Journal of Membrane Science 355 (2010) 18–27

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Simulations of solute concentration profile and mass transfer behavior near the membrane surface with finite volume method

Weidong Zhang*, Jiang Li, Geng Chen, Wei You, Zhongqi Ren*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 100029 Beijing, People's Republic of China

ARTICLE INFO

Article history:
Received 8 November 2009
Received in revised form 16 February 2010
Accepted 28 February 2010
Available online 6 March 2010

Keywords:
Gas absorption
Mass transfer
Mathematical model
Porous membrane
Porosity

ABSTRACT

Membrane gas absorption technique is one of the most attractive alternatives for CO_2 capture. In this paper, a mathematical model for membrane gas absorption process has been developed to describe the solute concentration profile and the mass transfer behavior near the membrane surface, which are important factors for the process. The finite volume method is used to solve the model. The modeling results show that the different solute diffusing distances in the vertical and parallel directions near the membrane surface result in varied concentration profiles. For the membrane with small pore size, the solute concentration profile near the membrane surface can reach uniform distribution instantly, and the membrane porosity has little effect on mass transfer. Contrarily, for the membrane with large pore size, especially at higher absorbent pH value or liquid velocity, the solute concentration distribution is comparatively non-uniform. The mass transfer is significantly affected by membrane porosity. That is the mass transfer coefficients are varied at different membrane porosities. Experiments are conducted to verify the model for CO_2 removal using flat sheet membrane contactor with de-ionized water or NaOH solution as absorbents. The comparison between the experimental results and the prediction results shows that the model is validated.

1. Introduction

Carbon dioxide (CO_2) has been considered as the top criminal for the greenhouse effect [1]. Among various technologies for CO_2 capture, membrane gas absorption technology has been identified as one of the most promising alternatives for CO_2 capture by the International Energy Agency in 1990s [2]. Qi and Cussler [3,4] first proposed membrane gas absorption technology in 1985. It can not only effectively overcome the conflict between selectivity and flux in membrane process, but also eliminate the drawbacks associated with conventional absorption such as flooding, foaming, and entrainment [5]. Since then, large numbers of researches have been done on the membrane gas absorption technology, focusing on mass transfer mechanism [6–8], various absorbents [9–12], design of membrane contactors [13,14] and so on.

In most studies on the membrane gas absorption processes, *resistance-in-series* model is used to describe the mass transfer process, in which the overall mass transfer resistance is assumed to consist of three partial resistances: the liquid phase resistance, the membrane resistance and the gas phase resistance. In most of the studies on membrane gas absorption, membrane porosity is merely considered to have the influence on the membrane phase mass transfer resistance [15–20]. Little attention has been given to the effect of the membrane porosity on mass transfer in the gas or liquid phase, and the concerned viewpoints somehow remain confused.

Kreulen et al. [21] absorbed pure CO_2 with water in hollow fiber modules. Membranes with porosities 70% and 3% were employed, and it was found that porosity had no effect on mass transfer in the liquid phase. The total membrane area can be taken as effective mass transfer area. However, Rangwala et al. [22] absorbed CO_2 in a hollow fiber contactor, and elicited that the effective mass transfer area was between the overall pore area and total membrane surface. Evren et al. [19] studied the mass transfer process when pure O_2 was absorbed into water, and they took the effect of membrane porosity into account in the model to describe the mass transfer in the liquid phase. It was pointed out that the solute in the gas phase transferred to the absorbent and diffused above the pores, but only diffusion occurred above the polymeric body. However, only one type of membrane with a porosity of 38% was used in their experiment. Moreover, some parameters were obtained by model fitting from experimental data, and the mechanism of the effect of the membrane porosity on mass transfer process was not presented in that work.

In our previous study [23], pure CO_2 gas was absorbed through flat membranes with different porosities. The overall mass transfer

---

* Corresponding authors at: PO Box 1#, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China. Tel.: +86 10 6442 3628; fax: +86 10 6443 6781.
E-mail addresses: zhangwd@mail.buct.edu.cn (W. Zhang), renzq@mail.buct.edu.cn (Z. Ren).

0376-7388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2010.02.071

resistance was controlled by the mass transfer in the liquid phase. When absorption processes were operated under the same conditions such as gas pressure, membrane area, absorbent pH value and velocity, different absorption rates were observed for CO_2/NaOH aqueous solution system as the membrane porosity varied. This proved that the membrane porosity could affect the mass transfer performance in the liquid phase. A mathematical model based on the advancing front model was developed to analyze the influence of the porosity in the membrane gas absorption process [24]. However, only the model for unsteady-state absorption has been developed, the steady-state absorption process has not been considered, which has more applications than the unsteady-state absorption process. So the applicability of the model based on advancing front model is limited.

In some other mass transfer processes beyond the membrane gas absorption process, some researchers investigated the effect of the membrane porosity on the mass transfer performance. Keller and Stein [25] studied the effect of membrane structure characteristics on the mass transfer flux, in a system where a species diffuses through a stagnant boundary layer and into a single isolated membrane pore. Their results indicated that the ratio of the distance between adjacent pores to the pore diameter (a parameter related to the membrane porosity) has a large effect on the mass transfer flux. Malone and Anderson [26] studied the diffusional mass transfer across membranes with uniform but low porosities (<10%) in a diaphragm cell of conventional design and measured the overall mass transfer coefficients. The results showed that the membrane porosity has a great effect on the overall mass transfer coefficient, and the effect of the membrane porosity on mass transfer becomes large with the increasing stirrer speed. However, the processes mentioned above are different from the membrane gas absorption process, in which process, the liquid phase in the membrane contactor is not stagnant and the mass transfer rate would be enhanced by chemical reaction when the chemical absorbent is used. Therefore, the effect of the membrane porosity on mass transfer becomes more complicated in the membrane absorption process than in the above mass transfer processes, and the effect of the fluid flow rate and the chemical reaction enhancement in the liquid phase should be taken into account.

In membrane gas absorption processes, the porous membranes can be treated as impermeable barriers penetrated with discrete pores. The solute from gas phase can only diffuse through the membrane pores into the liquid phase; however, it cannot diffuse through the membrane body into the absorbent. Therefore, the existence of the porous membrane has a significant influence on the solute concentration profile near the membrane surface. It is necessary to figure out the concentration profile near the membrane surface at different experimental conditions for the investigation of the effect of porosity on mass transfer in membrane gas absorption process.

In this work, a mathematical model is developed to describe the influence of the membrane porosity on mass transfer near the membrane surface in the steady-state absorption process. It is found that the existence of the porous membrane can affect the solute concentration profile near the membrane surface, and furthermore, affect the mass transfer performance. According to the solute diffusing distances in the vertical and parallel directions near the membrane surface, the effect of the membrane porosity can be determined.

2. Theory

A mathematical model is developed to analyze the effect of membrane porosity on mass transfer near the membrane surface. In order to eliminate the influence of mass transfer resistances in the gas and membrane phase, pure gas with constant pressure is used. In this case, mass transfer resistances in the gas and membrane phase can be neglected. The overall mass transfer resistance is controlled by the mass transfer in the liquid phase.

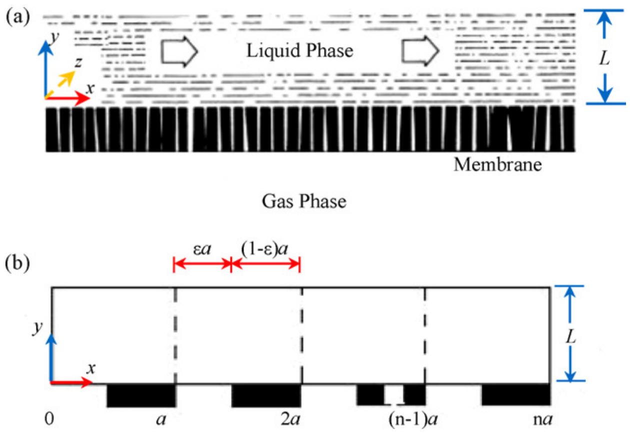

Fig. 1. Schematic representation of the membrane structure.

2.1. Model development

Pure CO_2 is absorbed by NaOH aqueous solution (chemical reaction absorption) or de-ionized water (physical absorption). Flat membranes are employed to minimize the influence of the non-ideal flow on the shell side of the hollow fiber module. Because of the strong hydrophobic property of the membranes, it can be assumed that the micro-pores in the membranes are not wetted under an appropriate gas pressure. So the mass transfer resistance in the gas phase or the membrane pores can be neglected. The CO_2 concentration at the gas–liquid interface is presumed to follow the Henry's law $c^* = p \times H$.

In general, micro-pores, distributed on the membrane, exhibit non-uniform sizes and shapes as shown in Fig. 1(a). The liquid phase flows along the x direction. To simplify the model, the structure of micro-porous membranes can be assumed as repeats of one pore and one polymeric body with invariant size, which is shown in Fig. 1(b). Under this assumption, any section in the z direction has the same concentration or velocity profile.

In the x direction in the liquid phase, solute diffusion can be neglected compared with the mass transfer in convection. It is assumed that the liquid flows through the membrane contactor with a fully developed laminar parabolic velocity profile, and the local velocity u_x is described as following:

$$u_x = 6u_{av}\left(\frac{y}{L} - \frac{y^2}{L^2}\right) \tag{1}$$

where u_{av} is the average velocity and L is the thickness of the liquid phase.

2.1.1. Mass transfer with chemical reaction

The reaction mechanism between CO_2 and OH^- can be represented as two steps:

$$CO_2 + OH^- \xrightarrow{k_1} HCO_3{}^- \tag{2}$$

$$HCO_3{}^- + OH^- \xrightarrow{k_2} CO_3{}^{2-} + H_2O \tag{3}$$

The reaction rate between CO_2 and OH^- can be calculated by Eq. (4) and (5):

$$R_A = -k_1 C_A C_B \tag{4}$$

$$R_B = -k_1 C_A C_B - k_2 C_B C_C \tag{5}$$