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Fabrication and characterization of superhydrophobic polypropylene hollow fiber membranes for carbon dioxide absorption

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ABSTRACT

The membrane wetting by amine absorbents results in performance deterioration of membrane gas absorption system for CO_2 post-combustion capture. To solve this problem, in this study, the polypropylene membrane fiber was modified by depositing a rough layer on the surface to improve its hydrophobicity. Weighing the coating homogeneity, hydrophobicity and modification process efficiency, the mixture of cyclohexanone and MEK system was considered as the best non-solvent. The contact angle increased dramatically from 122° to 158° by the modification, thereby obtaining superhydrophobic membrane surface. The membrane–absorbent interaction results demonstrated that the modification treatment effectively enhanced the stability and maintained the superhydrophobicity of fibers contacting with the absorbent. In addition, continuous CO_2 absorption experiments for up to 20 days were carried out in untreated and modified polypropylene hollow fiber membrane contactors, using 1 mol L^{-1} MEA solution as the absorbent. The long-term system operation results indicated that, even though additional mass transfer resistance was introduced by the surface coating, the modified polypropylene hollow fiber membrane contactor was still technically feasible for CO_2 capture from the power stations.

1. Introduction

Carbon dioxide capture and storage in geological formations (CCS) has been examined as one of technically viable options for mitigating atmospheric CO_2 levels due to human activities. Currently, a wide variety of technologies have been proposed to capture CO_2 from the combustion of fossil fuels, such as chemical and physical absorption, solid adsorption, cryogenic distillation and membrane techniques [1–4]. Among these, chemical absorption has been used in the chemical industry for decades as the most well established technology, but it has several disadvantages such as large space, high capital cost and a variety of operational problems, e.g. liquid channeling, flooding, entrainment and foaming. Therefore, many researchers have examined the possibilities by combining two or more technologies to enhance the efficiency of these processes and to reduce the effect of their drawbacks.

Membrane gas absorption technology completely integrates the membrane separation and the absorption processes in order to exploit the benefits of both technologies. In comparison with conventional absorption equipments such as packed towers or bubble columns, the membrane gas–liquid contactor has the features of flexible operation, high surface-area-to-volume ratio, compact size, linear scale-up and modularity, making them attractive for offshore applications [5–7]. Due to its excellent mass transfer properties, membrane gas absorption has currently been considered as one of promising alternatives to conventional technologies for CO_2 mitigation [8]. A feasibility study has also demonstrated that membrane gas absorption technology is a technically viable and economically feasible method for capturing CO_2 from large-scale power plants [9].

Although the membrane contactor offers many advantages over conventional contacting equipment, additional mass transfer resistance is introduced due to the existence of membrane phase. The membrane micropores can be theoretically filled with either gas for the hydrophobic membrane or liquid for the hydrophilic membrane, corresponding to non-wetting mode and overall-wetting mode, respectively. For membrane gas absorption system, it is essential to avoid a strong increase in mass transfer resistance in a liquid filled membrane pore compared to a gas filled pore. This indicates that the absorption liquid is not allowed to enter the membrane pores over prolonged period of operation time. However, in practical application, the aqueous solutions with organic absorbents can penetrate into partial pores of the hydrophobic membrane. Then the membrane pores are gradually wetted over

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long-period operation time, leading to the increase of overall mass transfer resistance and deterioration of membrane performance. Atchariyawut et al. [10] experimentally observed that, when 2 mol L^{-1} MEA was used as the absorbent in hydrophobic porous polyvinylidenefluoride (PVDF) hollow fiber membrane contactor, the CO_2 flux continuously decreased about 43% of the initial flux due to membrane wetting during 15 days' operation. The simulation results of Zhang et al. [11] also revealed that for the physical absorption of CO_2 by water, the proportion of membrane phase resistance in the overall mass transfer resistance increased from less than 5 to about 90% when the operation mode was shifted from non-wetted mode to wetted mode. Therefore, the membrane wetting has to be addressed first in order to ensure efficient absorption process and long-term operation stability.

The membrane with higher hydrophobicity is more resistant to wetting. Different polymeric materials such as polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidenefluoride (PVDF) have been used for CO_2 absorption in hollow fiber membrane contactors [12–15]. Only microporous PTFE membrane shows good gas absorption performance and stability without membrane wetting by MEA aqueous solutions for more than 6600 h due to its higher hydrophobicity [12]. However, the application of PTFE is limited for its high production cost and is unavailable in small diameters [16]. Compared with other fibers, PP membrane exhibits comprehensive applications due to wide size range, high void volume, well-controlled porosity, high thermal and chemical stability, and low cost [17].

In our previous work [18], the PP membrane fibers were immersed into different absorbents for up to 90 days to investigate the compatibility between the absorbents and the PP membrane fibers. The experimental results revealed that the membrane–absorbent interaction leads to a significant decrease in the membrane surface hydrophobicity, following more serious wetting phenomenon. It was also concluded that improving the membrane hydrophobicity is a more effective way to overcome wetting than decreasing the membrane pore size. The membrane hydrophobicity can be improved by pretreatment on the surface with fluorocarbonic material [12], but the modified membrane still tended to be wetted due to the capillary condensation. Other processing methods to achieve superhydrophobic surfaces might be time-consuming with high cost. Erbil et al. [19] successfully obtained a superhydrophobic isotactic-polypropylene (i-PP) porous membrane with the contact angle of 160° by dissolving granular PP in the solvent mixture and further evaporating the solvent. In their membrane modification experiments, this simple and low-cost method for forming a superhydrophobic coating was applied on a wide variety of dense substrates to obtain a homogeneous film of porous gel-like structure. Based on their work, Julianna et al. [20] applied such solvent casting techniques on the coating of porous polypropylene filter discs to achieve superhydrophobic surface. The 21.4 mg mL^{-1} concentration of polypropylene in solution was optimized to achieve the highest contact angle of 169°, which was 42° higher than that of the untreated PP membrane and even 30° higher than that of PTFE membrane. Therefore, it can be inferred that fabricating a superhydrophobic surface on porous PP hollow fiber membrane may be an alternative to eliminate the influence of membrane wetting on performance deterioration. However, compared with the above successfully modified substrates including the glass slides, high-density polypropylene, and 4.7 cm diameter polypropylene filter discs, it would be much more difficult to modify the microporous hollow fibers with the outer diameter of 500 μm using such solvent casting techniques at such a small size. In addition, the modification treatment may result in an increase in membrane thickness and a decrease in surface porosity, which may offset the advantages of membrane gas absorption technology. Therefore, detailed studies are needed to investigate the effects of surface modification on membrane characteristics, especially on the long-term performance of the modified membrane contactor for CO_2 post-combustion capture.

In this study, a rough layer was deposited on microporous PP hollow fibers used in practical membrane contactor. Then the membrane fibers before and after the modification were characterized by means of field emission scanning electron microscopy (FE-SEM), mercury intrusion porosimetry (MIP), atomic force microscopy (AFM) and contact angle goniometer measurements, to investigate the effects of modification on the membrane properties. After the modified fibers were assembled in a membrane contactor, a long-run test on the performance of membrane gas absorption system was carried out. This study aims to investigate the feasibility of enhancing the properties and durability of PP hollow fiber membrane contactor by surface treatment for CO_2 capture from power stations.

2. Experimental

2.1. Preparation of superhydrophobic membrane surface

Commercial grade PP hollow fibers (Tianjin Blue Cross Membrane Technology Co., Ltd., China) were used as the modification substrate. Xylene (Shanghai Bangcheng Chemical Co., Ltd., China) was selected as the solvent to dissolve the granular PP. Methyl ethyl ketone (MEK), cyclohexanone, and the mixtures of MEK and cyclohexanone with the weight ratio of 1:1 were used as the non-solvents, respectively, to accelerate the nucleation rate and create smaller aggregates.

The flask containing 0.7 g of granulated polypropylene and 30 mL of xylene was placed in a heating mantle and heated to 130 °C. The flask was constantly stirred by a magnetic stirring bar to prepare uniform polypropylene solution. After the granulated polypropylene was completely dissolved in the xylene, a 20 mL of the non-solvent was added in the solution to optimize the preparation process [20]. Then the prepared uniform hot solution was deposited onto the original PP hollow fiber membrane fibers which were positioned on a spin coater. The spin coater was rotated at 2000 rpm for 40 s. The coated membrane fibers were cleaned with ethanol to eliminate the residual solution and were subsequently dried under the vacuum oven at 70 °C for three hours. During the modification process, the following fiber module assembly and long-term system operation, no broken fibers were observed.

2.2. Membrane characterization and measurement

2.2.1. Field emission scanning electron microscope (FE-SEM)

The structural and morphological characteristics of the membrane fibers before and after the modification were characterized by FE-SEM. The PP hollow fibers were positioned on a metal holder and were gold coated using a sputter coating under vacuum for 40 s to prevent charging. The fibers were then observed under a JEOL JSM-7401F FESEM to investigate the surface morphologies. The accelerating voltage used was 5 kV. The images were captured by a video recorder attached to a Macintosh computer system. Images from three different areas of each sample surface were recorded.

2.2.2. Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry investigation was carried out under Poremaster GT-60 produced by USA Quantachrome Instruments, to characterize the total porosity and pore size distribution in the membrane fibers before and after the modification. Before the MIP testing, all the samples were dried up at 50 °C for 24 h and each MIP value was the average of three measurements.