CO$_2$ absorption intensification using novel DEAB amine-based nanofluids of CNT and SiO$_2$ in membrane contactor

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A R T I C L E   I N F O

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DEAB

A B S T R A C T

Recent developments in nanotechnology have a great impact to improve the mass transfer in gas-liquid systems. The effect of nanoparticles was taken into account considering Grazing effect and Brownian motion as main phenomena of mass transfer enhancement in nanofluids. In the present study, a sensitivity analysis was performed to evaluate the influence of nanoparticles on the CO$_2$ absorption inside a hollow fiber membrane contactor (HFMC). The distilled water and chemical system of 4-diethylamino-2-butanol (DEAB)-water nanofluid for CO$_2$ absorption was studied. The considered drops were nanofluids containing carbon nanotube (CNT) and nanosilica (SiO$_2$). A rigorous two-dimensional mathematical model for CO$_2$ absorption from a N$_2$/CO$_2$ gas mixture was developed. The predicted results indicated that the injection of nanoparticles to distilled water and DEAB amine solution improves the CO$_2$ absorption efficiency. Nanofluid of CNT represented better separation performance than nanosilica. Also, the CO$_2$ absorption efficiency of nanofluids was enhanced with the increasing amine and nanoparticle concentration, liquid flow rate and also, decreasing the gas flow rate. Although increasing the liquid temperature decreased the physical absorption of CO$_2$, it enhanced the chemical absorption of CO$_2$ due to improvement of the reaction rates and diffusion coefficients.

1. Introduction

In recent years, there is a progressive interest to develop novel technologies to improve process performance and reduce energy costs associated with CO$_2$ capture. Absorption process is an extensively used method for decreasing the CO$_2$ concentration in human activities and industrial applications [1-7]. In this regard, the efficient solvents are the critical factor to evaluate the CO$_2$ absorption performance [8,9]. Among different solvents, nanofluids are introduced as an efficient absorbent for CO$_2$ absorption. Nanofluids are stable suspended nanoparticles in conventional host liquids. The most advantages of nanofluids are their improved heat transfer related to have higher thermal conductivities and improved convective heat transfer, and also their modified mass transfer coefficients inside binary nanofluids in comparison to host liquids [10].

The enhancement of CO$_2$ absorption rate using nanofluids could be related to different phenomena which improve the diffusion and transport of CO$_2$ in the solutions. The presence of solid particles in a three-phase system (gas-liquid-solid) significantly increases the mass transfer coefficient and the gas absorption rate in the liquid phase based on Grazing effect [11]. Based on this phenomenon, due to strong absorption of the gas molecules into the dispersed solid particles, the concentration of gas molecules in the liquid phase near the interface will be decreased, leading to an increment in the absorption rate. Subsequently, after a specific contact time, the gas phase component will desorb and the solid particles will regenerate. Also, the presence of nanoparticles near the interface between the bubbles and the liquid leads to a thinner effective layer because of breaking the diffusion boundary layer. This phenomenon which is called gas-liquid boundary layer mixing, enhances the gas diffusion into the liquid film due to increasing the turbulence of the flow and the mass transfer coefficient [12].

In recent years, extensive researches have been carried out on the heat and mass transfer enhancement by introducing nanoparticles. Krishnamurthy et al. [13] inferred that the Brownian motion of nanoparticles which induces the micro-convections in nanofluids, increases the mass transfer performance. In another related study, Esmaeili-Faraj et al. [14] concluded that the absorption rate of hydrogen sulfide improves considerably according to Grazing effect of nano-particles. They reported that the absorption rate of H$_2$S into water raised up to 40 % by
adding 0.02 wt% of exfoliated graphene oxide. Kim et al. [15,16] observed that due to bubble breaking by nanoparticles, bubble size in nanofluid is smaller than that in base fluid and as a result, the absorption of ammonia in a bubble type absorber enhances by adding small amount of nanoparticles into the base fluid. Also, Lee et al. [17] studied the CO2 removal using methanol nanofluid in a bubble type absorber. Darvanjooghi et al. [18,19] considered the absorption of CO2 by using Fe3O4/water and SiO2/water nanofluids and observed intensified solubility of CO2 and absorption rate using nanofluids. Also, in related study, Komati et al. [20] used nanoferrofluids to enhance the absorption rate of CO2 in amine solutions. Their experimental results indicated that nanofluids with 0.39 vol% nanoparticles improve the mass transfer up to 92.6% with respect to base fluid. Golkhar et al. [21] investigated the CO2 absorption by CNT and silica nanofluids in membrane contactor and reported that the CO2 removal efficiency improves 40% using nanoparticles. Peyravi et al. [22] considered the effect of different nanoparticles such as Fe3O4, SiO2, Al2O3 and carbon nanotube (CNT) in distilled water on the mass transfer rate during CO2 absorption using a gas-liquid membrane contactor. They concluded that the nanofluid stability and hydrodynamic diameter of nanoparticles play an essential role in the selection of nanoparticles for CO2 absorption. Also the reported results by this group indicated that the concentration of nanoparticles and liquid flow rate have the most significant effects on the CO2 absorption. Similarly, Mohammadoost et al. [23] investigated the role of Al2O3, TiO2 and SiO2 nanoparticles to improve the mass diffusion in a water-based nanofluid using a membrane contactor.

Xuan [24] developed a mathematical model to predict the mass diffusivity, mass transfer coefficient and rate within the binary nanofluids. The results indicated that the micro-convection in nanofluids is one of the major factors enhancing the mass transfer rate. Also, Park et al. [25] considered the CO2 absorption into silica/water nanofluids and developed an empirical correlation based on rheological behavior of aqueous silica nanofluids to calculate the mass transfer parameters. In another theoretical study, Darabi et al. [3] developed a two-dimensional mathematical model to predict the CO2 absorption in the presence of nanoparticles in membrane contactor with considering Brownian motion and Grazing effect. Their modeling results approved that the CO2 absorption enhances 16% and 32% by adding 0.05 wt.% silica and CNT nanoparticles, respectively. Hajilary and Rezakazemi [26] applied computational fluid dynamics to evaluate the effects of nanoparticle content and liquid flow rate on the CO2 absorption and observed that increasing absorbent flow rate increases the CO2 absorption rate, especially at a low flow rate.

In this study, a two-dimensional mathematical model is developed to investigate the mass transfer and reaction kinetics of CO2 absorption from a gas mixture of CO2 and N2 into distilled water and DEAB (4-diethylamino-2-butanol) based nanofluids of carbon nanotube and nanosilica in HFMC. DEAB provides appropriate operating conditions related to its high mass transfer rate, high absorption and cyclic capacity, fast reaction kinetics, low solvent viscosity and low solvent lost due to vaporization [27]. The mass transfer performance was investigated in terms of absorption efficiency. A numerical method was applied to solve the simultaneous nonlinear mathematical equations. The model results were used to compare the absorption performance of different concentration of distilled water and DEAB based nanofluid
with respect to pure water and DEAB solutions as references. Also, the effect of different operating parameters of HFMC, including gas and liquid flow rates, liquid temperature, nanoparticle concentration, and amine concentration have been considered and the design consequences of different options have been discussed. The HFMC specifications and operating conditions are summarized in Table 1.

2. Kinetic investigation

The reaction network of capturing CO$_2$ by DEAB solution is presented in Table 2. In the present kinetic model development, since proton transfer reactions (including R = 3 to R = 5 in Table 2) are reversible and instantaneous with respect to mass transfer, (R = 1) and (R = 2) are considered as rate limiting reactions. At equilibrium condition, the reaction rate of (R = 1) can be expressed as:

$$r_1 = k_{(R=1)}[CO_2][DEAB] - k_{(R=1)}[DEABH]^+][HCO_3]^-$$

(1)

$k_{(R=1)}[CO_2][DEAB] = k_{(R=1)}[DEABH]^+][HCO_3]^-$(2)

$\eta = (k_{(R=1)}[DEAB])[CO_2] - [CO_2]$ $L$(3)

$r_1 = k_{(R=1)}[CO_2] - [CO_2]$ $L$(4)

where $k$ and [CO$_2$] are the rate constant and the CO$_2$ concentration at equilibrium conditions. Similar to above mentioned strategy, the reaction rate of (R = 2) can be expressed as bellow:

$$r_2 = k_{(R=2)}[OH^-][CO_2] - k_{(R=2)}[HCO_3]^-$$

(5)

$k_{(R=2)}[OH^-][CO_2] = k_{(R=2)}[HCO_3]^-$(6)

$r_2 = k_{(R=2)}[OH^-][CO_2] - [CO_2]$ $L$(7)

$r_1 = k_{(R=2)}[CO_2] - [CO_2]$ $L$(8)

The overall reaction rate will be determined as:

$\eta_{total} = \eta_1 + \eta_2 = (k_1 + k_2)[CO_2] - [CO_2]$ $L$(9)

$k = k_{(R=1)}[DEAB] + k_{(R=2)}[OH^-]$(10)

where $k$ is the overall apparent first-order rate constant. The kinetic and equilibrium constants are summarized in Table 3.

3. Model development

As illustrated in Fig. 1, the amine-based nano-fluid solvent and the CO$_2$ containing gas stream flow counter-currently inside (at z = L) and outside the fiber (at z = 0), respectively. To investigate the CO$_2$ absorption from CO$_2$/N$_2$ gas mixture (containing 20% CO$_2$ and 80% N$_2$) in a HFMC using nano-fluids, a steady state two-dimensional model was assembled on the following assumptions [28–30]: steady-state and isothermal condition, non-wetted membrane mode, homogeneous nanoparticles distribution, ideal behaviors in the gas phase, incompressible and non-wetted fluid flow for the nano-fluid, laminar and plug flow with fully developed velocity profile in the gas and liquid phases, negligible radial convection, applied Henry’s law at the gas-liquid interface, and applied Happel’s free surface model for gas flow.

The membrane material influences the CO$_2$ removal and wetting characteristics of the membrane. In the non-wetting mode (hydrophobic materials), the membrane are filled by gas molecules, whereas in the case of wetting mode (hydrophilic materials), the pores are occupied by solvent molecules. Generally, three commercially available microporous membranes are applied for CO$_2$ removal in HFMC including polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF). The main criterion to determine the membrane performance is the CO$_2$ mass-transfer coefficient of the membrane (k$_m$). As well documented in literature [2,31–34], although the PP and PVDF membranes are appropriate materials for the CO$_2$ absorption related to their high mass transfer coefficients between 10$^{-3}$ and 10$^{-2}$ m s$^{-1}$, they become easily wetted. By difference, the PTFE membranes which considered in the present study, represents high resistance to wetting with acceptable k$_m$ values between 10$^{-4}$ and 10$^{-3}$ m s$^{-1}$ [2,31–34]. Also, due to high diffusion rate of CO$_2$ in the presence of nanoparticles, the membrane fibers or pores are filled by gas molecules and it can be supposed the non-wetting mode. The characterizations of nanoparticles and model parameters are presented in Table 4.

3.1. Model development of tube side

As discussed in the literature review section, addition of nanoparticles can improve the mass transfer of the solute through the gas-liquid interface due to Brownian motions and Grazing effect [11,21]. The empirical relationship of mass diffusion coefficient in the nano-fluids has been reported as [10,35]:

$$D_{CO_2, tube} = D_{CO_2, tube}^0(1 + m_1Re^{m_2}Sc^{m_3}P^m_4)$$

(11)

where $m_1 = 1650$, $m_2 = 0.039$, $m_3 = -1.064$, and $m_4 = 0.203$ [10,35]. Also, $D_{CO_2, tube}^0$ is the mass diffusion coefficient in the base fluid, where for DEAB solution, $D_{CO_2, tube}$ is defined as [27]:

$$D_{CO_2, water}^{DEAB} = 1.89 \times 10^{-9}D_{CO_2, water}/D_{N_2, water}$$

(12)

$D_{CO_2, water}$ and $D_{N_2, water}$ are given by Eqs. 13 and 14 [36]:

$$D_{CO_2, water} = 2.35 \times 10^{-6} \exp(\frac{-2119}{T})$$

(13)

$$D_{N_2, water} = 5.07 \times 10^{-6} \exp(\frac{-2371}{T})$$

(14)

Also, in Eq. 11, $\Phi$ is the volume fraction of the nanoparticles, Sc and Re are the Schmidt and Reynolds numbers, respectively for the nanoparticles Brownian motion. Reynolds number is calculated as follows [37]:

$$Re = \frac{18KT^2}{\pi \eta_d \rho_d \mu^2}$$

(15)

where $K$, $T$, $\rho$, $\mu$, $d_\phi$, and $\mu$ are Boltzmann constant, temperature, carrier

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner tube diameter, $r_1$ [mm]</td>
<td>0.22</td>
</tr>
<tr>
<td>Outer tube diameter, $r_2$ [mm]</td>
<td>0.30</td>
</tr>
<tr>
<td>Module inner diameter, R [mm]</td>
<td>63.50</td>
</tr>
<tr>
<td>Total number of fibers [-]</td>
<td>3600</td>
</tr>
<tr>
<td>Fiber porosity, $\varepsilon$ [%]</td>
<td>25</td>
</tr>
<tr>
<td>Fiber tortuosity, $\tau$ [[48]]</td>
<td>4</td>
</tr>
<tr>
<td>Inner shell diameter, $d$ [mm]</td>
<td>0.529</td>
</tr>
<tr>
<td>Module length, L [m]</td>
<td>0.25</td>
</tr>
<tr>
<td>Temperature, $T$ [K]</td>
<td>298 – 318</td>
</tr>
<tr>
<td>Gas inlet pressure, P [kPa]</td>
<td>120</td>
</tr>
<tr>
<td>Gas velocity, $U_g$ [m s$^{-1}$]</td>
<td>0.01 – 0.20</td>
</tr>
<tr>
<td>Liquid velocity, $U_l$ [m s$^{-1}$]</td>
<td>0.01 – 0.10</td>
</tr>
<tr>
<td>Nanoparticle concentration, [wt.%]</td>
<td>0 – 0.5</td>
</tr>
<tr>
<td>CO$_2$ concentration, [M]</td>
<td>0.5 – 2.5</td>
</tr>
<tr>
<td>CO$_2$ concentration, [M]</td>
<td>0.5 – 2.5</td>
</tr>
<tr>
<td>Aminol solution density, $\rho$ kg m$^{-3}$</td>
<td>(1.0 – 1.1)×10$^3$</td>
</tr>
<tr>
<td>Gas phase density, $\rho$ kg m$^{-3}$</td>
<td>0.8 – 1.2</td>
</tr>
<tr>
<td>Specific heat of amine solution, $c_p$ J mol$^{-1}$ K$^{-1}$</td>
<td>(3.2 – 3.8)×10$^3$</td>
</tr>
<tr>
<td>Specific heat of gas phase, $c_p$ J mol$^{-1}$ K$^{-1}$</td>
<td>29 – 33</td>
</tr>
<tr>
<td>Thermal conductivity in the tube side, $W$ m$^{-1}$ K$^{-1}$</td>
<td>0.39 – 0.41</td>
</tr>
<tr>
<td>Thermal conductivity in the membrane section, W m$^{-1}$ K$^{-1}$</td>
<td>0.15</td>
</tr>
<tr>
<td>Heat of absorption of CO$_2$, $\Delta H$ J mol$^{-1}$</td>
<td>(2.4 – 2.8)×10$^{-2}$</td>
</tr>
</tbody>
</table>

* Estimated from Wakao-smith equation ($\tau = 1/\varepsilon$).
fluid density, nanoparticles density, nanoparticles diameter, and dynamic viscosity of the fluid. The second mechanism that can be proposed to mass transfer enhancement is Grazing effect or shuttle effect mechanism in gas-liquid systems [11,21]. Grazing is a phenomenon for gas transport from the interface of liquid-gas to the liquid bulk. In order to investigate the Grazing effect, the nanoparticle in the tube side is considered as two distinct liquid and solid phases, so the continuity governed to each phase, i.e., the amine solution and the nanoparticles, separately. Continuity equation for CO2 in the solid phase can be expressed as follows:

\[
\Phi \frac{q}{\rho} \frac{\partial q}{\partial z} = k_p a_p (C_{CO2-\text{tube}} - C_\text{S})
\]

(16)

where, \( q \) is the amount of CO2 adsorbed by the nanoparticles which could be obtained with Langmuir isothermal adsorption model as:

\[
q = q_m \frac{k_p C_\text{S}}{1 + k_p C_\text{S}}
\]

(17)

\( q_m \) is the maximum amount of adsorption by nanoparticles, \( k_p \) is Langmuir constant, and \( C_\text{S} \) is the CO2 concentration at the solid-liquid interface. By applying mass balance for CO2 in tube side and considering CO2 adsorption to nanoparticles, \( C_\text{S} \) will become apparent. Also, \( a_p \) and \( C_\text{S} \) are the specific surface area of nanoparticles and CO2 concentration in nanoparticles, and \( k_p \) is the mass-transfer coefficient between solid particles and liquid phase determined by [38]:

\[
Sh = \frac{k_p d_p}{D_{CO2}} = 2
\]

(18)

Table 2
Reactions network.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R - 1)</td>
<td>( CO_2 + \text{DEAB} + H_2O \rightarrow \text{DEABH}^+ + HCO_3^- )</td>
</tr>
<tr>
<td>(R - 2)</td>
<td>( CO_2 + \text{OH}^- \rightarrow HCO_3^- )</td>
</tr>
<tr>
<td>(R - 3)</td>
<td>( \text{DEAB} + H^+ \rightarrow \text{DEABH}^+ )</td>
</tr>
<tr>
<td>(R - 4)</td>
<td>( CO_2 + H_2O \rightarrow H^+ + HCO_3^- )</td>
</tr>
<tr>
<td>(R - 5)</td>
<td>( HCO_3^- \rightarrow H^+ + CO_2 )</td>
</tr>
<tr>
<td>(R - 6)</td>
<td>( H_2O \rightarrow H^+ + OH^- )</td>
</tr>
</tbody>
</table>

The effective density and thermal diffusivity of the nanoparticle are defined as follows [39]:

\[
\rho_{\text{n}}^\text{eff} = (1 - \Phi)\rho_p^\text{eff} + \Phi \rho_\text{f} \tag{19}
\]

The nanoparticle thermal conductivity, \( \chi_{\text{nf}} \), can be calculated using Maxwell equation [38]:

\[
\chi_{\text{nf}} = \chi_p \left( \frac{\chi_a + 2\chi_p}{\chi_a + \chi_p} \right) + \Phi \chi_f \tag{20}
\]

where \( \chi_{\text{nf}} \) and \( \chi_f \) are the thermal conductivity of dispersed nanoparticles and base fluid, respectively. The heat capacitance of the nanoparticle is given by [40]:

\[
(p\chi_{\text{nf}})^\text{eff} = (1 - \Phi)(p\chi_p)^\text{eff} + \Phi (p\chi_f) \tag{21}
\]

Also, Brinkman correlation can be used to calculate the effective dynamic viscosity of the nanoparticle as [41]:

\[
\mu_{\text{n}}^\text{eff} = \frac{\mu_p^\text{eff}}{(1 - \Phi)^{5.3}} \tag{22}
\]

The mass balance equations for each component and the corresponding boundary conditions are formulated as:

\[
D_{\text{C_{tube}}} \frac{\partial^2 C_{\text{tube}}}{\partial y^2} + \frac{1}{r} \frac{\partial C_{\text{tube}}}{\partial r} + \frac{\partial^2 C_{\text{tube}}}{\partial z^2} + R_i = V_{\text{C_{tube}}} \frac{\partial C_{\text{tube}}}{\partial t} + \frac{k_p d_p}{1 - \Phi} C_{\text{tube}} - C_\text{S}
\]

(23)

Table 3
Equilibrium, kinetics and transport parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{R-1}(m^3 \text{ mol}^{-1} \text{ s}^{-1}) )</td>
<td>( k_{R-1} = 4.01 \times 10^{13} \exp(-2271.5) )</td>
<td>[27]</td>
</tr>
<tr>
<td>( k_{R-2}(m^3 \text{ mol}^{-1} \text{ s}^{-1}) )</td>
<td>( \log(k_{R-2}) = 13.635 - \frac{2815}{T} )</td>
<td>[55]</td>
</tr>
<tr>
<td>( k_{R-3} )</td>
<td>( \ln(k_{R-3}) = -90.93 + \frac{430.0 \times 10^6}{T} - \frac{1008 \times 10^6}{T^2} + \frac{1}{T} + \frac{1}{T^2} )</td>
<td>[54]</td>
</tr>
<tr>
<td>( k_{R-4}(m^3 \text{ mol}^{-1} \text{ s}^{-1}) )</td>
<td>( \log(k_{R-4}) = 179.648 + 0.0192447 - 67.341 \log T - \frac{789.441}{T} )</td>
<td>[55]</td>
</tr>
<tr>
<td>( D_{CO2-N_2} )</td>
<td>( 1.8583 \times 10^{-7} \sqrt{1 + 1.6396 + 1.01325 \frac{1}{101325}} )</td>
<td>[36]</td>
</tr>
<tr>
<td>( D_{CO2-water} )</td>
<td>( 2.35 \times 10^{-14} \exp(-715) )</td>
<td>[36]</td>
</tr>
<tr>
<td>( D_{N_2-water} )</td>
<td>( 5.67 \times 10^{-14} \exp(-2771) )</td>
<td>[36]</td>
</tr>
<tr>
<td>( D_{CO2-DEAB} )</td>
<td>( 1.89 \times 10^{-9} )</td>
<td>[27]</td>
</tr>
<tr>
<td>( H_{CO2-N_2}(kPa \text{ m}^3 \text{mol}^{-1}) )</td>
<td>( 2.8249 \times 10^6 \exp(-2984) )</td>
<td>[36]</td>
</tr>
<tr>
<td>( H_{N_2-water}(kPa \text{ m}^3 \text{mol}^{-1}) )</td>
<td>( 8.5470 \times 10^6 \exp(-2268) )</td>
<td>[36]</td>
</tr>
<tr>
<td>( H_{CO2-DEAB} )</td>
<td>( \exp(-2268) \times RT )</td>
<td>[27]</td>
</tr>
</tbody>
</table>
The energy balance equation and related boundary conditions in the tube side are summarized as:

\[
\frac{\partial}{\partial z} \left( \frac{\delta C_{\text{absorbent}}}{\delta r} \right) = 0 \quad \text{where} \quad m = \frac{1}{H}
\]

\[
at r = 0: \quad C_{\text{CO}_2,\text{tube}} = m C_{\text{CO}_2,\text{membrane}}
\]

\[
at z = L: \quad \frac{\delta T_L}{\delta z} = 0
\]

\[
at r = 0: \quad \frac{\delta T_L}{\delta r} = 0
\]

\[
at r = r_i : \quad T_r = T_M
\]

Also, the velocity profile in the tube side is determined based on:

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

### 3.2. Model development of membrane section

In the membrane section under non-wetted mode, the dominant mass transfer mechanism is diffusion and no reaction takes place in this section of the contactor. For the approximate range of \(0.2 < d/\lambda < 20\), both ordinary and Knudsen diffusion should be considered, where \(d\) and \(\lambda\) denote the pore size and mean free path, respectively. In this study, the mean free path is determined by:

\[
\lambda = \left( \frac{3.2 \mu}{P} \right) \left( \frac{RT}{2\pi M} \right)^{0.4}
\]

The diffusion coefficient in the membrane section is expressed as follow:

\[
D_{\text{CO}_2,\text{membrane}} = \frac{\zeta}{r} \left[ \left( \frac{1}{\langle r \rangle_{\text{CO}_2}} \right) + \left( \frac{1}{\langle n_{\text{CO}_2} \rangle} \right) \right]
\]

where \(D_{\text{Kn}}\) is the Knudsen diffusivity and can be calculated as [42]:
The governing equations and the related boundary conditions in the membrane section are defined as:

\[
D_{\text{CO}_2\text{membrane}} \left[ \frac{\partial^2 C_{\text{CO}_2\text{membrane}}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{\text{CO}_2\text{membrane}}}{\partial r} + \frac{\partial^2 C_{\text{CO}_2\text{membrane}}}{\partial z^2} \right] = 0
\]

(31)

\[ at \ z = 0 \text{and} \ z = L: \nabla C_{\text{CO}_2\text{membrane}} = 0 \]

\[ at r = r_1: C_{\text{CO}_2\text{membrane}} = C_{\text{CO}_2\text{shell}} \]

\[ at r = r_f: C_{\text{CO}_2\text{membrane}} = C_{\text{CO}_2\text{tube}} \]

(32)

where, the thermal conductivity of membrane is calculated by:

\[ \chi_{\text{M,eff}} = \chi_M (1 - \varepsilon) + \chi_G \varepsilon \]

(35)

3.3. Model development of shell side

In the shell side, \( D_{\text{CO}_2\text{shell}} \) is calculated by [36,43]:

\[ D_{\text{CO}_2\text{shell}} = 1.8583 \times 10^{-7} \sqrt{T^3 \left( \frac{1}{M_{\text{CO}_2}} + \frac{1}{M_{\text{N}_2}} \right) \frac{101.325}{P_{\text{CO}_2-N_2}} \rho} \]

(36)

where, \( \sigma \) and \( \Omega \) denote Lennard-jones parameter (A) and collision integrals, respectively. The governing equations and also their corresponding boundary conditions in the shell side are formulated as:

Fig. 2. Flowchart of model validations steps.
Fig. 3. Comparison of modeling results with experiment data, (a) Effect of CO₂ partial pressure on CO₂ flux at T = 294 K, U_i = 0.011 m/s and U_g = 0.1 m/s [44], (b) Effect of liquid velocity on CO₂ flux at U_i = 0.211 m/s; T_g: 298 K; CO₂ volume fraction in feed gas: 14 vol.% and T_i: 308 K) [45].

Fig. 4 shows a conceptual flowchart that describes the steps of model validation based on reported data in literature.

4. Results and discussions

As conceptually illustrated in Fig. 1, the absorbent solution flows through the tube side of the contactor from the top (z = 1). Also, the gas stream enters the shell side of contactor from the bottom section (z = 0). The CO₂ molecules absorb by the solvent based on the convection and diffusion mass transfer mechanisms.

4.1. Model validation

Since DEAB is a novel absorbent, no related experimental data in the literature is available for CO₂ absorption in aqueous DEAB solution using HFMC. Accordingly, the validity of the model using amine solvent is evaluated by the experimental results of CO₂ absorption into MEA, DEA and MDEA reported in the literature [44,45]. The CO₂ absorption flux from a gas mixture of CO₂ and N₂ in to DEA and MDEA versus CO₂ pressure at atmospheric pressure is illustrated in Fig. 3-a. Also, as presented in Fig. 3-b, the CO₂ absorption flux as a function of liquid velocity is considered in comparison with the experimental data [45]. As demonstrated, the model predicted results satisfy the experimental data, appropriately.

The velocity profile in the shell side is expressed based on Happel’s free surface model as follow [28]:

\[
V_{z,\text{shell}} = 2(V)\left[1 - \left(\frac{r}{R}\right)^2\right]\frac{(\frac{r}{R})^2 - (\frac{r}{R})^4 + 2\ln\left(\frac{r}{R}\right)}{3 + (\frac{r}{R})^2 - 4\left(\frac{r}{R}\right)^4 + 4\ln\left(\frac{r}{R}\right)}
\]

 Parameter R in the above equation is calculated as:

\[
R = \frac{1}{2\sqrt{1 - \varphi}}
\]

where

\[
\varphi = 1 - \frac{n\pi^2}{n_L}
\]

3.4. Numerical approach

The governing equations are solved numerically based on finite element method (FEM) using MATLAB software. Because of large difference between r and z directions, a scaling factor of 800 is employed for the contactor in the z direction to create a large number of elements. To test and assess the grid independency of the solution scheme, an extensive scaling analysis was performed to determine the appropriate grid density. The convergence criterion is based on a tolerance function which considered to be less than 10⁻⁶.

Tolerance = \frac{\sum_{i=1}^{n} |\phi_{i+1} - \phi_i|}{\sum_{i=1}^{n} |\phi_i|} < 10^{-6}

In the above equation, \phi, i and n are the decision variable (CO₂ absorption flux), the number of iterations and the number of grid points in the z direction, respectively. Fig. 2 shows a conceptual flowchart that describes the steps of model validation based on reported data in literature.
4.2. Nanofluid effect on CO2 concentration profile in HFMC

The dimensionless CO2 concentration in the shell side of HFMC versus dimensionless length of contactor is illustrated in Fig. 5. Because of concentration difference, the CO2 molecules transferred through the membrane pores. As shown in the Fig. 5-a, the outlet concentration of CO2 in distilled water is about 0.72 of its initial concentration, but addition of 25 wt% of CNT and SiO2 nanoparticles to distilled water improves the outlet concentration to 0.63 and 0.66 of its initial concentration. It also shows a sharp decrease in the CO2 concentration in the entrance of contactor and approximately constant concentration in the following of contactor which is attributed to the fact that CO2 solubility in the liquid phase reduces and there is a high resistance to mass transfer. The absorption of CO2 by DEAB solutions is also presented in Fig. 5-b. It is found that, the outlet concentration of CO2 in 1 M DEAB solution is about 0.11 of its initial concentration, where it improves to 0.06 and 0.08 by addition of 25 wt% of CNT and SiO2 nanoparticles to amine solution, respectively.

4.3. Effect of nanofluid flow rate on CO2 absorption

Liquid flow rate is one of the main operating conditions of membrane gas-liquid contactors which has a great impact on the CO2 absorption efficiency. Figs. 6-a and -b indicate the CO2 absorption as a function of distilled water based and amine based nanofluid flow rate. It is observed from these figures that the CO2 removal enhances with the nanofluid flow rate. By increasing the nanofluid flow rate, the boundary layer thickness of the liquid phase in the tube side will reduce, which leads to decrease in the mass transfer resistance of the liquid phase, and enhance in the mass transfer and diffusivity. On the other hand, increasing the nanofluid flow rate in the tube side decreases the CO2 concentration at the inner surface of the fiber along the length of the contactor and provides higher concentration gradient at the interface which leads to higher CO2 absorption rate. As it can be seen from the Fig. 6, the nanofluid flow rate can significantly influence the CO2 absorption at lower rates, however at higher liquid rate, the CO2 absorption efficiency is not affected by liquid flow rate significantly. As illustrated in Figs. 6-a and -b, the CO2 removal reaches to a constant value depending on the composition of absorbent solution generally after a nanofluid flow rate of about 0.05 m/s. Also, in the case of amine based nanofluid solvents (Fig. 6-b), due to existence of chemical reaction which reduces the mass transfer resistance of liquid phase, the effect of liquid flow rate on the CO2 absorption is less significant with respect to physical absorption (Fig. 6-a). According to reported results flow rates for distilled water and aqueous-based CNT and SiO2 nanofluids confirms the good accuracy of the predicted model results.
in Fig. 6-a, addition of 0.25 wt% CNT and silica nanoparticle to distilled water increases the absorption efficiency up to 8 % and 5 %, respectively at liquid flow rate of 0.1 m/s, gas flow rate of 0.01 m/s and temperature of 298 K. Also, in the case of DEAB solution (Fig. 6-b), by addition of 0.25 wt% CNT and silica nanoparticle, the CO2 removal efficiency is improved up to 5 % and 3 %, respectively. CO2 absorption improvement is related to adsorption property of nanoparticles which can increase the driving force between two phases.

4.4. Effect of gas flow rate on CO2 absorption

It is obvious that the residence time of CO2 in the membrane contactor decreases with increasing the gas flow rate. Therefore, the mass transfer deriving force which is related to the amount of CO2 molecules at the interface reduces. As a result, the CO2 absorption efficiency decreases significantly. The effect of inlet gas flow rate on the CO2 absorption is investigated in Fig. 7. As illustrated in this figure, the percentage of CO2 absorption decreases considerably with increasing the gas flow rate in both case of distilled water (Fig. 7-a) and DEAB solution (Fig. 7-b). In particular, increasing the gas flow rate from 0.01 to 0.1 m/ s reduces the CO2 absorption into pure distilled water and DEAB solution from 28 % to 1 %, and 88 % to 13 %, respectively. The same trend can be observed using different nanofluid solvents. Again, it can be observed that CNT nanofluid provides higher absorption efficiency compare to silica nanofluid, distilled water and DEAB solution at all range of gas velocity.

4.5. Effect of liquid temperature on CO2 absorption

The impact of liquid temperature on the CO2 absorption efficiency has been considered for 0.25 wt% of CNT and silica nanofluids. In the case of physical absorption, increasing the liquid temperature restricts the performance of gas-liquid membrane contactors, since the solubility of CO2 in water reduces considerably with increasing the liquid temperature. It is necessary to mention that although CO2 diffusivity improves with temperature enhancement, but also in the membrane contactor, increasing the liquid temperature may enhance bulk water evaporation and subsequently membrane pore blockage due to vapor condensation at the interface. In summary, it prevents CO2 diffusion. As indicated in Fig. 8-a, the CO2 absorption using CNT-distilled water nanofluid decreases from 37 % to 3 % with rising the liquid temperature from 298 K to 318 K. Also, the CO2 absorption using silica-distilled water nanofluid reduces from 34 % to 2 % at the same conditions. According to the reported results in Fig. 8-a, it is inferred that the negative effects of temperature on the CO2 solubility and evaporation are dominant with respect to its positive effect on CO2 diffusivity.

Fig. 6. CO2 absorption percentage versus liquid flow rate at T = 298 K, Ptotal = 120 kPa and UG = 0.01 m/s; a) distilled water nanofluid, b) 1 M DEAB solution nanofluid.

Fig. 7. CO2 absorption percentage versus gas flow rate at T = 298 K, Ptotal = 120 kPa and UG = 0.1 m/s; a) distilled water nanofluid, b) 1 M DEAB solution nanofluid.
increasing the absorbent concentration enhances the reaction rate because increasing in the amount of active absorbent molecules. Indeed, in the case of the temperature is increased from 298 K to 318 K, the CO2 removal increases from 94 % to 100 % using 25 wt% CNT-DEAB nano fluids. This improvement in the CO2 removal of silica-DEAB nano fluids is from 92 % to 98 % at the same operating conditions.

4.6. Effect of DEAB concentration on CO2 absorption

DEAB concentration influences the rate of CO2 removal and the amount of required circulating solvent. The impact of amine concentrations on the CO2 removal in the HFMC is presented in Fig. 9. The results indicated that increasing the DEAB concentration over the range of 0 to 0.5 M in the tube side of HFMC improves the CO2 removal due to increasing in the amount of active absorbent molecules. Indeed, increasing the absorbent concentration enhances the reaction rate between CO2 and amine molecules which in turn leads in increment of CO2 mass transfer. By considering reported results in Fig. 9, it is inferred that the effect of absorbent concentration on the CO2 removal is more significant at lower concentrations. This performance can be attributed to this fact that at higher amine concentrations, the equilibrium condition is achieved and it prevents the CO2 removal in the contactor. Again, due to higher absorption efficiency of CNT nanofluid, the effect of amine concentration on the CO2 removal is more significant with respect to silica nanofluid. An increase in DEAB concentration from 0.5 to 2.5 M at 298 K results in an increase in CO2 absorption from 74 % to 100 % and, from 69 % to 98 % for CNT and silica nanofluids, respectively.

4.7. Effect of nano particle concentration on CO2 absorption

The absorption of CO2 using distilled water based nanofluid is compared with the performance of amine based nanofluids at the various concentrations of nanoparticles. Fig. 10 represents the effect of nanoparticle concentration on the CO2 removal in HFMCs. It could be found that the removal efficiency enhances with an increase in the nanoparticles concentration. The enhancement of the CO2 absorption can be justified based on Eqs. 11 and 16 in which Brownian motion and Grazing effect are directly related to the nanoparticle concentrations. Since the liquid flow rate inside the fibers is laminar, there is a slow rate of mass transfer in the liquid phase. Addition of nanoparticle to the liquid phase can make micro-convections because of the Brownian motion of nanoparticles and enhance mass transfer rate. Also, creation of micro-convection can avoid accumulation of CO2 molecules near the fibers wall and intensify the mass diffusion of CO2 in the fibers. Moreover, the presence of nanoparticles in the liquid solvent intensifies the removal efficiency based on CO2 molecules adsorption mechanism in the gas-liquid interface, where the concentration of CO2 is very high. The CO2 absorption for CNT and silica nanofluids at nanoparticle concentration in the range of 0 to 0.5 wt% is shown in Fig. 10. The results confirm that that the addition of both silica and CNT nanoparticles increases the CO2 absorption compared to distilled water and DEAB solution. The predicted results indicated that the injection of silica and CNT nanoparticles to distilled water at 298 K increases the removal efficiency from 28 % to 35 % and 38 % respectively. Also, the injection of silica and CNT nanoparticles to 1 M DEAB solution enhances the removal efficiency from 88 % to 92 % and 94 % respectively. It is necessary to mention that the nanoparticles concentration in the base fluid can lead to negative effect on the size of nanoparticles and nanofluid stability. It is well documented that at high nanoparticles concentration, the membrane pores block and subsequently, the absorption efficiency of HFMC decreases [22]. As reported by Peyravi et al. [22], increasing the concentration of nanoparticles enhances the hydrodynamic diameter of particles and subsequently, leads to less particle stability. Furthermore, increasing the hydrodynamic diameter limits the micro-convection phenomenon and shuttle effect in the
5. Conclusions

The performance of distilled water- and DEAB-based nanofluid for CO₂ absorption were investigated in a non-wetted gas-liquid HFMC. The modeling results indicated that the suspended CNT and SiO₂ nanoparticles remarkably improve the mass transfer performance of the base fluid. According to obtained results, it is found that increasing the gas flow rate has no positive effect on the absorption efficiency of nanofluids in the HFMC, however, increasing the liquid flow rate decreases the mass transfer resistance in the liquid phase and improves the CO₂ absorption, remarkably. Also, it is inferred that the nanoparticle concentration has a great impact on the absorption performance of nanofluids in HFMC, because increasing the nanoparticle concentration leads to intensification of Grazing effect of nanoparticles in the base fluid and also, more creation of micro-convection. Finally, due to appropriate properties of DEAB solvent including high mass transfer rate, high absorption and cyclic capacity, fast reaction kinetics, fast reaction kinetics, low solvent viscosity and low solvent lost due to vaporization, the nanofluid of DEAB can be used as an efficient solvent for CO₂ removal.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jecep.2020.107848.

References