Simultaneous Removal of SO₂ and NO by O₃ Oxidation Combined with Wet Absorption

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ABSTRACT: The effects of ozone concentration, NaOH concentration, type and concentration of additives, initial pH, temperature, and NO and SO₂ concentration on simultaneous removal of NO and SO₂ were studied through ozone oxidation combined with wet absorption. Results indicated that ozone concentration and the type and concentration of additives had the most significant effect on NO removal. The optimal ozone concentration was 250 ppm (NO/NO₂ = 1), and the best additive was KMnO₄. The removal efficiency of NO₂ was as high as 97.86% when NO/NO₂ = 1, and the concentration of KMnO₄ was 0.025 mol/L. Considering economic and other factors, the KMnO₄ concentration was selected to be 0.006 mol/L. At this time, the removal efficiencies of NO₂ and SO₂ were 81.35 and 100%, respectively. This method has potential application prospects for simultaneous removal of SO₂ and NO in the industrial flue gas.

1. INTRODUCTION

In China, the main contributor to severe smog pollution is the generation of various air pollutants such as particulate matter (PM), sulfur dioxide (SO₂), and nitrogen oxides (NO) during coal combustion, especially for power generation and supply.¹,² Even though coal is the main source of greenhouse gases, it is undeniable that coal will become a major energy source in the near future because of its supply and cost efficiency stability.³ Currently, 33–77% of PM₂.₅ in China can be attributed to secondary aerosols emitted by SO₂ and NO.⁴ At the same time, the use of biomass boilers is increasing rapidly with the replacement of coal, which also leads to more and more emissions of flue gas pollutants. Because of the variety and scale of biomass boilers, equipment operating conditions and the level of pollution control technologies vary widely, and the control of NO and SO₂ emissions from biomass boilers has always been the focus of attention.

At present, various techniques such as adsorption, catalytic reduction, nonthermal plasma, and electron beam have been developed to remove SO₂ and NO.⁵–⁸ Among the existing technologies for removing NOx, the selective catalytic reduction (SCR) technology has always been considered the most effective technology. However, it has disadvantages such as high investment operation cost, large equipment area, large changes to the original flue gas, strict temperature range requirements, ammonia escaping, and catalyst poisoning, which restricts its application in tail gas treatment. The difficulty in achieving wet scrubbing to get high efficiency in removing NOx is largely due to the low solubility of NO.⁹ The solubility of NO in water is increased by the oxidation of NO to higher oxidation states (NO₃, NO₂, and N₂O₅). In some studies, strong oxidants such as ozone (O₃), hydrogen peroxide (H₂O₂), chlorine dioxide (ClO₂), potassium permanganate (KMnO₄), sodium chlorite (NaClO₂), sodium hypochlorite (NaClO), sodium persulfate (Na₂S₂O₈), Co(NH₃)₆Cl₃, and Fe(II)/EDTA were added to the absorption liquid to oxidize NO.¹⁰–¹³ Shao et al. proposed a method using KI as an additive to remove NOx and SO₂ simultaneously.¹⁴ Adewuyi et al. utilized persulfate activated by Fe²⁺ and heat to achieve the purpose of simultaneous removal of NO and SO₂.¹⁵ Hao et al. studied the use of vaporized H₂O₂ as an oxidant and Na₂SO₃ as an absorbent to absorb NOx and NO.¹⁶ Liu et al. used H₂O₂/Fe₂(MoO₄)₃ as the oxidant in the study process.¹⁷ In the absence of SO₂ or the presence of SO₂, it is a common method to use ozone to oxidize NO into a high-valence mixture at the meteorological interface and then enter the wet scrubbing system. However, in reality, the sulfur concentration in coal is different from the subsequent SO₂ flue gas concentration. Therefore, some studies had already noted that it was necessary to investigate the removal efficiency of NOx at different SO₂ concentrations. Fang et al. used a urea...
solution to remove SO₂ and NOₓ by wet scrubbing and found that the SO₂ removal rate was maintained at 100% during the process of changing the concentrations of SO₂ from 1000 to 3000 ppm.²³ Si et al. studied a method of simultaneously removing NOₓ and SO₂ by using O₃ as an oxidant and a limestone slurry as an absorbent.²⁴ As the SO₂ concentrations increased from 2200 to 4500 mg/m³, the NOₓ removal efficiency increased by more than 10%.

In this study, these latest studies were extended by wet scrubbing of NO after oxidation with ozone. Ozone was used as an oxidant at the meteorological interface, and then the scrubbing of NO after oxidation with ozone. Ozone was used as the absorbing liquid. The purpose of this study was to explore the optimum reaction conditions.

2. EXPERIMENTAL SETUP

2.1. Materials. N₂ (99.999%), NO (10.02%), and SO₂ (4.01%) of Zhuozheng Gas Co., Ltd. from Guangzhou were used as standard gases during the experiment. Sodium chlorite (>78.00%, AR), nitric acid (65−68.00%, AR), sodium persulphate (≥98.00%, AR), sodium hydroxide (≥98.00%, AR), and potassium permanganate (≥99.50%, AR) were all purchased from Guangzhou chemical reagents and used without further purification.

2.2. Experimental System. Figure 1 shows the schematic diagram of the experimental apparatus, and the entire experimental system was roughly divided into four parts, namely, an experimental material supply system, an ozone oxidation system, a flue gas processing unit, and a sampling analysis system. NO, SO₂, and N₂ were obtained through steel cylinders, and their flow rate was controlled by a matching computer, while O₃ was produced by an ozone generator (FG-Y). NO and SO₂ were injected into the flue gas treatment system after being diluted by N₂ and reacted with the ozone generated by the ozone generator. After the mixing reaction, the gas entered the absorption tower through the pipeline, and finally, the gas from the absorption tower entered the flue gas analysis system, and the gas flow rate of 2 L/min was always maintained during the reaction process.

The absorption experiment was carried out in a bubble column made of borosilicate glass (25 cm in length and 10 cm in diameter). The mixed gas continuously passed through the meteorological and liquid phase systems during the reaction time. The flue gas analyzer (Testo350XL, Germany Detu Instrument International Trading Co., Ltd.) has been used to monitor the concentrations of O₂, NO, NO₂, and SO₂ in different time periods during the experiment in order to calculate the removal efficiencies of SO₂ and NO.

2.3. Data Analysis. The removal efficiencies of NO, NOₓ, and NO₂ can be calculated by the following formula

\[
\eta(\%) = \frac{\text{NO}_{\text{int}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{int}}} \times 100\%
\]

\[
\eta(\%) = \frac{\text{NO}_{\text{2int}} - \text{NO}_{\text{2out}}}{\text{NO}_{\text{2int}}} \times 100\%
\]

\[
\eta(\%) = \frac{\text{NO}_x\text{int} - \text{NO}_x\text{out}}{\text{NO}_x\text{int}} \times 100\%
\]

where \(\eta\) is the removal efficiency.

3. RESULTS AND DISCUSSION

3.1. Influence of Ozone Concentration on the Meteorological Interface. The experiment was carried out by changing the O₃ concentration from 110 to 460 ppm. Figure 2 shows the changes in NO and NO₂ concentrations at different ozone concentrations. The concentration of NO₂ gradually increased with the increase of ozone concentration, while the concentration of NO gradually decreased. The reaction between ozone and NO at the gas interface is as follows (4–6), and the final production is closely related to the O₃ concentration of the inlet.

\[
\text{NO(g)} + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)
\]

\[
\text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{NO}_3(g) + \text{O}_2(g)
\]

\[
\text{NO}_2(g) + \text{NO}_3(g) \rightarrow \text{N}_2\text{O}_5(g)
\]

At the same time, it can be seen that the concentration of NO converted to NO₂ was approximately equal to the concentration of ozone injected, which indicated that the...
reaction between O3 and NO was mainly reaction 4 when the ozone concentration was lower than the NO concentration. NO and NO2 with a concentration ratio of essentially 1:1 can be seen from Figure 2 when the injected ozone concentration was slightly higher than 250 ppm. When the ozone concentration was increased to 460 ppm, it was found that 91.11% of NO was oxidized to NO2. The concentration of SO2 only slightly changed with the increase of ozone concentration, which meant that the reaction between O3 and SO2 was almost negligible compared with the reaction of O3 with NO.

Figure 3. (a) NOx removal efficiency of different O3 concentrations. [NO] = 500 ppm and [NaOH] = 0.0125 mol/L. (b) NO, NO2, and NOx removal efficiencies of different NaOH concentrations. [NO] = 500 ppm, [SO2] = 1000 ppm, and [O3] = 250 ppm.

Figure 4. (a) NO removal efficiency under different oxidants; (b) NO2 removal efficiency under different oxidants; (c) NOx removal efficiency under different oxidants; and (d) average removal efficiency of NO, NO2, and NOx under different oxidants. [NO] = 500 ppm, [SO2] = 1000 ppm, [O3] = 250 ppm, and [NaOH] = 0.025 mol/L.
Reaction 7 is more difficult than reaction 4 for the activation energy of reaction 4 is greater than the activation energy of reaction 7, which may be the reason why O₃ preferentially reacts with NO.

\[ \text{SO}_2(g) + \text{O}_3(g) \rightarrow \text{SO}_3(g) + \text{O}_2(g) \]  

(7)

3.2. Influence of Wet Absorption. In the experiment, 0.5 and 1 g of NaOH were added to 1 L of distilled water as an absorbent (the molar concentrations were 0.0125 and 0.025 mol/L, respectively). Figure 3a shows the NO₂ removal efficiencies of different O₃ concentrations. It can be seen that in the absence of SO₂, the removal efficiency of NO₂ appeared to increase first and then decrease with the increase of O₃ concentration. When the O₃ concentration increased from 0 to 250 ppm, the NO₂ removal efficiency increased from 5.19 to 61.05%, and then as the O₃ concentration increased to 460 ppm, the NO₂ removal efficiency decreased to 52.17%. When the SO₂ concentration was 1000 ppm, the removal efficiency of NO₂ gradually increased, but when the O₃ concentration exceeded 250 ppm, the increasing trend was slow. At the same time, the presence of SO₂ made the removal efficiency of NO₂ slightly increased, indicating that SO₂ had promoted the removal of NO₂. The removal efficiency of SO₂ reached 100% during the whole reaction process. Therefore, we determined that the optimal O₃ concentration was 250 ppm (NO/NO₂ = 1); so, the O₃ concentration was taken as 250 ppm in subsequent experiments.

Figure 3b shows that with the increase of NaOH concentration, the average removal rate of NO decreased from 82.62 to 77.79%, but the average removal rate of NO₂ increased from 68.42 to 83.35%. From the removal rate of NO, increasing the mass of NaOH will increase the average removal rate of NO₂. The increase in NO₂ removal rate is mainly due to the persistence of SO₂ during reactions 8 and 9, and it has been reported that Na₂SO₃ can act as an absorbent for NO₂. In the absence of SO₂, the removal efficiency of NO decreased from 82.62 to 77.79%, but the average removal rate of NO₂ increased from 68.42 to 83.35%. From the removal rate of NO, increasing the mass of NaOH will increase the average removal rate of NO₂. The increase in NO₂ removal rate is mainly due to the persistence of SO₂ during reactions 8 and 9, and it has been reported that Na₂SO₃ can act as an absorbent for NO₂.

\[ 2\text{NO}_2(g) + \text{Na}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l) \rightarrow 2\text{NaNO}_2(aq) + \text{H}_2\text{SO}_4(aq) \]  

(8)

\[ \text{H}_2\text{SO}_4(aq) + 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l) \]  

(9)

The decrease in NO removal rate may be due to the involvement of NO₂ in the removal process of NO (10–13), and the lower concentration of NO₂ directly led to a lower NO removal rate after NO₂ preferentially reacted with Na₂SO₃. The degree of reduction in NO absorption was less than the extent of absorption of NO₂ resulting in an increase in the final NO absorption rate. To avoid repeated NaOH additions, the amount of NaOH added in the subsequent experiments was set to 1 g. The removal rate of SO₂ during the whole reaction process was basically 100%, which was consistent with many previous reports. The concentration of the inlet SO₂ was maintained at 1000 ppm during the subsequent experiments, and the removal rate of the SO₂ was found to be essentially 100%, so that the description will not be repeated later.

\[ \text{NO}(g) + \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_3(g) \]  

(10)

\[ \text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O}(g) \leftrightarrow 2\text{HNO}_2(g) \]  

(11)

\[ \text{N}_2\text{O}_3(g) \rightarrow \text{N}_2\text{O}_5(l) + \text{H}_2\text{O}(l) \rightarrow \text{HNO}_2(aq) \]  

(12)

\[ \text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HNO}_2(aq) + \text{H}_2\text{O}(l) \]  

(13)

3.3. Effect of Oxidant Type. Different types of oxidants are typically added to the scrubbing system to achieve the purpose of promoting the NO removal efficiency. In this study, three relatively common oxidants, Na₂S₂O₈, NaClO₂, and KMnO₄ were used. Na₂S₂O₈, NaClO₂, and KMnO₄ (1 g) were separately added (the molar concentrations were 0.004, 0.009, and 0.006 mol/L, respectively). Figure 4a–c shows the removal efficiencies of NO, NO₂, and NO₃ under different oxidizing conditions, and Figure 4d shows the average removal rates of NO, NO₂, and NO₃. It can be seen that the removal efficiencies of NO, NO₂, and NO₃ by the three oxidants were different. The ability to remove NO of the three catalysts was NaClO₂ > KMnO₄ > Na₂S₂O₈, which was related to the average removal rates of 98.34, 89.18, and 76.58%, respectively. The ability to remove NO₂ of the three catalysts was KMnO₄ > Na₂S₂O₈ > NaClO₂, and the average removal rates were 98.63, 76.97, and 45.29%, respectively. The ability to remove NO₃ of the three catalysts was KMnO₄ > NaClO₂ > Na₂S₂O₈, and the average removal rates were 88.45, 68.89, and 64.24%, respectively.

This phenomenon can be attributed to the different oxidizing properties of different oxidants. The oxidation of NO to NO₂ and the further oxidation to nitrate can be attributed to the strong oxidizing properties of NaClO₂ (eqs 14 and 15). The oxidation of NO to nitrate can also embed its oxidizing power (eq 16). To generate hydroxyl (OH⁻) and sulfate free radical (SO₄⁻), Na₂S₂O₈ can be activated in the solution. They can oxidize NO dissolved in water to nitrite and then further oxidize to NO₂, which is represented by the general formulae (17–23), and the final dissolved NO is oxidized to nitrate.

\[ 2\text{NO}(l) + \text{ClO}_2^- (aq) \rightarrow 2\text{NO}_2(l) + \text{Cl}^- (aq) \]  

(14)

\[ 4\text{NO}_2(l) + \text{ClO}_2^- (aq) + 4\text{OH}^-(aq) \rightarrow 4\text{NO}_3^- (aq) + \text{Cl}^- (aq) + 2\text{H}_2\text{O}(l) \]  

(15)

\[ 4\text{NO}(l) + 3\text{ClO}_2^- (aq) + 4\text{OH}^-(aq) \rightarrow 4\text{NO}_3^- (aq) + 3\text{Cl}^- (aq) + 2\text{H}_2\text{O}(l) \]  

(16)

\[ \text{OH}^-(aq) + \text{NO}(l) \rightarrow \text{H}^+(aq) + \text{NO}_2^-(aq) \]  

(17)

\[ \text{SO}_4^{2-}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{NO}(l) \rightarrow \text{HSO}_4^-(aq) + \text{H}^+(aq) + \text{NO}_2^-(aq) \]  

(18)

\[ \text{S}_2\text{O}_8^{2-}(aq) + \text{NO}_2^-(aq) \rightarrow \text{SO}_4^{2-}(aq) + \text{SO}_4^{2-}(aq) + \text{NO}_2(l) \]  

(19)

\[ \text{SO}_4^{2-}(aq) + \text{NO}_2^- (aq) \rightarrow \text{SO}_4^{2-}(aq) + \text{NO}_2(l) \]  

(20)

\[ \text{NO}_2(l) + \text{OH}^+(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq) \]  

(21)

\[ \text{S}_4\text{O}_6^{2-}(aq) + \text{NO}(l) + \text{H}_2\text{O}(l) \rightarrow 2\text{HSO}_4^-(aq) + \text{NO}_2(l) \]  

(22)
KMnO₄ (0.5, 1, 2, 3, and 4 g) was added to the absorbing liquid, respectively. Therefore, in the subsequent experiments, the pH was selected to be about 12. Consequently, in the subsequent experiments, K₂MnO₄ was determined to be the best additive for subsequent experiments.

3.4. Impact of pH. Figure 5 shows the average removal efficiencies of NO, NO₂, and NO₃ under different pH conditions. The initial pH was adjusted to about 5, 7, 9, 11, and 12 with HNO₃ and NaOH.

\[
\begin{align*}
\text{SO}_4^{2-}(aq) + \text{OH}^-(aq) + \text{NO}(l) \\
\rightarrow \text{HSO}_4^-(aq) + \text{NO}_2(l)
\end{align*}
\]  

Figure 5. Effect of pH on the removal rate of NO, NO₂, and NO₃.

It can be seen that the concentration of KMnO₄ is the key factor affecting the removal efficiencies of NO₃ and NO. From Figure 6a–c, it can be seen that with the increase of KMnO₄ concentration, the trend of NO and NO₂ removal rates changed basically similar. It can be seen from Figure 6b that when the mass of KMnO₄ was greater than 1 g, the removal rate of NO remained above 94%. Figure 6d shows that with the increase of the amount of KMnO₄, the average removal rate of NO₂ basically remained above 99%. When the dosage of KMnO₄ was increased from 0.5 to 1 g, the average removal rate of NO increased sharply from 44.15 to 84.56%. When the dosage of KMnO₄ was increased from 2 to 4 g, the average removal rate of NO increased from 88.15 to 97.86%, smaller than the previous increase. This may be because the probability of collision increased as the concentration of KMnO₄ increased, and the reactions of eqs 25–29 can be promoted, resulting in an increase in the removal efficiency of NOₓ.

The experiment found that the removal rate of SO₂ was as high as 100% in the whole process, and the denitration efficiency was obviously affected. When the pH was 5.55, the removal rates of NO, NO₂, and NO₃ were 79.26, 33.86, and 43.46%, respectively. Then, as the pH increased to 9, the removal rates increased to 80.40, 37.58, and 46.35%, respectively. This suggested that acidic conditions were not conducive to the removal of nitrogen oxides, which may be due to the fact that acidic conditions were detrimental to NO absorption and that nitrous acid may be accelerated under the strong acidic conditions (24). The optimum denitration efficiency was observed at a pH of 12.13. The removal rates of NO, NO₂, and NO₃ were 88.45, 70.11, and 57.15%, respectively. Therefore, in the subsequent experiments, the pH was selected to be about 12.

\[
\begin{align*}
3\text{HNO}_2(aq) \rightarrow \text{NO}(g) + \text{HNO}_3(aq) + \text{H}_2\text{O}(l)
\end{align*}
\]  

3.5. Effect of Potassium Permanganate (KMnO₄). Figure 6a–c shows the removal efficiencies of NO, NO₂, and NO₃ at different concentrations of KMnO₄. KMnO₄ (0.5, 1, 2, 3, and 4 g) was added to the absorbing liquid, respectively (the molar concentrations were 0.003, 0.006, 0.013, 0.019, and 0.025 mol/L, respectively).

It can be seen that the concentration of KMnO₄ is the key factor affecting the removal efficiencies of NO₃ and NO. From

\[
\begin{align*}
4\text{MnO}_4^- (aq) + 2\text{OH}^-(aq) + 3\text{NO}(g) + 3\text{NO}_2(g) \\
\rightarrow 6\text{NO}_2^-(aq) + 4\text{MnO}_2(s) + \text{H}_2\text{O}(l)
\end{align*}
\]

Considering the removal efficiencies of NO and NO₂ and the cost of KMnO₄, 1 g KMnO₄ was selected as the best dosage for the experiment.

3.6. Effect of NO Concentration. The initial NO concentrations were changed to 100, 300, 500, 700, and 1000 ppm, respectively. Figure 7 shows the removal rates of NO₂ and the outlet concentrations of NO₃ at different NO concentrations.

It can be seen that the average outlet concentration of NO₃ was kept below 1.2 ppm with the increase of the inlet NO concentration, and the average outlet concentration of NO₂ was 0 ppm when the NO inlet concentrations were 100 and 300 ppm. The average removal rates of NO and NO₂ were basically the same. It is observed that with the increase of the NO inlet concentration, the average removal efficiency of NO₂ first increased and then decreased. The average removal efficiency of NO₂ increased sharply from 55.24 to 84.55% under the condition that the inlet concentration of NO was from 100 to 500 ppm, but when the NO inlet concentration increased to 700 ppm, the average removal rate of NO₂ decreased. When the inlet concentrations of NO were 700 and 1000 ppm, the average removal rates of NO₂ were 67.54 and 54.14%, respectively. The reason for this trend was that the dosage of KMnO₄ is fixed at 1 g, and the higher the inlet concentration of NO, the more KMnO₄ reacted with them. However, when the NO content was higher than 500 ppm, the increase in the consumption of KMnO₄ made the remaining NO not fully react with KMnO₄, so the average removal rate of NO₂ tended to decrease.
3.7. Effect of SO2 Concentration. In the experiment, the initial SO2 concentrations were changed to 0, 200, 500, 1000, and 1500 ppm, respectively. Figure 8 shows the removal rates of NOx at different conditions of SO2 concentration.

Figure 8a,b shows that the SO2 concentration affected the NOx removal efficiency greatly. The average removal rate of NOx was 71.17% when the concentration of SO2 was 0 ppm. After the addition of SO2, the average removal rate of NOx will be improved, indicating that a certain amount of SO2 will promote the absorption of NOx. The reaction obtained the best NOx removal efficiency when the SO2 was 1000 ppm, and the average removal rate was as high as 88.15%. The reason was that a large amount of KMnO4 can be consumed when the concentration of SO2 in the solution reached a certain level and the reactions of eqs 30 and 31 can be promoted,13 so that the amount of KMnO4 reacted with NO was insufficient, resulting in a decrease in the average removal rate of NOx.
The average removal rate of NO during the entire reaction was similar to that of NO\textsubscript{x} for the average outlet concentration of NO\textsubscript{2} was less than 0.2 ppm. The removal rate of SO\textsubscript{2} was 100% for a high Henry’s constant appeared on SO\textsubscript{2}.

### 3.8. Effect of Temperature.

The effect of the reaction temperature on the removal efficiencies of SO\textsubscript{2} and NO was investigated due to the important role of the reaction temperature in the dissolution, diffusion behavior, and reaction characteristics of the ions or molecules in the solution. The reaction temperatures were changed to 30, 40, 50, 60, and 70 °C.

Figure 9a,b shows the removal rates of NO\textsubscript{x} at different temperature conditions. It can be seen that the removal efficiency of NO\textsubscript{x} increased first and then decreased with temperature, and the maximum removal rate occurred at a temperature of 40 °C. When the temperature was raised from 30 to 40 °C, the average removal rate of NO\textsubscript{x} increased from 71.61 to 81.35%. When the temperature rose from 50 to 70 °C, the removal rate of NO\textsubscript{x} decreased from 77.52 to 74.33%. Because the removal rate of NO\textsubscript{2} reached 100% during the reaction, the removal rate of NO was completely consistent with the removal rate of NO\textsubscript{x}. An increase in the reaction temperature led to an increase in the rate of chemical reactions and a decrease in the solubility of NO in aqueous solutions. At the same time, the high temperature led to the accelerated decomposition of nitrite, which reduced the efficiency of NO\textsubscript{x} removal. Although a small amount of SO\textsubscript{2} appeared in the initial stage of the reaction, the removal rate of SO\textsubscript{2} reached 100% with the increase of reaction time. The temperature also reduced the solubility of SO\textsubscript{2}, but this phenomenon occurred because of the high Henry’s constant (1.2 M/atm) in SO\textsubscript{2}.

Under the optimal experimental conditions, Fang et al. found that the removal efficiencies of NO\textsubscript{x} and SO\textsubscript{2} can reach 82 and 99%, respectively.\textsuperscript{35} Wang et al. found that the highest NO removal efficiency was 82%.\textsuperscript{36} Under the optimal conditions, Hao et al. found that the removal rates of NO and SO\textsubscript{2} reached 82.7 and 100%, respectively.\textsuperscript{37} Compared with other studies, the removal rate of NO\textsubscript{x} under the optimal conditions is as high as 81.35%, which indicates that we have successfully achieved the simultaneous removal of SO\textsubscript{2} and NO by ozone and wet absorption.
4. PRODUCT ANALYSIS

The reaction was monitored under the optimal conditions to determine intermediates and products. The ion chromatography system was used to detect ionic products in the absorption solution, and the entire reaction time was set to 2 h. Table 1 shows the IC analysis results of the ionic components and concentrations in the absorption solution during the entire reaction.

Table 1. Composition of Ions in the Absorption Solution (mg/L)

| T (min) | C(NO₃⁻) | C(NO₂⁻) | C(SO₄²⁻) |
|---------|---------|---------|---------|
| 30      | 69.71   | 276.24  |         |
| 60      | 126.56  | 538.84  |         |
| 90      | 179.86  | 780.82  |         |
| 120     | 222.76  | 0.745   | 1020.84 |

As shown in Table 1, the concentration of NO₃⁻ in the absorption solution gradually increased with the increase of the reaction time, which was similar to the increasing trend of SO₄²⁻. The concentration of NO₂⁻ in the first 1.5 h was 0 mg/L, and the concentration was 0.745 mg/L in 2 h. The strong oxidation of the system was the main reason for this result. Because a large amount of oxidants and free radicals existed in the system and NO₂⁻ was easily oxidized to NO₃⁻, but with the extension of the reaction time, the amount of oxidants in the absorption solution will decrease, resulting in the occurrence of the low NO₃⁻ concentration.

Figure 10a,b shows the actual removal efficiency and the removal efficiency calculated from the ion concentration in the absorption solution. As shown in Figure 10a,b, the calculated NOₓ and SO₂ removal efficiencies were basically similar to the actual removal rates, indicating that the theory is consistent with reality. The actual SO₂ removal rate was maintained at 100% throughout the reaction process. According to the experimental results and the literature, we believe that oxidation, absorption, and acid–base neutralization are the main pathways for SO₂ to SO₄²⁻. The elimination mechanism of NOₓ is relatively complicated, the mechanism of NOₓ removal can be explained by eqs 4–24, and most of the NO will be converted into NO₃⁻ in the absorption solution.

5. CONCLUSIONS

In this study, the simultaneous removal of SO₂ and NO in the industrial flue gas by ozone combined with wet absorption was successfully achieved. Experiments showed that in the absence of SO₂, the maximum NO removal efficiency was 64.60% when the injected O₃ concentration was 250 ppm (NO/NO₂ = 1). In the presence of 1000 ppm of SO₂, the removal efficiency of NO gradually increased, but the increase trend was slow after NO/NO₂ = 1. The addition of KMnO₄ was more conducive to the removal of NO, and the more the concentration of KMnO₄ increased, the more the removal efficiency of NO increased. The tendency of the NO removal rate increased first and then decreased when increasing the NO concentration. The experiment also found that a certain amount of SO₂ can promote the removal of NOx. After considering the NOₓ removal efficiency and the costs, the optimal conditions for NO removal were determined to be when the initial pH was about 12, the temperature was 40 °C, the concentration of KMnO₄ was 0.006 mol/L, and the concentrations of imported NO and SO₂ were 500 and 1000 ppm, respectively. The NO removal efficiency of 81.35% was obtained under the optimal conditions. In this paper, the detailed results can provide guidance on the promotion of simultaneous removal of NO and SO₂ by using O₃ combined with NaOH and KMnO₄.

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Figure 10. (a) Actual and calculated NOₓ removal efficiencies; (b) Actual and calculated SO₂ removal efficiencies. [NO] = 500 ppm, [SO₂] = 1000 ppm, [O₃] = 250 ppm, T = 40 °C, [KMnO₄] = 0.006 mol/L, and [NaOH] = 0.025 mol/L, initial pH = 12.
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Notes
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