Journal of Membrane Science 563 (2018) 31–42

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Polyvinylidene fluoride membrane modification via oxidant-induced dopamine polymerization for sustainable direct-contact membrane distillation

Nick Guan Pin Chew[a,b], Shanshan Zhao[b], Chandresh Malde[c], Rong Wang[b,d,*]

[a] Interdisciplinary Graduate School, Nanyang Technological University, Singapore 639798, Singapore
[b] Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore 637141, Singapore
[c] Johnson Matthey Technology Centre, Reading RG4 9NH, United Kingdom
[d] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore

ARTICLE INFO

Keywords:
Membrane distillation
Surfactant
Oxidant-induced
Polydopamine
Superoleophobic

ABSTRACT

Porous hydrophobic polyvinylidene fluoride (PVDF) membranes have been extensively used in direct-contact membrane distillation (DCMD) processes. However, these PVDF membranes are vulnerable to membrane fouling and pore wetting in low surface tension feeds, restricting its application for water recovery from challenging industrial wastewaters. Therefore, it is of paramount importance to engineer fouling- and wetting-resistant MD membranes for robust long-term applications. In this study, a superoleophobic composite hollow fiber membrane with sandwich structure has been developed via accelerated oxidant-induced polydopamine (PDA) deposition on both the outer and inner surfaces of a commercial hydrophobic PVDF membrane under slightly acidic conditions (pH = 5). The modified surface prevents organics adhesion ascribing to its underwater superoleophobicity while the unmodified pores remain hydrophobic for vapor transport. The long-term robustness of the PDA-decorated membrane in highly saline feeds containing low surface tension contaminants has been evaluated via bench-scale DCMD experiments. In contrast to the pristine PVDF membrane, the PDA-decorated membrane exhibits excellent fouling- and wetting-resistant properties in different surfactant solutions as well as oil-in-water emulsion. The PDA-decorated membrane has also been used for seawater desalination, during which it maintains a stable flux and high salt rejection rate. Furthermore, the PDA-decorated membrane presents a flux enhancement of up to 70% over the pristine PVDF membrane in 3.5 wt% NaCl solution at 333 K. This study demonstrates the potential of the PDA-decorated membrane for extended DCMD applications such as water recovery from industrial wastewater containing low surface tension substances.

1. Introduction

Membrane distillation (MD) is a continuous thermal-driven desalination process based on the vapor-liquid equilibrium [1–3]. In this process, water vapor molecules from the warm saline feed transport through a porous hydrophobic membrane and condense into highly purified distillate on the cold permeate side, driven by the water vapor pressure difference associated with the temperature gradient across the membrane. MD has been proposed as a promising candidate for water recovery from highly saline feeds over conventional pressure-driven membrane processes due to its merits of low sensitivity to feed salinity, moderate operating conditions, and ability to utilize low-grade thermal energy that is abundantly available within many industries [4–6].

In the MD process, the porous hydrophobic membrane is a crucial element for efficient vapor transport and preventing liquid permeation from the saline feed to the distillate. Hence, conventional MD membranes are typically fabricated from hydrophobic polymeric materials that include polypropylene, polyvinylidene fluoride (PVDF), and polytetrafluoroethylene. These membranes have shown stable performances for treating relatively clean feeds that contain mostly salt. However, they are vulnerable to membrane fouling and pore wetting when used to treat challenging feeds that contain hydrophobic (e.g. oil) and/or amphiphilic (e.g. surfactants) pollutants. Adsorption of these substances on the membrane surface can lower the pore liquid entry pressure or cause pore blockage, which compromises on the recovery rate and distillate quality [7]. Hence, it is paramount to develop robust MD membranes with fouling- and wetting-resistant properties. This could potentially extend the applications of the MD process to treating

---

[*] Corresponding author at: Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore 637141, Singapore.

E-mail address: rwang@ntu.edu.sg (R. Wang).

https://doi.org/10.1016/j.memsci.2018.05.035
Received 11 March 2018; Received in revised form 13 May 2018; Accepted 19 May 2018

oil-in-water (O/W) emulsions such as produced water as well as surfactant-containing wastewaters from the textile, food, paint, polymer, cosmetic, and pharmaceutical industries, to name a few. Recent studies have provided an insight on that [7,8]. It has been suggested that omniphobic and composite membranes can provide a solution to membrane fouling and pore wetting faced in low surface tension feeds via MD [6,9–11].

Hierarchical re-entrant structures, coupled with low surface energy, can improve the anti-wetting properties of omniphobic membranes as they represent a significant energetic barrier that has to be overcome in order to transit from the metastable Cassie-Baxter state to the fully wetted Wenzel state [6,12–15]. The other approach to mitigate fouling and wetting involves creating a superhydrophilic skin layer on the top of a hydrophobic or omniphobic substrate [11,16,17]. This forms a hydration layer surrounding the superhydrophilic skin and renders the membrane surface superoleophobic under water. Besides that, incorporation of low surface energy functional groups into the hydrophilic matrix can further facilitate the detachment of hydrophobic foulants such as oil [18]. It is evident from these studies that strides have been made in improving the anti-fouling and anti-wetting properties of MD membranes. Yet, most of these surface modification techniques are often too complex for practical applications. Therefore, developing a facile technique to engineer robust MD membranes that can handle wastewaters containing low surface tension pollutants is of high priority.

Moreover, to make MD membranes commercially viable, membranes with high vapor permeability have to be developed [19]. This can be achieved through altering vapor-membrane interaction, which is one of the major physicochemical factors determining permeability [20]. Apart from that, striking a balance between high mass transfer and low heat loss is also vital in enhancing vapor permeation flux in MD operations [21]. In line with this, much effort has been focused on performing surface modification on commercially available polymeric substrates to attempt to enhance flux, which includes the immobilization of carbon nanotubes (CNT) in membrane pores [19]. CNT's excellent thermal conductivity reduces the effect of temperature polarization, which in turn brings about an increase in vapor driving force across the membrane. In addition, CNT's remarkable sorption and desorption capacity contribute favorably to water-membrane interactions. Faster removal of water vapor from the membrane pores is also possible via CNT's atomic-scale smooth surface. Similar concepts have been proposed through incorporating nanodiamond and graphene oxide within the membrane matrix [22,23]. Besides that, reducing vapor transport distance while maintaining the membrane thickness can facilitate mass transport across the membrane [21]. These works have contributed tremendously to developing MD membranes with enhanced flux, but the performances of these membranes in saline feeds containing low surface tension pollutants are found to be undesirable.

Since 2007, the mussel-inspired chemistry of dopamine has opened up avenues for numerous applications due to its unique advantages of material-independent attachment and surface post-functionalization under relatively mild conditions [24]. However, most of the surface modification techniques involving dopamine investigated thus far have proven to be laborious and time-consuming. These techniques involve numerous preparation steps, and require long hours of coating [25]. Often, the deposition of polydopamine (PDA) through these conventional techniques is non-homogenous, of low thickness, and of limited hydrophilicity. In our previous study, the coating process took more than a day to achieve the desired thickness [11]. Even so, the deposited layer presented limited hydrophilicity. Furthermore, the modified membrane was especially vulnerable to wetting in some non-ionic surfactant solutions and fouling in anionic surfactant solutions. It has been suggested that the use of oxidants, in replacement of dissolved oxygen, can overcome these limitations [26,27].

This study focuses on developing a robust MD membrane with enhanced flux for water recovery from wastewaters containing low surface tension solutes via direct-contact membrane distillation (DCMD). Specifically, a superoleophobic composite membrane with sandwich structure was fabricated through facile single-step deposition of hydrophilic PDA layer in the presence of an oxidant, namely sodium periodate (SP), on both the outer and inner surfaces of a commercial hydrophobic PVDF hollow fiber substrate. The surface chemistry and hierarchical structure of the modified PVDF membrane were studied comprehensively through a range of characterization techniques. The fouling and wetting propensities of the modified PVDF membrane were investigated via a bench-scale DCMD experimental rig by feeding a series of low surface tension saline wastewater. Its performances were analyzed and then compared against those of the pristine PVDF and

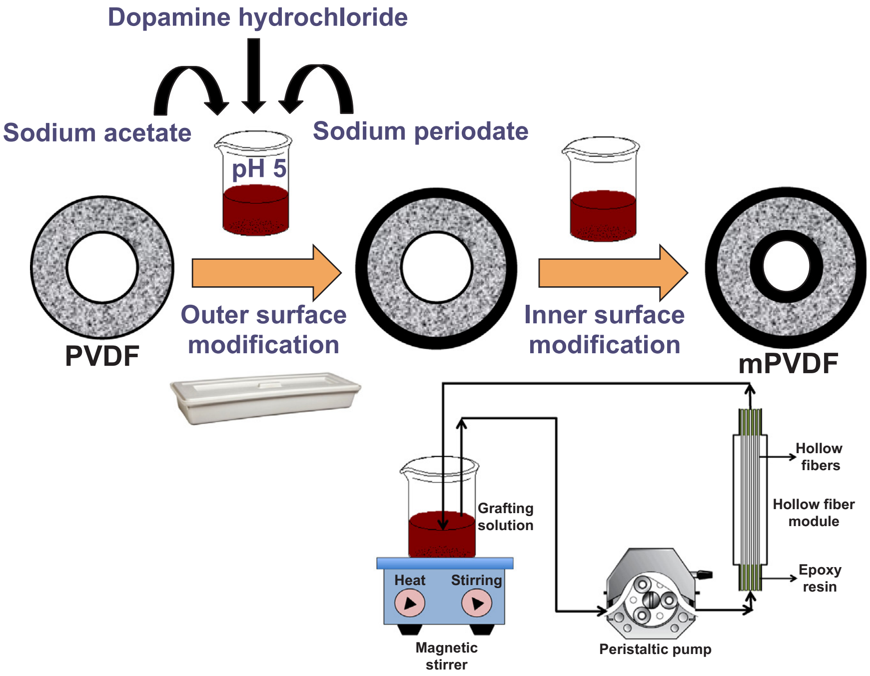

Fig. 1. Schematic of oxidant-induced deposition of PDA on the outer and inner surfaces of a PVDF hollow fiber membrane.