International Journal of Technology 14(3) 576-583 (2023)
Received February 2022 / Revised March 2022 / Accepted April 2022

International Journal of Technology

http://ijtech.eng.ui.ac.id

The Simultaneously Removal of NOx and SO_2 Processes through a Polysulfone Hollow Fiber Membrane Module

Sutrasno Kartohardjono[1*], Eva Fathul Karamah[1], Grace Nathalie Talenta[1], Thariq Ahmad Ghazali[1], Woei Jye Lau[2]

[1]*Process Intensification Laboratory, Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia*
[2]*Advance Membrane Technology Research Center, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*

Abstract. Hazardous pollutants such as NOx (NO and NO_2) and SO_2 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 SO_2 and NOx. The study aims to examine the performance of polysulfone membranes in removing NOx and SO_2 simultaneously using hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) solutions as absorbents. The presence of H_2O_2 and NaOH in absorbent solutions plays a role in oxidizing NOx into soluble species in water and in absorbing SO_2 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 NOx and SO_2 and the absorbent. The experimental results showed that the presence of SO_2 affected the NOx reduction efficiency. The NOx and SO_2 removal efficiencies decreased with the feed gas flow. This study's maximum NOx and SO_2 reduction efficiencies were 93.9 and 99.8%, respectively.

Keywords: Air pollution; H_2O_2; NOx; Removal efficiency; SO_2

1. Introduction

Air pollution in Indonesia increases yearly due to growing public energy consumption. Hazardous pollutants such as NOx (NO and NO_2) and SO_2 generally come from fossil combustion, harm the human respiratory system, and damage environmental ecosystems (Manisalidis *et al.*, 2020; Wang, Wang, and Shammas, 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 NOx and SO_2, 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 NOx and SO_2 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 NOx and SO_2 emissions requires two different technologies, namely SO_2

*Corresponding author's email: sutrasno@che.ui.ac.id, Tel.: 6221-7863516; Fax: 6221-7863515
doi: 10.14716/ijtech.v14i3.5544

reduction using FGD (Flue Gas Desulfurization) and NOx 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 NOx and SO_2 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 NOx and SO_2 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 NOx in water is lower than that of SO_2 (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 NOx using H_2O_2 and HNO_3 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 NOx and the absorbent. NO (nitrogen monoxide) in NOx 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 (H_2O_2). The H_2O_2 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 NOx and SO_2 simultaneously (Park *et al.*, 2019; Si *et al.*, 2019). In order to remove NOx and SO_2 simultaneously, an absorbent that can oxidize NOx into water-soluble species and an alkaline solution that can absorb SO_2 are required. This study utilized the polysulfone hollow fiber membrane module to remove NOx and SO_2 simultaneously using absorbents consisting of H_2O_2 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 SO_2 in the feed gas on NOx removal compared to NOx removal alone. The NaOH solution absorbs the reaction products between NOx gas and SO_2 and H_2O_2. Reactions (1-7) are reactions that may occur in the process of simultaneously removing NOx and SO_2 using a mixture of H_2O_2 and NaOH as absorbents: (Kartohardjono *et al.*, 2020; Sun, Zwolińska, and Chmielewski, 2016):

$$2NO_2 \leftrightarrow N_2O_4 \quad (1)$$

$$NO + NO_2 \leftrightarrow N_2O_3 \quad (2)$$

$$NO + NO_2 + H_2O \leftrightarrow 2HNO_2 \quad (3)$$

$$3HNO_2 \leftrightarrow 2NO + HNO_3 + H_2O \quad (4)$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \quad (5)$$

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \quad (6)$$

$$HNO_3 + H_2SO_4 + 3NaOH \rightarrow NaNO_3 + Na_2SO_4 + 3H_2O \quad (7)$$

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 NOx and 500 ppm of SO_2 in nitrogen, was supplied from PT EIN Jakarta, Indonesia. The chemicals used, H_2O_2 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 NOx, SO_2, H_2O_2, and NaOH, as shown in Reaction (1-8). The concentrations of NOx and SO_2 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 NOx and SO_2 gases, *Gas*Abs, removal efficiency, *R*, fluxes, *J*, and NOx and SO_2 loading, *Gas-loading*, can be calculated by Equations 8-11 (Kartohardjono *et al.*, 2020; Ding *et al.*, 2014):

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

$$R = \frac{X_{in}-X_{out}}{X_{in}} x100\% \quad (9)$$

$$J = \frac{Gas_{Abs}}{Am} \quad (10)$$

$$Gas - loading = \frac{Gas_{Abs}}{molH_2O_2} \quad (11)$$

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.

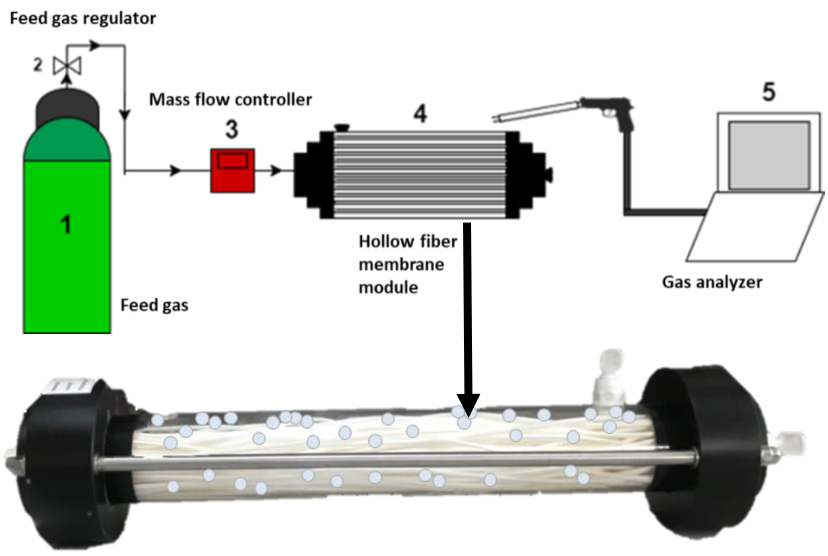

Figure 1 The experimental diagram schematic

3. Results and Discussion

Figure 2 shows the effect of the feed gas flow rate, containing 500 ppm SO_2 and 600 ppm NOx, on the simultaneous removal of SO_2 and NOx in the HFMM, which contains 0.1M of H_2O_2 and 0.5 M NaOH each of 200 ml. As demonstrated in Figure 2, the NOx 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 SO_2 removal efficiency is relatively constant to the feed gas flow rate changes because it is already close to 100%. The removal efficiency of SO_2 depends not only on the oxidant (H_2O_2), 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 NOx absorption efficiency decreases from 93.9 to 81.3% by increasing the feed gas flow from 100 to 200 mL/min. The NOx removal was more complex than the SO_2 removal, as the SO_2 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 NOx 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 H_2O_2 and HNO_3 solutions. It reveals that the presence of SO_2 in the feed gas decreases the efficiency of NOx 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).

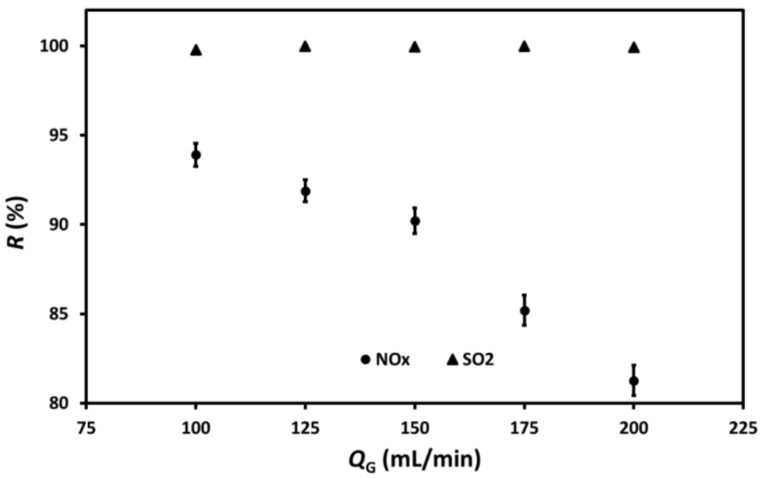

Figure 2 The dependency of NOx and SO_2 reduction efficiencies, R, on the feed gas flow, Q_G

The amount of absorbed NOx and SO_2 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 NOx and SO_2 and mass transfer flux (Liu *et al.*, 2019). The absorbed NOx and SO_2 rose from 3.8 to 6.6 x 10^{-5} mmol/s and 4.1 to 8.1 x 10^{-5} mmol/s, respectively, by increasing the feed gas flow from 100 to 200 mL/min. Meanwhile, the NOx and SO_2 flux increased from 4.9 to 8.4 x 10^{-8} mmol/cm^2.s and 5.2 x 10^{-8} to 1.0 x 10^{-7} mmol/cm^2.s, respectively, when the feed gas flow rate was increased from 100 to 200 mL/min. A previous study exhibited a similar result: single NOx flux increased from 5.6 x 10^{-8} to 1.1 x 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 SO_2 in the feed gas affects the transfer flux of NOx (Kartohardjono *et al.*, 2019).

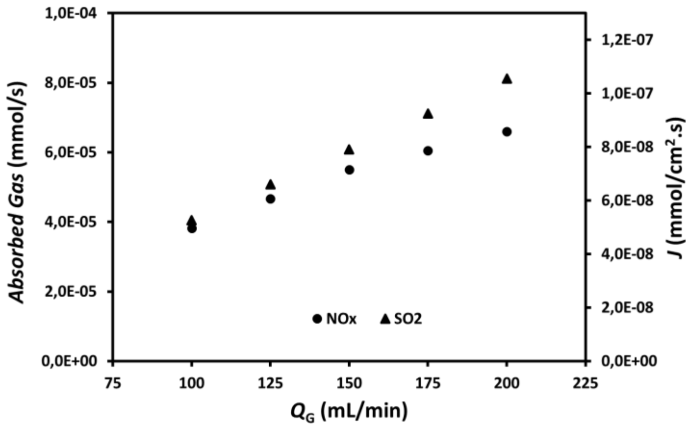

Figure 3 The dependency of absorbed NOx and SO_2, and mass transfer fluxes, J, on the feed gas flow, Q_G

As with flux, NOx and SO_2 loading increases with the feed gas flow rate due to the increased amount of absorbed NOx and SO_2. Figure 4 shows the dependency of NOx and SO_2 loading on the feed gas flow. The NOx and SO_2 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 NOx removal increased from 0.002 to 0.004 mmol/mol.s by doubling the feed gas flow rate, containing NOx 600 ppm, in the PVDF HFMM containing 0.5 wt.% H_2O_2 and 0.5M HNO_3 each of 25 ml (Purnawan *et al.,* 2021).

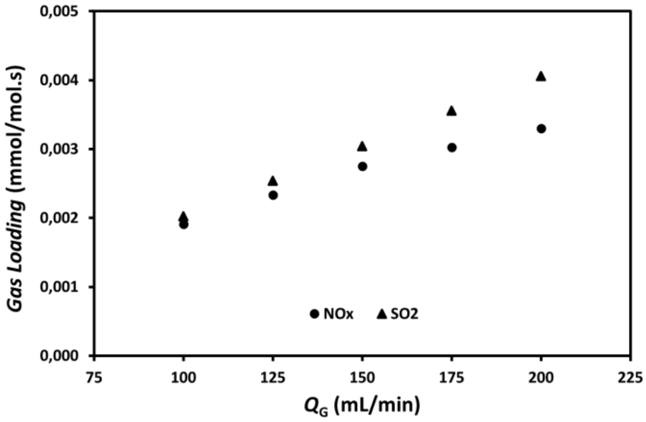

Figure 4 The absorbed NOx and SO_2 loading dependency on the feed gas flow, Q_G

Figure 5 shows the absorption efficiency (%R) for NOx and SO_2 as a function of H_2O_2 concentration. The efficiency of NOx removal increases with the increase in H_2O_2 concentration, while in SO_2 gas, the efficiency is relatively constant with the addition of H_2O_2 concentration. The increase in the concentration of H_2O_2 causes an increase in the number of moles of O2 produced in the solution to oxidize NOx. The highest absorption efficiency achieved was 97.53% for NOx and 99.79% for SO_2 at a 0.1 M H_2O_2 concentration. This study of simultaneous removal of mixed gases (NOx and SO_2) resulted in a lower %R compared to the utilization of hollow fiber membranes on single-gas NOx by H_2O_2/HNO_3 solvents in previous studies (Kartohardjono *et al.,* 2019). The absorption efficiency of NOx gas is about 95% at 0.25% H_2O_2 by mass. In the same polysulfone membrane module and H_2O_2 solvent, it is seen that the absorption efficiency decreases between mixed gas (NOx and SO_2) and single gas (NOx only) due to SO_2 compounds competing with NOx in consuming the absorbent (i.e., H_2O_2 and NaOH).

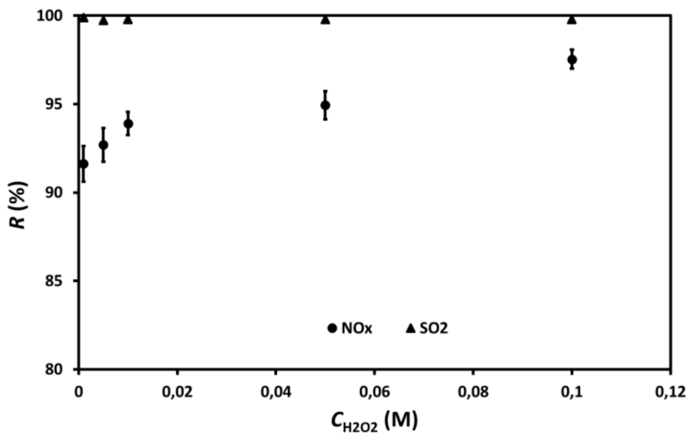

Figure 5 The dependency of NOx and SO_2 reduction efficiencies, *R*, on the H_2O_2 concentration in the absorbent solutions at the feed gas flow rate of 0.1 L/min

Figure 6 shows the effect of the concentration of H_2O_2 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 SO_2 gas absorbed and the mass transfer flux of SO_2 was constant, at about 4.05 x 10^{-5} mmol/s and

8.98 x 10^{-8} mmol/cm^2.s. Meanwhile, the amount of NOx absorbed and the mass transfer flux of NOx increased with the increase in the concentration of H_2O_2 in the absorbent solution. The amount of NOx absorbed and the mass transfer flux of NOx increased from 3.72 to 3.96 x 10^{-5} mmol/s and from 8.24 to 8.77 x 10^{-8} mmol/cm^2.s. The increase in the amount of absorbed gas and flux is relatively small, so it can be categorized as the concentration of H_2O_2 does not have much effect on the amount of gas absorbed and the flux of NOx and SO_2. The increasing concentration of H_2O_2 only affects the reaction rate between NOx with H_2O_2. Compared with other studies (Kartohardjono, 2019), the results also show an insignificant mass transfer flux from 1.153 x 10^{-9} mmol/cm^2.s at 0.1% w/w H_2O_2 to 1.486 x 10^{-9} mmol/cm^2.s at 0.4% w/w H_2O_2.

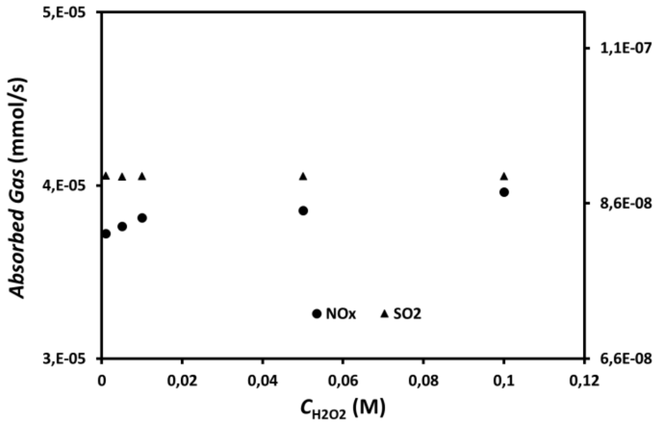

Figure 6 The dependency of NOx and SO_2 absorbed and flux, *J*, on the H_2O_2 concentration in the absorbent solutions at the feed gas flow rate of 0.1 L/min.

NOX and SO_2 loading decreased drastically as the feed gas flow rate increased, as shown in Figure 7. The NOx loading at a feed gas flow rate of 100 mL/min was 1.86 x 10^{-3} mmol NOx per mole H_2O_2 per second. It decreased drastically to 1.98 x 10^{-4} mmol NOx per mole H_2O_2 per second if the concentration of H_2O_2 in the absorbent solution increased from 0.001 to 0.1 M. Meanwhile, SO_2 loading decreased drastically from 2.03 x 10^{-2} mmol SO_2 per mole H_2O_2 per second to 2.03 x 10^{-4} mmol SO_2 per mole H_2O_2 per second if the concentration of H_2O_2 in the absorbent solution increases from 0.001 to 0.1 M. This decrease occurs because the increase in the amount of NOx and SO_2 gas absorbed is not proportional to the increase in the concentration of H_2O_2 in the absorbent. Similar results were also reported: the NOx loading decreased with increasing the concentration of absorbents (Karamah *et al.,* 2021; Purnawan *et al.,* 2021).

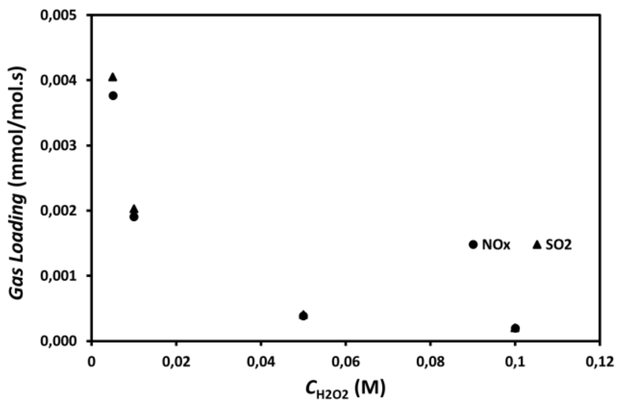

Figure 7 The dependency of NOx and SO_2 loading on the H_2O_2 concentration in the absorbent solutions at the feed gas flow rate of 0.1 L/min

4. Conclusions

The elimination of NOx and SO_2 simultaneously can be conducted in an HFMM using absorbents such as H_2O_2 and NaOH. The presence of SO_2 in the feed gas could reduce the removal efficiency of NOx because of the competition factor in consuming H_2O_2 in the process. The NOx and SO_2 removal efficiencies decrease with the feed gas flow rate, while the NOx and SO_2 absorbed, fluxes, and loadings increase with the feed gas flow. This study's maximum NOx reduction efficiency was 93.9%, while SO_2 can be almost entirely removed. In future work, the methods would be applied to remove NOx and SO_2 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.

References

Brandenberger, S., Kröcher, O., Tissler, A., Althoff, R., 2008. The state of the art in selective catalytic reduction of NOx by ammonia using metal-exchanged zeolite catalysts. *Catalysis Reviews,* Volume 50(4), pp. 492–531

Chang, M.B., Lee, H.M., Wu, F., Lai, C.R., 2004. Simultaneous removal of nitrogen oxide/nitrogen dioxide/sulfur dioxide from gas streams by combined plasma scrubbing technology. *Journal of the Air & Waste Management Association,* Volume 54(8), pp. 941–949

Chen, T.-L., Chen, Y.-H., Chiang, P.-C., 2020. Enhanced performance on simultaneous removal of NOx-SO2-CO2 using a high-gravity rotating packed bed and alkaline wastes towards green process intensification. *Chemical Engineering Journal,* Volume 393, p. 124678

Cheng, G., Zhang, C., 2018. Desulfurization and denitrification technologies of coal-fired flue gas. *Polish Journal of Environmental Studies*, Volume 27(2), pp. 481–489

Ding, J., Zhong, Q., Zhang, S., Song, F., Bu, Y., 2014. Simultaneous removal of NOx and SO_2 from coal-fired flue gas by catalytic oxidation-removal process with H_2O_2. *Chemical Engineering Journal,* Volume 243, pp. 176–182

Fang, P., Cen, C., Tang, Z., Zhong, P., Chen, D., Chen, Z., 2011. Simultaneous removal of SO_2 and NOx by wet scrubbing using urea solution. *Chemical Engineering Journal,* Volume 168(1), pp. 52–59

Febriasari, A., Huriya, Ananto, A.H., Suhartini, M., Kartohardjono, S., 2021. Polysulfone-polyvinyl pyrrolidone blend polymer composite membranes for batik industrial wastewater treatment. *Membranes,* Volume 11(1), pp. 1–17

Huang, X., Ding, J., Zhong, Q., 2015. Catalytic decomposition of H_2O_2 over Fe-based catalysts for simultaneous removal of NO_X and SO_2. *Applied Surface Science,* Volume 326, pp. 66–72.

Karamah, E.F., Arbi, D.S., Bagas, I., Kartohardjono, S., 2021. Hollow fiber membrane modules for NOx removal using a mixture of $NaClO_3$ and NaOH solutions in the shell side as absorbents. *International Journal of Technology,* Volume 12(4), pp. 690–699

Kartohardjono, S., Merry, C., Rizky, MS., Pratita, C.C., 2019. Nitrogen oxide reduction through absorbent solutions containing nitric acid and hydrogen peroxide in hollow fiber membrane modules. *Heliyon,* Volume 5(12), p. e02987

Kartohardjono, S., Paramitha, A., Putri, AA., Andriant, R., 2017. Effects of absorbent flow rate on CO_2 absorption through a super hydrophobic hollow fiber membrane contactor. *International Journal of Technology,* Volume 8(8), pp. 1429–1435

Kartohardjono, S., Rizky, M.S., Karamah, E.F., Lau, W.-J., 2020. The effect of the number of fibers in hollow fiber membrane modules for NOx absorption. *Chemical Engineering,* Volume 11(2), pp. 269–277

Krzyzynska, R. Hutson, N.D., 2012. Effect of solution pH on SO_2, NOx, and Hg removal from simulated coal combustion flue gas in an oxidant-enhanced wet scrubber. *Journal of the Air & Waste Management Association,* Volume 62(2), pp. 212–220

Li, Y., Che, D., Zhao, H., Yang, C., Zhao, T., Cheng, G., Yao, M., 2020. Tributyl phosphate additive enhancing catalytic absorption of NO_2 for simultaneous removal of SO_2/NOx in wet desulfurization system. *Journal of the Energy Institute,* Volume 932, pp. 474–481

Liu, X., Zhu, T., Lv, Q., Li, Y., Che, D., 2019. Simultaneous removal of NOx and SO_2 from coal-fired flue gas based on the catalytic decomposition of H_2O_2 over Fe_2 MoO_{43}. *Chemical Engineering Journal,* Volume 371, pp. 486–499

Manisalidis, I., Stavropoulou, E., Stavropoulos, A., Bezirtzoglou, E., 2020. Environmental and health impacts of air pollution: a review. *Frontiers in public health*, Volume 8, p. 14

Park, J.-H., Ahn, J.-W., Kim, K.-H., Son, Y.-S., 2019. Historic and futuristic review of electron beam technology for the treatment of SO_2 and NOx in flue gas. *Chemical Engineering Journal,* Volume 355, pp. 351–366

Purnawan, I., Kartohardjono, S., Wibowo, L., Ramadhani, A.F., Lau, W.J., Febriasari, A., 2021. Effect of absorbents on NOx removal through polyvinylidene fluoride PVDF hollow fiber membrane modules. *International Journal of Chemical Engineering,* Volume 2021, p. 8277082

Republic of Indonesia (RI), 1999. Government Regulation No. 41 of 1999 concerning Air Pollution Control. pp. 1–34

Serbanescu, O.S., Voicu, SI., Thakur, V.K., 2020. Polysulfone functionalized membranes: Properties and challenges. *Materials Today Chemistry,* Volume 17, p. 100302

Sharma, S.B., Jain, S., Khirwadkar, P., Kulkarni, S., 2013. The effects of air pollution on the environment and human health. *Indian Journal of Research in Pharmacy and Biotechnology,* Volume 13, pp. 391–396

Si, T., Wang, C., Yan, X., Zhang, Y., Ren, Y., Hu, J., Anthony, E. J., 2019. Simultaneous removal of SO_2 and NOx by a new combined spray-and-scattered-bubble technology based on preozonation: From lab scale to pilot scale. *Applied Energy*, Volume 242, pp. 1528–1538

Sun, Y., Zwolińska, E., Chmielewski, A.G., 2016. Abatement technologies for high concentrations of NOx and SO2 removal from exhaust gases: A review. *Critical Reviews in Environmental Science and Technology,* Volume 46(2), pp. 119–142

Sunarno, S., Purwanto, P., Suryono, S. 2021., Trend analysis of NO_X and SO_2 emissions in Indonesia from the period of 1990 -2015 using data analysis tool. *Advances in Science, Technology and Engineering Systems Journal,* Volume 61, pp. 257–263

Wang, M.-H. S., Wang, L.K., Shammas, N.K., 2019. Glossary of acid rain management and environmental protection. In: *Handbook of environment and waste management: Acid rain and greenhouse gas pollution control*, Hung, Y.T., Wang, L.K., Shammas, N.K., (ed.), World Scientific, Cleveland, USA, pp. 719-749

Wu, Y., Chu, B., Zhang, M., Yi, Y., Dong, L., Fan, M., Jin, G., Zhang, L., Li, B., 2019. Influence of calcination temperature on the catalytic properties of $LaCu0.25Co0.75O_3$ catalysts in NOx reduction. *Applied Surface Science,* Volume 481, pp. 1277–1286

Zhao, M., Xue, P., Liu, J., Liao, J., Guo, J., 2021. A review of removing SO_2 and NO_X by wet scrubbing. *Sustainable Energy Technologies and Assessments,* Volume 47, p. 101451