Research Article

UV-Enhanced NaClO Oxidation of Nitric Oxide from Simulated Flue Gas

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A wet de-NO\textsubscript{x} technique based on an UV-enhanced NaClO oxidation process was investigated for simulated flue gas of a diesel engine using a bench-scale reaction chamber. The effects of UV irradiation time, initial pH value, and available chlorine concentration of NaClO solution were studied, respectively. The results showed that when the UV irradiation time was 17.5 min and the initial pH value of NaClO solution was 6, NO removal efficiency of UV/NaClO solution was increased by 19.6% compared with that of NaClO solution. Meanwhile, when the available chlorine concentration of NaClO solution decreased from 0.1 wt% to 0.05 wt%, the enhancement in NO removal efficiency of UV/NaClO solution increased from 19.6% to 24%, compared with that of NaClO solution. The reaction pathways of NaClO solution photolysis and NO removal by UV/NaClO process were preliminarily discussed. The results suggested that HOCl might be the most active species that released many UV-induced photooxidants through photolysis reactions, which played an important role in NO removal process.

1. Introduction

More and more attention has been paid to nitrogen oxides (NO\textsubscript{x}) emissions in recent years. The risks posed by atmospheric NO\textsubscript{x} can be enormous, resulting in catastrophic consequences [1] (e.g., acid deposition, formation of tropospheric ozone, photochemical smog, and aerosol warming) to human health and environment. Atmospheric NO\textsubscript{x} originates from both anthropogenic and natural sources, and flue gas emission from burning fossil fuels by internal combustion engines is one of the most significant contributors to the anthropogenic sources [2]. Currently, the common practice in many industries is to implement more stringent regulations [3, 4] in order to control NO\textsubscript{x} emissions from vehicle, power plants, and ocean-going ships.

To mitigate NO\textsubscript{x} emissions from flue gas of internal combustion engines, a variety of technologies have been proposed to meet strict regulations on NO\textsubscript{x} emission. Such methods are divided into two main categories [1, 5]: (i) dry techniques and (ii) wet techniques. Technologies within the first classification mainly include exhaust gas recirculation (EGR) [6], selective catalytic reduction (SCR) [7], nonthermal plasma (NTP) [8], electrochemical reduction [9], and lean NO\textsubscript{x} traps [10]. For diesel engines, the commonly used commercial technologies are EGR and SCR at present. EGR can reduce the amount of NO\textsubscript{x} generated during combustion by lowering the oxygen content in the cylinder and increasing the specific heat capacity of the air [6]. However, this technique is so complex that it is not suitable for retrofit. SCR can be installed with few engine modifications and it can remove more than 90% of NO\textsubscript{x} from flue gas. But some problems with high working temperature (300–400°C) and catalyst poisoning effect will restrict the extensive applications of this technique [11]. Consequently, alternative cost-efficient wet techniques, which are capable of significantly absorbing nitric oxide (NO) in scrubbing water, are becoming more attractive over the past decades. As NO is the major component of NO\textsubscript{x} emissions and is of low solubility, it cannot be removed easily. Thus a number of recent studies take use of wet scrubbing agents [12] to oxidize NO to soluble NO\textsubscript{2}. The oxidants include H\textsubscript{2}O\textsubscript{2} [13], NaClO\textsubscript{2} [14], NaClO [15], KMnO\textsubscript{4} [16], Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} [17], and Fe(II) EDTA [18]. Among these oxidants, NaClO [19, 20] is found to be one of the most promising chemicals for NO oxidation because of its low cost [21] and self-regeneration.
characteristic with an electrochemical cell. The results of previous studies indicated that this technique achieved a comparatively high NO removal efficiency, but one of the concerns was the high consumption of NaClO reagent [15, 22, 23].

As a kind of inexpensive oxidant, NaClO was also used for wastewater treatment. In order to reduce the NaClO consumption, an advanced oxidation technique [24–26] by using a hybrid system of an UV lamp and NaClO solution was introduced in water treatment recently, and an enhancement effect had been achieved obviously. However, to the best of our knowledge, the effect of UV irradiation on the NO removal of NaClO solution has not been reported yet. In this work, the NO oxidation characteristic of UV/NaClO aqueous solution in a bench-scale spraying column was studied to demonstrate the significance and advantages over conventional NaClO wet scrubbing techniques previously reported. The effects of UV irradiation time, initial pH value, and available chlorine concentration (ACC) of NaClO solution were investigated experimentally. The results showed that UV/NaClO solution appeared to be a cost-effective method for removing NO from flue gas, and the possible reaction mechanism was discussed, although a number of questions regarding the chemistry of the process have been raised.

2. Materials and Methods

2.1. Experiment Apparatus. As shown in Figure 1, the experimental system consisted of a simulated flue gas system, a photochemical reactor, a bench-scale scrubber, and a flue gas analysis system.

The flue gas of a diesel engine was simulated by mixing different gas species: NO (9.8% NO with 90.2% N₂ as balance gas) and N₂ (99.9%). The flow rate of material gas was regulated by a mass flow controller (D07-19B, Sevenstar Electronics, China), and the NO concentration of the simulated flue gas was adjusted by controlling the mixing ratio. All pipes, valves, regulators, and fittings were made up of stainless steel 316 grade or Teflon.

The photochemical reactor included a LP-UV lamp (UV-C, 253.7 nm, 11 W, Philips, Holland), a column, and a magnetic stirrer. In order to reduce the interference of photochemical reaction by sunlight, the outside of the photochemical reactor was covered with aluminum foil.

The bench-scale scrubber (height: 30 cm; internal diameter: 5.0 cm) was a customized lucite spray column. The length of the reaction zone from the point at gas inlet to the spray nozzle (Bi/4TT-SS+TG-SS0.4, Spraying System Co., America) was 20 cm. The feed pump was a peristaltic pump (YZ1115, Longer Precision Pump, China).

The flue gas analysis system consisted of a U-shaped dryer and a gas analyzer (GA21-plus, Madur, Austria). The Madur GA21-plus gas analyzer was a portable electrochemical flue gas analyzer. It was equipped with two electrochemical sensors, which were used for measuring NO and O₂ concentrations.

2.2. Experimental Procedures. NaClO solution was prepared using NaClO stock solution (ACC 5.0 wt%, Aladdin, China) and deionized water (15.0 MΩ, ELGA LabWater, England). The initial pH value of NaClO solution was adjusted to the desired value by adding freshly diluted HCl solution (AR, Sinoreagent, China). Then, NaClO solution was pretreated with UV irradiation in the photochemical reactor and the pH value of NaClO solution was online monitored with a pH meter (S210, Mettler-Toledo, Switzerland). Finally, the
UV/NaClO solution was delivered into the scrubber using the feed pump.

The initial NO concentration was kept at 300 ppm and the gas flow rate was set to 1.5 L·min⁻¹. Liquid absorption reactions occurred when the simulated flue gas entered into the bench-scale scrubber. The gas-liquid contact time between gas inlet and spraying nozzle was approximately 1.0 s. Moreover, the NO concentration was measured by gas analyzer at an interval of 5 s during the absorption process. After being scrubbed, the simulated flue gas was discharged into atmosphere while the effluent of scrubbing liquid was collected in the bottom tank.

2.3. Data Processing. The scrubbing period for each set of experiments was kept for 5 min. NO removal efficiency was obtained at steady-state conditions. NO removal efficiency was calculated by

\[ \eta_{\text{NO}} (%) = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \]  

where \( C_{\text{in}} \) is the inlet NO concentration (ppm) and \( C_{\text{out}} \) is the outlet NO concentration (ppm).

3. Results and Discussions

3.1. Comparison of Different Reaction Conditions. In order to demonstrate the UV enhancement effect of UV/NaClO solution on NO removal through experiments, a set of comparative experiments were conducted (see Figure 2). As the major species in NaClO solution at pH 6 were Na⁺, Cl⁻, ClO⁻, and HClO, four different reaction conditions had been designed in our experiments. They were deionized water with UV irradiation (17.5 min), NaCl solution (0.1 wt%) with UV irradiation (17.5 min), NaClO solution (ACC 0.1 wt% and pH 6) without UV irradiation, and NaClO solution (ACC 0.1 wt% and pH 6) with UV irradiation (17.5 min), respectively. From Figure 2, one can see that NO was removed slightly by UV/H₂O or UV/NaCl solution, and the NO removal efficiencies of NaClO and UV/NaClO were 31.3% and 50.9%, respectively. The major ions in NaCl solution at pH 6 were Na⁺ and Cl⁻ ions. The result of UV/NaCl solution indicated that Na⁺ and Cl⁻ ions in aqueous solution with UV irradiation made no contribution to NO removal. Consequently, the comparison results between UV/NaCl and UV/NaClO demonstrated that mainly HClO and ClO⁻ in aqueous solution with UV irradiation played an important role in NO removal process. With the assistant of UV lamp, a remarkable improvement in NO removal efficiency using UV/NaClO solution was observed, compared with that of NaClO solution without UV treatment. Under the same condition, UV/NaClO scrubbing process has the potential to achieve the same NO removal efficiency with less consumption of NaClO reagent compared with that of NaClO wet scrubbing process. Therefore, NaClO solution with UV irradiation pretreatment appears to be an effective way to enhance NO removal efficiency and reduce the NaClO consumption.

According to the comparison results of four different reaction conditions, the UV-enhanced mechanism may be explained by the following reactions [24, 27–29]:

\[
\text{HOCl} + h\nu \rightarrow \text{HO}^* + \text{Cl}^-
\]  

\[
\text{OCl}^- + h\nu \rightarrow \text{O}^\cdot + \text{Cl}^-
\]  

\[
\text{OCl}^- + h\nu \rightarrow \text{Cl}^- + \text{O}(^{3}\text{P})
\]  

\[
\text{O}^- + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{OH}^-
\]

\[
\text{HO}^* + \text{HOCl} \rightarrow \text{ClO}^- + \text{H}_2\text{O}
\]

\[
\text{HO}^* + \text{OCl}^- \rightarrow \text{ClO}^- + \text{OH}^{-}
\]

\[
\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-
\]

\[
2\text{ClO}^- \leftrightarrow \text{Cl}_2\text{O}_2
\]

\[
2\text{Cl}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cl}_2\text{O}_3^- + \text{Cl}_2\text{O} + \text{OCl}^- + 2\text{H}^+
\]

\[
\text{Cl}_2\text{O}_2 \rightarrow \text{Cl}_2 + \text{O}_2
\]

\[
\text{ClO}^- + \text{NO} \rightarrow \text{ClNO}_2
\]

\[
\text{ClNO}_2 \rightarrow \text{Cl}^- + \text{NO}_2
\]

It was noteworthy that many UV-induced photooxidants (e.g., HO^*, O_3^-, O(^{3}\text{P}), and ClO^*) were generated in situ through photolysis of NaClO solution. As these UV-induced photooxidants have an extremely strong oxidation ability, a significant part of NO was oxidized and absorbed into the UV/NaClO solution. Without UV irradiation, HOCl/OCl⁻...
was the active species reacting with NO in liquid phase, and the main reactions were given as follows [15, 30]:

\[
\text{NO} + \text{HOCl} \leftrightarrow \text{NO}_2 + \text{HCl} \quad (14)
\]

\[
\text{NO} + \text{OCl}^- \rightarrow \text{NO}_2 + \text{Cl}^- \quad (15)
\]

\[
3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \quad (16)
\]

3.2. Effect of UV Irradiation Time. Figure 3 describes the influence of UV irradiation time on NO removal efficiency. One can see that although NO removal efficiency decreased in the first 5 min, there was a remarkable increase in NO removal efficiency when UV irradiation time increased from 5 min to 17.5 min. After that, when we further increased UV irradiation time from 17.5 min to 20 min, the NO removal efficiency decreased sharply. Moreover, more and more O$_2$ gas was released from scrubbing liquid with the increase of UV irradiation time (see Figure 4).

With the increase of UV irradiation time, photooxidants concentrations increased gradually via photochemical reactions ((2)–(11)) in UV/NaClO solution. Thus, NO removal efficiency of UV/NaClO solution was enhanced when the UV irradiation time increased from 5 min to 17.5 min. However, several side reactions ((10)-(11)) occurred with further increase of UV irradiation time, resulting in a loss of photooxidants. These side reactions were also confirmed by the phenomenon that more O$_2$ gas and bubbles were observed to escape from solution. Therefore, excessive UV irradiation resulted in a negative effect on NO removal efficiency of UV/NaClO solution.

3.3. Effect of Initial pH Value of NaClO Solution. The effect of initial pH value on NO removal efficiencies of NaClO solution with or without UV irradiation is investigated experimentally and the results are shown in Figure 5. Without UV irradiation, the NO removal efficiency decreased with the initial pH value varying from 2 to 10, which was similar to the experimental results of Mondal and Chelluboyana [20]. This phenomenon can be attributable to the following equations:

Free chlorine = $[\text{Cl}_2] + [\text{HOCl}] + [\text{OCl}^-] + [\text{Cl}^-]$ \quad (17)

\[
\text{HOCl} + \text{H}^+ + \text{Cl}^- \leftrightarrow \text{Cl}_2 + \text{H}_2\text{O} \quad (18)
\]

\[
pk_a = 3.33 \text{ (25°C)}
\]

\[
\text{OCl}^- + \text{H}^+ \leftrightarrow \text{HOCl} \quad pK_a = 7.53 \text{ (25°C)} \quad (19)
\]

\[
\text{Cl}_2 + \text{Cl}^- \leftrightarrow \text{Cl}_3^- \quad (20)
\]

When the initial pH value dropped below 4, Cl$_2$ was released from NaClO solution. Thus, direct gas phase reaction
of Cl₂ and NO [31] occurred in scrubbing chamber, which greatly enhanced the mass transfer efficiency and improved the NO removal efficiency. When the initial pH value increased from 4 to 10, NO conversion decreased slowly at first and then dropped sharply. The liquid oxidation reactions were shown in (14)–(16). As HOCl was a stronger oxidizing agent than OCl⁻ [15, 30], NO removal efficiency would decrease with the increase of the initial pH value, owing to the reduction of HOCl chlorine species in the solution.

As shown in Figure 5, with UV irradiation, UV/NaClO solution at pH 6 exhibited the characteristic of an excellent scrubbing medium. When the initial pH value increased from 2 to 4, the NO removal efficiency decreased because of outgassing of Cl₂ during UV irradiation and reduction of direct gas phase oxidation. When the initial pH value varied from 4 to 6, a significant increase of NO removal efficiency was measured. However, when the initial pH value increased from 6 to 10, the NO removal efficiency decreased gradually. According to the equilibrium concentrations of chlorine species with the change of pH in NaClO solution, when the initial pH value increased from 4 to 10, the main chlorine species in NaClO solution were HOCl/OCl⁻, which generated photolysis reactions ((2)–(11)). Although the molar absorption coefficient of OCl⁻ was higher than HOCl, the side reaction rate of HO· and OCl⁻ made OCl⁻ to be a more strong free radical scavenger than HOCl. The difference of NO removal efficiencies with the change of initial pH value indicated that HOCl was the most active species that released the largest amount of photooxidants through photolysis reactions under the same UV irradiation condition. In addition, from Figure 6, one can see that UV/NaClO solution at initial pH 6 showed an apparent drop of pH value with the increase of UV irradiation time. As ClO₃⁻ was one of the photooxidants, its oxidation ability increased with the decrease of pH value. As a consequence, ClO₃⁻ also enhanced NO removal efficiency when the initial pH value dropped from 10 to 6.

Moreover, as a kind of advanced oxidation technique, UV/NaClO was also applied to treat wastewater. According to some recent studies [25, 32], photooxidants concentrations of UV/NaClO solution were also changed as a function of the initial pH value. With this, UV irradiation was proved to make a remarkable improvement to the oxidability of NaClO solution at initial pH 6.

3.4. Effect of ACC of NaClO Solution. Figure 7 shows the effect of ACC on NO removal efficiencies of NaClO solution with or without UV irradiation, respectively. Without UV irradiation, as the ACC of NaClO solution increased from 0 to 0.2 wt%, NO removal efficiency varied from 3.6% to 41.7%, which was due to the increase of HClO concentration [20, 33]. With UV irradiation, one can see that NO removal efficiency of UV/NaClO solution was greatly enhanced when the ACC of NaClO solution was less than or equal to 0.1 wt%. However, when the ACC of NaClO solution was higher than 0.1 wt%, UV irradiation had a negative effect on NO removal efficiency compared with that of non-UV irradiation. In addition, Figure 8 shows the effect of UV irradiation time on the pH value of UV/NaClO solution under different ACC. It can be seen that the pH value dropped as the UV irradiation time increased for NaClO solution with a specific ACC, and under the same UV irradiation time, the pH value of UV/NaClO solution increased with the increase of ACC of UV/NaClO solution.

When the ACC of NaClO solution was less than or equal to 0.1 wt%, photooxidants concentrations increased via photolysis of HOCl/OCl⁻. However, under the same UV irradiation condition, side reactions between photooxidants and HOCl/OCl⁻ increased as the ACC of NaClO solution varied from 0.1 wt% to 0.2 wt%, which might explain that the NO removal efficiency was lower than that of NaClO solution without UV irradiation. In addition, as ClO₃⁻ was one of
3.5. Comparison with Other Wet de-NO\textsubscript{x} Technologies. Table 1 describes the comparison with other NaClO de-NO\textsubscript{x} technologies in literature regarding NO removal. As the absorption conditions used by various researchers were different, the comparison of the NO removal efficiencies by various NaClO de-NO\textsubscript{x} technologies was difficult. In order to demonstrate the enhancement effect of UV/NaClO process, an evaluation criteria \( \mu_{\text{NO}} = \frac{C_{\text{in}} \times \eta_{\text{NO}}}{C_{\text{NaClO}}} \) ppm/(mmol \cdot L\textsuperscript{-1}) was proposed and calculated by

\[
\mu_{\text{NO}} = \frac{C_{\text{in}} \times \eta_{\text{NO}}}{C_{\text{NaClO}}} \text{ ppm/(mmol \cdot L\textsuperscript{-1})},
\]

where \( C_{\text{in}} \) is the inlet NO concentration (ppm), \( \eta_{\text{NO}} \) is the NO removal efficiency (%), and \( C_{\text{NaClO}} \) is the NaClO concentration (mmol \cdot L\textsuperscript{-1}). Based on this criteria, the result of present work had a significant improvement as compared to previous NaClO solution wet scrubbing techniques [15, 22, 23].

From the equilibrium concentrations of chlorine species with the change of pH in NaClO solution, one can see that HClO was the main oxidizing agent in the result of Chen et al. [15] and Xiao et al. [23], while Cl\textsubscript{2} was the main oxidizing agent in the result of Yang et al. [22]. As the oxidation potential of UV-induced photooxidants is much stronger than that of HClO and Cl\textsubscript{2}, the NO removal per NaClO concentration of this work is higher than that of Chen et al. [15], Yang et al. [22], and Xiao et al. [23]. Therefore, the combined techniques of UV and NaClO solution have the potential to reduce the NaClO consumption in the future.

### Table 1: NaClO de-NO\textsubscript{x} technologies related investigations.

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Gas-liquid contact time (s)</th>
<th>NaClO concentration (mmol L\textsuperscript{-1})</th>
<th>Initial pH value</th>
<th>Temperature (°C)</th>
<th>Initial NO concentration (ppm)</th>
<th>NO removal efficiency (%)</th>
<th>NO removal per NaClO concentration (ppm NO/(mmol L\textsuperscript{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed tower</td>
<td>∼1.7</td>
<td>169</td>
<td>5.3</td>
<td>Room temperature</td>
<td>100</td>
<td>80</td>
<td>0.58</td>
<td>[15]</td>
</tr>
<tr>
<td>Bubbling reactor</td>
<td>—</td>
<td>176</td>
<td>3.18</td>
<td>20</td>
<td>1000</td>
<td>93.5</td>
<td>5.31</td>
<td>[22]</td>
</tr>
<tr>
<td>Bubbling reactor</td>
<td>—</td>
<td>87</td>
<td>5.5</td>
<td>25</td>
<td>500</td>
<td>66.21</td>
<td>3.81</td>
<td>[23]</td>
</tr>
<tr>
<td>Scrubbing tower</td>
<td>∼1 (with UV irradiation)</td>
<td>7</td>
<td>6</td>
<td>Room temperature</td>
<td>300</td>
<td>50.60</td>
<td>21.69</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Figure 8:** Effect of UV irradiation time on the pH value of UV/NaClO solution with different ACCs.
as reduce storage space for chemical reagents by in situ generation of NaClO solution using electrochemical cell. With these advantages, UV/NaClO process may be applicable to the treatment of flue gas from large power plants (e.g., coal-fired thermal power plants, marine diesel engines), which are sensitive to the reagent consumption and footprint of de-\(\text{NO}_x\) systems.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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