MASS TRANSFER ANALYSIS AND SIMULATION OF A HOLLOW FIBER GAS-LIQUID MEMBRANE CONTACTOR

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Abstract– A steady state model was developed for a hollow fiber membrane contactor to describe gas absorption performance. Countercurrent absorption of pure CO₂, pure SO₂, CO₂-N₂ and SO₂-N₂ mixtures in diethanolamine solution (DEA), and water as the absorbent were investigated. The model is able to predict gas phase concentration and the velocity profile in the axial direction inside the shell, as well as the liquid concentration profile in both the axial and radial direction inside the fibers. A numerical scheme was proposed to solve the simultaneous mathematical expressions that were obtained based on concepts of mass transfer, and the results were validated with experimental data found in the literature. Axial variations of gas velocity, gas concentration and a two dimensional concentration profile of the liquid phase were compared for three absorbing systems, including low (CO₂-water), moderate (CO₂-DEA) and high (SO₂-water) absorption rates. The effect of chemical reaction on the importance of external resistance was also studied using this model. It was found that the shell side and membrane resistances are negligible in comparison with the liquid resistance in low absorption rates, for example in a CO₂-water system, however they have significant effects when the chemical reaction is fast and the absorption rate is high, such as SO₂-water system.

Keywords– Membrane contactor, hollow fiber, gas absorption, modelling

1. INTRODUCTION

The application of the microporous hollow fiber membrane contactor for gas absorption and stripping has gained considerable attention recently and is still a relatively new concept. In comparison with most membrane separation processes which use a dense selective layer on one side of the fibers, the microporous membrane used in the membrane contactor is not selective. Instead of the selective layer, a liquid flow is introduced in one side of the fiber that can absorb gas components physically or chemically. This leads to a higher mass transfer rate due to lower membrane resistance. Additionally, because there is no selective layer, a very small pressure drop across the membrane is required for mass exchange. Compared to the traditional columns like packed and tray towers, bubble columns, venture scrubbers and spray towers, membrane contactor has several advantages. These include higher mass transfer rates, independent control of gas and liquid rates, a known and constant interfacial area, easy scale up and no operational problems such as foaming, flooding and entrainment [1, 2]. By forming the membranes as hollow fibers, a very compact unit can be made with a specific area 1600-6500 (m²/m³), which is higher than the 30-330 (m²/m³) offered by packed/tray towers and 160-500 (m²/m³) for mechanically agitated columns [1]. Although the membrane wall introduces an additional resistance that does not exist in conventional towers, a higher specific surface area in these type of modules offers much higher mass transfer rates.

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These advantages have led to a number of investigations on the use of membrane contactors for gas absorption and stripping. Absorption of various gases by a number of solvents in a hydrophobic contactor were first carried out by Zhang and Cussler [3, 4]. The same as in this preliminary study, in most other further researches, hydrophobic membranes have been employed with gas filled membrane pores. In a hydrophilic fiber, pores are filled with a stagnant liquid film and the mass transfer rate is much lower due to a lower diffusivity in the liquid. The liquid phase pressure should be slightly higher than the gas phase pressure to prevent the dispersion of gas bubbles into the liquid. On the other hand, the liquid pressure should not exceed the breakthrough pressure of the membrane to prevent membrane wetting.

Kreulen et al. [5, 6] studied the CO$_2$ absorption by water/glycol mixture as absorbent. Their results showed a better performance of the membrane contactor compared to the bubble column, especially for higher viscous liquids. Karoor and Sirkar [7] studied the absorption of CO$_2$ and SO$_2$ by water in a comprehensive experimental investigation and found that the mass transfer rate is about ten times higher than those typically obtained in packed towers. Some other experimental and theoretical studies have been carried out focusing on CO$_2$ absorption from flue gases using various absorbents such as sodium hydroxide, potassium hydroxide and alkanolamines [8-15]. The advantages of chemical absorption of CO$_2$ by alkanolamine solutions are quite obvious, since alkanolamines are weak basic compounds and their chemical bonds with CO$_2$ are easily broken at high temperatures, leading to efficient regeneration of the absorbents and, as a result, can be regenerated efficiently. Such a process has recently been studied by some researchers [16-18]. A theoretical analysis of cross flow membrane contactor for physical and chemical absorption of carbon dioxide and hydrogen sulfide was developed by Dindore et al. [19, 20]. They used water and aqueous potassium carbonate solution as absorbents and found that gas phase concentration distribution has a considerable influence on the CO$_2$ flux in the case of high recovery.

In most of the previous theoretical investigations, emphasis has focused mainly on physical or slow chemical absorptions. In some other studies, gas phases have been assumed to be pure. In such cases, external mass transfer resistance (combination of membrane and gas side resistances) is essentially negligible in comparison with liquid resistance. Therefore, applying component material balance on the liquid phase side could be sufficient to model the problem. In this paper, a theoretical analysis was performed for microporous hollow fiber membrane modules employed for gas absorption. Governing equations for both gas phase in the shell side and liquid phase in the lumen side of the module were developed. Physical absorption of pure CO$_2$ and mixed CO$_2$-N$_2$ with water, the chemical absorption of CO$_2$-N$_2$ with DEA solution, and SO$_2$-N$_2$ with water were investigated theoretically. The validation of the model was checked using the experimental data given by Karoor and Sirkar [7] and Wang et al. [18]. After the model validation, axial variations of gas velocity and gas concentration in the shell side were compared for three absorbing systems including low (CO$_2$-water), moderate (CO$_2$-DEA) and high (SO$_2$-water) absorption rates. Two-dimensional concentration profiles in the lumen side of three systems were also compared. Then, the effect of chemical reaction on the importance of external resistance was studied using the model for the mentioned absorbing systems.

2. MODEL DESCRIPTION

A mathematical model is developed here to describe pure or mixed gas absorption, physically or chemically. In all parts of this study, liquid is assumed to flow inside the fibers and countercurrent to gas flow inside the shell. Fig. 1 illustrates the mass transfer regimes for a single fiber. Gaseous component "i" can diffuse from the shell side to the membrane wall, pass through the pores of the membrane (which can be gas filled or liquid filled), and is finally followed by liquid phase diffusion/chemical reaction. The following assumptions were made in deriving the mathematical expressions:
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- Steady state and isothermal conditions
- Laminar parabolic velocity profile within the fibers
- Ideal gas behavior
- No axial mixing in all phases
- Uniform pore size distribution and membrane wall thickness
- Pores are fully gas filled or liquid filled (not partially)

Using the above assumptions, the mathematical formulation of the liquid and gas phases are given as follows.

**a) Governing equations in liquid phase**

The operation principle of gas absorption in a hollow fiber membrane contactor under countercurrent condition is shown in Fig. 2. Applying a component material balance on the liquid phase within the fibers for the $i$th diffusing component leads to the following two dimensional partial differential equations:

$$
U_z \frac{\partial C_{iL}}{\partial Z} = D_{iL} \left( \frac{\partial^2 C_{iL}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{iL}}{\partial r} \right) - R_i
$$ (1)

Where, $R_i$ is the rate of chemical reaction for component $i$. In the case of physical absorption, the term $R_i$ can be dropped.

Equation (1) consists of a set of partial differential equations that should be written for all diffusing components in the liquid phase. Since the chemical reaction term ($R_i$) is normally a function of concentration of several components, the partial differential equations are not independent and must be solved simultaneously. The initial condition for each diffusing component in the lumen is specified as:

$$
C_{iL} = C_{iL, \text{in}} \quad \text{for } Z=0 \text{ and all } r
$$ (3)

At the center of each fiber, symmetry is assumed in the radial direction, resulting in the following boundary condition:

**Fig. 1. Mass transfer regimes in a single fiber**

**Fig. 2. Operation of membrane contactor**

Liquid flow rate inside the fiber is laminar and can be given by:

$$
U_z = 2U_{av} \left[ 1 - \left( \frac{r}{r_i} \right)^2 \right]
$$ (2)

Equation (1) consists of a set of partial differential equations that should be written for all diffusing components in the liquid phase. Since the chemical reaction term ($R_i$) is normally a function of concentration of several components, the partial differential equations are not independent and must be solved simultaneously. The initial condition for each diffusing component in the lumen is specified as:

$$
C_{iL} = C_{iL, \text{in}} \quad \text{for } Z=0 \text{ and all } r
$$ (3)

At the center of each fiber, symmetry is assumed in the radial direction, resulting in the following boundary condition:
\[
\frac{\partial C_{iL}}{\partial r} = 0 \quad \text{for } r=0 \text{ and all } Z \quad (4)
\]

At the gas-liquid interface, a mass conservation for each diffusing species leads to:

\[
-D_{il} \frac{\partial C_{iL}}{\partial r} = K_{ex} \left( C_{ig} - C_{ig,\text{int}} \right) \quad \text{for } r = r_i \text{ and all } Z \quad (5)
\]

Also, Henry’s law can be applied at the gas-liquid interface as follows:

\[
C_{iL} = H C_{ig} \quad \text{for } r = r_i \text{ and all } Z \quad (6)
\]

External mass transfer coefficient \( (K_{ex}) \) is a combination of the membrane wall and the shell side mass transfer coefficient and will be discussed in detail later. For some species in the liquid phase which cannot diffuse to gas, such as water and diethanolamine, Eq. (5) can be simplified as:

\[
-D_{il} \frac{\partial C_{iL}}{\partial r} = 0 \quad \text{for } r = r_f \text{ and all } Z \quad (7)
\]

b) Governing equations in gas phase

Equation (5) indicates that the liquid phase concentration profile inside the fibers depends on the gas phase concentration distribution inside the shell. If the gas in the shell side is assumed to be pure or nearly pure, the assumption that is used frequently in previous research [8, 13, 15, 16], it is possible to use a constant gas concentration in Eq. (5), which leads to a simpler problem. However, in practical applications of membrane contactor for gas absorption, for example in flue gas treating or gas sweetening, the gas phase is a mixture of several components and gas phase concentration distribution must be considered.

By applying a component mass balance on the gas phase for ith diffusing components, the following ordinary differential equation is proposed:

\[
\frac{d}{dz} \left( U_g C_{ig} \right) - \frac{A_i}{A_s L} K_{ex} \left( C_{ig} - C_{ig,\text{int}} \right) = 0 \quad (8)
\]

where \( A_i \) and \( A_s \) are gas-liquid mass transfer area and shell side cross section area available for gas, respectively. An overall mass balance for gas phase also gives:

\[
\frac{d}{dz} \left( U_g \right) - \sum_i \frac{A_i}{A_s C_g L} K_{ex} \left( C_{ig} - C_{ig,\text{int}} \right) = 0 \quad (9)
\]

Equations (8) and (9) should be written for all diffusing components to give the velocity and concentration profile in the axial direction with the following boundary conditions:

\[
C_g = \frac{P_g}{RT} \quad \text{at } Z=L \quad (10)
\]

\[
U_g = \frac{Q_g}{A_s} \quad \text{at } Z=L \quad (11)
\]

When a gas mixture is analyzed, the sets of Eqs. (1) to (11) should be solved simultaneously for all diffusing components.
c) Chemical reactions

Mass transfer can be enhanced when a chemical reaction is present and is usually unavoidable for a high recovery gas absorption process. The absorption of carbon dioxide with water is essentially physical, while sulfur dioxide is absorbed by water according to the following chemical reactions [7, 21]:

\[
SO_2 + 2H_2O \rightleftharpoons k_1 \rightarrow H_3O^+ + HSO_3^- \quad , \quad K_E = 0.014 \text{ M}
\]  
(12)

\[
HSO_3^- + H_2O \rightleftharpoons k_2 \rightarrow H_3O^+ + SO_3^{2-} \quad , \quad K_E = 6.24 \times 10^{-8} \text{ M}
\]  
(13)

If pH is less than 4-5, \( SO_3^{2-} \) formation can be avoided and the second reaction can be dropped. The rate expression for reactions has been given by [7]:

\[
-R_{SO_2} = k_1[C_{SO_2}] - \frac{k_1}{k_E} [C_{HSO_3}]^2
\]  
(14)

Because this reaction depends on the concentration of \( HSO_3^- \), the diffusion of this anion in the liquid phase should also be considered.

\[
-R_{HSO_3} = -k_1[C_{SO_2}] + \frac{k_1}{k_E} [C_{HSO_3}]^2
\]  
(15)

The forward reaction rate constant (\( k_1 \)) is given as \( 3.17 \times 10^{-2} \) (1/s), [7].

The reaction of carbon dioxide with primary and secondary amines can be expressed by zwitterions mechanism. The first step is the production of zwitterion as follows [16, 22, 23]:

\[
CO_2 + R_2NH \rightleftharpoons k_2 \rightarrow R_2NH^+COO^-
\]  
(16)

The zwitterion can be deprotonated by any base present in the solution producing a carbamate ion and a protonate base:

\[
R_2NH^+COO^- + B \rightleftharpoons k_0 \rightarrow R_2NCOO^- + BH^+
\]  
(17)

Then, the overall chemical reaction of DEA with \( CO_2 \) is given by:

\[
CO_2 + 2R_2NH \rightleftharpoons R_2NCOO^- + R_2NH^+
\]  
(18)

The forward reaction rate of \( CO_2 \) is derived on the assumption of a quasi-steady state for the zwitterion:

\[
R_{CO_2} = \frac{[CO_2][R_2NH]}{k_2 + \frac{k_2k_{R_2NH}}{k_{-1}}[R_2NH] + \frac{k_2k_{H_2O}}{k_{-1}}[H_2O] + \frac{k_2k_{OH^-}}{k_{-1}}[OH^-]}
\]  
(19)

The concentration of \( OH^- \) is assumed to be negligible in comparison with much higher concentrations of \( R_2NH \) and \( H_2O \) [23-26].

The depletion rate of carbon dioxide depends on the \( R_2NH \) concentration, and therefore, the amine ion should also be considered as a defusing component. The value of rate constants and diffusion coefficients of the mentioned reactions are listed in Table 1.
Table 1. Physical and chemical properties used in this study [7,14,22,23]

<table>
<thead>
<tr>
<th>Liquid solution</th>
<th>Species</th>
<th>$D_{CO_2}$</th>
<th>$D_{SO_2}$</th>
<th>$D_{H_2O}$</th>
<th>$D_{DEA}$</th>
<th>H</th>
<th>$k_2$</th>
<th>$k_{2H_2O}$</th>
<th>$k_{2DEA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEA solution</td>
<td>$CO_2$</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
<td>0.497</td>
<td>0.833</td>
<td>2.38</td>
<td>$2.2 \times 10^{-6}$</td>
<td>$4.37 \times 10^{-4}$</td>
</tr>
<tr>
<td>Pure water</td>
<td>$CO_2$</td>
<td>1.92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.765</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure water</td>
<td>$SO_2$</td>
<td>-</td>
<td>1.76</td>
<td>2.34</td>
<td>-</td>
<td>25.86</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**d) External mass transfer coefficients**

External mass transfer coefficient ($K_{ex}$) used in previous equations, is a combination of membrane wall and gas phase mass transfer coefficients. Application of the resistance-in-series model for these two phases gives [1, 2]:

$$\frac{1}{K_{ex}} = \frac{1}{K_g} + \frac{1}{K_m}$$  \hspace{1cm} (20)

In the derivation of Eq. (20), the fiber wall is assumed to be flat, a routine assumption in gas absorption analysis. A more accurate formulation can be proposed by considering the fiber curvature:

$$\frac{1}{K_{ex}d_i} = \frac{1}{K_g d_i} + \frac{1}{K_m d_{ln}}$$  \hspace{1cm} (21)

The application of Eq. (21) is as simple as Eq. (20) in the model simulation, but it will be shown later that Eq. (20) is not an accurate relation in some conditions.

Membrane mass transfer coefficient depends on effective diffusivity and membrane thickness as shown in Eq. (22) [27]:

$$K_m = \frac{D_e e}{\delta \tau}$$  \hspace{1cm} (22)

Because of very small pore size, the gas diffusion can be affected by the pore wall, and Knudsen diffusion must be considered.

$$\frac{1}{D_e} = \frac{1}{D_{ik}} + \frac{1}{D_{ig}}$$  \hspace{1cm} (23)

Knudsen diffusion coefficient can be written as [27]:

$$D_{ik} = \frac{d_p}{3} \left( \frac{8RT}{\pi M} \right)^{1/2}$$  \hspace{1cm} (24)

The gas phase mass transfer coefficient ($K_g$) should be evaluated from empirical correlations [1, 28]. Lipnizki and Field [29] proposed a set of correlations to estimate shell side mass transfer coefficient for axial flow in the hollow fiber modules, based on the analogy between mass and heat transfer. In a laminar flow and for a fully developed hydrodynamic and concentration profile, they propose:

$$Sh_1 = 3.66 + 1.2 \left( \sqrt{1 - \epsilon} \right)^{0.8}$$  \hspace{1cm} (25)
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In the case of a developing concentration profile and fully developed hydrodynamic, it gives:

\[
Sh_2 = 1.615 \left(1 + 0.14\left(\sqrt{1 - e}\right)^{-0.5}\right)^{3/2} \left(\frac{Re Sc d_h}{L}\right)
\]  

At the beginning of the module, neither concentration nor hydrodynamic profile is fully developed. This condition is given by:

\[
Sh_3 = \left(\frac{2}{1 + 22Sc}\right)^{1/6} \left(\frac{Re Sc d_h}{L}\right)^{1/2}
\]  

An approximation for Sherwood number for the whole regime can be calculated as follows:

\[
Sh = \left(Sh_1^3 + Sh_2^3 + Sh_3^3\right)^{1/3}
\]

Table 2 shows the hollow fiber modules used in this study and their references.

<table>
<thead>
<tr>
<th>Module no.</th>
<th>Fiber o. d., ((\mu m))</th>
<th>Fiber i. d., ((\mu m))</th>
<th>Module leng., (cm)</th>
<th>No. of fibers</th>
<th>Porosity</th>
<th>Tortuosity</th>
<th>Pore size ((\mu m))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>300</td>
<td>240</td>
<td>30</td>
<td>132</td>
<td>0.4</td>
<td>2.5</td>
<td>0.03</td>
<td>[7]</td>
</tr>
<tr>
<td>II</td>
<td>300</td>
<td>240</td>
<td>18</td>
<td>75</td>
<td>0.4</td>
<td>2.5</td>
<td>0.03</td>
<td>[7]</td>
</tr>
<tr>
<td>III</td>
<td>300</td>
<td>220</td>
<td>11.3</td>
<td>1100</td>
<td>0.4</td>
<td>3.5</td>
<td>0.04</td>
<td>[18]</td>
</tr>
</tbody>
</table>

3. METHOD OF SOLUTION

The set of Eqs. (1) to (11) includes a number of partial and ordinary differential equations of first and second order. The partial differential equations are usually non-linear because of the chemical reaction term. These equations must be solved simultaneously to find liquid concentration profile in the radial and axial directions, and the gas concentration/velocity profile in the axial direction. Because of the mathematical complexity of the proposed system, a numerical technique should be applied to solve the equations. A finite difference scheme was applied to solve the equations by using MATLAB [30]. The diffusion terms were discretized by the Crank-Nicolson method, while nonlinear chemical reaction terms were linearized using the Newton-Raphson method. Then the set of linearized algebraic equations in the radial direction, which form a tridiagonal matrix, were solved simultaneously using Thomas algorithm [31]. Because the governing equation in gas and liquid phases cannot be solved separately, a value for \((C_{ig} - C_{ig, int})\) was assumed at the beginning. This value should be adjusted according to the solution algorithm for the system, which is given schematically in Fig. 3. A material balance error was evaluated at the end of the program to check the accuracy of the numerical technique. The average error is something around \(\pm 0.05\%\), which is essentially acceptable for a finite difference method.

4. RESULTS AND DISCUSSION

The results of the numerical study carried out with the proposed algorithm are presented below for countercurrent flow pattern. The liquid outlet part of the module was selected as zero (Z=0) in the axial direction for all parts of this study.
The absorption of pure carbon dioxide in pure water was analyzed initially by using the model and checked with the experimental results of Karoor and Sirkar [7] in Fig 4. This figure shows the liquid outlet concentration of carbon dioxide into water as a function of liquid flow rate. It is indicated that the liquid outlet concentration predicted by the model decreases with increasing the liquid flow rate, which is in good agreement with the experimental data for both wetted and non-wetted mode. The liquid phase diffusivity is much less than gas phase diffusivity, and as a result, gas absorption performance is lower under wetted condition, as shown in Fig. 4.

The chemical absorption of pure SO\textsubscript{2} with pure water is given in Fig. 5, which shows a good agreement between the proposed model and the experimental results. It should be noted that the performance of gas absorption is much higher for SO\textsubscript{2} removal by water in comparison with the CO\textsubscript{2}-water system, due to the effects of the chemical reaction. Another important parameter is the solubility of SO\textsubscript{2} in water, which is much higher than CO\textsubscript{2} solubility, according to Table 1.

The chemical absorption of sulfur dioxide from a 1% SO\textsubscript{2}-air mixture in module II is illustrated in Fig. 6. To evaluate the accuracy of the presented model, the obtained results were compared with the Karoor and Sirkar [7] model, which used Happel's free surface model to characterize the shell side velocity profile. The figure reveals a better agreement of the proposed model with the experimental results. The fibers within the shell side of a hollow fiber module are normally not packed uniformly, complicating shell side fluid hydrodynamics and mass transfer [28]. The real fibers are not, therefore, in a regular array and there is a fluid exchange between the fibers in the radial direction. As a result, Happel's
free surface model with the assumption of uniform flow distribution between the fibers cannot always give a good estimation of the flow pattern in the shell side.

![Graph 1](image1)

**Fig. 4.** Pure $CO_2$ absorption in pure water under wetted and non-wetted cases, module I, $Q_g = 75 \text{ cc/min}$

The molar flux of carbon dioxide in module III versus gas inlet velocity is given in Fig. 7 for a constant liquid flow rate. The absorbent is a 2 molar DEA solution, while gas phase is a mixture of $CO_2$ and $N_2$. Theoretical prediction of the model and the experimental results of Wang et al. [18], both show that a higher flux is reachable, especially for higher gas flow rates.

![Graph 2](image2)

**Fig. 5.** Absorption of pure $SO_2$ in pure water, module I, $Q_g = 715 \text{ cc/min}$

![Graph 3](image3)

**Fig. 6.** Absorption of $SO_2$ in pure water from a 1% $SO_2$-air mixture in module II, $Q_g = 200 \text{ cc/min}$

![Graph 4](image4)

**Fig. 7.** $CO_2$ molar flux for a 20%$CO_2$-$N_2$ gas mixture and DEA solution, module III, $U_L = 0.12 \text{ ms}^{-1}$

The proposed numerical model can be used as a useful tool for parameter evaluation and performance analysis of gas absorption in hollow fiber membrane contactors. Three absorbing systems were studied as follows:

a. System 1: Gas including 20%$CO_2$-80%$N_2$ and pure water as absorbent.
b. System 2: Gas including 20%$CO_2$-80%$N_2$ and 2 M DEA solution as absorbent.
c. System 3: Gas including 20%$SO_2$-80%$N_2$ and pure water as absorbent.

Module I was used for all three absorbing systems.

Figure 8 presents the two dimensional concentration distributions in the liquid phase of $CO_2/SO_2$ in their related absorbents for three absorbing systems. The figures reveal faster depletion of $CO_2/SO_2$...
concentration in both the radial and axial direction when the gas absorption is enhanced by chemical reaction. A comparison between systems b and c indicates that the rate of depletion in the CO$_2$-DEA system is faster than the SO$_2$-water system in the radial direction, while it is slower in the axial direction. This result can be attributed to a much higher Henry's constant of the SO$_2$-water system in comparison with the CO$_2$-DEA system, while the diffusivities are nearly the same. A high Henry's constant results in the absorption of a large amount of SO$_2$ in water near the point of liquid entrance and around the lumen wall (Z/L = 1, r/r$_i$ = 1), therefore, SO$_2$ can be significantly diffused in the radial direction. On the other hand, the absorption rate of CO$_2$ in DEA solution is lower and as a result, CO$_2$ can not diffuse far from the fiber wall, hence it will be consumed quickly by chemical reaction. It seems that an analytical solution with the assumption of "short contact time" in the radial direction can be established for an absorbing system such as CO$_2$-DEA with a low Henry's constant and relatively fast chemical reaction.

![Diagram](image-url)

Fig. 8. Two dimensional concentration distribution in the lumen of module I for three absorbing systems, Q$_L$ = 100 cc/min, Q$_g$ = 400 cc/min
Figure 9 illustrates the changes of gas velocity in the shell side of the module versus fiber length. This shows that the gas velocity is dropped by 20% for SO$_2$-water system, a system with fast chemical reaction and high recovery, while the reduction is about 2% for the physical absorption of CO$_2$-water system with low recovery. Fig. 10 presents the reduction of gas phase mole percent in the shell side of the module versus fiber length. The same results of Fig. 9 can be seen, which shows that higher variations can be obtained in the presence of a fast chemical reaction. These two figures reveal that the assumption of constant concentration and the velocity of the gas phase in the shell side, which has been used in some previous investigations for the simplification of mathematical formulation, is only valid when a system with a low absorption rate is analyzed.

Fig. 9. Gas velocity distribution along the fiber length, a comparison of three absorbing system, $Q_L=100$ cc/min, $Q_g=400$ cc/min

Fig. 10. Gas concentration distribution along the fiber length, a comparison of three system, $Q_L=100$ cc/min, $Q_g=400$ cc/min

The effect of liquid flow rate on the liquid phase concentration profile versus fiber length is shown in Fig. 11. The gas phase is a 20%SO$_2$-80%N$_2$, and gas flow rate is 400 (cc/min) and constant. This demonstrates that for low liquid flow rates, the whole fiber length is effective and a normal rise in the concentration with length can be seen. But for a high value of liquid rates, the initial parts of the fibers have essentially no effects on the gas absorption. Therefore, an increase in module length cannot increase the recovery. It should be emphasize that this result is only valid for a special case, when the chemical reaction is fast enough and the liquid flow rate is very high.

Fig. 12 presents the effects of external mass transfer coefficient on the module performance. To do this, Eq. (21) can be rewritten in the following form:

$$K_{ex} = \beta \frac{K_g K_m}{K_g + K_m}$$  \hspace{1cm} (29)

$\beta$ is an artificial factor and allows us to change the amount of external mass coefficient for parameter evaluation. The amount of $\beta$ is 1 according to Eq. (20) and is about 1.15 from Eq. (21) for module I. The relative error was defined as:

$$\text{Error} \% = \frac{C_{ig \ (out, \ I)} - C_{ig \ (out, \ II)}}{C_{ig \ (out, \ II)}}$$  \hspace{1cm} (30)

Where $C_{ig \ (out, \ I)}$ and $C_{ig \ (out, \ II)}$are gas outlet concentrations when Eqs. (29) and (21) are applied in the model respectively. The figure shows that the SO$_2$-water system is very sensitive to $\beta$, while the
sensitivity for the CO$_2$-DEA system is lower and for the CO$_2$-water system nearly zero. This means that the external mass transfer resistance is essentially negligible in comparison with the liquid resistance for a low absorption rate system. On the other hand, for a system with a fast chemical reaction and a high recovery, the liquid phase resistance is reduced significantly by chemical reaction, and therefore, the external mass transfer resistance can be very important and must be considered accurately in the membrane analysis.

![Fig. 11. Effect of liquid flow rate on the liquid phase concentration profile (bulk average in radial direction), 20%SO$_2$-80%N$_2$ system, $Q_g = 400$ cc/min](image1.png)

![Fig. 12. The effect of external mass transfer coefficient on the module performance, module I, $Q_L = 100$ cc/min, $Q_g = 400$ cc/min](image2.png)

The accuracy of Eq. (20) can also be checked by using the results of Fig. 12. The correct value of $\beta$ is about 1.15 according to Eq. (21) for module I, when fiber curvature is considered. This value is 1 when Eq. (20) is applied instead of Eq. (21), the simplification that has been used several times in previous studies. The figure reveals that the application of Eq. (20) instead of (21) can cause an error of about 17% in the given conditions for the SO$_2$-water system; 5% for the CO$_2$-DEA system, and almost no error for the water-CO$_2$ system. Because the application of Eq. (21) is as simple as Eq. (20) in the modeling and simulation studies, it is proposed to employ this equation for more accuracy.

5. CONCLUSION

In the present study, a mathematical model was developed for gas absorption in the hollow fiber membrane contactors. The chemical or physical absorption of pure SO$_2$ and pure CO$_2$, or a mixture of the gases with N$_2$ were analyzed using the model, where water and DEA solution were employed as absorbents. The results predicted by the model were in good agreement with the experimental data found in the literature. The developed model is able to calculate two-dimensional concentration distributions of diffusing components inside lumen, as well as axial concentration and velocity profile in the shell side in a countercurrent flow regime. The model was also applied as a tool to simulate the module performance under three absorbing systems including CO$_2$-water, CO$_2$-DEA and SO$_2$-water, at the same operating conditions. The simulation results showed that the velocity and concentration of the gas phase can change significantly in the presence of a fast chemical reaction in the liquid phase. The effect of liquid flow rate on the liquid phase concentration distribution revealed that an increasing in module length cannot increase the recovery when the chemical reaction is fast enough and the liquid flow rate is high. It was also found (by using the simulation) that the external mass transfer resistance has a significant influence in the module performance for an absorbing system with high absorption rate (SO$_2$-water system), while it is
essentially negligible for a physical absorption system with low recovery (CO$_2$-water system). The considerable reduction of liquid phase resistance in the presence of a fast chemical reaction is the reason for such behavior.

**NOMENCLATURE**

- $A_i$: gas-liquid mass transfer area ($m^2$)
- $A_s$: shell side cross section area available for gas ($m^2$)
- $C$: concentration ($mol m^{-3}$)
- $d$: diameter (m)
- $d_h$: hydraulic diameter of shell side (m)
- $D$: diffusivity ($m^2 s^{-1}$)
- $D_e$: membrane effective diffusivity ($m^2 s^{-1}$)
- $D_{ik}$: Knudsen diffusivity of species $i$ ($m^2 s^{-1}$)
- $e$: membrane porosity (dimensionless)
- $G_z$: Graetz number (dimensionless)
- $H$: dimensionless Henry's constant
- $K_{ex}$: external mass transfer coefficient ($m s^{-1}$)
- $K_E$: reaction equilibrium constant ($mol m^{-3}$)
- $K_g$: gas phase mass transfer coefficient ($m s^{-1}$)
- $K_m$: membrane mass transfer coefficient ($m s^{-1}$)
- $k_{Olm}$: overall mass transfer coefficient ($m s^{-1}$)
- $k_1$: reaction rate constant ($s^{-1}$)
- $k_{-1}$: reverse first order reaction rate constant ($s^{-1}$)
- $k_2$: second order reaction rate constant ($mol^{-1} m^{-3} s^{-1}$)
- $k_b$: second order reaction rate constant for base b ($mol^{-1} m^{-3} s^{-1}$)
- $L$: module length (m)
- $M$: molecular weight ($kg mol^{-1}$)
- $P$: pressure (Pa)
- $Q$: volumetric flow rate ($m^3 s^{-1}$)
- $r$: radial direction or Radius (m)
- $r_i$: inner radius of fiber (m)
- $R$: universal gas constant ($J mol^{-1} K^{-1}$)
- $R_i$: chemical reaction term ($mol m^{-3} s^{-1}$)
- $Re$: Reynolds number (dimensionless)
- $Sc$: Schmit number (dimensionless)
- $Sh$: Sherwood number (dimensionless)
- $T$: temperature (K)
- $U$: velocity ($m s^{-1}$)
- $Z$: axial coordinate (m)
- $\varepsilon$: fibers porosity in module (dimensionless)
- $\tau$: tortuosity (dimensionless)

**Subscripts**

- $av$: average
- $g$: gas
- $i$: any diffusing species
- $in$: input
- $int$: interface
- $L$: liquid
- $Im$: Log-mean average
- $p$: pore
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