

# 7 **Graphical abstract**



# 8

#### 9 Abstract

Due to the widespread use of fossil fuels, atmospheric levels of carbon dioxide ( $CO_2$ ), a major contributor to climate change, have increased dramatically. Through the simulation of a twodimensional (2D), bovine carbonic anhydrase (bCA)-mediated mechanism, this work presents a novel approach method for  $CO_2$  capture using membrane contactor, the technique uses aqueous carbonate solution as a chemical solvent. tt is tested both with and without bCA. The influence of

important parameters on the CO<sub>2</sub> capture performance, such as gas flow rate, liquid flow rate, bCA 15 concentration in both counter- and co-current flow are investigated. The results show that the 16 addition of 5 mg  $L^{-1}$  bCA improves the removal efficiency by 24%, it is found that increasing the 17 gas flow rate of CO<sub>2</sub> from 10 mL min-1 to 40 mL min<sup>-1</sup> reduces the CO<sub>2</sub> removal from 23.47% to 18 6.68% in pure solution, whereas with 5 mg  $L^{-1}$  bCA increasing the gas flow rate of CO<sub>2</sub> from 10 19 mL min<sup>-1</sup> to 40 mL min<sup>-1</sup> reduces the CO<sub>2</sub> removal from 57.17% to 19.79%. Increasing the liquid 20 flow rate from 10 mL min-1 to 40 mL min-1 increases the CO<sub>2</sub> removal from 23.47% to 56.33% 21 without the addition of bCA, with 5 mg  $L^{-1}$  bCA the CO<sub>2</sub> removal increases from 57.17% to 22 69.07%. The counter-current is better than the co-current by 3% improvement. The effect of the 23 bCA enzyme on CO<sub>2</sub> capture is limited by the availability of CO<sub>2</sub> (the substrate) and the catalytic 24 capacity of the enzyme. The proposed simulation approach for maximum enzyme concentration, 25 incorporates kinetic effects while maintaining the same parameters and operating conditions as 26 reported in the literature, maximum CO<sub>2</sub> removal efficiency, approaching almost total removal, is 27 achieved at an enzyme concentration of approximately 30 mg L<sup>-1</sup> for the same CO<sub>2</sub> load. 28

Keywords: Biocatalyst; Carbonate solution; Chemical CO<sub>2</sub> absorption, Enzyme, HFMC;
Modelling

#### 31 **1. Introduction**

Climate challenges today are mainly caused by global warming, changes in natural ecosystems, and economic and technological problems. Global warming is primarily driven by the gradual rise in Earth's average temperature. This rise in temperature is mostly due to greenhouse gas (GHG) emissions, especially carbon dioxide (CO<sub>2</sub>). GHGs are mainly released by the fossil fuel, petrochemical, steel, transport, and cement industries. CO<sub>2</sub> is known to be one of the main drivers of climate change. Its level in the atmosphere has grown quickly in recent years, mostly because

of the widespread use of fossil fuels (Sekartadji et al., 2023; Muthumari et al., 2024). Global 38 climate change is largely influenced by complex atmospheric dynamics and the accumulation of 39 greenhouse gases, particularly carbon dioxide (CO<sub>2</sub>). These disturbances directly affect 40 ecosystems, human health, agriculture, and global climate stability (Nirmal, Subramanian and 41 Surendran, 2025), a substantial growth of  $CO_2$  emissions over the past 150 years has resulted in a 42 43 significant increase of the atmospheric CO<sub>2</sub> concentration. The remarkable upward trend in Earth's average temperature could threaten human health, lives and industries associated with the 44 temperature rise (Ze and Sx, 2014a). Climate change is leading to an increase in extreme weather 45 events such as wildfires, heat waves and droughts, threatening ecosystems, food security and 46 human health. In response to this crisis, reducing CO<sub>2</sub> emissions particularly through advanced 47 technologies (Jasmine et al., 2025). Hollow fiber Membrane contactor (HFMC) has emerged as 48 an innovative alternative, offering numerous advantages such as prevention of interphase 49 dispersion, a high specific surface area, and a compact design (Ze and Sx, 2014; Mansourizadeh 50 et al., 2022). Membrane gas absorption has recently attracted much attention as one of the 51 promising technologies for CO<sub>2</sub> capture because of its superior mass transfer efficiency high 52 surface-to-volume ratio, flexible operation, modularity, compact design, and linear scalability 53 54 (Okabe, Mano and Fujioka, 2008; Han and Ho, 2018). Alkanolamine solvents, such as MEA, are commonly used for  $CO_2$  capture due to their rapid reaction rate with  $CO_2$ . However, they are 55 56 associated with high regeneration energy demands and evaporative losses (Zare, Keshavarz and 57 Mowla, 2019). To overcome these drawbacks, other absorbents have been tried, one of which is 58 carbonate aqueous solution. Carbonate solution is inexpensive, noncorrosive, and its regeneration 59 for CO<sub>2</sub> capture consumes less energy compared to MEA. However, it also presents a smaller 60 reaction rate with CO<sub>2</sub>, especially at low temperature and low partial pressure (Hu et al., 2016). A

feasible way to improve the performance of carbonate solution (e.g., K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>) is to add reaction promoters in it. Carbonic anhydrase is an extremely effective catalyst and promoter discovered in 1933 from red blood cells (Maćkowiaka *et al.*, 2018), which catalyzes the reversible conversion of CO<sub>2</sub> to HCO3<sup>-</sup>. Traditional CO<sub>2</sub> capture methods consume a lot of energy and degrade over time. Enzyme-enhanced absorption may solve these problems and provide a greener, faster, and cheaper method.

The aim of this research is to investigate and improve the efficiency of enzyme (bio-promoter) on CO<sub>2</sub> capture in carbonate solution using hollow fiber membrane contactor. This work evaluate To simulate the process using COMSOL, study of the effect of adding an enzyme on CO<sub>2</sub> absorption, key parametric study performance on HFMC such as gas and liquid flow rate.

With a focus on evaluating the effect of an industrial enzyme, α-carbonic anhydrase from Bovine ''Carbonic anhydrase'' (bCA), to accelerate the process of capture using HFMC. bCA was selected for exceptional catalytic efficiency. The enzyme's kinetic data,  $\mathbf{k}_{e}$  from the study by (Alper and Deckwer, 1980a). The study investigates CO<sub>2</sub> absorption using carbonate solutions, both with and without the addition of the enzyme, through process simulation supported in a hollow fiber membrane contactor. This innovative approach aims to enhance CO<sub>2</sub> capture efficiency and promote the sustainability of carbon capture processes

### 78 2.Membrane description and transport equation modeling for CO<sub>2</sub> capture

Figure 1 illustrates a schematic of module and a single hollow fiber membrane, showing thedirections of liquid and gas fluxes. It includes a view depicting the fiber's radius used in this study.



Figure 1. Depict a schematic diagram related to a CO<sub>2</sub> absorption process through HFMC.
The key assumptions made to simplify mass transfer calculations in the numerical model
development are as follows:

- Steady-state conditions are assumed,
- The system operates under isothermal conditions,
- Fully developed velocity profiles for gas and liquid phases are considered within,
- Co-current and counter-current are taken into account,
- Only CO<sub>2</sub> is transferred through the membrane into the tube side (no wetted for pores),
- Michaelis-Menten kinetics are applied to describe the enzymatic reaction rate of with
- 91 CO<sub>2</sub> in the carbonate solution.
- 92 2.1 Shell side equations

- 93 The steady-state mass transfer equation in the shell side in cylindrical coordinates is then derived
- 94 as (Faiz and Al-Marzouqi, 2009)

95 
$$D_{CO_2,shell} \left[ \frac{\partial^2 C_{CO_2,shell}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2,shell}}{\partial r} + \frac{\partial^2 C_{CO_2,shell}}{\partial z^2} \right] = V_{z,shell} \frac{\partial C_{CO_2,shell}}{\partial z}$$
(1)

96 Boundary conditions for shell side equations in counter-current are given as

97 at 
$$z = 0$$
,  $C_{CO_2-shell} = C_0$  (2)

98 at 
$$z = L$$
,  $\frac{\partial C_{CO_2,Shell}}{\partial z} = 0$  (3)

99 
$$at r = r_3, \quad \frac{\partial C_{CO_2,Shell}}{\partial r} = 0 \quad (insulated) \quad (4)$$

100 at 
$$r = r_2$$
,  $C_{CO_2-shell} = C_{CO_2-membrane}$  (5)

101 Assuming Happel's free sur face model (Happel, 1959), the velocity profile in the shell is given

103 
$$V_{z-shell} = 2\langle V \rangle \left[ 1 - \left(\frac{r_2}{r_3}\right)^2 \right] \times \frac{\left(\frac{r}{r_3}\right)^2 - \left(\frac{r_2}{r_3}\right)^2 + 2\ln\left(\frac{r_2}{r}\right)}{3 + \left(\frac{r}{r_3}\right)^4 - 4\left(\frac{r_2}{r_3}\right)^2 + 4\ln\left(\frac{r_2}{r_3}\right)}$$
(6)

# 104 2.2 Membrane side equations

105 The steady state continuity equation for the transport of  $CO_2$  inside membrane with cylindric 106 coordinates, taken only radial diffusion (no wetted pores), can be written as (Shirazian *et al.*, 2020):

107 
$$D_{CO_2,membrane} \left[ \frac{\partial^2 C_{CO_2,membrane}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2,membrane}}{\partial r} + \frac{\partial^2 C_{CO_2,membrane}}{\partial z^2} \right] = 0 \quad (7)$$
108 
$$D_{CO_2,membrane} = \varepsilon \frac{D_{CO_2,shell}}{\tau} \quad (8)$$

109 
$$\tau = \frac{(2-\varepsilon)^2}{\varepsilon}$$
(9)

110 Boundary conditions are given as

111 
$$at r = r_2, C_{CO_2-shell} = C_{CO_2-membrane},$$
 (10)

112 
$$at r = r_1, C_{CO_2-membrane} = \frac{C_{CO_2-tube}}{m}.$$
 (11)

# 114 **2.3** Tube side equations

115 On the tube side, there is reaction for  $CO_2$  in carbonate solution with enzyme, the transmission 116 continuity equation is as follows (Shirazian *et al.*, 2020):

117 
$$D_{CO_2,tube} \left[ \frac{\partial^2 C_{CO_2,tube}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2,tube}}{\partial r} + \frac{\partial^2 C_{CO_2,tube}}{\partial z^2} \right] = V_{z,tube} \frac{\partial C_{CO_2,tube}}{\partial z} - R_{CO_2}$$
(12)

118 Boundary conditions for tube side equations in counter-current flow are given as

119 
$$at z = 0, \ \frac{\partial C_{CO_2,Shell}}{\partial z} = 0,$$
 (13)

- 120  $at z = L, C_{solvent} = C_0,$  (14)
- 121  $at r = r_1, C_{CO_2-tube} = m \times C_{CO_2-membrane},$  (15)
- 122 Boundary conditions for tube side equations in co-current flow are given as

123 
$$at z = 0, C_{solvent} = C_0,$$
 (16)

124 at 
$$z = L$$
,  $\frac{\partial C_{CO_2-tube}}{\partial z} = 0$ , (17)

125 
$$at r = r_1, C_{CO_2-tube} = m \times C_{CO_2-membrane}.$$
 (18)

126 It is hypothesized that the velocity distribution within the tube will be in accordance with

127 Newtonian laminar flow (Bird, 1960)

128 
$$V_{z,tube} = 2\overline{V}_{T} \left[ \left(1 - \left(\frac{r}{r_{1}}\right)^{2} \right]$$
(19)

129 
$$\overline{V}_{T} = \frac{Q_{l}}{n\pi(r_{1})^{2}}$$
(20)

The  $r_3$  on the shell side, part of the membrane contactor can be estimated by the development of fluid around the fiber, the area of the free void can be predicted by Happel's free surface model (Srisurichan, Jiraratananon and Fane, 2006).

133 
$$r_3 = \left(\frac{1}{1-\phi}\right)^{1/2} r_2$$
 (21)

Where Ø is the volume fraction of the vacuum in the module, It can be calculated as follows(Happel, 1959).

136 
$$1 - \emptyset = \frac{\mathrm{nr}_2^2}{\mathrm{R}^2}$$
(22)

137 where n is the number of fibers, and R is the module's inner radius.

# 138 **3. Kinetics of CO<sub>2</sub> with carbonate solution**

The global reactions between CO<sub>2</sub> and carbonate solution are presented as follows (Pohorecki andMoniuk, 1988):

141 
$$CO_3^{2^-} + CO_2 + H_2O \quad \leftrightarrow \quad 2HCO_3^{-^-}$$
 Reaction 1

The above reaction is evidently made up of a sequence of elementary steps. The carbonate ion first
reacts with water to generate hydroxyl ions, which then react with CO<sub>2</sub> as follows (Astarita, Savage
and Longo, 1981).

145 
$$H_2O + CO_2 \iff H_2CO_3$$
 Reaction 2

146	$H_2O + CO_3^{2-}$	$\leftrightarrow$	$OH^{-} + HCO_{3}^{-}$	Reaction 3

148  $H_2O \leftrightarrow OH^- + H^+$  Reaction 5

 $CO_2 + OH^2$ 

147

Aqueous carbon dioxide may react with water to form bicarbonate as shown in *Reaction 2*. The contribution of this reaction to the overall absorption of  $CO_2$  is usually assumed to be negligible in basic solutions, Additionally, since Reaction 3 is an instantaneous reaction, Reaction 4 is the limiting reaction. So, the rate equation of  $CO_2$  with hydroxyl ion (Reaction 4) expresses as (Thee, 2013).

 $HCO_3^-$ 

Reaction 4

154 
$$R_{(CO_2)} = k_{OH} - [OH^-]([CO_2] - [CO_{2e}])$$
(23)

We can consider  $[CO_{2e}] = [CO_{2b}]$ , with  $[CO_{2e}]$  is equilibrium concentration of CO<sub>2</sub>,  $[CO_{2b}]$  is concentration of CO<sub>2</sub> in the bulk, since that the solution is alkaline (pH > 9), CO<sub>2</sub> concentration in the bulk can be negligible. So, we can write the reaction rate of CO<sub>2</sub> as follows (Russo *et al.*, 2013) :

159 
$$R_{(CO_2)} = (k_w + k_{OH} - [OH^-])[CO_{2,tube}]$$
 (24)

160 Where  $R_{(CO_2)}$  is the rate of reaction (mol m<sup>-3</sup> s<sup>-1</sup>),  $k_{OH}$ - is the second order rate constant, and 161  $[CO_{2,tube}]$  and  $[OH^-]$  are the concentrations of free CO<sub>2</sub> and base in the liquid phase.

The second order rate constant of reaction of CO<sub>2</sub> with OH<sup>-</sup> and constant of water can be found
from Equation 24 and Equation 25 (Danckwerts, 1966; Afza, Hashemifard and Abbasi, 2018).

164 
$$\log k_{OH^-} = 13.635 - \frac{2895}{T}$$
 (25)

165 
$$\log k_w = 329.85 - 110.541 \log(T) - \frac{17265.4}{T}$$
 (26)

167 **Parameters** Expression References  $1 - (C1[C0_3^{2-}] + C2[HC0_3^{-}])$ (Versteeg, Blauwhoff and  $D_{CO_{2,T}}$ 168  $+ C3[OH^{-}]) \times D_{CO_{20}}$ van Swaaij, 1987) 169  $3.59 \times 10^{-7} \text{ RT} \, \overline{e^{\left(\frac{2044}{T}\right)}}$ (Dindore, Brilman and  $m_{0,CO_2}$ 170 Versteeg, 2005) 171  $log(m_0/m')$  $\sum (h_{i_{+}^{-}} + h_G)C_i$ (Weisenberger and 172 Schumpe, 1996) 173  $h_{G,0} + 0.338 \times 10^{-3} (T$ (Weisenberger and h<sub>G</sub> - 298.15) Schumpe, 1996) 174 175

**Table 1**. physical parameters used in this work

Where C1, C2, and C3 are constant and equal to  $2.61 \times 10^{-4}$  (m<sup>3</sup> mol<sup>-1</sup>),  $1.40 \times 10^{-4}$  (m<sup>3</sup> mol<sup>-1</sup>),

and  $1.29 \times 10^{-4}$  (m<sup>3</sup> mol<sup>-1</sup>), respectively like it mentioned in Table 1. Diffusion coefficient D<sub>CO<sub>2,0</sub> of</sub>

178 CO<sub>2</sub> in water at 298 K is  $1.88 \times 10^{-9}$  (m<sup>2</sup> s<sup>-1</sup>) (Versteeg, Blauwhoff and van Swaaij, 1987).

**Table 2.** Constants  $h_{i_{+}}$  used in this work (Weisenberger and Schumpe, 1996).

Constant	Value	180
hCO <sub>2</sub>	-0.0172	101
hHCO <sub>3</sub>	0.0967	181
hCO <sub>3</sub> <sup>-2</sup>	0.1423	182

183

## 185 4. Kinetics of CO<sub>2</sub> with Carbonic Anhydrase (CA)

The catalyzed mechanism of Carbonic anhydrase (CA) for  $CO_2$  hydration was introduced by (Lindskog and Silverman, 2000a, 2000b). CA is an efficient hydration catalyst and its reaction with  $CO_2$  had been studied, the main reactions of CA with  $CO_2$  are expressed in equation (20), equation (21) (Lindskog and Silverman, 2000a).

190 
$$CO_2 + EZnOH^- \leftrightarrow EZnOH-CO_2 \leftrightarrow EZnHCO_3^-$$
 Reaction 6  
191  $EZnHCO_3^- + H_2O \leftrightarrow EZnH_2O + HCO_3^-$  Reaction 7

192 The enzymatic reaction which takes the form of a first order Michaelis-Menten equation, expressed193 as follows

194 
$$R_{CA} = k_e[E][CO_{2,tube}]$$
 (27)

With  $\mathbf{R}_{CA}$  (mol m<sup>-3</sup> s<sup>-1</sup>) is the reaction rate of enzyme bCA with CO<sub>2</sub>,  $\mathbf{k}_{e}$  (m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) or (m<sup>3</sup> kg<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-3</sup>) or (mol m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-1</sup>) is the first order Michaelis-Menten kinetic, [*E*] is enzyme concentration (kg m<sup>-1</sup>) is the first order Kinetic (kg m<sup>-1</sup>) is the first orde

198 For bCA enzyme, the  $\mathbf{k}_{\mathbf{e}}$  is 1.15 (L mg<sup>-1</sup> s<sup>-1</sup>) (Alper and Deckwer, 1980a).

199 In this work the reaction rate of CO<sub>2</sub> with enzyme and carbonate solution can expressed as:

200 
$$R_{CO_2} = (k_e[E] + k_w + k_{OH} - [OH^-])[CO_{2,tube}]$$
(28)

Materiel chosen for the membrane is PVDF from (Cao *et al.*, 2021), the dimension of fiber and module of membrane are listed in Table 3, also for porosity and tortuosity are 0.4585 and 5.18 respectively.

Table 3. Characteristics of HFMC module and fluid specification used in this work (Poling,

Prausnitz and O'connell, 2001; Cao *et al.*, 2021).

Parameters	value	Unit
Fiber length (L)	0.210	m
Number of fibers (n)	11	$\sim$
Membrane inner diameter (r <sub>1</sub> )	2.1 × 10 <sup>-4</sup>	m
Membrane outer diameter (r <sub>2</sub> )	5.5 × 10 <sup>-4</sup>	m
Module inner diameter (r <sub>3</sub> )	0.004	m
Membrane thickness $(\delta)$	$3.4 \times 10^{-4}$	m
D <sub>CO2</sub> ,Shell	1.39 × 10 <sup>-5</sup>	m²/s
D <sub>CO2</sub> ,membrane	$D_{CO_2,Shell^*}(\epsilon/\tau)$	m²/s
D <sub>CO<sub>2</sub>,tube</sub> (caculated)	$1.75  imes 10^{-9}$	m²/s
Henry's law physical constant m' (calculated)	0.66	-

### 207 **5. Numerical solution**

A set of governing partial differential equations of CO<sub>2</sub> mass transfer from gas phase (Shell side) passing through hollow fibers contactor using carbonate solution with bCA in liquid phase (Tube side), were solved based on finite elements method (FEM) by COMSOL Multiphysics software (Version 5.0), which can divide different domains in the hollow fiber membrane contactor into small dimension units to obtain the simulated results of important parameters such as CO<sub>2</sub> concentration profiles at each point of the domains. Overview of CO<sub>2</sub> gas capture using HFMC mentioned in Table 4. The Specifications of membrane and the related physical and chemical parameters are listed in Table 1, Table 2 and Table 3, respectively. An internal numerical solver
of COMSOL, PARDISO, is employed to achieve self-adaptive meshing and error control were
employed to minimize the calculations errors (Pishnamazi *et al.*, 2020).

### 218 **6. Results and discussions**

A simulation using a  $CO_2$  capture using carbonate solvent with carbonic anhydrase in a countercurrent and co-current using hollow fiber membrane contactor is given. The main parameters study is; Effects of enzyme concentration, gas and liquid flow rate on  $CO_2$  removal efficiency have been investigated in this study.

223 
$$CO_2 \text{ removal } \% = 100 \times \frac{(Q \times C)_{\text{inlet}} - (Q \times C)_{\text{outlet}}}{(Q \times C)_{\text{inlet}}} = 100 \times \left(1 - \frac{C_{\text{outlet}}}{C_{\text{inlet}}}\right)$$
(29)

In this equation,  $Q_g$  and C represent the volumetric flow rate and the concentration, respectively. Assuming that the maximum concentration of  $CO_2$  in the gas mixture at the inlet is 20%, it can be concluded that the variation in volumetric flow rate is negligible. This allows for the approximation of  $CO_2$  removal with this equation.

### 228 6.1 Velocity profile

Figure 3 depicts the gas and liquid velocity profile on the shell side and tube side expressed as Equation 2 and Equation 3 Respectively, Figure 3 demonstrates that the fully developed velocity profile is confirmed by the previously stated assumption.



Figure 2. Gas and liquid velocity profile,  $Q_l = 10$  ml min<sup>-1</sup>,  $Q_g = 10$  ml min<sup>-1</sup>

# 234 6.2 Gas flow rate effect on CO<sub>2</sub> removal

Figure 3 illustrates the relationship between gas flow rate of CO<sub>2</sub> and removal efficiency for 0.5M 235 Carbonate solution (Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>), pure and with the bCA (5 mg  $L^{-1}$ ). Figure 3.a shows that 236 increasing the gas flow rate of CO<sub>2</sub> from 10 mL min<sup>-1</sup> to 40 mL min<sup>-1</sup> reduces CO<sub>2</sub> removal from 237 23.47 % to 6.68% in pure solution, whereas with 5 mg  $L^{-1}$  of bCA increasing the gas flow rate of 238 CO<sub>2</sub> from 10 mL min<sup>-1</sup> to 40 mL min<sup>-1</sup> reduces CO<sub>2</sub> removal from 57.17 % to 19.79 %. An increase 239 in gas flow rate of CO<sub>2</sub> reduces the contact time between CO<sub>2</sub> and the absorbing liquid, which 240 241 decreases the capture efficiency. CO2 absorption is often limited by mass transfer between the gas and liquid phases. However, the bCA enzyme helps to overcome this limitation by maintaining a 242 high CO<sub>2</sub> concentration gradient and accelerating the chemical reaction, thereby increasing 243 absorption. Figure 3.b shows that increasing the gas flow rate from 10 to 40 mL/min reduces the 244

removal efficiency in both co-current and counter-current flow. However, counter current flow
improves efficiency by an average of 3% by maintaining a high concentration gradient, optimising
mass transfer and increasing gas-liquid contact time, resulting in better CO<sub>2</sub> capture.



Figure 3. CO<sub>2</sub> removal as function of gas flow rate,  $C_{CO_2} = 5.24 \text{ mol m}^{-3}$ , bCA enzyme concentration = 5 mg L<sup>-1</sup>, Q<sub>1</sub>= 10 ml min<sup>-1</sup>, 0.5M (Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>), T=298 K, pH= 9.6

**Table 4**. Overview of recent advancements in CO<sub>2</sub> gas capture using hollow fiber membrane.

Membrane	Absorbent	Gas	Absorption	References
	Solution	Mixture	Flux (mol/m <sup>2</sup> ·s)	
Polyvinylidene	Nanofluid of	$CO_2/N_2$	1.14×10 <sup>-3</sup>	(Cao <i>et al</i> .,
fluoride (PVDF)	MDEA + CNT	(20/80)		2021)
PP (3M Liqui-Cel <sup>TM</sup> )	Potassium	$CO_2/N_2$	2.27×10-4	(Nieminen et
	glycinate amino acid salt	(10/90)		al., 2020)
Superhydrophobic	Activated K <sub>2</sub> CO <sub>3</sub>	$CO_2/N_2$	2.5×10 <sup>-3</sup>	(Li et al.,
PEEK		(13/87)		2013)
Polyvinylidene	Carbonate	$CO_2/N_2$	2.44×10 <sup>-4</sup>	This work
fluoride (PVDF)	solution $+$ bCA	(20/80)		

### 253 **6.3 Liquid flow rate effect on CO**<sub>2</sub> removal

254 Figure 4 shows the impact of liquid flow rate on CO<sub>2</sub> removal efficiency with and without enzyme 255 in 0.5 M Carbonate solution (Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>). Figure 4.a shows that as the liquid flow rate increases from 10 mL min<sup>-1</sup> to 40 mL min<sup>-1</sup> CO<sub>2</sub> removal increase from 23.47 % to 56.33 % without 256 addition of bCA. With 5 mg/L of bCA it founds that CO<sub>2</sub> removal increase from 57.17 % to 69.07 257 %. This enhancement (  $\sim 24$  % to  $\sim 14$  %), from 10 mL min<sup>-1</sup> to 40 mL min<sup>-1</sup> (the main causes of 258 the decrease in effectiveness are the solvant's saturation with CO<sub>2</sub> and the shorter contact time) 259 due to bCA which lowers the mass transfer resistance by speeding up the process. 260 The enhancement is more noticeable at high flow rates, indicating that the enzyme enhances absorption 261 even more at high liquid renewal rates. Figure 4.b increasing in liquid flow rate from 10 mL min<sup>-</sup> 262 <sup>1</sup> to 40 mL min<sup>-1</sup> both in counter-current and co-current, removal efficiency increase, here the 263 counter-current flow enhances removal efficiency about  $\sim 3$  %. 264



Figure 4. CO<sub>2</sub> removal as function of gas flow rate,  $C_{CO_2} = 5.24 \text{ mol m}^{-3}$ , bCA enzyme = 5 mg L<sup>-</sup>

267 <sup>1</sup>,  $Q_g = 10 \text{ ml min}^{-1}$ , 0.5M (Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>), T = 298 K, pH=9.6

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## 269 6.4 Effect of enzyme bCA

270 Figure 5 presents the effect of concentration of bCA on CO<sub>2</sub> removal efficiency. An increase in 271 CO<sub>2</sub> removal is observed from 23.17% to 91.51%, when bCA concentration increases from 0 mg  $L^{-1}$ , to 50 mg  $L^{-1}$  respectively. Figure 5 shows that with 5 mg  $L^{-1}$  of bCA the efficiency of CO<sub>2</sub> 272 removal intensifies by average 24%. The use of bCA enzyme has a notable impact by accelerating 273 274 the CO<sub>2</sub> hydration reaction, which significantly increasing the effectiveness of the capture process. Beyond this concentration (40 mg L<sup>-1</sup>), the efficiency stabilizes, showing no significant further 275 improvement. bCA enzyme improves mass transfer by maintaining a high concentration gradient, 276 which implies a reduction in transfer resistance in the carbonate solution. From about 40 mg L<sup>-1</sup>, 277 the improvement CO<sub>2</sub> removal efficiency becomes very weak, indicating an enzyme saturation 278 effect. Adding more enzyme beyond 40 mg L<sup>-1</sup> hardly improves performance anymore. 279



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Figure 5. CO<sub>2</sub> removal as function of bCA enzyme concentration,  $C_{CO_2} = 5.24$  mol m<sup>-3</sup>, T= 298

K, pH= 9.6,  $Q_l$ = 10 ml min<sup>-1</sup>,  $Q_g$  = 10 ml min<sup>-1</sup>, n=11, Counter-current flow

In conclusion, this thesis explores the modelling and simulation of CO<sub>2</sub> capture using a hollow 284 285 fiber membrane with carbonate solutions enhanced by enzymes as bio-promoters. The developed 286 methodology has been successfully implemented, providing valuable insights into the theoretical impact of enzymatic enhancement on CO<sub>2</sub> absorption efficiency using, for COMSOL software. 287 288 Key parameters studied such as the gas flow rate, liquid flow rate both in counter-current and cocurrent, enzyme concentration. It founds that increasing the CO<sub>2</sub> gas flow rate from 10 ml min<sup>-1</sup> to 289 40 ml min<sup>-1</sup>, reduces removal efficiency due to decreased contact time and mass transfer 290 limitations, increasing the liquid flow rate from 10 ml min<sup>-1</sup> to 40 ml min<sup>-1</sup> CO<sub>2</sub> removal efficiency 291 increases. However, the presence of the bCA enzyme and the counter-current flow configuration 292 enhance CO<sub>2</sub> absorption both in term of gas and liquid flow rate by maintaining a high 293 concentration gradient Although the bCA enzyme improves CO<sub>2</sub> removal efficiency, its impact 294 becomes less significant at higher flow rates, as physical mass transfer limitations start to dominate 295 over reaction kinetics. Additionally. The bCA enzyme significantly enhances CO<sub>2</sub> removal in 296 carbonate solutions, reaching nearly almost total removal efficiency at 40 mg L<sup>-1</sup> enzyme 297 concentration. 298

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#### **300 Abbreviations**

С	Concentration (mol m <sup>-3</sup> )
bCA	Bovine Carbonic Anhydrase
$C_0$	CO <sub>2</sub> concentration at inlet (mol m <sup>-3</sup> )
$CO_2$	Carbon dioxide
C <sub>CO2</sub> ,Shell	$CO_2$ concentration in the shell side (mol m <sup>-3</sup> )

$C_{CO_2,membrane}$	$CO_2$ concentration in the membrane side (mol m <sup>-3</sup> )
C <sub>CO2</sub> ,tube	CO <sub>2</sub> concentration in the tube side (mol m <sup>-3</sup> )
D <sub>CO2</sub> ,Shell	Diffusion constant of $CO_2$ in the shell side (m <sup>2</sup> s <sup>-1</sup> )
D <sub>CO2</sub> ,membrane	Diffusion constant of $CO_2$ in the membrane side (m <sup>2</sup> s <sup>-1</sup> )
D <sub>CO2</sub> ,tube	Diffusion constant of $CO_2$ in tube side (m <sup>2</sup> s <sup>-1</sup> )
HFMC	Hollow fiber membrane contactor
k <sub>OH</sub> -	Specific reaction rate constant of amine (m <sup>3</sup> kmol <sup>-1</sup> s <sup>-1</sup> )
k <sub>Cat</sub>	Turnover Number (s <sup>-1</sup> )
k <sub>m</sub>	Michaelis Constant (mol m <sup>-3</sup> )
L	Length of the fiber (m)
m'	Physical solubility
n	Number of fibers
Q1	Liquid flow rate (m <sup>3</sup> s <sup>-1</sup> )
$Q_{\rm g}$	Gas flow rate of $CO_2$ (m <sup>3</sup> s <sup>-1</sup> )
R	Module radius (m)
$\mathbf{r}_1$	Outer membrane radius (m)
<b>r</b> <sub>2</sub>	Inner membrane radius (m)
<b>r</b> <sub>3</sub>	Shell radius (m)
$\overline{V}$	Average velocity (m s <sup>-1</sup> )
V <sub>z-Shell</sub>	Velocity in the shell side (m s <sup>-1</sup> )
V <sub>z-tube</sub>	Velocity in the tube side (m s <sup>-1</sup> )
ø	Module volume fraction
δ	Thickness
ε	Porosity
τ	Tortuosity factor

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