

Simultaneous removal of SO₂ and NO_x with ammonia absorbent in a packed column

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Abstract—Catalytic oxidation of NO followed by simultaneous removal of SO₂ and NO_x with ammonia is a promising method for control of coal-fired flue gas pollutants. We investigated simultaneous absorption of SO₂ and NO_x in a packed column with ammonia, and found that SO₂ and NO_x could promote absorption with each other in the process of simultaneous removal SO₂ and NO_x. The removal efficiency of SO₂ and NO_x was, respectively, about 98% and 70.9% at pH 5.5, temperature 323.15 K, SO₂ concentration 1,800×10⁻⁶, NO_x concentration 400×10⁻⁶ and m_{NO₂}/m_{NO} 1 in our experimental system. The experimental results also show that the formation of sulfite oxidized by reacting with dissolved NO₂ and the molar ratio of sulfite to total sulfur is more than 0.8 in the solution. Accordingly, the energy consumption for sulfite oxidation would be greatly reduced in the process of simultaneous desulfurization and denitrification with ammonia.

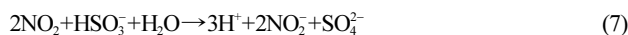
Key words: Sulfur Dioxide, Nitrogen Oxides, Ammonia, Simultaneous Absorption

INTRODUCTION

Sulfur dioxide (SO₂) and nitrogen oxide (NO_x), which lead to acid rain, are the main atmospheric pollutants from combustion of fossil fuels and have been a major environmental concern because of their hazardous effects on human health and ecosystems [1-4]. To respect the increasingly stringent regulations, the flue gas should be treated before being ejected into the atmosphere. SO₂ and NO_x are controlled, respectively, in prior art processes and selective catalytic reduction (SCR) to remove NO_x after wet flue gas desulfurization (WFGD) is the available method for flue gas desulfurization and denitrification [5-7]. However, SO₂, dust and vapor adversely affect the SCR catalyst and the cost of this technology is high [2,8]. Among various technologies, wet flue gas desulfurization (WFGD) is the most widely used technology because it remains the most economical and has the advantage of controlling other acid gases and particulates simultaneously [9,10]. An ongoing demand of desulfurization processes is the reduction of SO₂ emission. However, from an economics standpoint, it is also desirable for a desulfurization technology to produce valuable byproducts [11]. Accordingly, the ammonia-based wet flue gas desulfurization (WFGD) process has attracted a great deal of attention in China recently because of its high desulfurization efficiency, no secondary pollution, useful byproducts and lower investment [11-13].

Makansi indicated that a wet scrubbing combined SO₂/NO_x removal system was one of the best technologies [14]. If SO₂ and NO_x could be removed effectively in an ammonia-based desulfurization system after minor adjustment is made, it may be a compact and economical technology. However, NO is 90-95% of the NO_x present in typical flue gas streams and it is relatively insoluble [2,15]. Accordingly, effective removal of NO by wet scrubbing method may be achieved if the former is oxidized first to the more soluble NO₂.

In the past few years, NO absorption in alkali solutions by adding chemical oxidants (NaClO₂, H₂O₂ and KMnO₄, etc.) has been studied extensively [16-24]. However, these methods are still in laboratory exploration stage because of high cost or technical problems [25]. Selective catalytic oxidation (SCO) with oxygen is considered to be a promising NO oxidation method as it could be achieved by using SCO catalyst instead of SCR catalyst in the existing SCR reactor [26-29]. Then, using ammonia as absorbent, SO₂ and NO_x can be simultaneously absorbed to form valuable mixed byproducts of ammonium sulfate and ammonium nitrate, corresponding reactions could be expressed as follows [12,13,17-19,30]:



Selective catalytic oxidation of NO with O₂ has been studied extensively though it has not been commercialized. Yet till now, the study on simultaneous absorption of SO₂ and NO_x by using ammonia has been rarely reported in the literature. In this paper, the effect of operation parameters such as molar ratio of NO₂ and NO (m_{NO₂}/m_{NO}), NO_x concentration, SO₂ concentration and temperature on both SO₂ and NO_x removal was experimentally investigated.

EXPERIMENTAL

The absorption of SO₂ and NO_x was performed in a packed col-

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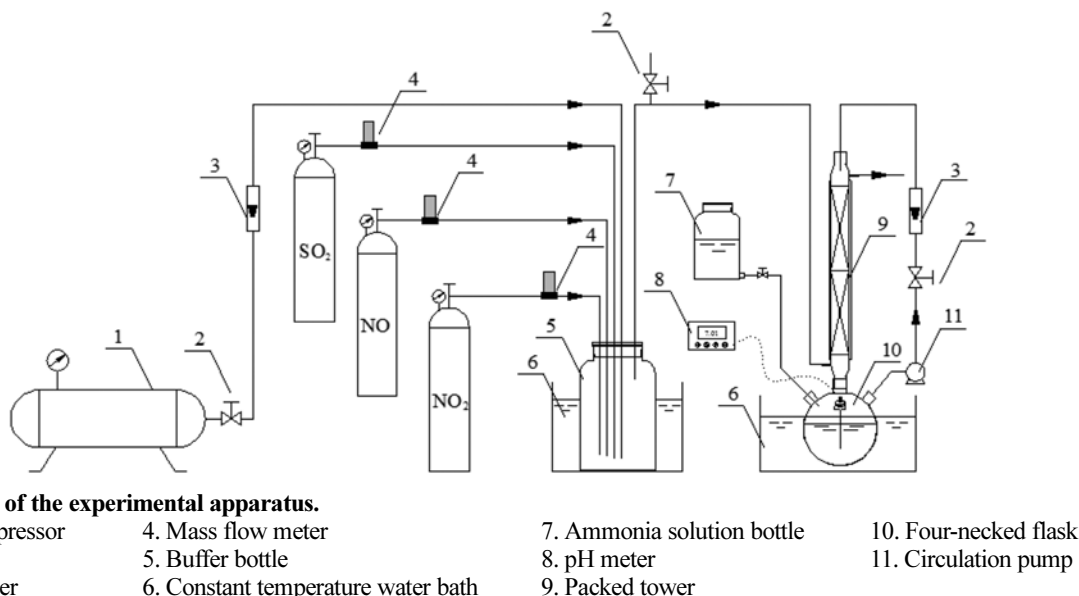


Fig. 1. Schematic of the experimental apparatus.

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|-------------------|------------------------------------|
| 1. Air compressor | 4. Mass flow meter |
| 2. Valve | 5. Buffer bottle |
| 3. Rotameter | 6. Constant temperature water bath |

- | | |
|----------------------------|-----------------------|
| 7. Ammonia solution bottle | 10. Four-necked flask |
| 8. pH meter | 11. Circulation pump |
| 9. Packed tower | |

umn. Fig. 1 shows the schematic diagram of the experimental system. The packed column is made of glass, 4 cm in internal diameter and 25 cm in height. There was a four-necked flask (volume of 500 ml) at the bottom of the packed column and the four-necked flask was immersed in a water bath. SO_2 (5% in N_2), NO (1% in N_2) and NO_2 (1% in N_2) were supplied from cylinders and the flow rate of these gases was controlled by mass flow meter separately. In the buffer bottle, SO_2 , NO and NO_2 were diluted by air to form simulated flue gas with a required concentration. Before each experiment was performed, 250 ml of distilled water was added into the four-necked flask and ammonia (12.5–14%) was added to maintain the absorption capacity of the liquid. The amount of ammonia added into the four-necked flask depended on the pH of solution. The absorption liquid in the four-necked flask circulated into the packed column by a recirculation pump. The simulated flue gas was fed into the packed column and countercurrently contacted with the descending liquid. The liquid and its absorbed gases were collected in the four-necked flask.

Before each preliminary test, the experimental system was stabilized for half an hour. Then, the inlet and outlet gas samples were analyzed for other experiments at the 10th minute. The inlet and outlet concentration of SO_2 and NO_x were measured by flue gas analyzer (MRU Vario Plus, Accuracy is $\pm 5\%$). The concentration of ions in the absorption solution was determined by ion chromatograph (DIONEX ICS-90). Each experiment investigated the effect of molar ratio of NO_2 and NO ($m_{\text{NO}_2}/m_{\text{NO}}$), NO_x concentration, SO_2 concentration and temperature on both SO_2 and NO_x removal was conducted within two hours. Accordingly, the amount of ammonia added into the four-necked flask was not very large and the liquid did not overflow. For most of the experimental runs, the temperature was maintained at 323.15 K, which simulated the temperature in existing FGD scrubbers.

RESULTS AND DISCUSSION

1. Separate Absorption of SO_2 and NO

To investigate the interaction between SO_2 and NO_x in the pro-

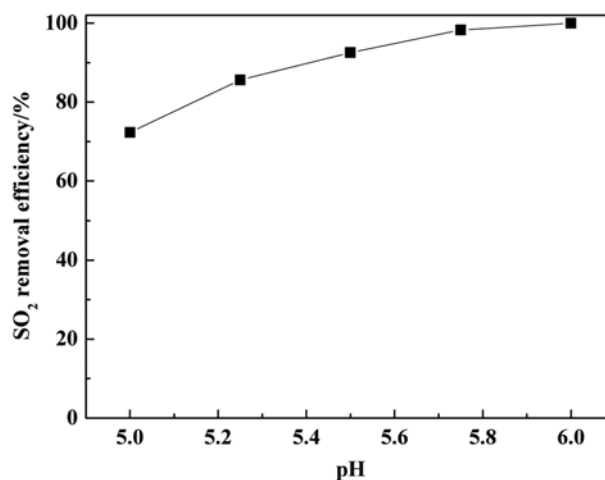


Fig. 2. Effect of pH on SO_2 removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{SO}_2}=1,800\times 10^{-6}$, $T=323.15 \text{ K}$).

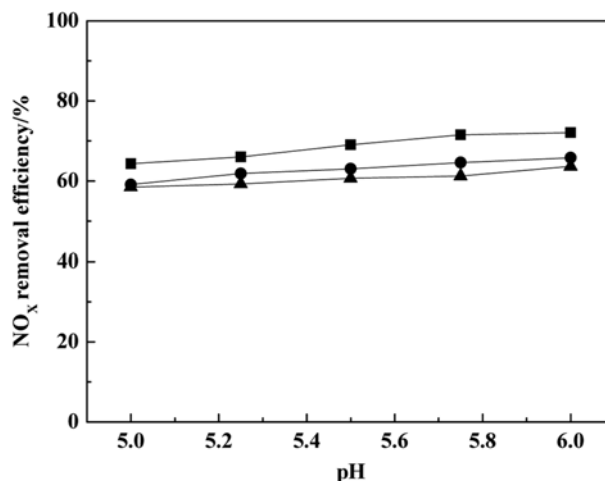


Fig. 3. Effect of molar ratio of NO_2 to NO on NO_x removal efficiency. \blacktriangle - $\text{NO}_2/\text{NO}=0.75$; \bullet - $\text{NO}_2/\text{NO}=1$; \blacksquare - $\text{NO}_2/\text{NO}=2$ ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{NO}_x}=600\times 10^{-6}$, $T=323.15 \text{ K}$).

cess of simultaneous desulfurization and denitrification, SO₂ and NO_x were absorbed with ammonia separately in the experimental system and results are plotted in Fig. 2 and Fig. 3.

It can be seen from Fig. 2 that SO₂ removal efficiency increased quickly with pH up to 5.7, above which it increased slowly. In the ammonia-based WFGD process, (NH₄)₂SO₃ and NH₄HSO₃ coexist in the desulfurization liquid with minimal free NH₃ and SO₂ [12]. According to the chemical balance, Eq. (1), the distribution coefficient of each species of total sulfite can be calculated according to the following equations:

$$\lambda_0 = \frac{[H^+]^2}{[H^+]^2 + K_{S1}[H^+] + K_{S1}K_{S2}} \quad (9)$$

$$\lambda_1 = \frac{K_{S1}[H^+]}{[H^+]^2 + K_{S1}[H^+] + K_{S1}K_{S2}} \quad (10)$$

$$\lambda_2 = \frac{K_{S1}K_{S2}}{[H^+]^2 + K_{S1}[H^+] + K_{S1}K_{S2}} \quad (11)$$

Where, λ_0 , λ_1 and λ_2 are the distribution coefficient of H₂SO₃, HSO₃⁻ and SO₃²⁻ respectively. Chemical equilibrium constants K_{S1} and K_{S2} could be calculated by the following equations [31]:

$$\log K_{S1} = 853/T - 4.74 \quad (11)$$

$$\log K_{S2} = 621.9/T - 9.278 \quad (12)$$

According to Eqs. (9)–(12), the concentration ratio of SO₃²⁻ to HSO₃⁻ is the single-valued function of pH at the at known temperature conditions. (NH₄)₂SO₃ is the key compound removing SO₂ from flue gas [12]. Fig. 4 shows that the distribution coefficient of SO₃²⁻ increases as pH increases; accordingly, the SO₂ removal efficiency increases with pH increases. Also, from Fig. 4, the distribution coefficient of SO₃²⁻ is 4.15×10⁻² at pH 6.0 and it drops from 1.35×10⁻² to 4.32×10⁻³ when the pH drops from 5.5 to 5.0. When the pH is below 5.0, the distribution coefficient of SO₃²⁻ is nearly zero. Therefore, the SO₂ removal efficiency drops drastically when

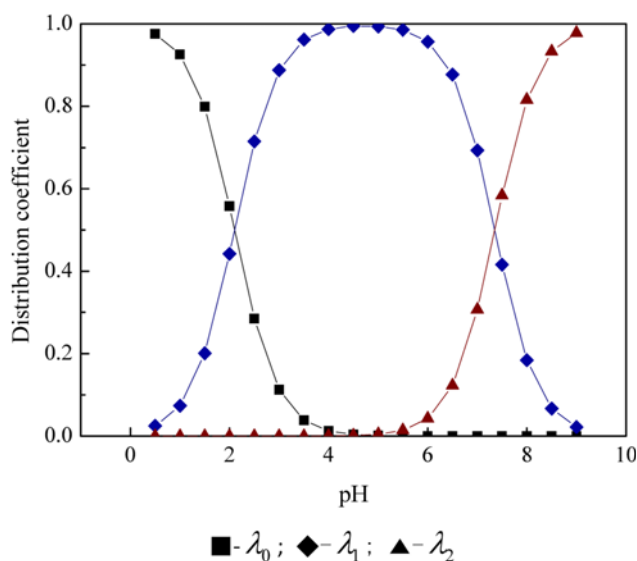


Fig. 4. Distribution coefficient of each species of total sulfite (temperature=323.15 K).

the pH is below 5.5.

Fig. 3 shows the effect of pH on denitrification efficiency at different molar ratio of NO₂ to NO. Obviously, NO_x removal efficiency increases as pH increases. It can be concluded from Eqs. (4)–(7) that the higher pH is conducive to the absorption of NO_x. Also, from Fig. 3, the NO_x removal efficiency increases as the molar ratio of NO₂ to NO increases. The NO_x removal efficiency increases from 61.2% to 71.5% when the molar ratio of NO₂ to NO increases from 0.75 to 2.

As can be seen from Eqs. (2), (4)–(8), the nitric oxide (NO), on its own does not react with ammonia. For reaction to occur, one mole of NO needs one mole of NO₂ to form HNO₂ and the corresponding reaction is given by Eq. (5). NO₂ reacts with ammonia, as already mentioned, according to Eqs. (2), (4) and (5). In addition to these reactions, NO₂ reacts with sulfite according to reactions (6) and (7). Therefore, the denitrification efficiency increases as the molar ratio of NO₂ to NO increases. Pradhan investigated the absorption of NO_x with NaOH, and reported a similar tendency [30].

2. Effect of Molar Ratio of NO₂ to NO

According to the description above, the NO in the flue gas should be partially oxidized into NO₂ before being absorbed simultaneously with SO₂. The molar ratio of NO₂ to NO (m_{NO_2}/m_{NO}) is the main influencing factor of simultaneous absorption of SO₂ and NO_x with ammonia. Therefore, a series of experiments were conducted to investigate the effect of m_{NO_2}/m_{NO} on the removal efficiency of SO₂ and NO_x, and the results are shown in Fig. 5 and Fig. 6.

It can be seen from Fig. 5 and Fig. 2 that the desulfurization efficiency is greater in the presence of NO_x than that in the absence of NO_x. The desulfurization efficiencies in Fig. 5 are nearly 98% at pH 5.5, while the desulfurization efficiency in Fig. 2 is about 92.6 at pH 5.5. The reason may be that the dissolved NO₂ reacts with sulfite (SO₃²⁻ and HSO₃⁻) according to Eqs. (6) and (7), and this promotes the absorption of SO₂. In addition, the concentration of SO₃²⁻, HSO₃⁻ and SO₄²⁻ in the solution was tested and the results show that the molar ratio of sulfite to total sulfur is more than 0.8. In the ammonia-based wet flue gas desulfurization process, the scrubbing solution is accumulated in a tank where the absorbed SO₂ reacts

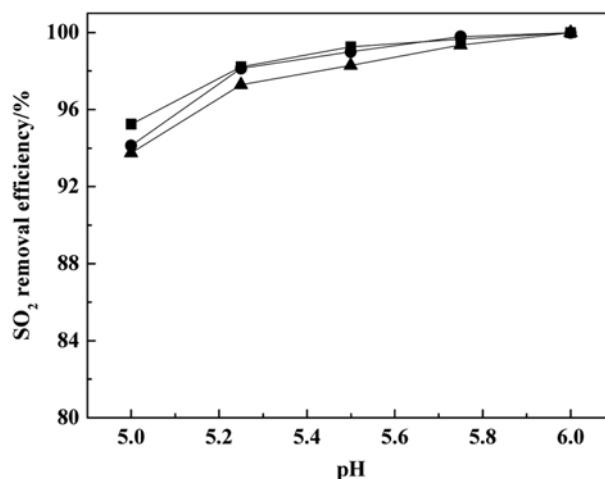


Fig. 5. Effect of m_{NO_2}/m_{NO} on SO₂ removal efficiency. ▲-NO₂/NO=3/4; ●-NO₂/NO=1; ■-NO₂/NO=2 (Q=80 L·h⁻¹, L=8 L·h⁻¹, C_{SO₂}=1,800×10⁻⁶, C_{NO_x}=600×10⁻⁶, T=323.15 K).

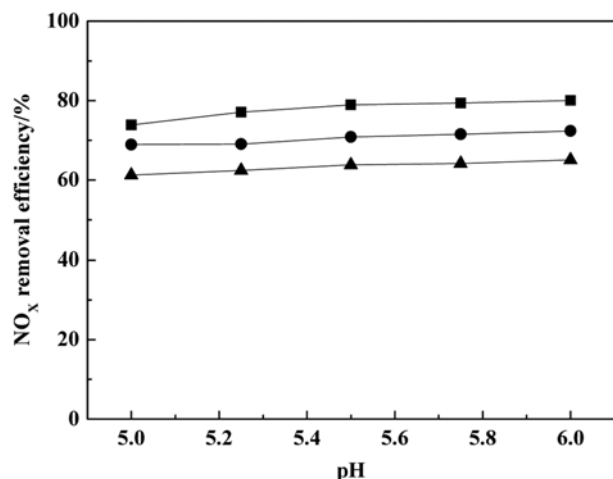


Fig. 6. Effect of $m_{\text{NO}_2}/m_{\text{NO}}$ on NO_x removal efficiency. \blacktriangle - $\text{NO}_2/\text{NO}=3/4$; \bullet - $\text{NO}_2/\text{NO}=1$; \blacksquare - $\text{NO}_2/\text{NO}=2$ ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{SO}_2}=1,800\times 10^{-6}$, $C_{\text{NO}_x}=600\times 10^{-6}$, $T=323.15 \text{ K}$).

with NH_3 to form $(\text{NH}_4)_2\text{SO}_3$ and NH_4HSO_3 , which are oxidized in the presence of sufficient oxygen to form $(\text{NH}_4)_2\text{SO}_4$ byproduct [11, 12]. Therefore, the amount of air needed for oxidation of sulfite in the process of simultaneous absorption of SO_2 and NO_x with ammonia would be much less than that in the ammonia-based wet flue gas desulfurization process. Accordingly, the energy consumption of the process of simultaneous absorption of SO_2 and NO_x with ammonia would be greatly reduced.

Also from Fig. 5, the response to an increasing $m_{\text{NO}_2}/m_{\text{NO}}$ is obviously a higher SO_2 removal efficiency, which could be mainly because the concentration of dissolved NO_2 increases with $m_{\text{NO}_2}/m_{\text{NO}}$ increases and dissolved NO_2 reacts with sulfite in the alkaline solution.

Fig. 6 illustrates the influence of $m_{\text{NO}_2}/m_{\text{NO}}$ on the NO_x removal efficiency in the presence of SO_2 . Obviously, increasing $m_{\text{NO}_2}/m_{\text{NO}}$ is favorable to the absorption of NO_x ; the denitrification efficiency increased from 63.8% to 70.9% as $m_{\text{NO}_2}/m_{\text{NO}}$ increased from 3/4 to 1. Because of Eqs. (4)–(7), the overall rate of NO_2 absorption is much higher than NO . On the other hand, Fig. 6 and Fig. 3 show that the NO_x removal efficiency in the presence of SO_2 is much higher than in the absence of SO_2 . The denitrification efficiency is 70.9% when pH is 5.5, $m_{\text{NO}_2}/m_{\text{NO}}$ is 1 and volume concentration of SO_2 is $1,800\times 10^{-6}$, while the denitrification efficiency is 63.1% in the absence of SO_2 at the same pH and $m_{\text{NO}_2}/m_{\text{NO}}$. The enhancement effect is due to reaction of dissolved NO_2 with SO_3^{2-} and HSO_3^- .

3. Effect of NO_x Concentration

The effect of NO_x concentration on simultaneous absorption of SO_2 and NO_x is shown in Fig. 7 and Fig. 8, respectively. Obviously, both desulfurization efficiency and denitrification efficiency increase as pH increases. An examination of Fig. 7 also shows that the higher the NO_x concentration, the greater the desulfurization efficiency. And the desulfurization increases from 96.5% to 98.0% when NO_x concentration increases from 200×10^{-6} to 400×10^{-6} at pH 5.5. The possible reason is that an appropriate increase in NO_x concentration promotes the reaction (Eqs. (6) and (7)) between NO_2 , SO_3^{2-} and HSO_3^- , and the chemical equivalent of absorbent did not sharply decline in our experimental conditions.

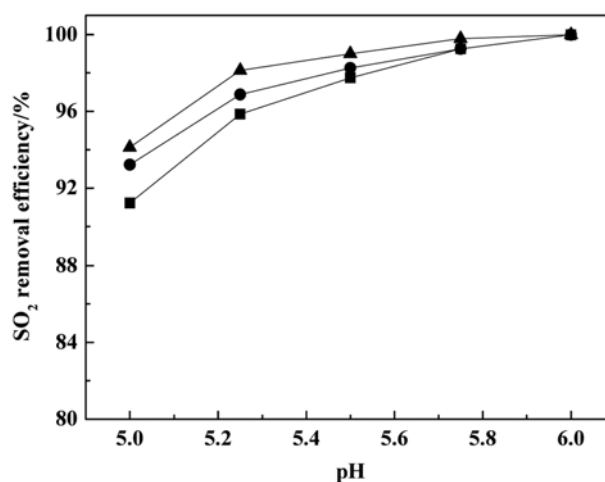


Fig. 7. Effect of NO_x concentration on SO_2 removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{SO}_2}=1,800\times 10^{-6}$, $m_{\text{NO}_2}/m_{\text{NO}}=1$, $T=323.15 \text{ K}$). \blacksquare - 200×10^{-6} ; \bullet - 400×10^{-6} ; \blacktriangle - 600×10^{-6} .

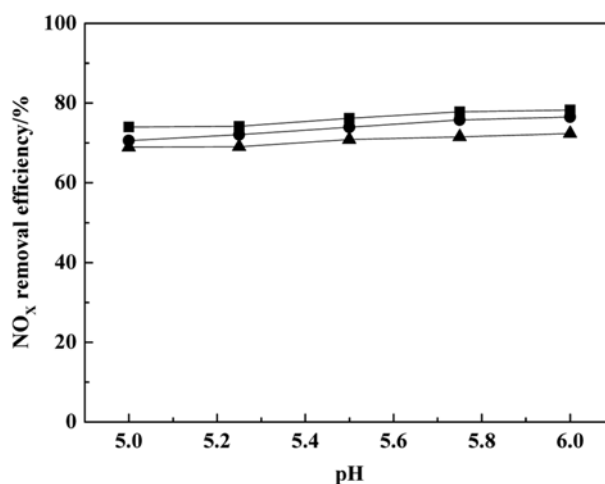


Fig. 8. Effect of NO_x concentration on NO_x removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{SO}_2}=1,800\times 10^{-6}$, $m_{\text{NO}_2}/m_{\text{NO}}=1$, $T=323.15 \text{ K}$). \blacksquare - 200×10^{-6} ; \bullet - 400×10^{-6} ; \blacktriangle - 600×10^{-6} .

Fig. 8 shows that the denitrification efficiency is 70.9% at pH 5.5, NO_x concentration 400×10^{-6} , $m_{\text{NO}_2}/m_{\text{NO}}$ 1 and the volume concentration of SO_2 $1,800\times 10^{-6}$. However, in the absence of SO_2 , the denitrification efficiency is 63.1% (Fig. 3) at the same pH, NO_x concentration and $m_{\text{NO}_2}/m_{\text{NO}}$. The reason is that NO_x reacts with dissolved SO_2 according to Eqs. (1), (6) and (7).

4. Effect of SO_2 Concentration

SO_2 plays an important role in the process of simultaneous absorption of SO_2 and NO_x . The effect of SO_2 concentration on desulfurization efficiency and denitrification efficiency is shown in Fig. 9 and Fig. 10, respectively.

Obviously, the desulfurization efficiency in Fig. 9 increases with elevated pH value and it decreases as SO_2 concentration increases. An examination of Fig. 9 and Fig. 2 also shows that the desulfurization efficiency in the presence of NO_x is greater than that in the absence of NO_x . The desulfurization efficiency in Fig. 9 is 98.9% at pH 5.5 and SO_2 concentration $1,800\times 10^{-6}$, while the desulfurization efficiency in Fig. 2 is 92.6% at the same pH and SO_2 concen-

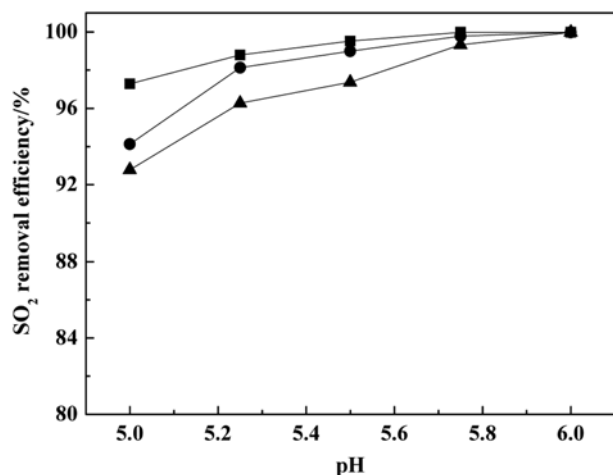


Fig. 9. Effect of SO₂ concentration on SO₂ removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{NO}_x}=600\times 10^{-6}$, $m_{\text{NO}_2}/m_{\text{NO}}=1$, $T=323.15 \text{ K}$). ■- 900×10^{-6} ; ●- $1,800\times 10^{-6}$; ▲- $2,700\times 10^{-6}$.

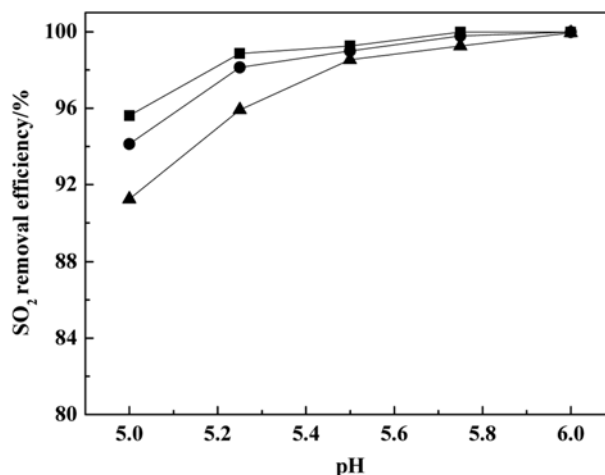


Fig. 11. Effect of temperature on SO₂ removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{SO}_2}=1,800\times 10^{-6}$, $C_{\text{NO}_x}=600\times 10^{-6}$, $m_{\text{NO}_2}/m_{\text{NO}}=1$). ■- $T=303.15 \text{ K}$; ●- $T=323.15 \text{ K}$; ▲- $T=343.15 \text{ K}$.

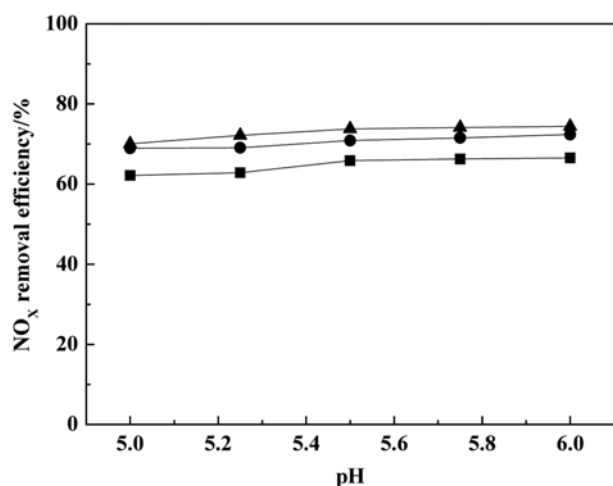


Fig. 10. Effect of SO₂ concentration on NO_x removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{NO}_x}=600\times 10^{-6}$, $m_{\text{NO}_2}/m_{\text{NO}}=1$, $T=323.15 \text{ K}$). ■- 900×10^{-6} ; ●- $1,800\times 10^{-6}$; ▲- $2,700\times 10^{-6}$.

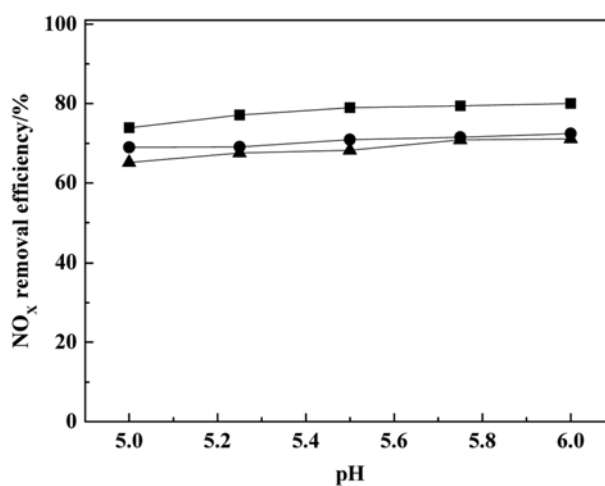


Fig. 12. Effect of temperature on NO_x removal efficiency ($Q=80 \text{ L}\cdot\text{h}^{-1}$, $L=8 \text{ L}\cdot\text{h}^{-1}$, $C_{\text{SO}_2}=1,800\times 10^{-6}$, $C_{\text{NO}_x}=600\times 10^{-6}$, $m_{\text{NO}_2}/m_{\text{NO}}=1$). ■- $T=303.15 \text{ K}$; ●- $T=323.15 \text{ K}$; ▲- $T=343.15 \text{ K}$.

tration. The possible reason is that the dissolved NO₂ may oxidize sulfite to sulfate (Eqs. (6) and (7)), which promotes the absorption of SO₂.

Fig. 10 shows that the denitrification efficiency increases linearly with pH increasing. Examination of Fig. 10 also shows that appropriate increase of SO₂ concentration is conducive to the absorption of NO_x. The reason for such observation may be that the formation of sulfite (SO₃²⁻ and HSO₃⁻) was oxidized by reacting with dissolved NO₂ and an appropriate increase of SO₂ concentration does not cause the absorption capacity to decline sharply in our experimental conditions.

5. Effect of Temperature

Temperature is an important parameter in the process of simultaneous absorption of SO₂ and NO_x with ammonia. The effect of temperature on absorption of SO₂ and NO_x is plotted in Fig. 11 and Fig. 12, respectively.

It is evident that the desulfurization efficiency in Fig. 11 is inversely proportional to temperature, and the desulfurization efficiency de-

creases from 99.2% to 98% at pH 5.5 when the temperature increases from 303.15 K to 343.15 K. A similar tendency of denitrification efficiency versus temperature is observed in Fig. 12, and the denitrification efficiency decreases from 81.6% to 74.2% at pH 5.5 when the temperature increases from 303.15 K to 343.15 K. On one hand, the increase of the temperature could promote the reaction rate. On the other hand, with the rise of the reaction temperature, the decomposition of (NH₄)₂SO₃, NH₄HSO₃ and HNO₂ was promoted, and the absorption of SO₂ was also inhibited because of the reduction of the solubility [32]. The negative effect may be greater than the positive effect in our experiments; then the removal efficiency of SO₂ and NO_x decrease as temperature increases accordingly.

CONCLUSIONS

Simultaneous absorption of SO₂ and NO_x with ammonia in a packed column was investigated, and experimental results indicate that SO₂ and NO_x could promote absorption with each other. The

removal efficiency of SO₂ and NO_x was about 98% and 70.9% at pH 5.5, temperature 323.15 K, SO₂ concentration 1,800×10⁻⁶, NO_x concentration 400×10⁻⁶ and m_{NO₂}/m_{NO} 1 in our experimental system. The experimental results also show that sulfite could be oxidized by reacting with dissolved NO₂, and the molar ratio of sulfite to total sulfur in the liquid is more than 0.8. Therefore, the amount of air needed for oxidation of sulfite and energy consumption in the process of simultaneous absorption of SO₂ and NO_x with ammonia would be much less than that of the ammonia-based wet flue gas desulphurization process. Accordingly, catalytic oxidation of NO followed by simultaneous removal of SO₂ and NO_x with ammonia is a promising method for control of coal-fired flue gas pollutants.

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