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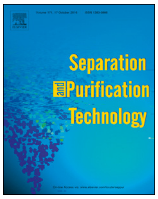

Enhanced fouling and wetting resistance of composite Hyflon AD/poly (vinylidene fluoride) membrane in vacuum membrane distillation

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ABSTRACT

Membrane fouling and pore wetting are the key problems affecting the separation performance of membrane distillation (MD). They can become more severe with increasing the operation time, which will have a negative impact on heat and mass transfers. In this paper, solutions containing $CaCO_3$, humid acid (HA), and/or silica sols (SiO_2) were used as the feed with different Hyflon AD/polyvinylidene fluoride (PVDF) composite membranes for vacuum membrane distillation (VMD). The evolutions of flux and salt rejection during the concentration process were examined, and the membranes with different properties were compared. The results showed that the original membrane was more prone to be fouled and wetted even at low concentration factors. In the single-component systems, $CaCO_3$ impacts the membrane performance most severely. With the hybrid component solutions, the flux declines for the composite membranes were lower than that of the original membrane. Compared with the single-component systems, the practical situation is more likely close to the hybrid-component system where fouling and wetting were easier to happen. Overall, the composite membranes showed enhanced fouling and wetting resistance and maintained stable salt rejections. Particularly, the composite membrane with smaller pore sizes (M-40L) performed best among all the membranes, suggesting its high potential for practical VMD applications.

1. Introduction

Membrane technology has been attracting considerable attention for many years. Its main functions are condensation, purification and separation. Membrane distillation (MD) is one of the emerging separation methods in membrane technology, which can be utilized in desalination [1,2], wastewater treatment [3], heat recovery [4,5] and volatile resource recovery [6–9]. It is a thermal driven process with vapor transport through non-wetted porous hydrophobic membranes by vapor pressure difference across the membrane pores. In MD, heat transfer and mass transfer through membrane pores take place simultaneously [10–12].

MD can be divided into four types according to different configurations: direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD) and air gap membrane distillation (AGMD) [3,13]. With lower temperatures compared with conventional distillation, lower hydrostatic pressures compared with pressure-driven membrane processes, and potential to use low-grade waste heat, MD requires less membrane mechanical strength but can achieve high rejection factors for non-volatile solutes. However, membrane wetting and fouling are main problems limiting the long-term stability performance of MD processes [14,15]. Membrane fouling is caused by the accumulation of unwanted deposits on the surface of membranes or in the membrane pores, reducing membrane permeability, which is particularly severe in pressure driven membrane processes [16–18]. Membrane fouling in MD is different from that in pressure driven membrane processes because of the difference in separation mechanisms.

Generally, fouling is affected by the solutes in the feed solution, properties of the membrane and operational conditions in MD operation. According to the location where fouling occurs, it can be divided into external surface fouling and pore blocking fouling [19]. External

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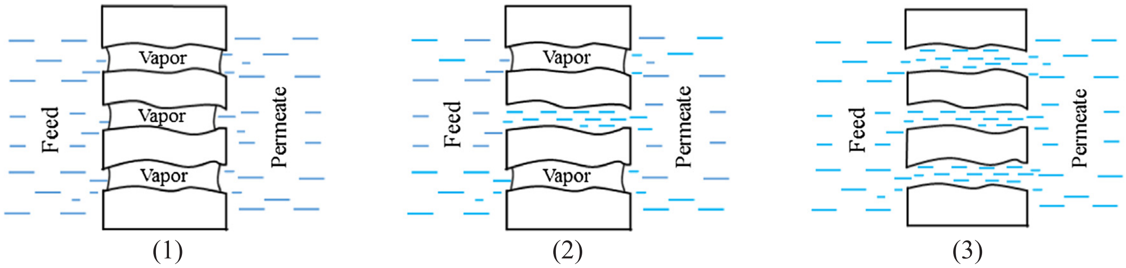

Fig. 1. Mechanism of membrane wetting: (1) surface wetting, (2) partial wetting, (3) fully wetting.

surface fouling is usually reversible and can be cleaned by various methods, while internal fouling or pore blocking is irreversible in most cases [20]. Foulants in MD can be classified into three types: inorganic materials, organic matters and microorganisms [21]. In most MD processes, membranes are fouled by a combination of different foulants. Various methods have been utilized in controlling membrane fouling in MD, such as feed pretreatment and membrane cleaning [22]. Developing anti-fouling membranes was also utilized in mitigating membrane fouling [23–25].

In addition to membrane fouling, wetting is another severe problem in long-term MD operations. Hydrophobic membrane wetting includes three stages: surface wetting (i.e. pores are non-wetted), partial wetting and fully wetting [16,26], and the mechanism can be seen in Fig. 1. Surface wetting means that only the membrane surface is wetted by the liquid, which will not influence the membrane performance. Partial wetting is that the membrane pores are partially filled with liquid, which may lead to the decline in salt rejection. When the membrane pores are completely filled with liquid, the membrane is fully wetted. The fully-wetted membrane will lose its function in separation via MD.

In our previous work, novel Hyflon AD/polyvinylidene fluoride (PVDF) composite membranes were developed and the preparation conditions were optimized [27,28]. After coating Hyflon AD, the hydrophobicity of the PVDF membranes was significantly enhanced, and the membrane pores became narrower. As a result, separation performance of the composite membranes in VMD was dramatically improved. However, the fouling and wetting behaviors of our composite membranes are still unclear.

In this paper, solutions containing $CaCO_3$, humid acid (HA), and/or silica sols (SiO_2), were selected as the feed to investigate the membrane fouling/wetting in MD. Effects of these feed solutions on the performance of the original PVDF membranes and the composite membranes were examined. The water vapor flux and salt rejection rate as a function of the concentration factor were investigated.

2. Experimental

2.1. Materials

Hyflon AD amorphous perfluoropolymers, including Hyflon AD40L (intrinsic viscosity: 0.4 dl/g @ 30 °C), Hyflon AD40H (intrinsic viscosity: 1.3 dl/g @ 30 °C) and Hyflon AD60 (intrinsic viscosity: 0.5 dl/g @ 30 °C) were kindly supplied by Solvay Specialty Polymer (Bollate, Italy). Commercial PVDF hollow fiber membranes developed by phase inversion were supplied by Nanjing Jiusi Hi-tech Co., Ltd. (Nanjing, China). Novec HFE-7100 Engineered Fluid (3 M Inc.) was used as the solvent for Hyflon AD copolymers. Ethanol (> 99.7%) was purchased from Wuxi Yasheng Chemical Co., Ltd. Sodium hypochlorite (NaClO) solution was purchased from Jiangsu Yangnong Chemical Group Co., Ltd. Commercial Humic acid (HA) was purchased from Aladdin (USA). Analytical grade sodium chloride (NaCl) and sodium bicarbonate ($NaHCO_3$) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Calcium chloride ($CaCl_2$) and sodium hydroxide (NaOH) were purchased from Xi Long Chemical Reagent Co., Ltd. Sodium silicate (Na_2SiO_3) was purchased from Shanghai shisihewei Chemical Co., Ltd.

2.2. Preparation of the composite membranes

The composite membranes were fabricated by dip-coating. Before coating, the membrane was pretreated to remove polyvinyl pyrrolidone (PVP), glycerol and other hydrophilic components used in membrane preparation, by immersing the commercial PVDF membranes in ethanol for 24 h, and in NaClO solution for 3 h, followed by washing and drying at room temperature for 12 h. The pretreated membranes were named as original membranes and also used as supports of the composite membranes. The optimizing process of coating conditions and parameters have been reported in our previous work [28,29]. Hyflon AD solutions as the coating liquids were prepared by mixing different Hyflon AD copolymers (Hyflon AD40L, Hyflon AD40H and Hyflon AD60) in Novec HFE-7100 Engineered Fluid. The solutions were stirred at room temperature until Hyflon AD was completely dissolved. The original PVDF membranes were dipped in the Hyflon AD solutions for 20 min. After dip-coating, the membranes were taken out of the Hyflon AD solution and dried in air, followed by heating in an oven at 45 °C for 9 h.

2.3. Preparation of feed solutions

Preparation of saturated $CaCO_3$ solution: $NaHCO_3$ was dripped into $CaCl_2$ solution and stirred continuously until precipitation appeared in the solution. Then, the prepared solution was filtered to remove the precipitation, and the filtered solution was used as feed for VMD concentration process.

Preparation of HA solution (1.0 g/L): 1.0 g HA was dissolved completely with 0.1 mol/L NaOH solution. Then, the solution was diluted with deionized water to 1.0 L, and was stored in a brown bottle. HA standard solutions were prepared with different concentrations. These solutions were measured with the absorbance at 235 nm by Ultraviolet–visible Light Detector (Lambda 950, PerkinElmer Instrument Co., Ltd, USA). A standard curve was drawn with the relation between the concentration of the HA standard solution and the absorbance. After VMD, the feed and permeate concentrations were estimated based on the standard curve.

Preparation of Na_2SiO_3 (SiO_2) solution: 4.72 g $Na_2SiO_3 \cdot 9H_2O$ was dissolved in deionized water and diluted to 1.0 L. The solution was stored in a plastic bottle placed in a refrigerator. The concentration of Na_2SiO_3 solution was 1.0 g/L.

These solutions were used to prepare feed solutions for simulating five different foulant systems. The concentration of the NaCl was 35 g/L in all the foulant systems. Different foulant systems are shown in Table 1.

Before VMD tests, all feed solutions were filtered to remove the precipitation. The pH of the solutions was adjusted to around 7.0 and was measured by a pH instrument (PH510, Shanghai Anlailisi Technology Co., Ltd, China).