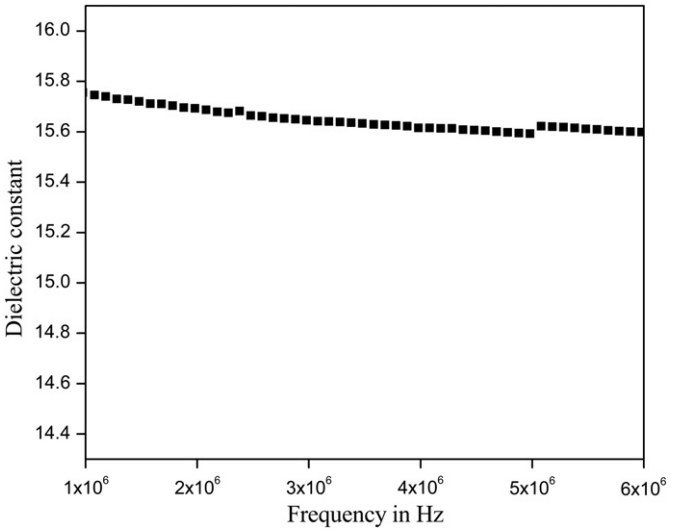

Fig 5. Dielectric constant of the membrane.

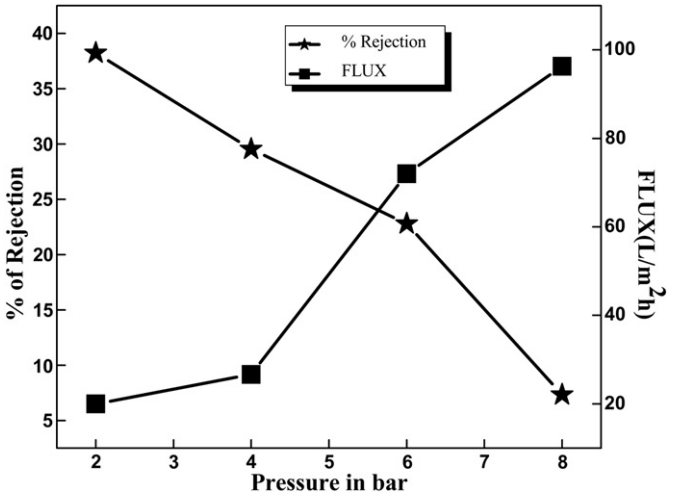

Fig 6. % rejection and flux of NaCl at different Pressure.

be 2.229×10^{-11} m/s Pa. According to the Spiegler–Kedem model [14] the membrane shows the nanonporous nature.

Fig. 5 represents the dielectric spectrum which are independent of the frequencies between 1×10^6–6×10^6 Hz. As discussed in [15], the greatest dielectric constant represented smallest void area of the membrane. This was also verified by the small water flux as shown in Fig. 4, by comparing these values with our recent report chitrakar et al, [16]. Hence the prepared membrane is in nanofiltration range.

Rejection of the NF membrane to inorganic electrolytes is related to the ion valency and size [17]. The transport mechanism and electrolyte rejection of amphoteric NF membrane are, convection (C), diffusion (D) and electron migration (EM) [18]. The charge effect of electrolyte ions is to be considered as a dominant factor for NF of inorganic electrolytes of low concentration [19].

The prepared membrane showed about 40 % salt rejection in lower pressure. Fig. 6 shows performance of the membrane at different pressures. All the experiments were repeated three times and the mean value was reported. Rejection experiments were carried out in different pH as well as at different pressure using 3500 ppm NaCl solution. The rejection study in different pH was carried out at 200 KPa. Table 1 shows percent rejection and flux of the membrane in different pH. Membrane behavior for different pH solutions was studied. At acidic pH, as chitosan is having NH_2 group in its back bone, it will get protonated and the membrane surface will become positively charged and therefore, the surface becomes hydrophilic in nature. So, when we study the salt rejection of the membrane, it is showing the highest rejection at lower pH. This is due to the fact that the presence of positive charge on the membrane surface facilitates for the exchange of cation and thereby shows highest rejection with flux of 43 L/m^{2}h, whereas in basic pH the free NH_2 remains as such and rejection is less. As a matter of fact, the water flux of the membrane increases as we go from basic to acidic pH range. This result also confirms that membrane has positive charge. In acidic pH of 5, membrane showed 45% of salt rejection with the flux of 43 L/m^{2}h, whereas in pH 11, it shows 12% of rejection with the flux of 5 L/m^{2}h.

4. Conclusion

The SEM micrograph pictures, showed two layers which are due to the polypropylene support and chitosan. Thermal study showed two separate Tg values, one ~90 °C due to chitosan and the other peak at around 170 °C is corresponding to the supporting polypropylene membrane. The membrane showed a low swelling ratio at pH 7, 9, and 11 as compared with pH 5. It showed 90 % water swelling in pH 5, whereas contact angle of the prepared membrane is 77.77°. Using Hydraulic permeability coefficient and dielectric constant it is confirmed that the prepared membrane is nanofiltration. The supported chitosan membrane has showed good performance in acidic pH compared to basic and neutral. In acidic media of 5 pH, membrane showed about 40% of salt rejection with the flux of 43 L/m^{2}h. However in pH 11, it showed 12% of rejection with the flux of 5 L/m^{2}h.

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