SO_2 Removal from the flue gas by hollow fibre membrane contactor

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Abstract. The combustion of fossils fuels is the main source of the environmental problems, such as acid rain, photochemical smog, and ozone depletion. To solve these problems, the appropriate technology to remove acid gasses such as SO2 is urgently required. In this work, SO2 removal was conducted using polypropylene and polysulfone-based hollow fiber membrane contactors. Water and sodium sulfite were used as sorbents. The results showed that the use of sodium sulfite as a sorbent provided 2 times higher SO2 permeation than water. Moreover, permeate flux of polypropylene membrane was higher than polysulfone membrane since the hydrophobic membrane is more suitable as membrane contactor for flue gas cleaning. In addition, a comparison between membrane contactor and conventional scrubber showed that membrane contactor can reduce the contact volume up to 27 times smaller than those used in the conventional scrubber.

1. Introduction

Most of the world energy production is made up from the combustion of fossil fuels such as oil, coal, and gas. The combustion of these fuels is the main source for environmental problems of major concern such as acid rain, photochemical smog, ozone depletion, and greenhouse effect [1, 2]. To cope with these problems, the appropriate technology to remove acid gasses such as SO_2 is urgently required.

The available SO_2 capture technology including physical and chemical absorption, cryogenic distillation solid adsorption, and membrane technologies. Among these, chemical absorption with conventional scrubbing tower is the most used technique to capture SO_2 from flue gas streams. However, this technique is characterized by huge space requirements and related high capital costs. The conventional wet scrubbing techniques also suffer from a number of deficiencies such as loading, flooding, and entrainment limitation [3].

The membrane processes is a promising alternative that rapidly gaining recognition as efficient, energy saving and compact separation technologies [4-6]. Microporous membranes can be used as gas-liquid contractors to remove gas components from gas phase [2, 7, 8]. The major advantage of the membrane contactor lies in the drastic reduction of the contactor volume and the related reductions in the investment and operating costs. Furthermore, due to the principles of contacting, many disadvantages present in conventional contacting equipment such as flooding, loading, and entrainment limitations can be overcome [9]. Hence, the operation of the membrane contactor can easily be adjusted to meet changes in plant load. In addition, due to their compactness and modular nature, membrane contactors are well suited for retrofit applications.

However, the majority of membrane contactor application is limited by membrane wetting phenomena which deteriorates its performance. Membrane wetting is caused by penetration of liquid absorbent into the pore structure. The presence of liquid absorbent inside of the pores add an additional mass transfer resistance causing a dramatic performance drop. Therefore, a material with the higher hydrophobicity is more recommended to assure long-term operation stability [10].

Membrane wetting problem can be overcome by increasing membrane hydrophobicity. The hydrophobic nature of membrane material will prevent penetration of liquid absorbent into the pore structure.

Polypropylene (PP), polyvinylidene fluoride (PVDF), polyethylene (PE), and polytetrafluoroethylene (PTFE) are the hydrophobic material which commonly used in porous membrane contactor fabrication, where polypropylene is considered as the most low-cost material with moderate hydrophobicity [11, 12].

The comprehensive review of the development of superhydrophobic membrane has available in the literature [13]. The coating method is a low-cost and simple approach to improve membrane hydrophobicity. The modification of low cost hollow fiber polypropylene membrane to improve its hydrophobicity by dip coating method was investigated by Himma et.al. [14]. The superhydrophobic membrane with a contact angle of 151.3^o can be obtained by using methyl ethyl ketone as nonsolvent.

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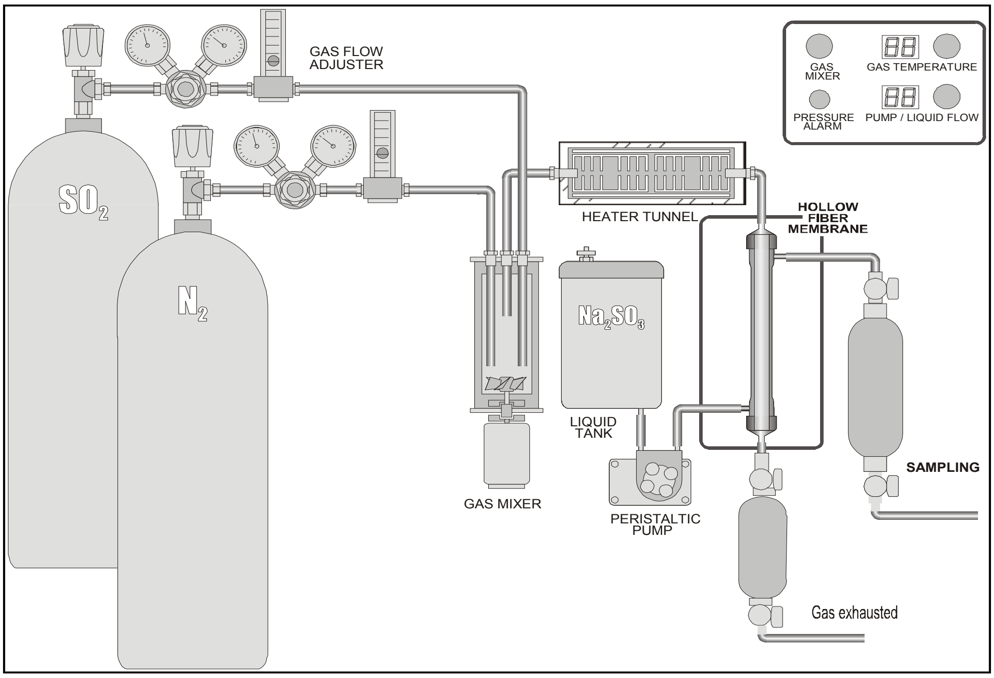


Figure 1 Schematic illustration of hollow fibre membrane contactor

In this work, SO_2 removal was conducted using polypropylene and polysulfone-based hollow fibre membrane contactors. Meanwhile, water and sodium sulfite were chosen as sorbents. Membrane characteristic, structure, and stability were investigated. Finally, the performance of membrane contactors was compared to the conventional scrubber.

2. Methodology

In this work, the comprehensive study of membrane characterization used for membrane contactor has been carried out experimentally and theoretically. Commercial polypropylene (MemTec) and polysulfone (self-preparation) were used in this work. Membrane was packed into units called modules. All experiments were conducted using hollow fibre modules due to the high packing densities obtained in such modules. Schematic illustration of hollow fibre membrane contactor can be seen in Figure 1.

The membrane parameters controlling the transport properties of the membrane such as wettability, porosity, wall thickness, pore size, pore area, and pore tortuosity has been assessed. Information about pore structure, pore area, etc. was obtained from scanning electron microscopy, measurement of the bubble point pressure, and measurement of mercury porosimetry. Chemical stability was studied by immersing membranes into any level pH of sodium sulfite solution for a month. Meanwhile, to measure its thermal stability, membrane contactor was operated at high temperatures.

3. Result and Discussion

3.1 Sorbent and Membrane Selection

In this work, both water and an aqueous solution of sodium sulfite have been used as sorbents. Comparison of the two sorbents is shown in Figure 2. As can be seen in this figure, SO_2 permeation is relatively same at the low gas flow rate. However, in high gas flow rate, an aqueous solution of sodium sulfite provides 2 times higher permeation of SO_2 than water. These results show that aqueous solution of sodium sulfite is more suitable than water. Figure 2 indicates that chemical reaction is controlling the overall process. In addition, an aqueous solution of sodium sulfite has a high absorption capacity for SO_2 so that mass transfer resistance in the liquid phase is negligible by proper selection of operating conditions.

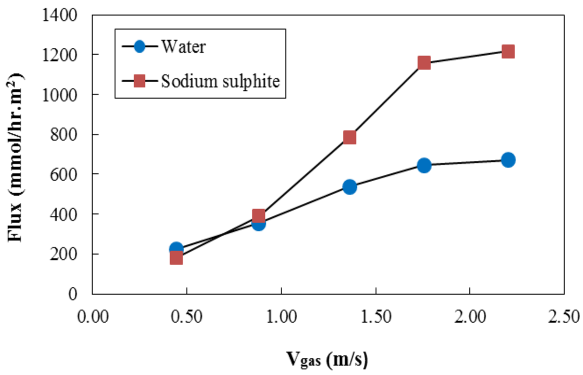


Figure 2 Comparison of SO_2 flux for sodium sulfite and water sorbent

Furthermore, the effect of membrane type is shown in Figure 3. This figure shows that the polypropylene membrane gives higher SO_2 flux than the polysulfone. It proves that the polypropylene membrane mass transfer coefficient is greater than the polysulfone since hydrophobic membrane is more suitable as membrane contactor for gas cleaning [14-17].

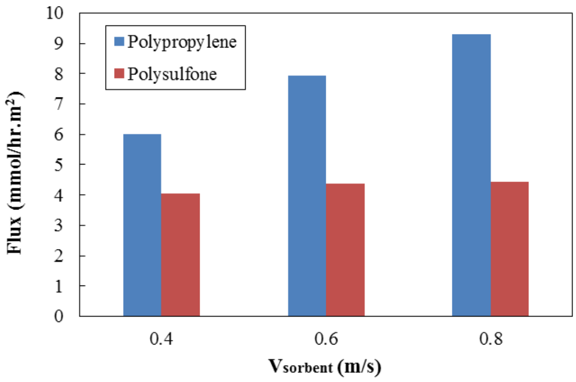


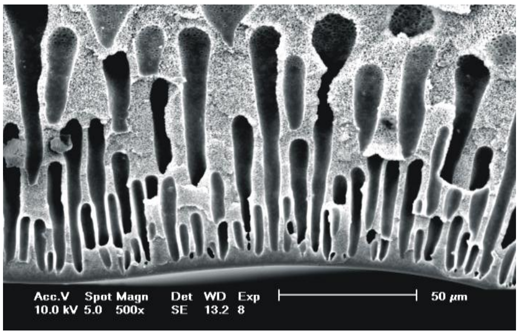
Figure 3 Comparison of SO_2 flux for polypropylene and polysulfone membrane (sorbent flow rate 0,001 m/s and sorbent concentration 0.26 M)

3.2 Membrane Characteristic and Structure

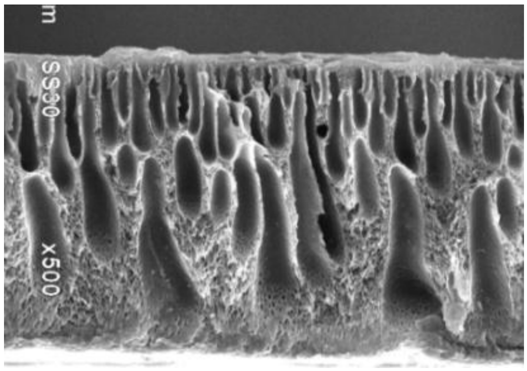
The key concern for selection of membranes used in membrane contactors is transport properties and membrane stability with respect to wettability, chemical, thermal, and mechanical properties. Parameters affected on transport properties are porosity, wall thickness, pore size, and tortuosity. The membrane wettability is influenced by the type of membrane used for membrane contactor. A hydrophobic microporous membrane will generally prevent liquid from penetrating into the pores, and hence the pores will be gases filled. In case of hydrophilic microporous membranes, the liquid will penetrate the pores. A commercial polymer such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinylidene fluoride (PVDF) and polysulfone) provide hydrophobic characteristics.

As regards to the thermal stability, PP membranes can be continuously operated in the range 50-90°C (depending on the grade of PP), while temperature ranges for PVDF and PTFE are 100-155°C and 130-260°C, respectively [18]. Typical flue gas temperatures after the dust removal system at coal fire boiler facilities are 110-150°C. For wet scrubbing systems the temperature is normally reduced by conditioning prior to scrubbing, thus the thermal stability of the membrane may not be a critical issue. However, a PVDF and PTFE do have a significance advantage in that an accidental exposure to higher temperatures will not be disastrous.

It is suggested to use a high porosity membrane as membrane contactor because it gives a large contact area between gas and sorbent. Two membranes, i.e. polypropylene and polysulfone have been used in this study. Porosities of the membranes used in this study are so high that they are good enough to be used as a membrane contactor. The experimental results of their characteristics are shown in Table 1. Based on their characteristics, both of them are microporous membranes with the pores sizes is in the range of 0.01-1 µm, the porosity between 0.3-0.85 % and membrane thickness between 25-500 µm.



(a)



(b)

Figure 4 SEM image of (a) polypropylene and (b) polysulfone membrane

Table 1 Membrane characteristics

	Polypropylene	Polysulfone
Pore diameter (µm)	0.2	0.2
Porosity (%)	70	82
Outside diameter (µm)	541	672
Membrane thickness (µm)	150	153

Furthermore, chemical stability of membranes was tested by pre-soaking polypropylene membranes in sodium sulphite solution in various pH for a month. Mercury porosimetry analysis results are listed in Table 2.

Table 2 Stability assessment of PP membrane

pH	Diameter (µm)
Initial	0.2
1	0.1
3	0.2
10	0.2

The results show that pore diameter remains stable before and after the treatment. At extreme acid condition, the membrane seems to shrink, as the pore size becomes smaller. However, the effect is not significant. This proves that extreme pH environment will not significantly influence membrane characteristic.

3.3 Comparison of Membrane Contactor Performance with Conventional Scrubber

Generally, the performance of membrane contactor is not enhanced by the increase of mass transfer coefficient but rather by increasing contact surface area. Absorption in many cases relies on providing a high interfacial area between the gas and liquid phase to achieve high overall rate of gas mass transport. Many commercial devices based on packed columns, plate columns, spray columns, venturi scrubbers, etc. are available. In many cases equipment design can be restricted by limitations in the relative flows of the fluid streams. The use of membrane, in the form of low cost hollow fibres gives a contact surface area between gas and liquid phases, which is independent of gas and liquid flows. The small dimensions of the hollow fibre membranes give high specific surface areas which are significantly larger than most conventional absorbers. Commercially available hollow fibre modules used for filtration duties can be used as absorbers with gas flow through the fibres.

In order to explain advantages of membrane contactor with conventional scrubbers, performance of both contactors is quantitatively compared. One of conventional scrubber i.e. packed column need 3.105 m on diameter and height 19.9 m for separation rate 0.5 kg/s. Membrane contactor with specifications pore size 0.2 μm, porosity 70%, fibre diameter 0.5 μm, module length 30 cm, module diameter 1.5 cm and number of fibre 100 is compared with the same separation rate. The comparison of both contactors is expressed using analytical dimension as shown in Table 3. Table 3 shows that flux of conventional scrubber is higher than hollow fibre contactor. However, membrane contactor volume is smaller than conventional scrubber for the same absorption capacity (27 times lower contactor volume).

Table 3 Analytical dimensions for membrane contactor and conventional scrubber

	Conventional Scrubber	Hollow Fiber Contactor
Capacity (kg/s)	0.5	0.5
Flux (mol/hr.m^2)	250	10
Contactor volume (m^3)	151	5.6

4. Conclusion

Theoretical and experimental investigations to explore the potential application of membrane contactor for flue gas cleaning were carried out. In the case of SO_2 absorption, aqueous solutions of sodium sulphite as listed in the commercial Wellman-Lord and Dual Alkali processes was selected for this study. The performance of the sorbent was compared with water. The result showed high absorption capacity for SO_2 by using aqueous solution of sodium sulphite as a sorbent. Moreover, hydrophobic membranes were more suitable as membrane contactor for flue gas cleaning. These membrane materials allow gas filled pores mechanism to govern the process.

Examination of membrane characteristic before and after treatment showed that pore size remained stable in wide pH range. Furthermore, the improved bubble point method could determine the pore size distribution and permeability of membrane. The nominal pore size obtained using this method was in agreement with the membrane data from the manufacturer. The pore size distribution obtained for each membrane was relatively narrow and shows good distribution.

Furthermore, comparison between membrane contactor and conventional scrubber showed that hollow fibres membrane contactor had higher contact surface area between gas and liquid phases. The small dimensions of hollow fibre membranes gave high specific surface areas which significantly larger than most conventional scrubbers. Analytical dimension were used to compare advantages of hollow fibre membrane contactor with conventional scrubbers quantitatively. The results showed that scrubber conventional had higher flux than membrane contactor, but membrane contactor could reduce the contact volume up to 27 times smaller than those used in conventional scrubber.

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