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CO₂ capture using a superhydrophobic ceramic membrane contactor

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Abstract

Wetting and fouling of membrane contactor result in performance deterioration of membrane gas absorption system for CO₂ post-combustion capture of coal-fired power plants. To solve these problems, in this study, a superhydrophobic ceramic (SC) membrane contactor was fabricated by chemically modification using 1H,1H,2H,2H-perfluorooctylethoxysilane (FAS) solution. The membrane contactor fabrication costs for both SC membrane and PP (polypropylene) membrane contactors per unit mass absorbed CO₂ were roughly the same. However, by using the SC membrane, the detrimental effects of wetting can be alleviated by periodic drying to ensure a high CO₂ removal efficiency (>90%), whereas the drying does not work for the PP membrane. The SC membrane contactor exhibited a better anti-fouling ability than the PP membrane contactor because the superhydrophobic surface featured a self-cleaning function. To ensure continuous CO₂ removal with high efficiency, a method that two SC membrane contactors alternatively operate combined with periodic drying was proposed.

Keywords: superhydrophobic; alumina; membrane contactor; CO₂ capture; wetting

1. Introduction

At present, most of the commercially available hollow fiber membranes are made from polymeric materials, most of which suffer from chemical and thermal stresses due to contact with absorbents in the
process of absorption, leading to membrane swelling and morphological changes \[1-3\]. In our previous reports, the membrane wetting mechanism and anti-wetting methods were proposed \[4-6\]. But, wetting is still a big challenge for polymer membranes. Compared with polymeric membranes, ceramic membranes show better structural, thermal, physical and chemical stability, which have been widely applied in the separation and purification processes \[7\]. Most ceramic membranes are made from metal oxides, such as alumina, zirconia, silica and so on, which are hydrophilic in nature because of the presence of hydroxyl (OH-) groups on the surface \[8\]. This surface property prevents them from being directly used in membrane gas-absorption process. However, ceramic membranes with hydrophobic surface could be prepared by surface modification \[8-9\]. There has been no report on the use of hydrophobic ceramic hollow fiber membrane for CO\(_2\) absorption so far.

In addition, fouling is one of the major problems in the industrial application of porous membranes. Fortunately, in the gas–liquid contactor applications, the contactors are less sensitive to fouling since there is no convection flow through the membrane pores. However, in industrial applications such as coal-fired power plant, gas and liquid streams with suspended particles can cause plugging due to the small membrane contactor diameter. No reports can be found on the fouling of membrane contactor for CO\(_2\) capture.

The aim of this study is to investigate the feasibility of using superhydrophobic ceramic (SC) membrane contactor for CO\(_2\) absorption. FAS was used as a surface modifier to change the membrane surface from hydrophilicity to superhydrophobicity. The performances of SC membrane contactor and PP hollow fiber membrane contactor were compared via experiments conducted in an CO\(_2\) absorption–desorption loop system using monoethanolamine (MEA) aqueous solution. The anti-fouling of the SC membrane contactor was investigated by operation in a coal-fired power plant.

2. Experimental

For the process of surface hydrophobic modification, the ceramic membrane tubes (Jiangsu Jiowu Hi-tech Co., Ltd.) were firstly cleaned by ultrasonication in ethanol and deionized water. The ceramic membrane was fabricated by coating a ZrO\(_2\) membrane layer on the interior surface of a highly permeable porous alumina support. Then, the ceramic membrane tubes were soaked in the mixture of ethanol and deionized water (2:1; volume) for 24 h and dried in an electrically heated drying oven at 60\(^\circ\)C for 24 h. The dried ceramic membrane tubes were immersed into the solution of 2 wt% FAS (Shanghai Hansi Chemical Co., Ltd.) and 98 wt% ethanol at room temperature for 24 h. After the immersion, the ceramic membrane tubes were rinsed by ethanol and deionized water to get rid of the residues of the unreacted FAS. The ceramic membrane tubes were subsequently dried at 100\(^\circ\)C for 24 h.

Fig 1. is the schematic diagram of CO\(_2\) absorption using a SC or PP membrane contactor. The detailed parameters of these two kinds of membrane contactors are shown in Table 1. The gas phase and liquid phase flowed countercurrent through the module (the the absorbent passed through the lumen side, and the gas flowed countercurrent through the shell side of the hollow fibers).

3. Results and discussion

3.1. Membrane characterization

The water contact angles of ceramic membranes ungrafted and grafted by FAS were measured. The contact angle of the ungrafted could not be obtained because the droplet of deionized water was quickly sucked into the porous membrane. After grafting by FAS, the ceramic membrane achieved a contact angle of 153\(^\circ\), revealing that the membrane surface was modified from hydrophilicity to superhydrophobicity.
The superhydrophobicity indicated that most of the hydroxyl groups on the membrane surface reacted with FAS because the hydrophilicity is heavily dependent on the density of hydroxyl groups [10]. The SC membrane is hereafter referred to the ceramic membrane grafted by FAS with a contact angle of 153°. Fig 2. shows N\textsubscript{2} permeance as a function of trans SC membrane pressure. The N\textsubscript{2} permeance of the SC membrane was 7.90×10\textsuperscript{-3} mol m\textsuperscript{-2} s\textsuperscript{-1} Pa\textsuperscript{-1}, which was only slightly lower than that of 8.9×10\textsuperscript{-3} mol m\textsuperscript{-2} s\textsuperscript{-1} Pa\textsuperscript{-1} for the ungrafted ceramic membrane; this suggests that the grafted FAS reduces the pore sizes of the membrane slightly. But the FAS grafting led to a drastic decrease in the permeance of clean water because of increased surface hydrophobicity. As shown in Fig. 3, the ungrafted ceramic membrane allowed liquid water to pass through at a fast rate of 1.94 m\textsuperscript{3} m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1}, whereas the SC membrane completely blocked water and 5% MEA aqueous solution at pressures less than 6.5 and 5.5 bar, respectively. Only at a pressure above those values, water and 5% MEA aqueous solution started to permeate through the membrane. These critical entry pressures agree well with the values calculated by the Laplace’s equation [11].

As presented in Table 1, the prices of SC membrane (Module 1) is 120 RMB, roughly one fifth of that of 650 RMB for PP membrane (Module 2). As presented in Table 2, for Module 1, the high CO\textsubscript{2} removal efficiency of 99.3% was achieved with a gas flow rate of 50 ml min\textsuperscript{-1}, which is one fifth of 250 ml min\textsuperscript{-1} for Module 2 (the CO\textsubscript{2} removal efficiency was 98.8%). Therefore, for the SC membrane and PP membrane contactors, the membrane contactor fabrication costs per unit mass absorbed CO\textsubscript{2} are roughly the same.

3.2. Performances of SC membrane in CO\textsubscript{2} absorption

The effects of operation time on the CO\textsubscript{2} absorption performances of PP membrane and SC membrane were investigated by running the system continuously for 7 days and then the membranes were dried at 50°C for 24 h. This procedure became on turn. As illustrated in Fig. 4, for the fresh PP membrane, the CO\textsubscript{2} removal efficiency maintained above 90% within the first 3 days and continuously dropped to 74.2% upon the 7th day. With the increase in turns, the CO\textsubscript{2} removal efficiency decreased obviously. That is, the performance of PP membrane could not be retrieved by drying. This tendency was attributed to the irreversible changes of PP membrane surface morphologies due to swelling during a long-term exposure of PP fibbers to MEA aqueous [4]. For the SC membrane, the CO\textsubscript{2} removal efficiency continuously decreases with operation time (see Fig. 5), indicating that wetting occurred despite its superhydrophobicity. However, after drying at 50°C, the membrane performance was resumed. The SC membrane exhibited a good chemical stability, suggesting that the grafted fluoroalkylsilane species on the membrane surface were not destroyed during exposure of membrane to MEA aqueous solution.

![Fig. 1. Schematic diagram of experimental setup](image)
Table 1. The specifications of membrane modules

<table>
<thead>
<tr>
<th>Module parameters</th>
<th>Module 1</th>
<th>Module 2</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane material</td>
<td>Support layer of alumina and membrane layer of ZrO$_2$ grafted by FAS</td>
<td>PP</td>
<td></td>
</tr>
<tr>
<td>Module inner diameter</td>
<td>30</td>
<td>42</td>
<td>mm</td>
</tr>
<tr>
<td>Module length</td>
<td>380</td>
<td>440</td>
<td>mm</td>
</tr>
<tr>
<td>Membrane fiber inner diameter</td>
<td>8</td>
<td>0.26</td>
<td>mm</td>
</tr>
<tr>
<td>Membrane fiber outer diameter</td>
<td>12</td>
<td>0.38</td>
<td>mm</td>
</tr>
<tr>
<td>Fiber length</td>
<td>360</td>
<td>440</td>
<td>mm</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>1</td>
<td>2000</td>
<td>-</td>
</tr>
<tr>
<td>Fiber porosity</td>
<td>0.38</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>Pore size</td>
<td>0.2</td>
<td>0.15</td>
<td>μm</td>
</tr>
<tr>
<td>Price</td>
<td>120</td>
<td>650</td>
<td>RMB</td>
</tr>
</tbody>
</table>

Fig. 2. N$_2$ permeance as a function of trans membrane pressure of ungrafted and SC membrane contactors.

Fig. 3. Flow-pressure curve of the SC membrane contactor measured using water and 5 wt% MEA aqueous solution at 25°C.

Table 2. Performance comparison between superhydrophobic ceramic membrane and PP membrane.

<table>
<thead>
<tr>
<th>Module parameters</th>
<th>Module 1</th>
<th>Module 2</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{gas}}$ (gas flow rate)</td>
<td>50</td>
<td>250</td>
<td>ml min$^{-1}$</td>
</tr>
<tr>
<td>$Q_{\text{absorbent}}$ (absorbent flow rate)</td>
<td>10</td>
<td>50</td>
<td>ml min$^{-1}$</td>
</tr>
<tr>
<td>$\eta$ (%) (CO$_2$ removal efficiency)</td>
<td>99.3</td>
<td>98.8</td>
<td></td>
</tr>
</tbody>
</table>

(Operation conditions: absorbent of 5 wt% MEA aqueous solution; CO$_2$ concentration in feed gas of 12.5%; 20°C.)

Fig. 4. Effects of operation time on CO$_2$ removal efficiency of PP hollow fiber membrane (CO$_2$ absorption at 293 K; $Q_{\text{gas}}$: 50 ml min$^{-1}$; $Q_{\text{absorbent}}$: 250 ml min$^{-1}$; absorbent: 5 wt% MEA aqueous solution; CO$_2$ concentration in feed gas: 12.5%).

Fig. 5. Effect of operation time on CO$_2$ removal efficiency of SC membrane (CO$_2$ absorption at 293 K; $Q_{\text{liquid}}$: 10 ml min$^{-1}$; $Q_{\text{gas}}$: 50 ml min$^{-1}$; absorbent: 5 wt% MEA aqueous solution; CO$_2$ concentration in feed gas: 12.5%).
3.3. Self-cleaning function

To investigate the anti-fouling of the SC membrane and PP membrane, the two membranes were connected to the by-pass of the flue gas main pipeline of Jinjiang Suyuan Thermal Power Plant (Jinjiang City, China). The dusty concentration of the flue gas from coal-fired boiler after deduster was 30 mg m$^{-3}$. The flue gas was introduced to the by-pass by a turbine fan and cooled to 50°C. The cooled flue gas flowed into the shell side of the two membranes with the gas flow rate of 3 L min$^{-1}$ controlled by a control value. The absorbent did not go through the tube side due to the experimental limitation on site. As shown in Fig. 6 (a) and (b), after one-month operation, no obvious dust was found for the SC ceramic membrane. In contrast, many fibers of PP membranes were fouled by dust in the flue gas (see Fig. 6 (c)). Therefore, the SC membrane exhibited a better anti-fouling ability than the PP membrane. Amount of water was observed in the shell side of the PP membrane because water of the flue gas was condensed (see Fig. 6 (c)). The condensed water in the shell side of SC membrane could wash the dust on the membrane surface. Because of the self-cleaning function of the superhydrophobic surface, the SC membrane exhibited a strong anti-fouling ability.

3.4. CO$_2$ capture using superhydrophobic ceramic membrane combined with periodic drying

To reduce the wetting effect, CO$_2$ capture using SC membrane combined with periodic drying was proposed. As shown in Fig. 7, Membrane contactors I and II were used alternatively to ensure continuous CO$_2$ removal with high efficiency. When Valve I and Valve III opened, Valve II and Valve IV closed, the flue gas was introduced into Membrane contactor I and CO$_2$ was absorbed by MEA aqueous solution. Meanwhile, Membrane module II was dried by the air from Heat exchanger where air was heated by flue gas. After 5 days running, the CO$_2$ removal efficiency decreased to about 90% according to the results shown in Fig. 5. At this moment, Membrane contactor II was used and the membrane contactor I was dried by closing Valve I and Valve III. Meanwhile, Valve I and IV opened. In this way, the SC membrane contactors can continuously remove above 90% CO$_2$ form flue gas of coal-fired power plant. Given the physical and chemical stabilities and strong anti-fouling ability of SC membrane, the proposed CO$_2$ capture combined with periodic drying should be feasible in real industrial applications.

![Fig. 6. Images of (a) fresh ceramic membrane, (b) SC membrane after one month on site operation in Jinjiang Suyuan Thermal Power Plant (Jinjiang City, China), and (c) PP membrane fibers after one month on site operation in Jinjiang Suyuan Thermal Power Plant (Jinjiang City, China).](image1)

![Fig. 7. Schematic diagram of CO$_2$ capture using SC membrane combined with periodic drying for coal-fired power plant.](image2)
4. Conclusions

A superhydrophobic ceramic membrane was developed by FAS grafting to handle the problems of wetting and fouling. After grafting with FAS, the ceramic membrane exhibited a contact angle value of $153^\circ$. For the SC membrane and PP membrane contactors, the membrane contactor fabrication costs per unit mass absorbed CO$_2$ are roughly the same. For the SC membrane, the detrimental effects of wetting could be alleviated by periodic drying to ensure a high CO$_2$ removal efficiency ($>90\%$), whereas the drying did not work for the PP membrane because the swelling of PP fibers was irreversible. The SC membrane exhibited a better anti-fouling ability than the PP membrane because the superhydrophobic surface featured a self-cleaning function. To ensure continuous CO$_2$ removal with high efficiency, a method that two SC membrane contactors alternatively operate combined with periodic drying was proposed.

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References