Desalination 347 (2014) 25–33

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Effects of calcium carbonate nano-particles on the properties of PVDF/nonwoven fabric flat-sheet composite membranes for direct contact membrane distillation

Deyin Hou [a,*], Guohua Dai [b], Hua Fan [c], Jun Wang [a,*], Changwei Zhao [a], Hongjing Huang [c]

[a] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China
[b] Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, PR China
[c] School of Environmental and Chemical Engineering, Nanchang University, Jiangxi 330031, PR China

HIGHLIGHTS

- PVDF flat-sheet composite membranes were prepared for membrane distillation.
- Influence of nano-particles on membrane properties was investigated.
- The calcium carbonate nano-particles narrowed membrane pore size distribution.
- The calcium carbonate nano-particles enhanced membrane roughness and contact angle.
- The composite membrane presented excellent permeability and performance stability.

ARTICLE INFO

Article history:
Received 13 January 2014
Received in revised form 2 May 2014
Accepted 21 May 2014
Available online 7 June 2014

Keywords:
Membrane distillation
Polyvinylidene fluoride
Calcium carbonate
Nano-particle
Flat-sheet membrane

ABSTRACT

The polyvinylidene fluoride (PVDF) flat-sheet composite membranes were prepared for membrane distillation using hydrophilic polyester nonwoven fabric as a support and the mixture of LiCl and PEG as non-solvent additive through coating and wet phase inversion process. The effects of hydrophobic calcium carbonate nano-particles on membrane morphology, porosity, pore size, pore size distribution, hydrophobicity, thermal properties and permeability were investigated. The nano-particles optimized membrane structure, enlarged pore diameter, narrowed pore size distribution and improved membrane porosity to some extent. In addition, the nano-particles could also enhance membrane surface roughness and contact angle while increasing the crystallinity degree of the prepared membranes. Nonetheless, the excess nano-particles addition would deteriorate membrane structure, reduce membrane porosity and decrease pore size. During the desalination process of 35 g/L sodium chloride solution, the maximum transmembrane permeate flux about 49.37 kg/m^{2}h was obtained with the feed solution at 83 ºC and the cold distillate water at 20.0 ºC. Furthermore, the flat-sheet composite membrane exhibited satisfying performance stability compared with the membrane without nano-particles addition in the 300 h continuous desalination experiments, indicating that the prepared PVDF/nonwoven fabric flat-sheet composite membrane may be of great potential to be utilized in membrane distillation process for desalination.

1. Introduction

Membrane distillation (MD) is an emerging membrane separation technology using temperature gradient created on membrane surfaces as a driving force and usually applied in which water is the major component present in the feed solution to be treated [1]. The MD process may be used as a substitute for conventional separation processes such as multistage vacuum evaporation, reverse osmosis and distillation [2]. Compared with those processes, the advantages of MD include: (1) lower operating temperature and vapor space required than conventional distillation, (2) lower operating pressure than RO, (3) 100% (theoretical) rejection of non-volatile solute, (4) unlimited by high osmotic pressure, and (5) lower energy consumption than multistage vacuum evaporation [3–5]. Extensive researches on MD have been done over the past three decades, and according to the different process configurations, four systems of MD have been identified including direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD) [6]. Up to the present, the application of MD has been extended to multiple areas, such as food processing, water desalination, wastewater treatment, juice

---

[*] Corresponding authors. Tel./fax: +86 10 62849150.
E-mail addresses: dyhou@rcees.ac.cn (D. Hou), junwang@rcees.ac.cn (J. Wang).

http://dx.doi.org/10.1016/j.desal.2014.05.028
0011-9164/© 2014 Elsevier B.V. All rights reserved.

concentration and some other industrial areas in lab or pilot plant scales [7–11].

Although the porous membrane only serves as a physical barrier, it plays a crucial role in MD process. At least the membrane surface directly contacting with the hot feed should be hydrophobic to prevent the aqueous solution from entering into its dry pores until the liquid entry pressure of water (i.e., *LEPw*) is exceeded [12]. Besides, some other membrane properties, such as pore size, pore size distribution, membrane thickness and porosity will also influence the MD performance [13–15]. Therefore, good hydrophobicity, appropriate pore size and narrow pore size distribution of porous membranes are necessary to ensure both the high permeate flux and high rejection in MD process.

Membranes designed for MD are mainly made of hydrophobic polymers such as polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). Among these three materials, only PVDF can be fabricated by non-solvent induced phase separation (NIPS) method because PVDF polymer is soluble at room temperature in several common organic solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), Dimethyl sulfoxide (DMSo) and *N*-methyl-2-pyrrolidone (NMP) [16,17]. So far, most commercial membranes used for MD are originally marketed for microfiltration or ultrafiltration, however, those commercial membranes are incompletely adequate for MD process because of weak hydrophobicity, poor permeability, low solute rejection rate, and so on.

In recent years, researchers have paid more attention to the preparation of hydrophobic membranes, particularly the PVDF membrane for MD process. Tomaszewska [18] fabricated hydrophobic PVDF flat-sheet membrane for MD by using LiCl as additive and studied the effect of the LiCl concentration in casting solution on permeate flux. Khayet and Matsuura [19] fabricated supported and unsupported PVDF membranes using pure water as pore-forming additive, while Fan et al. [20] prepared hydrophobic PVDF symmetric flat-sheet membranes for VMD by using double-layer casting process in vapor-induced phase separation method. Peng et al. [21] obtained a novel composite membrane with a polyvinyl alcohol/polyethylene glycol hydrophilic layer on PVDF hydrophobic substrate and the wetting problem could be prohibited by adopting the additional hydrophilic layer. Hou et al. [22] prepared a PVDF flat-sheet membrane by using a mixture of acetone and H_3PO_4 as mixed non-solvent additive. Feng et al. [23,24] fabricated flat-sheet membranes from poly(vinylidene fluoride-co-tetrafluoroethylene) and poly(vinylidene fluoride-co-hexafluoro propylene), which had a higher flux than the pure PVDF membrane. Wang et al. [25] added hydrophobic clay particles to the polymer dope to fabricate mixed matrix PVDF hollow fiber membranes, and the obtained fibers exhibited high porosity, high flux, good thermal insulation and reduced the risk of membrane pore wetting. Teoh and Chung [26] spun PVDF–PTFE hollow fibers, which exhibited good hydrophobicity and macrovoid free structure. Khayet firstly presented the concept of hydrophilic/hydrophobic composite membrane and prepared series novel composite flat-sheet membranes by phase inversion method in a single casting step [27–31]. Edwie et al. [32] fabricated hydrophobic/hydrophilic dual layer hollow fibers using methanol as a non-solvent additive and self-synthesized silica particle as a hydrophobic modifier to improve the membrane hydrophobicity. Bonyadi and Chung [33] utilized the dual-layer co-extrusion technology to fabricate hydrophobic/hydrophilic hollow fibers, and the produced fibers exhibited superior performance with a remarkable water flux of 55 kg/m^2h at 90 ºC.

Although most researchers have been working on the preparation of hydrophobic hollow fibers because of its higher packing density and lower cost than flat-sheet membranes [34], the latter possess higher heat and mass transfer coefficient and better antifouling properties compared with hollow fiber membranes. As for the flat-sheet membrane with a support layer, it presents stronger mechanical strength to withstand the intense hydraulic impact and flow disturbance, which is very important from an industrial application standpoint.

The present investigation was carried out to fabricate PVDF/nano-particles flat-sheet composite membranes for MD using polyester (PET) nonwoven fabric as a support through coating and wet phase inversion process. The prepared membranes contained a hydrophobic PVDF/nano-particles composite porous separation function layer and a hydrophilic nonwoven fabric support layer, which can be considered as a kind of developed hydrophilic/hydrophobic composite membrane in a broad sense. The hydrophobic modified calcium carbonate nano-particles were chosen as the inorganic phase of the membranes because it had good dispersity in organic solvent and high interface adhesive force with polymer matrix [35]. It has also been reported that nano-particles added into polymer dope can effectively optimize membrane pore distribution, improve permeate flux and surface hydrophobicity [25,26,33,36,37]. In this study, the influences of the hydrophobic modified calcium carbonate nano-particles on membrane properties were investigated comprehensively. The prepared flat-sheet composite membranes were also tested via DCMD process using 35 g/L sodium chloride solution as feed.

2. Materials and methods

2.1. Materials

PVDF (FR-904) was obtained from Shanghai 3 F new materials Co., Ltd. (China). The molecular weight (Mw) of PVDF is about 1.02×10^6 g/mol. DMAc (>99%) was employed as the solvent, purchased from Shanghai Jingwei Chemical Co., Ltd. (China). Hydrophobic calcium carbonate nano-particle (≥98.7%) modified with octadecyl dihydrogen phosphate was supplied by NanoMaterials Technology Co., Ltd. (China), its contact angle is about 120°. The mean particle size and specific surface area are about 36 nm and 45 m^2/g, respectively. A mixture of LiCl and polyethylene glycol (PEG) was used as non-solvent additive in the polymer solution, LiCl (95.0%) and PEG (Mw = 400, >99.5%) were supplied by Tianjin Guangfu Research Institute of Fine Chemical Engineering (China). Ethanol (GR grade, 99.9%) and NaCl (99.5%) were from Beijing Chemical works (China). PET nonwoven fabric was purchased from Teijin Ltd. (Japan), its area weight is about 100.6 ± 0.3 g/m^2. The SEM image and gas permeability of the nonwoven fabric are presented in Fig. 1. The ultrapure water used in all experiments was produced by a Milli-Q BIOCEL unit (MilliPore, USA) with the resistivity of 18 MΩ · cm.

2.2. Membrane preparation

The PVDF powder was dried at 100 ºC under vacuum for 24 h to remove its moisture content before being used for dope preparation. A desired amount of dried PVDF powder was weighed and poured into a tank containing DMAc solvent and non-solvent additive, then the

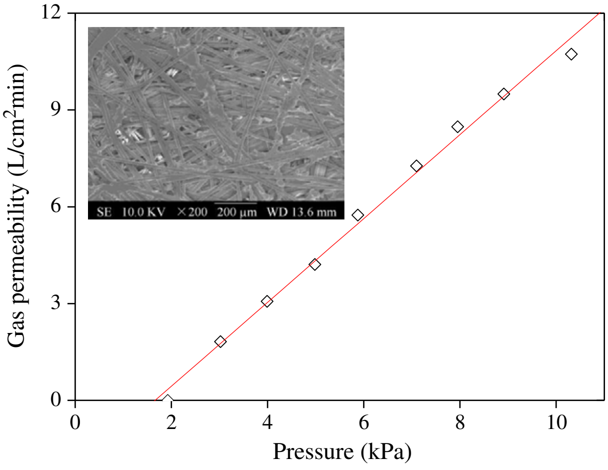

Fig. 1. SEM image and gas permeability of the polyester nonwoven fabric.