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Study on CO_2 stripping from water through novel surface modified PVDF hollow fiber membrane contactor

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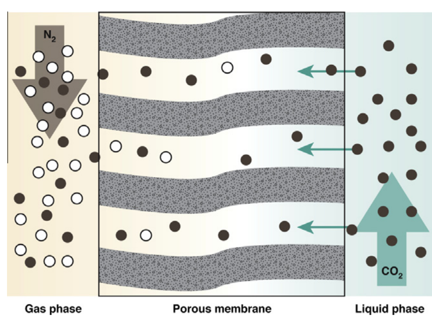
HIGHLIGHTS

- Different amounts of SMM were used to improve the surface hydrophobicity of PVDF HFM.
- The PVDF HFMs were used in contactor application for CO_2 stripping from water.
- The CO_2 stripping flux and efficiency increased by increasing SMM concentration.
- The gas flow rate has no significant effect on the CO_2 desorption flux.

GRAPHICAL ABSTRACT

Schematic of CO_2 stripping mechanism through gas–liquid membrane contactor.



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ABSTRACT

Dry–wet phased inversion method was used to fabricate polyvinylidene fluoride (PVDF) hollow fiber membranes. Different concentration of surface modifying macromolecules (SMM) i.e., 2, 4 and 6 wt.% were used as additives in the spinning dope. In the phase inversion SMM migrates to the membrane surface and changes the surface morphology with chemical properties on the membrane surface. This modification results into larger pore size, higher gas permeance, effective surface porosity and water contact angle. The surface modified membrane was used in membrane contactor for CO_2 stripping from water by using self-fabricated gas–liquid membrane contactor module. The result of CO_2 stripping experiment shows that the performance of surface modified membrane is better than plain PVDF membrane. CO_2 desorption flux increased with respect to SMM concentration, considerably. The membrane fabricated with 6 wt.% SMM as additive showed higher CO_2 desorption flux and efficiency of 2.1×10^{-3} (mol m^{-2} s^{-1}) and 80%, respectively at 200 ml/min of liquid flow rate. For this membrane CO_2 stripping flux was investigated for different liquid phase temperature. It was found that desorption flux increased by increasing liquid temperature and the highest stripping flux was obtained in the temperature of 90 °C. The enhancement of the gas flow rate increased the CO_2 desorption flux but this change was negligible.

1. Introduction

CO_2 is the main responsible for greenhouse effects and climate change. Recently, many techniques have been reported for CO_2

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Nomenclature

$C_{l,o}$	CO_2 concentration in the outlet liquid (mol m^{-3})	J_{CO_2}	CO_2 desorption flux (mol m^{-2} s^{-1})
$C_{l,i}$	CO_2 concentration in the inlet liquid (mol m^{-3})	η	stripping efficiency
d_i	inside diameter of membrane (m)		

capture/stripping by researchers. Hollow fiber membrane contactor is one of the interesting and promising methods for CO_2 absorption/desorption [1–5]. In this technique membrane acts as a barrier between gas and liquid phases and increases the contact area between the phases without dispersing if the differential pressure between the phases is effectively controlled. Hence, wettability property of the membrane is very important factor in gas–liquid contactor. The membrane wetting is directly proportional to mass transfer resistance of membrane and inversely proportional to CO_2 absorption and desorption flux. Therefore, pores of membrane should be gas filled to prevent membrane wetting.

Membrane pore wetting can be largely avoided by increasing hydrophobicity of membrane surface. Hydrophobic surface modifying macromolecule (SMM) is one of the best approaches to increase the membrane surface hydrophobicity and can be used as an additive to the spinning dope [6]. Rana and Matsuura reviewed the chemical structure and properties of the hydrophobic SMM. They stated that after casting or spinning the polymer solution which is contain SMM as additive SMM tends to migrate to the membrane–air interface to reduce the interfacial energy of the system due to lower surface energy of SMM [7]. The fluorohydrocarbon end group of SMM is exposed to the surface while PDMS polyurea prepolymer is embedded in the PVDF matrix, as shown schematically in Fig. 1. Therefore, accumulation of SMM on the membrane surface changes the surface properties such as surface hydrophobicity.

Several reports have been published on CO_2 capture and stripping using hollow fiber membrane contactor which were fabricated using different polymers [8–10]. Naim and Ismail [11] fabricated polyetherimide HFM and used for CO_2 stripping from aqueous diethanolamine (DEA) solutions. The maximum CO_2 stripping flux of 2.7×10^{-2} mol/m^2 s was achieved using their fabricated membrane. In our previous work [12], polysulfone (PSf) HFM was produced and applied for CO_2 stripping from water. Results showed that liquid velocity and temperature are two important factors for gas stripping process while, gas velocity has no significant effect. Mansourizadeh and Ismail [13] investigated membrane morphology of PVDF HFM for CO_2 desorption from water. They found that the membranes which fabricated using phosphoric acid and PEG-400 showed higher stripping flux compared with control PVDF membrane. A regeneration unit was developed for CO_2 desorption from CO_2 loaded MEA solution using membrane contactor [14]. PTFE HFM was used to study the stripping performance. It was found that the CO_2 stripping flux increased with increasing liquid velocity, liquid temperature and MEA concentration. The 5 kmol m^{-3} MEA concentration showed highest CO_2 desorption flux.

In this work PVDF HFM was fabricated using different concentration of SMM in the spinning dope. The performance of the surface modified membranes was studied in membrane contactor system for CO_2 stripping from water. The effect of liquid and gas velocity on the CO_2 stripping efficiency and flux and the effect of liquid phase temperature on CO_2 stripping flux were investigated.

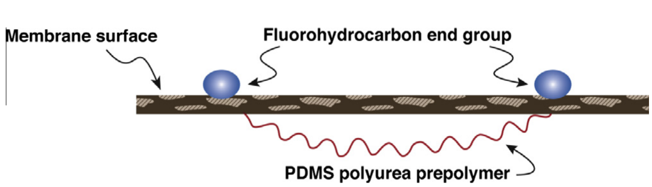

Fig. 1. Shematic of surface modified membranes surface and SMM.

2. Experimental

2.1. Preparation and characterization of hollow fiber membrane

Porous surface modified PVDF hollow fiber membranes were fabricated via the dry–wet spinning process for CO_2 absorption applications in our previous work [15]. Different amounts of SMM were used as additive in the spinning dope. The produced membranes were characterized in terms of gas permeation, wetting resistance, critical entry pressure for water, water contact angle, collapsing pressure and overall porosity. The details of fabrication and characterization of membranes were presented in our previous work [15]. The properties of the fabricated membrane are presented in Table 1.

2.2. CO_2 stripping experiment

Self-constructed membrane contactor module was used to study the CO_2 stripping efficiency of the prepared membrane. The total of 30 hollow fibers were packed randomly and used in membrane module. The details of the membrane contactor module are given in Table 2.

Pure nitrogen gas flowed through the shell side and distilled water preloaded with CO_2in another membrane contactor flowed through the lumen side of the hollow fibers in a counter-current flow mode. The pressure and the flow rate of both phases were controlled by control valves. In order to avoid bubbles formation in the liquid phase, the liquid phase pressure was set 0.2×10^5 Pa more than gas phase pressure. The temperature and pressure of the liquid phase in the experiment were maintained 80 °C and 0.5×10^5 Pa, respectively. The CO_2 concentrations of the liquid of the feed and outlet of the stripper module were measured to determine stripping flux and efficiency by using the double chemical titration method [16]. Initially, before collecting the samples the experiment was run for 30 min to achieve a steady state condition. Fig. 2 shows the flow diagram of the experimental setup. The CO_2 stripping efficiency (η) of the module was calculated as:

$$\eta(\%) = \left(1 - \frac{C_{l,o}}{C_{l,i}}\right) \times 100 \tag{1}$$

where $C_{l,o}$ and $C_{l,i}$ are the liquid phase CO_2 concentrations (mol/m^3) at outlet and inlet of the membrane module, respectively. The experimental CO_2 stripping flux was calculated based on the inner surface area of the hollow fibers as:

$$J_{CO_2} = \frac{(C_{l,i} - C_{l,o}) \times Q_l}{A_i} \tag{2}$$

where J_{CO_2} is the CO_2 stripping flux (mol/m^{2}s), Q_l is liquid flow rate (m^3/s), and A_i is inner surface area of the hollow fiber membranes.