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Poly(vinyl alcohol) incorporated with surfactant based electrospun nanofibrous layer onto polypropylene mat for improved desalination by using membrane distillation

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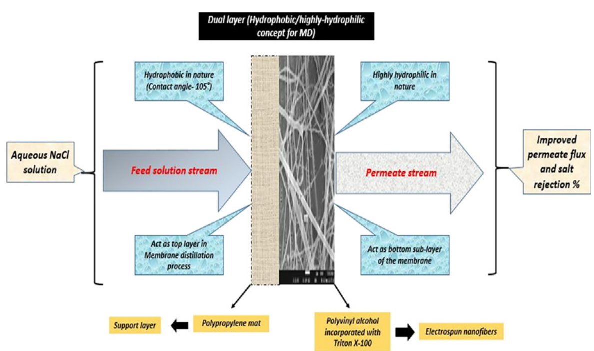
HIGHLIGHTS

- Hydrophobic/highly-hydrophilic dual layer concept utilized for Membrane distillation
- PVA-TX identified as novel nanofibers for surface modification of PP mats
- PP/PVA-TX membrane shows improved rejection % and permeate flux.
- PP/8% PVA-TX membrane shows best result in terms of mechanical and chemical stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel category of improved performance membrane consisting of a hydrophobic mat and a hydrophilic electrospun layer for membrane distillation (MD) application has been presented. The nanofibrous non-woven layer was fabricated by electrospinning of polyvinylalcohol (PVA) incorporated with Triton X-100 directly onto the polypropylene (PP) mat. To render the membrane distillation process effective in terms of high permeate flux and salt rejection %, the concept of dual layer membrane is utilized with hydrophobic PP mat on top and hydrophilic PVA layer on bottom. In this study, PVA nanofibrous layer has been fabricated by incorporating non-ionic surfactant Triton X-100 for uniformity and homogeneity in fiber diameter. Additionally, the PP mat acts as a top support layer and PVA-TX nanofiber acts as base layer which absorb the water molecules (condensed vapour), that enhances the vapour flux across the membrane. The modified bilayer PP/PVA-TX membranes were characterized by the pore size distribution, permeate flux, and rejection %, then compared with original PP mat. The salt rejection of the dual layered PP/PVA-TX membrane showed >99% and still maintained 2 times higher permeate flux compared to PP membrane for long term operation of 15 h.

1. Introduction

With the increase scarcity of water worldwide, there is an increase in water demand in industrial as well as agricultural areas. There are many modern methodologies based on membrane were developed for water

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reclamation and seawater desalination. Reverse osmosis (RO) is well known technology, but it is considerably expensive compared to other processes. However, there are certain aspects which make the application of RO difficult: (1) the limited quantity of water which can be recovered and (2) the environmental impact from the toxic residual after RO treatment. Hence, there is a need of a cheaper and sustainable technology with a high recovery rate for water reuse and reclamation [1].

In near future, membrane distillation emerges out as a prominent technology which may overcome the water scarcity issue. Recently, membrane based technologies are highly utilized for desalination, separation, and purification [2], such as removal of trace volatile organics, heavy metals, as well as water oil separation [3–5]. Typically, reverse osmosis (RO) process is one of the crucial membrane based technologies for desalination, and became an advantageous process for water reuse and reclamation [6]. Nevertheless, many brines (where salt concentration > 3.5%) are not applicable for desalination by utilizing RO process because of the high pressure that must be applied is expensive, in terms of pumping costs, and often lead to membrane scaling and fouling [7,8].

Membrane distillation primarily depends on the temperature differences (feed stream and permeate stream) across the membrane. Therefore, it is essential to mention that in membrane distillation technology, the driving force for diffusive transport is the difference in vapour pressure, that changes exponentially with the temperatures of the feed and permeate streams [9].

The membranes materials commonly utilized in membrane distillation process are made of highly hydrophobic materials, such as polyvinylidene fluoride (PVDF), polypropylene (PP), and polytetrafluoroethylene (PTFE). Typically, these membranes are commercially available casted by utilizing different techniques such as phase inversion, stretching, thermally induced phase separation [10, 11].Currently, electrospinning technique has been widely used to fabricate hydrophobic MD membranes. Electrospinning technique is one of the versatile methodologies for producing nonwoven sheets of nanofibrous material for the purpose of membrane based separation and purification [12]. The nanofibers can be spun into structures having high porosity, small pore size, and high surface area-to-volume ratio which can be further used for membrane distillation process possessing high permeate water flux and salt rejection.

Therefore, in the present research work, PVA solution has been electrospun for producing nanofibrous layer. The reasons of selecting the PVA polymer as an electrospinning solution are as follows: (1) non-toxic in nature (2) biologically compatible (3) highly hydrophilic (4) chemical and thermal stability (5) binding and adhesive in nature [13]. However, in order to fabricate a membrane with uniform fiber diameter, improved quality of fibers with reduced number of beads, Triton X-100 has been found to be ideal choice that was incorporated in PVA solution [14]. Triton X-100 being surfactant in nature, it was utilized in order to lower the surface tension and also influences the homogeneity of electrospun fibers. Typically, when enough surfactant molecules attach to a water molecule, it gets covered in surfactant and forms a unit. These units have a weaker force of attraction because only the non-polar head of the surfactant is exposed thereby lowering the surface tension. By decreasing the surface tension of polymeric solution, fibers could be obtained without beads [15]. Interestingly, Triton X-100 increases the conductivity of the solution which enhances the quality of fiber which apparently reduces the number of beads. Typically, beads are supposed to be defect of fibers. After thorough analysis 1% v/v of Triton X-100 was found to be optimum and finally incorporated in PVA solution. Higher concentration of Triton X-100 (2%, 5% and 10% v/v) directly influences the viscosity of the solution. Moreover, beyond a certain viscosity, the electrospinning jet may breaks up into droplets and no fiber will form. Consequently, this experiment has been executed with lower concentration of Triton X-100 so that there will not be much influence in the viscosity of the polymeric solution. Increasing the conductivity is having another benefit of lowering the critical voltage required to initiate the electrospinning process. Additionally, Triton X-100 being a surfactant improves binder adhesion and stability of the solution. Fig. 1 shows the mechanism how Triton X-100 enhances the quality of PVA nanofibers.

Being a polymer, PVA is inherently hydrophilic in nature, so it is not suitable for the use as an MD membrane in unmodified form. Apparently, it will need a supporting layer which must be hydrophobic in nature. Thus, the surface of the PP mat has been modified for improved flux and rejection % while utilizing in MD process. Fig. 2 indicates the detailed mechanism of the surface modification of PP mat by PVA-TX. Even the figure also reasons out why the hydrophobic PP mat has been kept at feed stream rather than the hydrophilic layer PVA-TX. Previously, composite dual layer MD membranes consisting of a hydrophobic top layer with a hydrophilic sub layer were patented in the 1980s by Cheng and Wiersma, so based on that a hydrophobic/hydrophilic composite membrane has been developed for improved performance in MD process.

In this present study of dual layer concept for membrane distillation, PP mat acts as a support thin top layer facing towards the feed stream consisting of numerous non-uniformly distributed pores whereas PVA-TX acts as bottom layer facing towards the permeate stream consisting of nanochannels. In addition to that, PVA-TX nanofibrous layer has the ability to absorb the water molecules (condensed vapour), which directly enhances the vapour flux across the membrane [16]. In other words, the hydrophilic sub-layer will help to absorb the condensed water molecule from the hydrophobic top layer, thus preventing the pore wetting. Moreover, the combination of hydrophobic/hydrophilic layer provides low resistance to mass flux and it also prevents conductive heat loss. Therefore, the dual layer PP/PVA-TX contributes to improved mass flux. Additionally, it has been well proven that, the higher mass transport in the MD by using the dual layer membrane is due to the shorter pathway needed for the vapour to move between the liquid/vapour interfaces [17–19]. Even, the results also supported that there is an improved permeate flux due to high surface area to pore volume ratio. Interestingly, due to lower pore diameter of the modified membrane, the rejection % was found to be >99%.

A summary of various attempts for membrane surface modification has been discussed along with the objectives (Table 1). Finally, in the present study surface modification of PP mat is compared with other membranes like PVDF, CNT bucky-paper and polyetherimide. In other words, these various attempts indicate the motivation of our present research work where high permeate flux and rejection % were achieved simultaneously.

With the advancements of membrane based technology, current research has focused on improving MD membranes by changing as well as modifying the surface chemistry. Recently, electrospinning technique has been utilized to fabricate nanofiber layers and their uses as MD membranes have been proposed [24,25]. In this present research study, there are certain factors such as considerably high rejection % (>99%) and high permeate flux as because of high surface area to pore volume ratio value also confirms the feasibility of the present surface modified membrane. Thus, certainly these characteristics are well enough to consider PP/PVA-TX as novel category dual layered membrane for MD application. Finally, the performance of modified membrane has been thoroughly analysed. Furthermore, a thermally driven membrane distillation (MD) operation was used for evaluating the permeate flux and salt rejection of 10 g/l NaCl aqueous solution while utilizing the PP/PVA-TX membrane. This research study provides the fundamental basics for developing other novel dual layered membrane for MD application.

2. Materials and methodology

2.1. Starting material

Polyvinylalcohol (PVA) was ordered from Sigma Aldrich with molecular weight of Mn 146,000–186,000 of 99.9% hydrolysed and Triton