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An ultrathin, porous and in-air hydrophilic/underwater oleophobic coating simultaneously increasing the flux and antifouling property of membrane for membrane distillation

Weishi Sun, Fei Shen*, Zhaoshuai Wang, Yan Zhang, Yinhua Wan

State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China
University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Surface modification is a useful method to enhance the antifouling ability of membranes for membrane distillation (MD). However, current surface modification strategies often tend to sacrifice the membrane flux. In this work, we decorated a commercial hydrophobic polytetrafluoroethylene (PTFE) membrane by coating dopamine (DA) alone. A unique surface coating being ultrathin, porous, and in-air hydrophilic/underwater oleophobic was constructed, which simultaneously increased the flux and fouling resistance of the PTFE membrane in MD desalination. When treating a 3.5 wt% NaCl aqueous solution at 70 °C through vacuum MD (VMD), compared with the pristine PTFE membrane flux of 28.8 kg/m^2·h, the flux of the modified membrane 0.5DA@PTFE-4 reached 89.6 kg/m^2·h, and the flux increased by 210%. Continuous VMD operations demonstrated that the 0.5DA@PTFE-4 membrane held a higher resistance to scaling than the pristine one. Moreover, the pristine PTFE membrane was incompetent to tackle an oily saline via VMD, showing an immediate membrane fouling and wetting. The 0.5DA@PTFE-4 membrane, however, exhibited a significant improvement in oil fouling resistance, rendering the VMD desalination process viable for more than 30 h. The findings in this work provided a new insight to develop the robust membrane with high performance used for MD.

1. Introduction

Membrane distillation (MD), a thermally driven membrane separation process, is considered as a promising technique candidate being able to efficiently remove volatile components from aqueous solutions [1–3]. Especially for desalination, high quality permeates can be obtained by MD process. MD even can further tackle the concentrated brine discharged from reverse osmosis (RO) process, since MD process isn't affected by osmotic pressure [4]. While, osmotic pressure significantly limits the water recovery rate of RO process. Plus, MD process is allowed to be operated at ordinary hydrostatic pressures, which are much lower than that required in RO process. In spite of such advantages, MD technique has not realized widely large-scale application yet, mainly due to the issues of low permeate flux, membrane fouling and wetting, as well as the instability of long-term performance [5]. That is, the overall performance of the membranes applied in MD process still needs to be improved, which has been highlighted in the recent reviews [6–8].

To get high MD flux, lots of efforts have been made from the viewpoint of optimization of membrane structure parameters including pore size, pore size distribution, porosity, thickness, and tortuosity, etc. [4]. Some of the parameters often have a contradictory effect on the membrane flux in MD process. For instance, larger pore size offers lower mass transfer resistance but is likely to reduce membrane's porosity and liquid entry pressure (LEP); Thinner membrane exhibits higher mass transfer coefficient yet probably encounters more thermal conduct loss thus decreasing the driving force across the membrane. Membrane porosity, however, monotonically impacts the flux in MD process, namely, higher porosity could produce higher flux. A mixed matrix polyvinylidene fluoride (PVDF) hollow fiber membrane with porosity up to about 90% and pore size less than 50 nm was specially designed for direct contact MD (DCMD) [9]. Such membrane fabricated by dry-wet phase inversion method yielded a flux as high as 79.2 kg/m^2·h when treating a 3.5 wt% sodium chloride (NaCl) aqueous solution via DCMD, where the hot and cold side inlet temperature was of 81.5 and 17.5 °C, respectively. Besides the porosity, it is identified that the

* Corresponding author at: State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China.
E-mail address: fshen@ipe.ac.cn (F. Shen).

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membrane cross-section morphology also has an important impact on flux improvement. A type of PVDF-based hollow fiber membrane with a unique dual-layer structure, consisting of a thin sponge-like outer-layer and a thick fully finger-like inner-layer, was engineered and made for DCMD. A high flux of 98.6 kg/m^2·h was obtained when treating a 3.5 wt % NaCl solution at the feed temperature of 80.2 °C via DCMD process [10]. Low mass transfer resistance provided by the finger-like macrovoids and high bulk porosity of over 84% could be the main contributors to achieve such high DCMD flux.

The concept of hydrophobic/hydrophilic composite membrane has been also proposed to enhance the membrane performance in MD [11–13]. This kind of composite membrane is always used in such scenario, in which the hydrophobic surface faces hot feed solution while the hydrophilic part serves as a support layer, which gives an opportunity to tune the properties of hydrophobic and hydrophilic parts separately. The hydrophobic layer for vapor transport can be adjusted to a desirable pore structure and thickness to reduce the mass transfer resistance, and the thermal conductivity and hydrophilicity of the hydrophilic layer can also be increased accordingly to enhance the driving force across membrane, which will together improve the membrane flux especially in the DCMD process [14,15]. Nevertheless, the existed hydrophilic layer inevitably produces an additional temperature polarization at permeate side in the DCMD mode, which is still an issue to be addressed further [4].

Recently, a couple of novel efficacies capable of improving MD flux was found via immobilizing nanomaterials onto membrane surface. One ascribed to the enhancement of driving force by conferring Joule heating [16] or photothermal effect [17] on a hydrophobic membrane surface to elevate the localized temperature of membrane surface at feed side, so that alleviating the temperature polarization. Another was inferred from the intensification of the interaction between water vapor and immobilized nanomaterial (e.g. functionalized carbon nanotubes) on membrane surface [18,19].

On the other hand, the demand for membrane fouling control in MD is a concern actually paralleling its demand for flux improvement. Despite the achieved advances in flux improvement, membrane fouling is still one of the main obstacles impacting the operation stability of MD process, particularly when separating a feed solution containing hydrophobic foulants (e.g. proteins, oily substances, etc.). Because there is a strong attractive interaction between hydrophobic foulants and a hydrophobic membrane surface, membrane fouling would be severer in that situation. Therefore, the ordinary hydrophobic membrane will be fouled soon in that case [20]. In order to improve the membrane antifouling property, surface modifications at the feed side of hydrophobic membranes were widely investigated to create a robust membrane with amphiphobic [21], omniphobic [22] or even hydrophilic surface [23–26]. Especially, the hydrophilic modifications on a hydrophobic membrane surface can transform the originally in-air oleophilic surface into an underwater oleophobic surface, endowing the membrane surface with an underwater anti-fouling ability while maintaining the hydrophobicity of the underlying membrane pores. Current hydrophilic modifications significantly reinforced the membrane fouling resistance in MD [21–26]. It is noteworthy that, the current hydrophilic decorations at the same time tend to sacrifice membrane flux as well, which can be clearly seen by the decline in MD flux after hydrophilic modification in comparison to their unmodified counterparts [25,26].

Actually, it is difficult to manipulate membrane chemistry and structure to simultaneously improve the membrane flux and resistance to fouling in MD. For hydrophilic/hydrophobic composite membrane, at least, the decorated hydrophilic layer should not furnish apparent mass transfer resistance. For example, it needs to be ultrathin and porous at the same time. Over the last decade, dopamine coating has been developed as a highly efficient approach being able to construct controllably ultrathin hydrophilic layer on almost any substrates [27–29]. Polydopamine (PDA) coatings seem to be an ideal candidate to meet the above requirements for MD. Very recently, a PDA/polyethylenimine (PEI) co-deposition was utilized to modify hydrophobic PVDF membrane's upstream side surface [24]. The co-deposited PDA/PEI coating presented underwater superoleophobic and exhibited an excellent antifouling ability in the DCMD process. However, it was not found that using such PDA/PEI co-deposition increased the PVDF membrane's flux.

In this study, based on a commercial polytetrafluoroethylene (PTFE) membrane, we fabricated a Janus membrane with an ultrathin, hydrophilic, and porous surface layer via a very simple surface coating method. Instead of using the existing PDA-based co-deposition approach, we adopted dopamine (DA) alone to modify the PTFE membrane. Through such modification, the modified membranes presented a simultaneous increase in flux and antifouling property in MD. To the best of our knowledge, there is no other membrane yet having such unique comprehensive property in MD to date; and, employing PDA only to modify a membrane for MD has not been reported either. Actually, with the exception of MD, almost all membrane processes have ever used the single deposition of PDA to decorate their membranes, such as microfiltration [30], ultrafiltration [31], nanofiltration [32], reverse osmosis [33], forward osmosis [34], electrodialysis [35], pervaporation [36], gas separation [37] and pressure retarded osmosis [38]. In addition, the surface modification strategy we propose here is obviously more facile and environment-friendly than those sophisticated methods of constructing other kinds of surfaces [21,22] and even the co-deposition of PDA/PEI [24]. The reason of opting for PTFE membrane as the substrate is that it possesses the highest hydrophobicity among the most used microfiltration membranes, which would make the PDA just deposit on the membrane surface rather than entry into its matrix. The effects of key coating parameters, such as DA concentration and coating time on membrane morphology, surface chemistry, and vacuum MD (VMD) performance were mainly investigated. Desalination durability of the membranes before and after the modification was compared during the VMD process of a synthetic saline wastewater with or without mineral oil. The possible mechanism that resulted in the simultaneous improvement in the membrane flux and the antifouling property was also discussed.

2. Experimental

2.1. Materials and chemicals

Hydrophobic porous PTFE flat-sheet membrane with a nominal 0.22 μm pore size and 7.5 μm PTFE layer thickness supported by polyethylene terephthalate (PET) scrim was purchased from Membrane Solutions Company. This PTFE membrane was used as the substrate for surface modification. Hydrochloric acid (HCl), NaCl, potassium chloride (KCl), tris-hydroxymethyl amino methane (Tris), sodium hydroxide (NaOH) were supplied by Xilong Chemical Co. Ltd., China. DA hydrochloride was obtained from Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 30 wt%) was bought from Beijing Chemical Works. Mineral oil (CAS: 8042-47-5) with a density of 0.88 kg/L was obtained from J&K Scientific Ltd., Beijing, China. All chemicals were used as received. Deionized water produced by Millipore Milli-DI® system was used in all tests. The purity or content of the relevant materials and chemicals has been listed in Table S1.

2.2. Membrane surface modification

DA hydrochloride with different weight was separately dissolved into the Tris buffer solution (10 mM, pH 8.5) prepared in advance to make the DA solution with the concentration of 0.1, 0.25, 0.5 and 2.0 g/L, respectively. A typical membrane surface modification procedure was that as follows. Firstly, a piece of round pristine PTFE membrane was fixed at the bottom of a homemade cylindrical cell made by polymethyl methacrylate. The cell (inner diameter 40 mm, height 50 mm and wall thickness 5 mm) had an open top connecting to the