Article

Simultaneous Removal of NO\textsubscript{x} and SO\textsubscript{2} through a Simple Process Using a Composite Absorbent

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Abstract: In this work, the feasibility of the simultaneous removal of NO\textsubscript{x} and SO\textsubscript{2} through a simple process using a composite absorbent (NaClO\textsubscript{2}/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) was evaluated. Factors affecting the removal of NO\textsubscript{x} and SO\textsubscript{2}, such as NaClO\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentrations, solution temperature, the initial pH of solution, gas flow rate, and SO\textsubscript{2}, NO, and O\textsubscript{2} concentrations were studied, with a special attention to NO\textsubscript{x} removal. Results indicate that a synergistic effect on NO\textsubscript{x} removal has been obtained through combination of NaClO\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}. NaClO\textsubscript{2} in the solution played a more important role than did Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} for the removal of NO\textsubscript{x}. The above factors had an important impact on the removal of NO\textsubscript{x}, especially the solution temperature, the initial pH of the solution, and the oxidant concentrations. The optimum experimental conditions were established, and a highest efficiency of NO\textsubscript{x} removal of more than 80% was obtained. Meanwhile, tandem double column absorption experiments were conducted, and a NO\textsubscript{x} removal efficiency of more than 90% was reached, using NaOH solution as an absorbant in the second reactor. A preliminary reaction mechanism for NO\textsubscript{x} and SO\textsubscript{2} removal was deduced, based on experimental results. The composite absorbent has the potential to be used in the wet desulfurization and denitration process, to realize the synergistic removal of multi-pollutants.

Keywords: NO\textsubscript{x}; SO\textsubscript{2}; NaClO\textsubscript{2}; Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}; wet scrubbing

1. Introduction

NO\textsubscript{x} (mainly NO) and SO\textsubscript{2} released from the fossil fuels burning process, are becoming increasingly well-known as the precursors for photochemical smog and regional haze \cite{1,2}. Coal-fired power plants, industrial boilers and furnaces are considered to be the main anthropogenic sources of these pollutants. Currently, wet flue gas desulfurization (WFGD) technology and selective catalytic reduction (SCR) technology are the mature commercial technologies for controlling SO\textsubscript{2} and NO\textsubscript{x}, and they are widely used in the flue gas treatment of power plant boilers in worldwide \cite{3}. At present, flue gas pollutants emitted from power plant are being effectively controlled. WFGD technology is often used to control SO\textsubscript{2} emitted from other industrial sources, such as industrial boilers and industrial furnaces; however, there is a lack of cost-effective NO\textsubscript{x} treatment technology. Due to the high investment and operating costs, a complicated system, and the large area required, the application of the SCR system in the field of industrial boilers and furnaces flue gas treatment is limited. Therefore, it is urgent that a cost-effective NO\textsubscript{x} control technology is developed, and it is better to develop an economical, and simplified method to achieve synergistic removal NO\textsubscript{x} and SO\textsubscript{2}.

The subject of multi-pollutant (NO\textsubscript{x}, SO\textsubscript{2}, etc.) cooperative control has been widely researched in recent years. According to a review of the literature, there are two major methods for realizing...
multi-pollutant removal: the dry method and absorption (solution scrubbing) [4]. The dry method includes catalysis oxidation [5], adsorbent adsorption [6], plasma degradation [7], photocatalytic methods [8], etc. The absorption method includes complex [9], oxidation [10], and reducing [11] absorption methods. Among these methods, the oxidation absorption method based on the WFGD process is generally considered to be one of cost-effective methods for controlling multi-pollutant in flue gas. Due to the low solubility of NO, in the wet oxidizing process, rapid and efficient oxidation of NO to NO2 is a key step. In order to increase the NO removal, a variety of reagents have been utilized to synergistically remove SO2 and NO, such as potassium permanganate (KMnO4) [12], potassium ferrate (K2FeO4) [13], sodium chlorite (NaClO2) [14], sodium hypochlorite (NaClO) [15], UV/H2O2 [16], ozone [17], and persulfate systems [18,19], and satisfactory SO2 and NO removal efficiencies have been achieved under laboratory conditions.

In the oxidation absorption method, NaClO2 and Na2S2O8 are considered to be effective reagents for controlling multi-pollutant in flue gas. Fang et al. [20] developed a novel oxidation–absorption system for SO2, NO, and Hg0 removal, and NaClO2 and NaOH were used as the oxidant and the absorbent, respectively. SO2, NOx, and Hg0 removal efficiencies of more than 99, 82, and 95% could be obtained, respectively, under optimal experimental conditions. Hao et al. [21] developed a new process for gas-phase oxidation, combined with liquid-phase absorption. The gas phase oxidants (mainly ClO2) was produced by vaporizing the mixed solution of sodium chlorite and sodium persulfate at a temperature of 413 K. NO in the simulated flue gas was first oxidized to NO2 by the gas phase oxidants, then NO, NO2, and SO2 were absorbed by the sodium humate solution. Finally, 82.7% of NO removal and 100% of SO2 removal could be reached under optimal conditions. Wang et al. [22] used a dual oxidant (H2O2/Na2S2O8) system to remove NO, and the highest NO removal efficiency (82%) was obtained under the optimal conditions. Khan et al. [23] used an aqueous solution of persulfate (0.01–0.2 M) to remove NO, and 92% of NO removal was obtained at 90 °C and 0.1 M persulfate concentration. However, these technologies included some shortages, such as a complex system, high reagent consumption, and more demanding process conditions. Thus, how to simply and cost-effectively perform the cooperative absorption of SO2 and NO in a single reactor is an urgent problem that needs to be solved.

According to our previous works [20], NaClO2 was a better oxidant in view of SO2 and NO removal, but there are issues with the actual usage of the reagent, such as its high price (10,000 ¥/t), its large rate of consumption, and its easy decomposition under acidic conditions. Na2S2O8 is easily soluble in water and environmentally friendly. It is a strong and nonselective oxidant, and its price is relatively low (5000 ¥/t); however, it needs to be activated by heating or other methods to reveal its strong oxidizing properties. According to the existing literature [23,24], the presence of Cl− could improve NO oxidation and absorption when using a persulfate solution to remove NOx. Hence, in this study, a composite absorbent consisting of NaClO2 and Na2S2O8 was utilized to simultaneously remove SO2 and NOx. The main purpose of this study is to evaluate the feasibility of simultaneous removal of SO2 and NOx by using a dual oxidant solution. Meanwhile, factors affecting the removal of NOx and SO2, such as NaClO2 and Na2S2O8 concentrations, solution temperature, the initial pH of solution, gas flow rate, and SO2, NO, and O2 concentrations were studied, with a special attention to NOx removal. The preliminary reaction mechanisms of SO2 and NOx removal were also hypothesized.

2. Materials and Methods

2.1. Reagents

Reagents used in this study were bought from Guangzhou Chemical Reagent Factory (Guangzhou, China), and directly used without purification. Deionized water was used to prepare the solution. The composite absorbent used in the first absorber (Figure 1) was prepared by NaClO2 (80%, AR) and Na2S2O8 (98%, AR), CO(NH2)2 (99%, AR), Ca(OH)2 (95%, AR), Na2S2O8 (98%, AR), and NaOH (96%, AR), were used in the second absorber when needed (Figure 1). The solution pH was adjusted using
When the tandem double column absorption experiments were conducted, the simulated flue gas flow (Q) was kept at 2 L/min. The two absorbers (4 cm i.d. × 65 cm length) were all made of borosilicate glass. The first absorber was filled with ceramic Raschig rings (1.25 cm i.d. × 1.25 cm length) of 20 cm height, heated by a temperature-controlled heating belt, and the second absorber was an empty column. The volume of the solution in the absorber was 1 L. The simulated flue gas was introduced into the first absorber through a gas distribution pipe fitted at the bottom of the absorber.

1 mol/L of H$_2$SO$_4$ and 1 mol/L of NaOH solutions. Anhydrous CaCl$_2$ (96%, AR) was used as a dryer to protect the flue gas analyzer.

![Schematic diagram of the experimental device.](image)

**Figure 1.** Schematic diagram of the experimental device.

### 2.2. Equipment

The experimental apparatus consisted of a simulated flue gas generation system, a wet scrubbing system, an online monitoring system and an exhaust gas adsorption system, as shown in Figure 1.

SO$_2$, NO, O$_2$, and N$_2$ gases were supplied by the compressed cylinders (Gas Co., Ltd. of Zhuo Zheng, Guangzhou, China), and metered by the mass flow controllers (Beijing Sevenstar Flow Co., Ltd., Beijing, China). Various gases flowed into the Mixer 1 to produce the flue gas, where the total flue gas flow (Q) was kept at 2 L/min. The two absorbers (4 cm i.d. × 65 cm length) were all made of borosilicate glass. The first absorber was filled with ceramic Raschig rings (1.25 cm i.d. × 1.25 cm length) of 20 cm height, heated by a temperature-controlled heating belt, and the second absorber was an empty column. The volume of the solution in the absorber was 1 L. The simulated flue gas was introduced into the first absorber through a gas distribution pipe fitted at the bottom of the absorber. When the tandem double column absorption experiments were conducted, the simulated flue gas flowed through two absorbers in sequence. The purified flue gas was then dried by anhydrous CaCl$_2$ and then it was introduced into the detection system. In this work, SO$_2$ concentration range was 0–2100 ppm, NO concentration range was 0–1000 ppm, O$_2$ concentration range was 1–15% (v/v). The time for each set of experiments was 1 h. The experimental conditions were summarized and shown in Table 1. An ECOM-J2KN flue gas analyzer (RBR Company, Germany) was utilized to detect online the inlet and outlet SO$_2$, NO$_2$, NO, and O$_2$ concentrations. An MP511 pH Detector (Shanghai Precision Instruments Co., Ltd., Shanghai, China) was used to detect the solution pH. Concentrations of NO$_3^−$, Cl$^−$, ClO$_2^−$, and ClO$_3^−$ were measured with an ion chromatography system (IC, Thermo ICS-1100, America). The NO$_x$ and SO$_2$ removal were calculated by Equation (1):

$$\eta = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\%$$

where $\eta$ is the removal efficiency of NO$_x$ or SO$_2$; $C_{\text{inlet}}$ and $C_{\text{outlet}}$ are the inlet and outlet concentrations of NO$_x$ or SO$_2$, respectively.
were considered as better NO oxidants. Thus, in this study, the contrast experiments for different oxidant solutions were NaClO4, KMnO4, and Na2S2O8. Hence, in this study, the authors hope to improve the denitration performance of NaClO4 by the NaClO4 solution was close to that of the NaClO4 solution with the increase of reaction time. However, a NOx removal efficiency of approximately 50% using the NaClO4 solution is relatively low. Hence, in this study, the authors hope to improve the denitration performance of NaClO4 solution.

<table>
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<th>No.</th>
<th>Experiment</th>
<th>Experimental Conditions</th>
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<tr>
<td>1</td>
<td>Removal of SO2 and NO with different oxidant solutions</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C</td>
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<td>2</td>
<td>Effect of NaClO2 concentration</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.%, pH = 12</td>
</tr>
<tr>
<td>3</td>
<td>Effect of Na2S2O8 concentration</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C, [NaClO2] = 0.2 wt.%, pH = 12</td>
</tr>
<tr>
<td>4</td>
<td>Effect of initial pH</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.%, [NaClO4] = 0.2 wt.%</td>
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<tr>
<td>5</td>
<td>Effect of solution temperature</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, [Na2S2O8] = 0.5 wt.% , [NaClO2] = 0.2 wt.% , pH = 12</td>
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<td>6</td>
<td>Effect of gas flow rate</td>
<td>Single absorber, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.% , [NaClO2] = 0.2 wt.% , pH = 12</td>
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<td>7</td>
<td>Effect of SO2 concentration</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, O2 = 10%, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.% , [NaClO2] = 0.2 wt.% , pH = 12</td>
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<td>8</td>
<td>Effect of NO concentration</td>
<td>Single absorber, Q = 2 L/min, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.% , [NaClO4] = 0.2 wt.% , pH = 12</td>
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<td>Effect of O2 concentration</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.% , [NaClO4] = 0.2 wt.% , pH = 12</td>
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<td>10</td>
<td>Tandem double column absorption experiments</td>
<td>Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%; Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.% , [NaClO4] = 0.2 wt.% , pH = 12 (the first absorber); Tabsorption = 25 °C, [reagent] = 5 wt.% (the second absorber)</td>
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<tr>
<td>11</td>
<td>Product analysis</td>
<td>Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO2] = 1000 ppm, O2 = 10%, Tabsorption = 50 °C, [Na2S2O8] = 0.5 wt.% , [NaClO4] = 0.2 wt.% , pH = 12</td>
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3. Results and Discussion

3.1. Simultaneous Removal of SO2 and NOx with Different Oxidant Solutions

Based on the literature and on our previous works [12,20,22,23], NaClO4, KMnO4, and Na2S2O8 were considered as better NO oxidants. Thus, in this study, the contrast experiments for different oxidants on SO2 and NOx removal were investigated, and the results are displayed in Figures 2 and 3. In this set of experiments, the concentrations of the single oxidants in the solutions were all 0.2 wt.%, and the initial pH values of NaClO4 + NaOH, KMnO4, and Na2S2O8 + NaOH solutions were 12.0, 8.0, and 12.0, respectively. The results indicate that all oxidant solutions had a good level of efficiency of removal on SO2, where the removal efficiency was close to 100%. However, different oxidant solutions had different effects on NOx removal, and the capacity on the NOx removal of three oxidant solutions was NaClO4 > KMnO4 > Na2S2O8, with the average NOx removal efficiencies being at 48.69%, 48.13%, and 23.98%, respectively. Although the average efficiency of NOx removal by KMnO4 solution was close to that of the NaClO4 solution, NOx removal efficiency by the KMnO4 solution decreased, with the reaction time increasing. Thus, it can be speculated that the NOx removal efficiency by the NaClO4 solution is significantly better than that of KMnO4 solution with the increase of reaction time. However, a NOx removal efficiency of approximately 50% using the NaClO4 solution is relatively low. Hence, in this study, the authors hope to improve the denitration performance of NaClO4 solution.
(0.2 wt.%) by adding a certain amount of Na$_2$S$_2$O$_8$ (0.1 wt.%), and the results are illustrated in Figures 2 and 3. The results show that SO$_2$ and NO$_x$ could be efficiently absorbed, and nearly 100% of the SO$_2$ and 73.51% of the NO$_x$ were simultaneously removed. NO$_x$ removal using a dual oxidant solution was much better than removal by using a single oxidant solution. SO$_2$ removal remained constant at about 100% in all tests, but the NO$_x$ removal was affected by many factors, so the emphasis was placed on the discussion of NO$_x$ removal by using a NaClO$_2$ + Na$_2$S$_2$O$_8$ solution, in subsequent experiments.

![Figure 2. Effect of different oxidants on NO$_x$ removal.](image2)

![Figure 3. Effect of different oxidants on SO$_2$ removal.](image3)

### 3.2. Effect of NaClO$_2$ Concentration

Several sets of experiments at various NaClO$_2$ concentrations (0, 0.05, 0.1, 0.15, 0.20, and 0.30 wt.%) were carried out to study the effect of NaClO$_2$ concentration on NO$_x$ removal efficiency at the same persulfate level (0.5 wt.%). Figure 4 shows that the NO$_x$ removal efficiency sharply increased with the increment of NaClO$_2$ concentration at first, and then it gradually increased; when the NaClO$_2$ concentration increased to 0.20 wt.%, a maximum NO$_x$ removal efficiency of 80.61% was obtained, and thereafter, NO$_x$ removal efficiency decreased from 80.61% to 72.83% with the increase of NaClO$_2$ concentration from 0.2 wt.% to 0.3 wt.%. NaClO$_2$ is a strong oxidant that can oxidize NO to NO$_2$, which then oxidizes NO$_2$ to nitrate (Equations (2) and (3)). It can also directly oxidize
NO to nitrate (Equation (4)) [20]. So, even the introduction of 0.05 wt.% of NaClO₂ had a very pronounced effect, where the NO₃ removal efficiency went increased from 29.16% without any NaClO₂ to 54.68% with NaClO₂. Moreover, Na₂S₂O₈ in the solution could be activated to generate sulfate-free radicals (SO₄²⁻) and hydroxyl radicals (OH•), and a large number of chlorine-free radicals (Cl•, ClO•, ClOH•) could be produced through complex reactions via the reactions of Equations (5)–(8) [23–25]. The chlorine-free radicals could react with dissolved NO to form nitrates and nitrites (Equations (9)–(11)). Therefore, the addition of Na₂S₂O₈ could increase the total number of reactive radical species, and enhance the NO₃ removal efficiency. In addition, as the reaction proceeded, the pH of the solution decreased, H⁺ could catalyze the decomposition of ClO₂⁻ to generate the strong oxidizing ClO₂ (Equations (12)–(14)). ClO₂ could oxidize NO to NO₂ and nitrate (Equations (15)–(17)) [20], leading to the increase of NO₃ removal. However, with an increasing concentration of NaClO₂, the NO concentration in the exhaust decreased, but the NO₂ concentration increased. A large amount of NO₂ was produced by the reactions (Equations (2), (10) and (15)) due to the high NaClO₂ concentration. On the one hand, the high NaClO₂ concentration was not conducive to the absorption of NO₂ [20]; on the other hand, a large amount of NO₂ escaped from the system, due to the limited gas–liquid contact time. The study found the average emission concentrations of NO₂ were 10.56, 13.44, 39.35, 64.17, 87.18, and 158.24 ppm when the NaClO₂ concentrations were 0, 0.05, 0.1, 0.15, 0.20, and 0.30 wt.%, respectively. Obviously, the NO₂ concentration in the exhaust significantly increased when the NaClO₂ concentration was more than 0.2 wt.%.

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

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

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

\[ \text{SO}_4^{\cdot-} (aq) + \text{Cl}^- (aq) \leftrightarrow \text{SO}_4^{2-} (aq) + \text{Cl}^\bullet (aq) \] 

\[ \text{Cl}^\bullet (aq) + \text{Cl}^- (aq) \leftrightarrow \text{Cl}_2^- (aq) \] 

\[ \text{OH}^\bullet (aq) + \text{Cl}^- (aq) \leftrightarrow \text{ClOH}^\bullet (aq) \] 

\[ \text{ClO}_2^\bullet (aq) + \text{Cl}^- (aq) \rightarrow \text{Cl}_2^- (aq) + \text{OH}^- (aq) \] 

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

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

\[ \text{ClO}_2^- (aq) + \text{NO}_2 (aq) \rightarrow \text{HNO}_3(aq) + \text{Cl}^- (aq) \] 

\[ 8\text{H}^+ (aq) + 8\text{ClO}_2^- (aq) \rightarrow 6\text{ClO}_2(l) + \text{Cl}_2(l) + 4\text{H}_2\text{O(l)} \] 

\[ 4\text{H}^+ (aq) + 5\text{ClO}_2^- (aq) \rightarrow 4\text{ClO}_2(l) + 2\text{H}_2\text{O(l)} + \text{Cl}^- (aq) \] 

\[ 4\text{ClO}_2^- (aq) + 2\text{H}^+ (aq) \rightarrow \text{Cl}^- (aq) + 2\text{ClO}_2(l) + \text{ClO}_3^- (aq) + \text{H}_2\text{O(l)} \] 

\[ 5\text{NO}(l) + 2\text{ClO}_2(l) + 2\text{H}_2\text{O(l)} \rightarrow 5\text{NO}_2(l) + 2\text{HCl}(aq) \] 

\[ 5\text{NO}_2(l) + \text{ClO}_2(l) + 3\text{H}_2\text{O(l)} \rightarrow 5\text{NO}_3^- (aq) + \text{Cl}^- (aq) + 6\text{H}^+ (aq) \]
The results in Figure 5 illustrate the effect of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration on NO\textsubscript{x} removal efficiency at a constant NaClO\textsubscript{2} concentration of 0.2 wt.% and at 50 °C. The addition of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} could effectively enhance the NO\textsubscript{x} removal efficiency, and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration had an important influence on the absorption of NO\textsubscript{x}. Figure 5 shows that when the Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration in the solution increased from 0.00 wt.% to 0.1 wt.%, the NO\textsubscript{x} removal efficiency rapidly increased from 48.69% to 72.34%, and then it slightly increased from 72.34% to 80.61% in the Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration range of 0.1 wt.% to 0.5 wt.% However, further increases in Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration resulted in a slight drop in NO\textsubscript{x} removal efficiency, which then maintained stability. For example, the NO\textsubscript{x} removal efficiencies were 78.96% and 79.42% when the Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentrations were 0.7 wt.% and 0.9 wt.%, respectively.

### 3.3. Effect of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} Concentration

Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} is a strong and nonselective oxidant, and it can be activated by heat and alkaline [21], to produce an intermediate sulfate free radical (SO\textsubscript{4}\textsuperscript{•−}) (Equation (17)) [23,26], then SO\textsubscript{4}\textsuperscript{•−} reacts with hydroxide ions or water molecules to produce a sulfate ion and hydroxyl radicals (OH\textsuperscript{•}) (Equations (18) and (19)). The reaction rate constant of Equation (19) (k = 7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}) is significantly greater than that of Equation (18) (k = 6.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}). So, the conversion of SO\textsubscript{4}\textsuperscript{•−} to OH\textsuperscript{•} via Equation (19)
becomes more important under alkaline conditions [23]. Both SO₄•⁻ and OH• are very strong oxidants in aqueous solution. They can oxidize NO dissolved in water to nitrite, which further oxidizes to NO₂ and, finally, the NO dissolved in water is oxidized to nitrate, as represented by the generalized Equations (20)–(26), respectively. The amount of SO₄•⁻ generation in the solution increased with the increase of Na₂S₂O₈ concentration at the constant reaction temperature. Therefore, the NOₓ removal efficiency increased as the Na₂S₂O₈ concentration increased. However, a further increase of Na₂S₂O₈ concentration could lead to the production of a large amount of SO₂•−. Then, the self-recombination and the intercombination of oxidative free radicals, and the scavenging reactions by free radicals with the remaining persulfate ions might become significant (Equations (27)–(30)). Those scavenging reactions could compete with the NOₓ removal reactions to consume a large amount of free radicals, finally leading to the decrease of NOₓ removal efficiency [23,26,27]. Thus, considering the NOₓ removal and economic costs, the optimum Na₂S₂O₈ concentration range of 0.3–0.5 wt.% and the optimal concentration of 0.5 wt.% were selected.

\[
\begin{align*}
S_2O_8^{2−}(aq) & \stackrel{Δ/\text{alkaline}}{\rightarrow} 2SO_4^{•−}(aq) \\
SO_4^{•−}(aq) + H_2O(l) & \rightarrow H^{+}(aq) + SO_2^{2−}(aq) + OH^{•}(aq) \\
SO_4^{•−}(aq) + OH^{−}(aq) & \rightarrow SO_4^{2−}(aq) + OH^{•}(aq) \\
OH^{•}(aq) + NO(l) & \rightarrow H^{+}(aq) + NO_2^{−}(aq) \\
SO_4^{•−}(aq) + H_2O(l) + NO(l) & \rightarrow HSO_4^{−}(aq) + H^{+}(aq) + NO_2^{−}(aq) \\
S_2O_8^{2−}(aq) + NO_2^{−}(aq) & \rightarrow SO_4^{2−}(aq) + SO_4^{•−}(aq) + NO_2(l) \\
SO_4^{•−}(aq) + NO_2^{−}(aq) & \rightarrow SO_4^{2−}(aq) + NO_2(l) \\
NO_2(l) + OH^{•}(aq) & \rightarrow H^{+}(aq) + NO_3^{−}(aq) \\
S_2O_8^{2−}(aq) + NO(l) + H_2O(l) & \rightarrow 2HSO_4^{−}(aq) + NO_2(l) \\
SO_4^{•−}(aq) + OH^{•}(aq) + NO(l) & \rightarrow HSO_4^{−}(aq) + NO_2(l) \\
OH^{•}(aq) + OH^{•}(aq) & \rightarrow H_2O_2(aq) \\
SO_4^{•−}(aq) + SO_4^{•−}(aq) & \rightarrow S_2O_8^{2−}(aq) \\
SO_4^{•−}(aq) + S_2O_8^{2−}(aq) & \rightarrow S_2O_8^{•−}(aq) + SO_4^{2−}(aq) \\
OH^{•}(aq) + S_2O_8^{2−}(aq) & \rightarrow S_2O_8^{•−}(aq) + OH^{−}(aq)
\end{align*}
\]

3.4. Effect of Initial pH

The effect of the solution initial pH ranging from 6.0–12.0 on NOₓ removal was studied. Figure 6 illustrates that NOₓ removal efficiency was much higher under alkaline rather than acidic conditions, and the NOₓ removal efficiency sharply increased with the increase of the initial pH. When the initial pHs of the solutions were 6.0, 8.0, 10.0, and 12.0, the NOₓ removal efficiencies were 3.54, 18.46, 38.36, and 80.61%, respectively. Meanwhile, it was discovered that the NO concentration gradually increased, and the NO₂ concentration gradually decreased in the exhaust with the increasing of initial pH. The average emission concentrations of NO were 0, 4.89, 11.22, and 20.39 ppm, and the average emission concentrations of NO₂ were 482.30, 402.81, 269.84, and 87.18 ppm, when the initial pHs of the solution were 6.0, 8.0, 10.0, and 12.0, respectively. The research found that the fractional conversion of NO to NO₂ could reach 100% at low pH. The literature reported that H⁺ could catalyze the decomposition of S₂O₈²⁻ to form SO₃ and HSO₄⁻ [23,27]. Hence, increasing the H⁺ concentration would promote the decomposition of S₂O₈²⁻, and inhibit the generation of free radicals, finally resulting in a decrease in the amount of reactive radicals produced, and the decrease of NOₓ removal. Meanwhile, H⁺ can also catalyze the decomposition of ClO₂⁻ to generate strongly oxidizing.
ClO₂ (Equations (12)–(14)) [20,28]. When the initial pH decreased from 12.0 to 6.0, the solution color varied from colorless to yellowish green, and then its color gradually deepened. The result indicated that large amounts of ClO₂ were being produced and dissolving into the solution under low pH conditions. Dissolved ClO₂ could react with dissolved NO to preferentially form NO₂ (Equation (15)) [29]. Although the NO₂ produced could be further oxidized to nitrate, it was more likely to escape from the solution under low pH conditions [20], leading to the increase of NO₂ concentration and the decrease of NO concentration in the exhaust with the decrease of solution pH [20]. When the initial pH of the solution increased, the NOx removal increased. This is because more free reactive radicals were generated (especially OH•) through the inhibition of the decomposition of S₂O₈²⁻ and ClO₂⁻ under alkaline conditions. In particular, alkaline conditions could promote the conversion of SO₄²⁻ to OH• by Equation (19). OH• is more reactive than SO₄²⁻ [23]. Meanwhile, the escape amount of NO₂ decreased significantly under alkaline conditions. So, NOx removal increased with the increase of initial pH. The study indicates that this new process is more suitable for operation under alkaline conditions, so in this study, the best pH was determined to be 12.0.

![Figure 6. Effect of initial solution pH on NOx removal.](image)

### 3.5. Effect of Solution Temperature

Several experiments were carried out at various temperatures (25, 40, 50, 60, and 70 °C) to study the effects of solution temperature on NOx removal, and the results are shown in Figure 7. As depicted in Figure 7, NOx removal efficiency decreased slowly at first, then it decreased rapidly as the temperature increased, with the turning point of the solution temperature being 50 °C. The NOx removal efficiencies were 91.77%, 84.48%, 80.61%, 66.29%, and 49.94% when the solution temperatures were 25, 40, 50, 60, and 70 °C, respectively. The research also found that NO concentration decreased and NO₂ concentration increased in the exhaust with the increase of the solution temperature. The average emission concentrations of NO were 33.72, 31.24, 20.39, 0.00, and 0.00 ppm, and the average emission concentrations of NO₂ were 7.43, 46.36, 87.18, 168.55, and 250.30 ppm, when the solution temperature changed from 25 to 70 °C, respectively. The fractional conversion of NO increased with increasing temperature, which is consistent with the results reported by Khan et al. [23]. Higher temperatures can significantly promote the activation of Na₂S₂O₈ to produce a large amount of sulfate free radicals [30], and then to generate a large number of other free radicals, such as OH•. These free radicals can oxidize NO to nitrite and nitrate, to promote NO removal. However, the high temperatures could also promote ClO₂ generation [20], leading to the fractional conversion of NO and an increase in the generation of NO₂. NO₂ can easily escape from solution into gas, due to the high temperature and limited gas–liquid contact time, so that the NOx removal efficiency is decreased.
The influence of solution temperature on NO\textsubscript{x} removal is ultimately determined by the above two aspects. The results indicate that the increase of absorption temperature is not conducive to the NO\textsubscript{x} removal. Thus, it shows that NaClO\textsubscript{2} in the dual oxidant solution plays a more important role than Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} for the NO\textsubscript{x} removal. The temperature of the absorption liquid of WFGD is usually approximately 40–50 °C. Considering the actual situation, in this study, the solution temperatures of the new process were all selected as 50 °C.

![Figure 7](image-url)

**Figure 7.** Effect of solution temperature on NO\textsubscript{x} removal.

### 3.6. Effect of Gas Flow Rate

The effect of gas flow rate on NO\textsubscript{x} removal is shown in Figure 8. Results indicate that the gas flow rate had an important effect on NO\textsubscript{x} removal, and NO\textsubscript{x} removal decreased with the increasing of the gas flow rate. When the gas flow rate increased from 1.0 to 3.0 L·min\textsuperscript{-1}, the NO\textsubscript{x} removal efficiencies were 88.28%, 83.30%, 80.61%, 72.07%, and 56.24%, respectively. Zhao et al. [2] also found that the removal efficiencies of SO\textsubscript{2}, NO\textsubscript{2}, and NO decreased as the gas flow rate increased. Meanwhile, it was also found that the average NO concentration increased sharply in the exhaust from 10.67 ppm to 195.56 ppm with the increase of gas flow rate from 1.0 to 3.0 L·min\textsuperscript{-1}. The gas–liquid contact time decreased with the increase in the gas flow rate. On the one hand, NO molecules in the gas could not have the necessary time to dissolve into the solution. On the other hand, the NO\textsubscript{2} generated by the reactions was taken out of the system without further reaction to form nitrates. Therefore, the NO\textsubscript{x} removal efficiency was reduced with an increase in the gas flow rate.

### 3.7. Effect of SO\textsubscript{2} Concentration

The effect of SO\textsubscript{2} concentration on NO\textsubscript{x} removal in the range of 0–2100 ppm was investigated. Figure 9 indicates that the SO\textsubscript{2} concentration in the flue gas had a very significant effect on NO\textsubscript{x} removal; the NO\textsubscript{x} removal efficiency was first rapidly increased, and then it decreased with the increase of SO\textsubscript{2} concentration. For example, when the SO\textsubscript{2} concentration increased from 0 to 500 ppm, the removal of NO\textsubscript{x} rapidly increased from 62.05% to 83.37%, then with the SO\textsubscript{2} concentration further increasing from 500 ppm to 2100 ppm, the NO\textsubscript{x} removal efficiency decreased from 83.37% to 70.66%. Results indicate that the removal of NO\textsubscript{x} could be promoted at low SO\textsubscript{2} concentration conditions, but higher concentrations of SO\textsubscript{2} inhibited NO\textsubscript{x} removal. SO\textsubscript{2} is very soluble in aqueous solution, and it dissolves into solution to generate HSO\textsubscript{3}\textsuperscript{−}, which can react with NO\textsubscript{2}\textsuperscript{−} to generate HON(SO\textsubscript{3})\textsuperscript{2−} and ONSO\textsubscript{3}\textsuperscript{−} (Equations (31)–(33)) [30–32]. Meanwhile, dissolved NO can also directly react with SO\textsubscript{3}\textsuperscript{2−} to form ON(SO\textsubscript{3})\textsuperscript{2−} and ON(NO)(SO\textsubscript{3})\textsuperscript{2−} (Equations (34) and (35)) [32]. These reactions promote the dissolution and oxidation of NO, while reducing the consumption of free radicals and oxidants.
finally promoting NO removal. On the other hand, HSO$_3^-$ and SO$_3^{2-}$ also can react with NO$_2$ to form NO$_2^-$ (Equations (36) and (37)) [32], then NO$_2^-$ can react with oxidants or free radicals to form NO$_3^-$, finally resulting in the inhibition of NO$_2$ volatilization from the solution, increasing NO$_x$ removal. The research found that the average NO$_2$ concentration in the exhaust decreased from 167.89 to 73.72 ppm when the SO$_2$ concentration changed from 0 to 500 ppm. This finding also confirmed the existence of the above reaction process. When the SO$_2$ concentration was further increased, the NO$_x$ removal efficiency decreased from 83.37% to 70.66%. Results indicate that the removal of NO$_x$ could be promoted at low SO$_2$ concentration conditions, but higher concentrations of SO$_2$ inhibited NO$_x$ removal. SO$_2$ is very soluble in aqueous solution, and it increases the pH of the solution drops sharply with the large amount of SO$_2$ dissolved, which will promote the decomposition of S$_2$O$_8^{2-}$ [23,27], and this is not conducive to NO$_x$ removal. In addition, the dissolved SO$_2$ also can react with NO$_3^-$ to form NO (Equation (41)); the NO can escape from the solution, leading to the decrease of NO$_x$ removal [20].

\[
\begin{align*}
\text{NO}_2^- (aq) + H^+ (aq) + 2\text{HSO}_3^- (aq) & \leftrightarrow \text{HON(SO}_3\)\text{)}_{2}^- (aq) + 2\text{H}_2\text{O(l)} \quad (31) \\
\text{NO}_2^- (aq) + H^+ (aq) + \text{HSO}_3^- (aq) & \leftrightarrow \text{ONSO}_3^- (aq) + 2\text{H}_2\text{O(l)} \quad (32) \\
\text{ONSO}_3^- (aq) + \text{HSO}_3^- (aq) & \rightarrow \text{HON(SO}_3\)\text{)}_{2}^- (aq) \quad (33) \\
\text{NO(aq)} + \text{SO}_3^{2-} (aq) & \rightarrow \text{ON(SO}_3\)\text{)}_{2}^- (aq) \quad (34) \\
\text{NO(aq)} + \text{ON(SO}_3\)\text{)}_{2}^- (aq) & \rightarrow -\text{ON(NO)}\text{SO}_3^- (aq) \quad (35) \\
2\text{NO}_2 (aq) + \text{HSO}_3^- (aq) + \text{H}_2\text{O(l)} & \rightarrow 2\text{NO}_2^- \text{aq} + \text{SO}_3^{2-} (aq) + 3\text{H}^+ (aq) \quad (36) \\
2\text{NO}_2 (aq) + \text{SO}_3^{2-} (aq) + \text{H}_2\text{O(l)} & \rightarrow 2\text{NO}_2^- \text{aq} + \text{SO}_4^{2-} (aq) + 2\text{H}^+ (aq) \quad (37) \\
\text{S}_2\text{O}_8^{2-} (aq) + \text{SO}_2(l) + 2\text{H}_2\text{O(l)} & \rightarrow 2\text{HSO}_4 (aq) + \text{H}_2\text{SO}_4 (aq) \quad (38) \\
\text{SO}_4^{2-} (aq) + 2\text{OH}^- & \rightarrow \text{H}_2\text{O(l)} + \text{SO}_4^{2-} (aq) \quad (39) \\
2\text{SO}_2(l) + \text{ClO}_2 (aq) + 2\text{H}_2\text{O(l)} & \rightarrow 4\text{H}^+ (aq) + 2\text{SO}_4^{2-} (aq) + \text{Cl}^- (aq) \quad (40) \\
3\text{SO}_2(l) + 2\text{NO}_3^- (aq) + 2\text{H}_2\text{O(l)} & \rightarrow 2\text{NO}(l) + 3\text{SO}_4^{2-} (aq) + 4\text{H}^+ (aq) \quad (41)
\end{align*}
\]

Figure 8. Effect of gas flow rate on NO$_x$ removal.
The driving force of the mass transfer of the NO absorption increases with NO concentration in flue gas. However, compared with NaClO, the oxidants in the liquid phase, which increased the concentration of the oxidants and free radicals increased with NO concentration increasing, and the pH value of the absorbent solution also dropped very quickly. These reasons all are not conducive for the NO removal. Therefore, the combined result is that the absolute amount of NO removal increased slowly from 78.33% to 80.61%, with an increase of NO concentration in the flue gas. Because the amount of oxidants and free radicals were relatively sufficient when the NO concentration was less than 500 ppm, therefore the NOx removal slightly increased with an increase of NO concentration. However, when the NO concentration in the flue gas exceeded 500 ppm, although the amount of dissolved NO increased, but more amount of NO was not absorbed by the solution and run out of the reactor with the flue gas due to the limited gas-liquid contact time. Meanwhile, the consumption rates of the oxidants and free radicals increased with NO concentration increasing, and the pH value of the absorbent solution also dropped very quickly. These reasons all are not conducive for the NO removal. Therefore, the combined result is that the absolute amount of NO removal increased, but the NO removal efficiency slightly reduced. For example, when the NO concentrations in flue gas were 500 ppm and 1000 ppm, the NOx removal efficiencies were 80.61% and 74.04%, and the absolute amount of NO removal were 86.85 mg and 159.54 mg, respectively.

3.9. Effect of O2 Concentration

The influence of O2 concentration on NOx removal, ranging from 1 to 15% (v/v), was investigated, and the results are shown in Figure 11. The results demonstrate that O2 concentration in the flue gas had a certain effect on NOx removal. When the O2 concentration increased from 1 to 15% (v/v), the NOx removal increased slowly from 79.11 to 81.74%. This is because increasing the O2 concentration could lead to an increase in the O2 concentration in the liquid phase, which increased the concentration of the oxidants in the liquid phase. However, compared with NaClO2 and Na2S2O8, the oxidation of O2 was so weak in the experimental conditions that the NOx removal increased slowly with an increase of O2 concentration.
3.10. Tandem Double Column Absorption Experiments

The study found that when using a single absorber for absorption experiments, a maximum NO\textsubscript{x} removal of 80.61% could be obtained, and so that the average concentration of NO\textsubscript{2} in the exhaust was about 80 ppm at the optimal experimental conditions. Compared to NO, NO\textsubscript{2} is more soluble, and it is more easily absorbed by the solution. Therefore, in order to increase the NO\textsubscript{x} removal, several tandem double column absorption experiments were conducted. Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} solution (5 wt.%), NaOH solution (5 wt.%), CO(NH\textsubscript{2})\textsubscript{2} solution (5 wt.%), and Ca(OH)\textsubscript{2} solution (5 wt.%) were used to absorb the NO\textsubscript{x} from the first absorber, and the results are illustrated in Figure 12. The results show that the NO\textsubscript{x} removal efficiency could be significantly increased by using a tandem double column absorption process, compared to using the single column absorption process. The absorption capacities of the four kinds of absorbents were in the order of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} > NaOH > Ca(OH)\textsubscript{2} > CO(NH\textsubscript{2})\textsubscript{2}, with NO\textsubscript{x} removal efficiencies of 92.41, 91.12, 84.06, and 82.66%, respectively. The NO\textsubscript{x} removal efficiency by using Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} as an absorbent was higher than that of the other three absorbents. This is because Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} as an oxidant has a good efficiency of removal for both NO and NO\textsubscript{2}. For alkaline absorbents, the solution pH had a significant effect on NO\textsubscript{x} removal. The initial pH values of NaOH, Ca(OH)\textsubscript{2}, and CO(NH\textsubscript{2})\textsubscript{2} solution were 13.6, 9.6, and 8.4, respectively. This was because the amount of NO\textsubscript{2}
in the composition of NO\textsubscript{x} was significantly higher than that of NO. Thus, NO\textsubscript{x} removal increased with the solution pH increasing. Considering the NO\textsubscript{x} removal and economic costs, NaOH is a better absorbent, due to its high initial pH.

![Tandem double column absorption experiments.](image)

Figure 12. Tandem double column absorption experiments.

In the study, when using a single column and double column to absorb NO\textsubscript{x}, the NO\textsubscript{x} removal efficiencies of 80.61% and more than 90% could be obtained, respectively. The NO\textsubscript{x} removal efficiencies obtained in this work are significantly higher than that of our previous work (53.05%) [12]. In other methods, a dual oxidant (H\textsubscript{2}O\textsubscript{2}/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) has been used to remove NO, and the highest NO\textsubscript{x} removal efficiency (82%) was obtained [22], but the concentrations of H\textsubscript{2}O\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} were 0.3 mol/L and 0.1 mol/L respectively which were higher than this work. UV/H\textsubscript{2}O\textsubscript{2} was also utilized to remove NO, and NO removal of 72% could be obtained [16]. Using NaClO\textsubscript{2} as absorbent, and using a wet scrubber combined with a plasma electrostatic precipitator as reactor, the NO\textsubscript{x} removal of 94.4% could be reached, but the absorption device of this method was complicated [33]. Therefore, this method has advantages in terms of NO\textsubscript{x} removal efficiency compared to other methods. The main difference between the method and the WFGD technology is the composition of the absorbent. Therefore, the investment cost of the method in practical engineering applications is comparable with that of WFGD technology. The operating cost of the method may be higher than that of WFGD technology due to the high cost of the absorbent of this method. However, this method can simultaneously remove SO\textsubscript{2} and NO\textsubscript{x} efficiently. Therefore, considering the economic and environmental aspects, this method has a good application prospect in the field of flue gas treatment.

4. Product Analysis

In this study, the ionic products in solution were detected by using an ion chromatography system. As the peak times of persulfate ion and sulfate ion are almost the same, it is impossible to measure persulfate ions and sulfate ions by the ion chromatography method when both are present. Fortunately, it is clear that the final decomposition product of persulfate is sulfate [21–23], and the SO\textsubscript{2} that dissolves in the solution is eventually oxidized to sulfate in the oxidation system. Therefore, the study focused on the other anions. The IC analysis results of the ionic components in the solution before and after the reaction are shown in Table 2.
Table 2. Analysis of ionic components in the absorption solutions (mg/L).

<table>
<thead>
<tr>
<th></th>
<th>NO$_2^-$</th>
<th>NO$_3^-$</th>
<th>Cl$^-$</th>
<th>ClO$_2^-$</th>
<th>ClO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>—</td>
<td>—</td>
<td>95.888</td>
<td>901.050</td>
<td>119.975</td>
</tr>
<tr>
<td>End</td>
<td>—</td>
<td>142.58</td>
<td>145.515</td>
<td>845.950</td>
<td>85.425</td>
</tr>
</tbody>
</table>

Results show that only Cl$^-$, ClO$_2^-$, and ClO$_3^-$ were detected in the solution before the reaction (irrespective of persulfate and sulfate). However, NO$_3^-$, ClO$_2^-$, Cl$^-$, and ClO$_3^-$ were detected after the reaction. From a comparison of ionic composition before and after the reaction, Cl$^-$ concentration significantly increased, while ClO$_2^-$ and ClO$_3^-$ concentration decreased. Equation (42) could be used to explain why the amount of ClO$_3^-$ was decreased. According to the calculation results of Cl material balance, the amounts of elemental Cl in the solution before and after the reaction were 620.78 and 626.74 mg/L, respectively. The results indicate that the Cl element was maintained with mass conservation during the reaction. It was also found that there existed a large amount of NO$_3^-$, but no NO$_2^-$, in the solution. This result is mainly attributed to the strong oxidizing properties of the system. Due to the presence of large amounts of free radicals and oxidants in the system, the NO$_2^-$ formed during the reaction are easily oxidized to NO$_3^-$:

\[
2\text{ClO}_3^-(aq) + \text{SO}_3^{2-}(aq) + 2\text{H}^+(aq) \rightarrow \text{SO}_4^{2-}(aq) + 2\text{ClO}_2(l) + \text{H}_2\text{O}(l) \quad (42)
\]

As listed in Table 2, NO$_3^-$ was measured in the absorption solution with a concentration of 142.58 mg/L. The average initial concentration of NO in the flue gas was 516 ppm (about 691 mg/m$^3$). The NO$_x$ removal efficiency was calculated to be 83.20%, according to the NO$_3^-$ concentration in the solution, which was close to the actual NO$_x$ removal efficiency of 81.12%.

One of the disadvantages of the liquid absorption method is the disposal of the wastewater. Table 2 indicates that a large amount of Cl$^-$ is present in the absorption solution. The presence of large amounts of Cl$^-$ in the solution will increase the difficulty of wastewater treatment. Fortunately, the Friedel’s salt precipitation method has been developed to effectively remove Cl$^-$ from wastewater. Meanwhile, the method can effectively synergistic remove SO$_4^{2-}$, F$^-$ and heavy metal ions. The purified wastewater can be reused to reduce the consumption of water and alkali, or discharged into the enterprise waste water treatment system. The precipitated solids can be used to replace part of alkali or landfilled [34]. Therefore, through the effective treatment of wastewater, the ecological risk caused by the use of absorbent can be avoided.

Figure 13 shows the NO and NO$_2$ emissions in the outlet flue gas at the optimal conditions. As the reaction progressed, the NO concentration sharply decreased to nearly 0 ppm, and this was maintained for nearly 25 min at first, then it slowly increased to about 25 ppm at the end of the experiment. The concentration of NO$_2$ increased sharply to about 85 ppm at first, then it decreased slowly to about 75 ppm. This is because the NaClO$_2$ and Na$_2$S$_2$O$_8$ concentrations in the solution decreased as the reaction proceeded, while the solution pH also decreased rapidly with the reaction time increasing. In addition, due to the strongly alkaline pH of the solution, the SO$_2$ concentration decreased drastically to 0 ppm, and this was maintained until the end of the reaction.

Based on experimental results and the literature, the mechanism of simultaneous removal of NO$_x$ and SO$_2$ using NaClO$_2$/Na$_2$S$_2$O$_8$ solution was deduced. The mechanism of SO$_2$ removal is clear and relatively simple; SO$_2$ is eventually converted to SO$_4^{2-}$ via absorption, acid–base neutralization, and oxidation. The removal mechanism of NO$_x$ is very complicated. Equations (2)–(42) can be used to explain the mechanism of NO$_x$ removal; finally, NO is partially converted into NO$_2$, while most of the NO is converted into NO$_3^-$, which exists in the solution. Finally, SO$_2$ and NO$_x$ are removed efficiently by the dual oxidant solution.
5. Conclusions

In this work, simultaneous removal of NO\textsubscript{x} and SO\textsubscript{2} through a simple process using a composite absorbent (NaClO\textsubscript{2}/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) has been studied in a bubble column reactor. In view of the high SO\textsubscript{2} removal efficiency, factors affecting the NO\textsubscript{x} removal were systematically investigated. The following conclusions can be obtained based on experimental results:

1. NaClO\textsubscript{2} in the solution played a more important role than Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} for NO\textsubscript{x} removal. NaClO\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentrations, solution temperature, the initial pH of the solution, the gas flow rate, and SO\textsubscript{2}, NO, and O\textsubscript{2} concentrations all had a certain impact on the NO\textsubscript{x} removal efficiency. Among them, solution temperature, the initial pH of the solution, and the oxidant concentrations had significant effects on the NO\textsubscript{x} removal efficiency.

2. Considering the NO\textsubscript{x} removal efficiency and its economic costs, the optimal conditions for NO\textsubscript{x} removal were determined to be when the solution temperature was 50 °C, the initial solution pH was 12, the gas flow rate was 2 L·min\textsuperscript{-1}, and NaClO\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentrations were 0.2 wt.% and 0.5 wt.%, respectively. A NO\textsubscript{x} removal efficiency of more than 80% could be obtained at optimal conditions. When using a NaOH solution as an absorbent in the second absorber, the NO\textsubscript{x} removal efficiency could reach more than 90%.

3. A preliminary reaction mechanism for the simultaneous removal of NO\textsubscript{x} and SO\textsubscript{2} was deduced, based on experimental results. The dual oxidant (NaClO\textsubscript{2}/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) solution can effectively remove multi-pollutants and, thus, it has the potential to be applied in the wet desulfurization and denitrification process to realize the synergistic removal of multi-pollutants.

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