

Removal of NO Research in A Polypropylene Hollow Fiber Membrane Contactor

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Abstract. Development of cost-efficient denitration technologies has been a challenging task in industry. Here we proposed a new denitration method by using polypropylene hollow fiber membrane contactor. The NO gas from a simulative flue gas was absorbed into a saline aqueous solution through a holly fiber membrane, and then oxidized by the added H₂O₂ in the solution. We examined the effects of different operation parameters including the gas and liquid flow rates, the concentrations of H₂O₂ in the solution and SO₂ in the mimic flue gas and the circulating time. The optimal operation parameters were identified. Finally, we make a conclusion that by using a PP hollow fiber membrane contactor and H₂O₂ aqueous solution with the addition of NaCl, is a new and effective method to remove NO.

Introduction

Nitrogen oxides (NO_x), referring to the mixture of NO and NO₂, are essentially formed in all combustion processes. The emission of NO_x becomes a serious global environmental problem because NO_x represents a key ingredient of photochemical smog and it accounts for about half of all acid deposition [1].

Many of those present technologies have been developed to reduce the NO_x emission. For example, there are several methods about the reduction of NO_x generation, such as SCR, SNCR, low NO_x burners, flue gas recirculation, and low excess air, but they may reduce the reaction efficiency and increase the cost of the combustion system[2]. Membrane gas absorption technology is a hybrid process that it completely integrates the advantages of membrane separation and absorption processes. The liquid flowing in the hollow fiber membrane contactors provides selective absorption to certain gas species, while the porous membrane acts as the contacting interface between the liquid and gas phases, allowing for the unidirectional transport of gas into liquid. Namely, the gas component to be removed is absorbed into the solution when the gas stream contacts with the liquid phase flowing on the other side of the membrane fibers. This technology has been widely adopted for acid gases removal due to its flexible operation, high surface-area-to-volume ratio, compact size, easily linear scale up or down, modularity and other benefits [3,4,5,6]. Because of its excellent mass transfer properties, the membrane gas absorption technology may provide one of the most promising alternatives to the conventional technologies for NO_x mitigation. However, little study can be found in the literature.

In this work, a membrane system for gas absorption was set up for the NO removal by using a polypropylene (PP) hollow fiber membrane contactor as the absorber. To enhance the NO solubility, NaCl was firstly added into the H₂O₂ aqueous solution. These effects of operation parameters such as liquid flow rate, gas flow rate, gas composition, the concentrations of H₂O₂ and SO₂ were investigated and discussed. We also do the long-term operation with the absorbent recycling.

Experimental

Materials

The HY/T 110-2008 type porous and hydrophobic PP hollow fiber membrane module (obtained from 718th Institute of China Shipbuilding Industry Corporation) was used as the membrane contactor. The specifications of the hollow fiber membrane module are listed in Table 1. Two gas cylinders

were used to provide the test gas: 190 ppm NO balanced with N₂, and 1.95% SO₂ balanced with N₂ obtained from Shanghai Wetry Standard Gas Co., Ltd. The H₂O₂ of 30% analytical grade (Shanghai Ling Feng Chemical Co., Ltd., China) and analytical-grade NaCl (Sino pharm Chemical Reagent Co., Ltd.) were dissolved in deionized water to prepare the aqueous solution, which served as the absorbent liquid in the membrane contactor.

Table 1. Specifications of the hollow fiber membrane module.

Parameter	Value
Module outer diameter (mm)	50
Module inner diameter (mm)	42
Module length (mm)	440
Fiber inner diameter (mm)	0.26
Fiber outer diameter (mm)	0.38
Fiber length (mm)	440
Number of fibers	3000
Fiber porosity	0.45
Pore size (m)	0.15

Experimental apparatus and procedures

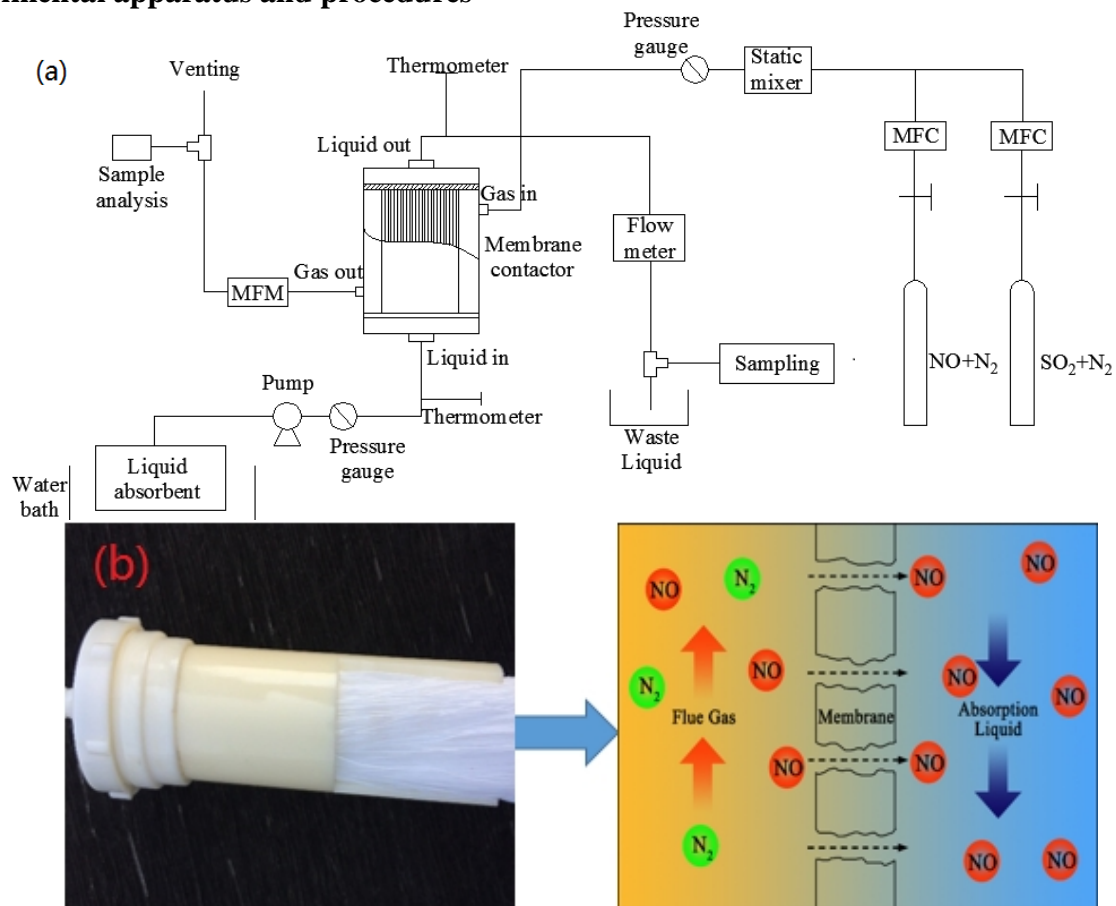


Fig. 1. (a) Schematic diagram of experimental setup for NO removal using a membrane contactor. (b) Principle of NO removal using a membrane contactor.

In the membrane contactor, the feed gas flow and absorbent liquid flow run on the both sides of the membrane. The membrane is selected so that the gas molecules can penetrate through the membrane while the liquid molecule cannot. During this process, the permeated gas molecules continue dissolving into the aqueous solution and reacting with H₂O₂. The flow chart of system setup for the NO absorption and reaction is displayed in Fig. 1. These gases from the two cylinders were mixed to form the feed gas, which has the concentration of NO around 200 ppm, similar to that in the flue gas after desulfurization. In this work, CO₂ and O₂ are not involved since they have little impact on the reaction according to our test experiments. The flow rate of the gas at the outlet was measured by a

mass flow meter (Seven Star Electronics Co., Ltd.) after dehydration. The NO concentration was measured by using a real-time NO analyzer (CLD 60, Chemiluminescence NO/NO_x, ECO PHYSICS Analyzer), and the SO₂ concentration was analyzed by SO₂ detector tubes (No. 5LC Gastec Co., Ltd.).

A stainless steel peristaltic pump (Tian Li liquid Industrial Equipment Factory) was used to pump the absorbent solution into the lumen side of the hollow fibers from a container, and the flow rate of liquid was controlled by a rotational flow meter. The absorbent container was immersed in a water bath (CU-600, Shanghai Precision Instruments Co., Ltd.), to control the temperature of the absorbent solution. The absorption temperature was calculated by taking average of the temperatures at the inlet and outlet of the absorbent solution measured by K-type thermocouples.

All data were collected at steady states, which were achieved after 30min of operation, when the NO concentration in the outlet gas didn't change with time. Each experiment was repeated for 5 times and the average values were reported.

Results and discussion

In this study, the removal efficiency and mass transfer rate of NO were used to evaluate the separation performance of hollow fiber membrane module, and they can be evaluated in inEqs. (1) and Eqs. (2)[5, 6]:

$$\eta = \frac{Q_{in} \times C_{in} - Q_{out} \times C_{out}}{Q_{in} \times C_{in}} \times 100\% \quad (1)$$

$$J_{gas} = \frac{(Q_{in} \times C_{in} - Q_{out} \times C_{out}) \times 273.15}{0.0224 \times T \times S} \quad (2)$$

where η denotes the NO removal efficiency, %; J_{gas} is the NO mass transfer rate, mol m² s⁻¹; Q_{in} and Q_{out} represent the inlet and outlet feed gas flow rate, respectively, m³ h⁻¹; C_{in} and C_{out} are the NO volumetric fraction at the gas inlet and outlet, respectively, %; S represents the gas-liquid mass transfer area and herein equals to the effective membrane area, m².

Effect of gas flow rate

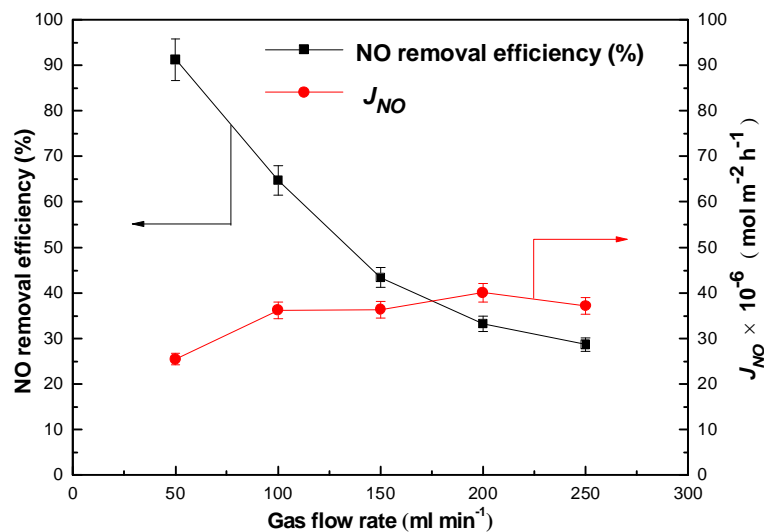


Fig. 2. Effect of gas flow rate on the NO removal efficiency and NO mass transfer rate (feed gas of 184.8 ppm NO balanced with N₂; absorbent of 0.2 wt. % H₂O₂ and 5 wt. % NaCl; absorbent flow rate of 40ml min⁻¹; absorption temperature of 323 K).

Fig. 2 shows the NO removal efficiency dropped continuously and remarkably with the increase in gas flow rate from 50 to 250 ml min⁻¹, coupled with a slight increase in the mass transfer rate. The mass transfer process consists of three consecutive steps: (i) diffusion from the bulk gas phase to the outer surface of the membrane; (ii) diffusion through membrane pores; and (iii) dissolution into the absorption liquid and liquid phase diffusion/chemical reaction. Consequently, for a hydrophobic hollow fiber membrane with gas-filled pores and liquid absorbent in the lumen side, the overall gas phase mass transfer coefficient (k_o) can then be expressed by a resistance in series model[7], as described in Eqs. (3):

$$k_o^{-1} = \left(k_g \cdot \frac{d_o}{d_i}\right)^{-1} + \left(k_m \cdot \frac{d_{lm}}{d_i}\right)^{-1} + H(E \cdot k_l)^{-1}.(3)$$

For the gas absorption, the resistance to gas diffusion from the bulk gas to the membrane external surface can be ignored compared to other resistances [8]. Accordingly, the increase of the gas flow rate obviously cannot enhance the NO mass transfer rate. On the other hand, the membrane resistance depends on the membrane operation mode, i.e., non-wetted, wetted or partially wetted mode. The high gas flow rate raised the gas pressure outside the membrane fiber, thus pushing some water out from the fiber pores and alleviating the membrane wetting. This resulted in an increase in the NO mass transfer rate as shown in Fig. 2 because the wetting surface increases the membrane mass transfer resistance rapidly and significantly [9]. Despite the increase in the NO mass transfer rate, the NO residence time declined, which is unfavorable for the NO absorption. The competition of both effects resulted in a decrease in the NO removal efficiency, indicating that the unfavorable effect played the major role.

Effect of absorbent flow rate

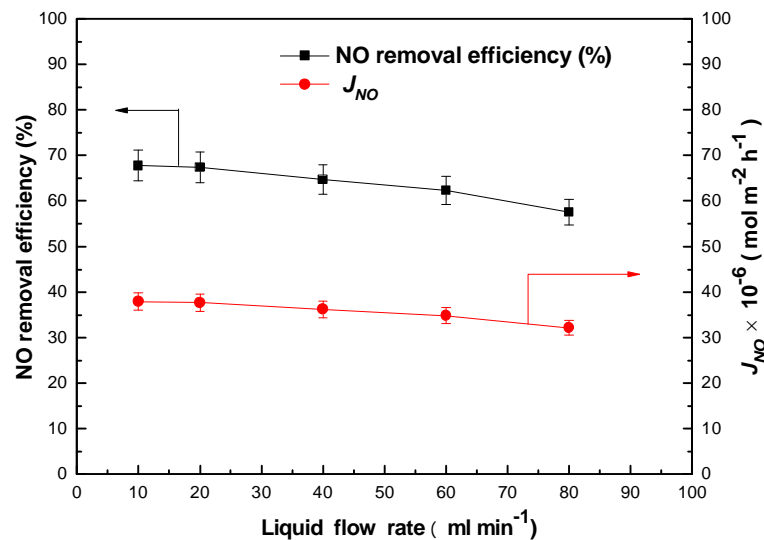


Fig. 3. Effect of absorbent flow rate on the NO removal efficiency and NO mass transfer rate (feed gas of 184.8 ppm NO balanced with N₂; feed gas flowrate of 100 ml min⁻¹; absorbent of 0.2 wt. % H₂O₂ and 5 wt.% NaCl; absorption temperature of 323 K).

Fig. 3 demonstrates the effect of absorbent flow rate on the NO absorption for the PP membrane. When the absorbent flow rate increased from 10 to 80 ml min⁻¹, both NO removal efficiency and NO mass transfer rate decreased rapidly from 67.8% to 37.9% and from 5.75×10⁻⁵ to 3.22×10⁻⁵ mol m⁻² h⁻¹, respectively. In the case of a liquid flowing through lumen of the hollow fiber, the Sherwood number of liquid phase (Sh_1) can be calculated in Eqs. (4):

$$Sh_l = \begin{cases} k_l d_i / D_l = 3.67 & Gz < 10 \\ Sh_l = (3.67^3 + 1.62^3 Gz)^{1/3} & 10 < Gz < 20 \\ Sh_l = 1.62(Gz)^{1/3} & Gz > 20 \end{cases} \quad (4)$$

For the PP membrane with absorbent flow rates from 10 to 80 ml min⁻¹, the corresponding Reynolds number ranged from 0.27 to 2.18 and the Graetz number (Gz) was far less than 1. A constant Sh_l of 3.67 was obtained over the membrane length in accordance with Eqs.1. Therefore, the increase in absorbent flow rate from 10 to 50 ml min⁻¹ had no influence on Sh_l and k_1 . On the other hand, the liquid pressure inside the membrane fiber increased with a rise in absorbent flow rate, pushing more water into the fiber pores and enhancing the membrane wetting. This results in a decrease in the NO mass transfer rate as shown in Fig. 4 because the wetting condition increases the membrane mass transfer resistance rapidly and significantly [11].

Effect of H₂O₂ concentrations

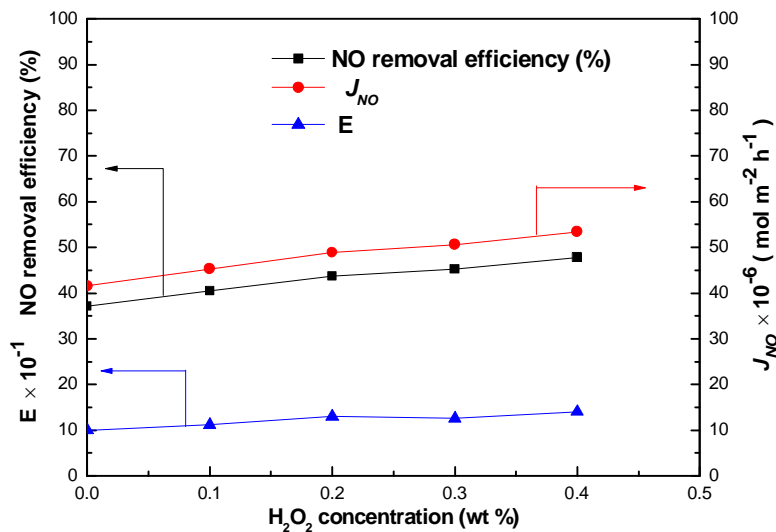


Fig. 4. Effect of H₂O₂ concentration on the NO removal efficiency and NO mass transfer rate (feed gas of 184.8 ppm NO balanced with N₂; feed gas flowrate of 200 ml min⁻¹; absorbent of H₂O₂ and 5 wt.% NaCl; absorbent flow rate of 40 ml min⁻¹; absorption temperature of 323 K).

The effect of H₂O₂ concentration was illustrated in Fig. 4. When the H₂O₂ concentration rose from 0 to 0.4 wt. %, both NO removal efficiency and NO mass transfer rate increased slightly from 37.2% to 47.8% and from 4.15×10⁻⁵ to 5.35×10⁻⁵ mol m⁻² h⁻¹, respectively. The enhancement factor E describes the effect of a chemical reaction on the mass transfer rate. Generally, E is defined as the ratio of the absorption flux in the presence of a chemical reaction (chemical absorption) to the absorption flux in the absence of a chemical reaction (physical absorption) for identical mass transfer force E, as calculated in accordance with the equations reported by Mansourizadeh et al. [7], rose from 1.0 to 1.40 with the increase in H₂O₂ concentration from 0 to 0.4 wt. %.

Effect of SO₂ concentration

As shown in Fig. 5, the NO removal efficiency and NO mass transfer rate decreased slightly first and then increased along with the increase of SO₂ concentration from 0 to 320 ppm. The lowest removal efficiency and mass transfer rate are 51.9% and 5.63×10⁻⁵ mol m⁻² h⁻¹ when the SO₂ concentration is 130 ppm. SO₂ exhibited a higher solubility than NO. Thus more SO₂ can be oxidized by H₂O₂ than NO in the feed stream. Due to the competition of oxidation, the addition of SO₂ is unfavorable for the NO removal. On the other hand, the pH value of the absorbent in the case with the addition of SO₂ is higher than that without SO₂ because the solubility and oxidation of SO₂ in the absorbent forming H₂SO₃ and H₂SO₄. The decline of pH can strengthen the H₂O₂ oxidation ability since it provides high concentration of H⁺ and is favorable for the reaction. The high H₂O₂ oxidation

ability suggests a high value of enhancement factor E, which is favorable for the NO removal. The two conflicting effects gave rise to the change of NO removal efficiency and NO mass transfer rate with the addition of SO₂ as illustrated in Fig. 5.

The SO₂ concentration at the absorber outlet kept below the SO₂ detector tube detection limit of 100 ppb with its removal efficiency of almost 100% throughout the whole operation time. The SO₂ concentration below 100 ppb is much lower than that required by SO₂ emission standard for flue gas from new-built coal fired power plant (35 ppm by China government [12]). It is also below the National Ambient Air Quality Standards for SO₂ proposed by United States Environmental Protection Agency (EPA) as follows: sulfur concentrations of 140 ppb measured over 24 h [13]. Therefore, this co-capture of NO and SO₂ could play an important role in further desulfuration, most likely alleviating the burden of desulfuration to some extent. This is an additional benefit of NO removal in our case.

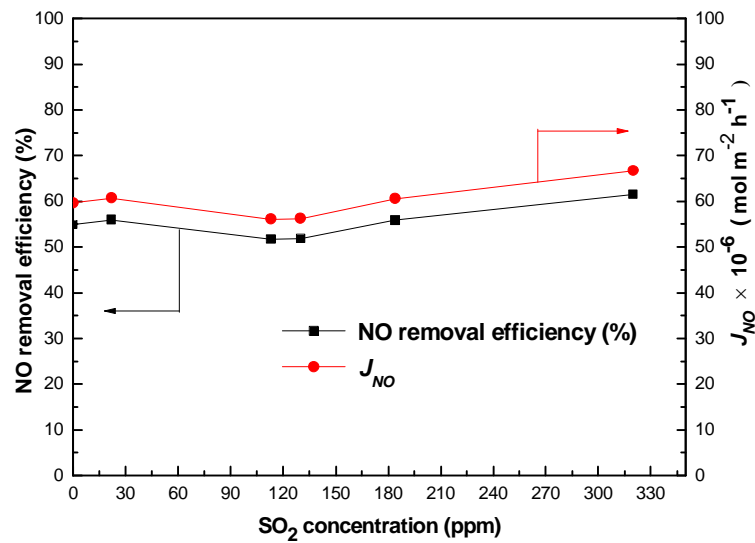


Fig. 5. Effect of SO₂ concentration on the NO removal efficiency and NO mass transfer rate (feed gas of 184.8 ppm NO balanced with N₂ and SO₂; feed gas flowrate of 200 ml min⁻¹ ; absorbent of 0.4 wt.% H₂O₂ and 30 wt.% NaCl; absorbent flow rate of 40 ml min⁻¹, absorption temperature of 333 K).

Effect of operation time with circulatory absorbent

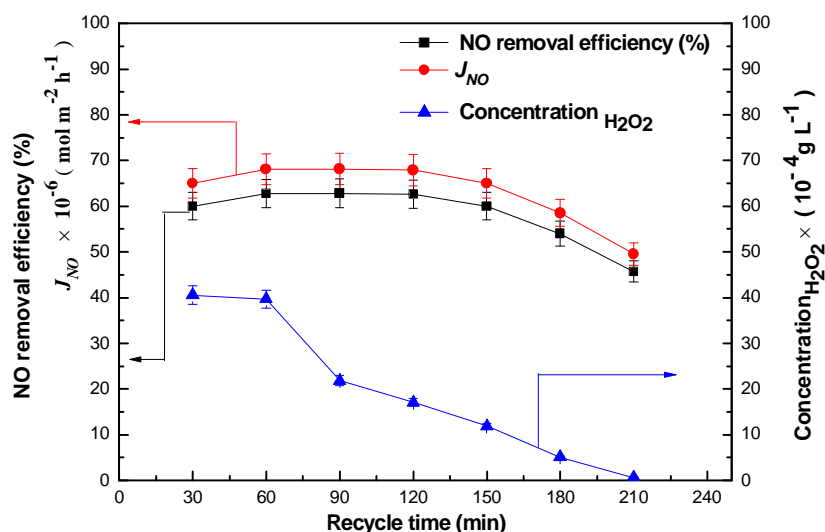


Fig. 6. Effect of operation time on the NO removal efficiency and NO mass transfer rate with circulatory absorbent (feed gas of 184.8 ppm NO; feed gas flow rate of 200 ml min^{-1} ; absorbent of 0.4 wt.% H_2O_2 and 30 wt.% NaCl; absorbent volume of 2 L; absorbent flow rate of 40 ml min^{-1} , absorption temperature of 333 K).

The effect of operation time on the NO removal efficiency is shown in Fig. 6. The NO removal efficiency and NO mass transfer rate decreased gradually from 60.0% to 45.7% and from 6.50×10^{-5} to $4.96 \times 10^{-5} \text{ mol m}^{-2} \text{ h}^{-1}$ when the operation time increased from 30 to 210 min. This is because the H_2O_2 concentration declined from 0.398 wt. % to 0.006 wt. % accordingly within this time interval. In the practical application, the H_2O_2 concentration of the circulatory absorbent can be stabilized by compensating the loss of H_2O_2 to ensure a high and steady NO removal efficiency. The mole ratio of the consumed H_2O_2 to the removed NO is 0.37 based on the data from 60 to 120 min of operation time as shown in Fig. 6.

Conclusions

By using a PP hollow fiber membrane contactor and H_2O_2 aqueous solution with the addition of NaCl, a new denitration method was proposed in this work. We demonstrated that the NO removal efficiency achieved 91.2% under the following condition: NO concentration of 184.8 ppm, absorbent of 0.2 wt.% H_2O_2 and 5 wt. % NaCl in water, gas flow rate of 50 ml min^{-1} , absorbent flow rate of 40 ml min^{-1} , and absorption temperature of 323 K. The SO_2 concentration at the outlet of the contactor kept below 100 ppb with the removal efficiency of almost 100% throughout the whole operation time, and this concentration is much lower than the SO_2 emission standard for the flue gas from a new-built coal fired power plant. The co-capture feature of NO and SO_2 could play an important role in further desulfuration, most likely alleviating the burden of desulfuration to some extent. The proposed denitration method is featured with high NO removal efficiency, medium investment and low removal costs and alleviating SO_2 removal burden, and thus provides a promising alternative to the current mainstream technologies for flue gas denitration.

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