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Flux enhancement in membrane distillation by fabrication of dual layer hydrophilic–hydrophobic hollow fiber membranes

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Abstract

For the first time, co-extrusion was applied for the fabrication of dual layer hydrophilic–hydrophobic hollow fibers especially for the direct contact membrane distillation (DCMD) process. The effect of different non-solvents on the morphology of the PVDF membranes was investigated and it was found that weak coagulants such as water/methanol (20/80, w/w) can induce a three-dimensional porous structure on PVDF membranes with high surface and bulk porosities, big pore size, sharp pore size distribution, high surface contact angle and high permeability but rather weak mechanical properties. Hydrophobic and hydrophilic clay particles were incorporated into the outer and inner layer dope solutions, respectively, in order to enhance mechanical properties and modify the surface tension properties in the membrane inner and outer layers. Different membrane characterizations such as pore size distribution, gas permeation test, porosity and contact angle measurements were carried out as well. Ultimately, the fabricated hollow fibers were tested for the DCMD process and flux as high as 55 kg/(m^2 h) at 90 °C was achieved in the test. This performance is much higher than most of the previous reports, indicating that the application of dual layer hydrophilic–hydrophobic hollow fibers may be a promising approach for MD.

Keywords: Membrane distillation; Hollow fiber; Flux enhancement; Hydrophilic; Hydrophobic

1. Introduction

As time goes by, the fresh water shortage will become a troublesome issue for human being. According to a report by United Nations in 1999, water shortage, besides the global warming, has been considered as the most worrying problem for the new millennium. In this respect, the importance of desalination technology becomes more and more evident. However, the conventional desalination technologies such as multi-stage flash vaporization (MSFV) and reverse osmosis (RO) suffer from disadvantages that make them rather expensive to be applied specially in poor countries. MSFV is an energy intensive process that suffers from high operating temperatures, high mechanical demanding and large space occupation [1]. On the other hand, RO is a pressure driven process that is greatly susceptible to fouling. In addition, the cost effectiveness of the RO plants is strongly dependant on the oil price. These facts have urged engineers to look for alternative approaches for conventional desalination technologies.

Membrane distillation was patented in 1963 by Bodell [2] as an alternative approach mainly for desalination. Being considered as a branch of membrane contactors, it offers many distinct advantages over conventional desalination technologies. The operating temperatures in this process can be maintained as low as 50 °C and the operating pressures are atmospheric [1,3–5]. As a result, this process has a great potential to be energy efficient and cost effective, especially if combined with low grade or waste energy sources. However, in contrast to its great potentials, this process has not been widely accepted by the industry during the last four decades. One important reason is probably due to its relatively lower flux compared to reverse osmosis process [5]. Therefore, flux enhancement in this process has become of great interest among membrane scientists and researchers.

In an MD process, a porous hydrophobic membrane is utilized to perform the separation among water and dissolved minerals. In this process, the liquid feed is heated up to about 50–90 °C and is brought into contact with one side of the

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hydrophobic membrane. On the membrane permeate side; a cold stream of pure water is in direct contact with the permeate side of the membrane to maintain the mass transfer driving force, which is the water vapor partial pressure across the membrane. This configuration is known as the direct contact membrane distillation (DCMD) which is the most common configuration applied in the literature. Other configurations can also be recognized when a sweeping gas or vacuum is applied in the membrane permeate side [1,3–5]. Because of the hydrophobic nature of the functional membrane, liquid water streams will be kept outside the membrane while water vapors will penetrate from the feed side with a higher partial pressure to the permeate side with a lower partial pressure. In this way, fresh water will be collected in the permeate side in a continuous manner [3–6]. According to the explained mechanism, MD involves a coupled mass and heat transfer phenomena. As a result of vaporization and convective heat transfer to the membrane matrix on the feed side of the membrane, the temperature on the surface of this side will be lower than the feed bulk temperature. This phenomenon is called temperature polarization [7–10]. A similar phenomenon occurs in a DCMD configuration on the permeate side when the temperature on the membrane permeate side surface becomes higher than the permeate bulk temperature. This is due to water vapor condensation and convective heat transport from the membrane matrix to the permeate stream.

According to the explained mechanism, the obtained flux in MD depends both on the membrane permeation properties as well as the flow geometry in the membrane modules. A good flow geometry maintaining turbulence among the fibers can minimize the undesirable temperature polarization which leads to a lower driving force across the membrane and consequently a lower obtained flux [11–13]. Therefore, research on the flux enhancement in MD can be divided into two large areas, the fabrication of highly permeable membranes and designing optimized membrane modules.

Most of the membranes applied for the MD process so far have not been specifically made for this process but initially fabricated for other processes such as microfiltration. The three most common materials applied in the literature are hydrophobic polyethylene (PE), polypropylene (PP) and polytetrafluoro ethylene (PTFE) polymers [7]. The membranes fabricated out of these polymers are made through a melt spinning process. However, these membranes designed originally not for MD suffer drawbacks such as low porosity and fixed pore size distributions, which limit their application as an efficient MD membranes. Polyvinyldine fluoride (PVDF) is the only hydrophobic polymer that can be easily dissolved in common organic solvents and has been considered to be utilized in the MD process. Tomaszewska [14] studied the preparation of flat-sheet PVDF membranes suitable for MD, while Khayet and Matsuura [15] and Feng et al. [16] fabricated and characterized single layer PVDF hollow fibers for this process. PVDF is a less hydrophobic polymer in its chemical nature compared to the other common polymers such as PP, PE and PTFE. As a result, PVDF membranes might be susceptible to the undesirable wetting phenomenon. Wetting occurs when the liquid stream penetrates into the membrane pores or vapor condensation occurs in the membrane matrix which leads to flux decay or lower separation efficiency [1,3–5]. Therefore, some research has been devoted to enhance the hydrophobicity of the fabricated PVDF membranes. Peng et al. [17] reported that a delayed demixing-induced through an open air gelation process could greatly enhance the contact angle in the fabricated flat-sheet PVDF membranes. They concluded that the observed phenomenon is due to the rough surface formed by a delayed demixing process. In another study by Yan et al. [18], particle-induced surface roughness was proved to be an effective approach to enhance the contact angle of surfaces in which PVDF/$CaCO_3$ nanocomposite coatings exhibited a super-hydrophobic behavior.

To enhance the flux in an MD process, one possible approach is to utilize hydrophilic–hydrophobic membranes. For the first time, Cheng and Wiersma [19] described the use of composite membranes in MD in a series of patents. They modified a cellulose acetate membrane via radiation graft polymerization of styrene onto the membrane surface, and a cellulose nitrate membrane via plasma polymerization of both vinyltrimethylsilicon/carbon tetrafluoride and octafluoro-cyclobutane. Wu et al. [20] applied hydrophilic porous supports such as cellulose acetate, and treated the membrane surface via radiation graft polymerization of styrene to enhance the hydrophobicity. In a similar way, Kong et al. [21] modified a cellulose nitrate membrane via plasma polymerization of both vinyltrimethylsilicon/carbon tetrafluoride and octafluoro-cyclobutane. However, both radiation graft and plasma polymerizations are expensive processes that limit their applications. Khayet and Matsuura [22] and Khayet et al. [23] fabricated flat-sheet hydrophilic–hydrophobic membranes based on the migration of hydrophobic macromolecules (SMM) to the membrane surface. However, the optimization of the hydrophobic layer thickness and morphology may be needed to enhance the flux through this approach. In addition, all the related reports in the literature so far have been limited to the flat-sheet membranes while hollow fibers are the most preferable membrane configuration for the industry because of providing high surface area per unit volume as well as ease of module fabrication.

In this paper, we propose and practice a novel approach to fabricate hydrophilic–hydrophobic hollow fiber membranes through a co-extrusion spinning process. Furthermore, we aim to optimize different membrane characteristics influencing the MD flux and finally we test our fabricated fibers in the DCMD process.

2. Theory

Based on the membrane distillation mechanism described in the previous section, a high performance membrane applied for this process should exhibit (1) low membrane resistance to mass transfer, (2) low thermal conductivity to prevent heat loss through the membrane matrix, (3) good thermal stability and chemical resistance toward different feed solutions, and (4) high liquid entry pressure to prevent wetting [5]. In the following sections, we will briefly overview the characteristics of high performance membranes for MD process.