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Improvement of PVDF-co-HFP Hollow Fiber Membranes for Direct Contact Membrane Distillation Applications

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Abstract

Objectives: Investigation the influence of PVP added into the dope solution with (0, 5, 7 and 9) wt. % on membrane characteristics, structure and performance for DCMD system. Determine the impact of process operating parameters on the performance of the (PVDF-co-HFP) hollow fibre membrane in DCMD applications such as hot feed temperature. **Methods/ Statistical analysis** Prepared and fabrication a PVDF-co-HFP hollow fibre membrane using a various parentage of PVP (0, 5, 7 and 9 wt. %) as a pore former into the dope solution. Characterisation the structure and morphology of the (PVDF-co-HFP) membrane via FESEM technique. Investigating the performance of the PVDF-co-HFP hollow fiber membrane through a DCMD system. Improvement of PVDF-co-HFP hollow fibers through the adding of PVP molecules into the dope solution was studied. **Finding** The addition of 5, 7, and 9 wt. % PVP into the dope solution resulted in repressed the sponge-like shapes and promoted the forming of two finger-like shapes. Modified the pore area per unit surface area (porosity) and the pore structure of the synthesized hollow fibres. The pore size of the hollow fibre was enhanced with the addition of 9 wt. % PVP into the dope solution. The PVDF-co-HFP fibres permeate flux with PVP additives was superior to that neat PVDF-co-HFP by about 75% at feed temperature (T_f) of 70 °C. The rejected salt factor for all PVDF-co-HFP hollow fibres was over 99.98%. The increase of hot feed temperature led to increased permeation flux for the DCMD process. **Application/ Improvements:** Outcomes give a good indication for the improvement of PVDF-co-HFP hollow fiber via adding the PVP particles onto the dope solution. It can be concluded that the PVDF-co-HFP hollow fiber appropriate for use in DCMD application for seawater desalination.

Keywords: Hollow Fiber, DCMD, Permeate Flux, PVDF-co-HFP, PVP Additives

1. Introduction

Membrane Distillation (MD) is a new technique which is able to produce high purity water utilizing hydrophobic fibers. Driving force for the MD can be achieved via the variance in vapor pressure which occurs due to difference in temperature across the fibers or by using a vacuum in the cold permeate stream[1,2]. It is recommended to use the DCMD configuration when the essential feed stream is water such as seawater desalination and solutions concentration in the food industries. Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) showed to be a highly promising polymer for fiber synthesizing which uses for diverse membrane applications. Due to the higher hydrophobicity, high solubility, low relative glass temperature and because of an amorphous phase of fluoro propylene (HFP) into the PVDF matrix a high free volume will be achieved[3].

A few studies have tested the impact of the addition of PVP upon the performance of PVDF-co-HFP hollow

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fiber membranes for MD water purification operations. Distilled water flux can be enhanced due to the utilizing the PVP as an additive mixed with polymer the casting solution. It was found that 5 wt. % PVP mixed with the polymer solution was able to rise the form of size and pores density within the membrane which one way or another leads to an increase of the membrane performance[3]. The aim is to synthesize and improving a PVDF-co-HFP hollow fibers membrane using PVP with various concentrations (0, 5, 7, and 9%wt.) as a pore former for MD implementation.

2. Materials and Methods

Polymer dope solution are consisting of three main materials; the main polymer is Poly (vinylidene fluoride-co-hexafluoropropylene), Mw 400,000 Da (average degree of polymerization 1040). Dimethylacetamide (DMAc), CH3C (O) N (CH3)2, was used as a polar solvent. Polyvinylpyrrolidone (PVP) (K30) (30,000 Da) as a pore-forming additive. All chemicals materials were purchased from Sigma–Aldrich Chemical Company.

2.1 Membrane Preparation

First step is to remove moisture from PVFD-co-HFP and PVP. A vacuum oven at 40 °C was utilized to remove the remains moisture. PVP with diverse concentrations (0, 5, 7 and 9 wt. %) was first dissolved with DMAc in a glass flask. Then, pellets of PVDF-co-HFP were added to the solution at 50 °C with continuous mixing using a magnetic stirrer until the solution become homogeneous. Homogeneous dope solution was transferred to a vertical stainless steel tube (dope container). For the synthesis of hollow fibers, a phase-inversion technique was used. The mechanism of spinning process is: The bore fluid (distilled water) was fed in the internal pipe using a precision gear pump, whilst the PVDF-co-HFP polymer solution flowed utilizing a pure nitrogen gas through a ring nozzle in the spinneret. Tap water was used as a coagulation bath.

2.2 Field Emission Scanning Electron Microscopy (FESEM)

FESEM technique was used to study the structure of the hollow fiber membrane. First of all, fibers were completely dried, then immersed in liquid nitrogen for 3 minutes before they were fractured to avoid the deformation of fibers cross sectional area. Subsequently, the samples coated with platinum and tested with FESEM (JSM-7800F Japan).

2.3 DCMD Consideration

Performance of PVDF-co-HFP fibers was investigated utilizing a DCMD system. Schematic diagram for DCMD process is shown in Figure 1. Five of PVDF-co-HFP hollow fiber membranes were bundled in a 1.5cm diameter stainless steel module in a Lab-scale, closing both ends with epoxy resin. Length of the hollow fiber membranes was 15 cm. DCMD experiments were implemented first with a feed of distilled water to check the system and make sure that there was no water leak during the operating. To prevent heat leakage into the surrounding, modules and all the system pipes were isolated with black rubber foam thermal insulation. Through the experiment, a counter current of 35000 ppm sodium chloride feed solution was pumped in the shell side of the hollow fiber membrane module, whilst the distilled water was pumped in the lumen side. Double-headed peristaltic pumps (WT600-1F- China) were used for pumping. (40, 50, 60, and 70 °C) were the hot feed stream temperature while the cold permeate stream temperature was kept constant at 20±1 °C. Permeate flux of the PVDF-co-HFP hollow fibers (in Kg/m^2 h) was estimated using the following formula:

$$\mathbf{J = G / n \pi D L} \tag{1}$$

where, **J** is the permeate flux (kg/m^2.hr), **G** is the accumulated permeate water per time (kg/h), **n** refers to the number of fibers that have been placed in the module, **D** is the outer diameter of fiber (m), and L refers to the active length of fibers (m).

2.4 Salt Rejection

In order to determine the membrane salt rejection index, electrical conductivity meter was used to measure both feed and permeate streams NaCl concentration. The NaCl rejection ratio was evaluated for the solution using Equation 2[4]:

$$\mathbf{R\% = [(C_F - C_P)/C_F] \times 100\%,} \tag{2}$$

Where R% is the rejection ratio of the aqueous NaCl solution, C_F is the feed concentration of the NaCl solution (ppm), and C_P is the concentration of the permeation solution[4].

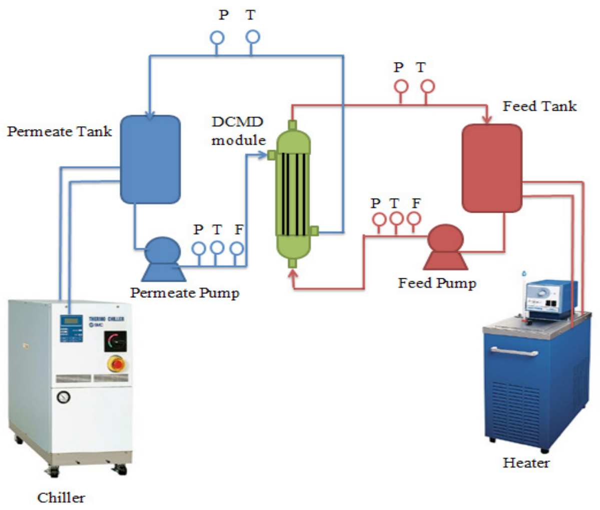

Figure 1. Schematic DCMD experimental setup.

3. Results and Discussion

3.1 Fibre's Structure Affected by PVP Content

Figure 2 shows Illustrates the FESEM cross-sectional images of the PVDF-co-HFP hollow fiber's structure. It can be noted clearly there are two finger-like layers are located near the edge of the internal and external fiber's surfaces, while, in the middle of the cross sectional area it can be recognized a sponge-like layer as clear in Figure 2a. It can be observed that when a 5 wt. % of PVP was added to the dope solution this will causes a turned the membrane's cross sectional area completely into two layers, with wide, finger-like structure, as depicted in Figure 2b. Two layers of skinny, finger-like structure were formed, and the average size of cavities will decrease when increasing the concentration of PVP in the PVDF-co-HFP dope solution into 7 wt. %. As shown in Figures 2c and 2d, due to the faster solvent/non-solvent rate exchanging enhances the creation of the finger-like structure or even macro-voids. The PVP-solvent and non-solvent demixing rates were accelerated through the phase inversion stage, this is due to of fact that the PVP is naturally hydrophilic and good miscible with water. A fast solvent/non-solvent demixing was occurred through the spinning dope (due to the influence of PVP content mixed with polymer solution), resulting in some thin selective layers and cavities with various sizes. The occurrence of macro voids was linked to the instantaneous mixing mechanism[5].

3.2 Impact of PVP Concentration on DCMD Performance

PVDF-co-HFP hollow fiber membrane prepared from the dope solution containing 9 wt. % PVP showed higher flux under the same conditions compared to hollow fibers prepared with PVP of 0, 5, and 7 wt. %. This is due to the fact that increasing the concentration of PVP in the dope solution leads to increase the pore size and also pore density. This will lead to improve the membrane porosity. The permeate flux is influenced by the membrane porosity and pore size, so highly porous structures lead to a high flux. The membranes of high porosity give a larger void fraction for the transfer of vapor and therefore provide a higher mass flux[6,7]. This behavior was also proposed by[8], who reported that high permeation flux could be observed with higher porosity and also pore sizes of the hollow fiber membranes fabricated at high PVP concentrations. In[9] concluded that with the porous composite membranes, a higher permeate flux can be obtained with higher porosity. In[10] also reported that when increasing PVP particles, the membrane pores and porosity were also increased. That in turn led to the flux enhancement.

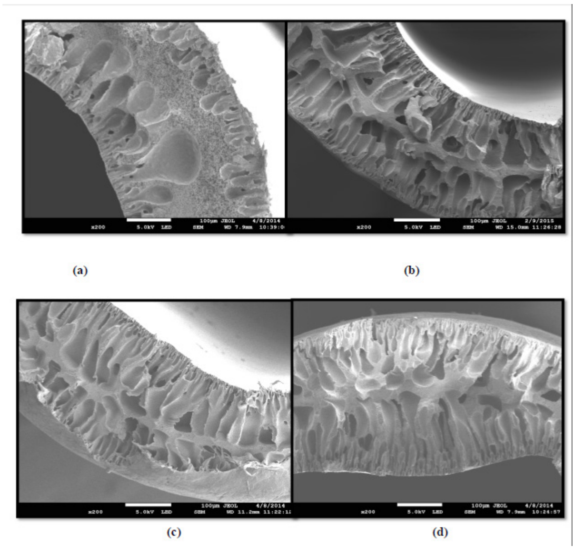

Figure 2. FESEM images of the Morphology for PVDF-HFP hollow fiber membranes prepared with: (a) 0% PVP, (b) 5% PVP, (c) 7% PVP, (d) 9% PVP.

3.3 Effectiveness of Feed Temperature on DCMD Performance

Impact of the hot feed temperature (i.e., 40 to 70 °C) at constant feed flow rate of about 0.6 L/min on PVDF-co-

HFP hollow fibers permeate flux was studied. Figure 3 shows that the temperature of the feed has a considerable impact on the membrane permeate flux. In the present study, the maximum permeation flux obtained was 15.0 (kg/m^2 h) of the hollow fiber prepared to 9 wt. % of PVP additive at T_f of 70 °C. The permeate flux was found to increase with the increasing of the feed temperature due to the increase of the vapour pressure[11]. The difference in vapour pressure across the membrane is the driving force of membrane distillation process. So any increase in feed temperature will lead to increased vapour pressure of the feed solution. Consequently, the transmembrane vapour pressure across the fiber is also increased, leading to high driving force which in turn causes an increase of mass flux. This is consistent with[12], who indicated that the temperature of the feed strongly affected on the membrane permeate flux.

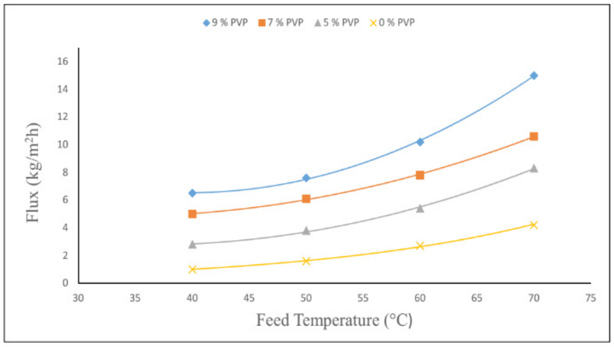

Figure 3. Flux as a function of feed temperature for (0.6 L/min) flow rate.

3.4 Salt Rejection

The salt rejection was as high as 99.98% for all PVDF-co-HFP hollow fibers fabricated with different PVP contents with the 35000 ppm NaCl solution as a feed of DCMD system. The main feature of the DCMD process is its tendency to provide a high rejection ratio, which cannot be achieved by conventional technique such as Reverse Osmosis (RO).

4. Conclusion

In the present study, Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) hollow fibers were fabricated using a phase inversion technique. Impact of PVP concentration in the polymer dope solution was studied. (0, 5, 7 and 9 wt. %) of PVP was used as a pore former additive. It was found that adding 5, 7, and 9 wt. % PVP into the dope solution could achieve the following:

- The pore size and pore density were improved with addition of PVP particles into the membrane dope solution.
- The permeate flux of PVDF-co-HFP hollow fibers with PVP is high compared with that of neat PVDF-co-HFP fibers by about 74% at a feed temperature (T_F) of 70 °C.
- The rejected salt of PVDF-co-HFP hollow fibers membrane is over 99.98%.

Finally, the PVDF-co-HFP fibers synthesized by an introduction PVP as additive onto the PVDF-co-HFP dope solution have a comparable and often better weight flux compared to most membranes synthesized from PVDF-co-HFP as a polymer material.

The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website[13] and organized by The Centre of Excellence for Advanced Research in Fluid Flow (CARIFF)[14]. The publications on fluid bulk volume flow, distillation technology, adsorption / absorption technology has been published as a special note in volume 1[15]. University Malaysia Pahang[16] the parent governing body is the host for the conference.

5. Acknowledgement

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