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Membrane fouling and wetting in membrane distillation and their mitigation by novel membranes with special wettability

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ABSTRACT

Membrane distillation (MD) has been identified as a promising technology to desalinate the hypersaline wastewaters from fracking and other industries. However, conventional hydrophobic MD membranes are highly susceptible to fouling and/or wetting by the hydrophobic and/or amphiphilic constituents in these wastewaters of complex compositions. This study systematically investigates the impact of the surface wetting properties on the membrane wetting and/or fouling behaviors in MD. Specifically, we compare the wetting and fouling resistance of three types of membranes of different wetting properties, including hydrophobic and omniphobic membranes as well as composite membranes with a hydrophobic substrate and a superhydrophilic top surface. We challenged the MD membranes with hypersaline feed solutions that contained a relatively high concentration of crude oil with and without added synthetic surfactants, Triton X-100. We found that the composite membranes with superhydrophilic top surface were robustly resistant to oil fouling in the absence of Triton X-100, but were subject to pore wetting in the presence of Triton X-100. On the other hand, the omniphobic membranes were easily fouled by oil-in-water emulsion without Triton X-100, but successfully sustained stable MD performance with Triton X-100 stabilized oil-in-water emulsion as the feed solution. In contrast, the conventional hydrophobic membranes failed readily regardless whether Triton X-100 was present, although via different mechanisms. These findings are corroborated by contact angle measures as well as oil-probe force spectroscopy. This study provides a holistic picture regarding how a hydrophobic membrane fails in MD and how we can leverage membranes with special wettability to prevent membrane failure in MD operations.

1. Introduction

Membrane distillation (MD) is a thermal desalination process capable of utilizing low-grade energy to desalinate highly saline water, such as RO brine and shale gas/oil wastewater (Lawson and Lloyd, 1997; Martinetti et al., 2009; Khayet and Matsuura, 2011; Souhaimi and Matsuura, 2011; Lin et al., 2014). In a typical MD process, a hydrophobic microporous membrane is used to separate a hot saline water stream (feed) and a cold fresh water stream (distillate). Driven by the trans-membrane temperature difference between the hot feed and cold distillate streams, water evaporates from the feed/membrane interface, transports down the partial vapor pressure gradient, and condenses on the distillate/membrane interface. Although MD has been studied for decades, it has recently gained momentum in academic research and industrial development because it has been proposed as one of the few promising solutions to the desalination of highly saline brine such as shale gas/oil produced water or briny wastewater in zero liquid discharge. (Camacho et al., 2013; Shaffer et al., 2013; Lin et al., 2014; Tong and Elimelech, 2016). Due to the very high salinity, the osmotic pressures of these wastewaters can be significantly higher than the allowable working pressure in reverse osmosis—the state-of-the-art technology for seawater desalination.

The MD membrane is a critical component in an MD system, serving as a barrier for direct liquid water transfer and a medium for water vapor transfer. Conventional MD membranes are hydrophobic and made of common polymeric materials such as polyvinylidene fluoride (PVDF), polypropylene (PP), and polytetrafluroethylene (PTFE). The hydrophobicity is required to prevent direct liquid permeation through the micropores. However, when hydrophobic membranes are used in MD to treat hypersaline wastewater of a complex composition, two potential problems may lead to MD operation failures. (Tijing et al., 2015).

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The first potential problem is membrane fouling in which fouling agents (or foulants) attach onto the hydrophobic membrane surface, block the membrane pores, and consequently cause significantly reduced water vapor flux (Gryta et al., 2001; Wang et al., 2016). Membrane fouling is a particular concern when hydrophobic membrane is used in MD to treat feed waters with an abundance of hydrophobic contaminants (e.g. oil, hydrophobic organics) due to the strong hydrophobic-hydrophobic interaction (Israelachvili and Pashley, 1982; Tsao et al., 1993; Meyer et al., 2006; Warsinger et al., 2014). Recent studies using hydrophobic MD membranes for desalinating brine water rich in oil or organics have shown the rapid and severe flux decline as a result of membrane fouling (Zuo and Wang, 2013; Wang et al., 2016a,b,c).

The second major problem that may lead to MD operation failure is membrane wetting. When a hydrophobic membrane is employed in an MD process to desalinate brine water containing amphiphilic molecules, such as surfactants and other amphiphilic organics, the hydrophobic tails of the amphiphilic molecules will attach onto the hydrophobic membrane pore surface, leaving the hydrophilic head exposed and eventually rendering the membrane pores hydrophilic. The consequence of membrane pore wetting is the direct permeation of feed water into the distillate stream and significantly undermined salt rejection rate (Razmjou et al., 2012; Liao et al., 2013; Lin et al., 2014; Boo et al., 2016a; Lee et al., 2016).

The potential problems of fouling and wetting constraint the applications of conventional hydrophobic MD membrane to treating only relatively “clean” feed water without hydrophobic and amphiphilic contaminants. For desalinating shale/gas wastewater or industrial brines, which are enriched in hydrophobic or/and amphiphilic contaminants, conventional hydrophobic membranes could readily fail due to wetting or/and fouling. In this case, either extensive pretreatments are required to remove the hydrophobic and amphiphilic contaminants before the MD process, which will significantly increase the treatment cost; or advanced membranes that can resist wetting and fouling need to be developed.

Significant advances have been made recently in the materials science community to elucidate the mechanisms of special wettability observed in biological systems and to apply those principles to fabricate artificial interfacial materials with similar special wettability (Wang et al., 2016). Two types of special wetting properties have been recently leveraged to enhance MD membrane performance. First, composite membranes with a hydrophobic substrate and a hydrophilic or superhydrophilic surface layer have been developed to impart robust resistance to oil fouling (Zuo and Wang, 2013; Wang et al., 2016a,b,c). Such an approach of integrating a superhydrophilic skin layer has also been employed for fouling control in other membrane processes (Xue et al., 2011; Hejazi et al., 2012; Wen et al., 2013; Zhu et al., 2013a,b; Rohrbach et al., 2014; Dudchenko et al., 2015). The underlying mechanism for fouling resistance is the formation of hydration shell on the superhydrophilic coating which renders the membrane surface superoleophobic underwater (Pashley, 1981; Rinaudo, 2006; Chen et al., 2010; Israelachvili, 2011; Tiraferri et al., 2012; Fe et al., 2016).

On the other hand, omniphobic membranes have been also developed to mitigate membrane wetting induced by surfactants (Lin et al., 2014; Boo et al., 2016a; Lee et al., 2016). These membranes resist wetting by water and low-surface-tension liquids (e.g. oil) in air, and prevent feed solutions containing surfactants from penetrating into the membrane pores. The key to impart omniphobicity, especially oleophobicity, is to create a rough surface of reentrant structure and very low surface energy (Tuteja et al., 2008; Kota et al., 2014). Detailed theory regarding the criteria of developing surfaces with robust resistance to wetting by low-surface-tension liquids has been established (Tuteja et al., 2008). Different methods have been also developed to create interfacial materials with omniphobicity using a variety of substrates (Hikita et al., 2005; Tuteja et al., 2007; Meng et al., 2008; Nyström et al., 2009; Vilčnik et al., 2009; Ceria and Hauser, 2010; Hsieh et al., 2010).

The development of omniphobic membranes and composite membranes with superhydrophilic skin layer has significantly expanded the applications of MD and enabled MD to desalinate more challenging feed water (Boo et al., 2016a; Wang et al., 2016). However, a systematic understanding is still lacking regarding how these membranes perform with feed water of different characteristics. For example, while omniphobic membranes robustly resist oil wetting in air, its underwater anti-fouling performance against oil has not been studied. On the other hand, a previous study has reported that a composite membrane with both hydrophilic and hydrophobic layers was effective in preventing the wetting by feed water containing ethanol, which seems to suggest that a composite membrane may also resist wetting by feed water with surfactants. It is also intriguing to investigate whether each of these two membranes, or both of them, can deliver stable MD performance in complex feed water, such as an oil-in-water emulsion stabilized by surfactants.

In this study, we employ direct contact membrane distillation (DCMD) to systematically investigate the impact of membrane wetting properties on their anti-fouling and anti-wetting performance when used to treat oil-in-water emulsion with and without added synthetic surfactants. Three types of membranes with distinct wetting properties, including a hydrophobic (but oleophilic) membrane, an omniphobic membrane, and a composite membrane with a hydrophobic substrate and a superhydrophilic skin layer, are compared for their wetting properties and MD performance. We also conduct force spectroscopy to assess the underwater interaction between an oil droplet and the three different membranes to elucidate the different observed fouling behaviors.

2. Materials and methods

2.1. Membranes and chemicals

The hydrophobic PVDF membrane and omniphobic membrane, both with a nominal pore size of 0.45 μm, were purchased from GE Healthcare Life Sciences (Pittsburg, PA), and Pall Corporation (Exton, PA), respectively. This commercial omniphobic membrane belongs to the Versapor® series and is made of acrylic copolymer. Although this Versapore® membrane is developed for venting and moisture control applications and has never been used for MD or any type of water treatment process, we have tested it to be applicable for MD, yielding a flux comparable to the PVDF membrane.

Chitosan (CTS, medium molecular weight, deacetylated chitin), silica nanoparticles, or SiNPs, (LUDOX® HS-40), perfluorooctanoic acid, Triton™ X-100, acetic acid, sodium hydroxide (NaOH) and sodium chloride (NaCl) were all procured from Sigma Aldrich (St. Louis, MO). The crude oil was purchased from Texas Raw Crude Oil (Midland, TX).

2.2. Fabrication of composite membrane with superhydrophilic skin layer

The composite membrane was fabricated following the procedures reported in literature (Yang et al., 2014; Wang et al., 2016). Briefly, a PFO/CTS nanoparticle-polymer composite was prepared via adding 20 mL of perfluorooctanoate (PFO) aqueous solution (0.1 M, acquired from reacting perfluorooctanoic acid with NaOH) to an 100 mL dispersion of CTS and SiNPs (0.2 g CTS dissolved in 1% acetic solution in the presence of 0.3 g SiNPs) dropwise under