Hollow Fiber Membrane Modules for NOx Removal using a Mixture of NaClO$_3$ and NaOH Solutions as Absorbents

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Abstract. Nitrogen oxide (NOx) is one of the polluting gases harmful to humans and the environment. Nitrous oxide gas is mostly found in air, namely nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$). NOx gas in the air, which mostly comes from exhaust gases, needs to be reduced to minimize the hazards to humans and the environment and comply with applicable regulations regarding hazards. The absorption process with a membrane contactor is an alternative to reduce NOx concentrations in the air. This study evaluates the hollow fiber membrane modules' performance in the NOx absorption process using sodium chlorate (NaClO$_3$) and sodium hydroxide (NaOH) as an absorbent solution. Based on the experimental results, the NOx reduction efficiency increased with an increase in the absorbent concentration and the amount of fibers in the membrane module but declined with an increase in the feed gas flow rate. The highest value of NOx reduction efficiency, the overall mass transfer coefficient, the flux, and the NOx loading obtained in the study were 99.7%, 0.01743 cm s$^{-1}$, $9.510 \times 10^{-8}$ mmole cm$^{-2}$ s$^{-1}$, and 0.026 mole NOx/mole NaClO$_3$, respectively.

Keywords: Absorption efficiency; hollow fiber membrane module; NaClO$_3$; NaOH; NOx

1. Introduction

In the 21st century, air pollution has become one of the global community's problems of concern. Pollutants cause air pollution from harmful gases, one of which is a nitrogen oxide (NOx) such as NO and NO$_2$. NOx gas is generally formed from the combustion process with a high temperature above 300°C (Tan, Guo, Liu, Feng, & Li, 2019). The primary source of NOx gas, namely 55%, comes from the combustion of motor vehicles, and 45% comes from the combustion process in the industry. High NOx levels in the atmosphere are the leading cause of acid rain, smog formation, decreased water quality, and global warming (Gao et al., 2018; Mohan, Dinesha, & Kumar, 2020; Skalska, Miller, & Ledakowicz, 2010; Sun et al., 2019). Moreover, exposure to NOx gas with a concentration in 50-100 ppm can cause lung inflammation from a health aspect. If the NOx concentration reaches 500 ppm, it is inevitable that the people who inhaled it will die within 2 - 10 days (Shaw & Chadwick, 1998).

Various technologies have been developed to reduce the NOx concentration in the air. These technological developments include dry methods such as Selective Catalytic Reduction & Selective Non-catalytic Reduction (Brandenberger, Kröcher, Tissler, & Althoff, 2008; Cheng & Bi, 2014; Jug, Homann, & Bredow, 2004; Roy & Baiker, 2009), and wet
methods such as absorption using absorbents (Fangyang, Jiali, Wei, Jiyun, & Jianfeng, 200; Kartohardjono, Merry, Rizky, & Pratita, 2019). The SCR method uses NH₃ as a reducing agent over catalysts based on V₂O₅-WO₃/TiO₂ or Cu- and Fe-zeolite, which is very efficient to reduce NOx but requires high temperatures around 300 to 400 °C (Grossale, Nova, & Tronconi, 2008; Mehring, Elsener, & Kröcher, 2012; Z.-y. Wang et al., 2019). The dry methods widely used are low-NOx burners and selective catalytic reduction (SCR), which have the disadvantages of low efficiency and high investment costs, respectively, making the wet methods attractive to many researchers (L. Guo et al., 2018; Kartohardjono, Merry, et al., 2019). The wet methods through absorption in the conventional gas-liquid contactor still have disadvantages such as the relatively low contact surface area between 25 - 75 ft²/ft³, thereby reducing the mass transfer. One alternative technology for NOx gas absorption that increase the contact surface area is using a membrane module as a gas-liquid contactor (Cai et al., 2019).

Several previous studies have been conducted regarding the absorption of NOx through a membrane contactor using a mixture of solutions functions as an oxidizer and absorbent. The effective oxidizing agents include NaClO₃, NaClO₂, KMnO₄, and H₂O₂; with the addition of NaOH or HNO₃ as absorbent (Kartohardjono, Merry, et al., 2019; Kartohardjono, Rizky, Karamah, & Lau, 2020; Yan, Chen, Zhang, O’Hare, & Wang, 2018). NaClO₃ and NaClO₂ showed good NOx absorption efficiency (> 90%) with the bubble column reactor media. A study by Shi et al. (Shi, Sun, & Cui, 2019) with NaClO₃/NaOH solvents conducted in the bubble column reactor media showed promising results with the highest NOx absorption efficiency achieved, namely 91.5%. This study investigates the hollow fiber membrane modules’ performance with polysulfone-based-material in the NOx gas absorption process using a mixture of NaClO₃ and NaOH solutions as absorbent. The reaction mechanism of NOx absorption by NaClO₃ that may occur as follows (Shi et al., 2019):

1. \( \text{NaClO}_3 + \text{H}^+ \leftrightarrow \text{Na}^+ + \text{HClO}_3 \)  
2. \( 13\text{NO} + 6\text{HClO}_3 + 5\text{H}_2\text{O} \rightarrow 6\text{HCl} + 3\text{NO}_2 + 10\text{HNO}_3 \)  
3. \( 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \)  
4. \( 2\text{NO} + \text{H}_2\text{O} + \text{HClO}_3 \rightarrow \text{HCl} + 2\text{HNO}_3 \)  
5. \( 2\text{NO} + \text{H}_2\text{O} + \text{NaClO}_3 + \text{H}^+ \rightarrow \text{Na}^+ + \text{HCl} + 2\text{HNO}_3 \)  
6. \( \text{NaClO}_3 + 2\text{NO} + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NaCl} \)

This study also aims to see the effect of NOx gas flow rate, solvent concentration, and the number of fibers on the NOx absorption performance, such as NOx absorption efficiency (\( R \)), mass transfer coefficient (\( k_0 \)), mass transfer flux (\( J \)), and NOx loading.

2. Methods

Figure 1 shows an experimental schematic for removing NOX from gas flow through a hollow fiber membrane module. The membrane modules used contained 50, 100, and 150 fibers, polysulfone-based and measuring 0.18 and 0.20 inside and outside diameters, purchased from GDP Filter Bandung, Indonesia. The NaClO₃ and NaOH used are supplied by Merck, Indonesia, while the gas feed, which contains NOx of around 560 ppm, is purchased from Energi Indogas Nusantara. During the experiment, the feed gas entered the membrane module through the lumen fibers, and the flow rate was adjusted using the CX series mass flow controller, Shanghai Instrument, while the composition was measured using the Gas Analyzer, Ecom-D. The fiber lumen’s feed gas then penetrates the membrane module’s fiber on the shell’s side, containing the absorbent solution to occur between the NOx gas and the absorbent solution. The feed gas flow rate variations applied in the experiment were 100,
Absorption efficiency ($R$) of NOx is one of the parameters to determine the amount of NOx gas absorbed by the absorbent in the hollow fiber membrane module. This parameter shows the ratio between the amount of NOx gas absorbed by the solvent and the amount of NOx gas in the feed. The higher the absorption efficiency indicates, the better the NOx absorption process. Other parameters observed in the experiment are the overall mass transfer coefficient, $K_G$, flux, $J$, and NOx loading, which are all calculated by (Kartohardjono, Merry, et al., 2019; D. Wang, Teo, & Li, 2004; Y. Wang & Yu, 2017):

$$R = \frac{C_{NOx_in} - C_{NOx_out}}{C_{NOx_in}}$$

(7)

$$K_G = \frac{Q_G}{A_m} \ln \left( \frac{C_{NOx_in}}{C_{NOx_out}} \right)$$

(8)

$$J = \frac{(C_{NOx_in} - C_{NOx_out})}{A_m} \frac{Q_G}{RT}$$

(9)

$$NOX_{loading} = \frac{\text{mole } NOX_{abs}}{\text{mole NaClO}_3}$$

(10)

$$\text{mole } NOX_{abs} = (C_{NOx_in} - C_{NOx_out}) \frac{Q_G}{RT}$$

(11)

$C_{NOx_in}$, $C_{NOx_out}$, $Q_G$, and $A_m$ are the concentration of NOx inlet and outlet of the membrane module, the feed gas flow rate, and the membrane surface area, respectively. Meanwhile, $P$, $T$, and $R$ are atmospheric pressure, temperature, and ideal gas constant, respectively.

Figure 1 Experiment set-up and apparatus: 1. Feed gas containing NOx of around 560 ppm; 2. Valve; 3. Mass flow controller; 4. Hollow fiber membrane module; 5. Gas analyzer.

3. Results and Discussion

3.1. Effects of Feed Gas Flow Rate

Figure shows the dependence of the NOx reduction efficiency on feed gas flow and the amount of fibers in the membrane module. As shown in Fig. 2, the NOx absorption efficiency declines with an increase in the flow rate of the feed gas. The process of gas transfer to the gas-liquid membrane contactor occurs in three stages: (a) the gas is transferred to the inner surface of the fibers; (b) the gas diffuses through the pores of the fibers; and (c) the gas is absorbed in the shell side of membrane module by absorbent, where the reaction occurred as shown in Eq. (1-6) (Kartohardjono, Merry, et al., 2019; Kartohardjono, Saksono, Supramono, & Prawati, 2019; Y. Wang & Yu, 2017). Of the three stages of the process, one
of the factors influencing the mass transfer process is the gas's residence time in the membrane fibers. The longer the gas's residence time in the membrane module, the better the transfer process due to the longer contact time between the gas and the membrane surface.

The experimental results indicated that an increase in the NOx gas flow rate reduced NOx absorption efficiency. The NOx reduction efficiency decreases with increasing the flow rate of feed gas due to the less residence time of the gas in the membrane fibers, which reduces the time for gas-absorbent contact so that the less NOx gas is absorbed (Kartohardjono, Merry, et al., 2019; Kartohardjono et al., 2020). The efficiency of NOx absorption in the study decreased from 99.6 to 98.9% if the flow rate of feed gas was increased from 0.1 to 0.2 L/min in the membrane module containing 100 fibers and 150 ml solutions of 0.05 M NaClO$_3$ and NaOH, respectively. Previous studies also showed a similar trend where NOx's absorption efficiency decreased from 98% to 94% using the same membrane module containing 150 ml of 0.25 wt.% H$_2$O$_2$ and 0.25 M HNO$_3$ solution as absorbent (Kartohardjono, Merry, et al., 2019). Meanwhile, another study reported NO removal efficiency declined from about 91% to 9% when the flow rate of feed gas increased from 0.05 to 0.25 L/min in a hollow fiber membrane module of polypropylene-based using the NO concentration in the feed gas of about 184.8 ppm, and the absorbent solution contains a mixture of 5 wt.% NaCl and 0.2 wt.% H$_2$O$_2$ (Y. Wang & Yu, 2017). Figure 2 also demonstrated that the efficiency of NOx absorption enhances with the increasing amount of fibers due to the increase in the gas-liquid phases' contact area in the hollow fiber membrane, thereby increasing NOx gas absorbed, leading to an increase in the NOx absorption efficiency (Kartohardjono et al., 2020).

Figure 2 The influences of the flow rate of the feed gas, $Q_G$, on the NOx removal efficiency, $R$, at various number of fibers in the membrane modules containing 150 mL of 0.05 M NaClO$_3$ and NaOH solutions

Figure 3 shows the dependence of the overall mass transfer coefficient and flux on feed gas flow and the number of fibers in the membrane module. The overall mass transfer coefficient and flux, as shown in Figure 3, increases with an increase in the flow rate of feed gas due to decreasing the gas-liquid boundary layer's thickness, thereby decreasing the mass transfer resistance. Figure 3 also presents that the overall mass transfer coefficient and flux declines with the increasing amount of membrane fibers used. The increasing number of membrane fibers means the gas-liquid phases contact area also increases, which causes the thickness of the gas-liquid boundary layer formed in the membrane fibers...
resulting gas transfer process that does not occur in the whole solvent but only occurs in the thin layer of the gas-liquid phases until it becomes saturated (Zhang et al., 2014). Figure 3 also shows that an increase in the feed gas flow rate also increases the overall mass transfer coefficient and flux due to the decrease in the boundary layer thickness in the gas phase, which leads to increasing the overall mass transfer coefficient and flux. The amount of NOx present in the feed gas increases with the feed gas flow rate, thereby increasing the NOx transfer’s driving force, which leads to increasing the overall mass transfer coefficient and flux. The thickness of the gas-liquid boundary layer decreases as the feed gas flow rate increases, enhancing the gas diffusion process (Kartohardjono et al., 2020). Similar results were also presented by Fangyang et al., where the flux of NOx increased from about 7.0 to 16.5 mole m$^{-2}$ h$^{-1}$ when the feed gas flow rate increased from about 60 to 200 cm$^3$ min$^{-1}$ in the ceramic membrane module using absorbent of 5 wt.% NaCl and 0.2 wt.% H$_2$O$_2$; the flow rate of absorbent of 40 cm$^3$ min$^{-1}$; and temperature of absorbent of 343 K (Fangyang et al., 2020). The overall mass transfer coefficient and flux, as presented in Fig. 2, declines with increasing the amount of fibers in the membrane module due to the increment in the gas-liquid contact area (Kartohardjono, Merry, et al., 2019).

\[ \text{Figure 3} \] The influences of the feed gas flow rate, $Q_G$, on the overall mass transfer coefficient, $K_G$, and flux, $J$, on the various amount of fibers in the membrane modules containing 150 mL of 0.05 M NaClO$_3$ and NaOH solutions

The dependence of NOx loading on the flow rate of the feed gas is demonstrated in Figure 4. The solvents used in the study were NaClO$_3$ and NaOH solutions. This parameter is determined by calculating the ratio of moles of NOx absorbed and the moles of absorbent used. The number of moles of solvent used in the calculation is only NaClO$_3$ species due to its role as an oxidizing agent for NOx gas based on the reaction (Shi et al., 2019):

\[ 2\text{NO} + \text{ClO}_3^- + 2\text{OH}^- \rightarrow 2\text{NO}_3^- + \text{Cl}^- + \text{H}_2\text{O} \]  \hspace{1cm} (12)

\[ 2\text{NO} + \text{NaClO}_3 + 2\text{NaOH} \rightarrow 2\text{NaNO}_3 + \text{NaCl} + \text{H}_2\text{O} \]  \hspace{1cm} (13)

As shown in Figure 4, the NOx loading increases with increasing the flow rate of the feed gas due to an increase in the concentration gradient in the gas-liquid phases and decreased the boundary layer’s thickness, which enhances the mass transfer process (Kartohardjono, Merry, et al., 2019). The mass transfer enhancement leads to an increase in the amount of NOx absorbed by the absorbents and finally increase the NOx loading. The NOx loading also increases with an increase in the amount of fibers used due to an increase in the gas-liquid
contact area. The higher the gas-liquid contact area, the more NOx can be absorbed by the solvent, which leads to an increase in NOx loading (Kartohardjono, Paramitha, Putri, & Andriant, 2017).

![Figure 4](image)

**Figure 4** The influences of the feed gas flow rate, $Q_G$, on the NOx loading at various membrane modules containing 150 mL of 0.05 M NaClO$_3$ and NaOH solutions.

The change in absorbents $pH$ for 1 hour of the absorption process is shown in Figures 5. The reaction occurred between NOx and NaClO$_3$ and NaOH during the absorption process to produce NO$_3^-$ and Cl$^-$ as presented in Eq. (12 and 13), causing a decrease in $pH$, as demonstrated in Figure 5. Figure 5a shows that as the number of fibers increases, the final measured $pH$ tends to decrease due to more NOx absorbed. As a result, more NOx in the feed gas reacts with the absorbents to increase NaNO$_3$ and NaCl products, which increase the $pH$ drop. Figure 5b, on the other hand, shows that the higher the flow rate of the feed gas, the lesser decrease in absorbent $pH$ due to less NOx absorbed.

![Figure 5](image)

**Figure 5** a) The $pH$ of absorbents before and after the absorption process at the feed gas flow rate, $Q_G$, of 0.2 L/min at the various amount of fibers in the membrane modules containing 150 mL of 0.05 M NaClO$_3$ and NaOH solutions; b) Figure 5. The $pH$ of absorbents before and after the absorption process in the membrane module consists of 150 fibers containing 150 mL of 0.05 M NaClO$_3$ and NaOH solutions at various feed gas flow rate, $Q_G$. 

3.2. Effects of Absorbent Concentration

Figure 6 shows that increasing the concentration of NaClO₃ in the absorbent solution causes an increase in NOx absorption efficiency. Sodium chlorate (NaClO₃) dissociates into ClO₃⁻ ions in water and NaOH solutions, where ClO₃⁻ then oxidizes NO to NO₂ and then re-oxidize to NaNO₃. The reactions, as shown in Eq. (12) and (13) are depending on the number of moles of NaClO₃, which is thermodynamically spontaneous and irreversible (R.-t. Guo et al., 2010). Increasing the concentration of NaClO₃ concentration is directly proportional to the number of moles of NaClO₃ in the solution so that the NOx absorption rate increase with the increasing concentration of NaClO₃. The study’s results follow previous studies stating that increasing the concentration of NaClO₃ can increase the absorption rate of NOx (R.-t. Guo et al., 2010). Another similar study conducted by Shi et al. (Shi et al., 2019) using a bubble column reactor also showed similar results where an increase in the concentration of NaClO₃ from 0.005 M to 0.1 M led to an increase in NOx absorption efficiency from 35.48% to 91.65%. As presented in Fig. 6, the increment of fibers also increases NOx absorption efficiency due to more contact surface area for gas-liquid phases in the membrane module. The highest NOx absorption efficiency obtained from this study was 99.2% at a flow rate of a feed gas of 200 mL/minute containing NOx of about 560 ppm, the number of fibers in the membrane module of 150 containing 0.05M NaClO₃ and NaOH in the 150 mL of absorbent solution. Meanwhile, Shi et al. (Shi et al., 2019), using a bubble column reactor, obtained the highest NOx absorption efficiency of 91.65% using 500 mL of 0.1 M NaClO₃ as absorbents, and the flow rate of a feed gas of 160 cm³/minute having NOx of about 800 ppm.

![Figure 6](image_url)

**Figure 6** The effects of the NaClO₃ concentration in absorbent solutions on the NOx removal efficiency, R, at various membrane modules containing 150 mL of absorbent solutions and the feed gas flow rate of 0.2 L/minute

The overall mass transfer coefficient and flux, as shown in Figure 7, were slightly enhanced with an increase in the NaClO₃: concentration in the absorbent solution. The overall mass transfer coefficient and flux only slightly increase with increasing NaClO₃ concentration as the main driving force in the NOx removal process in the membrane module is the NOx concentration difference in the gas and liquid phases (Kartohardjono, Merry, et al., 2019). The increase in the concentration of NaClO₃ only slightly affects the rate of reaction that occurs between NOx and NaClO₃, so that it only causes a slight ease in the overall mass transfer coefficient and flux.
Figure 7 The effects of the NaClO₃ concentration in absorbent solutions on the overall mass transfer coefficient, $K_G$, and flux, $J$, at the various membrane modules containing 150 mL of absorbent solutions and the feed gas flow rate of 0.2 L/minute.

Figure 8 presents the influence of NaClO₃ concentration in the absorbent solution on the NOx loading. NOx loading decreases with increasing NaClO₃ concentration due to the increase in the amount of NOx absorbed is not proportional to the increase in NaClO₃ concentration in the absorbent solution. Meanwhile, as predicted, NOx loading increases with increasing fibers due to more contact area in the gas-liquid phases. The highest NOx loading obtained was 0.026 mole NOx/mole NaClO₃ in a 150 fibers membrane module containing 0.01 M NaClO₃ in absorbent solution and a flow rate of a feed gas of 0.2 L/minute.

Figure 8 The variation of NOx loading with the concentration of NaClO₃ in absorbent solutions on the NOx loading at the various membrane modules containing 150 mL of absorbent solutions and the feed gas flow rate of 0.2 L/minute.
4. Conclusions

The study has been conducted to reduce the NOx concentration from the gas stream in the hollow fiber membrane modules using absorbent of a mixture of NaClO3 and NaOH solutions. The experimental results confirmed that the gas stream's NOx concentration could be drastically reduced through the proposed process. NOx's absorption efficiency increased with increasing NaClO3 concentration in the absorbent solution, and the amount of fibers in the membrane module but declined as the feed gas flow rate increased. The best results from experiments on the NOx absorption efficiency, the overall mass transfer coefficient, the flux, and the NOx loading were 99.7%, 0.01743 cm s⁻¹, 9.510 x 10⁻⁸ mmole cm⁻² s⁻¹, and 0.026 mole NOx/mole NaClO3, respectively.

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