

The Simultaneously Removal of NO_x and SO₂ Processes through a Polysulfone Hollow Fiber Membrane Module

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Abstract. Hazardous pollutants such as NO_x (NO and NO₂) and SO₂ generally come from fossil fuel combustion, harm the human respiratory system, and damage environmental ecosystems. The conventional technology that has been used so far consists of two methods: FGD (Flue Gas Desulfurization) and SCR (Selective Catalytic Reduction) or SNCR (Selective Non-Catalytic Reduction) to remove SO₂ and NO_x. The study aims to examine the performance of polysulfone membranes in removing NO_x and SO₂ simultaneously using hydrogen peroxide (H₂O₂) and sodium hydroxide (NaOH) solutions as absorbents. The presence of H₂O₂ and NaOH in absorbent solutions plays a role in oxidizing NO_x into soluble species in water and in absorbing SO₂ gas, respectively. During the experiment, the feed gas flowed through the lumen fiber and then passed through the fiber to the shell side of the membrane module, where the reaction happened between NO_x and SO₂ and the absorbent. The experimental results showed that the presence of SO₂ affected the NO_x reduction efficiency. The NO_x and SO₂ removal efficiencies decreased with the feed gas flow. This study's maximum NO_x and SO₂ reduction efficiencies were 93.9 and 99.8%, respectively.

Keywords: Air pollution; H₂O₂; NO_x; Removal efficiency; SO₂

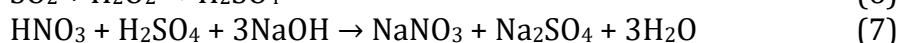
1. Introduction

Air pollution in Indonesia increases yearly due to growing public energy consumption. Hazardous pollutants such as NO_x (NO and NO₂) and SO₂ generally come from fossil combustion, harm the human respiratory system, and damage environmental ecosystems (Manisalidis *et al.*, 2020; Wang, Wang, and Shamma, 2020; Sharma *et al.*, 2013). Based on a study on the emissions prediction from the coal-fired power plants in Indonesia in 2016-2020, there was an exponential increase of 120.0 and 798.5 ktons of NO_x and SO₂, respectively, in that period (Sunarno, Purwanto, and Suryono, 2021). The Indonesian Government's efforts to prevent air pollution nationally set Ambient Air Quality Standards (BMUA) in Government Regulation No. 41 of 1999 (RI, 1999). However, the NO_x and SO₂ emissions produced by the coal-fired power plants in Indonesia are above the value of the BMUA, so efforts are needed to reduce emissions in PLTUs made from burning coal. Reducing NO_x and SO₂ emissions requires two different technologies, namely SO₂

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doi: [10.14716/ijtech.v14i3.5544](https://doi.org/10.14716/ijtech.v14i3.5544)

reduction using FGD (Flue Gas Desulfurization) and NO_x reduction using SCR (Selective Catalytic Reduction) or SNCR (Selective Non-Catalytic Reduction) (Chang *et al.*, 2004; Brandenberger *et al.*, 2008; Wu *et al.*, 2019). Simultaneous removal of NO_x and SO₂ with two separate technologies requires complex processes, high operational costs, and investment (Zhao *et al.*, 2021; Cheng and Zhang, 2018; Krzyzynska and Hutson, 2012). Both NO_x and SO₂ are acid gases (Li *et al.*, 2020); however, it needs to use different techniques to remove both gases due to differences in solubility, where the solubility of NO_x in water is lower than that of SO₂ (Fang *et al.*, 2011).

A previous study (Kartohardjono *et al.*, 2019; Kartohardjono *et al.*, 2017) has shown that the HFMM (hollow fiber membrane module) can be used as a bubble reactor to remove NO_x using H₂O₂ and HNO₃ solutions. The fibers' role is to distribute the feed gas into the solutions on the shell side of the HFMM so that reactions happen between NO_x and the absorbent. NO (nitrogen monoxide) in NO_x is an insoluble gas in water, so it needs to be oxidized to increase its solubility. One of the solutions that can be used to oxidize NO is hydrogen peroxide (H₂O₂). The H₂O₂ is superior as it is very stable under normal conditions, environmentally friendly, does not leave harmful residues, and the operating costs are pretty affordable. No conventional technology in the power generation industry can reduce NO_x and SO₂ simultaneously (Park *et al.*, 2019; Si *et al.*, 2019). In order to remove NO_x and SO₂ simultaneously, an absorbent that can oxidize NO_x into water-soluble species and an alkaline solution that can absorb SO₂ are required. This study utilized the polysulfone hollow fiber membrane module to remove NO_x and SO₂ simultaneously using absorbents consisting of H₂O₂ as an oxidant and sodium hydroxide (NaOH) as a base solution. The polysulfone membrane module was chosen because of its excellent stability over a wide pH range (2-13) and oxidant resistance (Febriasari *et al.*, 2021; Serbanescu, Voicu, and Thakur, 2021). Therefore, it can be expected to see the effect of SO₂ in the feed gas on NO_x removal compared to NO_x removal alone. The NaOH solution absorbs the reaction products between NO_x gas and SO₂ and H₂O₂. Reactions (1-7) are reactions that may occur in the process of simultaneously removing NO_x and SO₂ using a mixture of H₂O₂ and NaOH as absorbents: (Kartohardjono *et al.*, 2020; Sun, Zwolińska, and Chmielewski, 2016):



2. Methodology

The hollow fiber membrane module used contains 50 polysulfone fibers with a diameter of 3 cm and an effective length of 25 cm, supplied from GDP Filter Bandung, Indonesia. The fibers are 1.8 and 2 mm in the inside and outside diameters, respectively. The feed gas, which contained 600 ppm of NO_x and 500 ppm of SO₂ in nitrogen, was supplied from PT EIN Jakarta, Indonesia. The chemicals used, H₂O₂ and NaOH, are analytical grades Merck Indonesia supplies. The feed gas flowed inside the fiber in the membrane module throughout the experiment. The flow rate was adjusted using a CX Series mass flow controller. The feed gas diffused across the membrane pores to the shell side of the HFMM and contacted absorbent solutions so that reactions occurred between NO_x, SO₂, H₂O₂, and NaOH, as shown in Reaction (1-8). The concentrations of NO_x and SO₂ gases entering and

leaving the HFMM were recorded by the Gas Analyzer ECOM-D. The schematic of the experiment is presented in Figure 1.

The amount of absorbed NO_x and SO₂ gases, *GasAbs*, removal efficiency, *R*, fluxes, *J*, and NO_x and SO₂ loading, *Gas-loading*, can be calculated by Equations 8-11 (Kartohardjono *et al.*, 2020; Ding *et al.*, 2014):

$$Gas_{Abs} = (X_{in} - X_{out}) \frac{Q_{G,in}P}{RT} \tag{8}$$

$$R = \frac{X_{in} - X_{out}}{X_{in}} \times 100\% \tag{9}$$

$$J = \frac{Gas_{Abs}}{A_m} \tag{10}$$

$$Gas - loading = \frac{Gas_{Abs}}{molH_2O_2} \tag{11}$$

Where *X_{in}* and *X_{out}*, *Q_{G,in}*, *T*, *P*, and *R* are the concentration of gas inlet and outlet of the membrane module, feed gas flow rate, temperature, pressure, and gas constant, respectively.

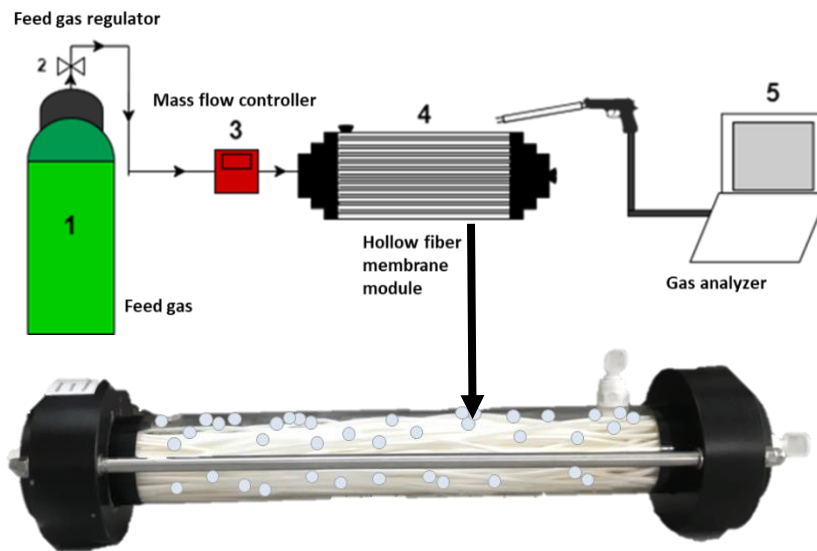


Figure 1 The experimental diagram schematic

3. Results and Discussion

Figure 2 shows the effect of the feed gas flow rate, containing 500 ppm SO₂ and 600 ppm NO_x, on the simultaneous removal of SO₂ and NO_x in the HFMM, which contains 0.1M of H₂O₂ and 0.5 M NaOH each of 200 ml. As demonstrated in Figure 2, the NO_x removal efficiency declines with increasing the feed gas flow rate due to the reduced gas residence time in the HFMM (Kartohardjono *et al.*, 2019). Meanwhile, the SO₂ removal efficiency is relatively constant to the feed gas flow rate changes because it is already close to 100%. The removal efficiency of SO₂ depends not only on the oxidant (H₂O₂), as expressed in Eq. 6, but also mainly on the alkaline solution present in the adsorbent (NaOH) so that it can be removed entirely (removal efficiency » 100%) (Chen, Chen, and Chiang, 2020; Liu *et al.*, 2019; Huang, Ding, and Zhong, 2015). The NO_x absorption efficiency decreases from 93.9 to 81.3% by increasing the feed gas flow from 100 to 200 mL/min. The NO_x removal was more complex than the SO₂ removal, as the SO₂ solubility in water was about 700 times higher than that of NO (Fang *et al.*, 2011). A previous study showed a slight decrease in single NO_x removal efficiency from 94.6 to 94.0% by increasing the same feed gas flow rate in a polysulfone HFMM containing 48 fibers using absorbents of H₂O₂ and HNO₃ solutions. It reveals that the presence of SO₂ in the feed gas decreases the efficiency of NO_x removal

due to the competition factor in consuming H_2O_2 as an oxidation agent, as expressed in Equations 5 and 6 (Chen, Chen, and Chiang, 2020; Kartohardjono *et al.*, 2020).

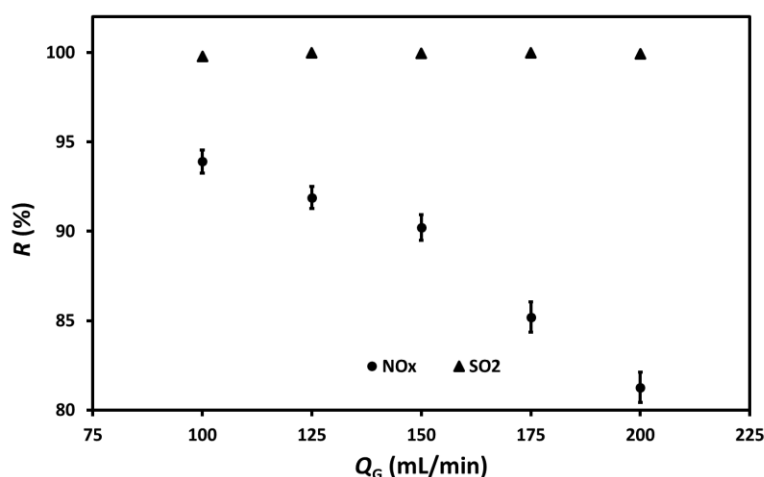


Figure 2 The dependency of NO_x and SO₂ reduction efficiencies, R , on the feed gas flow, Q_G

The amount of absorbed NO_x and SO₂ and mass transfer flux, J , rise with the feed gas flow, as presented in Figure 3. The increase in the feed gas flow increases the number of gas molecules and resulting a higher concentration of the bulk gas. This condition creates a higher concentration driving force, bringing the higher absorbed NO_x and SO₂ and mass transfer flux (Liu *et al.*, 2019). The absorbed NO_x and SO₂ rose from 3.8 to 6.6×10^{-5} mmol/s and 4.1 to 8.1×10^{-5} mmol/s, respectively, by increasing the feed gas flow from 100 to 200 mL/min. Meanwhile, the NO_x and SO₂ flux increased from 4.9 to 8.4×10^{-8} mmol/cm².s and 5.2×10^{-8} to 1.0×10^{-7} mmol/cm².s, respectively, when the feed gas flow rate was increased from 100 to 200 mL/min. A previous study exhibited a similar result: single NO_x flux increased from 5.6×10^{-8} to 1.1×10^{-7} by doubling the feed gas flow from 100 to 200 mL/min in a polysulfone HFMM with 48 fibers containing absorbents of H_2O_2 and HNO_3 solutions. It is also revealed that the existence of SO₂ in the feed gas affects the transfer flux of NO_x (Kartohardjono *et al.*, 2019).

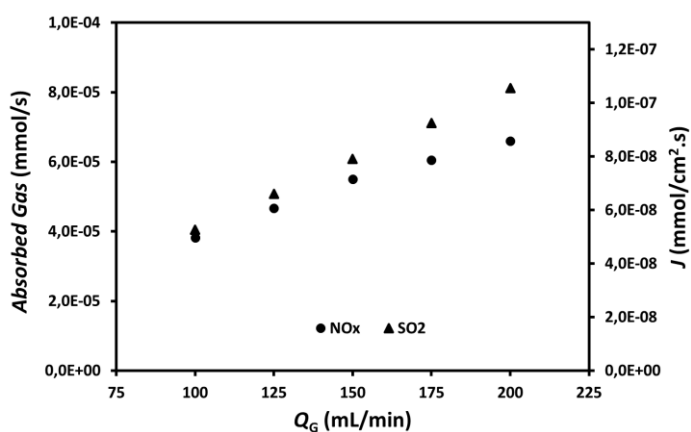


Figure 3 The dependency of absorbed NO_x and SO₂, and mass transfer fluxes, J , on the feed gas flow, Q_G

As with flux, NO_x and SO₂ loading increases with the feed gas flow rate due to the increased amount of absorbed NO_x and SO₂. Figure 4 shows the dependency of NO_x and SO₂ loading on the feed gas flow. The NO_x and SO₂ loading increased from 0.0019 to 0.0033 mmol/mol.s and 0.0020 to 0.0041 mmol/mol.s, respectively, by doubling the feed gas flow

from 100 to 200 mL/min. Similar results were also reported that the NO_x removal increased from 0.002 to 0.004 mmol/mol.s by doubling the feed gas flow rate, containing NO_x 600 ppm, in the PVDF HFMM containing 0.5 wt.% H₂O₂ and 0.5M HNO₃ each of 25 ml (Purnawan *et al.*, 2021).

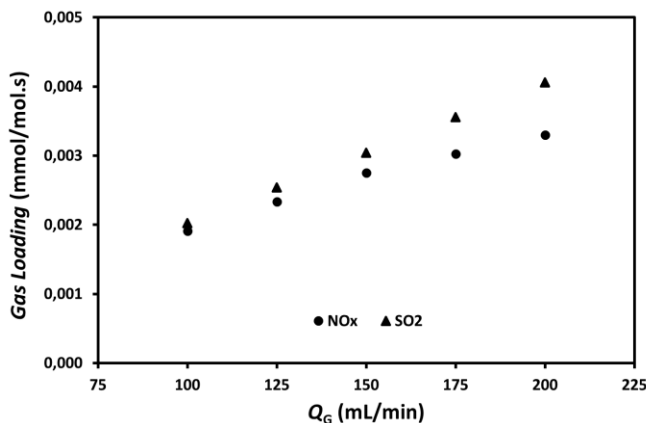


Figure 4 The absorbed NO_x and SO₂ loading dependency on the feed gas flow, Q_G

Figure 5 shows the absorption efficiency (%R) for NO_x and SO₂ as a function of H₂O₂ concentration. The efficiency of NO_x removal increases with the increase in H₂O₂ concentration, while in SO₂ gas, the efficiency is relatively constant with the addition of H₂O₂ concentration. The increase in the concentration of H₂O₂ causes an increase in the number of moles of O₂ produced in the solution to oxidize NO_x. The highest absorption efficiency achieved was 97.53% for NO_x and 99.79% for SO₂ at a 0.1 M H₂O₂ concentration. This study of simultaneous removal of mixed gases (NO_x and SO₂) resulted in a lower %R compared to the utilization of hollow fiber membranes on single-gas NO_x by H₂O₂/HNO₃ solvents in previous studies (Kartohardjono *et al.*, 2019). The absorption efficiency of NO_x gas is about 95% at 0.25% H₂O₂ by mass. In the same polysulfone membrane module and H₂O₂ solvent, it is seen that the absorption efficiency decreases between mixed gas (NO_x and SO₂) and single gas (NO_x only) due to SO₂ compounds competing with NO_x in consuming the absorbent (i.e., H₂O₂ and NaOH).

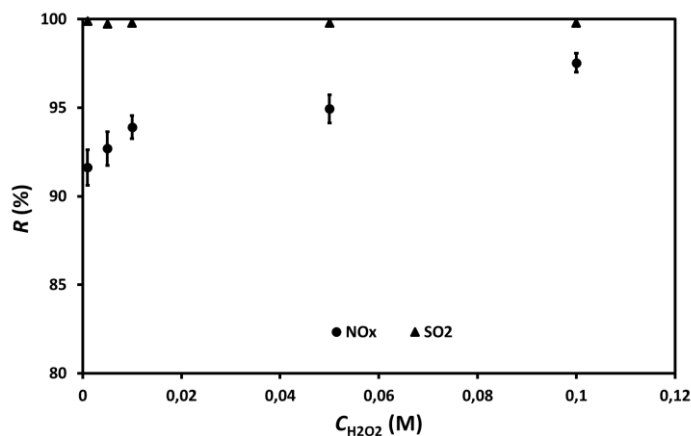


Figure 5 The dependency of NO_x and SO₂ reduction efficiencies, R, on the H₂O₂ concentration in the absorbent solutions at the feed gas flow rate of 0.1 L/min

Figure 6 shows the effect of the concentration of H₂O₂ on the amount of gas absorbed and the mass transfer flux at a feed gas flow rate of 0.1 L/min. The amount of SO₂ gas absorbed and the mass transfer flux of SO₂ was constant, at about 4.05 x 10⁻⁵ mmol/s and

8.98×10^{-8} mmol/cm².s. Meanwhile, the amount of NO_x absorbed and the mass transfer flux of NO_x increased with the increase in the concentration of H₂O₂ in the absorbent solution. The amount of NO_x absorbed and the mass transfer flux of NO_x increased from 3.72 to 3.96×10^{-5} mmol/s and from 8.24 to 8.77×10^{-8} mmol/cm².s. The increase in the amount of absorbed gas and flux is relatively small, so it can be categorized as the concentration of H₂O₂ does not have much effect on the amount of gas absorbed and the flux of NO_x and SO₂. The increasing concentration of H₂O₂ only affects the reaction rate between NO_x with H₂O₂. Compared with other studies (Kartohardjono, 2019), the results also show an insignificant mass transfer flux from 1.153×10^{-9} mmol/cm².s at 0.1% w/w H₂O₂ to 1.486×10^{-9} mmol/cm².s at 0.4% w/w H₂O₂.

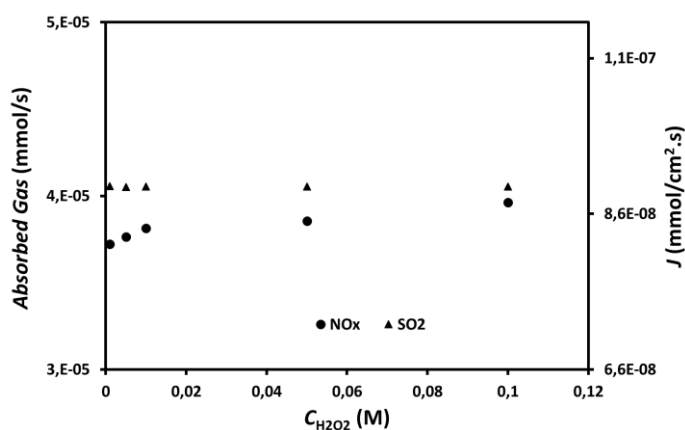


Figure 6 The dependency of NO_x and SO₂ absorbed and flux, J , on the H₂O₂ concentration in the absorbent solutions at the feed gas flow rate of 0.1 L/min.

NO_x and SO₂ loading decreased drastically as the feed gas flow rate increased, as shown in Figure 7. The NO_x loading at a feed gas flow rate of 100 mL/min was 1.86×10^{-3} mmol NO_x per mole H₂O₂ per second. It decreased drastically to 1.98×10^{-4} mmol NO_x per mole H₂O₂ per second if the concentration of H₂O₂ in the absorbent solution increased from 0.001 to 0.1 M. Meanwhile, SO₂ loading decreased drastically from 2.03×10^{-2} mmol SO₂ per mole H₂O₂ per second to 2.03×10^{-4} mmol SO₂ per mole H₂O₂ per second if the concentration of H₂O₂ in the absorbent solution increases from 0.001 to 0.1 M. This decrease occurs because the increase in the amount of NO_x and SO₂ gas absorbed is not proportional to the increase in the concentration of H₂O₂ in the absorbent. Similar results were also reported: the NO_x loading decreased with increasing the concentration of absorbents (Karamah *et al.*, 2021; Purnawan *et al.*, 2021).

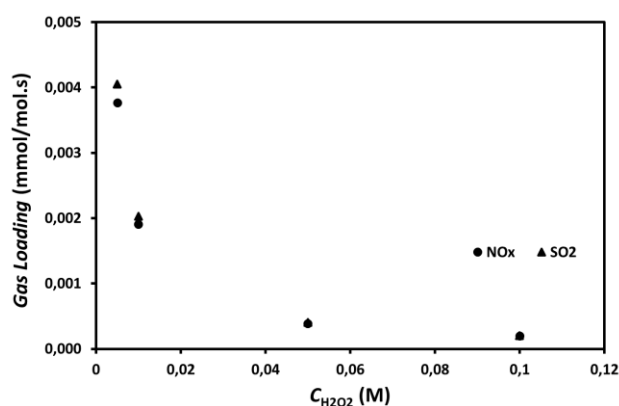


Figure 7 The dependency of NO_x and SO₂ loading on the H₂O₂ concentration in the absorbent solutions at the feed gas flow rate of 0.1 L/min

4. Conclusions

The elimination of NO_x and SO₂ simultaneously can be conducted in an HFMM using absorbents such as H₂O₂ and NaOH. The presence of SO₂ in the feed gas could reduce the removal efficiency of NO_x because of the competition factor in consuming H₂O₂ in the process. The NO_x and SO₂ removal efficiencies decrease with the feed gas flow rate, while the NO_x and SO₂ absorbed, fluxes, and loadings increase with the feed gas flow. This study's maximum NO_x reduction efficiency was 93.9%, while SO₂ can be almost entirely removed. In future work, the methods would be applied to remove NO_x and SO₂ simultaneously from the flue gas resulting from fossil fuel combustion.

Acknowledgments

The authors wish to acknowledge the PDUPT Project via the Directorate of Research and Services Universitas Indonesia through Contract No. NKB-213/UN2.RST/HKP.05.00/2021.

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