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Optimization of novel composite membranes for water and mineral recovery by vacuum membrane distillation

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ABSTRACT

In mining industries, the process combining ultrafiltration (UF) and reverse osmosis (RO) is often used for wastewater treatment, but RO brine discharge is a big issue. Membrane distillation (MD) has been proposed to solve this problem by significantly increasing the water recovery ratio, and recovering minerals. However, membranes with high hydrophobicity targeting for MD, particularly for vacuum membrane distillation (VMD) are still scarce. Hyflon AD is a novel candidate for fabricating membranes for MD. In this paper, the effects of membrane fabrication parameters, such as coating time, heat treatment and pre-filling were investigated and optimized. Membrane morphology, mechanical properties and VMD performance of the composite membranes were tested. The results showed that the hydrophobicity and elongation at break of the membrane were significantly improved after coating. The coating polymer concentration, coating time, heat treatment temperature and heat treatment time for the membrane coated by Hyflon AD40L and Hyflon AD40H, respectively were optimized. Monovalent alcohols can be excellent pre-filling agents to improve membrane performance. Separation performance of the membrane coated by Hyflon AD40H was better than that of the one coated by Hyflon AD40L.

1. Introduction

The shortage of resources such as fresh water and raw materials is an increasingly important problem, hindering the improvement of people's life quality [1]. Recovering potable water and extracting useful minerals from wastewater are an efficient and economical way to achieve sustainable development in the modern world. Wastewaters like industrial wastewater, municipal wastewater, dye wastewater and domestic sewage are applicable water resources to be explored. Among them, mining wastewater takes a large part in the whole wastewater system. Today, mining industry is facing many problems, such as shortages in sustainable water and renewable energy, and mineral depletion [2].

Traditional methods treating mining wastewater include neutralization, chemical precipitation, microbiological treatment, and membrane separation [3]. Membrane technology, such as ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) has been applied to dispose mining wastewater for decades [4]. Currently, the combined membrane method (UF + RO), is widely used for mining wastewater treatment and recovery. The advantage of this method is that it can reject more than 80% COD, more than 95% chroma and almost all the ferrous irons and bacteria [5]. However, the water recovery ratio of RO is limited to around 30% to 60% [2]. Disposal of RO brine is still a big problem. Most methods of disposing RO brine still rely on deep well injection or direct discharge to barren land. However, these methods cause negative impacts on the environment [6]. Membrane distillation (MD) is an emerging desalination technology with high water recovery and drawing growing attentions.

MD is driven by the difference of the saturated vapor pressure across the membrane. In MD, only vapor molecules are allowed to pass through a hydrophobic porous membrane. The operating pressure is not too high, and low-grade heat can be utilized to cut the energy cost [1,6–9]. MD has four types of configurations [10], one of which is vacuum membrane distillation (VMD). It provides a promising way to increase the water recovery ratio and extract some useful minerals as by-products at the same time [11]. For example, lithium was recovered

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from high concentrated aqueous solutions by different MD configurations. However, VMD performed best in recovering lithium from extremely high concentration (saturation level) [12]. Hence, hydrophobic membranes for VMD to recover minerals like lithium need to be more robust and have long-term stabilities. Since there are no mining industry-oriented proper membranes for VMD, it is important to develop robust hydrophobic VMD membranes.

In VMD, heat loss by conduction and molecular diffusion resistance on permeate side are almost negligible comparing with those in other MD configurations [13–15]. In addition, due to the applied vacuum on the penetration side, the transmembrane pressure difference in VMD is larger than that in other configurations, which could help achieve higher permeate flux [14]. Therefore, VMD requires high quality membranes to prevent pore wetting and loss in separation performance [16]. There are several polymer materials, such as polypropylene (PP) [17], poly(vinylidene fluoride) (PVDF) [18,19] and polytetrafluoroethylene (PTFE) [20] for preparing porous MD membranes. PVDF membranes have been widely used in membrane contactor applications due to their high mechanical and chemical stabilities, and good processability. However, original properties of commercial PVDF membranes like hydrophobicity are not satisfied in VMD. Thus, hydrophobic modification to achieve composite membranes with desired properties for VMD is essential [21–23].

Several modification methods, such as radiation grafting, plasma polymerization, surface coating and blending to optimize membrane properties have been investigated [24–31]. Some hydrophobic materials were applied to modify PVDF membranes to improve MD performance [32–34]. A commercial product called Hyflon AD copolymer, which is a family of copolymers of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), has attracted much attention. Hyflon AD exhibits excellent hydrophobicity, high temperature stability and chemical resistance [35–38]. In addition, it can provide uniform and thin films by casting or coating techniques and different thermal treatments [39]. Gugliuzza et al. [40] selected PVDF and Hyflon AD60 as raw polymers to prepare composite membranes. The combination of these two fluorinated polymers obviously improved the hydrophobicity of the PVDF membranes. The composite membrane with well-controlled structures and excellent surface properties is suitable for membrane contactors.

It is interesting to combine Hyflon AD with PVDF hollow fiber membranes to prepare Hyflon AD/PVDF composite membranes for VMD. In our previous work [41], Hyflon AD60 was utilized to prepare Hyflon AD60/PVDF composite hollow fiber membrane. The properties of PVDF hollow fiber membrane were significantly improved and exhibited favorable stability in VMD. However, depending on the composition contents of TFE and TTD, there are three different Hyflon AD copolymers. They possess various chemical structure and properties, and thus may lead to different performances in the preparation of the composite membranes. In addition, the effects of the fabrication parameters on membrane separation performance are still unclear.

Therefore, in this paper, two kinds of Hyflon AD materials (Hyflon AD40L, Hyflon AD40H) were selected to prepare Hyflon AD/PVDF composite membranes for VMD. The properties, such as morphology, water contact angles, mechanical strength and VMD performance of the composite membranes were studied. The effects of a number of fabrication parameters, such as pre-filling, coating polymer concentration, coating time, heat treatment temperature and heat treatment time on membrane properties and separation performance were systematically investigated.

2. Experimental

2.1. Materials

Hyflon AD amorphous perfluoropolymers, Hyflon AD40L (intrinsic viscosity: 0.4 dl/g @ 30 °C) and Hyflon AD40H (intrinsic viscosity: 1.3 dl/g @ 30 °C), were kindly supplied by Solvay Specialty Polymer (Bollate Italy) [42]. 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 (3M Inc.) was used as the solvent for Hyflon AD copolymers. Analytical grade sodium chloride (NaCl) and pore pre-filling agents (methyl alcohol, ethanol, ethanediol, glycerin and n-hexane) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Sodium hypochlorite (NaClO) solution was purchased from Jiangsu Yangnong Chemical Group Co., Ltd. Wetting liquid (GQ-16) was purchased from Jiangsu Gaoqian Function Material Co., Ltd.

2.2. Preparation of Hyflon AD/PVDF composite hollow fiber membranes

The commercial PVDF hollow fiber membranes were prepared by phase inversion and post-treated by glycerol solution to protect the pore structure. To remove the protective glycerol and poly(vinyl pyrrolidone), the PVDF membranes were immersed in ethanol for 1 h, and then in sodium hypochlorite solution with a concentration of 8 g/L for 3 h before coating. The treated membranes were named as original membranes. Treated membranes were coated with Hyflon AD and labeled as Hyflon AD/PVDF composite membranes. The fabrication procedure of the composite membranes can be found in our previous study [41]. Different Hyflon AD solutions with a series of concentration were prepared by mixing Hyflon AD powder (Hyflon AD40L or Hyflon AD40H) and Novec HFE-7100. Original PVDF hollow fiber membranes were blocked at both ends and dipped into the Hyflon AD solutions for different period of time. Finally, the coated membranes were taken out and heated at desired temperatures for several hours.

2.3. Membrane characterization

2.3.1. Scanning electron microscopy (SEM)

Field emission scanning electron microscopy (FESEM, Hitachi S4800, Japan) was used to examine the cross-section and surface morphologies of the hollow fiber membranes. The original and composite membrane samples were frozen in liquid nitrogen and fractured, then positioned on a holder and sputtered with gold/palladium alloy under vacuum using an E-1010 Ion Sputtering device (HITACHI, Japan), before taking SEM images.

2.3.2. Porosity

The gravity method was selected to measure the overall porosity. Hollow fiber membranes were blocked at both ends and immersed in kerosene for 24 h. After blotting the surface, the wetted membranes were weighed by a digital microbalance. Then, the wet membranes were dried in an oven at 80 °C until the weight of the membrane became stable. The porosity of the hollow fiber membrane (ε) was calculated by:

$$\varepsilon = \frac{(w_w - w_d)/\rho_k}{(w_w - w_d)/\rho_k + w_d/\rho_p} \times 100\% \tag{1}$$

where w_w is the weight of the wet membrane (g), w_d is the weight of the dry membrane (g), ρ_p and ρ_k are the densities of PVDF (1.78 g/cm^3), and kerosene (0.82 g/cm^3), respectively.

2.3.3. Hydrophobicity characterization

The hydrophobicity of the PVDF membrane and composite membrane was characterized by measuring water contact angle using DropMeter A-100 (MAIST Measurement Co., Ltd., China). DI water droplets with a diameter of 0.4 μL were dropped onto membrane surface at room temperature. The images were captured by a digital camera allowing apparent static contact angles to be measured. Each sample was measured at five different positions to obtain the average value.