

Mathematical Analysis of Removal of Dissolved Acidic Gases from Aqueous Stream Using Membrane Contactor

Ashutosh Rawat, Gunjan K. Agrahari, Niharika Pandey, and Prashant K. Bhattacharya

Abstract—A mathematical analysis was performed on an acid-gas removal process applied to an aqueous feed stream using a hollow fiber membrane contactor in liquid-liquid extraction mode. Furthermore, a comparison was made between the obtained simulation results and with the earlier published experimental results. The model development is based on a process setup wherein synthetic wastewater feed solution was considered to be passing through the lumen side and later recycled back to the feed tank. On the shell side of the membrane contactor, an extractant was circulated in the counter direction. The model is developed considering radial and axial diffusion mechanisms and convection on the lumen side. Mass transfer across the pore by diffusion from Knudsen and bulk flow has also been considered. The partial differential equations obtained, were solved by converting them into a number of ordinary differential equations by using the finite difference method. The model was solved and simulated using MATLAB. The effect of various membrane contactor parameters such as the number of fibers and their effective lengths on the removal of gases have also been studied in this analysis. The simulated results obtained were observed to be in excellent agreement with the experimental results obtained for the acidic gas, H₂S.

Index Terms—Waste water treatment, membrane separation, hollow fiber membrane contactor, degasification of water, modeling and simulation.

I. INTRODUCTION

Large amounts of dissolved acidic gases such as CO₂ and H₂S are generally found in natural water reservoirs and industrial wastewater. CO₂ is present in natural water reservoirs because of the respiration and photosynthesis of marine animals and plants, decay of organic substances, and dissolution of carbonate salts present at the reservoir bottoms [1]. H₂S is also present in thermal sulfur springs [2].

Industrial plants manufacturing ammonia and urea generate wastewater streams containing high CO₂ contents. In general, industries that manufacture viscose rayon, paper, and pulp discharge wastewater streams containing high H₂S concentrations. Dissolved H₂S may also be found in untreated agricultural water output and in effluent streams generated from the hydrocracking of crude oil [3], [4]. Conventional processes for wastewater treatment, such as aeration, forced draft degasification, and vacuum degasification may involve high cost as these processes

require high duty equipments like blowers etc. In such cases, membrane contactor could become a viable alternative. Methods including vacuum sweep mode and gas-liquid extraction in membrane contactors may have some operational drawbacks; moreover, precise design is required to avoid loading or flooding in columns [5]. In recent years, membrane contactors have evolved as very important tool for separation. These contactors consist of a cylindrical cartridge which contains number of microporous hollow fibers constituting the lumen side of the contactor. Fibers in the membrane contactor are polymeric and can be either hydrophobic or hydrophilic. Polypropylene and polytetrafluoroethylene are the polymeric materials used for making hydrophobic membranes, which can be used for removing volatile species and gases from water.

The degasification of feed streams using membrane contactors has been studied by many researchers. CO₂ removal from gas using monoethanolamine as the extractant in the membrane contactor has been studied by Bottino *et al.* [6], while experimental study and numerical analysis of carbon dioxide removal from water in liquid-liquid extraction mode have been performed by Agrahari *et al.* [7]. Keshavarz *et al.* [8] have presented a mathematical model for membrane contactors used for the simultaneous absorption of CO₂ and H₂S from gaseous feed to diethanolamine (DEA) solution. McDermott *et al.* [9] studied the removal of volatile and semi-volatile organic components from water using membrane contactors in the vacuum sweep mode. More specifically, Mandowara and Bhattacharya [10] have also performed a mathematical analysis on the removal of ammonia from water using a membrane contactor in the gas-liquid mode operation, while Agrahari *et al.* [11] performed an experimental study of H₂S extraction from an aqueous stream where the model was developed by defining the transport of a gas molecule by adsorption/desorption.

The mathematical analysis used in the present study aims at improving the modeling of the contactor system by considering radial and axial diffusion mechanisms, convection on the lumen side, and mass transfer across the porous membrane. The Knudsen and bulk diffusion mechanisms are assumed to represent mass transfer in the membrane pores. This model predicts results that are in better agreement with the experimental data than any previous mathematical analysis.

II. MODEL DESCRIPTION

A schematic of hollow fiber membrane contactor is shown

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in Fig. 1, which describes the flow pattern and various mass transfer steps taking place in the contactor system. Synthetic wastewater feed is passed through the lumen side of the contactor at a particular flow rate, while monoethanolamine is passed through the shell side in the counter flow direction. Both streams are recycled back to their respective original tanks. Gaseous molecules are desorbed from the lumen side to the shell side. Here they are assumed to instantaneously react with monoethanolamine as the latter is considered to be at a high concentration in the extract phase.

A. Assumptions

The mathematical model for the system makes the following assumptions:

- 1) Physical and transport conditions for the feed solution remain unchanged as the solution is dilute.
- 2) Isothermal operating conditions.
- 3) No wetting or swelling in the membrane, and pores are filled with air.
- 4) A Fully developed parabolic velocity profile is assumed on the lumen side. The operational experimental conditions for flow on the lumen side are chosen to be at very small Reynolds number.
- 5) The pH of the feed solution is controlled so that the gas remains in the molecular form.
- 6) The respective volumes of the feed and extract used in the process are very large in comparison to the volume of the membrane contactor.
- 7) An instantaneous reaction is assumed to occur on the shell side as the extract phase is highly concentrated.

B. Governing Equations on the Lumen Side

Transport of gas on the lumen side can be expressed by the unsteady-state convective-diffusive equation, which accounts for diffusion components in both the radial and axial directions and convection in the axial direction:

$$\frac{\partial C_l}{\partial t} + v_z \frac{\partial C_l}{\partial z} = D_l \left(\frac{1}{r} \frac{\partial}{\partial r} \left(\frac{\partial C_l}{\partial r} \right) + \frac{\partial^2 C_l}{\partial z^2} \right) \quad (1)$$

Here, C_l is the concentration of gas, and D_l denotes the diffusivity of the gas in the aqueous feed solution. A fully developed parabolic velocity profile for laminar flow condition has been assumed on the lumen side of the contactor; therefore, v_z can be defined as [12]:

$$v_z(r) = 2\bar{V} \left[1 - \left(\frac{r}{r_l} \right)^2 \right] \quad (2)$$

Here, r_l is the inner radius of the fiber, and \bar{V} is the average velocity of the fluid flowing on the lumen side that can be defined as:

$$\bar{V} = \frac{Q}{N\pi r_l^2} \quad (3)$$

The Feed flow rate and the number of fibers in the membrane contactor are denoted by Q and N , respectively.

C. Initial Condition (at $t = 0$)

For all values of r and z , i.e., $0 < r < r_l$ and $0 < z < L$:

$$C_l = C_{o,in} \quad (4)$$

$C_{o,in}$ is the initial concentration of gas in the feed solution.

D. Boundary Conditions

At $r = 0$, for all values of t and z , an axial symmetry condition can be applied:

$$\left(\frac{\partial C_l}{\partial r} \right)_{r=0} = 0 \quad (5)$$

At $z = 0$, for all values of r and t :

$$C_l = C_{tank}(t) \quad (6)$$

For $z = L$, for all values of r and t , it is assumed that diffusion of the gaseous species in the axial direction, at the outlet of the lumen side, becomes negligible in comparison to the bulk convection flow:

$$D_l \left(\frac{\partial^2 C_l}{\partial z^2} \right) = 0 \quad (7)$$

At $r = r_l$, for all values of z and t , the flux of the gas in the aqueous phase is equal to the flux of the gas diffusing through the pore [10]:

$$D_l \frac{\partial C_l}{\partial r} \Big|_{r=r_l} = k_{g,pore} \left(\frac{p_{int}^g - p_b^g}{RT} \right) \quad (8)$$

According to our assumption that instantaneous reaction occurs on the shell side (i.e. $p_b^g = 0$), the above equation reduces to:

$$D_l \frac{\partial C_l}{\partial r} \Big|_{r=r_l} = k_{g,pore} \left(\frac{p_{int}^g}{RT} \right) \quad (9)$$

At $r = r_l$, Henry's law can be applied (at the liquid-gas interface) [13]:

$$p_{int}^g = H_a C_{l,int} \quad (10)$$

Now, the mass transfer coefficient inside the pore can be estimated by using following equation [10]:

$$k_{g,pore} = D_{c,pore} \left(\frac{\varepsilon}{\tau b} \right) \quad (11)$$

Here, τ , ε , b , and $D_{c,pore}$ denote the tortuosity of the pore, porosity of the membrane, thickness of the membrane, and combined diffusivity, respectively. As discussed earlier, the pores of the hydrophobic membrane are filled by air, and the transfer of gas can occur by either Knudsen flow or bulk diffusion, depending upon the ratio of the pore radius to the mean free path across the pore. In this study, we have assumed that both flows coexist; hence combined diffusivity can be obtained from the following correlation [13]:

$$\frac{1}{D_{c,pore}} = \frac{1}{D_{k,pore}} + \frac{1}{D_{air}} \quad (12)$$

Here, $D_{k,pore}$ is the Knudsen diffusivity and can be defined as:

$$D_{k,pore} = 4850d_{pore} \sqrt{\frac{T}{M_w}} \quad (13) \quad \text{The units of } D_{k,pore} \text{ are } \text{cm}^2 \cdot \text{s}^{-1}.$$

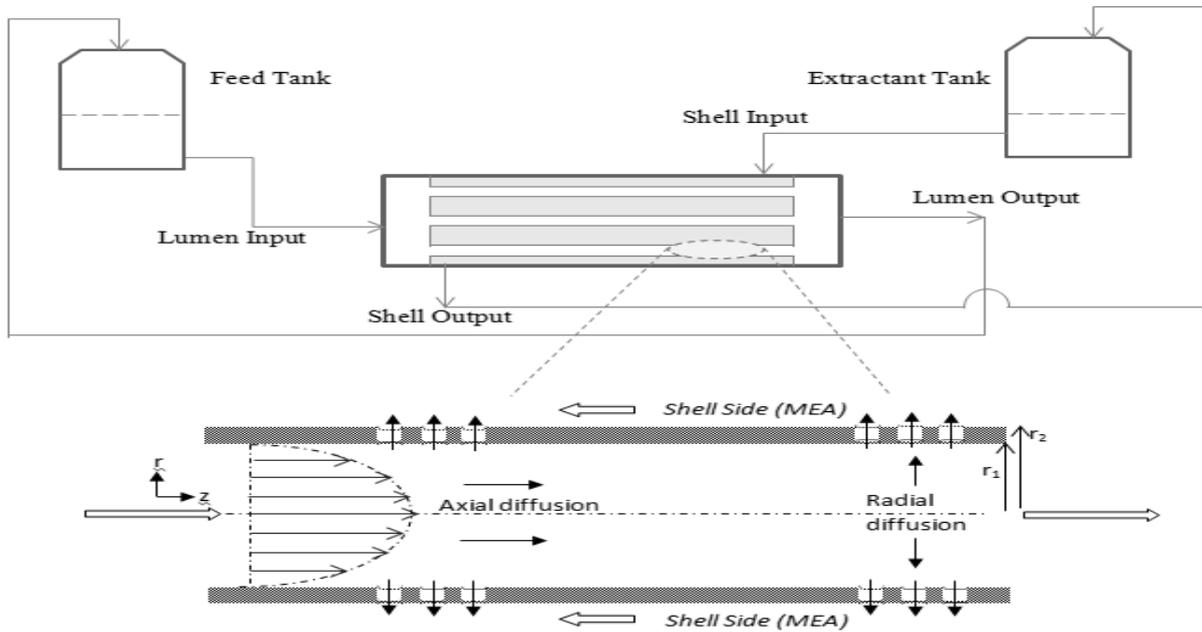


Fig. 1. Schematic representation of the process and various transport steps in the fiber module.

A. Mass Balance across Feed Tank

During the experiment, an aqueous feed solution is continuously recycled, and uniform mixing in the tank is assumed. The mass balance equation across the tank can be written as:

$$V \frac{dC_{l,tank}}{dt} = Q(C_{l,z=1} - C_{l,tank}) \quad (14)$$

Here, $C_{l,tank}$ and $C_{l,z=1}$ denote the concentrations of gas in the tank and at the exit of the membrane contactor, respectively. Q is the flow rate of feed solution, and V is the volume of the aqueous solution.

The initial condition for $C_{l,tank}$ can be written as:

$$\text{For } t = 0; C_{l,tank} = C_0 \quad (15)$$

TABLE I: PHYSICAL PARAMETERS FOR H₂S AT 298K

Properties	Values
Diffusivity in water, D_l (cm ² /s)	1.88×10^{-5}
Diffusivity in air, D_{air} (cm ² /s)	0.15
Molecular weight of H ₂ S, M_w (g/mol)	34.08

TABLE II: SPECIFICATION OF LIQUI-CEL[®] MODULE

Parameters	Values
Porosity, ϵ	0.4
Tortuosity factor for pore, τ	2.54
Inner diameter of fiber, d_i (mm)	0.24
Outer diameter of fiber, d_o (mm)	0.3
Effective fiber length, L (m)	0.16
Total number of fibers in contactor, N	10,200
Pore diameter, d_{pore} (nm)	30
Thickness of membrane, b (μm)	60
Contact area, (m ²)	1.4

B. Values of Parameters

In this study, for modeling purposes, we have used the physical parameter values of H₂S to represent the acidic gas, which are given in Table I. The contactor parameters used in this analysis are also described in Table II.

III. RESULTS AND DISCUSSIONS

A. Comparison between Experimental Results [11] and Simulated Results

Agrahari *et al.* [11] obtained experimental results for the removal of H₂S from aqueous feed using Liqui-Cel[®] hollow fiber membrane contactor. In this study, the parameters of the same membrane contactor are used for solving the model. Fig. 2 compares the experimental and simulated results for the concentration variation and fractional removal of gas from the aqueous feed solution.

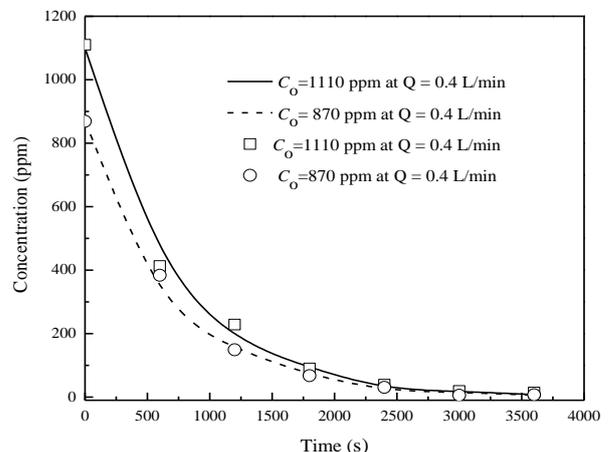


Fig. 2. Simulated and experimental results for variation in concentration of gas in aqueous feed solution with time

B. Influence of Feed Flow Rate on Concentration of Gas on Lumen Side

Fig. 3 depicts the effect of increasing the feed flow rate on concentration variation with time. It can be observed from Fig. 3 that the rate of gas removal increases as the feed flow rate increases. This is evident because the increased convection on the lumen side leads to a lower viscous membrane resistance.

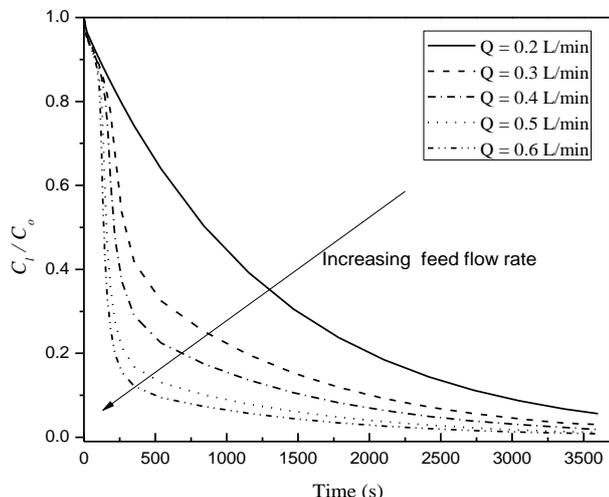


Fig. 3. Variation in fractional residual concentration of solution with $C_0=1100$ ppm with time for different feed flow rates

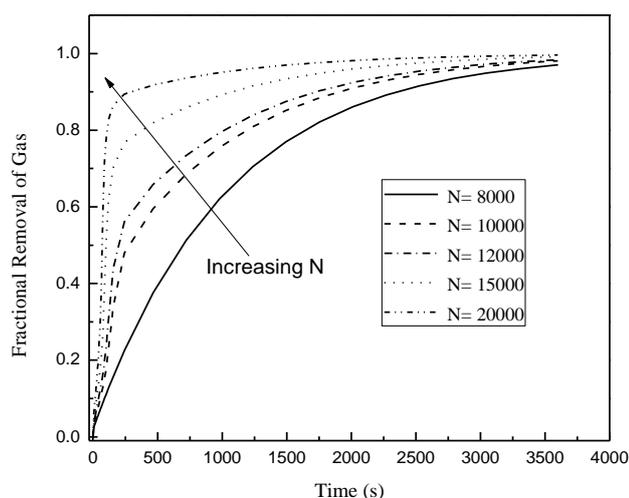


Fig. 4. Variation in fractional removal of gas with $C_0=1100$ ppm $Q=0.4$ L/min with time for different values of numbers of fibers

C. Effect of Membrane Contactor Variables on Fractional Removal of Gas over Time

1) Number of fiber in contactor

Fig. 4 illustrates the effect of the number of fibers on the fractional removal of gas, with the number of fibers ranging from 8,000 to 20,000. It can be seen from the graph that the removal efficiency increases as the number of fibers increases. This is because the area of the porous membrane available for desorption also increases with an increase in the number of fibers.

2) Effective lengths of fibers in contactor

Fig. 5 depicts the effect of varying the lengths of fibers on the fractional removal of gas. It is observed that the gas removal becomes faster as length increases, because the area,

from which the radial diffusion can occur, also increases for longer tubes. Further, above a certain value of L, not much variation is observed because of the dilution of the feed solution.

D. Variation in Concentration over Time at Different Axial Points

Fig. 6 illustrates the variation in gas concentration over time at different points across the length of the lumen side.

As expected, the concentration of gas at the same time across the length of the lumen side is observed to be decreasing. This is because of the radial diffusion and subsequent transfer of gas molecules to the shell side between the two axial points.

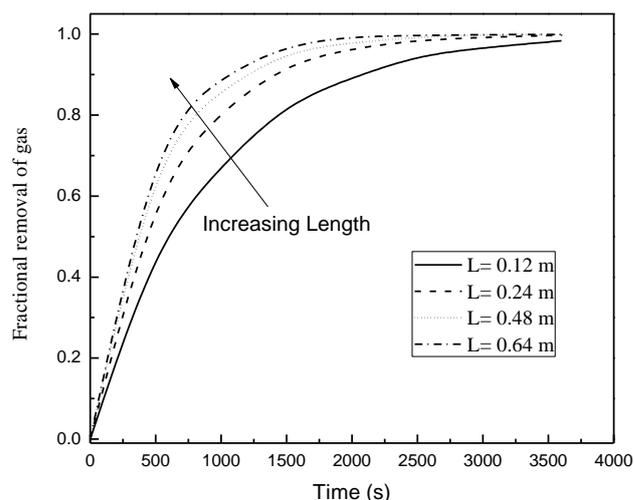


Fig. 5. Variation in fractional removal of gas with $C_0=1100$ ppm $Q=0.4$ L/min with time for different length of lumen fibers

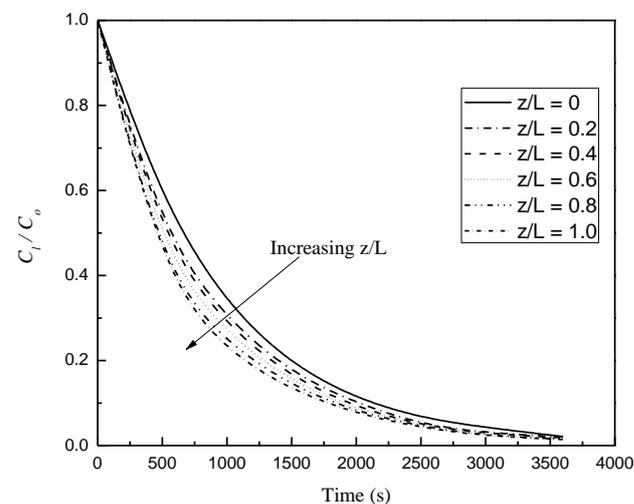


Fig. 6. Variation in fractional residual gas concentration with $C_0=1100$ and ppm $Q=0.4$ L/min with time for different points in axial direction

IV. CONCLUSION

Degasification of water using a membrane contactor has been successfully analyzed, and the obtained results show an excellent agreement with the available experimental results. Further, the variation in the gas concentration in the aqueous feed solution over time has been obtained for different operating conditions such as feed flow rate and initial concentration. The effects of various parameters of the membrane contactor on the fractional removal of gas have

also been discussed. In particular, it has been found that the degasification efficiency of the contactor increases with increase in the number of fibers and with the length of the lumen side.

NOTATIONS

- C_o Initial feed concentration (moles/m³)
 C_l Gas concentration on lumen side (moles/m³)
 $C_{b,tank}$ Gas concentration in the tank (moles/m³)
 d_{pore} Diameter of pore (m)
 $D_{c,pore}$ Combined diffusion coefficient (m²/s)
 D_l Diffusion coefficient of gas in water (m²/s)
 $D_{k,pore}$ Knudsen diffusion coefficient of gas (m²/s)
 D_{air} Diffusion coefficient of gas in air (m²/s)
 H_a Henry's law constant (Pa.m³/mol)
 L Length of fiber (m)
 M_w Molecular weight of gas (kg/mol)
 N Number of fibers in the Contactor module
 p_{int}^g Partial pressure of gas at $r = r_1$ (Pa)
 p_b^g Partial pressure of gas at $r = r_2$ (Pa)
 Q Feed flow rate (m³/s)
 r Radial distance from the lumen-axis (m)
 r_1 Inner radius of the lumen (m)
 r_2 Outer radius of fiber (m)
 R Universal gas constant (J/(mol.K))
 z Axial length (m)
 t Time (s)
 t_0 Initial time (s)
 T Temperature (K)
 v_z Axial velocity on the lumen side (m/s)
 V Volume of feed solution in the tank (m³)
 ε Porosity
 τ Tortuosity factor for pore
 \bar{V} Average velocity on the lumen side (m/s)

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