



Post-combustion CO₂ membrane absorption promoted by mimic enzyme

Muhammad Saeed, Liyuan Deng*

Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim 7491, Norway



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ABSTRACT

This work presents a CO₂ membrane absorption process using a K₂CO₃ solvent promoted by a Zinc complex containing a cyclic ligand of 1,4,7,10-tetracyclododecane (Zn-cyclen) in a membrane contactor. Zn-cyclen (referred as mimic enzyme in this work) resembles the natural enzyme carbonic anhydrase (CA), but is more stable, has a much longer life time and much smaller molecular weight (235 g/mol) compared with CA. The mass transfer resistances in the membrane, gas and liquid phases in the membrane contactor were determined. The effects of gas film and liquid film resistances on the overall mass transfer coefficient were studied by varying the gas and liquid velocities. A tubular, hydrophobic porous glass membrane contactor with pore size of 200 nm was used to study the CO₂ absorption in potassium carbonate (0.5 M K₂CO₃) solution promoted by different concentrations of mimic enzyme. The kinetic rate constant for absorption of CO₂ in the K₂CO₃ solvent promoted by mimic enzyme was increased by 10 fold compared to the experiment without mimic enzyme. The significantly improved CO₂ separation performance demonstrates a novel approach to the effective enhancement of CO₂ absorption by using a low cost, chemically stable mimic enzyme.

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1. Introduction

Carbon dioxide (CO₂) is the primary greenhouse gas emitted through human activities, and the combustion of fossil fuel accounts for 90% of the total CO₂ emissions [1]. Carbon capture and storage (CCS) has been acknowledged as an efficient and economical technique to regulate these emissions. Currently chemical absorption of acidic gases in a liquid stream is the most investigated technique for CO₂ capture. However, it is also known as an energy intensive process, which requires high capital investment and suffers several operational challenges [2–7].

The application of membranes to ensure a non-dispersive mass transfer interface between the gas and liquid phases (membrane contactor) is an emerging technique in gas/liquid contacting equipment. Compared with a conventional packed column (specific surface area 100–800 m²/m³), a membrane contactor can offer a much higher specific surface area (3000–30,000 m²/m³), smoother operation, and can evade several common operational problems seen with conventional contactors such as loading, flooding, channeling and entrainment [3,8,9]. The membrane in a membrane contactor determines the mass transfer area which remains constant at all operational conditions [10,11]. Several

studies on CO₂ capture technology show that membrane contactors have potential to perform better than packed column and other conventional contactors [12–17]. For instance, the defined geometry and simple hydrodynamics of a membrane contactor makes it easier to study the mass transfer and to take the advantages of different configurations such as parallel flow, cross flow, co-current and countercurrent flow of the contacting fluids [13].

The membrane in a membrane contactor should be highly permeable, gas filled inert interface with a low mass transfer resistance. For this purpose hydrophobic porous membranes have been extensively investigated in combination with aqueous absorbents for membrane contactors [18,19]. However, due to the loss of hydrophobicity over time and a relatively broad pore size distribution in most of the porous polymeric membranes, phase breakthrough or pore wetting has been a common problem in porous membrane contactors. Pore wetting and its effects have been investigated by several researchers [15,20–24]. Wang et al. [21] predicted a 20% decline in the overall performance with 5% pore wetting.

Inorganic membranes on the other hand have seldom been investigated for application in membrane contactors due to their hydrophilic nature [19]. Several inorganic membranes with hydrophobic surfaces have been reported in literature [25–28], but few used glass membranes. Glass membranes have a big advantage for application in a gas/liquid contactor, as they have well-

* Corresponding author.

E-mail address: deng@ntnu.no (L. Deng).

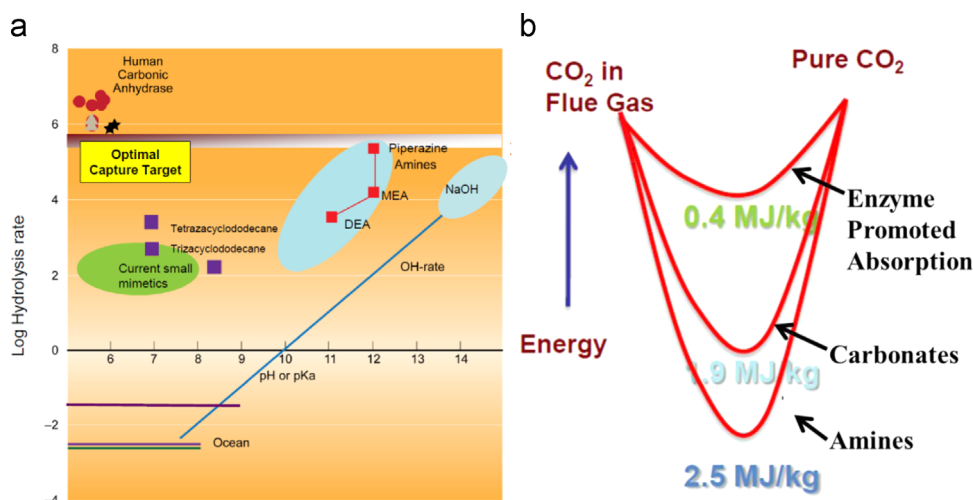


Fig. 1. (a) CO₂ hydration rate of different absorbents, and (b) energy demand for CO₂ capture by different absorbents, reprinted from [45].

structured pores with narrow pore size distribution, which enables an easy control to avoid pore wetting.

Absorption of CO₂ in a liquid stream usually involves a reversible reaction between acidic gas and the absorbent. Chemically absorbed CO₂ is then stripped from liquid stream by temperature swing to reverse the reaction and regenerate the absorbent. This regeneration of solvent is an energy intensive process and results in high operational costs. To address this challenge research is ongoing to find novel absorbents with low heat of reaction and high absorption capacity [29–31].

The absorption of CO₂ in the fast reactive solvent NaOH is a well-established technique [16,32]. Reaction between CO₂ and NaOH is fast, irreversible and literature on its kinetic data, is abundantly available. NaOH is often used as the absorbent in membrane contactors in order to investigate the contribution of membrane resistance. The influence of chemisorption of CO₂ in a membrane contactor using NaOH has been investigated by several researchers [10,11,16,28,32–35]. Atchariyawut [16,33] studied the absorption of CO₂ in water and NaOH solution to determine the contribution of membrane, gas/liquid films on mass transfer and evaluate different polymeric membranes. Constantinou et al. [28] evaluated nickel and silica mesh membranes by studying absorption of CO₂ in NaOH. The CO₂ absorption rate and kinetics using membrane contactors have also been investigated by several other researchers [15,36–38].

Aqueous solution of carbonate/bicarbonate of alkali metal and alkali earth metals have been widely recognized as absorbents for CO₂ capture due to their high CO₂ loading capacity and low heat of reaction. Absorption of CO₂ using potassium carbonate (K₂CO₃) in membrane contactors has also been studied. Due to its slow reaction kinetics K₂CO₃ needs to be promoted by some catalyst. The Benfield process is a commercial CO₂ capture process which use amine promoted aqueous K₂CO₃ absorbent [4]. Amines are highly reactive absorbents, yet the regeneration of the solvents is energy intensive. To address this challenge and reduce the energy consumption, a catalyst can be used as promotor for CO₂ capture. One option is the use of enzymes, such as carbonic anhydrase (CA).

The use of carbonic anhydrase (CA) to promote CO₂ absorption has become a research highlight in recent years [39–41]. Naturally occurring CA in human body has a fast and reversible reaction with CO₂ while producing minimal heat of reaction. The CA enzyme can speed up the hydration of CO₂ to bicarbonate and the reverse bicarbonate dehydration; CA has the ability to catalyze the hydration of 600,000 molecules of CO₂ per molecule of CA per second, 4000 times faster than MEA in terms of catalytic

activity whereas its energy consumption is almost 7 times less [42–44].

Although CA has shown appreciable enhancement in CO₂ separation properties, the limited lifetime of enzyme and the loss of activity by pH or temperature fluctuation have been proven to be major constraints in their commercial application [46–48]. Metal organic complexes that mimic the active sites of CA have gained much attention [49–54]. There are many metal organic complexes that can mimic the natural enzyme. Among them zinc (Zn) organic complexes have shown the highest activity [55,56]. Many different types of ligands can be attached to Zn metal to achieve the catalytic function. These ligands play an important role in determining the performance of the catalyst. Recently a facilitated transport membrane containing a mimic enzyme was reported with significantly improved CO₂ separation performance in a highly water swollen condition [57]. Zhang et al. [49,50] investigated the kinetics of CO₂ hydration and speciation of some Zn complex catalysts with cyclic ligands. Davy [51] compared the CO₂ hydration/dehydration of Zn complexes with CA and other complexes. William et al. [47] investigated the effect of Zn complexes concentration, pH of absorbent, operating temperature and bicarbonate concentration on the kinetics of CO₂ hydration by the Zn complexes (i.e., Zn-cyclen), and found that the catalytic activity of Zn-cyclen increased with increasing temperature (100–130 °C) and pH (> 12) and was retained after exposure to a 45% w/w K₂CO₃ solution at 130 °C for 6 days (Fig. 1).

This paper presents a novel CO₂ membrane absorption process using K₂CO₃ aqueous solution promoted by a zinc based metal-organic complex in a hydrophobic glass membrane contactor. Based on literature data, Zn based metal organic complex containing a cyclic ligand of 1,4,7,10-tetracyclododecane (Zn-cyclen) has a high catalytic activity and stability, and was therefore selected as the mimic enzyme in this work. The molecular weight of Zn-cyclen (235 g/mol) is much lower than CA, and its dissociation constant (pKa) is close to CA [49]. A highly efficient, hydrophobic porous tubular glass membrane with narrow pore size distribution was used for gas liquid contact to ensure well-structured pores for a simplified mass transfer study and to avoid pore penetration. The effect of pore size on the membrane contribution to mass transfer resistance was investigated. To the best of our knowledge, this membrane configuration and effect of membrane pore size have not been reported for membrane absorption applications. Membrane and gas/liquid film resistances were determined by studying CO₂ absorption in 1 M NaOH solution at various gas/liquid flow-rates. 0.5 M K₂CO₃ promoted by 3 different concentrations of

mimic enzyme (5,10 and 20 mM) were used to investigate the effect of mimic enzyme on the overall CO₂ removal efficiency with simulated flue gas at 25 °C, atmospheric pressure and different gas/liquid flow rates. Mimic enzyme shows significant influence on the CO₂ removal efficiency even at low concentrations (less than 20 mM). The experiment results in this study exhibit the potential of using highly efficient green solvents enhanced with mimic enzyme in membrane contactors for post-combustion CO₂ capture.

2. Theoretical background

2.1. Mass transfer in a membrane contactor

Mass transfer in a membrane contactor is analogous to heat transfer in a heat exchanger. The resistance-in-series model is commonly applied to determine the overall mass transfer coefficient in a membrane contactor, where resistance offered by each phase can be studied individually and minimized separately [33,58,59]. In this study, it is designed so that the gas stream flows in the tube side, and the liquid stream flows in the shell side of a tubular membrane contactor in a counter current flow. The CO₂ concentration profile in the gas, membrane and liquid phase is illustrated in Fig. 2. The relation between the mass transfer coefficient of each phase and the overall mass transfer coefficient is presented in Eq. (1).

$$\frac{1}{k_g} + \frac{1}{k_m} + \frac{1}{k_l} = \frac{1}{K_{ov}} \quad (1)$$

Where k_g , k_m and k_l are individual mass transfer coefficients of the gas, membrane and liquid film, respectively, and K_{ov} is the overall mass transfer coefficient. An elaborative form of this correlation is to involve phase equilibrium and reaction kinetics as is presented in Eq. (2). Here H is the Henry's law constant, where d_i , d_o and d_{in} are inner, outer and log mean diameters of the tubular membrane and E is the enhancement factor due to chemical reaction [16,59–62].

$$\frac{Hd_o}{k_g d_i} + \frac{Hd_o}{k_m d_{in}} + \frac{1}{Ek_l} = \frac{1}{K_{ov}} \quad (2)$$

For the shell side mass transfer coefficient, the most suited for this case is given in Eq. (3) [60].

$$Sh = 1.25(Re, d_h/L)^{0.93} Sc^{0.33} \quad (3)$$

Here Sh is Sherwood number, Re is the Reynolds number, Sc is the Schmidt number and G_z is the Graetz number. D is the diffusion

coefficient, L is the tube length and V_L is liquid velocity, d_i is tube internal diameter and d_h is hydraulic diameter of shell.

For the tube side mass transfer coefficient, fewer correlations are available as the flow regime is simpler and much better defined in the tube side compared with the shell side. As in this work gas stream containing 10% CO₂ in N₂ was used in the tube side, for calculation of individual mass transfer coefficient in the gas phase, the well-known Graetz–Leveque is used in this work as presented in Eq. (4) [16,60,63].

$$Sh = 1.62(G_z)^{1/3} \quad (4a)$$

$$G_z = \frac{v_L \cdot d_i^2}{D \cdot L} \quad (4b)$$

The calculation of membrane mass transfer coefficient is simpler compared with those in the liquid or gas phase, as in this work porous, hydrophobic glass membranes were used for gas/liquid contact with gas filled pores. Mass transfer coefficient in membrane can be calculated as per Eq. (5) [16].

$$k_m = \frac{D_E \epsilon}{l\tau} \quad (5)$$

Here k_m is the membrane mass transfer coefficient, D_E is the effective diffusivity of CO₂ in the membrane, $\frac{\epsilon}{\tau}$ is the ratio of porosity and tortuosity in the membrane (a dimensionless factor) and l is the thickness of the membrane [64]. In this case effective diffusivity of CO₂ in membrane is the same as in gas phase because the membrane pores are gas filled.

2.2. Chemical absorption of CO₂

The reactions between CO₂ in NaOH are presented as in (Eqs. (6a) and (6b)) [65]:



When CO₂ is absorbed in aqueous carbonate system, the overall reaction can be written as in Eq. (7) [66]:



The produced bicarbonate (HCO₃[−]) then reacts with hydroxyl (OH[−]) ions dissociated from water and reverts back to carbonate (CO₃^{2−}) as in Eq. (6b). The overall kinetics is governed by Eq. (6b), which is first order with respect to CO₂ and OH[−]. The expression for the reaction rate is given as:

$$r = k_{OH}[\text{CO}_2][\text{OH}^-] \quad (8)$$

Where r is the rate of reaction, k_{OH} is the second order rate constant, and $[\text{CO}_2]$ and $[\text{OH}^-]$ are the concentrations of free CO₂ and base in the liquid phase. As in this case, at low CO₂ loadings and high concentrations of OH[−], the reaction become independent of OH[−] concentration and is hence considered to be the first order with respect to CO₂. Mimic enzyme promotes the hydration of CO₂ but it does not appear in the overall reaction, functioning as a catalyst. The hydration mechanism of CO₂ by the mimic enzyme (Zn-cyclen) is presented in Fig. 3.

3. Experimental

3.1. Materials

The specially customized tubular glass membrane with

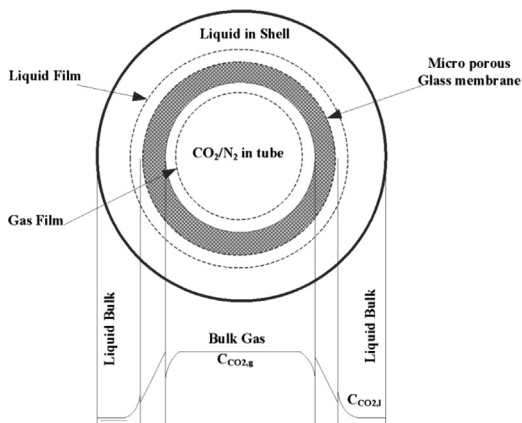


Fig. 2. CO₂ concentration gradients in gas, membrane and liquid phase.

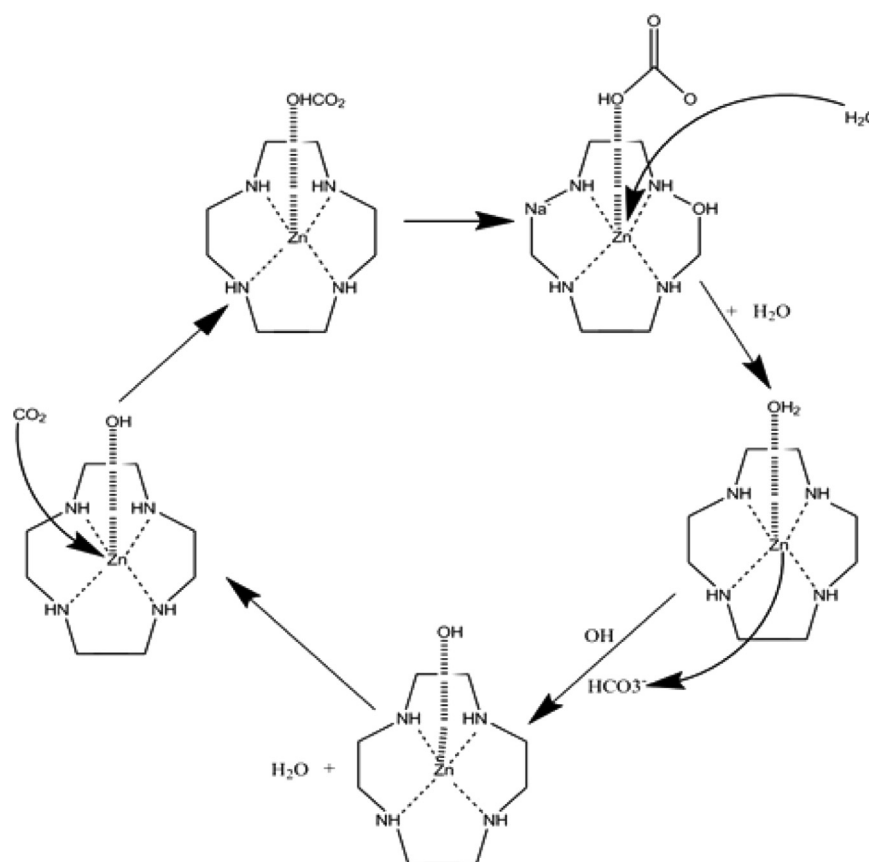


Fig. 3. CO₂ hydration promoted by mimic enzyme (Zn-cyclen).

Table 1
Membrane and contacting cell details.

	Membrane A	Membrane B
Radius of membrane (m)	5.0E−3	5.0E−3
Thickness of membrane (m)	2.0E−4	2.0E−4
Outer radius (m)	5.2E−3	5.2E−3
Shell IR (m)	6.5E−3	6.5E−3
Membrane pore size (nm)	200	100
Membrane area (m ²)	9.8E−03	9.8E−03
Porosity	0.57	
Tortuosity	1.25	

Table 2
List of chemicals.

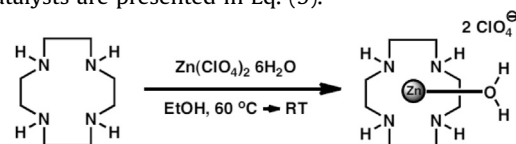
Chemical	Supplier	Purity
Sodium hydroxide (NaOH)	VWR	99%
Potassium carbonate (K ₂ CO ₃)	Sigma Aldrich	99%
Zinc perchlorate hexahydrate	Sigma Aldrich	crystalline
Cyclen	Sigma Aldeich	97%
Hydrochloric acid (HCl) 0.1 M	MERCK	
Barium chloride (BaCl ₂)	Sigma Aldeich	99.9%
Ethanol	VWR	100%

hydrophobic coating on the out skin was supplied by SPG Technology Co. Ltd. Japan. Details of the membranes and the contacting cell are given in Table 1. A list of the chemicals used in this work are presented in Table 2.

3.2. Synthesis of Zn-cyclen (mimic enzyme)

The synthesis of Zn-cyclen (mimic enzyme) involves the

treatment of the aza-macrocyclic scaffold with the perchlorate salt of the metal, and heating the mixture at 50–60 °C. All the raw materials for the synthesis of Zn-cyclen are soluble in ethanol, but the Zn-cyclen is insoluble in ethanol. A 5 ml solution of cyclen in ethanol was added with 10 ml of Zn(ClO₄)₂ solutions in ethanol over a period of 1.5 h [49,53]. Both reactants were added in a molar ratio of 1:1. The reactions involved in the synthesis of the catalysts are presented in Eq. (9).



At the end of the reaction, the product was separated from the solution using vacuum filtration and then washed several times with absolute ethanol. H¹ NMR 400 and MS were used to verify the completion of the reaction.

3.3. Membrane contactor setup

The membrane contactor setup developed for this work is presented in Fig. 4. Absorption of CO₂ in the aqueous solutions was carried out at near room temperature (25 °C) and atmospheric pressure. Gas streams of pure CO₂ and N₂ were mixed to generate a mixed gas containing 10% CO₂ in N₂ at various flowrates. This mixed gas was then passed to the membrane contactor placed in a heating cabinet maintained at 25 °C. Gas flowrates were controlled by mass flow controllers from Bronchorst (0–1000 ml/min ± 0.5% for N₂ and 0–500 ml/min ± 0.5% for CO₂). Liquid from the feed liquid tank was pumped into the membrane contactor by a non-pulsating micro gear pump. The liquid flowrate was measured by a digital flowmeter from Alicat at various flowrates (10–60 ± 5% ml/min). The CO₂ concentrations in the feed and retentate gas streams

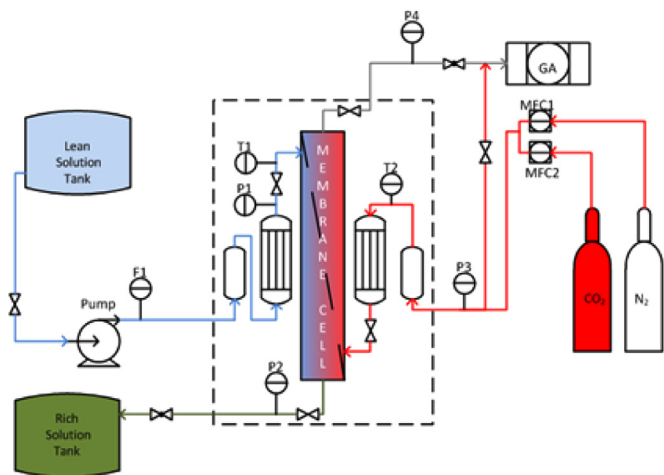


Fig. 4. Schematic diagram of the membrane contactor setup.

were measured by IR based analyzer from Emerson with a detection range of 0–100% CO₂.

In this work gas stream analysis was used as the basis for calculation. However, liquid samples were also analyzed by titration to confirm the absorbed CO₂ concentration in liquid. The gas stream with 10% CO₂ in N₂ or 100% CO₂ at various flowrates was fed into the tube side of membrane, whereas the liquid stream was fed in the shell side from the opposite direction. Liquid stream was kept in shell side for a low mass transfer resistance and well mixed bulk liquid [60,67], whereas counter-current flow was used because the average driving force (concentration difference) across the membrane is higher and more constant throughout the contactor compared with that in a co-current flow [19]. The membrane contactor cell and the flows of the fluids in it are presented in Fig. 5.

The gas flowrate was adjusted to maintain Reynolds number in a range of 900–2000, and liquid flowrate was also adjusted to maintain laminar regime ($Re \leq 500$). All experimental data were collected after 30–45 min of stable operation, and parallel samples were analyzed to confirm the results. All experiments were conducted at 25 °C and atmospheric pressure. The pressure in the

liquid stream was kept slightly higher (1.15 Bar) than that of the gas stream to maintain a continuous film and avoid bubbling of the gas into the liquid phase. Flux of CO₂ was calculated based on Eq. (10) [68].

$$J_{CO_2} = \frac{Q_F (C_{CO_2,F} - C_{CO_2,R}) \times 273.15 \times 1000}{22.4 \times T_g \times A_m} \quad (10)$$

Where J_{CO_2} is the CO₂ flux, $C_{CO_2,F}$ and $C_{CO_2,R}$ are the CO₂ concentrations in the feed and retentate streams, respectively. Q_F is the gas flow rate at the inlet of the membrane module. T_g is the gas temperature and A_m is the mass transfer area.

Absorption of CO₂ is a three step process in a membrane contactor, which involves (i) the diffusion of CO₂ through gas film, (ii) CO₂ transport through membrane to the membrane/liquid interface, and (iii) the absorption of CO₂ in liquid film and the absorbed CO₂ transport to the liquid bulk. Based on the film model, the driving force for mass transfer is the concentration gradient in liquid film and the partial pressure difference in gas phase [69], therefore the equilibrium CO₂ absorption can be defined as Eq. (11).

$$J_{CO_2} = \left(\frac{1}{\frac{1}{k_g} + \frac{1}{k_m}} \right) (P_{CO_2,bulk} - P_{CO_2,i}) = Ek_L^o (C_{CO_2,i} - C_{CO_2,bulk}) \quad (11)$$

Where $P_{CO_2,bulk}$ and $P_{CO_2,i}$ are the bulk and the interfacial partial pressure of CO₂ in gas phase, whereas $C_{CO_2,i}$ and $C_{CO_2,bulk}$ are the liquid phase interfacial CO₂ concentration and the bulk CO₂ concentration. k_g , k_m and k_L^o are the individual mass transfer coefficients of the gas, membrane and liquid phase, respectively, and can be calculated using (Eqs. (3)–(5)). E is the enhancement factor that accounts for the influence of the reactions between CO₂ and the solvent.

The overall mass transfer coefficient can be calculated by dividing CO₂ flux with the driving force (concentration difference or partial pressure difference of CO₂). In this work the gas stream analysis is used for calculations, as shown in Eq. (12).

$$K_{ov} = \frac{J_{CO_2}}{LMPD} \quad (12)$$

Where $LMPD$ is the log mean pressure difference. The overall mass transfer coefficient is related to the individual phase resistance in Eq. (2). Enhancement factor (E) is typically calculated by Hatta number (Ha) which is defined as shown in Eq. (13):

$$Ha = \frac{\sqrt{k_1 D_{CO_2}}}{k_L^o} \quad (13)$$

Here, k_1 is the 1st order kinetic rate constant, D_{CO_2} is the diffusivity of CO₂ in liquid phase and k_L is the physical mass transfer coefficient. The requirement for using pseudo first order assumption given in literature [70] is $3 < Ha \ll E^\infty$.

The 2nd order rate constant k_2 can then be calculated by simply dividing k_1 with the bulk concentration of NaOH:

$$k_2 = \frac{k_1}{[OH^-]} \quad (14)$$

3.4. CO₂ analysis

The liquid stream analysis was conducted using precipitation titration of samples with HCl. Each collected sample was titrated twice using an automated titration system. Each sample was added with calculated amount of barium chloride solution and was boiled. Solution containing precipitates was cooled and filtered. Precipitated particles separated using vacuum filtration and then were

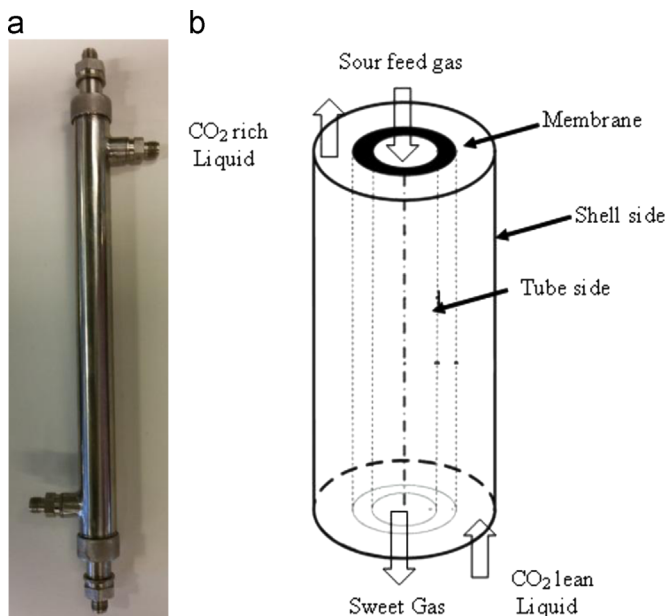


Fig. 5. Picture of the membrane contactor module (a) and the counter current flow of fluids in the membrane contactor (b).

added with HCl solution and stirred to dissolve the particles. Clear solution was titrated against NaOH of known concentration to determine the liquid loading. The method is adopted from Hoff [61].

3.5. Contact angle

Contact angle of water on membrane surface was measured with an automated dosing system and analyzed by “Attention software”. Advancing and receding contact angles were calculated and the average value was recorded. Multiple runs were conducted to verify the readings.

4. Results and discussion

4.1. Phase breakthrough

The most common operational challenge in a porous membrane contactor is the pore penetration/phase breakthrough of liquid. The maximum pressure difference between the two phases which allows operation without pore wetting can be calculated using Young–Laplace Eq. (15a) [64].

$$\Delta P = P_L - P_G = - \frac{2\gamma \cos(\theta)}{r} \quad (15a)$$

here ΔP is the minimum pressure difference across the membrane for pore wetting, γ is the surface tension of the liquid, θ is the contact angle of the membrane and r is the pore radius. Pore wetting and its effects have been investigated by several researchers [14,20,33]. Porous polymeric membranes reported in literature usually have a pore size distribution, as such the pore penetration pressure is usually much lower than the theoretical value calculated based on Young–Laplace equation using the average pore size. Narrow pore size distribution of the glass membrane can reduce or even eliminate this risk and is therefore used in this study.

Pores of a membrane should be gas filled to minimize membrane resistance and achieve mass transfer efficiency. However, gas can bubble into the liquid phase if gas pressure is higher than the breakthrough pressures as can be calculated by Eq. (15b)

$$\Delta P = P_G - P_L = - \frac{2\gamma \cos(\theta)}{r} = \frac{2\gamma}{r} \quad (15b)$$

Since all absorbents were dilute aqueous solutions, the surface tension was close to water (72.1–75.2 mN/m), and therefore the pore penetration pressure was calculated to be in the range of 4.30–4.50 bar for membrane with 200 nm pore size and 8.6–8.9 bar for membrane with 100 nm pore size. The theoretical breakthrough of gas in water was calculated to be around 7.2 bar. However, since the gas stream simulates the post combustion flue gas at near atmospheric pressure, the gas breakthrough into liquid phase is unlikely. Taking advantage of the high hydrophobicity of the glass membrane used in the membrane contactor, all experiments in this work were conducted with liquid stream at a pressure slightly higher than that in the gas stream ($\Delta P=150$ –200 mbar) to avoid pore-wetting. It was further confirmed by experiments.

One operational challenge reported in literature regarding porous polymeric membrane is the loss of hydrophobicity with time. Most of the absorbents used for CO₂ capture may interact with membrane surface and gradually reduce the hydrophobicity of the membrane. This loss of hydrophobicity eventually results in pore wetting and a decline in overall performance. To study the long term effect of the solvent on the membrane surface properties in the glass membrane contactor, a piece of glass membrane was dipped in a 1 M NaOH solution for several days and its

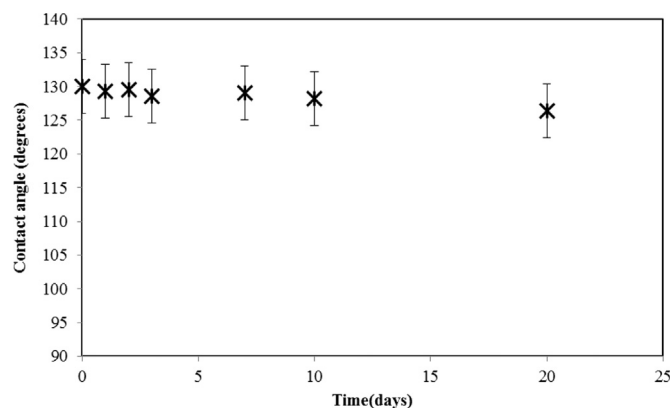


Fig. 6. Effect of soaking time in 1 M NaOH solution on contact angle of water with the glass membrane.

hydrophobicity was periodically tested by determining the contact angle. Results presented in Fig. 6 show that the glass membrane retains its hydrophobicity over a period of 20 days. The pressure difference across the membrane was maintained to be less than 200 mbar in this work, which is much less than phase breakthrough pressure of both membranes.

4.2. Effect of membrane pore size

In this study, liquid stream was fed into the shell side of the membrane contactor while the gas stream was fed into the tube side in counter-current flow. To investigate the performance of membrane contactor, the overall mass transfer coefficient based on gas stream analysis and the percentage of CO₂ removed were used as the evaluation basis. Membranes with two different pore sizes were used to determine the effect of membrane pore size on the overall efficiency of the system. Gas and liquid velocities were varied to investigate the effects of flow regime on mass transfer efficiency of the two membranes.

The effect of liquid flowrate on the overall CO₂ removal efficiency was studied by varying the liquid velocity in a range of (0.03–0.2 m/s). The feed gas containing 10% CO₂ in N₂ was supplied at a constant gas velocity of 0.1 m/s. The percentage of CO₂ removal from gas stream was calculated based on the feed/re-tentate gas analysis. Fig. 7 presents the effect of the liquid velocity on the CO₂ removal efficiency. The CO₂ removal efficiency increases with increase in liquid velocity. This trend is more pronounced in the range of 0.03–0.1 m/s. As the velocity increases from 0.1 m/s to 0.2 m/s, the CO₂ removal efficiency remains constant. The absorption of CO₂ in NaOH solution mainly takes place

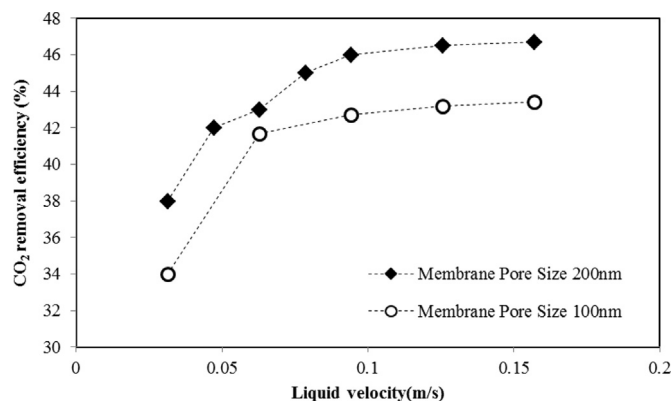


Fig. 7. Effect of liquid velocity on CO₂ removal efficiency for glass membranes contactor operating with 1 M NaOH (absorption temperature 25 °C, gas velocity 0.1 m/s, feed gas 10/90 (v/v) CO₂/N₂).

by chemical reaction between the two the reactants in the liquid film. The product then diffuses through the liquid film towards the liquid bulk. At low liquid flow rates, the Reynolds number (< 200) is very small and within the laminar liquid flow regime with a stagnant film. At these conditions the diffusion of the reactants and the products through the liquid film becomes the rate limiting step in the overall mass transfer. Under these conditions, the absorption of CO_2 in the liquid phase is governed by diffusion of reactants/products in liquid film.

The mass transfer in liquid phase shifts from diffusion to kinetic limiting regime as the liquid velocity is increased and over 0.1 m/s liquid velocity ($\text{Re} > 200$) the mass transfer in liquid phase is purely governed by kinetics of the reaction between CO_2 and NaOH . Beyond this point the liquid velocity does not have a significant effect on CO_2 removal efficiency. The effect of membrane resistance to mass transfer on the CO_2 removal efficiency is also evident in Fig. 7. Compared with the membrane with the pore size of 100 nm, CO_2 removal efficiency of membrane with pore size of 200 nm is higher due to its bigger pore size and lower mass transfer resistance. For post CO_2 combustion capture where the CO_2 partial pressure is low, membrane with large pore size is preferred for an efficient gas liquid contact. Similar trends were observed by researchers in their studies on CO_2 absorption in chemical absorbents at different liquid velocities [16,32,71].

4.3. Effect of gas velocity and liquid velocity

To study the effect of gas velocity on the overall CO_2 removal efficiency in the membrane contactor, experiments were conducted at various gas velocities (0.10–0.21 m/s) at a constant liquid velocity (0.125 m/s). Liquid flowrate was adjusted so that absorption takes place in the kinetic limited regime. Results presented in Fig. 8 compares the effect of gas velocity on the overall CO_2 removal efficiency in two membrane contactors using membranes with different pore sizes. CO_2 removal efficiency decreases with increase in gas velocity. The CO_2 removal efficiency was calculated based on gas stream analysis of the feed and retentate gas composition. Retentate CO_2 concentration increases with the increase of gas velocity and hence the overall capture efficiency decreases. The effect of membrane resistance can also be seen in this Fig. 8. At higher gas velocities the membrane with the pore size of 200 nm shows better separation performance compared with that of 100 nm due to its higher CO_2 permeance and lower resistance to mass transfer.

From discussion on Figs. 7 and 8 it can be concluded that glass membrane with pore size of 200 nm has a higher separation

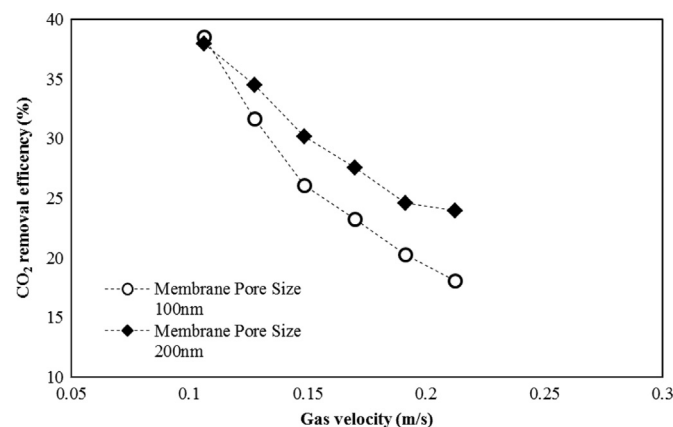


Fig. 8. Effect of gas velocity on CO_2 removal efficiency for glass membrane contactors operating with 1 M NaOH (absorption temperature 25 °C, liquid velocity 0.125 m/s, feed gas 10/90 (v/v) CO_2/N_2).

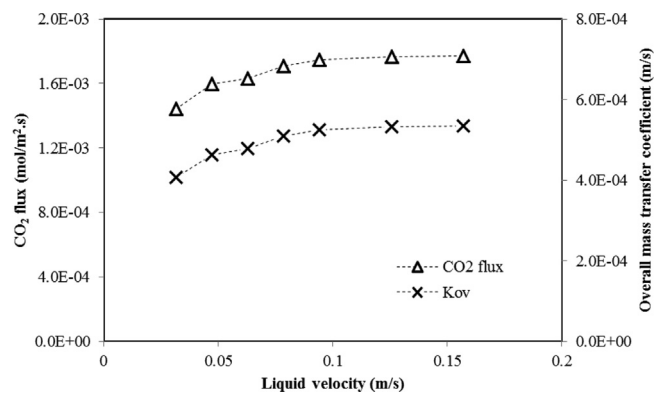


Fig. 9. Effect of liquid velocity on CO_2 flux and overall mass transfer coefficient (K_{ov}) in glass membrane contactor operating with 1 M NaOH (absorption temperature 25 °C, gas velocity 0.1 m/s, feed gas 10/90 (v/v) CO_2/N_2).

efficiency. The consistency in experimental data also indicates no pore wetting so membrane with pore size of 200 nm can be preferred over membrane with pore size of 100 nm. Effect of liquid velocity on flux of CO_2 and overall mass transfer coefficient (K_{ov}) is presented in Fig. 9. Both CO_2 flux and overall mass transfer coefficient shows an increase with respect to liquid velocity and transition from diffusion to kinetic limited regime is observed at a liquid velocity of 0.1 m/s. An increase in CO_2 flux, K_{ov} and CO_2 removal efficiency is observed as the liquid velocity is increased from 0.05 m/s to 0.1 m/s. This indicates that the liquid flow regime has a significant effect on mass transfer through the liquid film and hence the diffusion of reacting species through liquid film has a significant contribution to mass transfer. As the liquid velocity increases over 0.1 m/s, both the CO_2 flux and K_{ov} becomes constant. This shows that absorption of CO_2 in NaOH is now independent of liquid flow regime and is governed by the reaction kinetics only.

The effect of the gas velocity on CO_2 flux and the overall mass transfer coefficient is presented in Fig. 10. Unlike the decreasing trend of CO_2 removal efficiency in Fig. 8, both the CO_2 flux and overall mass transfer coefficient remains constant. The flux of CO_2 is dependent on its concentration difference between gas phase and liquid phase. The transport of CO_2 in gas phase takes place by the diffusion of molecules from gas bulk to gas film and gas-membrane interface. The diffusivity of CO_2 in nitrogen is much higher as compared to its diffusivity in water or NaOH solution. Hence the gas phase mass transfer is independent of its flow regime.

Overall mass transfer coefficient is a function of membrane and gas/liquid film resistances which is independent of driving force. A

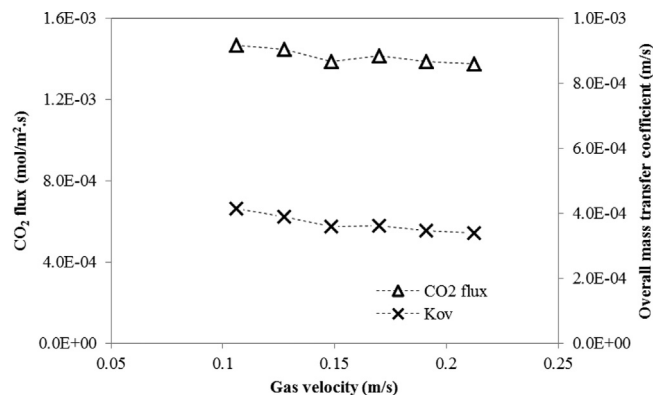


Fig. 10. Effect of gas velocity on CO_2 flux and overall mass transfer coefficient (K_{ov}) in glass membrane operating with 1 M NaOH (absorption temperature 25 °C, liquid velocity 0.125 m/s, feed gas 10/90 (v/v) CO_2/N_2 , Membrane pore size 200 nm).

constant value of K_{ov} with respect to gas velocity at constant liquid velocity in kinetic limited absorption regime also indicates the validity of experimental procedure. Similar trends were reported by researchers in their study of CO_2 absorption in chemical absorbents at different gas velocities [16,32,71].

4.4. Membrane resistance to mass transfer

Based on above experimental results from the membrane contactor using 1 M NaOH as absorbent, it is evident that membrane resistance has a significant contribution to the overall mass transfer. Furthermore, Wilson plot was used to quantify the individual mass transfer resistance. Feed gas containing pure CO_2 at a velocity of 0.1 m/s was feed to the glass membrane contactor to eliminate gas film resistance. Experiments were conducted with 1 M NaOH at various liquid velocities. In this way, pure gas is absorbed in a fast reacting liquid, the gas/liquid film resistance can be neglected and membrane resistance to mass transfer can be determined experimentally. The overall mass transfer resistance calculated using Eq. 9–11 was plotted as a function of liquid velocity ($V^{-0.93}$). The coefficient (-0.93) was chosen based on Eq. 4, and a linear trend line was plotted to determine the membrane resistance as suggested in literature [16, 33]. The value of R^2 in Fig. 11 shows that the experimental data agrees well with the chosen model. Based on these results, the membrane mass transfer resistance is the highest among the three phases.

Based on the Wilson model, the membrane resistance to mass transfer ($1/k_m$) was calculated to be 2954.3 s/m. Mass transfer resistance calculated for this membrane by using Eq. 5 is 2211.69 s/m which is close to the one experimentally calculated. This confirms that membrane operation took place with gas filled pores. The absorption study of CO_2 from the feed gas containing 10% CO_2 in N_2 by a fast reacting absorbent like NaOH indicated that membrane contribution to mass transfer resistance is about 85% of overall resistance to mass transfer. The transport of CO_2 through membrane and the gas film is the limiting steps in overall performance of the contactor. However, when absorption study was conducted with K_2CO_3 solution, contribution of gas film and membrane resistance to mass transfer was found to be around 43% of overall mass transfer resistance. Kinetics for absorption of CO_2 in K_2CO_3 is much slower as compared to that of NaOH. The transport of CO_2 in the liquid film is the limiting step for mass transfer in a membrane contactor when the K_2CO_3 solution is used as absorbent. To improve the performance of the membrane contactor operating with K_2CO_3 as absorbent, mimic enzyme can be used to decrease liquid film resistance by promoting CO_2 hydration.

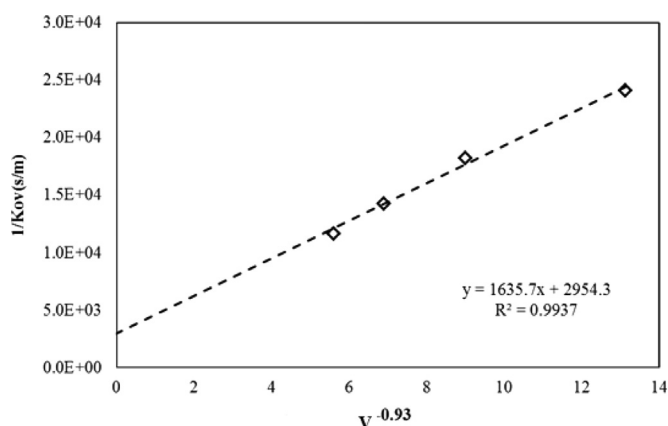


Fig. 11. Wilson plot model of tubular glass membrane contactor with pore size 200 nm (absorption temperature 25 °C, gas velocity 0.1 m/s, feed gas pure CO_2).

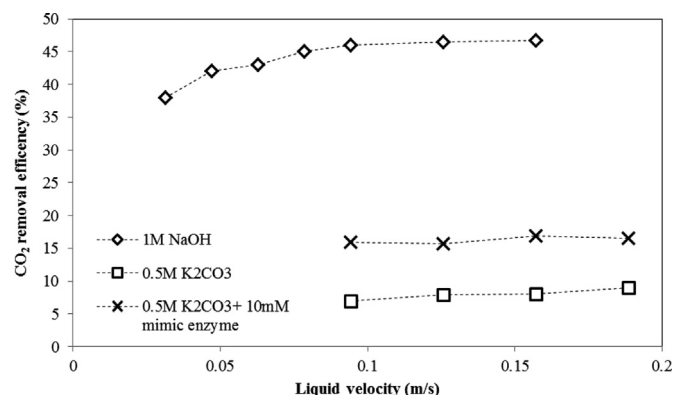


Fig. 12. Effect of liquid velocity on CO_2 removal efficiency in the membrane contactor with respect to absorption in NaOH, K_2CO_3 with and without mimic enzyme (absorption temperature 25 °C, gas velocity 0.1 m/s, feed gas 10/90 (v/v) CO_2/N_2 , membrane pore size 200 nm).

4.5. Effect of Zn-cyclen (mimic enzyme)

Aqueous carbonate/bicarbonate based CO_2 absorbents are one of the oldest and well-studied solutions for CO_2 capture. Potassium carbonate has a high CO_2 loading capacity and a low heat of reaction with CO_2 , but a low kinetic rate constant. In-order to take the advantages of K_2CO_3 as CO_2 absorbent, usually the solvent is promoted by the addition of fast reacting amines. However, the regeneration of amines is energy intensive. In this study, mimic enzyme is added to promote the process. Mimic enzyme is a small catalyst with appreciable thermal stability, high rate of hydration and low heat of reaction. Absorption of CO_2 in K_2CO_3 solution containing different concentrations of mimic enzyme was studied in the membrane contactor. Fig. 12 presents the effect of liquid velocity on CO_2 capture efficiency by using 0.5 M K_2CO_3 solution with and without mimic enzyme.

Compared with the absorption in 1 M NaOH, CO_2 removal efficiency by 0.5 M K_2CO_3 solution is much lower. However, with addition of a small quantity of mimic enzyme (10 mM) the removal efficiency is doubled. William et al. [47] studied the kinetic of CO_2 hydration with mimic enzyme in K_2CO_3 solution and also observed an appreciable increase in rate of CO_2 absorption by adding small quantity of mimic enzyme.

The effect of mimic enzyme concentration on the CO_2 removal efficiency was studied at various liquid flowrates in order to find the optimum mimic enzyme concentration. The absorption of CO_2 from feed gas containing 10% CO_2 in N_2 at constant flowrate of

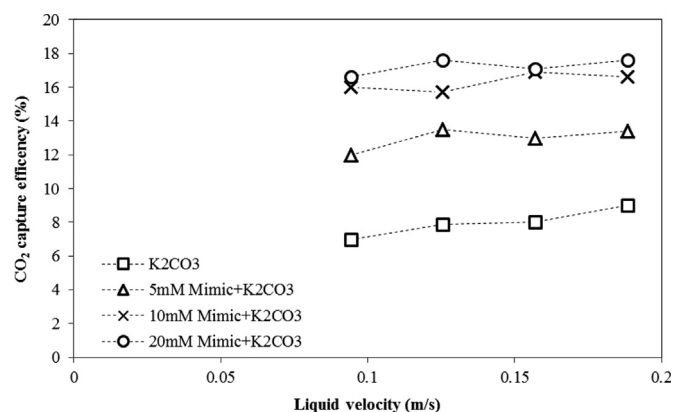


Fig. 13. Effect of mimic enzyme concentration on CO_2 removal efficiency at various liquid velocities in a membrane contactor (absorption temperature 25 °C, gas velocity 0.1 m/s, feed gas 10/90 (v/v) CO_2/N_2 , membrane pore size 200 nm).

Table 3
Parameters for calculation of kinetics.

Parameter	Value	Reference
Shell side mass transfer coefficient (k_L^o)	5.39E-6~2.85E-5 (m/s)	This work
Tube side mass transfer coefficient (k_g)	2.13E-3~2.67E-3 (m/s)	This work
Kinetic rate constant of 1 M NaOH (k_2)	1.519E+4 (m ³ /kmol-s)	This work
Kinetic rate constant of 1 M NaOH (k_2)	1.520E+4 (m ³ /kmol-s)	[65]
Kinetic rate constant for 0.5 M K ₂ CO ₃ (k_2)	1.871E+3 (m ³ /kmol-s)	This study
Kinetic rate constant for 5 wt% (~0.35 M) K ₂ CO ₃ (k_2)	1.322E+3 (m ³ /kmol-s)	[66]
Kinetic rate constant for 0.5 M K ₂ CO ₃ + 10 mM Mimic (k_2)	1.124E+4 (m ³ /kmol-s)	This work

0.1 m/s, temperature of 25 °C and 1 bar in 0.5 M K₂CO₃ solution without mimic enzyme was tested to establish a base case. Afterwards, experiments were conducted at the same operating conditions with liquid stream containing 0.5 M K₂CO₃ with mimic enzyme of 3 different concentrations (5, 10 and 20 mM). Experimental results for CO₂ removal efficiency with respect to different concentrations of mimic enzyme at various liquid velocities are presented in Fig 13. An appreciable increase in CO₂ removal efficiency was observed by adding 5 mM of mimic enzyme to 0.5 M K₂CO₃ solution. The CO₂ removal efficiency went up to 15% by adding 10 mM mimic enzyme to 0.5 M K₂CO₃ solution. However, very little increase in CO₂ removal efficiency was observed as concentration of mimic enzyme was increased from 10 to 20 mM in 0.5 M K₂CO₃ solution. Similar trends have been observed in literature [47,51,56].

4.6. Kinetic study

The main objective of kinetic study is to quantify the effect of mimic enzyme on CO₂ absorption rate. Due to its simple geometry and well controlled gas/liquid flow regimes, the membrane contactor has been widely acknowledged as a contacting equipment to study the reaction kinetics of novel absorbents. However, Kinetic study of known absorbents can also be used to validate the experimental procedure and authenticity of newly commissioned setup. Sodium hydroxide has been extensively studied for CO₂ capture and kinetic data for absorption of CO₂ in NaOH is abundantly available in literature. First order kinetic rate constant (k_2) for NaOH was calculated based on experimental results by using Eqs. (10–14). Liquid film resistance for physical absorption (k_L^o) was calculated using Eq. 4. Based on laborious calculation procedure elaborated by Gondal et al. [65], kinetic rate constant (k_2) for absorption of CO₂ in 1 M NaOH was calculated and compared with the literature. For the calculation of kinetic rate constant CO₂ solubility in NaOH and K₂CO₃ aqueous solutions was taken from literature. [72,73]. Diffusivity of CO₂ in water and N₂ was taken from Versteeg et al. [74].

The first order rate constant (k_2), liquid film and gas film mass transfer coefficients for physical absorption calculated from this experimental study is presented in Table 3. A comparison of first order kinetic rate constant for absorption of CO₂ in 1 M NaOH and 0.5 M K₂CO₃ are in good agreement with literature data. This validates the experimental procedure.

Kinetic rate constant (k_2) for absorption of CO₂ in 0.5 M K₂CO₃ with and without mimic enzyme was calculated using the same procedure. Kinetics of CO₂ absorption in K₂CO₃ has seldom been reported in literature data and even fewer data is available for K₂CO₃ promoted by mimic enzyme. Kinetic rate constant for CO₂ absorption in 0.5 M K₂CO₃ was calculated and compared with literature data [66]. Rate constants for CO₂ absorption in NaOH, K₂CO₃ and mimic enzyme promoted K₂CO₃ is listed in table 3. This study shows that mimic enzyme has significant influence on absorption of CO₂ in K₂CO₃ and small quantity of mimic enzyme can

appreciably promote CO₂ capture by aqueous K₂CO₃ in a membrane contactor at post combustion conditions.

5. Conclusions

The mimic enzyme promoted CO₂ absorption in a gas–liquid membrane contactor presented in this work shows high CO₂ separation performance and is stable. Porous glass membrane retains its hydrophobicity over a long period of time and provides high mass transfer rate without pore wetting. The membrane mass transfer study in the membrane contactor was conducted by using a fast reacting absorbent (NaOH), where the membrane contributes (85%) in the overall mass transfer resistance, and is the limiting factor. The membrane resistance only accounts for 43% of the overall mass transfer resistance when absorption takes place in a K₂CO₃ solution.

Mimic enzyme is a catalyst that promotes CO₂ hydration even at low concentrations (10 mM). Kinetic study indicates that with addition of 10 mM mimic enzyme to 0.5 M K₂CO₃ solution, the kinetic rate constant for absorption of CO₂ in the K₂CO₃ solvent increased by 10 fold compared to the experiment without mimic enzyme.

This study demonstrates a novel, easy approach to effectively promoting CO₂ absorption using a low cost, chemically stable mimic enzyme. It opens the possibilities of replacing the traditional chemical absorbents (amines) with more environmentally-friendly and less energy intensive green absorbents.

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Nomenclature

ΔP	pressure difference across membrane (bar)
A_m	membrane mass transfer area (m ²)
γ	surface tension of solvent (mN/m)
θ	contact angle between liquid and membrane
r	pore radius (mm)
K_o	overall mass transfer coefficient (m/s)
K_{ov}	overall mass transfer coefficient based on gas phase analysis (m/s)
k_m	mass transfer coefficient through membrane (m/s)
k_L	liquid film mass transfer coefficient for physical absorption (m/s)

k_L^o	liquid film mass transfer coefficient for physical absorption (m/s)
D	molecular diffusivity coefficient of a component in film (m^2/s)
D_E	effective diffusivity in membrane (m^2/s)
ε	porosity
E	enhancement factor
J	flux of CO_2 by chemical/physical absorption
τ	tortuosity
l	thickness of membrane (m)
L	length of membrane tube (m)
H	henry's law constant ($\text{bar m}^3/\text{mol}$)
Q_l	liquid flowrate (m^3/s)
$C_{L(\text{out/in})}$	concentration of gas (CO_2) in liquid stream at outlet and inlet (mol/m^3)
d_o, d_i, d_n	outer, inner and log mean diameter of hollow fiber membrane (m)
d_h	hydraulic diameter (m)
R	general gas law constant ($\text{mol}/\text{m}^3 \text{ s}$)
T	temperature (K)
v_z	liquid velocity in a fiber (m/s)
Sh	Sherwood number
Sc	Schmidt number
Re	Reynold number
Gz	Greatz number
$k_{[\text{OH}^-]}$	second order rate constant (1/s)
k_2	First order kinetic rate constant ($\text{m}^3/\text{kmol s}$)

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