



Anti-fouling membranes by manipulating surface wettability and their anti-fouling mechanism



Xuemei Lu^a, Yuelian Peng^{a,*}, Haoran Qiu^a, Xinrui Liu^a, Lei Ge^b

^a Beijing Key Laboratory for Green Catalysis and Separation, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

^b School of Chemical Engineering, the University of Queensland, Brisbane 4072, Australia

HIGHLIGHTS

- Two routes were used for superhydrophobic and superhydrophilic surface modification.
- Three organic foulants examined in membrane distillation.
- The anti-wetting and anti-fouling behaviors of three membranes were compared.
- Superhydrophobic modification displayed much better self-cleaning property.
- Superhydrophilic modification only slowed down wetting and fouling.

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ABSTRACT

This study aims to compare the anti-wetting and anti-fouling surface behavior in membrane distillation (MD) by two surface modification routes on porous polyvinylidene fluoride (PVDF) membranes. A superhydrophobic membrane (SiO₂-PFTS/PVDF) was obtained by dynamically forming 1H,1H,2H,2H-perfluorooctyl trichlorosilane containing SiO₂ nanoparticles on the membrane surface as in our previous study; whereas a superhydrophilic membrane (PVA/PVDF) was developed by attaching a thin layer of poly(vinylalcohol) hydrogel onto the membrane's surface. The effects of surface modification on their anti-wetting or anti-fouling properties were examined in MD using an aqueous NaCl solution with various organic foulants (e.g., kerosene, humic acid (HA), and sodium dodecyl benzene sulfonate (SDBS)). The results showed that the superhydrophobic SiO₂-PFTS/PVDF membrane displayed excellent self-cleaning characteristics and wetting resistance against all three studied foulants. In contrast, the hydrophilic surface layer of the PVA/PVDF membrane only slowed down wetting and fouling when in contact with kerosene and HA. Nonetheless, when dealing with SDBS, its anti-wettability performance was comparable to that of the SiO₂-PFTS/PVDF membrane. The superhydrophobic SiO₂-PFTS/PVDF membrane exhibited anti-fouling and anti-wetting behaviors even though the extended Derjaguin–Landau–Verwey–Overbeek theory indicated the attraction force between the membrane surface and all three foulants.

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1. Introduction

Membrane distillation (MD) is an emerging separation membrane technology based on the vapor pressure gradient across a porous hydrophobic membrane [1]. The advantages of applying MD for desalination include relatively low operating temperatures, lower operating pressures and fewer requirements on membrane mechanical properties [2]. With these unique advantages, MD processes have demonstrated promising results in seawater desalination, wastewater treatment and many other applications [3].

The issues of membrane fouling and wetting have been frequently discussed for improving the MD performance. Membrane fouling, which is defined as the deposition of contaminants (organic and/or inorganic materials) on the membrane's surface or into the membrane's pores, decreases the water purification performance of the membrane and increases operational cost by adding extra processing requirements, such as periodical membrane cleaning and/or replacement [4]. In particular, membrane fouling can be accelerated by a hydrophobic interaction between contaminants and membrane surface [5]. Membrane wetting includes two steps: surface wetting and partial wetting [6]. An increase of the permeate conductivity usually suggests the occurrence of partial wetting [7,8]. Generally, membrane wetting depends on the membrane materials, the content and type of foulants [9], membrane's pore size and porosity [10], as well as membrane surface morphology and

* Corresponding author.

E-mail address: pyl@bjut.edu.cn (Y. Peng).

structure [11]. Moreover, membrane wetting can be caused by the adhesion of bio-organisms (biofoulants) [12], membrane degradation by long time operation [13], as well as mechanical and thermal damage by heating and cooling cycling [8].

As a popular hydrophobic membrane material, polyvinylidene fluoride (PVDF) is widely used in MD [14]. The hydrophobic PVDF membranes are susceptible to fouling when treating aqueous solutions containing various organic matters, e.g. oily substances, humic acid, surfactants [7,8,15]. Furthermore, the long-term stability for an enhanced PVDF membrane performance in MD is a significant issue, so further membrane modification becomes critical [16]. Therefore, chemical modification of the membrane's surface is necessary to improve anti-fouling and anti-wetting properties. There are two major strategies for hydrophobic surface modification: changing the PVDF's intrinsic hydrophobicity towards either super-hydrophobicity or super-hydrophilicity.

The superhydrophobic nature of the surface renders the membrane with anti-wetting properties, while retaining high flux. Super hydrophobicity helps to introduce an air gap between the liquid droplet and the membrane's surface [17], thereby increasing the allowable pore size prior to the occurrence of pore wetting, and consequently ensuring higher mass flux and throughput [18]. Generally, a superhydrophobic surface is acquired for the modification with fluorosilanized nanoparticles [19–23]. In a previous work, we have also fabricated amphiphobic PVDF composite membranes with excellent anti-wetting and anti-fouling properties against various organic foulants such as humic acid and surfactant [24].

Shifting the PVDF's hydrophobicity towards super-hydrophilicity is a major strategy for hydrophobic surface modification. A pure water layer is easily formed on a highly hydrophilic surface, preventing the adsorption and deposition of hydrophobic pollutants onto the membrane's surface [25]. Surface grafting [7] and coating [26] can be effective in improving the hydrophilicity of PVDF membranes. A highly hydrophilic membrane surface was developed via plasma induced grafting of polyethylene glycol (PEG) and TiO₂ particles deposition onto the PVDF membrane surface, and the resulted hydrophilic-modified composite membrane was tolerant to salty feed solution containing mineral oil [7]. Liang et al. [27] combined the plasma treatment with the coating of silica nanoparticles for the hydrophilic modification of PVDF ultrafiltration (UF) membranes. The surface modification significantly improved the wettability and anti-biofouling properties of PVDF membranes. Fane et al. [28] successfully developed composite membranes with a poly (vinylalcohol)/PEG hydrophilic layer on a PVDF substrate for desalination. A similar composite membrane was synthesized by attaching a thin layer of agarose hydrogel on the surface of a Teflon membrane, which displayed anti-fouling properties against the studied surfactant [16]. Du et al. [29] modified a PVDF membrane by coating with a poly (vinylalcohol) (PVA) solution followed by crosslinking. The treated membrane displayed both a high flux and a slow fouling rate. Rahimpour et al. [30] immobilized acrylic and amino moieties on a PVDF membrane surface, the hydrophilicity, antifouling properties, and flux recovery of the composite membrane were all enhanced.

As above discussion, previous literatures have shown that both hydrophobic and hydrophilic treatment can contribute to the membrane anti-fouling, however it is difficult to evaluate various surfaces modification methods based on different membrane supports. The aims of this study are to compare the anti-fouling and anti-wetting mechanisms of the PVDF based composite membranes derived from hydrophobic and hydrophilic treatment in same direct-contact membrane distillation (DCMD) process. Humic acid, oily substances and surfactants were chosen as the organic pollutants in DCMD, representing natural organic matter, hydrophobic and amphiprotic pollutants, respectively. Since the process of fouling and wetting on membrane surface can be a slow process, the long-term stability test (>100 h) is critical to evaluate the effectiveness of different modification routes. The XDLVO theory was also applied in this study to explore the mechanisms of wetting and fouling by various organic matters in MD process, providing some

insights in developing high performance membranes via membrane modifications.

2. Theory

2.1. Concept of surface tension

The wettability of a solid surface can be expressed by the contact angle, θ , which is governed by Young's Eq. [7]:

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \quad (1)$$

where γ_s , γ_{sl} and γ_l refer to the surface tensions of solid in contact with air, solid in contact with liquid, and liquid in contact with air, respectively. The surface tension of a solid surface can be written as the following when the Good–Van Oss model is applied [31]:

$$\gamma_s^{\text{TOT}} = \gamma_s^{\text{LW}} + \gamma_s^{\text{AB}} \quad (2)$$

$$\gamma_s^{\text{AB}} = 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (3)$$

$$\gamma_l^{\text{TOT}}(1 + \cos\theta) = 2\left(\sqrt{\gamma_s^{\text{LW}} \gamma_l^{\text{LW}}} + \sqrt{\gamma_s^+ \gamma_l^+} + \sqrt{\gamma_s^- \gamma_l^-}\right) \quad (4)$$

where θ is the contact angle, and the surface tension parameters (γ_s^{LW} , γ_s^+ , γ_s^-) of a solid can be obtained by determining the contact angles between the solid and three probe liquids with well-known surface tension properties (γ_l^{LW} , γ_l^+ , γ_l^-); γ^{TOT} is the total surface tension; and γ^{AB} is the AB components of surface tension [32]. In this study, the pristine and modified membrane surfaces were treated as the solid. The calculation of all components of the surface tension of a polymer (γ_s^{LW} , γ_s^+ , γ_s^-) was carried out using Eq. (4) for three liquids with known values of γ_l^{LW} , γ_l^+ , γ_l^- . The liquid surface tension data of water, diiodomethane and glycerol are listed in Table S1.

2.2. The XDLVO theory

The extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory describes the total interaction energy, or adhesion energy, between a colloid and a membrane surface as the sum of Lifshitz–van der Waals (LW), acid–base (AB) and electrostatic double layer (EL) interactions [33].

$$\Delta G^{\text{XDLVO}} = \Delta G^{\text{LW}} + \Delta G^{\text{EL}} + \Delta G^{\text{AB}} \quad (5)$$

where ΔG^{XDLVO} is the total interaction energy between a membrane surface and a colloid immersed in water, ΔG^{LW} is the LW interaction term, ΔG^{EL} is the EL interaction term, and ΔG^{AB} is the AB interaction term. In Eq. (8), ϵ_0 is the permittivity of free space, ϵ_r is the relative dielectric constant of water, κ is the reciprocal of the Debye length, ζ_p and ζ_m are Zeta potentials of membrane and foulant respectively, d_0 is the minimum contact distance between foulant and membrane. The input values used for the XDLVO module are listed in Table S2. And the interfacial free energy for the interaction between solid and liquid immersed in an aqueous medium can be further expressed as following [26]:

$$\Delta G^{\text{LW}} = 2\left(\sqrt{\gamma_s^{\text{LW}} \gamma_w^{\text{LW}}} + \sqrt{\gamma_l^{\text{LW}} \gamma_w^{\text{LW}}} - \sqrt{\gamma_s^{\text{LW}} \gamma_l^{\text{LW}}} - \gamma_w^{\text{LW}}\right) \quad (6)$$

$$\Delta G^{\text{AB}} = 2\left[\sqrt{\gamma_w^+ (\gamma_s^- + \gamma_l^- - \gamma_w^-)} + \sqrt{\gamma_w^- (\gamma_s^+ + \gamma_l^+ - \gamma_w^+)} - \sqrt{\gamma_s^+ \gamma_l^+} - \sqrt{\gamma_s^- \gamma_l^-}\right] \quad (7)$$

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