Modeling the absorption of CO$_2$ in solvents enhanced by nanoparticle in polymeric membranes

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Abstract. Lately nanomaterial received substantial consideration by several researchers. Solid nanoparticles prove to have extensive applications in composite materials and in the enhancement of mass and heat transfer. Adding nanoparticles to a base fluid improves the performance of mass and heat transfer. The effect of the addition of nanoparticles to base fluids, such as pure water and aqueous sodium hydroxide, show significant improvement in the percent removal of carbon dioxide from a gas composed of 15% CO$_2$ balance is CH$_4$ using gas-liquid hollow fiber membrane contactor. Results reveal that the rate of absorption of carbon dioxide increases with an increase in the concentration of nanoparticles up to certain extent beyond which insignificant removal rate is observed. Predicted results revealed that the percent removal of CO$_2$ in the existence of CNT and NaOH is 35% and 40%, respectively.

1. Introduction

The major source of the world energy supply is said to be natural gas. Methane is the key component of natural gas with trivial percentages of carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S), and nitrogen. There do exist water vapor, which is normally removed by dehydration process using ethylene glycol or its alternatives. The existence of acid gases in natural gas in addition of lowering the natural gas heating value, it can cause pipe corrosion [1-3]. Accordingly, prior to using of natural gas as an energy source in power generation and water desalination plants, the impurities should be removed. The conventional absorption methods used is primarily packed bed towers. In spite of the successful removal of acid gas using the traditional absorption columns, this method suffers from difficulties such as flooding at high inlet gas flow rate, channeling and foaming that can weaken the mass transfer between liquid and gas [1,4].

Several researchers thought that gas-liquid hollow fiber membrane contactor is an encouraging substitute gas absorption technology. Gas elimination process via membrane contactor is a non-dispersive process; gas is not dispersed in liquid. In membrane contactor absorption of pollutant component is taking place at the membrane liquid interface without dispersion of one phase into the other phase. Membrane contactor is supposed to overcome the drawbacks of conventional absorption columns [5]. Absorption of CO$_2$ using membrane contactor covers effect of liquid and gas flow rate, membrane partial wetting, membrane packing density, type of polymer used in the fabrication of hollow fiber membranes, variety of solvents used in the absorption process [6]. Various mathematical model were developed to describe the separation process using membrane contactor [7-10].

Solvent used in CO$_2$ absorption are mainly alkanolamine aqueous solutions, such as monoethanolamine (MEA), diethanolamine (DEA). In spite of the successful performance of these solvents in removing most of CO$_2$ from natural gas and flue gas, they have disadvantages of being
corrosive to pipes and absorber walls and if used in membrane contactor they can cause membrane degradation [11]. Accordingly, seeking for user friendly absorbent took the attention of many researchers to replace the traditional amine family solvent. Water-based nanofluids is anticipated to be encouraging alternative solvents, various nanofluids were experimentally investigated for CO2 absorption such Fe3O4, silica (SiO2), alumina (Al2O3) and carbon nanotube (CNT) in distilled water and there effect on CO2 absorption [12]. Absorption of carbon dioxide in hollow fiber membrane contactor were investigated using water based nanofluid containing solid nanoparticles (Al2O3, TiO2, SiO2). Results revealed there is an optimum concentration of the these nanoparticles on the percent removal of CO2 [13]. Various mathematical models to describe the CO2 absorption in the presence of water-based solid nanoparticles were developed. Models took into consideration Brownian motion and Grazing effect. These models focused on physical absorption [14-16]. In the present work a mathematical model will be used to simulate the chemical absorption of aqueous sodium hydroxide (NaOH)-based solid nanoparticles. The effect of liquid flow rate, gas flow rate on the percent removal will be investigated.

2. Model equations

The presence of solid nanoparticles in a nanofluid generates several mechanisms that can play a positive or negative impact on the rate of absorption of the pollutant gas. The adsorption of gas component by particles in the gas-liquid interfacial area and desorb in the bulk liquid increases mass transfer coefficient and is named Grazing effect. The random motion of particles dispersed in liquid phase is called Brownian motion. The particle motion produced momentum that enhanced the mass transfer coefficient due to intensifying liquid motion near the gas-liquid interface. There are negative effect of particles on mass transfer coefficient such as particle clustering, particle agglomeration, increase of liquid viscosity [17]. Accordingly, there is optimum nanoparticle concentration in the base fluid. The absorption mechanism in gas-liquid hollow fiber membrane contactor enhance by nanoparticles is illustrated in figure 1.

![Figure 1. Schematic of segment of membrane contactor used in developed model.](image)

The mathematical model is developed for the segment shown in figure 1 considering Happel’s free surface and non-wetting model. The liquid nanofluid flow at z = 0 in the tube side, by contrast, the gas flow at z = L counter-currently. The model is developed considering isothermal steady state operation, ideal gas, incompressible liquid solvent, and negligible radial convection. The model consists of three segments: tube, membrane, and shell side. The system governing equations is as follows:

2.1. Tube side

The material balance equation represents CO2 in the tube side is expressed as per equation (1):
\[
D_{CO_2,t} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{CO_2,t}}{\partial r} \right) + \frac{\partial^2 C_{CO_2,t}}{\partial z^2} \right) = V_{z,t} \frac{\partial C_{CO_2,t}}{\partial z} + \frac{k_p S_p}{1 - \phi} (C_{CO_2,t} - C_s) - k_r C_{CO_2,t} C_{NaOH,t} \quad (1)
\]

Where \(D_{CO_2,t}\) is the diffusion coefficient of CO\(_2\) in liquid phase in the tube side, \(C_{CO_2,t}\) is concentration of carbon dioxide in the tube side, \(V_{z,t}\) is the liquid velocity of the liquid inside the membrane tubes, \(k_p\) is the mass transfer coefficient between liquid and solid nanoparticles, \(S_p\) is the specific surface area of the nanoparticles, \(k_r\) is the reaction rate constant, \(C_s\) is the concentration of CO\(_2\) at the liquid-solid interface [11]. The material balance equation represents NaOH in the tube side (equation (2)):  

\[
D_{NaOH,t} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{NaOH,t}}{\partial r} \right) + \frac{\partial^2 C_{NaOH,t}}{\partial z^2} \right) = V_{z,t} \frac{\partial C_{NaOH,t}}{\partial z} - 2k_r C_{CO_2,t} C_{NaOH,t} \quad (2)
\]

The fully developed velocity in the tube side is calculated as per equation (3):  

\[
V_{z,t} = 2V_{z,avg} \left( 1 - \left( \frac{r}{R_1} \right)^2 \right) \quad (3)
\]

The adsorption of CO\(_2\) in the solid particles is presented in equation (1) is calculated using the following auxiliary continuity equations of carbon dioxide adsorption in the solid nanoparticles (equation (4)).

\[
\phi V_z \rho_p \frac{\partial q}{\partial z} = k_p a_p (C_{CO_2,t} - C_s) \quad (4)
\]

Where \(q\) is the amount of CO\(_2\) adsorbed by nanoparticle is determined by Langmuir isothermal adsorption mode [18] as expressed in equation (5):

\[
q = q_m \frac{k_d C_s}{1 + k_d C_s} \quad (5)
\]

where \(q_m\) is the maximum adsorption capacity of nanoparticles, \(k_d\) is the Langmuir constant.

### 2.2. Membrane

The steady state diffusion mechanism of the gas components inside the membrane pores occurs by diffusion only (equation (6)):

\[
D_{CO_2,m} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{CO_2,m}}{\partial r} \right) + \frac{\partial^2 C_{CO_2,m}}{\partial z^2} \right) = 0 \quad (6)
\]

### 2.3. Shell side

The steady state material balance equation of CO\(_2\) in the shell side is represented by equation (7):

\[
D_{CO_2,s} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{CO_2,s}}{\partial r} \right) + \frac{\partial^2 C_{CO_2,s}}{\partial z^2} \right) = V_{z,s} \frac{\partial C_{CO_2,s}}{\partial z} \quad (7)
\]

The velocity in the shell side is given by equation (8) [19]:

\[
V_{z,s} = 2V_{z,avg} \left[ 1 - \left( \frac{r}{R_3} \right)^2 \right] \left\{ \frac{(r_2^2 - (r_2/R_3)^2)^2 + 2ln \left( \frac{r_2}{R_3} \right)}{3 + (r_2/R_3)^4 - 4 \left( \frac{r_2}{R_3} \right)^2 + 4ln \left( \frac{r_2}{R_3} \right)} \right\} \quad (8)
\]

where \(V_{z,avg}\) is the average velocity of the gas stream in the shell side. The boundary conditions are summarized in table 1.
Table 1. Boundary conditions of mass transfer equations [20].

| Boundary Condition | Tube side | Membrane | Shell side |
|--------------------|-----------|----------|-----------|
| \( z = 0 \)       | \( C_{CO_2,t} = 0 \) | Insulated | Convective flux |
| \( z = L \)       | Convective flux | Insulated | \( C_{CO_2,m} = C_{CO_2,o} \) |
| \( r = 0 \)       | Symmetry | - | - |
| \( r = r_1 \)     | \( C_{CO_2,t} = m \cdot C_{CO_2,m} \) | \( C_{CO_2,m} = C_{CO_2,r} / m \) | - |
| \( r = r_2 \)     | - | \( C_{CO_2,m} = C_{CO_2,s} \) | \( C_{CO_2,s} = C_{CO_2,m} \) |
| \( r = r_3 \)     | - | - | \( \frac{\partial C_{CO_2}}{\partial r} = 0 \) |

Where \( m \) is the solubility of \( CO_2 \) in the absorbent liquid. The nanofluid parameters used in the model is shown in Table 2.

Table 2. The characterization of water-based carbon nanoparticles (CNT) [11].

| Property                        | Value          | Property of hollow fiber | Value   |
|---------------------------------|----------------|--------------------------|---------|
| Morphology                      | Tubular        | Fiber out diameter       | 1.10 mm |
| True density (g/cm\(^3\))       | 2.2 g/cm\(^3\) | Inner diameter           | 0.42 mm |
| Particle capacity (\( q_m \))   | 29.45 mol/kg  | Number of fibers         | 11      |
| Langmuir constant (\( k_d \))   | 0.00049 m\(^2\)/mol | Module active length     | 0.21 m  |
| Specific surface area (\( S_p \))| 500 m\(^2\)/g | Module diameter          | 0.08 m  |
| Inner diameter                  | 2.5 nm         |                          |         |

The governing model equations with the appropriate boundary conditions for coupling the tube, membrane, and shell sides are solved simultaneously using COMSOL Multiphysics version 5.4. The commercial software uses finite element method in the numerical solution of the set of differential equations.

3. Results and discussion

The 2D and 3D surface plot for the concentration of \( CO_2 \) throughout the membrane contactor is portrayed in figures 2(a) and 2(b), respectively. The \( CO_2 \) total flux and the track of the \( CO_2 \) diffusion pathway through the gas phase, membrane pores, and diffusion in water-based liquid nanofluid is categorized by white arrows. The carbon dioxide in the \( CO_2/CH_4 \) gas mixture enters at the upper side of the membrane module (i.e. \( z = L \)). The \( CO_2 \) is depleted from the gas mixture during the flow of the gas.
mixture in the gas phase. The CO\(_2\) diffused through the membrane pores to the membrane-liquid interface based on concentration gradient where it is dissolved in the nanofluid.

The change in the concentration of CO\(_2\) in the shell side along the length of the membrane is simulated in figure 3(a). It is clear that concentration of CO\(_2\) decreased throughout the gases flow from \(z = L\) downward to \(z = 0\) of the membrane modules, attributed to the continuous absorption of CO\(_2\) into the solvent in the tube side. Figure 3(b) illustrated the CO\(_2\) concentration outlined crosswise the membrane module at the top of module (\(z = 1\)), middle of the module (\(z = 0.5\)) and close to the bottom of the module (\(z = 0.1\)) in the shell, membrane and tube side. The straight horizontal line (0.42 to 1) represents the CO\(_2\) concentration in the shell side, the concentration is then start to drop, attributed to the diffusion of CO\(_2\) in the membrane toward the solvent in the tube. The straight line between the dimensionless radiuses of 0 to 0.18 is the concentration of CO\(_2\) in the solvent which is almost very small compared to the bulk concentration of sodium hydroxide solution. This is attributed to the continuous absorption of CO\(_2\) during the gas flow inside the shell side of the membrane and its diffusion through the membrane micropores to the tube side where CO\(_2\) dissolved in the liquid; being adsorbed in the solid nanoparticles, react with sodium hydroxide, and portion dissolved in water.

**Figure 3.** Concentration profile of CO\(_2\) in the shell-membrane interface along the length of membrane (a), Concentration of CO\(_2\) across various point (\(z = 1\), \(z = 0\), \(z = 0.1\)) of the module (b). Gas flow rate, 100 ml/min and liquid flow rate, 10 ml/min.

**Figure 4.** Effect of solvent type on CO\(_2\) concentration along the membrane-gas interface, liquid flow rate, 10 m/min and gas flow rate of 100 ml/min.
The effect of solvent type is exposed in figure 4. The figure revealed that the drop in CO$_2$ concentration in pure water is insignificant. The presence of CNT in pure water causes a significant drop in the CO$_2$ concentration, which is attributable to the fact that the dynamic motion of the solid nanoparticles in the water-based nanofluid and the accompanying grazing and Brownian motion enhanced the CO$_2$ removal rate meaningfully. The percent removal of CO$_2$ in this case is around 36%. The addition of aqueous sodium hydroxide to water-based CNT nanoparticle fluid improves the removal rate of CO$_2$ as shown from the drop of the CO$_2$ concentration during gas flow in the shell side. The percent removal of carbon dioxide in the presence of 0.1 M NaOH is approximately 40% due to the chemical reaction between CO$_2$ and NaOH.

4. Conclusion
The CO$_2$ absorption using nanofluid composed of water, CNT, and sodium hydroxide in gas-liquid hollow fiber membrane contactor was modelled and simulated using computational fluid dynamics method. The numerical model composed of the material balance equations represent the component mass transport in the tube, membrane and shell side. The coupling equations were solved using COMSOL software version 5.4. The predicted results revealed that the presence of CNT in pure water increased the percent removal of CO$_2$ significantly compared pure water as absorbent without the addition of CNT nanoparticles. The addition of NaOH to the water-based CNT nanofluid improved the CO$_2$ removal rate. The percent removal of CO$_2$ in the water-CNT-NaOH nanofluid is estimated to be around 40% and can be increased by increasing liquid inlet flow rate.

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