CFD Analysis of CO\textsubscript{2} Sequestration Applying Different Absorbents Inside the Microporous PVDF Hollow Fiber Membrane Contactor

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Abstract
The sequestration process of greenhouse contaminants such as CO\textsubscript{2} via hollow fiber membrane contactor (HFMC) is regarded as a promising technology to manage the deleterious impressions of CO\textsubscript{2} on environment such as global warming and air pollution. This investigational paper renders a wide-ranging 2D simulation in order to assess the removal performance of CO\textsubscript{2} from CO\textsubscript{2}/CH\textsubscript{4} gaseous stream (containing 80 % CH\textsubscript{4} and 20 % CO\textsubscript{2}) in the HFMC. As the novelty, the evaluation of CO\textsubscript{2} acid gas removal from gaseous mixture applying four novel absorbing agents (potassium threonate (PT), piperazine (PZ), pure water (H\textsubscript{2}O) and methyldiethanolamine (MDEA)) is implemented in the HFMC with the aim of introducing a more efficient liquid absorbent for CO\textsubscript{2} sequestration.

Model validation is done based on the comparison of mathematical model outcomes and experimental data in a wide range of H\textsubscript{2}O velocity and confirms a desirable agreement with an average relative deviation (ARD) of approximately 3 % for CO\textsubscript{2} flux. It is perceived from the results that PZ is introduced as the most efficient liquid absorbent for CO\textsubscript{2} sequestration and MDEA, PT and H\textsubscript{2}O are in the next category (100 % removal using PZ > 96 % removal using MDEA > 89 % removal using PT > 57 % removal using H\textsubscript{2}O). The results corroborate that increase in membrane tortuosity and gas velocity negatively affects the sequestration process while increment of module length and porosity improve the separation of CO\textsubscript{2}.

Keywords
absorbent, CO\textsubscript{2} sequestration, membrane contactor, modeling and simulation, CO\textsubscript{2}/CH\textsubscript{4} gaseous stream

1 Introduction
Nowadays, increase in the emission of greenhouse contaminants has eventuated in serious climate change and caused worldwide concern in environmental, scientific and political fields. Therefore, major impurities of industrial gaseous flows such as CO\textsubscript{2} and H\textsubscript{2}S are required to be removed efficiently with the aim of mitigating the deleterious influences of them on environment and industry such acid rain, global warming and the corrosion of pipelines [1-3]. Different techniques such as cryogenic distillation, absorption and currently membrane separation process have been emerged in order to eliminate carbon dioxide from gaseous streams [4-6]. Gas-liquid membrane contactor is a novel technology that has been able to solve the serious disadvantages of conventional absorbers / disrobers affect on the removal efficiency of membrane contactor as like as foaming, unloading and also channeling [7].

Apart from decreasing the abovementioned disadvantages, the hollow fiber membrane contactor (HFMC) is modular and easy to scale up which eventuates in higher proportion of surface area to volume [7]. Despite various advantages, membrane may decline the performance of the hollow fiber membrane contactor by increasing the overall resistance [8]. The investigation on CO\textsubscript{2} separation from gaseous mixtures using hollow fiber membrane contactor has been conducted since 1980. Qi and Cussler [9] were the first investigators who developed the first membrane with the aim of removing carbon dioxide acid gas from gas stream. Liquid absorbent plays an essential role for carbon dioxide elimination in the HFMCs. Based on the physicochemical properties of absorbent solvents as like as thermal stability, reaction rate with CO\textsubscript{2} and the ease of regeneration, various alkanolamine solutions such
as diethanolamine (DEA), monoethanolamine (MEA), diisopropanolamine (DIPA) and triethanolamine (TEA) were applied as liquid absorbents for the separation of CO$_2$ acid gas from gaseous stream [10-15].

Generally, there are two prevalent liquid absorbents for selective separation of CO$_2$, SO$_2$ and H$_2$S acid pollutants from gaseous flows: physical and chemical liquid solvents [16-18]. Alavinasab et al. [17] used both distilled water as a physical absorbing agent and 2-aminomethyl-1-propanol (AMP) as a chemical liquid solvent with the aim of comparing the difference between physical absorption and chemical absorption of CO$_2$. They discovered that in the counter-current flow arrangement, the utilization of AMP increased the sequestration efficiency of CO$_2$ by about 16% compared to distilled water [17]. The sequestration behavior of CO$_2$ applying three conventional alkanolamines such as diethanolamine (DEA), 2-aminomethyl-1-propanol (AMP) and diisopropanolamine (DIPA) through hollow fiber membrane contactor was presented by Boucif et al. [19]. They corroborated that AMP could sequester CO$_2$ acidic contaminant from gaseous mixture better than DEA and DIPA [19]. Achariyawat et al. [16] investigated the influence of temperature and velocity of liquid absorbent on CO$_2$ flux along with the mass transfer analysis of sequestration process. Hot potassium carbonate (K$_2$CO$_3$) and liquid absorbent was applied by Mehdipour et al. [20] to evaluate the separation efficiency of CO$_2$ from gaseous mixtures via a microporous HFMC. They understood that increment in the velocity of gaseous flow from 0.1 to 0.3 m s$^{-1}$ significantly enhanced the CO$_2$ absorption flux from $6.25 \times 10^{-4}$ to $7.75 \times 10^{-4}$ mol m$^{-2}$ s$^{-1}$ [20]. The influence of potassium glycinate (PG), sodium hydroxide (NaOH) and potassium argininate (PA) absorbents on the sequestration performance of CO$_2$ was studied by Nakhjiri et al. [21]. They perceived that PA could sequester about 95% of inlet CO$_2$ while the sequestration efficiency of CO$_2$ using PG and NaOH was only 62 and 57% of CO$_2$, respectively [21].

Currently, different investigators developed the finite element method (FEM) with the aim of evaluating the sequestration percentage of greenhouse pollutants such as CO$_2$ and H$_2$S from various gaseous mixtures [12, 13, 22-25]. Besides, numerous researchers applied COMSOL software, which is based on FEM to implement the computational fluid dynamics (CFD) simulation of CO$_2$ separation from gaseous mixtures [12, 13, 20, 26]. They reported reasonable precision compared to experimental data. Considering the abovementioned items, COMSOL is applied in this article to provide CFD analysis of CO$_2$ sequestration from CO$_2$/CH$_4$ gaseous stream under non-wetting mode of operation.

In this investigational paper, a wide-ranging 2D simulation is presented with the goal of studying the CO$_2$ sequestration efficiency from gaseous stream containing 20% CO$_2$ and 80% CH$_4$. Numerical simulation is implemented under non-wetting mode of operation and counter-current pattern of gas and liquid. As the novelty, physical solvent (H$_2$O) and chemical solvents (potassium threonate (PT), piperazine (PZ) and methyl diethanolamine (MDEA)) are utilized for CO$_2$ separation. Various parameters which affect the sequestration efficiency of CO$_2$ via HFMC such as gas velocities, porosity and tortuosity of hollow fiber membrane contactor and module length are under the investigation.

2 Mass Transfer in Microporous HFMC

The transport of interested gas (CO$_2$) from the gas phase through the microporous PVDF membrane into liquid phase is vividly demonstrated by Fig. 1 and can be explained by the resistance-in-series model, presented by Eq. (1) [27]:

$$\frac{1}{k_{ol}} = \frac{1}{k_d} \left( \frac{H_d}{k_d d_{in}} + \frac{H_d}{k_d d_i} \right).$$

Where in this equation, $k_{ol}$ is expressed as the overall mass transfer coefficient in the liquid phase. $k_d$, $k_m$ and $k_i$ are the local mass transfer coefficients in the gas phase, membrane phase and liquid phase, respectively. $H$, $d_{in}$ and $d_i$ are respectively denoted as Henry’s constant, the outer, inner and logarithmic average diameters of the fibers. Eq. (2) presents the Yang and Cussler [28] mass transfer correlation with the aim of predicting the CO$_2$ transfer coefficient inside the shell compartment:

$$S_h = \frac{k_{CO_2,de} d_i}{D_{CO_2,de}} = 1.25 \left( \frac{d_i}{L} \right) Re^{0.93} Sc^{0.33}.$$

In this equation, $d_i$ is denoted as the hydraulic diameter of shell. The CO$_2$ mass transfer coefficient in the membrane side ($k_{CO_2,de}$) is derived by Eq. (3):

$$k_{CO_2,de} = \frac{D_{CO_2,de} \tau}{\tau \delta}.$$

Where $\tau$, $\delta$ and $\epsilon$ are membrane’s porosity, tortuosity and thickness, respectively. Equation (4) renders the reputable Graetz-Leveque mass transfer correlation for accurate estimation of liquid mass transfer in the tube compartment ($k_v$) [29]:

$$S_h = \frac{k_v d_i}{D_{CO_2,de}} = 1.62 \left( \frac{d_i}{L} Re Sc \right)^{\frac{1}{3}}.$$

Where $S_h$, $Re$ and $Sc$ are respectively expressed as the Sherwood number, Reynolds number and Schmidt number.
3 Theory of Model

The major purpose of this article is to represent a comprehensive dynamic modeling and a wide-ranging 2D numerical simulation of CO₂ separation from gaseous flow via hollow fiber membrane contactor utilizing PT, PZ, H₂O and MDEA absorbents. Continuity equations are derived and consequently solved in three main domains including tube side (liquid phase), porous membrane side and shell section (gas phase). The diagrammatic scheme and circular approximation of the porous PVDF hollow fiber membrane contactor is apparently demonstrated in Fig. 2. Based on the Happel's [30] free surface model, the fiber's cross sectional region is assumed to be circle-shaped which is clearly demonstrated in Fig. 2. It is obvious from the schematic diagram that the gaseous stream is fed into the shell segment of the HFMC, passes through the pores of membrane and eventually is absorbed by PT, PZ, H₂O and MDEA stripping absorbents. Due to the assumption of non-wetting mode of operation, only the diffusion of gas phase occurs in the membrane side of the hollow fiber membrane contactor and liquid absorbents flow in the tube side of HFMC based on counter-current form.

Module specification, operating conditions and also physicochemical properties of CO₂ acid gas and PT, PZ, H₂O and MDEA absorbents utilized in modeling and numerical simulation are illustrated in Table 1 and Table 3, respectively. Following assumptions are implemented to develop the dynamic modeling and numerical simulation:

1. Steady state and isothermal conditions,
2. Non wetting mode of operation,
3. The utilization of Henry's law for the interface of gas and liquid,
4. The application of Happel's free surface model with the purpose of anticipating the species velocity profile in the liquid phase (tube section),
5. The existence of ideal gas behavior in the tube segment of hollow fiber membrane contactor,
6. The consideration of laminar liquid flow in the tube side and laminar gas flow in the shell side,
7. The existence of a fully developed laminar parabolic gas velocity profile in the shell side of the hollow fiber membrane contactor and
8. Counter-current arrangement of liquid-gas flow.

Fig. 3 shows the molecular structures of PT, PZ, H₂O and MDEA used as absorbing agents in this investigation.

| Parameter          | Value | Unit |
|--------------------|-------|------|
| Type of membrane   | PVDF  | --   |
| Inner fiber radius (r₁) | 3.25×10⁻⁴ | m   |
| Outer fiber radius (r₂) | 5×10⁻⁴    | m   |
| Module inner radius (R)  | 5×10⁻³    | m   |
| Effective contact area | 0.019      | m²   |
| Module length       | 0.27   | m    |
| ε (Porosity)        | 0.75   | --   |
| τ (Tortuosity)      | (2 – ε)² / ε | --   |
| Number of fibers    | 50     | --   |
| Temperature (T)     | 303.15 | K    |
| Gas velocity (V₉)   | 0.07   | m s⁻¹|
| Liquid velocity (V₇) | 2.3    | m s⁻¹|
| P                   | 1      | atm  |
3.1 Governing Equations in the Tube Region

The steady state material balance for species \( i \) (CO\(_2\), PT, PZ, H\(_2\)O and MDEA liquid absorbents) in the tube side of HFMC considering principal mechanisms (diffusion, convection and also reaction) may be derived as Eq. (5) [13]:

\[
D \frac{\partial^2 C_{i,\text{tube}}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{i,\text{tube}}}{\partial r} + \frac{\partial^2 C_{i,\text{tube}}}{\partial z^2} = \frac{V_{\text{tube}}}{V_{\text{tube}}} \frac{\partial C_{i,\text{tube}}}{\partial z} - R_i. 
\]

It can be denoted from the equation that \( D_{i,\text{tube}} \) is diffusion coefficient of components \( i \) (CO\(_2\), PT, PZ, H\(_2\)O and MDEA) inside the tube region of HFMC and also \( R_i \) and \( V_{\text{tube}} \) are described as the reaction rate and the velocity in the axial direction, respectively. On the basis of Newtonian laminar flow, the estimation of axial velocity distribution is as Eq. (6) [13]:

\[
V_{\text{tube}} = 2V_{\text{t}} \left[ 1 - \left( \frac{r}{r_f} \right)^2 \right]. 
\]

In Eq. (6) \( V_{\text{t}} \), \( r \) and \( r_f \) express the average velocity inside the tube section, radial coordinate and the radius of inner fiber, respectively. Table 2 lists the reaction of CO\(_2\) with physical absorbent (H\(_2\)O) and chemical absorbents (PT, PZ, H\(_2\)O and MDEA) involved in CO\(_2\) sequestration.

The reaction rates of CO\(_2\) acid pollutant with PT, PZ, H\(_2\)O and MDEA absorbent solutions inside the tube compartment of hollow fiber membrane contactor are rendered by Eqs. (7) to (10), respectively [34-37],

\[
r_{\text{CO}_2,\text{PT}} = -4.1310^4 \exp(3580/T) C_{PT} \exp(0.9C_{PT}) C_{\text{CO}_2} \tag{8} 
\]

\[
r_{\text{CO}_2,\text{H}_2\text{O}} = -1.210^4 C_{\text{H}_2\text{O}} \exp(C_{\text{CO}_2}) \tag{9} 
\]

\[
r_{\text{CO}_2,\text{MDEA}} = -8.74110^12 \exp(-8625/T) C_{\text{CO}_2} C_{\text{MDEA}} \tag{10} 
\]

Table 2 Reaction of CO\(_2\) with physical and chemical absorbents

| Absorbent | Reaction | Ref |
|-----------|----------|-----|
| PT        | CO\(_2\) + 2RNH\(_2\) → RNHCOO\(^-\) + RNH\(_3\)\(^+\) | [32] |
| PZ        | PZ + CO\(_2\) + H\(_2\)O → HCO\(_3\)^- + PZCOO\(^-\) | [33] |
| H\(_2\)O   | H\(_2\)O + CO\(_2\) ↔ H\(^+\) + HCO\(_3\)^- | [34] |
| MDEA      | R, R, R, N + H\(_2\)O + CO\(_2\) → R, R, R, NH\(^+\) + HCO\(_3\)^- | [35] |

Table 3 CO\(_2\), PT, PZ, H\(_2\)O and MDEA physicochemical properties used for dynamic modeling and simulation.

| Parameter | Value | Unit | Ref |
|-----------|-------|------|-----|
| \( D_{\text{CO}_2,\text{shell}} \) | 1.8 \times 10^{-5} | m\(^2\) s\(^{-1}\) | [13] |
| \( D_{\text{CO}_2,\text{mem}} \) | \( D_{\text{CO}_2,\text{shell}} \)/\( \varepsilon \tau \) | m\(^2\) s\(^{-1}\) | [13] |
| \( D_{\text{CO}_2,\text{PT}} \) | 1.38 \times 10^{-9} | m\(^2\) s\(^{-1}\) | [38] |
| \( D_{\text{CO}_2,\text{PZ}} \) | 1.51 \times 10^{-9} | m\(^2\) s\(^{-1}\) | [34] |
| \( D_{\text{CO}_2,\text{H}_2\text{O}} \) | 2.35 \times 10^{-6} \exp(-2199/T) | m\(^2\) s\(^{-1}\) | [39] |
| \( m_{\text{CO}_2,\text{PT}} \) | 1.5 | 1 | [37] |
| \( m_{\text{CO}_2,\text{PZ}} \) | 1.06 | 1 | [37] |
| \( m_{\text{CO}_2,\text{H}_2\text{O}} \) | 0.83 | 1 | [37] |
| \( m_{\text{CO}_2,\text{MDEA}} \) | 0.82 | 1 | [37] |
| OH concentration | \( K_w / K_p (1 - m_{OH}) / m_{OH} \) | mol m\(^{-3}\) | [42, 43] |
3.2 Governing Equations in the Membrane Region
In the membrane side of HFMC, non-wetting mode of operation is assumed. Therefore, the only mechanism which may be considered for CO₂ transport inside the microporous PVDF membrane is diffusion. The governing mass balance in the steady state mode can be presented as Eq. (11) [13]:

\[ D_{CO_2 \text{-mem}} \left[ \frac{\partial^2 C_{CO_2 \text{-mem}}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2 \text{-mem}}}{\partial r} + \frac{\partial^2 C_{CO_2 \text{-mem}}}{\partial z^2} \right] = 0. \]  

(CO₂ \text{-mem} and D_{CO_2 \text{-mem}} in this equation indicate the concentration and diffusion coefficient of CO₂ across the microporous polyvinylidene fluoride (PVDF) membrane. The diffusion coefficient of carbon dioxide in the microporous PVDF membrane depends on two variables: 1) membrane porosity (ε) and 2) membrane tortuosity (τ) and may be defined as Eq. (12) [13]:

\[ D_{CO_2 \text{-mem}} = \frac{C_{CO_2 \text{-mem}} \cdot \tau}{\varepsilon}. \]  

3.3 Governing Equations in the Shell Region
The governing differential mass transfer balance under the steady state mode of operation in order to transport of CO₂ inside the shell is given as Eq. (13) [13]:

\[ D_{CO_2 \text{-shell}} \left[ \frac{\partial^2 C_{CO_2 \text{-shell}}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2 \text{-shell}}}{\partial r} + \frac{\partial^2 C_{CO_2 \text{-shell}}}{\partial z^2} \right] = V_{e-shell} \frac{\partial C_{CO_2 \text{-shell}}}{\partial z}. \]

Based on the assumption of Happel’s free surface model, the profile of velocity inside the shell region of HFMC is presented as Eq. (14) [13]:

\[ V_{e-shell} = 2\pi \left[ 1 - \left( \frac{r_f}{r_i} \right)^2 \right] \times \left[ \frac{(r_f/r_i)^2 - (r_f/r_i)^2 + 2 \ln (r_f/r_i)}{3 + (r_f/r_i)^2 - 4 (r_f/r_i)^2 + 4 \ln (r_f/r_i)} \right]. \]

In Eq. (14), \( V_{e} \) is average velocity inside the shell region of HFMC. Also, \( r_i \) is the shell’s effective radius and may be presented as Eq. (15) [13]:

\[ r_i = r_s \sqrt{\frac{1}{1 - \phi}}. \]

ϕ is the void’s volume fraction and can be calculated by Eq. (16):

\[ 1 - \phi = \frac{m_e^2}{R^2}. \]

In which, \( R^2 \) and \( n \) are defined as the inner radius of module and number of fibers, respectively. Therefore, using Eqs. (10) and (11), the effective radius of shell based on Happel’s free surface model is achieved \( 8.45 \times 10^{-4} \) m.

Boundary conditions utilized inside the tube, porous membrane and shell regions of hollow fiber membrane contactor are listed in Table 4.

3.4 Numerical Scheme
The prominent purpose of this research article is to present a dynamic modeling and a wide-ranging 2D comprehensive simulation for CO₂ capture from CO₂/CH₄ gaseous stream applying novel liquid stripping absorbents (PT, PZ, H₂O and MDEA) in microporous HFMC using CFD technique. According to this reason, COMSOL Multiphysics software which is based on finite element method (FEM) was utilized to solve the governing equations in the tube, membrane and shell sides of HFMC. Due to undeniable and various abilities such as memory efficiency, robustness and the simplicity to use for solving widespread symmetric linear systems, PARDISO numerical solver was used to control the material balance error. In order to solve partial differential equations, a computational platform consisting of 64-bit operating system, Intel core™ i5-4200U CPU at 1.60 GHz and 4 Gigabyte RAM was used. The computational duration for solving the equations of the model was approximately 3 minutes. Fig. 4 and Fig. 5 demonstrate the triangular mesh elements employed to analyze gaseous mixture behavior inside the microporous HFMC and convergence status of 2D simulation, respectively. It is apparent from the Fig. 4 that due to the existence of reaction and gas-liquid contact inside the pores of membrane.

| Table 4 Boundary conditions utilized for model development |
|---------------------------------|-----------------|-----------------|-----------------|
| Boundary | Tube side | Membrane side | Shell side |
|---------|-----------|-----------------|-----------------|
| z = 0 | \( C_{CO_2 \text{-in}} = 0 \) | Insulated | \( \frac{\partial C_{CO_2 \text{-out}}}{\partial r} = 0 \) |
| z = \( L \) | \( C_{CO_2 \text{-out}} = C_{init} \) | Insulated | \( C_{CO_2 \text{-shell}} = C_{init} \) |
| \( r = 0 \) | \( \frac{\partial C_{CO_2 \text{-shell}}}{\partial r} = 0 \) | \( r = r_1 \) | \( C_{CO_2 \text{-shell}} = m_{CO_2} C_{CO_2 \text{-shell}} C_{CO_2 \text{-shell}} = \frac{C_{CO_2 \text{-shell}}}{m_{CO_2}} \) |
| \( r = r_2 \) | \( C_{CO_2 \text{-shell}} = C_{CO_2 \text{-shell}} C_{CO_2 \text{-shell}} = C_{CO_2 \text{-shell}} C_{CO_2 \text{-shell}} = C_{CO_2 \text{-shell}} \) |
compartment, the mesh size and density in this region is smaller than other areas to increase the outputs accuracy and reduce the computational discrepancies. Fig. 5 clearly illustrates that this system is non-stiff which provides confidence in the solution process and after 13 iterations the system reaches convergence.

It is worth mentioning that although increase in the number of meshes declines the computational errors, it dramatically increases the iterations and calculation time. Therefore, achieving the optimal number of meshes is mandatory. The influence of mesh numbers on the CO$_2$ concentration at the outlet of the microporous HFMC’s shell compartment is illustrated in Fig. 6. It is understood from the Fig. 6 that increment in the mesh numbers leads in better convergence of simulation’s results, but after the 260th mesh, no significant changes in CO$_2$ concentration at the shell side’s outlet using different chemical absorbents occurs which implies the convergence of the simulation outcomes. Therefore, the computational precision is independent of the applied mesh numbers in values greater than 260.

4 Results and Discussion

4.1 Model Validation

Up to now, based on the knowledge of the authors, there is only one experimental article about the sequestration of CO$_2$ from CO$_2$/CH$_4$ gaseous stream using H$_2$O inside the microporous PVDF HFMC [16]. Hence the results of developed model are validated with the experimental data reported in the literature by Atchariyawut et al. [16]. Fig. 7 corroborates that there is an excellent agreement between the results of simulation and experimental data with an average absolute deviation (ARD) of about 3 % for CO$_2$ flux. The deviation between modeling results and experimental data are able to be justified due to the anticipation of reaction kinetics and constants.
4.2 Concentration Distribution of CO₂

Fig. 8 demonstrates the dimensionless concentration distribution of CO₂ \(\frac{C_{\text{CO}_2}}{C_{\text{CO}_2,0}}\) inside the shell compartment of microporous hollow fiber membrane reactor using PT, PZ, H₂O and MDEA absorbing agents. Counter-current mode of operation justifies the movement of liquid absorbents inside the tube segment of HFMC where the concentration of CO₂ is zero \(z = 0\) and also the flow of CO₂/CH₄ gaseous stream in the other compartment (shell side) where the concentration of CO₂ is in the highest amount (maximum) \(z = L\). Overall, diffusion and convection can be regarded as two prominent mechanisms of gas transfer inside the HFMC. Diffusion mechanism happens in the radial direction \(r\) because of the gradient of concentration. Also, convection mechanism takes place in axial direction \(z\) due to the velocity of fluid. However, in the tube region of hollow fiber membrane reactor, diffusional mass transfer is preferred due to increasing CO₂ sequestration. The mechanism of CO₂ removal in the hollow fiber membrane reactor can be interpreted based on the transfer of gaseous stream into the pores of membrane to the other side and the absorption of CO₂ by moving absorbent agents (PT, PZ, H₂O and MDEA) inside the shell compartment.

4.3 Axial Concentration Profile of CO₂ along the Shell-Membrane Interface

The axial concentration distribution of CO₂ along the shell-membrane interface of the HFMC utilizing PT, PZ, H₂O and MDEA liquid absorbents can be illustrated by Fig. 9. It is apparent from the Fig. 9 that at \(z = L\), the concentration of CO₂ is maximum and decreased to the minimum amount at the outlet of shell side \(z = 0\). Also, it is understood from the Fig. 9 that the dimensionless concentration of CO₂ at the outlet of shell side \(z = 0\) using PZ absorbent is about 0 while the dimensionless concentration of CO₂ at the outlet of shell side using MDEA, PT and H₂O is 0.04, 0.11 and 0.33, respectively which indicate the excellent removal performance of CO₂ with PZ compared to MDEA, PT and H₂O (100 % removal using PZ > 96 % removal using MDEA > 89 % removal using PT > 57 % removal using H₂O).

4.4 The Effect of Membrane Porosity on CO₂ Removal

The influence of membrane porosity on CO₂ sequestration from CO₂/CH₄ gaseous stream using various absorbents (PT, PZ, H₂O and MDEA) is rendered by Fig. 10. The percentage of CO₂ removal is derived from Eq. (17) [44]:

\[
\% \text{ CO}_2 \text{ removal} = 100 \times \left(1 - \frac{C_{\text{CO}_2}}{C_{\text{CO}_2,0}}\right)
\]

where \(C_{\text{CO}_2,0}\) is the initial concentration of CO₂ and \(C_{\text{CO}_2}\) is the concentration of CO₂ at any point in the membrane reactor.
% CO_2 removal \( = 100 \left( \frac{C_{\text{inlet}}}{C_{\text{outlet}}} \right) \). (17)

It is entirely apparent from the Fig. 10 that increment in the porosity of membrane from 0.1 to 0.9 eventuates in a significant increase in CO_2 removal from about 82 to approximately 100 % when PZ is used as the absorbent solution of process. However, using PT, H_2O and MDEA liquid solvents cause a relatively considerable increase in the sequestration percentage of CO_2 from almost 54 to 91 %, from 18 to 76 % and from 66 to 98 % while increasing the membrane porosity from 0.1 to 0.9. It means that a considerable removal of CO_2 from CO_2/CH_4 gaseous flow may be taken place by applying a microporous PVDF membrane with a porosity equal to 0.9 and PZ absorbent. Also it is clear that the efficiency of H_2O as absorbing agent for removing CO_2 from gaseous flow is considered insufficient. As it is clear from the Eq. (12) mentioned above, increment in the porosity of membrane increases the CO_2 diffusion coefficient inside the membrane segment of HFMC \( (D_{\text{CO}_2},_{\text{mem}}) \) and also improves the CO_2 mass transfer through the membrane. Consequently, whenever the membrane porosity increases, the transfer rate of CO_2 acidic gas inside the membrane wall improves significantly that leads to more superior CO_2 separation efficiency.

4.5 The Effect of Membrane Tortuosity on CO_2 Removal

Fig. 11 depicts the influence of membrane tortuosity on CO_2 removal using PT, PZ, H_2O and MDEA liquid absorbents. As can be seen in the abovementioned Eq. (11), the effective diffusion coefficient of CO_2 inside the membrane segment of HFMC \( (D_{\text{CO}_2},_{\text{mem}}) \) is in inverse relation with the membrane tortuosity. Hence, by increasing the tortuosity of membrane, a substantial increment in the mass transfer resistance of membrane takes place which results in a significant reduction in total mass transfer of CO_2. By decreasing total mass transfer resistance of the membrane, the diffusivity of CO_2 in the membrane declines which leads in the reduction of CO_2 absorption percentage. Increment in the tortuosity of membrane (from 1 to 5) leads in reducing the percentage of CO_2 removal from about 100 to 96 % using PZ, from about 92 to 82 % using PT, from about 90 to 82 % using MDEA and from 77.5 to 48 % using H_2O absorbent. Different decrements in CO_2 removal can be justified due to the difference of some constants and kinetics of reactions such as the reaction rates and the solubility of CO_2 in PS, PZ, MDA and H_2O liquid absorbents utilized for developing the computational simulation.

4.6 The Effect of Module Length on CO_2 Removal

Fig. 12 represents the influence of module length on the sequestration rate of CO_2 from CO_2/CH_4 gaseous stream in the microporous PVDF hollow fiber membrane contactor using four various absorbents (PT, PZ, H_2O and MDEA). As can be seen from the Fig. 12, by increasing the module length, residence time and also contact area between two phases (gas and liquid phases) through the HFMC increases substantially. Therefore, increase in the contact area and residence time inside the microporous HFMC provides better circumstances for efficient reaction of CO_2 molecules and liquid absorbents that positively encourages the CO_2 separation efficiency from gaseous stream. According to the
Fig. 12, while using PZ absorbent, the sequestration percentage of CO\textsubscript{2} from CO\textsubscript{2}/CH\textsubscript{4} gaseous mixture improves from around 96 to 100 % when the module length increases from 0.1 to 0.5 m. Also using PT, H\textsubscript{2}O and MDEA absorbing agents causes a substantial linear increment in the sequestration percentage of CO\textsubscript{2} from 60 to almost 97 %, from 40 to almost 78 % and from 79 to 99 %, respectively when the module length increases from 0.1 to 0.5 m.

4.7 The Effect of Gas Velocity on CO\textsubscript{2} Removal

Fig. 13 depicts the removal efficiency of CO\textsubscript{2} in a wide range of gas velocities applying PT, PZ, H\textsubscript{2}O and MDEA liquid absorbents. As expected, increment of gas velocity results in a substantial decrease in the residence time in the hollow fiber membrane module. Even in the low velocity of gas, decrease in the sequestration percentage of CO\textsubscript{2} is completely apparent. As can be seen from the Fig. 13, by increasing the velocity of gas from 0.15 to 0.5 m s\textsuperscript{-1}, the removal percentage of CO\textsubscript{2} decreases dramatically from about 100 to nearly 96 % while using PZ absorbent solvent. Also Fig. 13 indicates that the increment of the velocity of gas from 0.15 m s\textsuperscript{-1} to 0.5 m s\textsuperscript{-1} results in a considerable decrease in the sequestration percentage of CO\textsubscript{2} from about 66 to nearly 30 %, from 15 to nearly 20 % and from 80 to 40 % while using PT, H\textsubscript{2}O and MDEA, respectively.

5 Conclusion

In this investigational study a dynamic modeling and two dimensional comprehensive simulation is presented in order to assess the sequestration performance of CO\textsubscript{2} from CO\textsubscript{2}/CH\textsubscript{4} gaseous stream in the hollow fiber membrane contactor. Four novel liquid absorbing agents including potassium threonate (PT), piperazine (PZ), pure water (H\textsubscript{2}O) and methyldiethanolamine (MDEA) are applied with the aim of comparing their efficiency for CO\textsubscript{2} sequestration. The results of dynamic modeling and simulation indicated the superiority of PZ for removing CO\textsubscript{2} in comparison with PT, H\textsubscript{2}O and MDEA liquid absorbents. Based on the abovementioned results, the amount of CO\textsubscript{2} removal from gaseous stream using PZ is approximately 100 % while the maximum CO\textsubscript{2} removal using MDEA, PT, and H\textsubscript{2}O is about 96, 89 and 57 %, respectively. Comparison of modeling and two dimensional simulation results with the experimental data is implemented for investigating the accuracy of simulation and validating the simulation results. An average deviation of 3 % is seen between the results of two dimensional simulation and experimental data which confirms an excellent agreement. Increment of some operational parameters such as module length and porosity encourage the sequestration percentage of CO\textsubscript{2} from gaseous stream while some other parameters such as membrane tortuosity and gas velocity had negative effect on the removal of CO\textsubscript{2} from CO\textsubscript{2}/CH\textsubscript{4} gaseous stream.
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