Ozone mass transfer behaviors on physical and chemical absorption for hollow fiber membrane contactors

Yong Zhang, Kuiling Li, Jun Wang, Deyin Hou and Huijuan Liu

ABSTRACT

To understand the mass transfer behaviors in hollow fiber membrane contactors, ozone fluxes affected by various conditions and membranes were investigated. For physical absorption, mass transfer rate increased with liquid velocity and the ozone concentration in the gas. Gas flow rate was little affected when the velocity was larger than the critical value, which was $6.1 \times 10^{-3}$ m/s in this study. For chemical absorption, the flux was determined by the reaction rate between ozone and the absorbent. Therefore, concentration, species, and pH affected the mass transfer process markedly. For different absorbents, the order of mass transfer rate was the same as the reaction rate constant, which was phenol, sodium nitrite, hydrogen peroxide, and oxalate. Five hydrophobic membranes with various properties were employed and the mass transfer behavior can be described by the Graetz–Lévêque equation for the physical absorption process. The results showed the process was controlled by liquid film and the gas phase conditions, and membrane properties did not affect the ozone flux. For the chemical absorption, gas film, membrane and liquid film affected the mass transfer together, and none of them were negligible.

Key words | bubbleless, chemical absorption, hydrophobic membrane, membrane contactor, ozone, physical absorption

INTRODUCTION

Ozone is a powerful oxidant, which is widely considered for environmental applications. In water and wastewater treatments, ozone is applied in a wide range of processes, including disinfection, decoloration, organics degradation and mineralization, inorganics oxidation, and so on (Gottschalk et al. 2000; Beltrán 2004). The ozone utilization efficiency and water/wastewater treatment efficiency are dramatically affected by the mass transfer process. Conventionally, ozone is diffused into water through bubble columns, stirred tank reactors, packed towers, or tube reactors (Gottschalk et al. 2000). These reactors are practical and economic for ozone mass transfer. However, severe problems may hinder the applications; for instance, flooding, emulsion, unloading, and foaming (Gabelman & Hwang 1999). Moreover, the reactors are large and the non-reacted gas must be treated.

Membrane contactors can be an excellent alternative instead of the traditional one. In the contactor, gas and liquid are separated by a hydrophobic membrane. Under the driving force of the concentration differential, the gas diffuses through the membrane and then dissolves into the liquid. Therefore, the mass transfer process is bubbleless and the disadvantages that occur in traditional contactors, such as foaming and flooding, can be avoided. Additionally, high volumetric mass transfer efficiency can be achieved as the specific surface area is rather large, especially in a hollow fiber membrane contactor. Thus, the size of the contactor can be smaller compared to the traditional one (Gabelman & Hwang 1999; Gottschalk et al. 2000). Due to these unique advantages, it is widely applied for CO$_2$ and SO$_2$ capture (Luis et al. 2010), ammonia and phenol removal, and so on. As for the ozone membrane contactors, the application for ozonated water production has been popular in the semiconductor industry (Gottschalk et al. 2000). Meanwhile, the environmental applications for ozonation of natural organic matters,
humic substances, phenols, iodides, and dyes were concerning researchers too (Shanbhag et al. 1995; Jansen et al. 2005; Leiknes et al. 2005; Atchariyawut et al. 2009; Wenten et al. 2012).

Mass transfer behavior, which is pivotal for membrane contactor optimization, is one of the most important issues of the membrane contactor studies. Shen et al. (1990) investigated a polypropylene hollow fiber membrane contactor for physical absorption, and the liquid velocity was considered to be a crucial parameter. Pines et al. (2003) investigated the effect of membrane parameters for physical absorption, and showed membrane thickness, porosity and pore size had little effect on ozone flux (Pines et al. 2003). Although there has been research on mass transfer behaviors, some issues need further study, including the influence of feed solution characteristics and membrane properties for chemical absorption, the difference between physical and chemical absorption, the importance of gas flow rate, and so on. In this study, systematic research into both physical and chemical absorption processes was undertaken for various conditions and membranes; and the resistance-in-series model was also employed to clarify the principles.

THEORIES

In an ozone membrane contactor, the gas and liquid phases are separated on different sides of the membrane. As shown in Figure 1, ozone diffuses from the gas to liquid bulk through the gas boundary layer, membrane, and liquid boundary layer, successively. Thus, the mass transfer process can be described by the resistance-in-series model (Equation (1)) (Kreulen et al. 1993a):

\[ R_{TOT} = R_G + R_M + R_L \]

where \( R_{TOT} \), \( R_G \), \( R_M \) and \( R_L \) are total resistance, gas boundary layer resistance, membrane resistance, and liquid boundary layer resistance, respectively.

In a hollow fiber membrane contactor, with liquid in the tube side and gas in the shell side, the resistance-in-series model can be expressed as follows (Equation (2)) (Rongwong et al. 2013, 2015):

\[ \frac{1}{K_L} = \frac{Hd_i}{k_Gd_o} + \frac{Hd_i}{k_Md_{in}} + \frac{1}{Eh_L} \]

where \( K_L \) is the overall mass transfer coefficient based on the liquid phase. \( k_G \), \( k_M \), \( k_{L} \) are individual mass transfer coefficients of the gas film, membrane, and liquid film without chemical reaction, respectively. \( d_i \), \( d_o \), \( d_{in} \) are the inner, outer, and logarithmic mean diameters of the membrane. \( H \) is the Henry's constant and \( E \) is the enhancement factor. \( E \) equals 1 for physical absorption and greater than 1 when chemical reaction takes place.

The individual mass transfer coefficients of the liquid and gas film are described by the Graetz–Lévêque equation (Equation (3)) (Gabelman & Hwang 1999) and the correlation proposed by Yang & Cussler (Equation (4)) (Yang & Cussler 1986), respectively:

\[ Sh = \frac{k_Gd_e}{D_{O_3,G}} = 1.62 \left( \frac{d_e}{Z} \frac{Re}{Sc} \right)^{1/3} = 1.62Gz^{1/3} \]
\[ Sh = \frac{k_Gd_e}{D_{O_3,L}} = 1.25 \left( \frac{d_e}{Z} \frac{Re}{Sc} \right)^{0.93} Sc^{0.33} \]

where \( Sh \), \( Re \), \( Sc \), \( Gz \) are the Sherwood, Reynolds, Schmidt, and Graetz numbers, respectively. \( D_{O_3,L}, D_{O_3,G} \) are the diffusivity of ozone in the liquid and gas streams, respectively. \( d_e \) is the equivalent diameter of the gas passage.

For hydrophobic membrane contactors, the membrane pores are assumed to be dry. However, membrane wetting can occur even if the hydraulic pressure is low, possibly due to the capillary condensation of water. Thus, the mass transfer process can be described by a partially wetted
model. Both the non-wetted and partially wetted models are presented in Figure 1.

When the membrane is dry, the individual mass transfer coefficient of membrane can be calculated by Equation (5) (Kreulen et al. 1993a; Bamperng et al. 2010):

$$k_M = \frac{D_{G,eff}\epsilon_M}{\tau_M \delta}$$

where $D_{G,eff}$ is the effective diffusion coefficient, $\delta$, $\epsilon_M$, $\tau_M$ are membrane thickness, porosity, and tortuosity, respectively.

When the membrane is partially wetted, the membrane resistance is composed of dry and wetted membrane resistances:

$$R_M = R_M^{dry} + R_M^{wetted}$$

The membrane individual mass transfer coefficients for the dry and wetted membranes are expressed as:

$$k_M^{dry} = \frac{D_{O_3,L}\epsilon_M}{\tau_M\delta_{wetted}}$$

$$k_M^{wetted} = \frac{D_{O_3,L}\epsilon_M}{\tau_M\delta_{wetted}}$$

where $R_M^{dry}$, $R_M^{wetted}$, $k_M^{dry}$, $k_M^{wetted}$, $\delta_{wetted}$, and $\delta_{dry}$ are the resistance of the dry membrane, the resistance of the wetted membrane, the mass transfer coefficient of the wetted membrane, the mass transfer coefficient of the dry membrane, the wetted membrane length, and the dry membrane length, respectively.

In addition, ozone flux can be calculated by the overall mass transfer coefficient and driving forces (Equation (9)) (Rongwong et al. 2015). The overall mass transfer coefficient can be calculated from the resistance-in-series model, which is expressed by Equations (1)–(8) for different occasions.

$$N_{O_3,a} = v_L \frac{dC_{O_3,L}}{dZ} = k_L a (C_G - C_{O_3,L})$$

where $N_{O_3}$ is the ozone flux, $C_{O_3,L}$, $C_G$, $v_L$, and $a$ are the ozone concentration of the liquid stream, the equilibrium concentration of ozone, the liquid stream velocity, and the specific surface area of the membrane, respectively.

As for physical absorption, the inlet water ozone concentration is zero and the self-decomposition is assumed to be negligible. Thus, the ozone concentration of outlet liquid stream can be calculated by the integration form (Equation (10)) of Equation (9) (Kreulen et al. 1993b):

$$C_{O_3,L} = C_G \left(1 - \exp\left(-\frac{K_L a Z}{v_L}\right)\right)$$

For chemical absorption, the mass transfer rate improves as chemical reaction occurs in the liquid phase. The enhancement factor is calculated by the following equation (Decourse 1974), where $E$, $Ha$, and $E_\infty$ are the enhancement factor, Hatta number, and infinite enhancement factor, respectively.

$$E = \frac{-Ha^2}{2(E_\infty - 1) + \sqrt{\frac{Ha^4}{4(E_\infty - 1)} + \frac{E_\infty Ha^2}{(E_\infty - 1)}}}.$$  

The Hatta number and infinite enhancement factor are defined by the following equations:

$$Ha = \sqrt{\frac{k_{A,O_3} D_{O_3,L} C_A}{k_L^L}}$$

$$E_\infty = \left(1 + \frac{D_{A,L} C_A}{v_R D_{O_3,L} C_{O_3,L}}\right)\left(D_{O_3,L} D_{A,L}\right)^{1/3}$$

where $k_{A,O_3}$, $k_L^L$, and $v_R$ are the reaction rate constant between ozone and absorbent, the liquid phase mass transfer coefficient, and the stoichiometric coefficient of ozone and absorbent, respectively. $C_A$, $C_{O_3,L}$, and $D_{A,L}$ are the absorbent concentration, the ozone concentration of the interface, and the diffusivity of the absorbent in the liquid stream, respectively.

As well, ozone solubility varies with temperature. The relationship between the Henry’s law constant and temperature can be described by the following equation (Rischbieter et al. 2000):

$$\log H = 5.12 - \frac{1230}{T}$$

where $T$ is temperature in degrees Kelvin.

**METHODS**

Six hollow fiber membranes were applied in the experiments. Membranes 1 to 4 were made from PTFE (DD...
Water Science & Technology | 76.6 | 2017

Ozone in deionized water was measured by a UV-photometric method using an ultraviolet-visible spectrophotometer (DR 5000, Hach, USA). The molar absorptivity of ozone was 3,000 M\(^{-1}\) cm\(^{-1}\) at 260 nm (Hart et al. 1983). For physical absorption, the ozone flux was determined by the concentration of water. For chemical absorption, the ozone flux was calculated by the concentrations of the inlet and outlet gas stream. The membrane structure was observed through a scanning electron microscope (SEM) (S-3000N, Hitachi, Japan). Before observation, membrane samples were dried and sputtered with platinum using a Hitachi-1010 ion sputtering a device at pressure less than 10 kPa.

RESULTS AND DISCUSSION

Mass transfer behaviors for physical absorption

To understand the physical absorption behaviors in the ozone membrane contactor, the effects of water velocity, gas ozone concentration, gas velocity, and water temperature were investigated with acidified deionized water in a PVDF hollow fiber membrane contactor (5).

As depicted in Figure 3, the ozone flux increased markedly with the liquid velocity and ozone concentration. When the water velocity increased from 0.04 to 0.67 m/s, the flux improved by 1.95 to 3.85 times for different ozone concentrations. According to Equations (2) and (3), the individual mass transfer coefficient of the liquid film (\(K_{L}^{f}\)) and the overall mass transfer coefficient (\(K_{L}\)) increased with the water velocity; therefore, the ozone flux increased. For the two-film theory (Yang & Cussler 1986; Kreulen et al. 1993a; Mavroudi et al. 2006), the liquid film resistance was caused by the boundary layer. When the velocity increases, the mixture of water at the vertical direction of the membrane surface becomes more drastic. Therefore, the thickness of the boundary layer reduces and then the mass transfer resistance decreases. When the ozone concentration increased from 10 to 100 mg/L, the flux improved by 8.32 to 18.33 times for different water velocities. As the ozone concentration increased, the driving force, which is determined by concentration differential, increased (Equation (9)); therefore, the flux increased with the ozone concentration.

For physical absorption, an efficient approach to improve the mass transfer rate is by increasing the liquid velocity or ozone concentration of the gas stream. However, the energy consumption should be considered as the pressure drop increases with the velocity. In addition, the ozone usage efficiency decreases when the ozone supply

Table 1 | Specifications of membranes and membrane modules

<table>
<thead>
<tr>
<th>Parameters</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
<th>5#</th>
<th>6#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane material</td>
<td>PTFE</td>
<td>PTFE</td>
<td>PTFE</td>
<td>PTFE</td>
<td>PVDF</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>Contact angle (°)</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>96</td>
<td>48</td>
</tr>
<tr>
<td>Outer diameter (mm)</td>
<td>2.23</td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
<td>1.40</td>
<td>3.53</td>
</tr>
<tr>
<td>Inner diameter (mm)</td>
<td>0.97</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.89</td>
<td>2.43</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.63</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.255</td>
<td>0.55</td>
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<tr>
<td>Porosity</td>
<td>0.50</td>
<td>0.50</td>
<td>0.40</td>
<td>0.30</td>
<td>0.67</td>
<td>0.33</td>
</tr>
<tr>
<td>Pore size (μm)</td>
<td>0.35</td>
<td>0.35</td>
<td>0.25</td>
<td>0.15</td>
<td>0.17</td>
<td>0.37</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>10</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Effective length (m)</td>
<td>0.155</td>
<td>0.155</td>
<td>0.155</td>
<td>0.155</td>
<td>0.155</td>
<td>0.155</td>
</tr>
<tr>
<td>Effective area (x10(^{-3}) m(^2))</td>
<td>4.72</td>
<td>6.72</td>
<td>6.72</td>
<td>6.72</td>
<td>8.66</td>
<td>2.37</td>
</tr>
</tbody>
</table>
far exceeds the demand when the gas phase ozone concentration increases. The optimization should, overall, consider the mass transfer rate, energy consumption, and ozone usage efficiency.

Gas velocity was always considered to be an irrelevant factor for ozone mass transfer in a membrane contactor (Atchariyawut et al. 2009; Bamperng et al. 2010). According to Equations (2)–(4), the gas film resistance was much smaller compared to that of the liquid film, as the ozone diffusivity of the gas stream ($D_{O_3,G} = 1.24 \times 10^{-5}$ m$^2$/s) was much larger than that of the liquid stream ($D_{O_3,L} = 1.75 \times 10^{-9}$ m$^2$/s). Thus, the gas film is negligible and the gas velocity did not affect the mass transfer in most cases.

However, our experiments show something different. As presented in Figure 4, when the gas flow rate was larger than $6.1 \times 10^{-3}$ m/s, which can be defined as critical velocity, the ozone flux remained almost unchanged. However, when the gas flow rate decreased from $6.1 \times 10^{-3}$ to $6.1 \times 10^{-4}$ m/s, the ozone flux decreased by 2.27 and 3.51 times for 25 and 50 mg/L gas phase ozone concentration, respectively. In these cases, the gas film resistance cannot be ignored. The gas phase mass transfer coefficient ($k_G$) decreased as the gas flow rate reduced, according to Equation (4). When the gas flow rate was smaller than the critical velocity, the gas film resistance was comparable to the liquid one and turned into an important factor for ozone mass transfer. In addition, based on mass balance of ozone, for 25 mg/L gas...
phase ozone concentration, when the gas flow rate was larger than $6.1 \times 10^{-3} \text{ m/s}$, less than 9.9% of the ozone in the gas was transferred to the water. When the gas flow rate decreased to $6.1 \times 10^{-4} \text{ m/s}$, 44.1% of the ozone in the gas crossed the membrane. As a result, the driving force provided by the concentration differential decreased with gas flow rate. Thus, the ozone flux reduced as the gas film resistance increased and the driving force decreased at the same time. Obviously, the optimized gas flow rate should be the critical velocity. It is worth noting that the critical velocity varies with the conditions of the liquid and gas streams.

As illustrated in Figure 5, the ozone flux was measured when the water temperature was varied from 278 to 318 K. The ozone flux decreased sharply as the temperature increased. As mentioned before, the mass transfer rate was controlled by the concentration differential between the equilibrium and the liquid concentration; and the equilibrium concentration ($C_{eq} = HP_O^3$) decreased with the Henry constant when the temperature increased. Thus, it was advantageous to obtain a high ozone concentration or to achieve a good mass transfer rate at a low temperature.

**Mass transfer behaviors for chemical absorption**

For chemical absorption, the mass transfer process was much different from that of the physical one. To understand the mass transfer behaviors, absorbent concentrations, species, pH, and gas flow rate were investigated.

In Figure 6, ozone fluxes for different concentrations of phenol and pure water are presented. The ozone flux of phenol was greater than pure water, and the flux increased with the phenol concentration. When the liquid flow rate was 0.11 m/s, the ozone flux was 1.6, 4.5, 11.6, and 25.5 times higher than that of deionized water for 0.05, 0.5, 5, and 50 mM phenol, respectively. The enhancement factor increased with the concentration of the absorbent, according to Equations (11)–(13), and the overall resistance decreased accordingly. Thus, the ozone mass transfer rate increased with phenol concentration. The reaction rate constant between ozone and phenol was very large through an electrophilic substitution reaction (Beltrán 2004), which was reported as $1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 8 (Hoigne & Bader 1983). As a result, the flux of phenol was much larger than that of pure water even though the concentration was only 0.05 mM. In addition, the ozone flux increased with the liquid flow rate, just like that of the physical one. However, the flux increment decreased when the phenol concentration increased. The flux increased by 2.56, 2.24, 1.75, 1.29, and 1.07 times as the liquid velocity increased from 0.11 to 0.67 m/s for pure water, and 0.05, 0.5, 5, and 50 mM phenol solution, respectively. As the enhancement factor improved with phenol concentration, the proportion of liquid film resistance decreased. Thus, the liquid velocity became less important compared to the physical absorption process.

Ozone is a highly selective oxidant, and the reaction rate varied with species in a very wide range. Four chemicals were chosen for typical absorbents: phenol (as a model contaminant in wastewater), sodium nitrite and oxalate (as model contaminants in drinking water), and hydrogen peroxide (as an oxidant coupled with the ozonation process). The results are shown in Figure 7. The ozone fluxes were very different from each other and the order of mass transfer rate was: phenol, sodium nitrite, hydrogen peroxide, and

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**Figure 5** Effect of water temperature on ozone flux (gas velocity: 0.024 m/s; ozone concentration: 50 mg/L).

**Figure 6** Ozone fluxes for pure water and phenol solutions with different concentrations (gas flow rate: 0.0061 m/s; ozone concentration: 50 mg/L; water temperature: 293 K).
oxalate. As reported in the literature, the reaction rate constants were $1.8 \times 10^7$, $1.6 \times 10^5$, $1.4 \times 10^3$, $4 \times 10^{-2}$ M$^{-1}$ s$^{-1}$ (pH = 8) for phenol, sodium nitrite, hydrogen peroxide, and oxalate, respectively (Hoigne & Bader 1983; Hoigne et al. 1985). The enhancement factor increased with the reaction rate constant according to Equations (11)–(13). Thus, the mass transfer resistance decreased and the flux increased.

OH$^-$ could accelerate the ozone decomposition; therefore, the enhancement factor and ozone mass transfer rate increased with pH value. Ozone flux depending on pH is presented in Figure 8. For pure water, the ozone flux increased by a large extent when the pH was over 10, while the change was relatively smaller when the pH was 2 to 10. For phenol solution, the ozone flux increased obviously along with pH. The reaction rate constant between ozone and phenol increased with pH (Hoigne & Bader 1983). In addition, the ozone self-decomposition contributed a lot at high alkalinity. Therefore, we can see that the increment was much larger when pH was over 10.

Figure 9 depicts the influence of gas flow rate on flux for chemical absorption. For 50 mM phenol solution, the flux increased 1.93 times as the gas velocity increased from $3 \times 10^{-3}$ to $1.2 \times 10^{-2}$ m/s and the flux remained unchanged when the gas velocity was over $1.2 \times 10^{-2}$ m/s. Similar to that of physical absorption, when the velocity was lower than the critical velocity, the flux was highly affected by the gas velocity, and while the velocity exceeded the critical velocity, the flux was not influenced. The critical velocity for pure water and 50 mM phenol solution was $6.1 \times 10^{-3}$ m/s and $1.2 \times 10^{-2}$ m/s, respectively. For chemical absorption, the flux was larger and the ozone demand was greater, and as a result the critical velocity increased. From another perspective, the gas boundary layer became more important for chemical absorption than the physical one.

Influence of membrane properties on mass transfer

Six kinds of hollow fiber membranes were employed to understand the influence of membrane properties on ozone mass transfer. Thickness, porosity, pore size, and contact angle were very different from each other for these membranes. The details of membrane properties are shown in Table 1. Both physical and chemical absorption processes were investigated and the results are depicted in Figures 10 and 11, respectively.
In a hydrophobic membrane contactor, the resistance of gas film and membrane were assumed to be negligible for physical absorption. Therefore, overall mass transfer coefficient ($K_L$) can be replaced by the local mass transfer coefficient of the liquid phase ($k^*_L$). According to Equation (9), mass transfer coefficient determined the ozone flux. $k^*_L$ is described by the Graetz–Lévêque equation (Equation (3)), which is the relationship between mass transfer rate (Sherwood number) and water velocity (Graetz number). As we can see in Figure 10, the results are presented as the relationship between Sherwood and Graetz number. For 1# to 5# hollow fiber membranes, the experimental data followed the Graetz–Lévêque equation. Although the membranes were different, the mass transfer rate was not much affected under the same water velocity. Therefore, for physical absorption, membrane properties, including pore size, porosity and thickness, were unimportant. The results also proved the validity of the non-wetted mode for hydrophobic membranes.

However, for membrane 6, the mass transfer rate was an order of magnitude lower than the simulation result based on the Graetz–Lévêque equation. Number 6 membrane was made from aluminum oxide and the contact angle was 48°, which was hydrophilic. Thus, the non-wetted mode was not applicable and the Graetz–Lévêque equation was invalid. For the hydrophilic membrane, the pores were partially wetted. Therefore, the membrane resistance increased by a large scale according to Equations (6)–(8). Thus the flux was much lower than that of the hydrophobic one.

For chemical absorption, mass transfer fluxes for different membranes are shown in Figure 11. As can be seen, the differences in flux between membranes became greater and greater as the phenol concentration increased from 0 to 5 mM. The enhancement factor increased with the absorbent concentration, according to Equations (11)–(13). Thus, the liquid film resistance proportion of the overall resistance decreased according to Equation (2). In other words, the membrane resistance becomes more and more important as the phenol concentration increases. Therefore, the importance of the membrane properties increases. According to the fluxes of membranes 2, 3 and 4, where the thickness of the three membranes was the same, it can be found that the mass transfer rate increased with porosity and mean pore size. For membranes 1 and 2, where the porosity and mean pore size were the same, the flux of membrane with smaller thickness (2#) was higher. The membrane mass transfer coefficient can be calculated from Equation (5); the order was 5, 2, 1, 3, and 4, which was the same as the order of ozone flux for most cases. However, for membrane 6, the flux was only 12.2% to 23.8% of that of membrane 5. The mass transfer rate was significantly affected by the partially wetted pores. Therefore, the membrane hydrophobicity was extraordinarily important for ozone mass transfer in membrane contactors.

The section and surface SEM images are presented in Figure 12, and the PTFE (4#) and PVDF (5#) membranes were chosen for comparison. From the SEM images, the surface pores of membrane 4 were more abundant than those of membrane 5, which was considered to be an advantage for mass transfer. However, the flux of membrane 4 was smaller than that of membrane 5. Compared to the thickness, the distance between pores was much smaller.
(Gabelman & Hwang 1999; Zhang 2010); therefore, the absorbent could instantaneously diffuse uniformly on the membrane surface and the surface pore density was less important. The pore structure of PVDF membrane 5 was richer than that of PTFE membrane 4, according to Figure 12, and the membrane thickness was less. As a result, the ozone diffusion distance was shorter for a PVDF membrane and thus the flux was larger. According to the results above, a membrane with a thin wall and large porosity was a good candidate for an ozone membrane contactor.

**CONCLUSIONS**

Physical and chemical absorption processes for ozone mass transfer were investigated in hollow fiber membrane contactors for various operating conditions and membranes. A resistance-in-series model was also employed for better understanding of the mass transfer principles. For the physical absorption process, the mass transfer was liquid film controlled. The liquid velocity was the vital factor, while the membrane properties were not. Thus, it was an efficient way to improve ozone flux by increasing the water velocity. The ozone concentration in the gas stream and the temperature controlled the mass transfer rate by influencing the driving force. For chemical absorption, the gas film and the membrane resistance were no longer negligible. When the absorbent concentration and reaction coefficient increased, the overall resistance decreased and the flux increased. In addition, the importance of the gas film and membrane increased. Thus, the membrane properties affect the mass transfer to a large extent. For chemical absorption, membrane optimization was meaningful. An ideal membrane has high porosity, a thin wall, high hydrophobicity and good ozone resistance.

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