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Preparation and properties of PVDF hollow fiber membrane for desalination using air gap membrane distillation

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HIGHLIGHTS

- PVDF hollow fiber membrane was prepared through TIPS method.
- GTA and DBS were used as the mixed diluents.
- The bicontinuous structure of membrane pore was obtained.
- The prepared PVDF membrane was tested in an AGMD process for desalination.
- J_D and GOR simultaneously can reach to 5.5 kg/m^{2}h and 6.2.

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ABSTRACT

The polyvinylidene fluoride (PVDF) hollow fiber membrane was prepared for membrane distillation through thermally induced phase separation (TIPS) using glyceryl triacetate (GTA) and dibutyl sebacate (DBS) as the mixed diluents. The bicontinuous structure of membrane pore was obtained in the case: PVDF/GTA/DBS is 25 wt.%:22.5 wt.%:62.5 wt.%, and the coagulation bath is the water of 20 °C. The membrane porosity and mechanical strength are 0.64 and 2.7 MPa, respectively. The PVDF membrane was characterized using the measurement of the liquid entry pressure (LEPw), scanning electron microscopy (SEM), mean pore, porosity and mechanical strength. The prepared PVDF membrane was tested in an AGMD process for desalination with 7.0 wt.% NaCl solution as the feed. The permeate water flux (J_D) and gained output ratio (GOR) simultaneously reach to 5.5 kg/m^{2}h and 6.2. The prepared PVDF membrane can be operated continuously for 240 h without any significant change to J_D and GOR, indicating that the prepared PVDF hollow fiber membrane by TIPS method may be of great potential to be utilized in AGMD process for desalination.

1. Introduction

Membrane distillation (MD) has been known as a feasible separation technology for desalination using the vapor pressure gradient across the micro-porous hydrophobic membrane as a driving force. Now MD is a promising separation technology in the 21st century for solving the water scarcity all over the world [1]. Recent studies on MD technology focus on the MD membrane [2,3], MD module [4,5] and membrane separation technology integrated with multi-effect distillation (MED), multi-stage flash evaporation (MSF) and reverse osmosis (RO). Membrane distillation despite being introduced since 1960s has not been widely used in wastewater treatment industry. A limitation for implementation of MD is the high energy consumption and the difficulties with long term operation connected with the risk of membrane wettability. And the fundamental cause lies in the MD membrane and membrane module with high performance [2]. The performance of MD module mainly depends on MD membrane and the structure of membrane module. MD has several advantages compared with other membrane separation technology including high rejection rate, low operating pressure and the capability to use low-grade energy [6,7]. In order to improve the performance of MD process for desalination, developing appropriate MD membrane and MD module with energy recovery has been being studied.

MD membranes must be hydrophobic and micro-porous and have high liquid entry pressure (LEPw). The membrane with bicontinuous membrane pore structure, high porosity, and large pore size (less than the allowed maximum pore size based on Laplace Law) is conducive to improve the performance of MD module. The most common hydrophobic polymer materials are polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). Of these materials,

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PTFE has the highest hydrophobicity, good chemical and thermal stability and oxidation resistance, but it has the highest conductivity which will cause great heat transfer through PTFE membranes. PVDF has good hydrophobicity, thermal resistance and mechanical strength and has been widely applied in microfiltration, ultra-filtration and many other membrane processes because of the excellent comprehensive properties [8–11]. Although many researchers have been working on the preparation of PVDF membranes with high permeate flux and surface hydrophobicity. Commercial PVDF membranes are usually prepared by non-solvent induced phase separation (NIPS) method and often have a large membrane pore size distribution inducing a low NaCl rejection, while membranes prepared by TIPS often have narrow membrane pore size distribution and outstanding mechanical performance. And the membranes with bicontinuous structure have higher water flux and greater mechanical strength than those of the membrane with cellular structure [12]. In recent years, membranes prepared by TIPS method have attracted much attention [13].

The diluents significantly affect membrane structure due to their extents of compatibility with polymer. Due to the strong compatibility of polymer with sulfolane, S–L phase separation occurred prior to L–L phase separation during the cooling of polymer/diluent solution. Thus spherulitic structure was obtained [14]. However, when diphenyl ketone (DPK) was selected as the diluent, cellular or bicontinuous structure can be observed in the cross section of PVDF membrane via TIPS method [15]. On the other hand, the mixed diluents, whose compatibility with PVDF can be adjusted by varying its compositions, has also attracted researchers' attention to prepare PVDF membrane via TIPS method. Using glyceryl triacetate (GTA)/glycerol as the mixed diluents, the phase separation from S–L phase separation to L–L phase was changed in TIPS process, thus the bicontinuous structure near the outer surface of PVDF hollow fiber membrane was obtained [13]. Song et al. [16] prepared PVDF membrane using the mixed diluents of γ-butyrolactone (GBL) and dioctyl phthalate (DOP). When the volume fraction of DOP in the mixed diluents increases from 53.5% to 58.4%, the spherulitic structure of membrane became ambiguous and the cellular structure of membrane became obvious.

In this study, the PVDF membrane with bicontinuous structure, high porosity and mechanical strength for desalination using air gap membrane distillation was prepared by TIPS method. GTA and DBS were used as the mixed diluents. The properties of PVDF membrane in terms of the AGMD modules with energy recovery (Fig. 1) were designed to concentrate 7.0 wt.% NaCl solution. The performance of AGMD process using PVDF hollow fiber membrane was investigated in different operating parameters such as the feed inlet temperature including the hot feed side and the cold feed side, the feed flow rate and the membrane module length. A long-term separation test was introduced to investigate the retaining performance of AGMD process for high salty water desalination using the prepared PVDF hollow fiber membrane.

2. Experimental

2.1. Materials

PVDF (Mw = 350,000) was obtained from Kureha Company (Japan). GTA and DBS were purchased from Tianjin Jiangtian Chemical Reagents (China). The iPP heat exchange hollow fibers with a inter diameter of 0.4 mm and outer diameter of 0.52 mm were provided by Tianjin Chemical Separating Technologies Co., Ltd.

2.2. PVDF hollow fiber membrane preparation

PVDF hollow fiber membrane was prepared through TIPS method using GTA and DBS as the mixed diluents. The PVDF powder was dried at 100 °C for 24 h to remove its moisture content before it was used for the casting solution preparation. The dried PVDF powder was weighed and poured into a tank containing GTA and DBS solvents, then the polymer mixture was subjected to continuous stirring at 200 °C for 12 h under the protection of nitrogen until it was homogeneous. Afterwards, the stirring was stopped and the gas bubbles in the casting solution were released for about 2 h with a vacuum pump. The homogenous casting solution was fed into the spinneret under the nitrogen pressure of 0.2 MPa, and the casting solution flow rate was adjusted by a gear pump with a speed controller. The temperatures remained stable at the gear pump and spinneret was adjusted by temperature regulating device. The nitrogen, used as the core gas, was adjusted by a gas flow meter. The hollow fiber was extruded from the spinneret and entered into a water bath kept at 20 °C to induce the complete phase separation and solidify the membrane. When the hollow

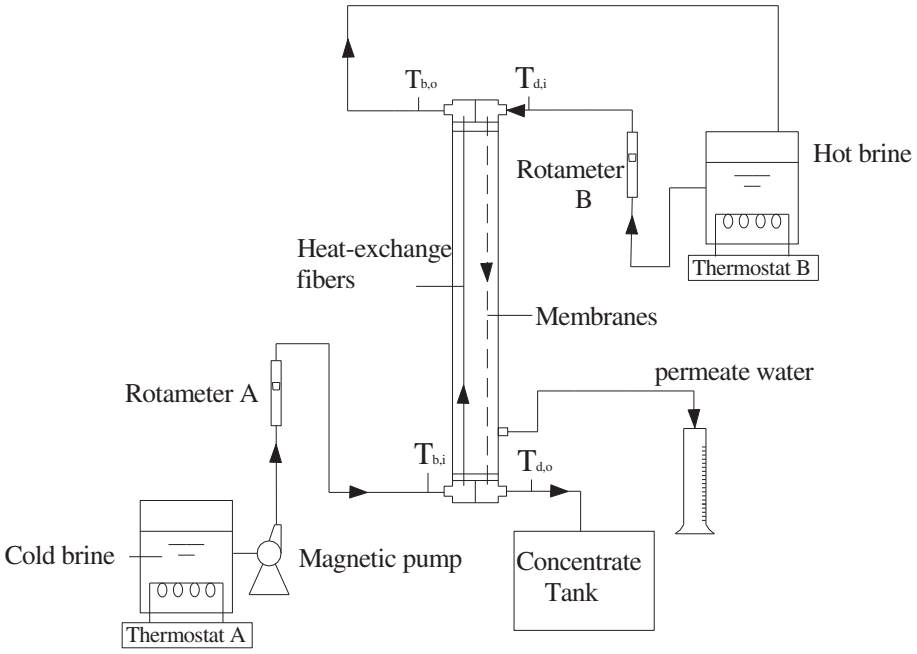

Fig. 1. Schematic diagram of AGMD experimental apparatus.