

Article

NO Removal from Simulated Flue Gas with a NaClO_2 Mist Generated Using the Ultrasonic Atomization Method

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Abstract: In order to enhance the mass transfer efficiency between gas–liquid interfaces, NaClO_2 mist generated by an ultrasonic humidifier was used to remove NO from simulated flue gas. The effects of some key parameters (the gas flow rate, the NaClO_2 concentration in the solution, the inlet NO concentration, the NaClO_2 solution pH) on NO removal efficiency were investigated preliminarily. The results showed that NaClO_2 mist could oxidize NO with a much higher efficiency compared with other mists containing either NaClO or H_2O_2 as oxidants. With an increase in the gas flow rate from 1.5 to 3.0 $\text{L} \cdot \text{min}^{-1}$, the atomizing rate of the NaClO_2 solution increased almost linearly from 0.38 to 0.85 $\text{mL} \cdot \text{min}^{-1}$. When the gas flow rate was 2.0 $\text{L} \cdot \text{min}^{-1}$, a complete removal of NO had been reached. NO removal efficiency increased obviously with an increase in the NaClO_2 concentration in the solution. With an increase in the inlet NO concentration, the ratio of NO in the flue gas and NaClO_2 in the mist increased almost linearly. Furthermore, the NaClO_2 mist exhibited a relatively stable and high NO_x removal efficiency in a wide pH range (4–11) of NaClO_2 solutions. The reason for the high NO removal efficiency was mainly ascribed to both the strong oxidative ability of NaClO_2 and the improved mass transfer at the gas–liquid interface.

Keywords: nitric oxide; ultrasonic atomization; sodium chlorite; mist

1. Introduction

A great deal of air pollutants are emitted from the combustion of fossil fuels in stationary sources and mobile sources every year, which results in serious damage to the ecological environment [1,2]. During the past decades, numerous efforts have been made to effectively remove sulfur oxides (SO_x), nitrogen oxides (NO_x), particle matters (PMs), and other air pollutants, from the waste gas [3]. Comparatively speaking, it is easy to decrease the emission of SO_x and PMs with a high efficiency by adopting a wet scrubbing method [4,5]. As to NO_x , NO accounts for more than 90% of the total makeup and it is insoluble in water, so NO_x cannot be removed effectively within the desulfurization scrubbers [6]. At present, a lot of NO_x emission control technologies have been developed, in which selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) are commercially available. SCR can remove NO_x with an efficiency of 80–95% and it has been successfully applied in power plants, heavy-duty vehicles, and ocean-going ships [7,8]. But there are still some challenges for SCR to deal with. It requires a large installation space and has a high investment cost [9]. When SO_2 and NO_x in flue gas are treated step-by-step through an integrated system, ammonium bisulfite salt formed in flue gas may deactivate the SCR catalyst. In addition, SCR requires a complicated control

system to avoid ammonia slip. For SNCR, its NO_x removal efficiency is obviously lower than that of SCR. Furthermore, a very high reaction temperature of 850–1100 °C is essential for SNCR to facilitate the reduction reaction between NO_x and the reductants [10]. Since both SCR and SNCR belong to the dry methods for NO removal, they have to be combined in series with a wet scrubbing desulfurization process for the simultaneous removal of NO_x and SO_2 . Such an integrated system suffers from some obvious drawbacks, such as the high cost, large size, complicated operation, and so on. To a great extent, these factors limit the application of the integrated system in some industrial areas.

In recent years, more and more researchers have been interested in developing new methods for the simultaneous removal of NO_x and SO_2 based on wet scrubbing processes [11]. In such cases, appropriate additives are required to improve the water solubility of NO_x . A number of reports have suggested NO removal with the help of an iron chelating agent such as Fe^{2+} -EDTA (Ethylene Diamine Tetraacetic Acid) because of its fast absorption rate for NO and high absorption capacity. However, the chelating agent could be easily oxidized by NO, NO_2 , and O_2 in flue gas to form Fe^{3+} -EDTA that is not capable of binding with NO [12]. It also needs to overcome other main drawbacks such as the high cost of EDTA, and the need to remove the N-S complex [13]. Another possible way is to oxidize the insoluble NO into soluble NO_2 , and then the NO_x molecules can be absorbed through wet scrubbing using the proper absorbents [14]. Although both nonthermal plasma and ozone can be used as excellent oxidants to oxidize NO effectively, they usually require expensive equipment and a large energy supply [15,16].

Since oxidants in a solution can oxidize NO effectively and economically, more and more interest is being focused on various inorganic reagents, such as KMnO_4 [17], H_2O_2 [18], oxone [19], $\text{Na}_2\text{S}_2\text{O}_8$ [20,21], NaClO [22–24], NaClO_2 [25–27], ClO_2 [28] and so on. Among these oxidants, NaClO_2 is found to be one of the most promising chemicals for the oxidation and absorption of NO. Some studies on the simultaneous removal of NO and SO_2 using a NaClO_2 solution have been published in the past decades [29,30]. Most of the work done till now has concentrated more or less on chemical scrubbing experimentation. However, the traditional chemical scrubbing method requires a large volume of reactors, expensive pipes, and powerful fans. In order to improve the economic feasibility of chemical scrubbing, a novel wet reaction system based on the ultrasonic atomization process has been proposed by Park et al. [31,32]. A very fine NaClO_2 mist generated by the ultrasonic atomization method was used to absorb NO and SO_2 simultaneously, and then the formed aerosol particles were collected in an electrostatic precipitator. Since the size of the ultrasonic mist was much smaller than that of the spraying droplets, it was beneficial to increase the gas–liquid contact area between the reactants and waste gas. Park et al. had preliminarily investigated the simultaneous removal performance and kinetics for NO and SO_2 using NaClO_2 mist. But more research is still necessary to further explore the feasibility of the process of NO removal with NaClO_2 mist. In this work, a NaClO_2 mist generated by an ultrasonic humidifier was used to remove NO from simulated flue gas, and the effects of some key operating parameters (the different oxidants, the gas flow rate, the concentration of the NaClO_2 solution, the inlet NO concentration, the initial solution pH) on the NO removal efficiency were investigated experimentally; the possible reaction pathways are also discussed.

2. Experimental Section

2.1. Experimental Apparatus

The experimental system is shown in Figure 1. Two kinds of gases, pure N_2 gas (99.999%) and NO span gas (10.04% NO with N_2 as a balance gas), were used to prepare the simulated flue gas. A custom-made ultrasonic humidifier with an ultrasonic atomizer (16.8 W, 1.67 MHz) situated inside was used to produce NaClO_2 mist. A column reactor was located at the top of the ultrasonic humidifier. Both the ultrasonic humidifier and reactor column were made of polymeric methyl methacrylate (PMMA). The height and inner diameter of the column reactor were 300 mm and 50 mm, respectively. An electric condenser was used to remove moisture from the flue gas before it entered the gas analyzer.

A gas analyzer (MGA5, MRU) with non-dispersive infrared (NDIR) sensors was used to measure the concentrations of multi-pollutants such as NO, NO₂, and NO_x. Here the concentration of NO_x in the experiments referred to the total sum of the NO and NO₂ concentrations. The measurement accuracy of the analyzer was $\pm 2\%$ of full scale. Since the change of liquid level in humidifier will affect the atomizing rate of the mist to some extent, a peristaltic pump (BT100-2J, Longer, Baoding, China) was used to continuously feed NaClO₂ solution into the ultrasonic humidifier to keep the liquid level constant during the atomization process.

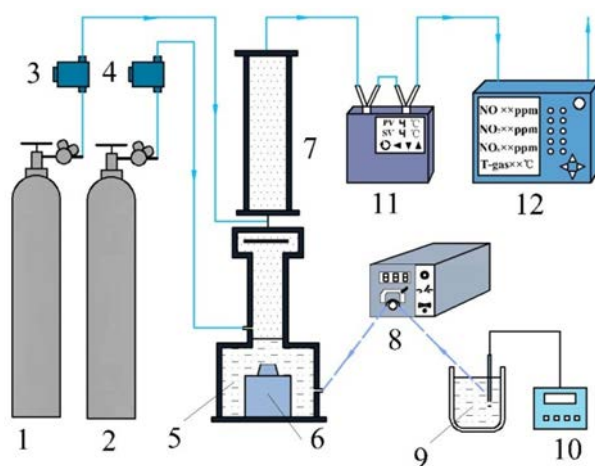


Figure 1. Schematic diagram of the experimental system. (1—N₂ pure gas bottle; 2—NO span gas bottle; 3,4—mass flow controllers (MFC); 5—ultrasonic humidifier; 6—ultrasonic atomizer; 7—column reactor; 8—peristaltic pump; 9—NaClO₂ solution; 10—pH meter; 11—electric condenser; 12—gas analyzer).

2.2. Experimental Procedures

The NaClO₂ solution was prepared using NaClO₂ powder (80%, Aladdin) and deionized water. The initial pH value of the NaClO₂ solution was adjusted by adding 1 mol/L HCl or 1 mol/L of NaOH solution, and measured with a pH meter (S210, Mettler-Toledo, Zurich, Switzerland). The flow rates of the pure N₂ gas and NO span gas were metered through mass flow controllers (MFCs, D07-19B, Sevenstar, Beijing, China). At first, the N₂ was introduced into the ultrasonic humidifier to activate the generated NaClO₂ mist. NO span gas was injected into the pipe that connected the humidifier and the column reactor. An extra electric condenser was used to remove the mist from the flue gas before it entered the flue gas analyzer. Each part of the experiment was conducted at room temperature (20 °C). The concentrations of NO, NO₂, and NO_x were recorded using the gas analyzer at an interval of 10 s.

2.3. Data Processing

Before the ultrasonic atomization of NaClO₂ solution, the concentrations of NO and NO_x in the simulated flue gas were measured as inlet concentrations. At the beginning of the atomization process, the NO_x concentrations decreased and stabilized within tens of seconds. Then, the atomization process lasted for another 10 min. The averaged concentrations of NO and NO_x measured in a stable state were used as the outlet concentrations. Thus, the removal efficiencies of the pollutants could be calculated by the following equation:

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

where η is the removal efficiency of the targeted pollutant (%), C_{in} and C_{out} are the inlet and outlet concentrations of the targeted pollutants (ppm), respectively.

3. Results and Discussion

3.1. Comparison of Different Oxidants in Mist

NaClO_2 , NaClO , and H_2O_2 are common oxidants that are used to remove NO from flue gas through wet scrubbing. Here they are chosen to combine with the ultrasonic atomization process in order to investigate the effect of various oxidants on NO_x removal efficiency; the results are shown in Figure 2. The concentration of oxidants in the solution was $0.02 \text{ mol} \cdot \text{L}^{-1}$. The flow rate of the simulated flue gas was 2 L/min. The inlet concentrations of NO and NO_2 were 500 and 0 ppm, respectively. The initial pH values of oxidant solution were adjusted to 4, 7, and 10, respectively. The atomization rate of the oxidant solution was measured to be about 0.6 mL/min.

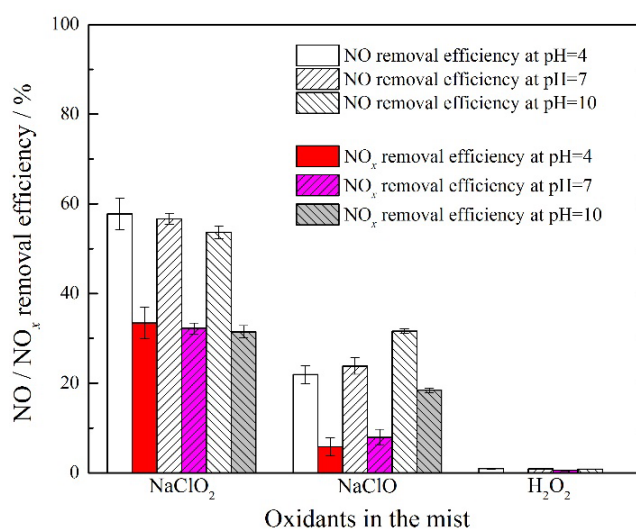


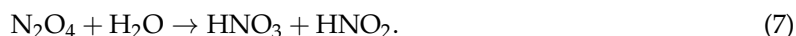
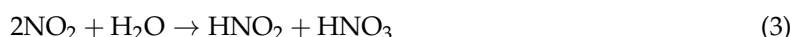
Figure 2. The change of NO removal efficiencies with different oxidants in mist.

It can be seen from Figure 2 that NO_x removal efficiencies changed greatly for the various oxidants in the mist. For the H_2O_2 mist, NO removal efficiencies were below 1%. That is due to the low oxidative ability of H_2O_2 compared with other oxidants. Some enhancement techniques are usually required for H_2O_2 oxidant to improve its NO removal efficiency [33–35].

For the NaClO mist, NO removal efficiency increased slightly from 21.9% to 23.8% and NO_x removal efficiency increased from 5.8% to 7.9% with NaClO solution pH increasing from 4 to 7. As the solution pH was increased from 7 to 10, NO removal efficiency increased obviously up to 31.6% and NO_x removal efficiency increased up to 18.4%. The variation trend of NO removal efficiency is the same as that for NO_x removal efficiency. Since a part of the generated NO_2 had not been absorbed by the scrubbing solution, NO_x removal efficiency was obviously lower than the corresponding NO removal efficiency. It was reported in a previous study that an acidic or a basic condition was favorable for NO removal by wet scrubbing using a NaClO solution, because HClO was considered as the effective oxidant among the active chlorine species [36,37]. However, for the ultrasonic atomization process, the effect of the initial pH of NaClO solution on the NO removal efficiency was quite different from that for the wet scrubbing process. Here HClO is still considered as the effective composition in the NaClO mist. NO_x removal efficiency for pH 10 NaClO mist is obviously higher than pH 7 NaClO mist. The reason might be that on one hand, the pH of NaClO mist generated from the pH 10 NaClO solution may be different from the pH 10 NaClO solution. It is possible that the former is a little lower than the latter. On the other hand, the size of the NaClO mist is much finer than the spraying droplets. The size of the ultrasonic mist has been measured using a Laser Particle Sizer (DP-02, OMEC, Zhuhai, China), and it is in the range of 2–5 μm . The size of the spraying droplets are usually in the range of 100–300 μm . This means that the fine mist can be acidized easily during the NO absorption process,

as a result the NaClO mist pH decreases to below 7 quickly in the reactor. Thus, it leads to a high NO_x removal efficiency for the NaClO mist ultrasonically generated from a pH 10 NaClO solution. Moreover, it is worth noting that the molar ratio of the NO concentration in flue gas and the NaClO concentration in the solution is approximately 3.45:1, suggesting that the molar ratio of reactants of NO and NaClO in the reactor is nearly 1:1. The result showed that the utilization of the NaClO oxidant in the mist is high.

As shown in Figure 2, when the NaClO₂ oxidant was used to oxidize NO, the NO removal efficiency decreased slightly from 57.8% to 53.6% and the NO_x removal efficiency decreased from 33.4% to 31.5% with the NaClO₂ solution pH increasing from 4 to 10. With the change of solution pH, the variation trend of the NO_x removal efficiency for the NaClO₂ mist was different from that for the NaClO mist. At first, the oxidation power of NaClO₂ is much higher than NaClO. A high and stable NO_x removal efficiency can be reached by wet scrubbing using NaClO₂ solution in a wide pH range of 3–10. So it is understandable that one could get a high and stable NO_x removal efficiency by using NaClO₂ mist ultrasonically generated from a NaClO₂ solution with a wide pH range of 4–11. Note that the active components in the NaClO₂ solution are different from those in the NaClO solution. HClO₂ in the NaClO₂ solution is considered as the effective composition for NO oxidation. We think that a very small fractional composition of HClO₂ can oxidize NO efficiently, so it is normal for NaClO₂ mist to obtain an excellent NO removal performance. As the fractional composition of HClO₂ in NaClO₂ mist decreases gradually with the increase of solution pH, it can explain the slight decrease in NO_x removal efficiency for the NaClO₂ mist when the initial solution pH increases from 4 to 10. The molar ratio of NO concentration in flue gas and NaClO₂ concentration in the solution is 3.45:1, but NO removal efficiency for the NaClO₂ mist is approximately twice compared with that for the NaClO mist. It implies that the molar ratio of reactants of NO and NaClO₂ in the reactor increased up to 2:1. One could deduce that the oxidation and absorption process of NO by the NaClO₂ mist might involve the reactions below [26,38]:



It is known that the oxidative ability of NaClO₂ is much higher than those of NaClO and H₂O₂. The results demonstrate that the NO removal performance for the oxidants in mist is in the order of NaClO₂ > NaClO >> H₂O₂. As both NO removal efficiency and the utilization of the NaClO₂ oxidant in mist are much higher than those for NaClO and H₂O₂, NaClO₂ is chosen as the oxidant in this study.

3.2. Effect of Gas Flow Rate

During the ultrasonic atomization process, with the increase in the gas flow rate, the amount of ultrasonic mist will increase accordingly. The effect of the flow rate of the simulated flue gas on the atomizing rate of the NaClO₂ solution was investigated, and the results are shown in Figure 3. The concentration of NaClO₂ in the solution was 0.04 mol·L^{−1}, and the solution pH was adjusted to 7. The flow rate of the simulated flue gas was in the range of 1.5–3.0 L·min^{−1}. It can be seen from Figure 3 that with the increase in gas flow from 1.5 to 3.0 L·min^{−1}, the atomizing rate increased almost linearly from 0.38 to 0.85 mL·min^{−1}. A fitted line was obtained with a high correlation coefficient of 0.99891 and a slope of 0.28894. Since the intercept of the fitted line was 0, the slope of the fitted line was equal to the ratio of the atomizing rate and gas flow, namely the liquid–gas ratio in the column

reactor. Thus, the liquid–gas ratio in this study could be considered as constant, which was much smaller than that for the spraying droplets.

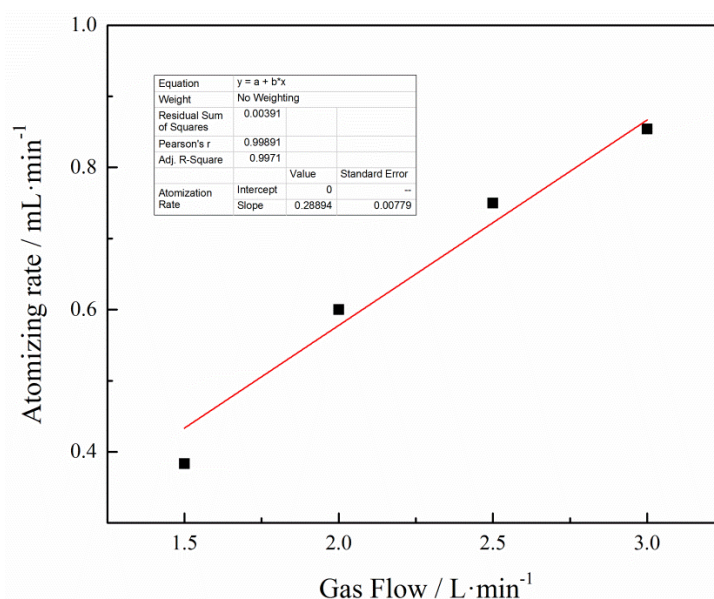


Figure 3. The change of atomizing rate of the NaClO₂ solution with gas flow.

Figure 4 presents the effect of gas flow on NO_x removal efficiency. The concentration of the NaClO₂ in the solution was 0.04 mol·L^{−1}, and the initial pH value was 10.4. The inlet concentrations of NO and NO₂ were 500 and 0 ppm, respectively. The flow rate of the simulated flue gas was in the range of 1.5–3.0 L·min^{−1}. As shown in Figure 4, the NO removal efficiency increased from 78.3% to 100% as the gas flow increased from 1.5 to 2.0 L·min^{−1}. Accordingly, the NO_x removal efficiency increased from 46.2% to 61.5%. However, on further increasing the gas flow from 2.0 to 3.0 L·min^{−1}, both the NO and NO_x removal efficiencies dropped slowly. Generally, the atomizing rate of the ultrasonic humidifier is mainly affected by the solution surface tension, the liquid height, the ultrasonic power, and gas flow. The liquid height and the ultrasonic power were kept constant in our experiments. As the concentration of the oxidant in the solution was comparatively low, the effect of the oxidant additive on the surface tension of the deionized water solution was neglected. Thus, the flow rate of the simulated flue gas became the major factor that determined the atomizing rate of the NaClO₂ solution. On one hand, the gas disturbance in the ultrasonic humidifier would be enhanced with the increase of gas flow, which increased the probabilities of inelastic collision and aggregation between the mist droplets after they left the liquid surface. This might adversely increase the diameter of the mist droplets. On the other hand, the mist droplets could quickly leave the atomization zone when the gas flow increased. To some extent, it was helpful to decrease the probabilities of inelastic collision and aggregation, resulting in more mist droplets flowing out together with the flue gas as the gas flow increased. This might be the reason for the change in the NO_x removal efficiency as the gas flow increased from 1.5 to 2.0 L·min^{−1}. When the gas flow increased from 2.0 to 3.0 L·min^{−1}, the residence time in the column reactor decreased obviously, though the atomizing rate of the NaClO₂ solution had increased proportionally. The less the residence time was, the lower the NO_x removal efficiency was. Therefore, a gas flow of 2 L·min^{−1} was chosen for the subsequent experiments in order to achieve a relatively high NO_x removal efficiency.

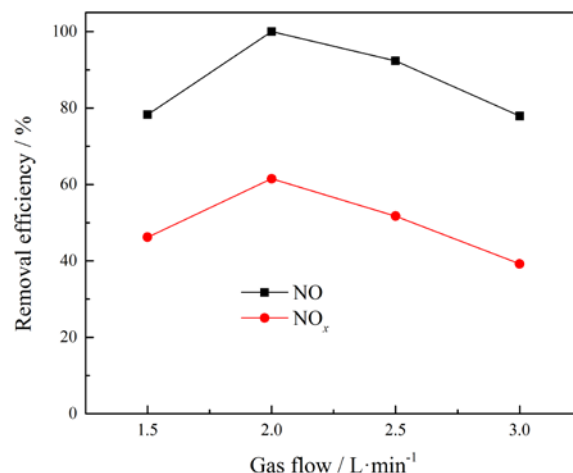


Figure 4. Effect of gas flow on the NO_x removal efficiencies.

3.3. Effect of NaClO₂ Concentration

Figure 5 shows the effect of NaClO₂ concentration in the solution on the change of the outlet concentration of NO in the flue gas during the denitrification process. The gas flow of the simulated flue gas was 2 L/min. The inlet concentrations of NO and NO₂ were 700 and 0 ppm, respectively. NaClO₂ concentrations in the solutions were 0.01, 0.02, 0.04, and 0.08 mol·L⁻¹. The corresponding pH values of the NaClO₂ solutions without adjustment were 10.1, 10.3, 10.5, and 10.7, respectively. It can be seen that when there was no addition of HCl or NaOH to adjust the initial solution pH, the pH values of the NaClO₂ solution increased almost linearly with the increment of the NaClO₂ oxidant. As shown in Figure 5, when the NaClO₂ mist was introduced into the reactor at the beginning, the NO concentration in outlet gas dropped quickly. The higher the NaClO₂ concentration in the solution was, the lower the outlet NO concentration was. When the NaClO₂ concentration in the solution was 0.08 mol/L, NO had been removed completely.

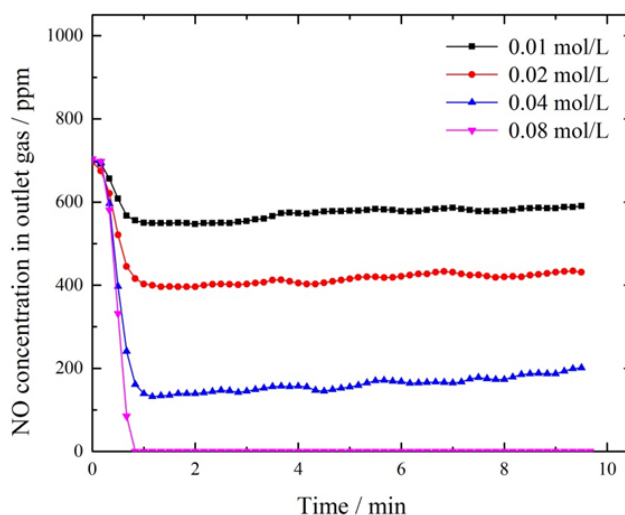


Figure 5. The effect of NaClO₂ concentration on the change of NO concentration in outlet gas during the denitrification process.

The change in the NO_x removal efficiency and the outlet NO₂ concentration in the flue gas with the NaClO₂ concentration in the solution are shown in Figure 6. NO removal efficiency increased greatly from 18.4% to 85.0% with the NaClO₂ concentration in the solution increasing from 0.01 to

$0.04 \text{ mol}\cdot\text{L}^{-1}$. Accordingly, the NO_2 concentration in outlet gas increased from 37 ppm to 215 ppm, and the NO_x removal efficiency increased from 13.1% to 42.5%. The result implied that the NaClO_2 mist could oxidize NO efficiently. When the NaClO_2 concentration in the solution was $0.04 \text{ mol}\cdot\text{L}^{-1}$, the molar ratio of NO in the flue gas and NaClO_2 in the mist was about 2.38:1. The results suggest that the reaction between NO and NaClO_2 possibly occurred as described in Equation (2). It also demonstrates that the generated NO_2 could be effectively absorbed by the mist.

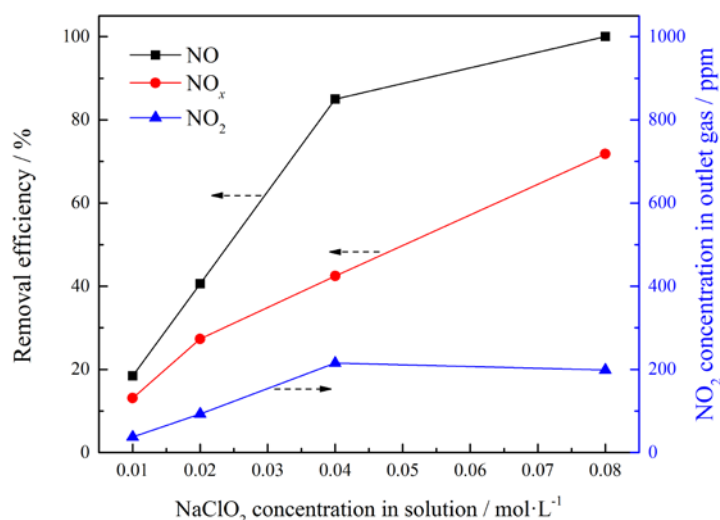


Figure 6. The change of the NO_x removal efficiency and outlet NO_2 concentrations with NaClO_2 concentration in the solution.

3.4. Effect of NO Concentration

The effect of the inlet NO concentration on the NO removal efficiency was investigated, and the results are shown in Figure 7. The flow rate of the simulated flue gas was 2 L/min. The inlet NO concentrations were in the range of 100–900 ppm, and the inlet NO_2 concentrations were 0 ppm. NaClO_2 concentrations in the solutions were 0.01, 0.02, 0.04, and $0.08 \text{ mol}\cdot\text{L}^{-1}$, and the initial solution pH values were 10.1, 10.3, 10.5, and 10.7 accordingly. As shown in Figure 7, when the NaClO_2 concentration in the solution was $0.01 \text{ mol}\cdot\text{L}^{-1}$, the NO removal efficiency decreased from 50.5% to 12.7% with the increase of the inlet NO concentration from 100 to 900 ppm. Figure 8 presents the change of the molar ratio between NO in the flue gas and NaClO_2 in the mist with the inlet NO concentration. It can be seen that with the inlet NO concentration increasing from 100 to 900 ppm, the molar ratio between NO in the flue gas and NaClO_2 in the mist increased from 1.6 to 13.0. Generally, the increase of molar ratio would promote the mass-transfer driving force of NO, which improves the oxidation and absorption of NO. However, NO concentration in the gas was relatively much higher than that of the NaClO_2 mist, it seemed to be reasonable to obtain a declining NO removal rate [39]. As shown in Figure 7, when the NO concentration changed from 100 ppm to 300 ppm, the NO removal efficiency for $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaClO_2 concentration decreased from 50.5% to 41.5%, but the NO removal efficiency for $0.02 \text{ mol}\cdot\text{L}^{-1}$ NaClO_2 concentration increased from 72.1% to 78.8%. That is because the NaClO_2 concentration of $0.01 \text{ mol}\cdot\text{L}^{-1}$ was a little low in this experiment, and so the reaction rate between NaClO_2 and NO played a dominant role at that moment. Thus, there was a decline trend in the NO removal efficiency for $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaClO_2 concentration. When the NaClO_2 concentration in the solution increased from $0.01 \text{ mol}\cdot\text{L}^{-1}$ to $0.02 \text{ mol}\cdot\text{L}^{-1}$, the increase of the NaClO_2 concentration will enhance the mass transfer rate at the liquid–gas interface to some extent. Therefore, the NO removal efficiency for $0.02 \text{ mol}\cdot\text{L}^{-1}$ NaClO_2 concentration increased at the beginning, and then decreased slowly after further increasing the inlet NO concentration from 300 ppm to 900 ppm.

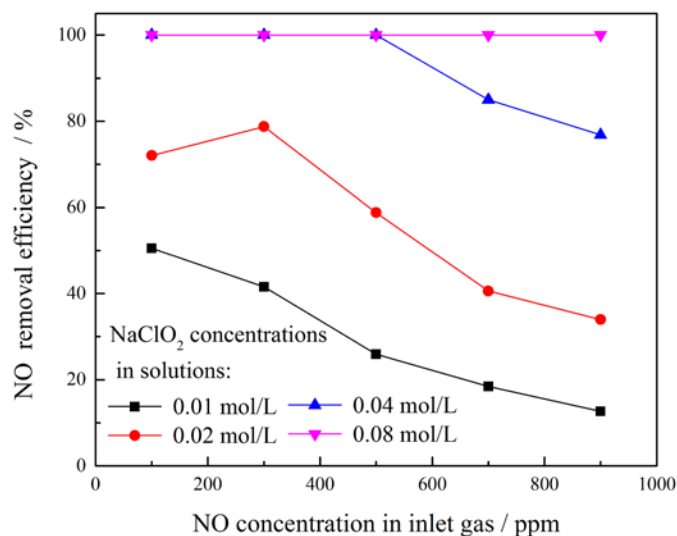


Figure 7. The change of the NO removal efficiency with the NO concentration of the inlet gas.

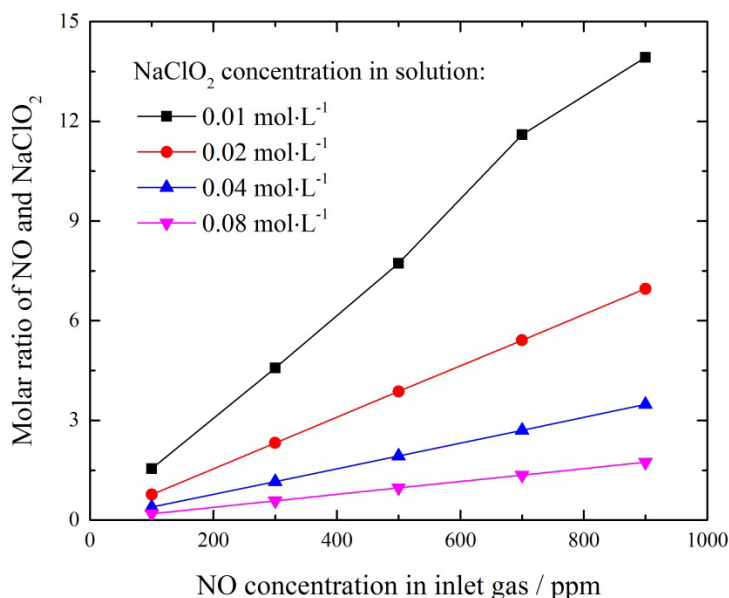


Figure 8. The change of the molar ratio of NO and NaClO₂ with inlet NO concentration.

The change of the NO_x removal efficiency with inlet NO concentration is shown in Figure 9. It can be seen that when the NaClO₂ concentrations in the solution were $\leq 0.02 \text{ mol}\cdot\text{L}^{-1}$, the NO_x removal efficiency increased as the inlet NO concentration increased from 100 ppm to 300 ppm, and then decreased gradually on further increasing inlet NO concentration from 300 ppm to 900 ppm. When NaClO₂ concentrations in the solution were in the range of $0.04\text{--}0.08 \text{ mol}\cdot\text{L}^{-1}$, the NO_x removal efficiency increased as the inlet NO concentration increased from 100 ppm to 500 ppm, and then decreased gradually on further increasing inlet NO concentration from 500 ppm to 900 ppm. This indicates that the mass transfer between NaClO₂ in the mist and NO in the flue gas imposed a great impact on the NO_x removal efficiency. At the beginning, the increase of the NaClO₂ concentration in mist and the NO concentration in the flue gas will enhance the mass transfer rate, resulting in an obvious increase in the NO_x removal efficiency. However, with the increase of the NaClO₂ concentration in the mist and NO concentration in flue gas, the reaction rate at the liquid–gas interface

becomes dominant. Thus, NO_x removal efficiency decreased slowly on further increasing the inlet NO concentration.

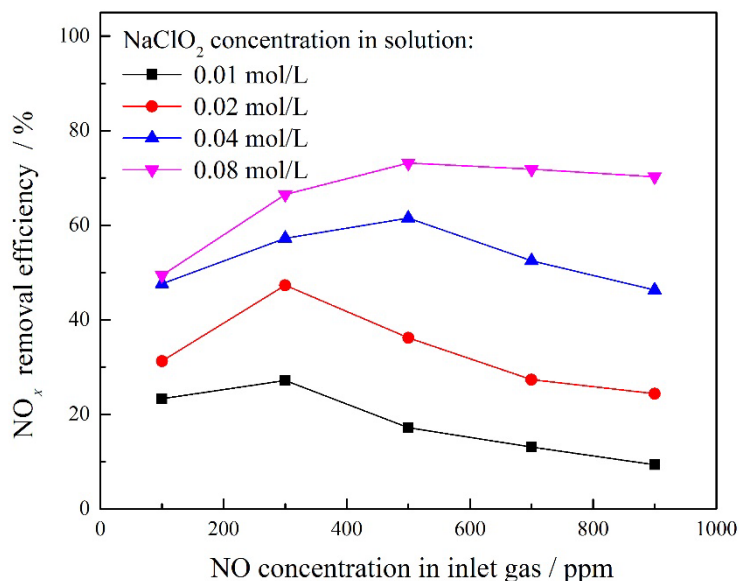


Figure 9. The change of the NO_x removal efficiency with the NO concentration of the inlet gas.

When the NaClO_2 concentration in the solution was higher than $0.04 \text{ mol}\cdot\text{L}^{-1}$ and the molar ratio of NO and NaClO_2 was below 2, a complete removal of NO could be obtained, indicating that all of NO had been oxidized by the NaClO_2 mist. But when the NaClO_2 concentration in the solution was lower than $0.02 \text{ mol}\cdot\text{L}^{-1}$, it was difficult to remove NO completely from the flue gas even if the molar ratio of NO and NaClO_2 was below 2. It could be ascribed to the mass-transfer between NO and NaClO_2 . When the NaClO_2 concentration in the mist was relatively low, it imposed a negative effect on the mass-transfer rate [40]. The lower the NaClO_2 concentration in mist was, the more obvious the adverse effect was. When the NaClO_2 concentration in the solution was $0.02 \text{ mol}\cdot\text{L}^{-1}$, with the inlet NO concentration increasing from 100 to 300 ppm, NO removal efficiency increased from 72.1% to 78.8%. However, on further increasing the inlet NO concentration, the NO removal efficiency began to decrease gradually. This also resulted from the change of the mass transfer efficiency between NO in gas phase and NaClO_2 in liquid phase.

3.5. Effect of Solution pH

The effect of the NaClO_2 solution pH on the NO removal performance was investigated, and the results are shown in Figure 10. The flow rate of the simulated flue gas was $2 \text{ L}/\text{min}$. The NO and NO_2 concentrations in the inlet gas were 500 and 0 ppm, respectively. The NaClO_2 concentrations in the solution were $0.02 \text{ mol}\cdot\text{L}^{-1}$. The initial solution pH values were adjusted to be in the range of 4–12. As shown in Figure 10, both the NO and NO_x removal efficiencies were kept almost stable when the initial NaClO_2 solution pH was changed in the range of 4–11. However, when the solution pH increased from 11 to 12, the NO removal efficiency decreased sharply from 55.3% to 4.4%. It indicated that a strong alkaline medium greatly suppresses the oxidative ability of NaClO_2 in the mist [41]. The results illustrated that for the ultrasonic atomization process, NaClO_2 could reach a relatively stable and high NO_x removal efficiency in a wide range of pH, which could be very favorable for industrial application.

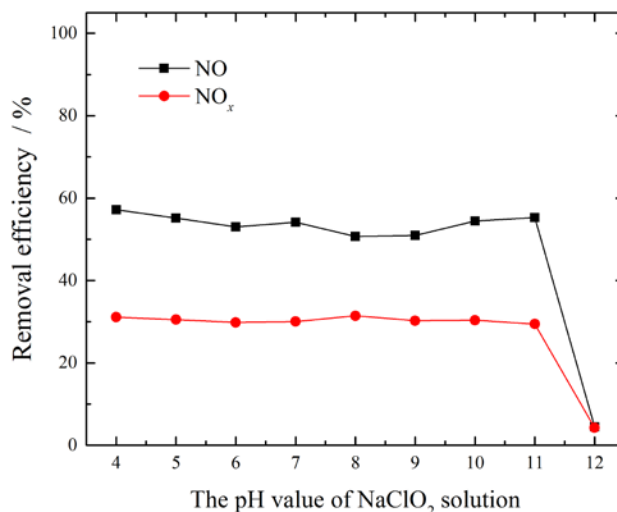


Figure 10. Effect of the pH value on the NO and NO_x removal efficiencies.

3.6. Parallel Tests and Reaction Chemistry

A group of parallel tests were carried out to investigate the repeatability and reproducibility of the NO removal efficiency by ultrasonic atomizing NaClO₂ solution, and the results are shown in Figure 11. The flow rate of the simulated flue gas was 2 L/min. NO and NO₂ concentrations in the inlet gas were 700 and 0 ppm, respectively. The NaClO₂ concentrations in the solution were 0.04 mol·L^{−1} with the corresponding pH value of 10.5. As shown in Figure 11, the minimum and maximum NO removal efficiencies were 78.2% and 82.1%, respectively. The average NO removal efficiency was 80.3%. The minimum and maximum NO_x removal efficiencies were 47.95% and 51.01%, respectively. The averaged NO_x removal efficiency was 49.75%. The results demonstrate that the NO removal process based on the ultrasonic atomization method possesses an excellent repeatability and stability as was shown in our experiments.

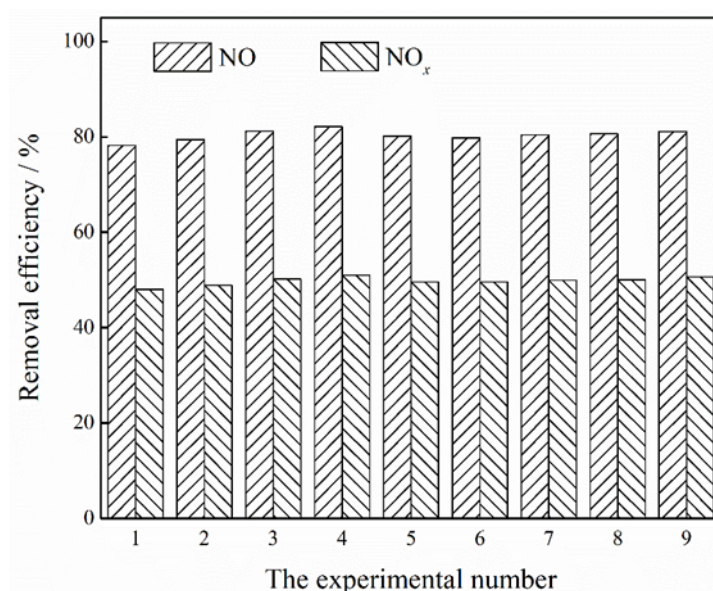


Figure 11. The effect of repetition times on NOx removal efficiency.

Compared with traditional wet scrubbing modes, such as spraying, bubbling, and packing, the liquid–gas ratio for the ultrasonic atomization process is much lower. For example, the liquid–gas

ratio for our experiment was only ~ 0.3 . In addition, the NO removal efficiency reached almost 100% when the molar ratio of NO in the flue gas and NaClO₂ in the mist was below 2. It implied that the reaction between NO in the flue gas and NaClO₂ in the mist is extremely efficient, and the utilization of NaClO₂ is very high. This is mainly ascribed to the gas–mist reaction mode, in which the diameters of the NaClO₂ mist generated by ultrasonic atomization are very small. Thus, the gas–liquid contact area is much larger than that found in traditional wet scrubbing processes, and it enhances the mass-transfer rate at the gas–liquid interface to a great extent [31]. Here the diameters of the NaClO₂ mist generated by ultrasonic atomization could be approximately calculated according to Lang's relation [42,43]:

$$d = 0.34 \left(\frac{8\pi\sigma}{\rho F^2} \right)^{1/3} \quad (8)$$

where d is the mist diameter (m), σ is the surface tension coefficient ($7.275 \times 10^{-2} \text{ N}\cdot\text{m}^{-1}$), ρ is the liquid density ($1.0 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$), and F is the forcing sound frequency ($1.67 \times 10^6 \text{ Hz}$). The diameter of the NaClO₂ mist in this study is calculated to be $\sim 2.95 \text{ }\mu\text{m}$, which is much smaller than those of the spraying droplets. It is favorable for increasing the contact area between the gas phase and liquid phase. Thus, the ultrasonic atomization process is favorable when attempting to achieve a high NO removal efficiency when compared with traditional wet scrubbing methods.

According to the experimental results mentioned above, one can deduce that NO was effectively oxidized into NO₂ by the NaClO₂ mist during the ultrasonic atomization process. The possible reaction pathways are summarized in Figure 12:

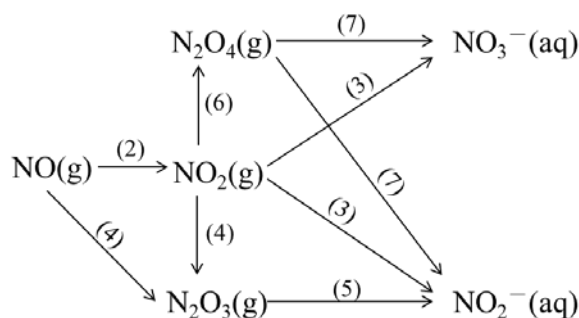


Figure 12. Reaction pathways of NO with the NaClO₂ mist.

4. Conclusions

NaClO₂ mist generated by the ultrasonic atomization process was used to remove NO from simulated flue gas, and the effects of various operating parameters on the NO removal efficiency were investigated preliminarily. Compared with other oxidants such as NaClO and H₂O₂, NaClO₂ mist could achieve a much higher NO removal efficiency because of its strong oxidative ability. With the increase in gas flow from 1.5 to 3.0 L·min^{−1}, the atomizing rate increased almost linearly from 0.38 to 0.85 mL·min^{−1}. However, a complete NO removal efficiency was only achieved at the gas flow rate of 2.0 L·min^{−1}. NO removal efficiency increased obviously with the increasing of the NaClO₂ concentration in the solution from 0.01 to 0.08 mol·L^{−1}. The increase of the inlet NO concentration resulted in a decrease in the molar ratio between NO in the flue gas and NaClO₂ in the mist. When the NaClO₂ concentration in the solution was higher than 0.04 mol·L^{−1} and the molar ratio of NO and NaClO₂ was below 2, a complete removal of NO could be obtained. When the initial pH values of the NaClO₂ solution were in the range of 4–11, NO removal efficiency for the NaClO₂ mist was relatively stable. However, it decreased sharply to 4.4% when the solution pH increased up to 12; this was because a strong alkaline medium greatly suppressed the oxidative ability of NaClO₂ in the mist. The parallel tests indicated that the ultrasonic atomization process possessed excellent repeatability and stability for NO removal applications. The possible reaction pathways were also discussed.

Author Contributions: Zhitao Han conceived and designed the experiment. Zhitao Han, Dongsheng Zhao and Dekang Zheng carried out the experiment and writing of the initial manuscript. Xinxiang Pan, Bojun Liu, and Zhiwei Han participated in the analysis of the data. Yu Gao, Junming Wang, and Zhijun Yan revised the manuscript and adjusted the data presentation. All authors have read and approved the manuscript.

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