Kinetic study and process model development of \( \text{CO}_2 \) absorption using hollow fiber membrane contactor with promoted hot potassium carbonate

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ABSTRACT

In this study, application of hollow fiber membrane contactor (HFMC) as an appropriate technology for absorption of \( \text{CO}_2 \) from gas mixture is proposed. A mathematical model is developed based on a new kinetic for prediction of "non-wetted" mode of HFMC performance in the presence of hot potassium carbonate promoted by diethanolamine (DEA). The model validation results show an appropriate agreement with experimental data which is reported in literature. Study of some related parameters on \( \text{CO}_2 \) removal efficiency indicates that increasing the liquid flow rate and number of fibers have positive effect on the \( \text{CO}_2 \) absorption, whereas enhancing the gas flow rate decreases the rate of absorption. The results show that the counter – current operation mode has better performance with respect to co-current flow. Also when gas and liquid phases pass through the tube and shell sides respectively, due to increasing the contact surface in the liquid phase, the \( \text{CO}_2 \) absorption will occur with higher efficiency than the case of gas flow in the shell side. Investigation of different absorption solvents indicates that the order of absorption rate of solvents is as follows: promoted hot potassium carbonate > 2-amino-2-methyl-1-propanol (AMP) > DEA > methyldiethanolamine (MDEA) > blend of MDEA and DEA. Modeling analysis reveals that due to higher absorption rate of promoted hot potassium carbonate with respect to other solvents, the required operating temperature for chemical absorption is lower than other solvents and as a result, this advantage also improves physical absorption.

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- \( \text{CO}_2 \) absorption
- Hollow fiber membrane contactor
- Potassium carbonate

1. Introduction

Nowadays, due to development of industrial activities, the concentration of greenhouse gases has been increased rapidly in the atmosphere and it leads to global warming [1-3]. \( \text{CO}_2 \) as a main greenhouse gas has been produced largely from burning different fossil fuels such as coal, natural gas and oil. These sources include coal – fired power plants, oil and gas operations and other industries [4-6]. The researches of World Bank’s Global Gas Flaring Reduction Partnership (GGFR) represent that about 400 million tons emission of \( \text{CO}_2 \) into the air – roughly 1.5% of the global \( \text{CO}_2 \) – was generated by almost one third of Europe’s natural gas burning in flares in one year [7]. Therefore \( \text{CO}_2 \) capture is essential to prevent the menace of global warming [8]. In recent years, researchers have focused on developing effective methods with economic and safety consideration for the separation of \( \text{CO}_2 \) from gases mixed stream in many industries such as fuel cell technology, ammonia production, and flue gas purification [9-11]. There are various ways for \( \text{CO}_2 \) capture such as gas hydrates formation, chemical – looping combustion process, membrane process, chemical absorption and bioelectrochemical process. Chemical absorption with alkanolamine solutions such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and methyldiethanolamine (MDEA) in absorption columns is a common industrial way [12-15]. Also, bioelectrochemical techniques is an interesting \( \text{CO}_2 \) capture technique in which electricity can be used as an energy source for the microbial catalytic production of fuels and other organic products from \( \text{CO}_2 \). ElMekawy et al. [16] and Bajracharya et al. [17] reviewed the recent progress of bioelectrochemical \( \text{CO}_2 \) reduction to valuable products. They investigated the different technologies for the bioelectrochemical utilization of \( \text{CO}_2 \) and considered the potential opportunities for the commercialization of these methods.

Although membranes have been employed commercially for gas separation since 1980, researchers have studied on membrane more than 150 years [18-20]. Many studies have been done to develop membrane contactor systems and membranes mass transfer rate [21-24]. Membrane gas absorption has been introduced as one of the favorable technologies for preventing emission of \( \text{CO}_2 \) owning to its excellent mass transfer abilities [25]. Many researchers compared the performance of \( \text{CO}_2 \) capture from flue gases using amine absorption (packed towers or bubble columns) as a conventional technology with respect to membrane gas absorption technology [26,27]. Their investigation showed that membranes have high surface area to volume...
ratio, flexible operation features, linear scale-up, compact size and modularity [28–30]. In addition, conventional absorption columns have many defects such as channeling, foaming, flooding, air entrainment, and also high operational and capital costs [31]. Application of membranes solves the above problems, because CO₂ absorption happens in a membrane contactor when the gas stream contacts with the liquid phase on the other side of membrane. Indeed, membrane acts as a barrier between gas and liquid phases for preventing inter penetration of them. Also, increasing the length of membranes could be enhanced the mass transfer between phases [31]. Furthermore membrane processes introduced as an environment friendly alternative because they always have a little loss of solvent (amine solution) to the atmosphere during the process [32].

Many researchers have been worked on hollow fiber membrane contractors (HFMC) and developed microporous hollow fibers, as a new method for gas separation [8,33,34]. HFMC is one of the main types of commercialized membrane modules. The membrane modules have excellent mass transfer performance, because of its large surface area per unit volume (about 3000 ft²/ft³) [35]. Membrane contacting as a process which combines the advantages of modularity and compactness, has been widely studied for CO₂ capture [36–40].

CO₂ capture is recognized as an important technology to achieve significant greenhouse gas emission reduction before 2050. The main challenging issue in this field is the high cost of avoided CO₂ related to capture (~40 €/t). A significant effort to decrease this cost is necessary for its large-scale deployment. In conventional amine-based CO₂ capture process, the main factors driving the cost of avoided CO₂ are the solvent regeneration duty, the compression works, the compressor cost and the solvent make-up cost. In a related study, Yan et al. [41] investigated and compared economically the CO₂ absorption from coal-fired flue gas by three typical CO₂ capture systems such as (a) chemical absorption process in packed column using MEA solvent; (b) chemical absorption process in packed column using aqueous ammonia solution, and (c) hollow fiber membrane contactors (HFMC) using MEA solvent. Their investigations indicated that CO₂ capture using aqueous ammonia solution is cheapest among all the three CO₂ capture technologies. Also they inferred that the CO₂ capture using HFMC is still less expensive than chemical absorption process in packed column using MEA solvent even membrane price is higher [41]. Kreulen et al. [42,43] considered the effective parameters such as porosity, liquid viscosity, hollow fiber dimension and also the effect of chemical reaction on the mass transfer in the HFMC using the gas–liquid systems of CO₂–water/glycerol and CO₂ (N₂O, H₂S)–NaOH aqueous solutions. Qi and Clussler [34] were the first group which used microporous polypropylene membranes for CO₂ absorption. In another related study, Herzog [4] mentioned that application of membrane technology decreases the size of the absorber and stripper units by 65% and reduces solvent loss and the reboiler duty. Wang et al. [44] developed a theoretical model simulates the CO₂ absorption by water in microporous HFMC under two extreme operating conditions, non–wetted and wetted modes. They reported CO₂ absorption rate in the non–wetted mode is six times higher than the wetted operation. Mavroudí et al. [45] and Khaisri et al. [46] developed mathematical based model for wetting gas absorption membrane and simulated the concentration profile for CO₂ capture. Zhang et al. [47] studied the CO₂ absorption in a HFMC by experimental and modeling investigation. Their research showed that the CO₂ flux increases with the liquid velocity, whereas the inlet gas velocity hasn’t major effect on the CO₂ flux. Atcharyayut et al. [48] considered the structural effect of membrane in microporous polyvinylidene fluoride (PVDF) hollow fibers on mass–transfer rate of gas–liquid contacting process. Khaisri et al. [38] compared membrane resistance and absorption performance of three different membranes, including polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF) in a gas absorption membrane contactor. Their observations showed that the highest CO₂ absorption ability belongs to PTFE. Also Sandru et al. [49] worked on composite hollow fiber

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am</td>
<td>Amine (Diethanolamine)</td>
</tr>
<tr>
<td>C</td>
<td>Concentration (mol m⁻³)</td>
</tr>
<tr>
<td>C₀</td>
<td>Initial concentration (mol m⁻³)</td>
</tr>
<tr>
<td>C_CO₂</td>
<td>Equilibrium CO₂ concentration in the bulk of liquid (kmol m⁻³)</td>
</tr>
<tr>
<td>C_{CO₂, mem}</td>
<td>CO₂ concentration in the membrane (mol m⁻³)</td>
</tr>
<tr>
<td>C_{CO₂, shell}</td>
<td>CO₂ concentration in the shell side (mol m⁻³)</td>
</tr>
<tr>
<td>C_{CO₂, tube}</td>
<td>CO₂ concentration in the tube (mol m⁻³)</td>
</tr>
<tr>
<td>D_{CO₂, mem}</td>
<td>Diffusion coefficient of CO₂ in the membrane (m² s⁻¹)</td>
</tr>
<tr>
<td>D_{CO₂, shell}</td>
<td>Diffusion coefficient of CO₂ in the shell side (m² s⁻¹)</td>
</tr>
<tr>
<td>D_{CO₂, tube}</td>
<td>Diffusion coefficient of CO₂ in the tube (m² s⁻¹)</td>
</tr>
<tr>
<td>D_{DEA}</td>
<td>Diffusion coefficient of DEA in the membrane (m² s⁻¹)</td>
</tr>
<tr>
<td>D_{DEA, pure}</td>
<td>Diffusion coefficient of CO₂ in pure water (m² s⁻¹)</td>
</tr>
<tr>
<td>J</td>
<td>Diffusive flux</td>
</tr>
<tr>
<td>H</td>
<td>Solubility of CO₂ in solution (kmol atm⁻¹ m⁻³)</td>
</tr>
<tr>
<td>h</td>
<td>Henry’s constant</td>
</tr>
<tr>
<td>k_{DEA}</td>
<td>Second order rate constant of DEA (m³ kmol⁻¹ h⁻¹)</td>
</tr>
<tr>
<td>k_{f,OFF}</td>
<td>Forward rate constant of reaction (24) (m³ kmol⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>k_{b,OFF}</td>
<td>Backward rate constant of reaction (24) (m³ kmol⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>K_1</td>
<td>First ionization constant for carbonic acid (kmol m⁻³)</td>
</tr>
<tr>
<td>K_2</td>
<td>Second ionization constant for carbonic acid (kmol m⁻³)</td>
</tr>
<tr>
<td>L</td>
<td>Length of fiber (m)</td>
</tr>
<tr>
<td>m</td>
<td>Physical solubility (dimensionless)</td>
</tr>
<tr>
<td>n</td>
<td>Number of fibers</td>
</tr>
<tr>
<td>Q_{gas}</td>
<td>Feed gas volume flow rate (mL min⁻¹)</td>
</tr>
<tr>
<td>Q_{liquid}</td>
<td>Feed liquid volume flow rate (mL min⁻¹)</td>
</tr>
<tr>
<td>Q_g</td>
<td>Gas volume flow rate (mL min⁻¹)</td>
</tr>
<tr>
<td>Q_L</td>
<td>Liquid volume flow rate (mL min⁻¹)</td>
</tr>
<tr>
<td>R</td>
<td>Inner shell radius (m)</td>
</tr>
<tr>
<td>R_i</td>
<td>Reaction rate</td>
</tr>
<tr>
<td>r_i</td>
<td>Inner tube radius (m)</td>
</tr>
<tr>
<td>r_o</td>
<td>Outer tube radius (m)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>V</td>
<td>Velocity (m s⁻¹)</td>
</tr>
<tr>
<td>V_L</td>
<td>Velocity in the shell side (m s⁻¹)</td>
</tr>
<tr>
<td>V_g</td>
<td>Velocity in the tube side (m s⁻¹)</td>
</tr>
</tbody>
</table>

### Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε</td>
<td>Porosity (−)</td>
</tr>
<tr>
<td>τ</td>
<td>Tortuosity (−)</td>
</tr>
<tr>
<td>φ</td>
<td>Volume fraction of void space (−)</td>
</tr>
</tbody>
</table>

### Fig. 1. Schematic diagram of an industrial split-flow absorber–stripper unit.
membranes for CO₂ capture. Ghasem et al. [50] studied the effect of temperature on the performance of poly(vinylidene fluoride) microporous hollow fiber membranes. Their results showed that at lower quenching temperatures, the structure of the membrane will condense and the water and gas permeability will decrease. Lv et al. [51] worked on fabrication and characterization of super hydrophobic hollow fiber membranes for CO₂ absorption.

Another challenge in CO₂ capture is spent solution regeneration after CO₂ absorption process. Usually, solvent regeneration is performed by stripping agent such as steam or heated inert gas in stripping column. In common industrial units, stripping column operates at low pressure about atmospheric pressure. Essentially, the regeneration process depends on the pressure difference between the absorber unit and stripping column, whereas significant temperature difference is not necessary. In industrial stripping column, generated steam from a reboiler or hot air is used to strip the CO₂ from absorbent. The quantity of required stripping vapor depends to the target solution purity, the stripping column specification and the nature of the solution. As represented in Fig. 1, the CO₂–rich liquid stream from the bottom of the absorber unit is first flashed nearly to 1.15 atm in a throttling valve and subsequently passes through the stripper where it is stripped counter–currently by the stripping agent. As the solution flows downward through the stripping column in the counter–current mode with steam, CO₂ is stripped from the solution. For better performance, a portion of the lean solution from the regenerator is cooled and fed into the top of the absorber while the major portion is added at a point below the top without any change in temperature. This simple modification, which is called split–flow process, raises the temperature of the rich liquid and lowers the amount of heat needed for heating the solution to the regeneration temperature. The acid gases together with some water vapor

Table 1
Membrane contactor characteristics and model parameters [47,52,54,55].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner tube diameter [mm]</td>
<td>0.22</td>
</tr>
<tr>
<td>Outer tube diameter [mm]</td>
<td>0.30</td>
</tr>
<tr>
<td>Inner module diameter [mm]</td>
<td>63.5</td>
</tr>
<tr>
<td>Total number of tubes [−]</td>
<td>3600</td>
</tr>
<tr>
<td>Inner shell diameter [mm]</td>
<td>0.529</td>
</tr>
<tr>
<td>Module length, l [m]</td>
<td>0.2286</td>
</tr>
<tr>
<td>T [K]</td>
<td>318</td>
</tr>
<tr>
<td>DCO₂,exp [m³ s⁻¹]</td>
<td>4.967 × 10⁻¹⁰</td>
</tr>
<tr>
<td>DCO₂–absor [m³ s⁻¹]</td>
<td>0.303 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Table 2
The kinetic and equilibrium parameters [55].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>α = [K⁺] − 2[CO₂⁻] / [K⁺]</td>
</tr>
<tr>
<td></td>
<td>+ [HCO₃⁻] / [K⁺]</td>
</tr>
<tr>
<td>pCO₂ (atm)</td>
<td>K₂[H] 1 − α</td>
</tr>
<tr>
<td>K₁ (kmol m⁻³)</td>
<td>log(K₁) = −1340.7 / T + 14.843 − 0.03279T</td>
</tr>
<tr>
<td>K₂ (kmol m⁻³)</td>
<td>log(K₂) = −1340.7 / T + 14.843 − 0.03279T</td>
</tr>
<tr>
<td>H₂O (kmol atm⁻¹ m⁻³)</td>
<td>log(H₂O) = 1140 / T − 5.30</td>
</tr>
<tr>
<td>k₁H (m³ (kmol atm⁻¹ m⁻³)⁻¹)</td>
<td>log(k₁H) = 13635 − 2895 / T + 0.08I</td>
</tr>
<tr>
<td>k₁H₂O (m³ (kmol h⁻¹)⁻¹)</td>
<td>6.4 × 10⁶ exp [14.97(1 − 3551 / T)]</td>
</tr>
</tbody>
</table>

Table 3
The mechanism and reaction rate for various aqueous absorbent solutions [8,55–59].

<table>
<thead>
<tr>
<th>Aqueous absorbent solution</th>
<th>Mechanism of the reaction:</th>
<th>Rate (mol m⁻³ s⁻¹)</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃ (B) + DEA (C)</td>
<td>CO₂ + K₂CO₃ + H₂O₂ ⇌ 2KHC₃O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEA (B)</td>
<td>CO₂ + K₂CO₃ + H₂O₂ ⇌ 2KHC₃O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MDEA (B)</td>
<td>CO₂ + R₂NH + H₂O ⇌ R₂NH⁺ + HCO₃⁻</td>
<td>R₈ = k₈([CO₂] − [CO₂]ₖ)</td>
<td></td>
</tr>
<tr>
<td>AMP (B)</td>
<td>CO₂ + R₂NH + H₂O ⇌ R₂NH⁺ + HCO₃⁻</td>
<td>R₈ = k₈([CO₂] − [CO₂]ₖ)</td>
<td></td>
</tr>
<tr>
<td>DEA (B) + MDEA (C)</td>
<td>CO₂ + R₂NH + H₂O ⇌ R₂NH⁺ + HCO₃⁻</td>
<td>R₈ = k₈([CO₂] − [CO₂]ₖ)</td>
<td></td>
</tr>
</tbody>
</table>
pass overhead from the stripper and through a condenser.

In this study, two-dimensional mathematical model is developed for separation of CO$_2$ from multi component gas mixture by HFMC. The proposed model considers chemical absorption based on non-wet mode. The effect of some important parameters such as initial CO$_2$ concentration, gas and liquid flow rates, operation modes and number of fibers on HFMC performance is investigated. The gas mixture includes carbon dioxide, carbon monoxide, methane, hydrogen, argon and water, and the liquid stream contains potassium carbonate, potassium bicarbonate, DEA and water which enters in the tube side. Table 1 represents the physical and chemical properties of membrane and mole fraction of the liquid and gas inlet flows which are used in the present work.

2. Reaction network and kinetic analysis

The overall reaction of aqueous hot potassium carbonate solution and CO$_2$ takes place as (R – 1). Since potassium carbonate and
bicarbonate are strong electrolytes, so (R−1) can be rewritten as (R−2).

\[
\text{CO}_2 + K_2\text{CO}_3 + H_2O \leftrightarrow 2K\text{HCO}_3^- \quad (R-1)
\]

\[
\text{CO}_2 + \text{CO}_3^{2-} + H_2O \leftrightarrow 2\text{HCO}_3^- \quad (R-2)
\]

The above reversible reaction (R−2) takes place based on the below proposed mechanism:

\[
\text{CO}_3^{2-} + H_2O \leftrightarrow \text{HCO}_3^- + \text{OH}^- \quad (R-3)
\]

\[
\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^- \quad (R-4)
\]

Since (R−3) is instantaneous reaction, (R−4) is the rate limiting reaction. So the rate equation expresses as below form:

\[
\frac{d[H]}{dr} = k_{\text{for}}[\text{OH}^-][\text{CO}_3^{2-}] - k_{\text{off}}[\text{HCO}_3^-]
\]

\[ r_{\text{OH}} = k_{\text{OH}}[\text{OH}^-][\text{CO}_3^{2-}] - k_{\text{OH}}[\text{HCO}_3^-] \quad (1) \]

where, \( k_{\text{for}} \) and \( k_{\text{off}} \) are forward and backward rate constants, respectively. At equilibrium condition, Eq. (1) results:

\[
k_{\text{for}}[\text{OH}^-][\text{CO}_3^{2-}] = k_{\text{off}}[\text{HCO}_3^-] \quad (2)
\]

where \([\text{CO}_3^{2-}]_e\) is the \text{CO}_2 concentration at equilibrium conditions. By combining Eqs. (1) and (2):

\[
\frac{dC_{\text{CO}_2}}{dr} = \left( k_{\text{for}}[\text{OH}^-][\text{CO}_3^{2-}] - k_{\text{off}}[\text{HCO}_3^-] \right) \]

Because the membrane mainly passes \text{CO}_2, the concentration of \text{OH}^- ion can be assumed constant, therefore Eq. (3) can be rewritten as below form:

\[
\frac{dC_{\text{CO}_2}}{dr} = k_{\text{OH}}[\text{OH}^-][\text{CO}_3^{2-}] - k_{\text{OH}}[\text{HCO}_3^-] \quad (4)
\]

where, \( k_i \) is an apparent first−order rate constant. When a little amount of DEA is added into the solution, the \text{CO}_2 consumption rate in the tube side will increase, because DEA reacts with \text{CO}_2 as follows.

\[
\text{CO}_2 + \text{R}NH \leftrightarrow \text{R}N\text{COOH} \quad (R-5)
\]

\[
\text{R}N\text{COOH} + \text{OH}^- \leftrightarrow \text{HCO}_3^- + \text{R}N\text{H} \quad (R-6)
\]

Since (R−6) is the rate limiting reaction, the reaction rate can be expressed as bellow:

\[
\frac{dC_{\text{CO}_2}}{dr} = k_{\text{for}}[\text{OH}^-][\text{CO}_3^{2-}] - k_{\text{off}}[\text{HCO}_3^-] \quad (5)
\]

and \( k_3 \) is an apparent first−order rate constant. In simultaneous presence of potassium carbonate and DEA, the overall reaction rate will be equal to the summation of Eqs. (4) and (5):

![Model validation using experimental data](image-url)
Fig. 4. Axial concentration profile of CO₂ in the shell side of HFMC at the presence of different solvents (n = 3600, Q₆ = 50 ml min⁻¹, Q₇ = 100 ml min⁻¹, T = 303 K).

Fig. 5. Effect of temperature on the CO₂ absorption in the presence of – (a) promoted hot potassium carbonate solution, (b) DEA solution, (c) MDEA solution (Q₇ = 100 ml min⁻¹, Q₆ = 200 ml min⁻¹ and n = 3600).
where \( k \) is the overall apparent first-order rate constant. The kinetic parameters of DEA, potassium carbonate and equilibrium parameters of CO2 absorption are summarized in Table 2.

For more investigation, the performance of promoted hot potassium carbonate is compared with respect to other commercial solvents. The reactions mechanisms, overall rates and kinetic constants for CO2 absorption at the presence of different solvent such as DEA, MDEA, AMP and blend of DEA and MDEA is presented in Table 3.

3. Model development

Fig. 2a shows a conceptual diagram of HFMC with counter-current flows of the gas phase (H2, CH4, H2O, N2, Ar, CO, CO2) and liquid phase (K2CO3, KHOCH3, DEA, H2O). The present model is developed based on some essential assumptions including steady state condition, fully developed gas and liquid velocity profile, laminar flow and ideal behavior of the gas mixture, “non-wetted mode” and finally supposed that the happele’s free surface model and Henry’s law are applicable. According to these assumptions, the overall mass balance equation is as follows:

\[
- \left( \frac{1}{r} \frac{\partial (r(C_2V))}{\partial r} + \frac{1}{r} \frac{\partial (C_2V)}{\partial r} + \frac{\partial (C_2V)}{\partial z} \right) - \left( \frac{1}{r} \frac{\partial (r(J_{2l}))}{\partial r} + \frac{\partial (J_{2l})}{\partial r} + \frac{\partial (J_{2l})}{\partial z} \right) + R_1 = 0
\]  

(7)

According to above mentioned assumption, the mass balance equation for absorption of CO2 in the membrane, shell and tube segments can be written as below.

\[
D_{CO2,membrane} \left( \frac{\partial^2 C_{2,membrane}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{2,membrane}}{\partial r} + \frac{\partial^2 C_{2,membrane}}{\partial z^2} \right) = 0
\]  

(8)

\[
D_{CO2,shell} \left( \frac{\partial^2 C_{2,shell}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{2,shell}}{\partial r} + \frac{\partial^2 C_{2,shell}}{\partial z^2} \right) = V_{c,shell} \frac{\partial C_{2,shell}}{\partial z}
\]  

(9)

\[
D_{c,tube} \left( \frac{\partial^2 C_{2,tube}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{2,tube}}{\partial r} + \frac{\partial^2 C_{2,tube}}{\partial z^2} \right) + R_t = V_{c,tube} \frac{\partial C_{2,tube}}{\partial z}
\]  

(10)

where \( D_{CO2,tube} \) and \( D_{w,CO2} \) are given by [52]:

\[
\frac{D_{CO2,tube}}{D_{w,CO2}} = 1 - (0.154[K_2CO_3] + 0.00723[KHOCH_3])
\]  

(11)

\[
D_w = 2.35 \times 10^{-4} \exp \left( \frac{-2199}{T} \right)
\]  

(12)

For determining the velocity profile in the shell side of membrane, it is assumed that Happel’s free surface model holds, so that velocity profile is given by Eq. (13) [53]. Also the flow in the tube side is assumed laminar and therefore the velocity profile determined as Eq. (14).

\[
V_{c,shell} = 2(V) \left[ 1 - \left( \frac{r}{R} \right)^3 \right] \left( \frac{R^3}{V} - \left( \frac{r}{R} \right)^3 \right) + 2 \ln \left( \frac{R}{r} \right)
\]  

\[
(13)
\]

\[
V_{c,tube} = 2(V) \left[ 1 - \left( \frac{r}{R} \right)^3 \right]
\]  

(14)

The relationship between \( R \) and \( r \) are given by:

\[
R = n_2 \sqrt{\frac{1}{1 - \Phi}}
\]  

(15)

In the membrane, diffusion is dominant mass transfer mechanism and there is no reaction.

4. Numerical approach

In this work, finite element method (FEM) is applied for numerical solution of the governing equations and their boundary conditions. The model is solved for a HFMC includes shell, membrane and tube segments. A large number of elements are created with scaling. A scaling factor of 600 is employed for the contactor in the \( z \) direction due to large difference between \( r \) and \( z \). Fig. 2b represents a schematic diagram of an element. The boundary conditions which are used for solving Eqs. (8)-(10) are reported in Table 4. In the boundary conditions, \( m \) is the quantity of physical solubility of CO2 in the solution, and it is given by Eq. (16) [54]:

\[
m = \frac{1}{h} = RT/(2.82 \times 10^8 \exp \left( \frac{-2044}{T} \right))
\]  

(16)

5. Model validation

Chemical reactions which are suggested in this paper are different from other proposed chemical reactions in this field. The present model includes CO2 reaction with two chemical components. Since there is no related experimental or literature data for this simulation, the model is validated for CO2 absorption by NaOH solution. Al-Marzouqi et al. [54] examined the CO2 absorption by MEA and NaOH solution in a HFMC. Their experiments were carried out in a shell and tube polypropylene hollow fiber membrane contactor with an inner shell diameter of 63.5 mm, which housed the 3600 microporous hollow fibers. The feed gas mixture was introduced into the shell side of the HFMC using mass flow controllers. The gas composition was quantified with a special CO2/CH4 gas analyzer. An online gas drier based on a single Nanoflow tube and flowing dry nitrogen was applied to dry the treated gas stream to avoid condensation inside the analyzer. Also, the liquid solvent was introduced into the tube side of the HFMC at different concentrations using a peristaltic pump [54]. The comparison between the predicted CO2 concentration and experimental data is presented in Fig. 3 [54]. According to this figure, modeling results satisfy the experimental data.

6. Results and discussion

6.1. Performance investigation of different solvents

The absorption rate of CO2 using aqueous solution of promoted hot potassium carbonate as a solvent has been compared with respect to different solvents such as DEA, MDEA, AMP and aqueous blends of DEA and MDEA. As indicated in Fig. 4, the variation of CO2 concentration at the entrance of the shell (at \( z = L \)) sharply decreases, but the
decreasing rate reduces through the length of HFMC. The decreasing rate is even rather sharper for the case of promoted hot potassium carbonate having high reaction rate. According to Fig. 4, it is inferred that the aqueous solution of promoted hot potassium carbonate has the highest CO₂ absorption rate and it is proposed as an appropriate absorption solvent. The order of absorption rate of solvents is as follows: promoted hot potassium carbonate > AMP > DEA > MDEA > blend of MDEA and DEA. The amount of C/C₀ of CO₂ for blend of MDEA and DEA, MDEA, DEA, AMP and promoted hot potassium carbonate are 0.41, 0.37, 0.34, 0.17 and 0.02 at z/L = 0.5, respectively. Among different solvents for the CO₂ absorption, the amine− promoted hot potassium carbonate provides an economic and efficient process for absorption of large quantities of CO₂ from gas mixture. Amine solvents generally provide high absorption rates, while the carbonate− bicarbonate buffer offers advantages of large capacity for CO₂ absorption, low cost, ease of handling, and ease of regeneration. The overall absorption rate of CO₂ in ordinary carbonate solutions is influenced by both chemical and physical processes, but due to small concentration of hydroxyl ion, the rate of reaction is relatively low. The combination of amine and carbonate solution offers advantages for gas treating in terms of both efficiency and capacity. When CO₂ is absorbed into a carbonate− bicarbonate buffer, the carbonate ion is converted stoichiometrically to the bicarbonate ion, but the local rate of reaction of CO₂ is proportional to the concentration of hydroxyl ion, rather than to the concentration of carbonate ion. The limitations associated with pure amine solvent have led to the use of mixtures of potassium carbonate and amine as an alternative which can simultaneously, overcome the slow CO₂ absorption kinetics of potassium carbonate solutions. Addition of DEA to hot potassium carbonate solution promotes the absorption of CO₂ via two pathways. The first pathway is the increase in OH⁻
concentration in the solvent when DEA is added and the carbamate forms and thus more $\text{OH}^-$ ions are present to react with $\text{CO}_2$. The second is the zwitterion mechanism pathway, which is the dominant promoting for DEA. DEA reacts with $\text{CO}_2$ in aqueous solution via the zwitterion mechanism, in which DEA reacts with $\text{CO}_2$ to form a zwitterion intermediate first, and then the intermediate reacts with a base to form bicarbonate ions and regenerate DEA. DEA promoted potassium carbonate solutions is the most mature promoted systems for $\text{CO}_2$ absorption. The addition of DEA increases the regeneration energy requirement for solvent regeneration and the degradation and corrosion problems still exist.

6.2. Effect of temperature on HFMC performance

Based on proposed kinetic model, it is obvious that increasing temperature improves chemical absorption, but reduces the physical absorption. The effect of temperature on the outlet $\text{CO}_2$ concentration is represented in Fig. 5. As shown in Fig. 5a, the absorption performance of promoted hot potassium carbonate at 298 and 303K are approximately the same. But as represented in Fig. 5b and c, the effect of temperature on $\text{CO}_2$ absorption rate in the presence of DEA or MDEA is more sensible than promoted hot potassium carbonate. However the performance of promoted hot potassium carbonate is better than other solvents. Since promoted hot potassium carbonate has an excellent absorption at 298 K ($C/C_0 = 0.012$ at the outlet of shell side), it is inferred that another advantage of using promoted hot potassium carbonate is better chemical absorption performance at lower temperatures.

Activation energy is an important kinetic parameter which is determined in this work. On the basis of the Arrhenius equation, the apparent rate constant of the reaction of the promoted hot potassium carbonate solution is plotted vs. inverse temperature (Fig. 6). Based on this figure, the apparent activation energy and Arrhenius constant for this reaction are 55.42 kJ mol$^{-1}$ and $5.19 \times 10^{13}$ m$^3$ kmol$^{-1}$ s$^{-1}$, respectively.

![Fig. 8. Axial concentration of potassium carbonate in the tube side with $c_{0,\text{CO}_2} = 3.883$ mol m$^{-3}$, $n = 3600$, (a), $Q_L = 100$ ml min$^{-1}$, (b) $Q_L = 200$ ml min$^{-1}$.](image-url)
6.3. Comparison of Co- and counter-current operation modes

The CO₂ concentration profile in the shell side of the contactor for co- and counter-current modes is shown in Fig. 7 for different liquid to gas ratio (L/G) and at the presence of chemical reaction. As shown in Fig. 7a, at constant gas flow rates, the CO₂ concentration decreases along the axial direction of the contactor and it illustrates that when L/G ratio is close to one, the C/C₀ ratio of CO₂ will be the same for both co- and counter-current modes. According to this figure, at L/G = 0.5, counter-current mode has the lower C/C₀ ratio respect to co-current mode, for example C/C₀ ratio of CO₂ at the outlet of the shell side for both co- and counter-current are 0.16 and 0.11, respectively. Fig. 7b illustrates the axial concentration of CO₂ in the shell side at constant liquid flow rates. As shown in this figure, the C/C₀ ratio of CO₂ decreases when L/G ratio increases. It means that, at constant liquid flow rates, the CO₂ adsorption will enhance with decreasing the gas flow rate.

6.4. Concentration profiles of K₂CO₃

Fig. 8 represents that the potassium carbonate concentration decreases along the length of the tube side, because it consumes during chemical reaction with CO₂. As shown in Fig. 8, the concavities of diagrams are downward for counter-current flow and it is vice versa.
for co–current, because potassium carbonate consumption will increase where the CO₂ concentration is high. So the maximum slope exists at the entrance of tube side. According to this figure, at Z = 0, the slope of counter–current flow diagrams is small, while there is a sharp slope in the co–current flow diagrams. Also the absorption rate of CO₂ in the counter–current flow is so higher than the co–current flow.

6.5. Effect of initial CO₂ concentration

Fig. 9a illustrates the outlet concentration of CO₂ in the gas phase versus its initial CO₂ concentration at constant gas flow rates. As shown in this figure, at constant gas flow rate, with increasing the initial concentration of CO₂, the outlet concentration of CO₂ in the gas phase reaches to the identical value for all L/G ratios. Fig. 9a shows that the worst performance is at L/G = 2 in the co–current flow mode, while the counter–current flow has a better performance, because in the counter–current flow, the driving force for reaction between liquid and CO₂ is more than co–current flow through the length of the contactor. As an example, at L/G = 2, the outlet concentration of CO₂ in the phase gas is 4.64 and 0.79 mol m⁻³ in co– and counter–current modes, respectively. Also according to this figure, the variation of outlet concentration of CO₂ at L/G = 2 is less than L/G = 3, because the gas flow rate increases. At constant liquid flow rate (Fig. 9b), application of counter–current flow for extraction of CO₂ is more
effective than co-current flow. As shown in Fig. 9b, the difference between outlet concentrations of CO2 will enhance with increasing initial concentration of CO2 for both co- and counter-current modes.

6.6. Effect of number of fibers

The effect of number of HFMC fibers on the efficiency of CO2 removal for both co-current and counter-current operation modes at a constant gas and liquid flow rate is presented in Fig. 10. This figure represents that increasing the number of fibers has a direct effect on the CO2 removal efficiency. This manner is due to increasing the contact area for CO2 absorption. The percentage removal of CO2 is defined as follows:

\[
\text{Percentage removal of CO2} = \frac{100 \left( \nu \times C_{\text{inlet}} - (\nu \times C_{\text{outlet}}) \right)}{(\nu \times C_{\text{inlet}})}
\]

where, \( \nu \) and \( C \) are the volumetric flow rate and concentration, respectively and \( C_{\text{outlet}} \) is the outlet concentration of CO2 in the shell side. According to this figure, due to enhancing the contact area, increasing the number of fibers leads to improvement of CO2 removal efficiency. Fig. 10a shows that the efficiency of CO2 removal is equal for both flow modes at \( L/G = 1 \); however, the counter-current flow has still a better performance than the co-current flow at \( L/G = 0.5 \). The figure shows that at 4000 fibers number, the percentage removal of CO2 is 83.85% and 90.59% for co-current and counter-current operation mode at
Fig. 10b represents the effect of number of HFMC fibers on the efficiency of CO₂ removal for both co-current and counter-current operation modes at a constant liquid flow rate. This figure shows that using counter-current flow enhances the CO₂ absorption. As shown in this figure, after using more than 2500 fibers in the membrane contactor, the percentage removal of CO₂ does not change notably. Also Fig. 10b illustrates that the removal of CO₂ in the gas phase is better than counter-current flow at L/G = 0.5. The percentage removal of CO₂ in the gas phase is 83.75% and 90.58% for co-current and counter-current operation modes, respectively.

6.7. Effect of gas and liquid flow rates on HFMC performance

Fig. 11 demonstrates the effects of gas and liquid flow rates on the CO₂ absorption for co- and counter-current flow modes. According to Fig. 11a, at constant liquid flow rates, the percentage removal of CO₂ reduces with increasing the gas flow rate in the shell side, because the residence time decreases. As mentioned in previous sections, at L/G ratio near or greater than one, the CO₂ removal efficiency is
is shown in Fig. 12. At the gas outlet point (z/L = 0), the concentration of CO2 is maximum. The CO2 concentration decreases along the axial direction of the contactor. As represented in Fig. 12, the CO2 outlet concentration decreases as the L/G ratio increases at a constant liquid flow rate. The figure shows that when the gas phase flows in the tube side, the CO2 absorption is higher than the case in which the gas phase flows in the shell side, because the contact surface area of liquid reactants and membrane increases. Therefore, by flowing the gas stream in the tube side, the reaction of liquid and CO2 enhances and higher amounts of CO2 pass through the membrane.

Fig. 13 shows the outlet concentration of CO2 in the gas phase versus its initial concentration. When the gas and liquid streams pass through the shell and tube sides, respectively, the outlet of CO2 at the case of L/G = 2 is more than L/G = 3. According to this figure, the absorption of CO2 when the gas phase passes through the tube side is better than the case in which the gas stream flows through the shell side. Also as represented in this figure, at low initial concentration of CO2 (less than 11.5 and 14.5 mol m$^{-3}$ for gas flow through shell and tube sides, respectively), increasing L/G ratio has not significant effect on the CO2 adsorption.

Figs. 14 and 15 show the effect of number of fibers, gas and liquid flow rates on the efficiency of CO2 removal when the gas phase passes through the tube or shell sides. Fig. 14 shows that at L/G = 2, increasing the number of fibers from 500 to 2000 has a significant effect on the CO2 absorption. As demonstrated in these figures, the percentage removal of CO2 improves when the gas stream flows in the tube side of the contactor.

7. Conclusions

In this paper, a 2-D mathematical model is proposed for absorption of CO2 from the gas mixture using HFMC at the presence of promoted hot potassium carbonate solution. The proposed model is based on a new kinetic model and is applicable for “non-wetted mode”. Also the axial diffusion in the tube, membrane and shell side is considered. The model validation results showed an appropriate agreement with respect to experimental data which is reported in the literatures. In this work, the performance of co-current and counter-current operation modes in the HFMC is compared. The modeling results indicated that the counter-current mode has a better performance with respect to the co-current mode. Also investigation of some effective parameters on the CO2 adsorption showed that increasing the liquid flow rate and number of fibers have a positive effect on the CO2 absorption, whereas enhancing the gas flow rate decreases the rate of absorption. Also, when the gas and liquid streams flow through the tube and shell sides of contactor respectively, the diffusion of CO2 through the membrane enhances due to increasing the contact surface area between the liquid reactants and the gas phase, and as a result, the absorption efficiency increases respect to the case in which the gas stream flows in the shell side.
References


