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Preparation and characterization of highly micro-porous PVDF membranes for desalination of saline water through vacuum membrane distillation

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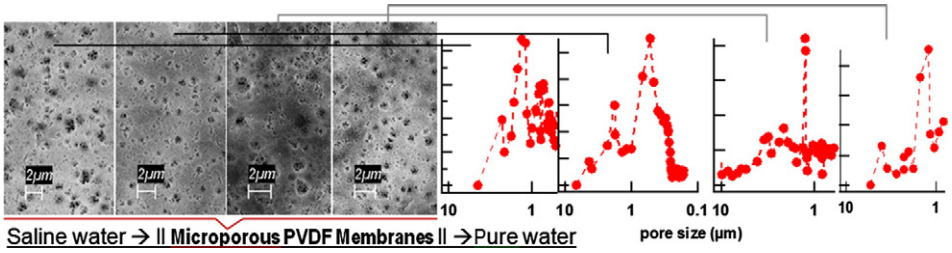
HIGHLIGHTS

- Flat-sheet PVDF membranes supported on polyester non-woven fabric
- Highly porous membrane with average pore size > 1 μm
- A controlled preparation in a continuous mode using motorized machine
- Demonstrated potential for seawater desalination through membrane distillation

GRAPHICAL ABSTRACT



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ABSTRACT

Highly porous PVDF membranes supported on non-woven polyester fabric were prepared by the phase inversion method from the solutions of different concentrations at identical conditions of casting as temperature, relative humidity and air drying time before immersion in non-solvent using motorized machine to study the microstructures formed in the resulting membrane and correlate membrane morphology to membrane performance in membrane distillation process. The membranes were extensively characterized for porosity, hydrophobicity and surface topography. Morphology study indicated an anisotropic nature of the membranes resulting from phase inversion occurred through liquid–liquid demixing process. The membrane prepared from casting solution of low polymer content is highly porous compared to those prepared from solution of higher polymer content. The membranes demonstrated potential for desalination from 30,000 to 100,000 ppm synthetic seawater through membrane distillation. The membranes exhibited 99.0 +% salt rejection efficiency and varied water flux ranging from 2 to 12 $l \cdot m^{-2} \cdot h^{-1}$ (LMH) depending on the membrane pore structure feed concentration and processing parameters. All the membranes exhibited practically uniform performance in all feed concentration ranges which indicated that there is no adverse effect of increased salinity in the feed on the performance of the membrane.

1. Introduction

The global demand for drinking water is increasing day-by-day. Although there is abundance of seawater which is not drinkable, it is imperative to desalinate seawater to make it drinkable. According to the World Watch Institute, more than two-thirds of the world's population may experience water shortages by 2025 [1]. Therefore desalination of saline water has become essential to meet the growing need of potable water. The membrane based reverse osmosis is a well-established desalination process however it is energy intensive and has many operational complexities such as pre and post treatment, and membrane fouling. Membrane distillation is relatively new process and differs from other membrane based desalination processes such as reverse osmosis in respect of nature of the membrane used in the process and driving force for separation which is vapor pressure gradient across the membrane rather than positive pressure as in the reverse osmosis. The vapor pressure gradient is created by keeping the feed solution at atmospheric pressure and ambient temperature and cooling/purging/sucking the condensate

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under reduced pressure in the permeate side. In membrane distillation process separation occurs below the normal boiling point of the feed solution. Thus membrane distillation also differs from conventional thermal distillation as membrane distillation could occur at a much lower temperature in comparison to conventional thermal distillation. The membrane distillation is potentially advantageous over conventional distillation processes on account of low energy consumption, simplicity in operation etc. hence it can be explored as an alternative method for the desalination of saline water (seawater/brackish water). Further the phenomenon of concentration polarization and membrane fouling which are very common in reverse osmosis does not encounter in membrane distillation process and ultrapure water can be produced. In general the membrane with low resistant to mass transfer, low thermal conductivity as to prevent heat loss across the membrane, thermally stable and high resistance to chemicals is most suitable for membrane distillation process [2]. Hydrophobic membranes are considered the most ideal for the vacuum membrane distillation process because hydrophobic membranes do not wet easily thus allow only vapors to pass through but not liquid solution which is the prime requisite of the membrane for vacuum membrane distillation process. Polymers such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE) and polyvinylidenefluoride (PVDF) are hydrophobic in nature due to their low surface energy and have excellent chemical resistance and good physical and thermal stability therefore these polymers are suitable for making hydrophobic membranes for membrane distillation and other applications [3]. The hydrophobic membranes are produced by various ways depending on the properties of the polymer. For example, PTFE membranes are prepared by thermal heating and stretching while PP and PE membranes are prepared by thermally induced phase separation (TIPS) and PVDF membranes are prepared preferably through a phase separation achieved by diffusion of non-solvent. The process is commonly known as the non-solvent induced phase separation (NIPS) method. PVDF has been chosen for this study because it is a commercially available, hydrophobic by nature and rubbery polymer having good physical and mechanical properties thus an ideal polymer for making membrane and easily soluble in common organic solvents. The properties of the membrane depend on the bulk properties of polymer and also on the method of membrane preparation including solvent used for the preparation of polymer solution. The morphology of the membrane largely depends on the diffusional exchange between solvent and non-solvent during the phase separation process of membrane preparation [4]. Many authors have investigated the formation of PVDF membrane through the phase inversion method using solvents like *N*,*N*-dimethylacetamide (DMAc), triethyl phosphate (TEP), *N*,*N*-dimethylformamide (DMF), however the preparation conditions in the phase inversion method had been different in each case and had not been discussed elaborately. Flat PVDF membranes with controlled morphology, pore dimensions, mechanical properties and crystal structure were prepared by wet and dry wet phase inversion [4] while the tubular PVDF membranes were prepared by water immersion of a binary PVDF-solvent solution cast on the outer surface of a porous tubular support [5]. This study aims to fabricate highly porous PVDF membranes from PVDF solution of various concentrations in DMF solvent under controlled conditions of temperature, relative humidity, air drying time etc., using in house developed motorized casting machine. The fabricated membranes were tested for desalination of synthetic seawater having varied salt concentration through membrane distillation. The influence of operating conditions such as temperature, vacuum and concentration of feed on the membrane performance was studied.

2. Experimental

2.1. Materials

PDVF homo-polymer trade name SOLEF® 1015/1001, density 1.78 g/cc was obtained from Solvay Advanced Polymer, USA. Polyester fabric Nordyls TS 100 was obtained from Polymer group Inc., France. Dimethylformamide (DMF) solvent and other chemicals were obtained from Qualigen Fine chemicals, India. They were of analytical grade and used without further purification.

2.2. Methods

2.2.1. Preparation of membrane

PVDF membranes were prepared by the non-solvent induced phase separation (NIPS) technique. In this process, degassed homogeneous solution of polymer in an appropriate solvent is spread into a uniform thick layer on a non-woven polyester fabric support using the Dr's blade technique and then immersed in a coagulation bath containing a non-solvent. The exchange of the solvent in polymer solution with the non-solvent from the coagulation bath results in the phase separation wherein polymer precipitates into a very thin layer on the support. For this study, homogeneous solutions having different concentrations of PVDF (16 to 22%, w/w) were prepared by dissolving SOLEF (PVDF) in DMF (solvent) at 70 °C under continuous stirring at fixed speed (400 rpm) with the help of mechanical stirrer for 8–10 h. The solutions were cooled to ambient temperature and evacuated to remove air bubble before casting. The solution was cast on the support under controlled conditions of temperature, relative humidity and speed of casting using in-house developed motorized machine which is shown as Fig. 1.

The polyester fabric of length 10 m and width 0.2 m was mounted in the mounting roll (A) of casting machine. The fabric is then passed through the next roller (B) attached with a microprocessor sensor connected to motor speed control device (I). The fabric then went through the casting blade (D) where the gap between the casting blade and fabric was adjusted by micro-meters fixed on the top of casting blade (C). The casting solution was poured on the top of fabric from a sealed container under the influence of regulated nitrogen gas pressure. The casting chamber was kept under controlled environmental conditions throughout casting process. The humidity of the casting chamber was monitored by humidity meter (H) and kept at about 30% with the help of a dehumidifier (K) connected to the casting chamber. This nascent polymer film casted on the fabric was then passed through a distance of 72 cm in air (E) before immersing in a gelling water bath of 100 l capacity where gelation of the PVDF solution layer takes place by phase inversion process in a continuous mode. The resultant membrane was then rolled on the receiving roller (G), washed with running deionized water stream and finally preserved in deionized water for a period of 48 h for the removal of residual DMF. The properties of asymmetric micro-porous membrane largely depend on the microstructure or morphology of membrane which in turn depends on casting process parameters therefore it is most important to control casting process parameters precisely. As described above, the motorized casting unit has relative humidity, casting speed and thickness controllers to control humidity, casting speed and thickness of polymer layer precisely.

2.2.2. Characterization of membranes

The performance of a membrane depends, by and large, on bulk properties of polymer and membrane morphology. The morphology of membrane depends on the composition of casting solution and conditions of preparation. Therefore characterization of membrane for its morphology, composition and porosity is essential to understand membrane properties and performance.

2.2.2.1. Membrane morphology. The scanning electron microscopy (SEM) is widely used to study the surface microstructures and cross sectional structures of porous materials, such as sorbents, catalysts and membranes. The surface microstructures and transverse sections of the membranes were examined on a scanning electron microscope (LEO, SEM, model 1430VP) at an accelerating voltage from 15 to 20 kVA in back-scattering electron detection mode using dried, fractured (for transverse section) and gold sputtered samples. Atomic force microscopy (AFM) is employed to obtain topographical images