SO₂ Emissions Removal in a Hollow Fiber Membrane Contactor

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Abstract

SO₂ is the component of greatest concern and is used as an indicator for the larger group of gaseous sulfur oxides (SOₓ) which should be reduced in the air. In this paper, DMA (Dimethylamine) solution was used as absorbent under the conditions of 0.1 L min⁻¹ gas velocity, 0.1 L min⁻¹ liquid velocity, and 290 K operating temperature. The effects of gas and liquid phase properties and module configuration on SO₂ absorption efficiency in the α-Al₂O₃ hollow fiber membrane contactor were investigated. Simulation results show that the changes of gas phase velocity, liquid phase velocity, concentration have great influences on the absorption efficiency of SO₂. Gas and liquid phase flow rate decreases and increases SO₂ absorption efficiency, respectively. Because gas in the membrane module stays for a longer time, more absorption time promotes the gas and liquid reaction. However, the changes of the liquid velocity and the volume fraction of SO₂ in the mixed gas are not significant to SO₂ absorption. In addition, the fluid in the turbulent state provides better SO₂ absorption efficiency than that in the laminar condition.

Keywords: SO₂ emission; air pollution; membrane; dimethylamine

1. Introduction

Currently, fossil fuels (coal, oil, and natural gas) are the primary energy sources throughout the world. As a result, fuel combustion will continue to emit sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) at an astonishing annual rate. In addition, SO₂ emissions lead to acid rain, air pollution, urban smog, and harm to human health and ecosystems (Bokotiko et al., 2005; Rahmani et al., 2015). Thus, it is very urgent to removal SO₂ from air. Currently, there are several common methods for SO₂ removal, i.e., wet scrubbing (Jin et al., 2006), dry scrubbing (Neatherby 1996), and wet sulfuric acid process (Kikkawa et al., 2002). But there are some shortcomings using these approaches, i.e., foaming, entrainment, flooding, and channeling issues, and a large required space. Membrane gas absorption (MGA) is an effective way for SO₂ removal providing a large gas and liquid contact surface using a hollow fiber membrane contactor with a high packing density. In addition, the membrane only acts as a fixed interface while gases transfer takes place across the membrane. Gas and liquid can be operated separately using the contactor (Park et al., 2007). The MGA method was first used for gas absorption in 1985 by Qi and Cussler (1985). The gas and liquid system were operated without flooding problems even at high gas flow rates. This was due to the indirect contact between gas and liquid. CO₂ capture using MGA method has been a popular topic and widely investigated (Zhang et al., 2014, 2014a; Hoff et al., 2004). However, there were much fewer publications reported on the membrane absorption process of SO₂ (Luis et al., 2010; Yu et al., 2016). Karoor and Sirkar (1993) carried out SO₂ absorption experiments in pure water in a packed tower and a hollow fiber contactor. They found that efficient contacting was achieved in the case of a hollow fiber membrane contactor when compared to conventional reactors. In addition, the K_a value using MGA was around 10 times higher than that using conventional methods. Park et al. (2008) performed a series of SO₂ absorption experiments in a polyvinylidenefluoride (PVDF) hollow fiber membrane. A variety of chemicals including NaOH, Na₂CO₃, NaOH and NaHCO₃ were compared regarding the SO₂ absorption performance. It was proved that the Na₂CO₃ solution showed the best performance for SO₂ absorption. Most previous studies have focused on experimental research and a few modeling works have been conducted (Fasih et al., 2012; Luis et al., 2010; Yu et al., 2016). In our previous work (Zhang et al., 2015), the effects of membrane and contactor geometry parameters on SO₂ absorption performance were studied theoretically. The proposed model could provide guidelines for selecting the optimum contactor parameters. The purpose of this current work is to focus on the fluid properties and module configuration influences on SO₂ absorption efficiency in a hollow fiber membrane. The governing equations for material balances in three sections, i.e., the tube, membrane, and shell sides, were calculated and solved with the given boundary conditioning.

2. Physical Model

Figure 1 shows a physical model of SO₂ absorption inside a hollow fiber membrane contactor. A mixed gas containing SO₂ and air entered into the module and reacted with the absorbent of DMA. The mixed gas flowed out of the hollow fibers (shell side), and the absorbent flowed on
the other side of the membrane contactor (tube side). Meanwhile, SO$_2$ was absorbed into the absorbent in the tube side to complete the desulfurization after mixed gas entered into the fibers. When gas and liquid were operated under the ideal conditions, the model could be simplified to the process of a hollow fiber absorbing SO$_2$.

3. **Numerical Model**

In this case, some assumptions are made to simplify the mass continuity equations for calculating the developed model: The liquid phase in the tube is a steady flowing fluid under the constant temperature condition, with stable physical properties, and the liquid velocity distribution in the tube is characterised by a parabolic curve; The effect of the axial diffusion and radial convective mass transfer is neglected; The gas in the shell side is an ideal gas, and the fluid inside the tube is a Newtonian-type fluid. They have stable physical properties; both the velocity distribution and the concentration distribution in the tube are axisymmetric; The solute at the gas-liquid phase contact surface follows Henry’s law. The parameters of hollow fiber membrane contactor in this paper are presented in Table 1. The finite element method using COMSOL Multiphysics software was applied in the numerical solution of the control equations in the developed model. The numerical solver UMFPACK is mainly used in solving the nonlinear, rigid and stiff boundary, which is also a good two-dimensional model numerical solver. The computer configuration of numerical simulation is a 64-bit operating system, with a 4.00GB memory space and Inter core AMD A8-4500M APU. Furthermore, Table 2 presents the physical and chemical property parameters of SO$_2$ as well as liquid absorbent, and reactive kinetic parameters between two phases. The software generates a series of isotropic triangular grid with a triangle smallest unit and creates cells according to a certain proportion. There are 24156 grids in this figure. Meanwhile, the area with dense meshes means large changes in the fluid concentration. This is due to that the absorbent inside the membrane contactor reacting with SO$_2$.

**Figure 1.** The internal structure of Hollow Fiber Membrane absorbing SO$_2$

| Table 1. Parameters of hollow fiber membrane contactor (Luis et al., 2008) |
|---------------------------------|---------------------|--------------------------|
| Parameter                       | Symbol              | Value |
| Fiber materials                 | $\alpha$-Al$_2$O$_3$|        |
| Canning material                | 316 stainless steel |        |
| Packing material                | epoxide resin       |        |
| Fiber outside diameter (μm)     | $d_o$               | 4000   |
| Fiber inside diameter (μm)      | $d_i$               | 3000   |
| Fiber length (m)                | L                   | 0.44   |
| Fiber number                    | n                   | 280    |
| Effective membrane contact area (m$^2$) | S              | 0.8    |
| Fiber pore size (nm)            | $d_p$               | 100    |

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<th>Table 2. Parameters of hollow fiber membrane contactor</th>
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<tr>
<td>Name</td>
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<tr>
<td>Henry’s coefficient between SO$_2$ and water</td>
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<td>Diffusion coefficient between SO$_2$ and water</td>
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<td>Henry’s coefficient between SO$_2$ and DMA solution</td>
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<tr>
<td>Diffusion coefficient between SO$_2$ and DMA solution</td>
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<td>SO$_2$ diffusion coefficient in the gas mixture</td>
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4. Results and discussions

4.1. Concentration distributions

It is an effective way to describe visually the SO$_2$ concentration distribution inside the membrane contactor with three-dimensional concentration schematic. Figure 2 (a-f) shows the SO$_2$ three-dimensional concentration schematic inside the membrane contactor when reacting with 2 mol L$^{-1}$ DMA solution at various gas velocities, respectively. As observed, the SO$_2$ concentration in the shell side of the membrane contactor gradually decreases from 2.0 to 1.06, 1.23, 1.35, 1.43, 1.48, and 1.53 mol L$^{-1}$. It is obvious that SO$_2$ in the mixed gas reacts continually with the DMA solutions, resulting in the continuous decrease in SO$_2$ contributes at the exit of the shell side. According to Figure 3, the SO$_2$ concentration increases from z=0 to z=L. This was due to the DMA solution absorbed SO$_2$ in the tube, and then the SO$_2$ concentration at the exit of tube reached to the highest value. Due to the concentration gradient of SO$_2$ between the tube and membrane sides, SO$_2$ concentration gradually reduced from the interface between the tube and membrane sides to the central axis of the membrane contactor.

4.2. Effect of the gas flow velocity (model verification)

Figure 4 demonstrates the comparison between the simulation results of SO$_2$ removal efficiency and the experimental data at different gas velocities. It can be seen from this figure that when the gas velocity increased from 0.0006 to 0.0035 m s$^{-1}$, SO$_2$ removal efficiency decreased from 46.82 to 23.5%. The reason was that when the velocity of gas phase increased, the gas and liquid reaction time reduced significantly, which led to inadequate reacting in the absorption process and affected the SO$_2$ removal efficiency. Although the SO$_2$ removal efficiency was high with a low gas velocity, the mass transfer effect of the whole process was relatively poor. The conclusion in literature (Eslami et al., 2011) had a similar result trend. Thus, it was necessary to consider comprehensively the influence of the gas velocity on the removal efficiency and the mass transfer rate of SO$_2$ while selecting the optimal gas velocity condition of the whole system.

Figure 2. The three-dimensional concentration distribution of SO$_2$ reacting with DMA in the shell side (mixed gas of 5% SO$_2$ and air, the liquid phase flow rate is 1 L min$^{-1}$, the operating temperature is 290 K. $V_g$ represents the gas phase flow velocity, a: $V_g$=0.0006 m s$^{-1}$; b: $V_g$=0.0008 m s$^{-1}$; c: $V_g$=0.0012 m s$^{-1}$ ; d: $V_g$=0.0023 m s$^{-1}$; e: $V_g$=0.0029 m s$^{-1}$; and f: $V_g$=0.0035 m s$^{-1}$).
Figure 3. The three-dimensional concentration distribution diagram of the SO$_2$ concentration in tube side (mixed gas of 5% SO$_2$ and air, the gas phase flow rate is 0.1 L min$^{-1}$, the liquid phase flow rate is 1 L min$^{-1}$, the operating temperature is 290 K).

Figure 4. Effect of the gas phase velocity on SO$_2$ absorption efficiency (mixed gas of 5% SO$_2$ and air, the liquid phase flow rate is 1 L min$^{-1}$, the operating temperature is 290K).

5. Conclusions
In allusion to atmospheric pollution aggravating, this paper mainly focused on the absorption problems of SO$_2$. A promising method of membrane technology has been used in this paper. The effect of the gas and liquid phases properties and module configuration on SO$_2$ absorption was investigated numerically. In this study, the three-dimensional distribution of SO$_2$ concentration in the hollow fiber membrane contactor was observed visually by applying COMSOL Multiphysics. The distribution of SO$_2$ concentration was shown intuitively with changing the gas and liquid phase parameters. Then, the model validation was carried out between the experimental data and the simulation results at different gas flow velocities and showed that the developed model was feasible and reliable. In all, this model could efficiently predict the influence of the gas and liquid parameters and module configuration on SO$_2$ absorption, which could optimize the system data and provide guidelines for the operation of the actual application in the future.

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