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CO_2 absorption in flat membrane microstructured contactors of different wettability using aqueous solution of NaOH

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Abstract: CO_2 absorption in solutions of sodium hydroxide (NaOH) was performed in three membrane/mesh microstructured contactors: a single-channel polytetrafluoroethylene (PTFE) membrane contactor, a nickel mesh contactor and an eight-channel PTFE membrane contactor. A membrane/mesh was used to achieve gas/liquid mass transfer without dispersion of one phase within the other. The PTFE membrane consisted of a pure PTFE layer 20 μm thick laminated onto a polypropylene (PP) layer of 80 μm thickness. The pure PTFE layer contained pores of ~0.5 to 5 μm diameter and was hydrophobic, while the PP layer consisted of rectangular openings of 0.8 mm × 0.324 mm and was hydrophilic. The nickel mesh was 25 μm thick and contained pores of 25 μm diameter and was hydrophilic. Experiments were performed with a 2 M NaOH solution and an inlet feed of 20 vol % CO_2/N_2 gas mixture. Numerical simulations matched reasonably well the experimental data. CO_2 removal efficiency increased by increasing the NaOH concentration, the gas residence time and the exchange area between gas and liquid. Higher removal of CO_2 was achieved when the PP was in the gas side rather than in the liquid side, due to lower mass transfer resistance of the gas phase. For the same reason, CO_2 removal efficiency was higher for the eight-channel PTFE contactor compared to the nickel mesh contactor. Average CO_2 flux was higher for the eight-channel contactor (8×10^{-3} mol/min·cm^2 with PP on the gas side) compared to the nickel mesh contactor (3×10^{-3} mol/min·cm^2) for the same gas and liquid residence times. The eight-channel PTFE membrane contactor removed around 72% of CO_2 in 1.2 s gas residence time, demonstrating the potential for CO_2 absorption using flat membrane contactors.

Keywords: CO_2 capture; membrane contactor; microstructured contactor; NaOH absorbent.

1 Introduction

Carbon dioxide contributes significantly to global warming, which is considered as one of the most important challenges the world is facing. Current technologies for CO_2 absorption (packed or spray towers) [1–3] involve many environmental and economic drawbacks [4]. An alternative technology is the use of membrane contactors. These modules achieve gas/liquid or liquid/liquid mass transfer without dispersion of one phase within the other. Membrane modules are widely used for many industrial applications such as distillation, absorption and stripping [5–10].

CO_2 absorption in hollow fiber membrane modules has been widely explored during the last decades from different research groups. Atchariyawut et al. [11] studied the separation of CO_2 from CH_4 using polyvinylidene fluoride (PVDF) membranes. During chemical absorption of CO_2, a higher CO_2 flux was attained when aqueous sodium hydroxide (NaOH) solution was used compared to an equal concentration of aqueous amine solution of monoethanolamine (MEA). This was because of the higher reaction rate constant for CO_2 and OH^- compared to CO_2 and MEA. Sadoogh et al. [12] performed experimental studies to examine the stability of the PVDF hollow fiber membrane modules for CO_2 capture with MEA and diethanolamine (DEA) solutions. A decline of 43% on CO_2 flux was observed during the operation with MEA, while with DEA, 26% reduction was observed within 10 h of operation. In addition, membrane mass transfer resistance increased by ca. 16.8% for DEA and 20% for MEA. It was found that the increase of mass transfer resistance and the decline in CO_2 flux were due to the deformation of the membrane structure after a long time of operation.

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Khaisri et al. [13] considered CO_2 absorption using an aqueous solution of MEA in polytetrafluoroethylene (PTFE) hollow fiber membrane modules. They examined the influence of membrane wetting on the CO_2 absorption capability and the overall mass transfer coefficient. It was found that the overall mass transfer coefficient and CO_2 flux declined with an increase of membrane wetting. In addition, they compared experimental results with a model and showed that the absorption performance dropped by ~56% at 10% wetting. Masoumi et al. [14] investigated the absorption of CO_2 using alkanolamines and amino acids in hollow fiber membrane contactors (HFMCs). It was found that potassium glycinate (PG) had better performance on capturing CO_2 compared to other absorbents such as methyl diethanolamine, DEA and potassium sarcosine (PS) when relative high partial pressures of CO_2 were used. Furthermore, they showed that an increase of temperature, amino acid concentration and gas/liquid flowrates can increase CO_2 flux, while an increase of the membrane wetting can lead to the decline of the CO_2 flux.

Dindore et al. [15] studied CO_2 absorption in an HFMC using water and aqueous NaOH solutions as absorbents. They showed that the contactor can be used successfully for the determination of various physicochemical properties such as reaction rate constant, diffusivity and solubility. Lv et al. [16] studied experimentally the simultaneous removal of CO_2 and SO_2 in polypropylene (PP) HFMC using MEA as the absorbent. They observed that the absorption of SO_2 and CO_2 was enhanced by the increase in liquid flowrate and decrease in gas flowrate. Furthermore, CO_2 mass transfer rate significantly decreased with operating time due to partial wetting of membrane pores. Makhloufi et al. [17] performed CO_2 absorption experiments in ammonia using PP membranes and composite hollow fibers with two different dense skin layers (Teflon AF2400 and TPX). They showed that microporous membranes do not offer stable performance due to salt precipitation; however, dense skin membranes showed stable performance and higher CO_2 mass transfer compared to packed column. Mansourizadeh and Mousavian [18] fabricated microporous PVDF hollow fiber membranes to examine CO_2 absorption in DEA solution. They observed a steep change in CO_2 flux when liquid flowrate was altered due to the existence of the main mass transfer resistance in the liquid phase. Furthermore, CO_2 flux increased with increasing gas pressure and decreasing temperature. Rajabzadeh et al. [19] examined the stability of PVDF membranes using aqueous MEA solutions for CO_2 absorption. It was noticed that membranes with lower porosity and pore diameter were stable for a longer time (200 h), compared to membranes with larger porosity and pore diameter which were completely wetted during the first 100 h of operation, and absorption flux declined steeply.

Membrane microstructured contactors can be useful in reducing cost, saving energy, increasing safety and improving process efficiency due to their small channel size. In our previous studies [20], we used a microstuctured mesh contactor to absorb CO_2 using NaOH and DEA aqueous solutions as absorbents. NaOH showed higher CO_2 removal efficiency as compared to DEA. The comparison of the microstructured mesh contactor with other contactors exhibited it had the best performance. Recently [21], PTFE membrane contactors using amine solutions were investigated. Significant CO_2 capture was found for gas residence time <0.2 s. CO_2 removal was increased using a multi-channel PTFE contactor with higher surface area. In this work, these contactors are evaluated for CO_2 absorption in NaOH solution. In addition, emphasis is given on wetting by comparing membranes/meshes with different wetting characteristics. We also demonstrate that for supported membranes, the orientation of the membrane plays an important role.

2 Contactor design and experimental conditions

Three different contactors were used (UCL Mechanical Workshop, London, UK), an eight-channel nickel mesh contactor, a single-channel PTFE contactor and an eight-channel PTFE contactor. Their characteristics can be seen in Table 1, while more details about them can be found

Table 1: Geometrical characteristics of membrane/mesh contactors.

Contactor type/key properties	Eight-channel PTFE membrane contactor	Eight-channel nickel mesh contactor	Single-channel PTFE membrane contactor
Membrane/mesh pore size (μm)	0.5–5	25	0.5–5
Membrane/mesh porosity (%)	70	15	70
Membrane/mesh thickness (μm)	20	25	20
Gas-liquid exchange area (cm^2)	55.9	39.4	4.9

All contactors had overall dimensions of 192 mm × 97 mm, gas channel depth of 0.85 mm and liquid channel depth of 0.2 mm.

elsewhere [20–22]. To avoid breakthrough of one phase into the other (see Figure 1), the contactors were operated with pressure difference between the liquid and gas phase P_L-$P_G \approx 100$ cm H_2O for the PTFE membrane and P_G-$P_L \approx 30$ cm H_2O for the nickel mesh. Breakthrough of liquid to the gas phase occurred at P_L-$P_G \approx 200$–220 cm H_2O for the PTFE membrane, while for the nickel mesh at P_L-$P_G \approx 31$ cm H_2O. The apparent contact angle on porous PTFE membrane was found to be 145°. During typical operation, pressure drop was negligible (ca. 2 cm H_2O for the gas and liquid phases). Continuous operation of the PTFE membrane over a month did not show any sign of decreased performance. The PTFE membrane (Sterlitech, OH, USA) used in the experiments consisted of 20 μm thick pure PTFE supported on an 80 μm thick PP layer [21], while the nickel mesh (Tecan, Weymouth, UK) was 25 μm thick. In all experiments, gas was flowing above the membrane/mesh and liquid at the bottom of the membrane/mesh co-currently. Experiments were performed changing the flowrate of a 2 M NaOH (Sigma-Aldrich, Gillingham, UK) between 1.66 and 2.56 ml/min and that of CO_2/N_2 (20 vol %) between 160 and 354 ml/min for the single-channel PTFE contactor, and between 1.66 and 2.56 ml/min (liquid flowrate) and between 230 and 354 ml/min (gas flowrate) for the eight-channel PTFE and the nickel mesh contactor. All experimental data were collected at room temperature (ca. 20°C).

The CO_2 removal efficiency, X_{CO_2}, was obtained by the following equation:

$$X_{CO_2} = 1 - \frac{F_{CO_2,\,out}}{F_{CO_2,\,in}} \quad (1)$$

where F is the molar flowrate of CO_2. Each experiment was repeated at least three times, and the relative differences were less than ±5.0%.

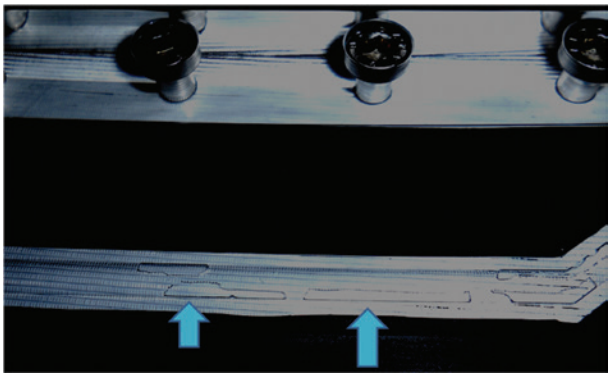

Figure 1: Picture of the top (gas) side of the single-channel contactor during breakthrough. The arrows indicate breakthrough of the liquid into the gas phase.

3 Numerical model

A two-dimensional (2D) model was developed to validate the experimental data of the PTFE membrane contactor. The concentration fields in the gas, membrane and liquid phase are governed by convection-diffusion-reaction equations and were presented in previous studies [21, 22]. The membrane was considered as a uniform medium with $D^M_{CO_2} = \frac{\varepsilon}{\tau} D^G_{CO_2}$, where ε is the membrane porosity (ca. 70%) and τ is the tortuosity (ca. 2.4) [23]. $D^M_{CO_2}$ is the diffusivity of CO_2 in the membrane, and $D^G_{CO_2}$ is the diffusivity of CO_2 in the gas phase. The following were the main assumptions: (1) steady-state operation; (2) ideal gas behavior is applicable; (3) Henry's law is valid for the equilibrium between the two phases; (4) plug flow profiles are assumed for both phases; (5) membrane pores are considered gas filled; (6) gas flowrates are considered constant; and (7) gas and liquid phases are considered to flow in the same direction. COMSOL Multiphysics 5.2a (Cambridge, UK) was used to solve the convection-diffusion-reaction equations. A mesh consisting of 561,421 number of elements and 1,252,378 degrees of freedom was used to perform the simulations in Windows 7 with Intel Core i5 2.7 GHz CPU and 64 GB of RAM, and computational time was around 3 min. No significant variation in the results was observed when the degrees of freedom were increased up to three times, proving that the solution was mesh independent.

4 Results and discussion

4.1 Effect of gas flowrate on CO_2 removal

To study the effect of the gas flowrate on CO_2 removal efficiency for the single-channel PTFE contactor, the experimental results were compared with the model predictions from CO_2 capture in the NaOH solution. Figure 2 shows the comparison of the experimental results with the model for CO_2 removal when the gas flowrate was varied from 160 to 247 ml/min. The experimental results were in reasonable agreement with model prediction. Differences between the experiments and the modelling may be due to the partial membrane wetting. By increasing the gas flowrate, the residence time in the contactor was reduced, and as a result, CO_2 removal efficiency decreased. Approximately 15%–20% of the initial CO_2 feed was captured within 0.102–0.157 s experimental gas residence time. These residence time values were calculated based on the contact of the gas volume (0.419 cm^3) with the membrane area. In a previous work [21] for the same residence times, CO_2

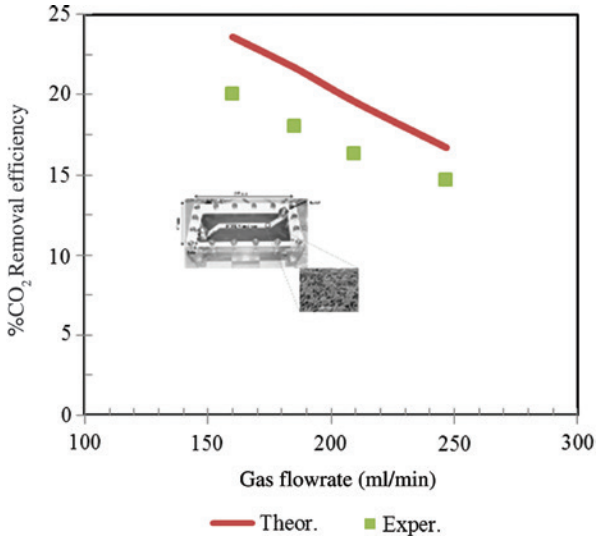

Figure 2: Amount of CO_2 removed from the gas phase as a function of gas flowrate, obtained experimentally and theoretically for the single-channel PTFE membrane contactor. PP support layer on the gas side. The gas to liquid flowrate ratio was 96.4.

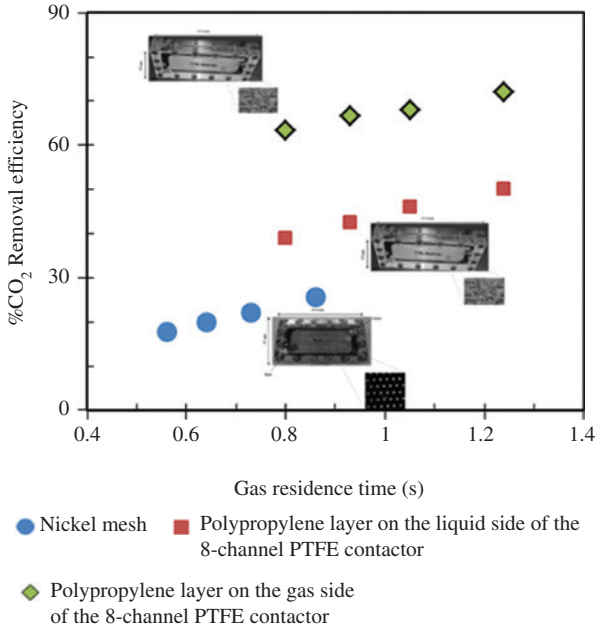

Figure 3: Amount of CO_2 removed from the gas phase as a function of gas-phase residence time for the eight-channel PTFE membrane contactor and the nickel mesh contactor. Gas to liquid flowrate ratio was 139.5.

removal efficiency was up to 14% using 2 M DEA solution with a flux of 0.008 mol/min·cm² and 18% using 2 M MEA solution with a flux of 0.011 mol/min·cm², showing that the NaOH solution in this work with a flux of 0.013 mol/min·cm² has higher CO_2 removal efficiency due to higher reaction rate constants.

4.2 Effect of membrane wetting characteristics on CO_2 removal

Figure 3 shows the results of the eight-channel (PTFE) membrane contactor and compares them with those of the nickel mesh contactor described previously [22]. Experiments were executed varying the liquid and gas flowrates within the range of 1.66–2.56 ml/min and 230–354 ml/min, respectively, for both contactors. The corresponding residence times for these flowrates were 0.8–1.24 s for the gas and 26.3–40.5 s for the liquid when the eight-channel PTFE membrane contactor was used, while for the nickel mesh, residence times were 0.56–0.86 s for the gas and 18.5–28.5 s for the liquid. Increasing the gas residence time increased the CO_2 removal efficiency. Despite the fact that the residence times were only slightly larger in the PTFE membrane contactor (PP in the gas side), the CO_2 removal efficiency was higher than the nickel mesh contactor. For a gas flowrate of 354 ml/min (gas residence time of 0.8 s), a liquid flowrate of 2.56 ml/min and a CO_2 removal efficiency of 63.2%, the average flux was 8×10^{-3} mol/min·cm² (PP in the gas side). When the PP was in the liquid side for the same gas and liquid flowrates and for a CO_2 removal efficiency of 39%, the flux was 4.9×10^{-3} mol/min·cm². For the nickel mesh for a gas flowrate of 230 ml/min (gas residence time of 0.86 s), a liquid flowrate of 1.66 ml/min and a CO_2 removal efficiency of 25.5%, the flux was 2.97×10^{-3} mol/min·cm². Hence, the flux on the PTFE membrane (PP in the gas side) was approximately 2.7 times higher than the flux of the nickel mesh and 1.6 times higher than the PTFE membrane (PP in the liquid side), indicating that the resistance to mass transfer is lower in the PTFE membrane (PP in the gas side) compared to nickel mesh and the PTFE membrane (PP in liquid side). The pores of the nickel mesh were liquid filled, and thus, there was more resistance to mass transfer than the PTFE membrane, whose pores were expected to be gas filled. As a result, the CO_2 removal efficiency was higher for the eight-channel PTFE membrane contactor. CO_2 removal efficiency was higher when the PP supporting layer was on the gas side rather than when it was on the liquid side. This was because the PP layer had large openings of 0.3 mm × 0.8 mm [21], which was filled with liquid when it was placed on the liquid side. Therefore, the resistance to mass transfer was larger.

4.3 Effect of the gas-liquid exchange area on CO_2 removal

The results of CO_2 removal for the eight-channel PTFE membrane contactor as a function of gas flowrate are

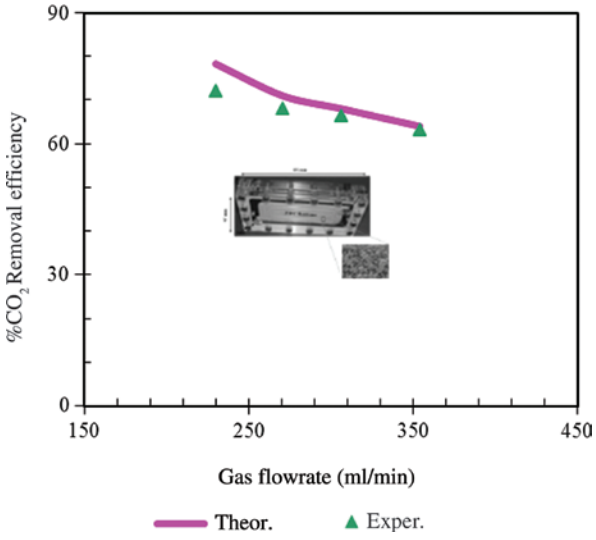

Figure 4: Amount of CO_2 removed from the gas phase as a function of gas flowrate, obtained experimentally and theoretically for the eight-channel PTFE contactor. PP support layer on the gas side. Gas to liquid flowrate ratio was 139.5.

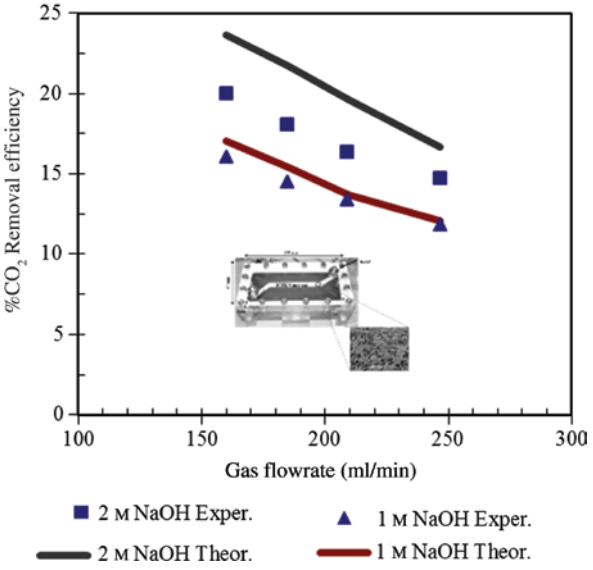

Figure 5: Amount of CO_2 removed from the gas phase as a function of gas flowrate, obtained experimentally and theoretically for the single-channel PTFE membrane contactor. PP support layer on the gas side. Gas to liquid flowrate ratio was 96.4.

presented in Figure 4. Numerical simulation predictions matched reasonably well the experimental data and indicated the decrease of CO_2 removal by increasing the gas flowrate. Comparing Figure 2 with Figure 4, it can be seen that the CO_2 removal efficiency was higher for the eight-channel PTFE contactor compared to the single-channel one. Under the same gas flowrates, it acquired between 0.1 and 0.16 s (experimental residence times) to achieve ca. 14.7%–20% CO_2 removal with the single-channel PTFE contactor, while ca. 63%–72% of the initial CO_2 feed was captured between 0.8 and 1.24 s using the eight-channel PTFE contactor. The larger gas/liquid exchange area (55.9 cm^2) of the eight-channel contactor (ca. 11.3 times bigger than the exchange area of the single-channel contactor) resulted in higher gas residence time for CO_2 to react with the NaOH solution, leading to higher CO_2 removal efficiency.

4.4 Effect of NaOH concentration on CO_2 removal

The experimental and theoretical results for two different NaOH concentrations for CO_2 removal as a function of gas flowrates are shown in Figure 5. Lower NaOH concentration leads to less CO_2 removal efficiency due to the associated lower reaction rate. The same observation was reported by Al-Marzouqi et al. [24] in their work of chemical absorption of CO_2 in PP membrane contactors; they showed that by increasing the concentration of NaOH from 0.005 M to 0.01 M, CO_2 removal efficiency increased. Similarly, Aroonwilas et al. [25] showed that increasing the NaOH concentration improved the CO_2 absorption performance.

4.5 Comparison with other absorbents and contactors from the literature

The comparison of our experimental results obtained by the eight-channel and the single-channel PTFE contactors with HFMCs from the literature is discussed below based on a modified gas residence time (defined as the surface area of gas/liquid exchange area over inlet volumetric gas flowrate), which is more appropriate as it includes the exchange area of the membrane. Kim and Yang [26] studied CO_2 absorption through hollow fibers using different aqueous absorbents. They aimed to capture 85%–100% of CO_2 from an inlet stream of 40 vol % CO_2/N_2 using solutions of MEA (2 M) within 16 s (gas residence time) and 74 s/cm modified residence time. Marzouqi et al. [24] performed experiments with PP HFMCs. They removed up to 80% of CO_2 from an inlet stream of 10 vol % CO_2/CH_4 in 58 s gas residence time using 0.005 M NaOH solution and modified residence time of 257 s/cm. In this work, in the eight-channel contactor, around 72% of CO_2 was removed in 15 s/cm modified residence time with a 2 M NaOH. The

eight-channel contactor removed similar % of CO_2 at lower modified residence time than the other studies, due to a higher concentration of NaOH used and the lower reaction rate constant of MEA. An overall liquid-phase mass transfer coefficient, $K_L\alpha$, was obtained from $K_L\alpha = R_{CO_2}/\Delta C_M$, where R_{CO_2} is the CO_2 absorption rate per unit volume of the contactor (kmol m^{-3} s^{-1}), α is the gas-liquid contact area (m^2 m^{-3}) and ΔC_M is the logarithmic mean concentration difference of CO_2 [27]. Only the volume of the contactor occupied by the gas, the liquid and the membrane was considered. For the four experimental points of Figure 4, $K_L\alpha$ was found to be in the range 0.92–1.2 s^{-1}. Rangwala [28] obtained similar $K_L\alpha$ values in the range 1.09–1.23 s^{-1} for a 0.0254 m diameter module containing 0.3 mm outer diameter, 30 μm thick PP hollow fibers, during CO_2 absorption in a 2 M NaOH solution. The author further showed that overall mass transfer rates in that module were 8.6 times higher than those of a column packed with Raschig rings when using DEA as absorbent. The above indicates that flat membrane configurations give comparable performance with hollow fiber contactors, offering the possibility of process intensification.

5 Conclusions

CO_2 capture using NaOH solution was studied in a single-channel PTFE membrane contactor, a nickel mesh contactor and an eight-channel PTFE membrane reactor. Twenty percent of CO_2 was removed with gas residence times below 0.2 s. A numerical model was utilized to simulate the contactor, and the experimental results matched reasonably well the model predictions. It was observed that the wetting of the membrane plays a significant role in performance because it affects the resistance to mass transfer. The eight-channel PTFE membrane contactor showed higher CO_2 removal efficiency compared to the nickel mesh contactor because of the hydrophobic nature of the PTFE membrane, thus offering less resistance to mass transfer. Furthermore, the PP support layer of the PTFE membrane increased the resistance to mass transfer when it was placed in the liquid side of the contactor. These findings indicate the importance of using gas-filled membranes. CO_2 removal efficiency reduced with a lower concentration of NaOH, because a lower concentration provided lower reaction rate, and it increased by increasing the exchange area between gas and liquid. Comparing the eight-channel PTFE membrane contactor with HFMCs from the literature demonstrated that it has great potential for CO_2 capture and can be used as an alternative technology.

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