


## Article

# Simultaneous Removal of NO<sub>x</sub> and SO<sub>2</sub> through a Simple Process Using a Composite Absorbent

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**Abstract:** In this work, the feasibility of the simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> through a simple process using a composite absorbent (NaClO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was evaluated. Factors affecting the removal of NO<sub>x</sub> and SO<sub>2</sub>, such as NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentrations, solution temperature, the initial pH of solution, gas flow rate, and SO<sub>2</sub>, NO, and O<sub>2</sub> concentrations were studied, with a special attention to NO<sub>x</sub> removal. Results indicate that a synergistic effect on NO<sub>x</sub> removal has been obtained through combination of NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. NaClO<sub>2</sub> in the solution played a more important role than did Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> for the removal of NO<sub>x</sub>. The above factors had an important impact on the removal of NO<sub>x</sub>, 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<sub>x</sub> removal of more than 80% was obtained. Meanwhile, tandem double column absorption experiments were conducted, and a NO<sub>x</sub> removal efficiency of more than 90% was reached, using NaOH solution as an absorbent in the second reactor. A preliminary reaction mechanism for NO<sub>x</sub> and SO<sub>2</sub> 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<sub>x</sub>; SO<sub>2</sub>; NaClO<sub>2</sub>; Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; wet scrubbing

## 1. Introduction

NO<sub>x</sub> (mainly NO) and SO<sub>2</sub> released from the fossil fuels burning process, are becoming increasingly well-known as the precursors for photochemical smog and regional haze [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<sub>2</sub> and NO<sub>x</sub>, and they are widely used in the flue gas treatment of power plant boilers in worldwide [3]. At present, flue gas pollutants emitted from power plant are being effectively controlled. WFGD technology is often used to control SO<sub>2</sub> emitted from other industrial sources, such as industrial boilers and industrial furnaces; however, there is a lack of cost-effective NO<sub>x</sub> 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<sub>x</sub> control technology is developed, and it is better to develop an economical, and simplified method to achieve synergistic removal NO<sub>x</sub> and SO<sub>2</sub>.

The subject of multi-pollutant (NO<sub>x</sub>, SO<sub>2</sub>, 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 NO<sub>2</sub> is a key step. In order to increase the NO removal, a variety of reagents have been utilized to synergistically remove SO<sub>2</sub> and NO, such as potassium permanganate (KMnO<sub>4</sub>) [12], potassium ferrate (K<sub>2</sub>FeO<sub>4</sub>) [13], sodium chlorite (NaClO<sub>2</sub>) [14], sodium hypochlorite (NaClO) [15], UV/H<sub>2</sub>O<sub>2</sub> [16], ozone [17], and persulfate systems [18,19], and satisfactory SO<sub>2</sub> and NO removal efficiencies have been achieved under laboratory conditions.

In the oxidation absorption method, NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> are considered to be effective reagents for controlling multi-pollutant in flue gas. Fang et al. [20] developed a novel oxidation–absorption system for SO<sub>2</sub>, NO, and Hg<sup>0</sup> removal, and NaClO<sub>2</sub> and NaOH were used as the oxidant and the absorbent, respectively. SO<sub>2</sub>, NO<sub>x</sub>, and Hg<sup>0</sup> 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 ClO<sub>2</sub>) 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 NO<sub>2</sub> by the gas phase oxidants, then NO, NO<sub>2</sub>, and SO<sub>2</sub> were absorbed by the sodium humate solution. Finally, 82.7% of NO removal and 100% of SO<sub>2</sub> removal could be reached under optimal conditions. Wang et al. [22] used a dual oxidant (H<sub>2</sub>O<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) 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 SO<sub>2</sub> and NO in a single reactor is an urgent problem that needs to be solved.

According to our previous works [20], NaClO<sub>2</sub> was a better oxidant in view of SO<sub>2</sub> 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. Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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<sup>−</sup> could improve NO oxidation and absorption when using a persulfate solution to remove NO<sub>x</sub>. Hence, in this study, a composite absorbent consisting of NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was utilized to simultaneously remove SO<sub>2</sub> and NO<sub>x</sub>. The main purpose of this study is to evaluate the feasibility of simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> by using a dual oxidant solution. Meanwhile, factors affecting the removal of NO<sub>x</sub> and SO<sub>2</sub>, such as NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentrations, solution temperature, the initial pH of solution, gas flow rate, and SO<sub>2</sub>, NO, and O<sub>2</sub> concentrations were studied, with a special attention to NO<sub>x</sub> removal. The preliminary reaction mechanisms of SO<sub>2</sub> and NO<sub>x</sub> 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 NaClO<sub>2</sub> (80%, AR) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (98%, AR). CO(NH<sub>2</sub>)<sub>2</sub> (99%, AR), Ca(OH)<sub>2</sub> (95%, AR), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (98%, AR), and NaOH (96%, AR), were used in the second absorber when needed (Figure 1). The solution pH was adjusted using

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

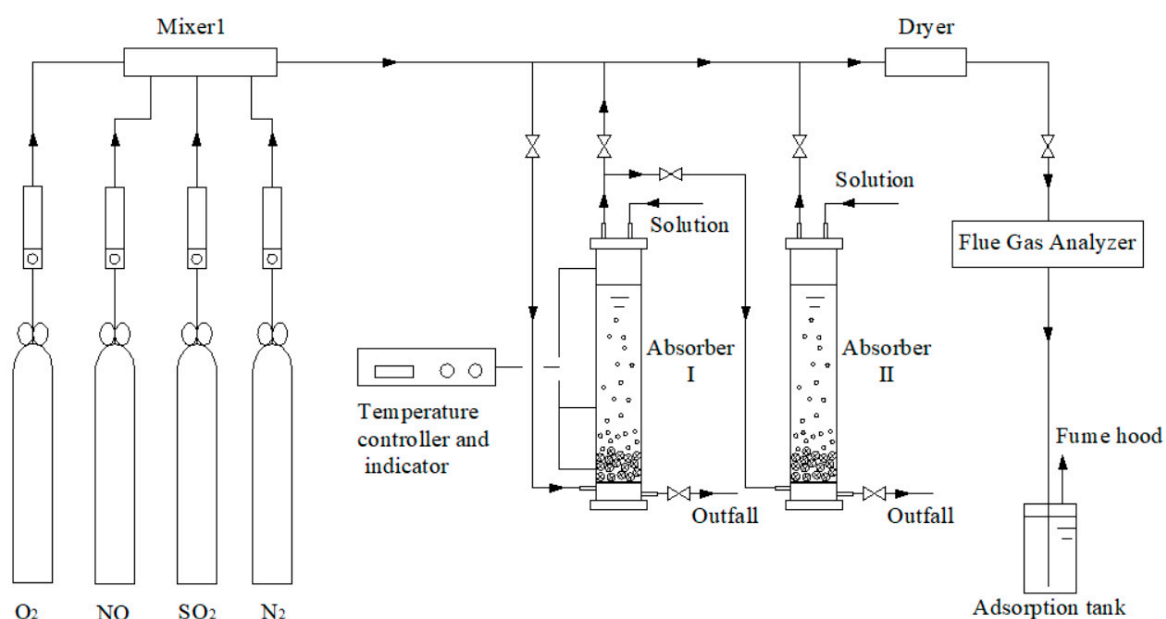


Figure 1. Schematic diagram of the experimental device.

## 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.

$\text{SO}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{N}_2$  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.  $\times$  65 cm length) were all made of borosilicate glass. The first absorber was filled with ceramic Raschig rings (1.25 cm i.d.  $\times$  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  $\text{CaCl}_2$  and then it was introduced into the detection system. In this work,  $\text{SO}_2$  concentration range was 0–2100 ppm,  $\text{NO}$  concentration range was 0–1000 ppm,  $\text{O}_2$  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  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{O}_2$  concentrations. An MP511 pH Detector (Shanghai Precision Instruments Co., Ltd., Shanghai, China) was used to detect the solution pH. Concentrations of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}_3^-$  were measured with an ion chromatography system (IC, Thermo ICS-1100, America). The  $\text{NO}_x$  and  $\text{SO}_2$  removal were calculated by Equation (1):

$$\eta = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\% \quad (1)$$

where  $\eta$  is the removal efficiency of  $\text{NO}_x$  or  $\text{SO}_2$ ;  $C_{\text{inlet}}$  and  $C_{\text{outlet}}$  are the inlet and outlet concentrations of  $\text{NO}_x$  or  $\text{SO}_2$ , respectively.

**Table 1.** Experimental conditions of the individual experiments.

No.	Experiment	Experimental Conditions
1	Removal of SO <sub>2</sub> and NO with different oxidant solutions	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C
2	Effect of NaClO <sub>2</sub> concentration	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, pH = 12
3	Effect of Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> concentration	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12
4	Effect of initial pH	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%
5	Effect of solution temperature	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12
6	Effect of gas flow rate	Single absorber, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12
7	Effect of SO <sub>2</sub> concentration	Single absorber, Q = 2 L/min, [NO] = 500 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12
8	Effect of NO concentration	Single absorber, Q = 2 L/min, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12
9	Effect of O <sub>2</sub> concentration	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12
10	Tandem double column absorption experiments	Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%; T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12 (the first absorber); T <sub>absorption</sub> = 25 °C, [reagent] = 5 wt.% (the second absorber)
11	Product analysis	Single absorber, Q = 2 L/min, [NO] = 500 ppm, [SO <sub>2</sub> ] = 1000 ppm, O <sub>2</sub> = 10%, T <sub>absorption</sub> = 50 °C, [Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] = 0.5 wt.%, [NaClO <sub>2</sub> ] = 0.2 wt.%, pH = 12

### 3. Results and Discussion

#### 3.1. Simultaneous Removal of SO<sub>2</sub> and NO<sub>x</sub> with Different Oxidant Solutions

Based on the literature and on our previous works [12,20,22,23], NaClO<sub>2</sub>, KMnO<sub>4</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were considered as better NO oxidants. Thus, in this study, the contrast experiments for different oxidants on SO<sub>2</sub> and NO<sub>x</sub> 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 NaClO<sub>2</sub> + NaOH, KMnO<sub>4</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 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 SO<sub>2</sub>, where the removal efficiency was close to 100%. However, different oxidant solutions had different effects on NO<sub>x</sub> removal, and the capacity on the NO<sub>x</sub> removal of three oxidant solutions was NaClO<sub>2</sub> > KMnO<sub>4</sub> > Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, with the average NO<sub>x</sub> removal efficiencies being at 48.69%, 48.13%, and 23.98%, respectively. Although the average efficiency of NO<sub>x</sub> removal by KMnO<sub>4</sub> solution was close to that of the NaClO<sub>2</sub> solution, NO<sub>x</sub> removal efficiency by the KMnO<sub>4</sub> solution decreased, with the reaction time increasing. Thus, it can be speculated that the NO<sub>x</sub> removal efficiency by the NaClO<sub>2</sub> solution is significantly better than that of KMnO<sub>4</sub> solution with the increase of reaction time. However, a NO<sub>x</sub> removal efficiency of approximately 50% using the NaClO<sub>2</sub> solution is relatively low. Hence, in this study, the authors hope to improve the denitration performance of NaClO<sub>2</sub> solution

(0.2 wt.%) by adding a certain amount of  $\text{Na}_2\text{S}_2\text{O}_8$  (0.1 wt.%), and the results are illustrated in Figures 2 and 3. The results show that  $\text{SO}_2$  and  $\text{NO}_x$  could be efficiently absorbed, and nearly 100% of the  $\text{SO}_2$  and 73.51% of the  $\text{NO}_x$  were simultaneously removed.  $\text{NO}_x$  removal using a dual oxidant solution was much better than removal by using a single oxidant solution.  $\text{SO}_2$  removal remained constant at about 100% in all tests, but the  $\text{NO}_x$  removal was affected by many factors, so the emphasis was placed on the discussion of  $\text{NO}_x$  removal by using a  $\text{NaClO}_2 + \text{Na}_2\text{S}_2\text{O}_8$  solution, in subsequent experiments.

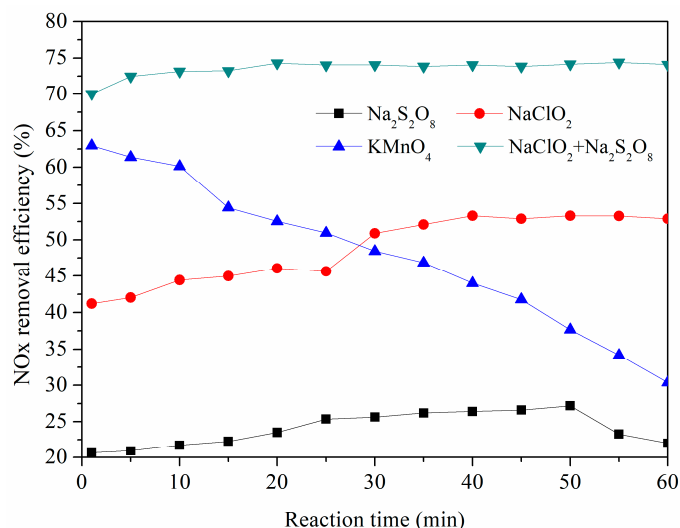


Figure 2. Effect of different oxidants on  $\text{NO}_x$  removal.

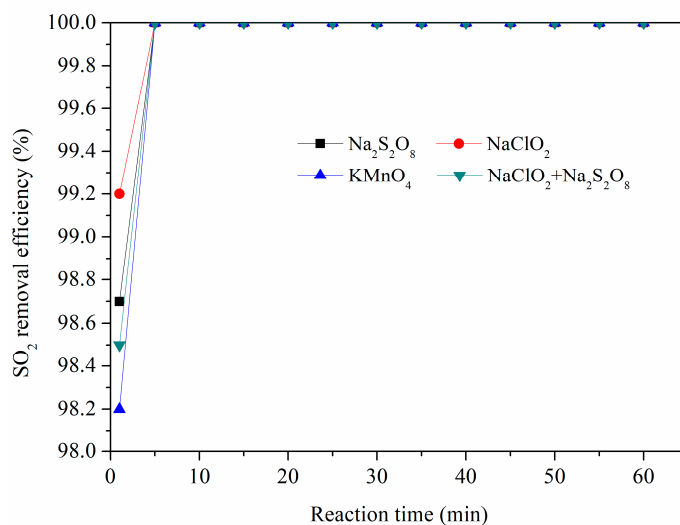
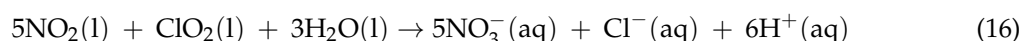
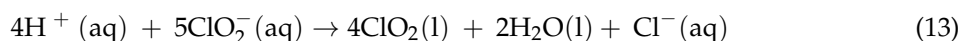
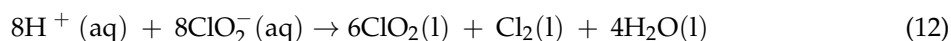
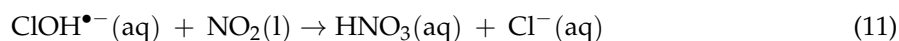
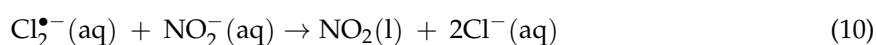
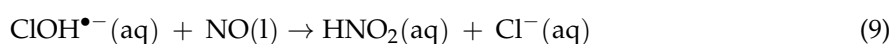
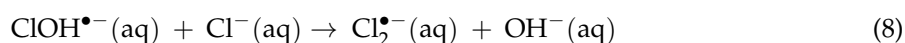
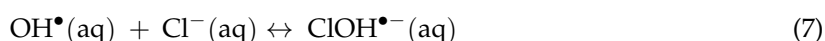
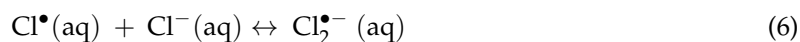
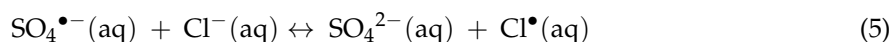
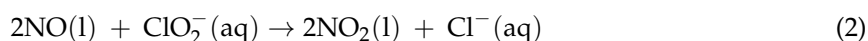


Figure 3. Effect of different oxidants on  $\text{SO}_2$  removal.

### 3.2. Effect of $\text{NaClO}_2$ Concentration

Several sets of experiments at various  $\text{NaClO}_2$  concentrations (0, 0.05, 0.1, 0.15, 0.20, and 0.30 wt.%) were carried out to study the effect of  $\text{NaClO}_2$  concentration on  $\text{NO}_x$  removal efficiency at the same persulfate level (0.5 wt.%). Figure 4 shows that the  $\text{NO}_x$  removal efficiency sharply increased with the increment of  $\text{NaClO}_2$  concentration at first, and then it gradually increased; when the  $\text{NaClO}_2$  concentration increased to 0.20 wt.%, a maximum  $\text{NO}_x$  removal efficiency of 80.61% was obtained, and thereafter,  $\text{NO}_x$  removal efficiency decreased from 80.61% to 72.83% with the increase of  $\text{NaClO}_2$  concentration from 0.2 wt.% to 0.3 wt.%.  $\text{NaClO}_2$  is a strong oxidant that can oxidize  $\text{NO}$  to  $\text{NO}_2$ , which then oxidizes  $\text{NO}_2$  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 NaClO<sub>2</sub> had a very pronounced effect, where the NO<sub>x</sub> removal efficiency went increased from 29.16% without any NaClO<sub>2</sub> to 54.68% with NaClO<sub>2</sub>. Moreover, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in the solution could be activated to generate sulfate-free radicals (SO<sub>4</sub><sup>•−</sup>) and hydroxyl radicals (OH<sup>•</sup>), and a large number of chlorine-free radicals (Cl<sup>•</sup>, Cl<sub>2</sub><sup>•−</sup>, ClOH<sup>•−</sup>) 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 Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> could increase the total number of reactive radical species, and enhance the NO<sub>x</sub> removal efficiency. In addition, as the reaction proceeded, the pH of the solution decreased, H<sup>+</sup> could catalyze the decomposition of ClO<sub>2</sub><sup>−</sup> to generate the strong oxidizing ClO<sub>2</sub> (Equations (12)–(14)). ClO<sub>2</sub> could oxidize NO to NO<sub>2</sub> and nitrate (Equations (15)–(17)) [20], leading to the increase of NO<sub>x</sub> removal. However, with an increasing concentration of NaClO<sub>2</sub>, the NO concentration in the exhaust decreased, but the NO<sub>2</sub> concentration increased. A large amount of NO<sub>2</sub> was produced by the reactions (Equations (2), (10) and (15)) due to the high NaClO<sub>2</sub> concentration. On the one hand, the high NaClO<sub>2</sub> concentration was not conducive to the absorption of NO<sub>2</sub> [20]; on the other hand, a large amount of NO<sub>2</sub> escaped from the system, due to the limited gas–liquid contact time. The study found the average emission concentrations of NO<sub>2</sub> were 10.56, 13.44, 39.35, 64.17, 87.18, and 158.24 ppm when the NaClO<sub>2</sub> concentrations were 0, 0.05, 0.1, 0.15, 0.20, and 0.30 wt.%, respectively. Obviously, the NO<sub>2</sub> concentration in the exhaust significantly increased when the NaClO<sub>2</sub> concentration was more than 0.2 wt.%. Thus, there was an optimal NaClO<sub>2</sub> concentration range of 0.15–0.2 wt.%, and the best NaClO<sub>2</sub> concentration was determined as 0.2 wt.%.





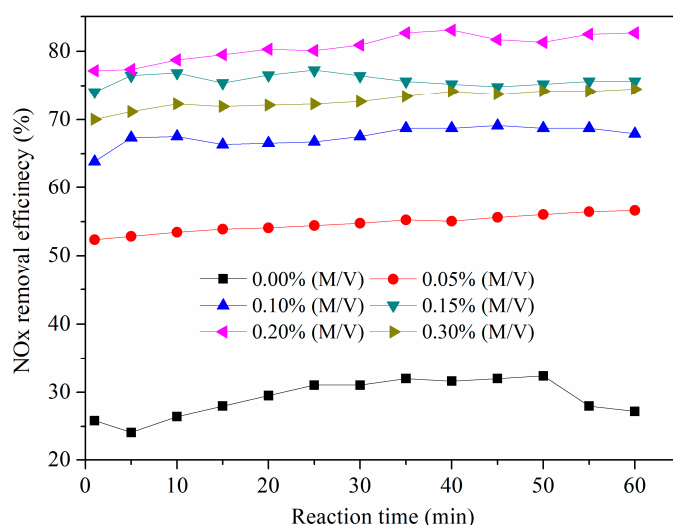


Figure 4. Effect of  $\text{NaClO}_2$  concentration on  $\text{NO}_x$  removal.

### 3.3. Effect of $\text{Na}_2\text{S}_2\text{O}_8$ Concentration

The results in Figure 5 illustrate the effect of  $\text{Na}_2\text{S}_2\text{O}_8$  concentration on  $\text{NO}_x$  removal efficiency at a constant  $\text{NaClO}_2$  concentration of 0.2 wt.% and at 50 °C. The addition of  $\text{Na}_2\text{S}_2\text{O}_8$  could effectively enhance the  $\text{NO}_x$  removal efficiency, and  $\text{Na}_2\text{S}_2\text{O}_8$  concentration had an important influence on the absorption of  $\text{NO}_x$ . Figure 5 shows that when the  $\text{Na}_2\text{S}_2\text{O}_8$  concentration in the solution increased from 0.00 wt.% to 0.1 wt.%, the  $\text{NO}_x$  removal efficiency rapidly increased from 48.69% to 72.34%, and then it slightly increased from 72.34% to 80.61% in the  $\text{Na}_2\text{S}_2\text{O}_8$  concentration range of 0.1 wt.% to 0.5 wt.%. However, further increases in  $\text{Na}_2\text{S}_2\text{O}_8$  concentration resulted in a slight drop in  $\text{NO}_x$  removal efficiency, which then maintained stability. For example, the  $\text{NO}_x$  removal efficiencies were 78.96% and 79.42% when the  $\text{Na}_2\text{S}_2\text{O}_8$  concentrations were 0.7 wt.% and 0.9 wt.%, respectively.

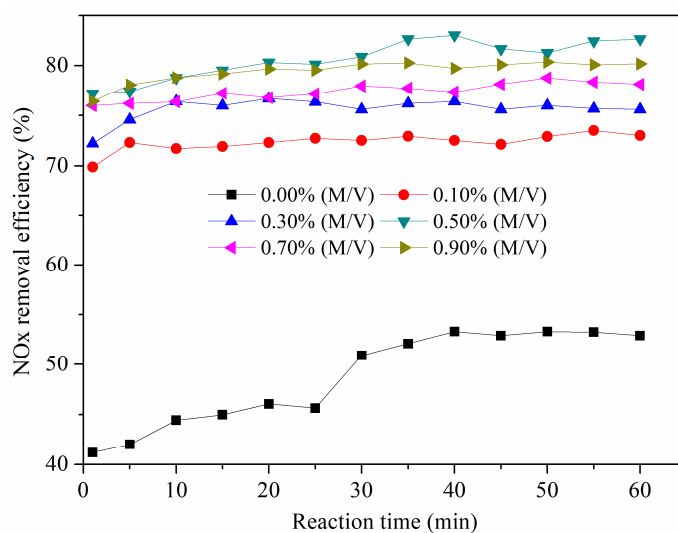
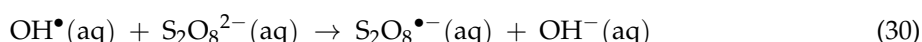
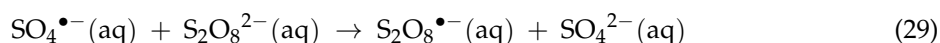
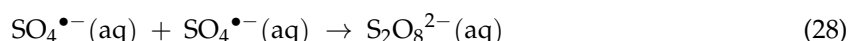
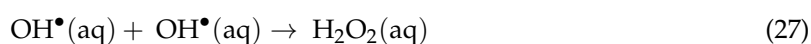
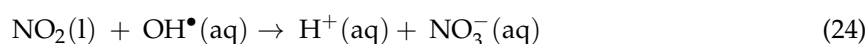
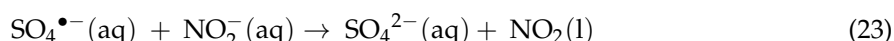
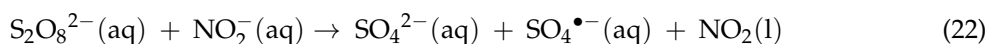
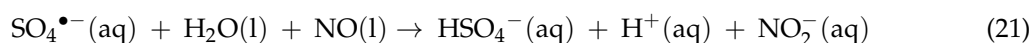
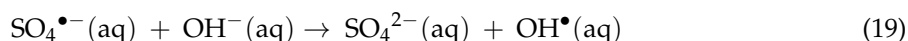
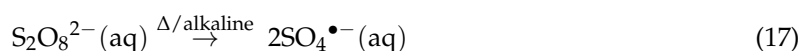


Figure 5. Effect of  $\text{Na}_2\text{S}_2\text{O}_8$  concentration on  $\text{NO}_x$  removal.

$\text{Na}_2\text{S}_2\text{O}_8$  is a strong and nonselective oxidant, and it can be activated by heat and alkaline [21], to produce an intermediate sulfate free radical ( $\text{SO}_4^{\bullet-}$ ) (Equation (17)) [23,26], then  $\text{SO}_4^{\bullet-}$  reacts with hydroxide ions or water molecules to produce a sulfate ion and hydroxyl radicals ( $\text{OH}^{\bullet}$ ) (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) ( $k = 6.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ). So, the conversion of  $\text{SO}_4^{\bullet-}$  to  $\text{OH}^{\bullet}$  via Equation (19)

becomes more important under alkaline conditions [23]. Both  $\text{SO}_4^{\bullet-}$  and  $\text{OH}^\bullet$  are very strong oxidants in aqueous solution. They can oxidize NO dissolved in water to nitrite, which further oxidizes to  $\text{NO}_2$  and, finally, the NO dissolved in water is oxidized to nitrate, as represented by the generalized Equations (20)–(26), respectively. The amount of  $\text{SO}_4^{\bullet-}$  generation in the solution increased with the increase of  $\text{Na}_2\text{S}_2\text{O}_8$  concentration at the constant reaction temperature. Therefore, the  $\text{NO}_x$  removal efficiency increased as the  $\text{Na}_2\text{S}_2\text{O}_8$  concentration increased. However, a further increase of  $\text{Na}_2\text{S}_2\text{O}_8$  concentration could lead to the production of a large amount of  $\text{SO}_4^{\bullet-}$ . 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  $\text{NO}_x$  removal reactions to consume a large amount of free radicals, finally leading to the decrease of  $\text{NO}_x$  removal efficiency [23,26,27]. Thus, considering the  $\text{NO}_x$  removal and economic costs, the optimum  $\text{Na}_2\text{S}_2\text{O}_8$  concentration range of 0.3–0.5 wt.% and the optimal concentration of 0.5 wt.% were selected.



### 3.4. Effect of Initial pH

The effect of the solution initial pH ranging from 6.0–12.0 on  $\text{NO}_x$  removal was studied. Figure 6 illustrates that  $\text{NO}_x$  removal efficiency was much higher under alkaline rather than acidic conditions, and the  $\text{NO}_x$  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  $\text{NO}_x$  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  $\text{NO}_2$  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  $\text{NO}_2$  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  $\text{NO}_2$  could reach 100% at low pH. The literature reported that  $\text{H}^+$  could catalyze the decomposition of  $\text{S}_2\text{O}_8^{2-}$  to form  $\text{SO}_3$  and  $\text{HSO}_4^-$  [23,27]. Hence, increasing the  $\text{H}^+$  concentration would promote the decomposition of  $\text{S}_2\text{O}_8^{2-}$ , and inhibit the generation of free radicals, finally resulting in a decrease in the amount of reactive radicals produced, and the decrease of  $\text{NO}_x$  removal. Meanwhile,  $\text{H}^+$  can also catalyze the decomposition of  $\text{ClO}_2^-$  to generate strongly oxidizing



$\text{ClO}_2$  (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  $\text{ClO}_2$  were being produced and dissolving into the solution under low pH conditions. Dissolved  $\text{ClO}_2$  could react with dissolved NO to preferentially form  $\text{NO}_2$  (Equation (15)) [29]. Although the  $\text{NO}_2$  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  $\text{NO}_2$  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  $\text{NO}_x$  removal increased. This is because more free reactive radicals were generated (especially  $\text{OH}^\bullet$ ) through the inhibition of the decomposition of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{ClO}_2^-$  under alkaline conditions. In particular, alkaline conditions could promote the conversion of  $\text{SO}_4^{\bullet-}$  to  $\text{OH}^\bullet$  by Equation (19).  $\text{OH}^\bullet$  is more reactive than  $\text{SO}_4^{\bullet-}$  [23]. Meanwhile, the escape amount of  $\text{NO}_2$  decreased significantly under alkaline conditions. So,  $\text{NO}_x$  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.

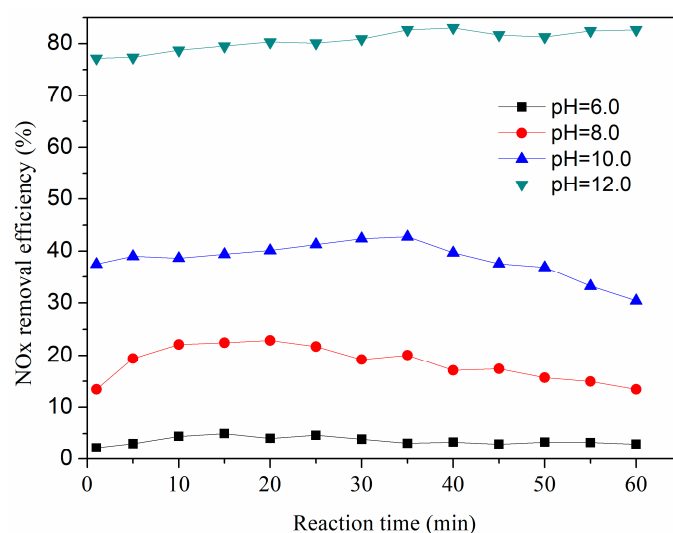


Figure 6. Effect of initial solution pH on  $\text{NO}_x$  removal.

### 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  $\text{NO}_x$  removal, and the results are shown in Figure 7. As depicted in Figure 7,  $\text{NO}_x$  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  $\text{NO}_x$  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  $\text{NO}_2$  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  $\text{NO}_2$  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  $\text{Na}_2\text{S}_2\text{O}_8$  to produce a large amount of sulfate free radicals [30], and then to generate a large number of other free radicals, such as  $\text{OH}^\bullet$ . These free radicals can oxidize NO to nitrite and nitrate, to promote NO removal. However, the high temperatures could also promote  $\text{ClO}_2$  generation [20], leading to the fractional conversion of NO and an increase in the generation of  $\text{NO}_2$ .  $\text{NO}_2$  can easily escape from solution into gas, due to the high temperature and limited gas–liquid contact time, so that the  $\text{NO}_x$  removal efficiency is decreased.

The influence of solution temperature on  $\text{NO}_x$  removal is ultimately determined by the above two aspects. The results indicate that the increase of absorption temperature is not conducive to the  $\text{NO}_x$  removal. Thus, it shows that  $\text{NaClO}_2$  in the dual oxidant solution plays a more important role than  $\text{Na}_2\text{S}_2\text{O}_8$  for the  $\text{NO}_x$  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.

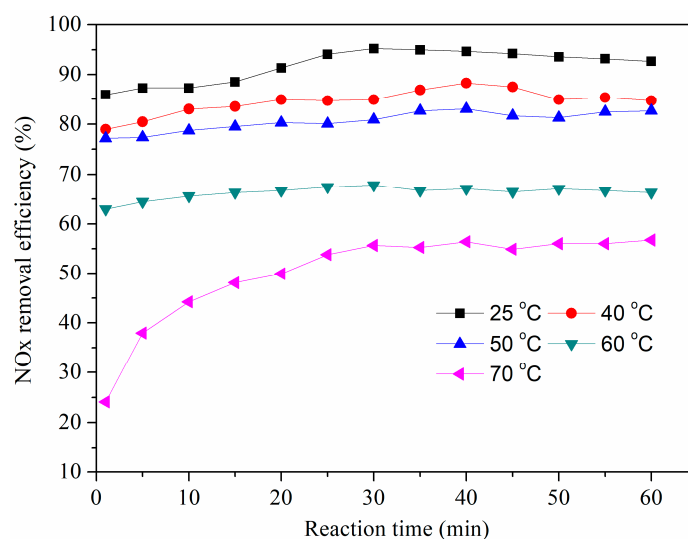


Figure 7. Effect of solution temperature on  $\text{NO}_x$  removal.

### 3.6. Effect of Gas Flow Rate

The effect of gas flow rate on  $\text{NO}_x$  removal is shown in Figure 8. Results indicate that the gas flow rate had an important effect on  $\text{NO}_x$  removal, and  $\text{NO}_x$  removal decreased with the increasing of the gas flow rate. When the gas flow rate increased from 1.0 to 3.0  $\text{L}\cdot\text{min}^{-1}$ , the  $\text{NO}_x$  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  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{NO}$  decreased as the gas flow rate increased. Meanwhile, it was also found that the average  $\text{NO}$  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  $\text{L}\cdot\text{min}^{-1}$ . The gas–liquid contact time decreased with the increase in the gas flow rate. On the one hand,  $\text{NO}$  molecules in the gas could not have the necessary time to dissolve into the solution. On the other hand, the  $\text{NO}_2$  generated by the reactions was taken out of the system without further reaction to form nitrates. Therefore, the  $\text{NO}_x$  removal efficiency was reduced with an increase in the gas flow rate.

### 3.7. Effect of $\text{SO}_2$ Concentration

The effect of  $\text{SO}_2$  concentration on  $\text{NO}_x$  removal in the range of 0–2100 ppm was investigated. Figure 9 indicates that the  $\text{SO}_2$  concentration in the flue gas had a very significant effect on  $\text{NO}_x$  removal; the  $\text{NO}_x$  removal efficiency was first rapidly increased, and then it decreased with the increase of  $\text{SO}_2$  concentration. For example, when the  $\text{SO}_2$  concentration increased from 0 to 500 ppm, the removal of  $\text{NO}_x$  rapidly increased from 62.05% to 83.37%, then with the  $\text{SO}_2$  concentration further increasing from 500 ppm to 2100 ppm, the  $\text{NO}_x$  removal efficiency decreased from 83.37% to 70.66%. Results indicate that the removal of  $\text{NO}_x$  could be promoted at low  $\text{SO}_2$  concentration conditions, but higher concentrations of  $\text{SO}_2$  inhibited  $\text{NO}_x$  removal.  $\text{SO}_2$  is very soluble in aqueous solution, and it dissolves into solution to generate  $\text{HSO}_3^-$ , which can react with  $\text{NO}_2^-$  to generate  $\text{HON}(\text{SO}_3)_2^{2-}$  and  $\text{ONSO}_3^-$  (Equations (31)–(33)) [30–32]. Meanwhile, dissolved  $\text{NO}$  can also directly react with  $\text{SO}_3^{2-}$  to form  $\text{ON}(\text{SO}_3)_2^{2-}$  and  $^-\text{ON}(\text{NO})(\text{SO}_3)_2^{2-}$  (Equations (34) and (35)) [32]. These reactions promote the dissolution and oxidation of  $\text{NO}$ , while reducing the consumption of free radicals and oxidants,

finally promoting NO removal. On the other hand,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  also can react with  $\text{NO}_2$  to form  $\text{NO}_2^-$  (Equations (36) and (37)) [32], then  $\text{NO}_2^-$  can react with oxidants or free radicals to form  $\text{NO}_3^-$ , finally resulting in the inhibition of  $\text{NO}_2$  volatilization from the solution, increasing  $\text{NO}_x$  removal. The research found that the average  $\text{NO}_2$  concentration in the exhaust decreased from 167.89 to 73.72 ppm when the  $\text{SO}_2$  concentration changed from 0 to 500 ppm. This finding also confirmed the existence of the above reaction process. When the  $\text{SO}_2$  concentration was further increased, the  $\text{NO}_x$  removal efficiency decreased. The main reason for this outcome was that severe competitive reactions of NO and  $\text{SO}_2$  for the limited oxidants and free radicals existed in the solution. As the solubility of  $\text{SO}_2$  is significantly greater than that of NO, so dissolved  $\text{SO}_2$  preferentially reacts with oxidants and free radicals in the solution (Equations (38)–(40)), and inhibits the oxidation of NO, finally resulting in a decrease of  $\text{NO}_x$  removal. Meanwhile, the pH of the solution drops sharply with the large amount of  $\text{SO}_2$  dissolved, which will promote the decomposition of  $\text{S}_2\text{O}_8^{2-}$  [23,27], and this is not conducive to  $\text{NO}_x$  removal. In addition, the dissolved  $\text{SO}_2$  also can react with  $\text{NO}_3^-$  to form NO (Equation (41)); the NO can escape from the solution, leading to the decrease of  $\text{NO}_x$  removal [20].

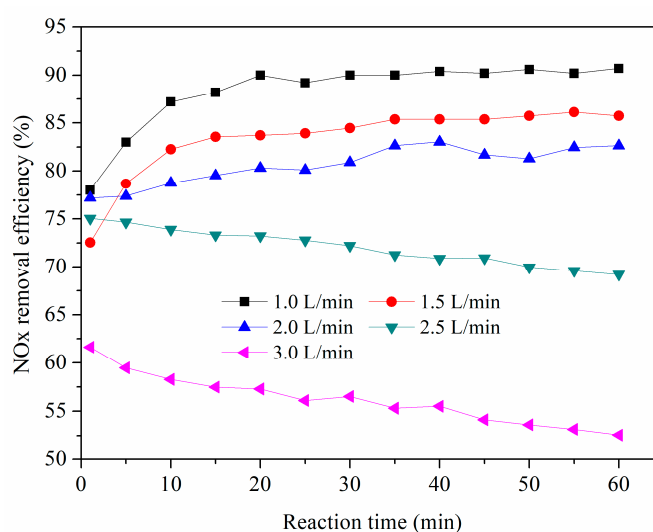
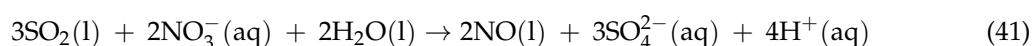
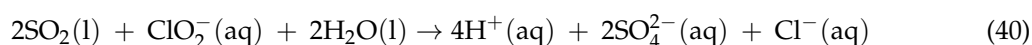
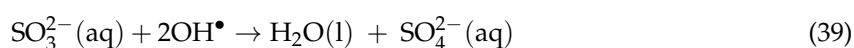
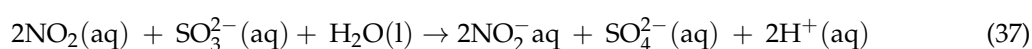
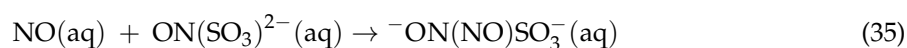
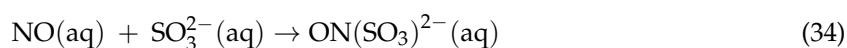
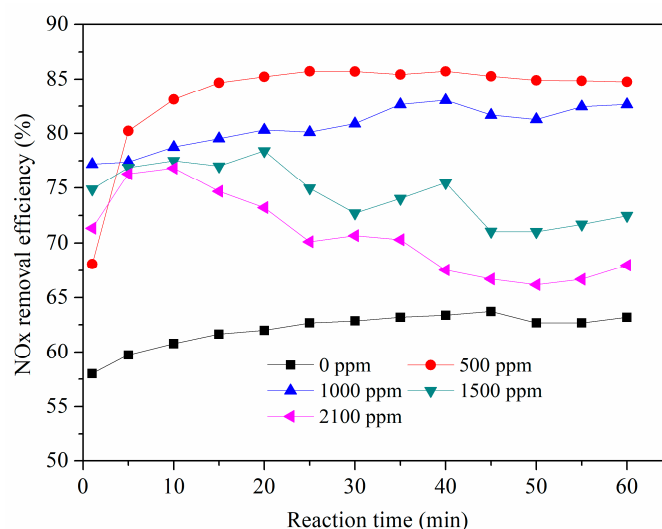


Figure 8. Effect of gas flow rate on  $\text{NO}_x$  removal.



**Figure 9.** Effect of SO<sub>2</sub> concentration on NO<sub>x</sub> removal.

### 3.8. Effect of NO Concentration

Figure 10 indicates that the effect of NO concentration on NO<sub>x</sub> removal. The results show that NO<sub>x</sub> removal was slightly affected by NO concentration. NO<sub>x</sub> removal increased slowly from 78.33% to 80.61%, with an increase of NO concentration from 100 to 500 ppm, and then it slowly decreased from 80.61% to 74.04%, with the NO concentration changing from 500 to 1000 ppm. The key step in the removal of NO by using oxidation absorption method is to promote the NO dissolution. The driving force of the mass transfer of the NO absorption increases with NO concentration in flue gas increasing. Hence, the amount of dissolved NO increases with an increase of NO concentration in flue gas. Because the amount of oxidants and free radicals were relatively sufficient when the NO concentration was less than 500 ppm, therefore the NO<sub>x</sub> 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 NO<sub>x</sub> 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 O<sub>2</sub> Concentration

The influence of O<sub>2</sub> concentration on NO<sub>x</sub> removal, ranging from 1 to 15% (v/v), was investigated, and the results are shown in Figure 11. The results demonstrate that O<sub>2</sub> concentration in the flue gas had a certain effect on NO<sub>x</sub> removal. When the O<sub>2</sub> concentration increased from 1 to 15% (v/v), the NO<sub>x</sub> removal increased slowly from 79.11 to 81.74%. This is because increasing the O<sub>2</sub> concentration could lead to an increase in the O<sub>2</sub> concentration in the liquid phase, which increased the concentration of the oxidants in the liquid phase. However, compared with NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, the oxidation of O<sub>2</sub> was so weak in the experimental conditions that the NO<sub>x</sub> removal increased slowly with an increase of O<sub>2</sub> concentration.

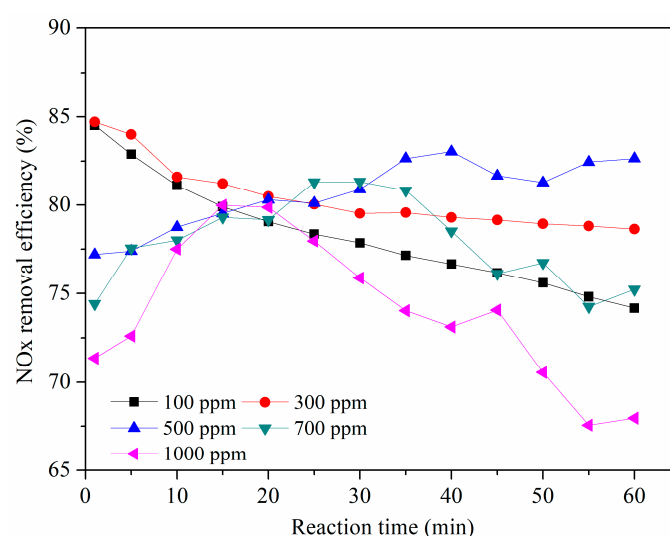


Figure 10. Effect of NO concentration on NO<sub>x</sub> removal.

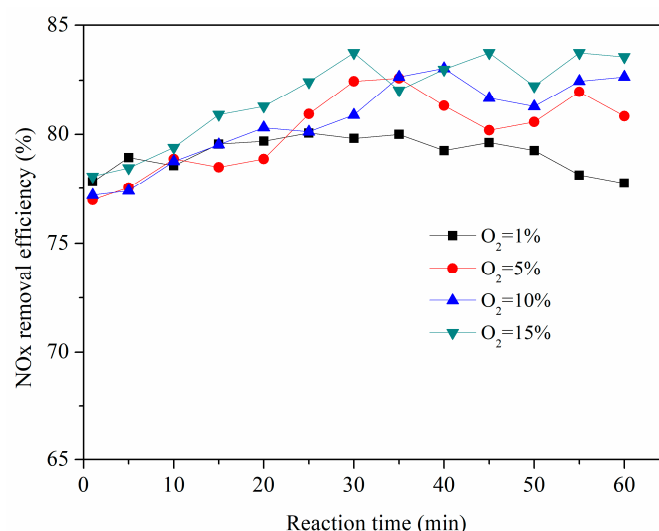


Figure 11. Effect of O<sub>2</sub> concentration on NO<sub>x</sub> removal.

### 3.10. Tandem Double Column Absorption Experiments

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

in the composition of  $\text{NO}_x$  was significantly higher than that of  $\text{NO}$ . Thus,  $\text{NO}_x$  removal increased with the solution pH increasing. Considering the  $\text{NO}_x$  removal and economic costs,  $\text{NaOH}$  is a better absorbent, due to its high initial pH.

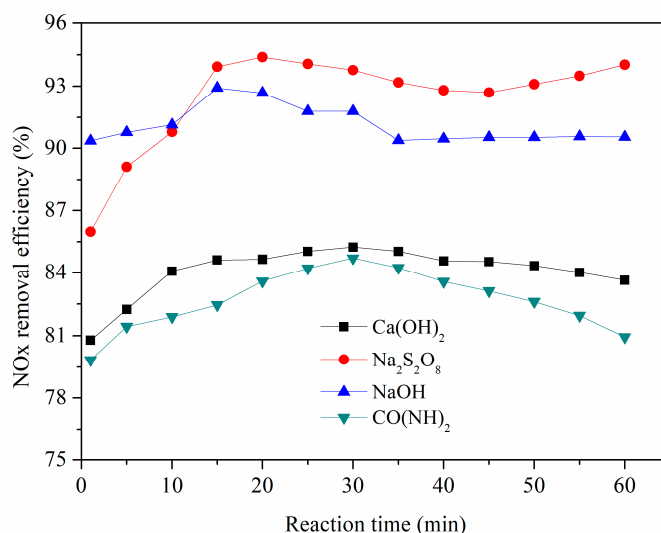


Figure 12. Tandem double column absorption experiments.

In the study, when using a single column and double column to absorb  $\text{NO}_x$ , the  $\text{NO}_x$  removal efficiencies of 80.61% and more than 90% could be obtained, respectively. The  $\text{NO}_x$  removal efficiencies obtained in this work are significantly higher than that of our previous work (53.05%) [12]. In other methods, a dual oxidant ( $\text{H}_2\text{O}_2/\text{Na}_2\text{S}_2\text{O}_8$ ) has been used to remove  $\text{NO}$ , and the highest  $\text{NO}$  removal efficiency (82%) was obtained [22], but the concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$  were 0.3 mol/L and 0.1 mol/L respectively which were higher than this work.  $\text{UV}/\text{H}_2\text{O}_2$  was also utilized to remove  $\text{NO}$ , and  $\text{NO}$  removal of 72% could be obtained [16]. Using  $\text{NaClO}_2$  as absorbent, and using a wet scrubber combined with a plasma electrostatic precipitator as reactor, the  $\text{NO}$  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  $\text{NO}_x$  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  $\text{SO}_2$  and  $\text{NO}_x$  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  $\text{SO}_2$  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).

	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{ClO}_2^-$	$\text{ClO}_3^-$
Initial	—	—	95.888	901.050	119.975
End	—	142.58	145.515	845.950	85.425

Results show that only  $\text{Cl}^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}_3^-$  were detected in the solution before the reaction (irrespective of persulfate and sulfate). However,  $\text{NO}_3^-$ ,  $\text{ClO}_2^-$ ,  $\text{Cl}^-$ , and  $\text{ClO}_3^-$  were detected after the reaction. From a comparison of ionic composition before and after the reaction,  $\text{Cl}^-$  concentration significantly increased, while  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  concentration decreased. Equation (42) could be used to explain why the amount of  $\text{ClO}_3^-$  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  $\text{NO}_3^-$ , but no  $\text{NO}_2^-$ , 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  $\text{NO}_2^-$  formed during the reaction are easily oxidized to  $\text{NO}_3^-$ :



As listed in Table 2,  $\text{NO}_3^-$  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<sup>3</sup>). The  $\text{NO}_x$  removal efficiency was calculated to be 83.20%, according to the  $\text{NO}_3^-$  concentration in the solution, which was close to the actual  $\text{NO}_x$  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  $\text{Cl}^-$  is present in the absorption solution. The presence of large amounts of  $\text{Cl}^-$  in the solution will increase the difficulty of wastewater treatment. Fortunately, the Friedel's salt precipitation method has been developed to effectively remove  $\text{Cl}^-$  from wastewater. Meanwhile the method can effectively synergistic remove  $\text{SO}_4^{2-}$ ,  $\text{F}^-$  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  $\text{NO}_2$  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  $\text{NO}_2$  increased sharply to about 85 ppm at first, then it decreased slowly to about 75 ppm. This is because the  $\text{NaClO}_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$  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  $\text{SO}_2$  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  $\text{NO}_x$  and  $\text{SO}_2$  using  $\text{NaClO}_2/\text{Na}_2\text{S}_2\text{O}_8$  solution was deduced. The mechanism of  $\text{SO}_2$  removal is clear and relatively simple;  $\text{SO}_2$  is eventually converted to  $\text{SO}_4^{2-}$  via absorption, acid–base neutralization, and oxidation. The removal mechanism of  $\text{NO}_x$  is very complicated. Equations (2)–(42) can be used to explain the mechanism of  $\text{NO}_x$  removal; finally, NO is partially converted into  $\text{NO}_2$ , while most of the NO is converted into  $\text{NO}_3^-$ , which exists in the solution. Finally,  $\text{SO}_2$  and  $\text{NO}_x$  are removed efficiently by the dual oxidant solution.

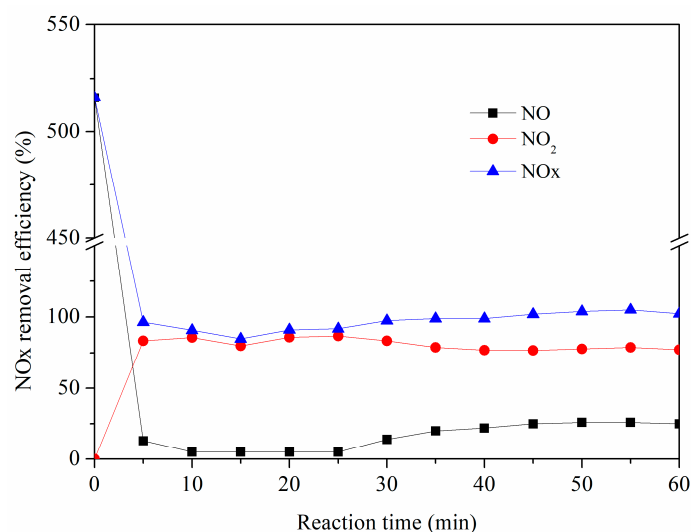


Figure 13. NO and NO<sub>2</sub> emissions in the outlet flue gas.

## 5. Conclusions

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

- (1) NaClO<sub>2</sub> in the solution played a more important role than Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> for NO<sub>x</sub> removal. NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentrations, solution temperature, the initial pH of the solution, the gas flow rate, and SO<sub>2</sub>, NO, and O<sub>2</sub> concentrations all had a certain impact on the NO<sub>x</sub> removal efficiency. Among them, solution temperature, the initial pH of the solution, and the oxidant concentrations had significant effects on the NO<sub>x</sub> removal efficiency.
- (2) Considering the NO<sub>x</sub> removal efficiency and its economic costs, the optimal conditions for NO<sub>x</sub> 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<sup>-1</sup>, and NaClO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentrations were 0.2 wt.% and 0.5 wt.%, respectively. A NO<sub>x</sub> 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<sub>x</sub> removal efficiency could reach more than 90%.
- (3) A preliminary reaction mechanism for the simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> was deduced, based on experimental results. The dual oxidant (NaClO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) solution can effectively remove multi-pollutants and, thus, it has the potential to be applied in the wet desulfurization and denitration process to realize the synergistic removal of multi-pollutants.

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