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Microporous polyvinylidene fluoride hollow fiber membrane contactors for CO₂ stripping: Effect of PEG-400 in spinning dope

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A B S T R A C T

In order to develop the structure of microporous PVDF membranes, PEG-400 was introduced into the polymer dope as a non-solvent additive. The hollow fiber membranes were prepared via a wet phase-inversion process and then used in the membrane contactor modules for CO₂ stripping from water. By addition of different amounts of PEG-400, cloud points of the polymer dope were obtained to examine phase-inversion behavior. From FESEM analysis, the membrane structure changed from a finger-like to an approximately sponge-like morphology with the addition of 4 wt.% of PEG-400. The prepared membranes presented smaller mean pore size (0.13 μm) and significantly higher wetting pressure (550 kPa) compared to the plain membrane. From CO₂ stripping test, at water velocity of 0.4 m/s, the PVDF membranes prepared by 4% PEG-400 demonstrated an approximate CO₂ stripping flux of 4.5×10^{-5} (mol/m² s) which is 125% higher than the flux of the plain membrane. It could be concluded that structurally developed hydrophobic PVDF hollow fiber membranes can be prepared by a controlled phase-inversion process to enhance the performance of gas-liquid membrane contactor.

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Keywords: PVDF hollow fiber membrane; Non-solvent additive; Phase-inversion; Characterization; CO₂ stripping; Membrane contactor

1. Introduction

Carbon dioxide (CO₂), which is rising due to combustion of fossil fuels worldwide, has been responsible for global climate change because of its greenhouse effect. So far, several technologies such as absorption column, cryogenic distillation, scrubbers and adsorption column have been developed to capture CO₂ from the outlet gas streams (Lecomte et al., 2010). Recently, membrane technology has gained a wide range of applications in different industrial areas owing to small footprint and low capital cost. Polymeric membranes due to ease of fabrication, availability and low cost of different polymers have also attracted considerable attentions. Using membrane contactor technology for CO₂ capture has been started since 1980s and numerous studies are going on thanks to the advantages over traditional contacting devices (Gabelman and Hwang, 1999; Klaassen et al., 2005; DeMontigny et al., 2006; Mansourizadeh and Ismail, 2009, 2011a). Despite CO₂

absorption by membrane contactors, the studies on CO₂ stripping from physical and chemical liquid absorbents have started recently and there are a few reports documented in the open literature (Koonaphapdeelert et al., 2009; Mansourizadeh and Ismail, 2011b; Khaisri et al., 2011; Mansourizadeh, 2012; Naim et al., 2012a,b). Since CO₂ stripping for regeneration of the liquid absorbents in gas separation industries is the most energy consuming process due to high heat requirement, further investigations to develop the technology is deemed necessary. It should be noted that the absorbed CO₂ in the liquid phase can cause serious operational and economical problems. In the case of dissolved CO₂ in water, it can increase acidity and corrosion nature of the water which results in increasing maintenance costs. A common method to remove CO₂ from water is the aeration process using columns. However, CO₂ stripping using membrane contactors can be an alternative; in fact, pH level of water can be increased by stripping without addition of chemicals which causes

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lower environmental and economical impacts. Furthermore, the scaling species such as CaCO_3 , Mg(OH)_2 and $\text{Ca}_3(\text{PO}_4)_2$ can possibly be removed from brackish and waste waters by increasing PH using CO_2 stripping method (Lisitsin et al., 2008).

In gas–liquid membrane contactor, the porous membrane acts as a barrier between the phases. The membrane is not selective and the pores should be filled with the gas phase. The driving force of mass transfer is the concentration difference between the gas and liquid phases and there is no convective flow through the membrane pores. Due to indirect contact of the phases, the membrane adds an extra resistance to the mass transfer process compared to the traditional contactors. Moreover, partial wetting of the membrane pores can significantly decrease separation performance (Wang et al., 2005). Therefore, the porous membrane is required to possess essential properties like high surface porosity (permeability), high wetting resistance and good mechanical and chemical stability. These requirements can be fulfilled by using hydrophobic polymers such as polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), which possess low values of surface energy (Khayet et al., 2006). PVDF is the only hydrophobic polymer that can be dissolved in common solvents to prepare asymmetric membranes via phase-inversion process. In fact, the fabrication parameters during phase-inversion can be controlled to develop the membrane structure for contactor applications. Research on the improvement of PVDF membrane structure for CO_2 stripping is limited in the literature. Naim et al. (2012a) studied the effect of lithium chloride (LiCl) in the spinning dope on the structure and performance of the PVDF hollow fiber membranes for CO_2 stripping from the diethanolamine (DEA) solution. By addition of 5 wt.% of LiCl, the highest stripping flux of $1.61 \times 10^{-2} \text{ mol/m}^2 \text{ s}$ was achieved at 110 ml/min of the liquid flow rate. This was related to the improved membrane structure. Rahbari-Sisakht et al. (2013a,b) used surface modifying macromolecules (SMM) to enhance hydrophobicity of the PVDF hollow fiber membranes for CO_2 stripping from diethanolamine solutions. In a previous study (Mansourizadeh, 2012), by introducing 5% glycerol in the spinning dope, the PVDF membrane structure was developed for CO_2 absorption/stripping via gas–liquid membrane contactors and the effect of main operating conditions on CO_2 absorption/stripping flux of the membrane was investigated.

Polymeric non-solvent additives like poly (vinylpyrrolidone) PVP and polyethylene glycol (PEG) have extensively introduced into the PVDF solutions in order to improve porous membrane structure for different applications (Shi et al., 2008; Hou et al., 2009; Wongchitphimon et al., 2011; Mansourizadeh and Ismail, 2011c; Tang et al., 2012). It was found that by addition of 5 wt.% of PEG-400 in the PVDF solution the prepared membranes presented enhanced properties (compared to the other non-solvent additives) for CO_2 stripping from the DEA solution (Naim et al., 2012b). Due to outstanding property of PEG for PVDF membrane preparation, an attempt was made to improve the membrane structure by optimizing PEG-400 in the spinning dope based on the ternary phase diagrams of polymer/solvent-additive/water system. Phase-inversion behavior of the polymer solutions was studied via cloud point measurements. The prepared membranes were characterized in terms of morphology, gas permeation, wetting resistance, hydrophobicity, mechanical stability and overall porosity. CO_2 stripping performance of the membranes was investigated through the gas–liquid membrane contactor module using CO_2 loaded water as the liquid phase.

Table 1 – Characteristics of PVDF spinning dopes.

Polymer dope	PEG-400 (wt.%)	Dope viscosity (cp at 25 °C)
M1	0	2075
M2	2	2270
M3	4	2465

2. Experimental

2.1. Preparation of PVDF hollow fiber membranes

Commercial PVDF polymer pellets (Kynar® 740) were supplied by Arkema Inc., Philadelphia, USA and dried in a vacuum oven at 60 °C before preparing polymer solutions. 1-methyl-2-pyrrolidone (NMP, >99.5%) (Merck) was used as polymer solvent. PEG-400 was supplied by Merck and used as non-solvent additive in the polymer dope.

The spinning dopes, containing 17 wt.% of PVDF and PEG-400, were prepared at 60 °C using constant stirring until the solutions became homogeneous. The composition and viscosity of the spinning dopes are given in Table 1. The solutions were de-bubbled using 30 min sonication and kept at room temperature for 24 h before spinning. The hollow fiber spinning process by the dry–wet phase-inversion was explained elsewhere (Ismail et al., 1999). The details of spinning conditions are given in Table 2. The prepared nascent membranes were immersed in tap water for 3 days to induce solvent/non-solvent exchange. By immersion of fibers in pure ethanol (Merck) for 15 min, post treatment process was conducted to prevent pore collapse and shrinkage before drying at room temperature.

2.2. Cloud points measurements of the polymer dopes

In order to measure cloud point data, the polymer dopes with different polymer concentrations (range: 1–17 wt.%) were prepared by setting the amount of 6 and 3 wt.% of PEG-400 in additive/solvent mixture. The cloud point data were obtained using titration method by adding distilled water into the polymer dope under constant magnet stirring at 25 °C. In cases of local precipitation in the solutions, especially at higher polymer concentration, stirring was continued until the solution became homogeneous again. Further addition of water was performed until the solution became permanently turbid at low polymer concentration or showed signs of gelation at high polymer concentration, which are the titration end point. Subsequently, the compositions at the cloud point were calculated by weight.

Table 2 – Hollow fiber spinning conditions.

Dope extrusion rate (ml/min)	4.0
Bore flow rate (ml/min)	1.6
Bore composition (wt.%)	NMP/H ₂ O 70/30
External coagulant	Tap water
Air gap distance (cm)	0.0
Spinneret o.d./i.d. (mm)	1.2/0.55
Spinning dope temperature (°C)	25
External coagulant temperature (°C)	25

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