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Modeling and Preparation of ABS Blend Membrane and Nanoparticles for Separation of CO_2 and CH_4

[1]Mahmoud Salimi, [2]Sadegh Moradi and [1]Saeed Shirazian

[1]Department of Chemical Enginering, Islamic Azad University, Arak Branch, Arak, Iran
[2]Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak 38156-8-8849, Iran

Abstract: Simulation of gas separation in a flat sheet membrane was investigated theoretically and experimentally in this study. A flat sheet ABS membrane blended with nanoparticles was prepared using cast method. Numerical simulation was performed using computational fluid dynamics (CFD) of mass transfer in the membrane for laminar flow conditions. Physical absorption was considered in the simulations for absorption of CO_2 in pure water. Simulation results were validated with the experimental data obtained from literature for physical absorption of CO_2 in pure water. Simulation results were in good agreement with the experimental data for different values of liquid flow rates. The modeling predictions indicated that the removal of CO_2 increased with increasing liquid velocity in the membrane. Also increasing temperature and gas velocity in the flat sheet membrane have an opposite effect. CFD also represents a design and optimization tool for membrane gas separation processes.

Key words: ABS Cast membrane · Simulation · Gas separation · Modeling · Mass transfer

INTRODUCTION

Expansion of industrial activities has caused the concentration of greenhouse gases to rise significantly in the atmosphere. This has contributed to global warming, which in turn has resulted in serious environmental problems [1]. Carbon dioxide is representing about 80% of greenhouse gases. It is reported that half of the CO_2 emissions are produced by industry and power plants using fossil fuels [2]. From the global environmental perspective, it is important to remove CO_2 to avert the threat of global warming, thereby attaining the carbon emission reduction targets set out by the Kyoto Agreement. Additionally, the CO_2 concentrations are typically 3-5% in gas-fired power plants and 13-15% in coal plants [3].

Current carbon dioxide removal technologies are based on a variety of physical and chemical processes including, absorption, adsorption, cryogenic and membrane techniques [4-5]. Conventional processes for the removal of CO_2 suffer from many problems such as flooding, foaming, entraining, channeling and high capital and operating costs. Therefore, many researchers have examined the possibilities of enhancing the efficiency of these processes to reduce the effect of their problems. Gas-liquid membrane s are expected to overcome the disadvantages of the conventional equipment when incorporated into the gas treating processes [5]. The characteristic of gas-liquid membrane s is that the gas stream flows on one side and the absorbent liquid flows on the other side of the membrane without phase dispersion, thus avoiding the problems often encountered in the conventional equipment such as flooding, foaming, channeling and entrainment. For the non-wetted mode, the flat sheet membrane pores are filled with gas phase because the flat sheet membrane is hydrophobic and the pressure difference of gas-liquid is not exceeded the critical pressure. Many researchers indicated that the non-wetted mode is better than wetted mode because mass transfer in non-wetted mode is much higher than wetted mode [5].

Some experimental and theoretical studies about the gas-liquid membrane s had been conduscted since Zhang and Cussler first studied the membranes [5]. Using polypropylene membrane, Kreulen *et al.* [6] studied absorption of CO_2 into water/glycerol mixtures. The authors studied the membrane as gas-liquid s in the case of both physical and chemical absorption. Separation of CO_2 from offshore gas using membrane s was investigated by Falk-Pederson and Dannstrom [7], who optimized

Corresponding Author: Mahmoud Salimi, Department of Chemical Enginering, Islamic Azad University, Arak Branch, Arak, Iran, E-mail: s-morady@araku.ac.ir & m-salimi@iau-arak.ac.ir.

the process with respect to sizes, weight and costs. Many researchers have reported the use of gas-liquid membrane s for absorption of CO_2 in a hydroxide solution [8], the CO_2 removal in membrane using amino acid salts [9]. Qi and Cussler [5] studied development of a theory of the operation of gas-liquid membrane s and calculated mass transfer coefficients in liquid phase. They also obtained the overall mass transfer coefficients, including resistances in both liquid and membrane and compared the performance of membrane s with that of packed towers [5].

Karoor and Sirkar [10] investigated the separation of CO_2 and SO_2 from CO_2/N_2 and SO_2/air gas mixtures, using water as an absorbent in a parallel module employing microporous polypropylene membrane. A similar system has been recently studied by Zhang *et al.* [11] for co-current gas-liquid contact. In both studies, the authors assumed negligible axial diffusion, which may not be a good assumption, especially for low gas velocities. Kim and Yang [12] investigated the separation of CO_2/N_2 mixtures using membranes theoretically and experimentally. Although there was an agreement between the model predictions with experimental results, the authors assumed a linear decrease of gas flow rate for the simulation purposes.

Thus, there is a definite need for a mass transfer model that can provide a general simulation of the chemical and physical absorption in gas-liquid flat sheet membranes. The main purpose of this study is to solve a 2D mathematical model for absorption of CO_2 in flat sheet membranes. The model is then validated using experimental data obtained from literature for absorption of CO_2 in water. Influence of different process parameters will be investigated on the mass transfer and absorption of CO_2 in membrane.

Experimental

Materials: Acrylonitrile-butadiene-styrene (ABS) terpolymer, T_g=108°C, containing 25% acrylonitrile, was supplied from Bayer companey and was dried about 3 h at 85°C in an oven before use. Dichloromethane (Acros) was used as solvent without further purification.

Membrane Preparation: In order to prepare the ABS cast membranes, predetermined quantities of ABS granuals dissolved in dichloromethane. The solution was stirred for about 5 h at room temperature. Silica nanoparticles were added into the solution under stirring. The resulting suspension was then sonicated for 40 min to promote the dispersion of nanoparticles. Then it was cast onto a glass plate. By solvent evaporation for 3 days at ambient temperature and pressure, the flat sheets were put into an oven for 15 h. Finally, the solvent-free membranes were used in permeation tests.

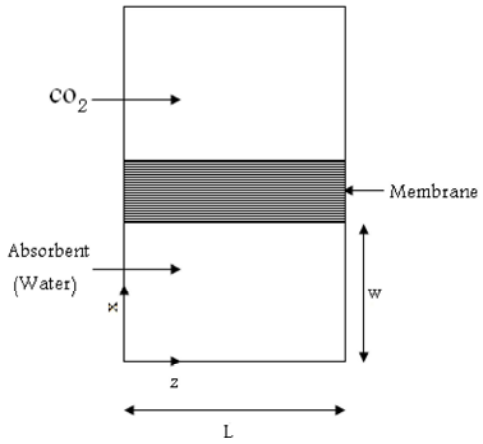

Fig. 1: Schematic drawing of CO_2 absorption in flat sheet membrane.

Theory: A comprehensive two-dimensional mathematical model was used for the transport of carbon dioxide through flat sheet membranes. In this work we study the absorption of pure CO_2 and absorption of CO_2 from CO_2/N_2 gas mixture in pure water as absorbent in a flat sheet membrane. The model was based on "non-wetted mode" in which the gas phase filled the membrane pores for co-current gas-liquid contacts. Laminar velocity distributions were used for the gas and liquid flow in the membrane.

Model Equations: A 2D mass transfer model was used for a flat sheet membrane, as shown in Fig. 1. The gas flows with a fully developed laminar velocity in the one side and the liquid absorbent (pure water) flows with laminar flow in the other side. Fig. 1 shows the cross sectional area of the flat sheet membrane. The steady state two-dimensional mass balances are carried out for membrane. The gas phase is fed to the one side (at $z = 0$), while the absorbent is passed through the other side (at $z = 0$). CO_2 is removed from the gas mixture by diffusing through the membrane and then is absorbed in the solvent (water).

The Model Is Built Considering the Following Assumptions:

- Steady state and isothermal conditions.
- Fully developed gas and liquid velocity profile in the flat sheet membrane.

- Ideal gas behavior is imposed.
- The Henry's law is applicable for gas-liquid interface.
- Laminar flow for gas and liquid flow in the contactor.
- Non-wetted mode in which the gas filled the membrane pores.

The Continuity Equation for Each Species in a Reactive Absorption System Can Be Expressed as [13]:

$$\frac{\partial C_i}{\partial t} = -(\nabla \cdot C_i V) - (\nabla \cdot J_i) + R_i \quad (1)$$

where C_i, J_i, R_i, V and t are the concentration, diffusive flux, reaction rate of species i, velocity and time, respectively. Either Fick's law of diffusion or Maxwell-Stefan theory can be used for the determination of diffusive fluxes of species i.

The continuity equation for steady state for CO_2 in the three sections of flat sheet membrane is obtained using Fick's law of diffusion for estimation of diffusive flux:

$$D_{CO2}\left[\frac{\partial^2 C_{CO2}}{\partial x^2} + \frac{\partial^2 C_{CO2}}{\partial z^2}\right] = V_z \frac{\partial C_{CO2}}{\partial z} \quad (2)$$

In a laminar flow, a fully developed velocity profile can be described as [13]:

$$V_z = 6\overline{V}\left[\left(\frac{x}{w}\right) - \left(\frac{x}{w}\right)^2\right] \quad (3)$$

where $\overline{V}$ is the average velocity in the flat sheet membrane.

The Boundary Conditions for Mass Transfer Equations Are: For liquid phase

at z=0, C_{CO2}=0 (4)

at $X = 0, \frac{\partial C_{CO2}}{\partial x} = 0$ (5)

at x=w, C_{CO2}=$C_{membrane}$×m (6)

where m is the physical solubility of CO_2 in the liquid absorbent (pure water).

For Membrane:

at $Z = 0, \frac{\partial C_{CO2}}{\partial z} = 0$ (7)

at x=w, $C_{membrane}$=C_l/m (8)

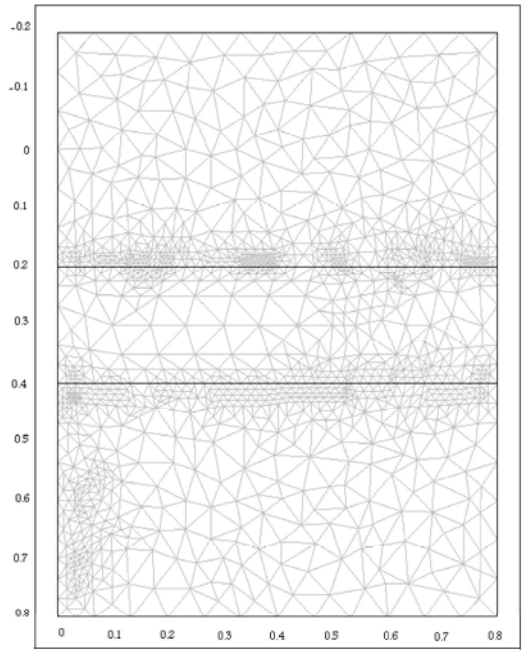

Fig. 2: Magnified segment of the mesh used in the numerical simulation. There are 1025 elements in total for the whole domain. z-Direction scale factor = 100. The three domains from left to right are liquid phase, flat sheet membrane and gas phase, respectively.

For Gas Phase:

at z=0, C_{co2}= C_0 (9)

at z=L, Convective flux (10)

at x=w, $C_{CO2,gas}$= $C_{membrane}$ (11)

Method of Numerical Solution: The dimensionless model equations with the appropriate boundary conditions were solved using COMSOL software, which uses finite element method (FEM) for numerical solutions of differential equations. The finite element analysis is combined with adaptive meshing and error control using numerical solver of UMFPACK. This solver is an implicit time-stepping scheme, which is well suited for solving stiff and non-stiff non-linear boundary value problems [5]. An IBM-PC-Pentium4 (CPU speed was 2800 MHz) was used to solve the set of equations. The computational time for solving the set of equations was about 8 minutes. Fig. 2 shows a segment of the mesh used to determine the gas transport behavior in flat sheet membrane. It should be pointed out that the COMSOL mesh generator creates tetrahedral that are isotropic in size. A large number of elements are then created with scaling. A scaling factor of 100 has been employed in z-direction due to large

difference between *x* and *z*. COMSOL automatically scales back the geometry after meshing. This generates an anisotropic mesh around 1025 elements.

RESULTS AND DISCUSSION

The calculations are performed for the cases of pure CO_2 and CO_2/N_2 mixture. The CO_2 inlet concentration in case of CO_2/N_2 mixture is taken as 20 vol.%. The gas phase concentration was assumed constant in the simulations. The length of the flat sheet membrane considered in this study, is 0.8m and the distance between the wall and the membrane is 0.02 m. A liquid velocity of 0.1 m s^{-1} is used in the simulations.

The solubility of CO_2 in pure water and the diffusion coefficient of CO_2 in the water and N_2 were taken from the Appendix [14, 15].

Model Validation: In order to validate the mass transfer model and the numerical solution, our modeling predictions for the physical absorption of 20% CO_2 in pure water using flat sheet membrane is compared with the experimental values reported by Wang *et al.* [16] (Fig. 3). The membrane geometry and operating parameters used in the simulation are the same as those used by Wang *et al.* [16]. As shown in Fig. 3, the simulation results are in good agreement with the literature data of Wang *et al.* [16] for different values of liquid flow rates, the average deviation being about 7%. It is worth mentioning here that while studying the effect of liquid velocity or liquid flow rate on the CO_2 absorption flux in water for different liquid flow rates, it was found that much lower values of liquid velocity has distinct influence on the CO_2 absorption flux.

Effect of Liquid Flow Rate on the Absorption of CO_2: The percentage removal of CO_2 can be calculated from the equation below:

$$\%\ \text{removal}\ CO_2 = 100\frac{(v\times C)_{inlet} - (v\times C)_{Outlet}}{(v\times C)_{inlet}} = 100\left(1 - \frac{C_{outlet}}{C_{inlet}}\right) \quad (7)$$

where *v* and *C* are the volumetric flow rate of gas phase and concentration, respectively. C_{outlet} is calculated by integrating the local concentration at outlet of membrane (*z* = L):

$$C_{outlet} = \frac{\int_{z=L} C(x)\,dx}{A} \quad (8)$$

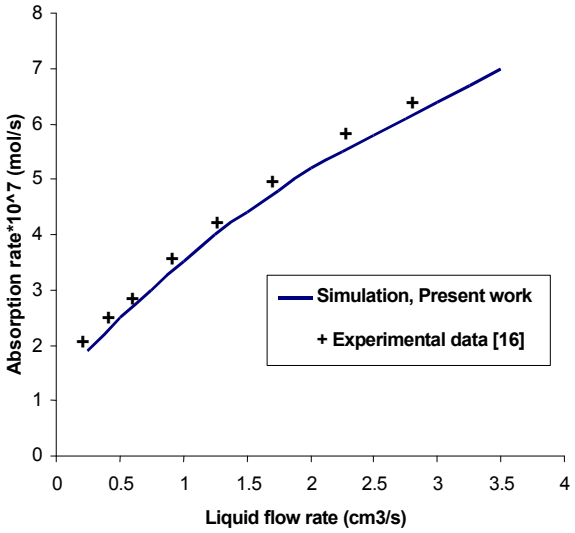

Fig. 3: Comparison of the CO_2 absorption rate in water with the experimental data [16].

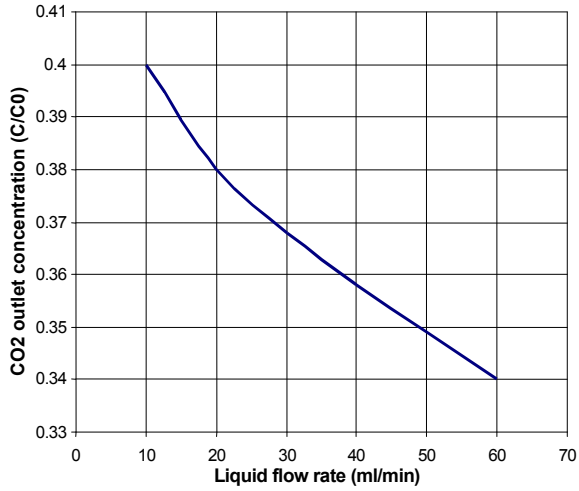

Fig. 4: Relationship between CO_2 outlet concentration in the gas phase and liquid flow rate. Gas pressure= 121.3 kPa, temperature= 298 K, Gas flow rate=100 ml/min. Inlet gas phase is 20% CO_2 and 80% N_2.

The change in volumetric flow rate is assumed to be negligible and thus % CO_2 removal can be approximated by Eq. (7).

In Fig. 4, the CO_2 outlet concentration in the gas phase is plotted as a function of absorbent flow rate or velocity and Fig. 5 illustrates the variation of the percentage removal of CO_2 as a function of liquid flow rate or velocity. As the absorbent flow rate increases, the mass transfer rate of carbon dioxide into the liquid increases because the concentration gradients of CO_2 and

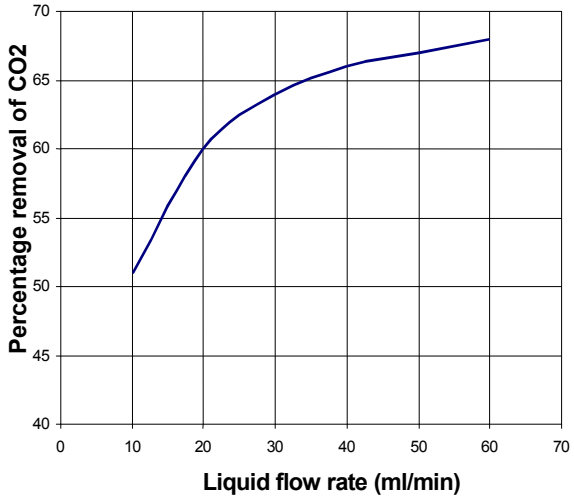

Fig. 5: Relationship between percentage removal of CO_2 and liquid flow rate. Gas pressure= 121.3 kPa, temperature= 298 K, Gas flow rate= 300 ml/min. Inlet gas phase is 20% CO_2 and 80% N_2.

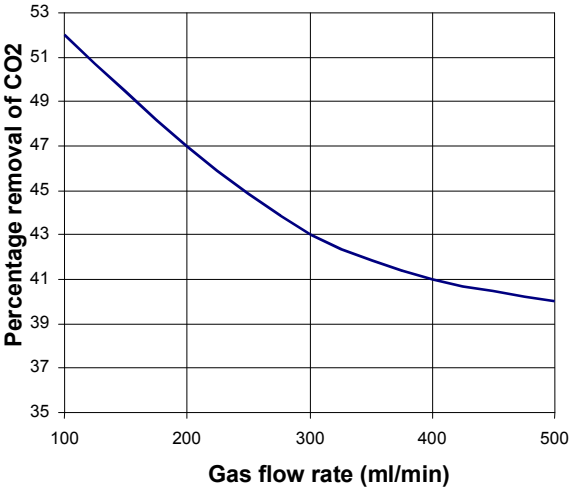

Fig. 6: Effect of gas phase flow rate on the removal of CO_2. Gas pressure= 121.3 kPa, liquid flow rate= 100 ml/min. Inlet gas phase is 20% CO_2 and 80% N_2.

absorbent in the liquid increase, thus the CO_2 outlet concentration in gas decreases (Fig. 4) and the percentage removal of CO_2 increases (Fig. 5). The figures clearly indicate that liquid flow rate in the flat sheet membrane has significant effect on the removal of CO_2.

Effect of Gas Flow Rate on the Removal of CO_2: The percentage removal of CO_2 in the gas phase along the length of flat sheet membrane for different values of gas flow rates (the effect of convection term) is presented in Fig. 6. As expected, the increase in the gas flow rate

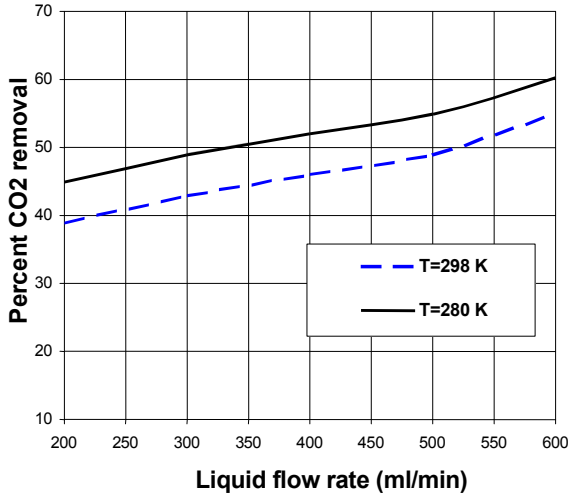

Fig. 7: Effect of temperature on the CO_2 removal in the gas phase. Gas pressure= 121.3 kPa, Gas flow rate= 500 ml/min. Inlet gas phase is 20% CO_2 and 80% N_2.

reduces the residence time in the membrane , which in turn reduces the removal rate of CO_2 in the . The percentage removal of CO_2 decreases from 52% to 40% when the gas flow rate in the flat sheet membrane changes from 100 ml/min to 500 ml/min. Also the Fig. 6 indicates that gas flow rate dose not greatly affect the CO_2 removal in the membrane.

Effect of Temperature: The change in temperature affects the key process parameters such as solubility of CO_2 in water, diffusion coefficients of gas and liquid phase and gas flow rate. Therefore, temperature variations are expected to results in significant changes in the mass transfer of CO_2. Fig. 7 shows the effect of temperature on the CO_2 removal. It is seen from figure that with decreasing temperature, the CO_2 removal increases. This can be attributed to the fact that as the temperature decreases, the physical solubility of CO_2 in water increases and the volumetric gas flow rate decreases, which gives combined favorable effects on the CO_2 removal. On the other hand, with decreasing temperature, liquid-phase diffusion coefficients decrease, giving unfavorable effect on the CO_2 removal. Since the favorable effect is more pronounced than the unfavorable effect, a net enhancement of CO_2 removal is observed with decreasing temperature.

CONCLUSIONS

This work presents a numerical simulation of mass transfer in a flat sheet membrane for gas-liquid phase

process. The numerical simulation was based on solving the conservation equations for gas in the membrane. The influence of various process parameters on the mass transfer of CO_2 was investigated. The simulation results were compared with the experimental data obtained from literature for absorption of CO_2 in pure water. The simulation results were in good agreement with the experimental data for different values of liquid flow rate. The results for the physical absorption of CO_2 in water indicated that the removal of CO_2 increased with increasing liquid velocity in the flat sheet membrane. On the other hand, increasing temperature and gas velocity in the membrane seemed to have an opposite effect. The liquid flow rate in the flat sheet membrane has significant effect on the removal of CO_2 whereas, the gas flow rate dose not greatly affect the CO_2 removal in the membrane.

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Nomenclature

A	Cross section of membrane (m^2)
C_0	Inlet gas concentration (mol/m^3)
C	Concentration (mol/m^3)
C_{CO2}	CO_2 concentration in the membrane (mol/m^3)
D	Diffusion coefficient (m^2/s)
D_{CO2}	Diffusion coefficient of CO_2 (m^2/s)
$D_{W,CO2}$	Diffusivity of CO_2 in pure water (m^2/s)
D_{CO2-N2}	Diffusion coefficient of CO_2 in N_2 (m^2/s)
$m_{wi}CO2$	Diffusive flux (mol/m^2s)
L	Length of the flat sheet (m)
m	Physical solubility (dimensionless)
$m_{w,CO2}$	Distribution coefficient of CO_2 in pure water (dimensionless)
P	Pressure (Pa)
T	Temperature (K)
$\overline{V}$	Average velocity in the membrane (m/s)
Vz	z-velocity in the (m/s)
w	Width between wall and membrane (m)
x	Distance (m)
z	Distance (m)

Greek Symbols

v	Volumetric flow rate (m^3/s)

Subscripts

i	Species i
g	Gas
in	Inlet
out	Outlet
I	Liquid

Appendix

A.1 Solubility: The distribution coefficient of CO_2 in pure water was taken from Versteeg and van Swaaij [14]:

$$m_{W,CO2} = 3.59\times10^{-7} RT \exp(\frac{2044}{T}) \text{ (dimensionless)} \quad (A.1)$$

A.2. Diffusivity: The diffusivity of CO_2 in pure water, $D_{W,CO2}$ was taken from Versteeg and van Swaaij [14]:

$$D_{W,CO2} = 2.35\times10^{-6} \exp(\frac{-2119}{T})\ m^2/S \quad (A.2)$$

The diffusivity of CO_2 in N_2 can be calculated based on Chapman-Enskog theory [15]:

$$D_{CO2-N2} = 1.85\ 10^{-5} \quad m^2/S \quad (A.3)$$

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