

## ORIGINAL RESEARCH PAPER

# Experimental study on the influence of H<sub>2</sub>O vapor and O<sub>2</sub> for desulfurization and denitrification of the diesel exhaust in marine application by non-thermal plasma

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## Abstract

To improve the pollutant removal efficiency by non-thermal plasma (NTP), the effect of H<sub>2</sub>O vapor and O<sub>2</sub> on removal efficiency of NO and SO<sub>2</sub> as well as the reduction of CO was investigated in H<sub>2</sub>O/O<sub>2</sub>/SO<sub>2</sub>/NO/C<sub>3</sub>H<sub>6</sub>/CO<sub>2</sub>/N<sub>2</sub> system. To analyse the reaction mechanism, the effects of H<sub>2</sub>O vapor and O<sub>2</sub> on the emission intensity of O(<sup>3</sup>p<sup>5</sup>P → 3s<sup>5</sup>S<sub>2</sub><sup>0</sup>) and OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) were investigated. The experimental results show that the increase of H<sub>2</sub>O vapour (0%–9.8%) promotes the generation of OH radicals, increases the removal efficiency of NO from 18.9% to 57.3%, decreases the energy per NO removed from 449.0 to 148.1 eV/NO, increases SO<sub>2</sub> removal efficiency from 4.8% to 35.3%, decreases the energy per SO<sub>2</sub> removed decreases from 2784.0 to 582.9 eV/SO<sub>2</sub>, and reduces the generation of CO from 460 to 229 ppm. In the range of 0%–15%, the increase of O<sub>2</sub> content promotes the formation of O radicals, increases the removal efficiency of NO from 8.5% to 54.2%, and decreases the energy per NO removed from 994.3 to 156.4 eV/NO. In the range of 0%–5%, increasing O<sub>2</sub> content promotes SO<sub>2</sub> removal efficiency from 8.7% to 24.8%, and decreases the energy per SO<sub>2</sub> removed from 2485.7 to 876.6 eV/SO<sub>2</sub>. However, CO generation increases from 200 to 350 ppm with the increase of O<sub>2</sub> in 0%–5% due to the incomplete oxidation of C<sub>3</sub>H<sub>6</sub>. In the range of 5%–15%, the increase of O<sub>2</sub> produces more O radicals, decreases the removal efficiency of SO<sub>2</sub> from 24.8% to 23.5% and the generates of CO from 350 to 311 ppm. This study is helpful for improving the efficiency of NTP for desulfurization and denitrification, while reducing the by-product CO.

## 1 | INTRODUCTION

Sea transportation forms an important part of the transportation sector, and 90% of world trade is carried across the oceans [1]. Diesel engines are dominant as the main power and generation power units in the marine sector [2]. Exhaust pollutants such as hydrocarbons (HC), particulate matter, SO<sub>x</sub> and NO<sub>x</sub> are inevitably generated during the operation of the diesel engine, which caused serious air pollution problems [3–6]. In order to control the exhaust pollution, the International Maritime Organization regulated the emission of NO<sub>x</sub> and SO<sub>x</sub> for marine diesel engine [7, 8].

Selective catalytic reduction (SCR) system is the main technology for NO removal [9]. But this technology may not be

available for two stroke low speed marine diesel engine because of the lower temperature of the exhaust gas and ammonium sulphate deposits formation problem [10, 11]. For SO<sub>x</sub> removal, wet flue gas desulfurization (WFGD) system can achieve a higher removal efficiency (more than 95%) However, for NO<sub>x</sub> removal, wet scrubbing has a low removal efficiency (less than 20%). This is due to more than 90% of NO<sub>x</sub> in the exhaust gas of marine diesel engine is NO, and NO has low solubility in water and does not react with alkali solution [12].

Some studies indicated that NO<sub>2</sub> can promote removal of NO by the WFGD system, and non-thermal plasma (NTP) can effectively oxidize NO so that the WFGD system can simultaneously remove SO<sub>x</sub> and NO<sub>x</sub> [12, 13]. Therefore, NTP combined with WFGD, as a technology for simultaneous

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desulfurization and denitrification, can activate flue gas at room temperature, along with highly reactive species including high energy electrons, free radicals (such as O and OH) being generated, which can contribute to the removal of gas pollutants [13, 14].

To improve the removal efficiency of pollutants by NTP, many gases are used as chemical additives, such as H<sub>2</sub>O, O<sub>2</sub>, C<sub>3</sub>H<sub>6</sub> [15–21]. Yin studied the effect of water vapour and oxygen on NO removal. The experimental results showed that increasing the content of water vapour can significantly reduce the removal efficiency of NO in NO/N<sub>2</sub>/H<sub>2</sub>O gas mixture, O<sub>2</sub> in the flow gas always hampered the removal of NO in NO/O<sub>2</sub>/N<sub>2</sub> gas mixture [15]. Wang Tao studied the effect of water vapour on NO removal, the experimental results indicated that H<sub>2</sub>O can greatly enhance the NO removal efficiency in NO/O<sub>2</sub>/N<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>O system [16]. Wang Tao studied the effect of O<sub>2</sub> and water vapour on SO<sub>2</sub> removal. The experimental results showed that increasing O<sub>2</sub> content enhances the removal of SO<sub>2</sub> in the SO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures and H<sub>2</sub>O can promote SO<sub>2</sub> removal efficiency, but a higher H<sub>2</sub>O content reduces SO<sub>2</sub> removal efficiency in SO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/N<sub>2</sub> gas mixture [17]. Jiang studied the effect of water vapour on NO oxidation by plasma in air/O<sub>2</sub>/NO/H<sub>2</sub>O/N<sub>2</sub> system. The experimental results showed that increasing the water vapour content is effective to the improvement of NO oxidation efficiency [18]. In 2012, Teodoru studied the effect of O<sub>2</sub> concentration on NO removal in NO/O<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> system by numerical simulation. The simulation results showed that increasing O<sub>2</sub> concentration is conducive to the formation of O, OH, HO<sub>2</sub> and other oxidative radicals, which can promote NO removal and promote the formation of NO<sub>2</sub> [19]. In 2010, Cai studied the effect of C<sub>3</sub>H<sub>6</sub> on NO removal. The experimental results showed that when C<sub>3</sub>H<sub>6</sub> was added to the NO/O<sub>2</sub>/N<sub>2</sub> gas mixture, the NO conversion rate was significantly increased and the energy consumption was dramatically reduced, and Schmidt obtained similar conclusions [20, 21].

In particular, the effects of H<sub>2</sub>O and O<sub>2</sub> in different gas components on the removal of NO by NTP are different, because NO is mainly removed by oxidation under oxygen-enriched conditions, while NO is mainly removed by reduction under low oxygen conditions. However, most of the studies were carried out under the condition of simple gas components, which are different from the practical diesel emission conditions. There are few researches on the effect of various gas components on simultaneous desulfurization and denitrification and its mechanism under a more similar diesel exhaust conditions [21]. In this article, the effects of two gas components (H<sub>2</sub>O and O<sub>2</sub>) on simultaneous desulfurization, denitrification and the generation of oxidative free radicals (O, OH) will be studied in N<sub>2</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/NO/SO<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> gas mixture, and the optical emission spectra (OES) of the plasma will be measured to study their effect mechanism.

## 2 | EXPERIMENTAL SETUP

The schematic diagram of the experimental setup is shown in Figure 1. It consists of a simulated gas supply unit, dielectric barrier discharge (DBD) reactor driven by a high voltage alternating current (HVAC) power supply, a discharge power

measuring unit, a gas analyzer, and an optical emission detection system.

The gas mixer was wrapped and heated by a resistance heater. These gases flowrates were controlled using mass flow controllers and mixed via a gas mixer to obtain the desired concentrations and temperature. The gas temperature was measured by temperature sensor PT100 at the inlet of DBD reactor. The water vapour was controlled by the water bath temperature and added to the N<sub>2</sub> carrier gas. The main components of the feed gas used to simulate practical exhaust gases of purity are N<sub>2</sub> (99.999%), O<sub>2</sub> (99.999%), CO<sub>2</sub> (99.999%), C<sub>3</sub>H<sub>6</sub> (99.5%), NO (99.5%), and SO<sub>2</sub> (99.5%). The gas mixture is prepared with reference to the exhaust conditions of marine diesel engine YC6C (fuel sulphur content is ~1%), as shown in Table 1. The total flow rate is 5 L/min. And the velocity of the gas flow in DBD reactor is ~5.2 m/s.

The DBD reactor is coaxial cylindrical, and the material of the dielectric layer tube is quartz. A cross-sectional view of DBD reactor is shown in Figure 2. The length of the quartz tube is 200 mm, the outer diameter is 18 mm, the inner diameter is 15 mm, and the thickness is 1.5 mm. The quartz tube was wrapped with copper foil as the outer electrode with 100 mm length. The inner electrode is a stainless steel rod with diameter of 14 mm.

The high voltage alternating current (HVAC, CTP2000K, Nanjing Suman Plasma Technology Co., Ltd) was used as the power supply of DBD reactor. The discharge power was calculated by Lissajous figure (Figure 3b). The measurement capacitance ( $C_m$ ) of DBD discharge transmission charge is 0.47  $\mu$ F, and the applied voltage was decreased 1000 times by high voltage probe (TEK P6015A), which was the input into oscilloscope (TEK TBS1052b).

The concentrations of NO, NO<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, and SO<sub>2</sub> were measured by flue gas analyzer (TESTO Pro.350). The information of TESTO Pro.350 is shown in Table 2. The water vapour content was measured by a psychrometer (TESTO 635). A spectrometer (Princeton Instruments Acton SpectraHub2500i) was used to measure the OES of the plasma. For measurement of OES, a 1 mm wide and 4 mm long hole was punched on the copper foil of the outer electrode. A convex lens (focal length: 30 mm) was used to focus the light generated by the discharge between the inner electrode and the outer electrode behind the hole into the spectrometer entrance slit. The entrance and exit slits of the spectrometer are fixed at 150  $\mu$ m and a grating of 1200 groove  $\text{mm}^{-1}$  is used to measure the OES in the wavelength ranging from 300 to 800 nm. The integration time and the resolution of the spectrometer are 500 ms and 0.5 nm, respectively. In order to obtain high resolution spectra, the entrance and exit slits were adjusted to 100  $\mu$ m and the resolution of the spectrometer was adjusted to 0.01 nm. A grating of 3600 groove  $\text{mm}^{-1}$  was used to obtain the spectra of OH ( $A^2\Sigma^+ \rightarrow X^2\Pi$ ), and for O ( $3p^5P \rightarrow 3s^5S_2^0$ , 777.8 nm), a grating of 1200 groove  $\text{mm}^{-1}$  was used. Typical emission spectra generated by DBD is shown in Figure 4. In the range of 300–450 nm, the emission spectra of plasma mainly contain the bands of OH ( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) and the second positive bands of N<sub>2</sub> ( $C^3\Pi_u \rightarrow B^3\Pi_g$ ). In the range of 500–800 nm, the emission spectra of plasma mainly contain the bands of O ( $3p^5P \rightarrow 3s^5S_2^0$ , 777.8 nm) and N<sub>2</sub> ( $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ ).

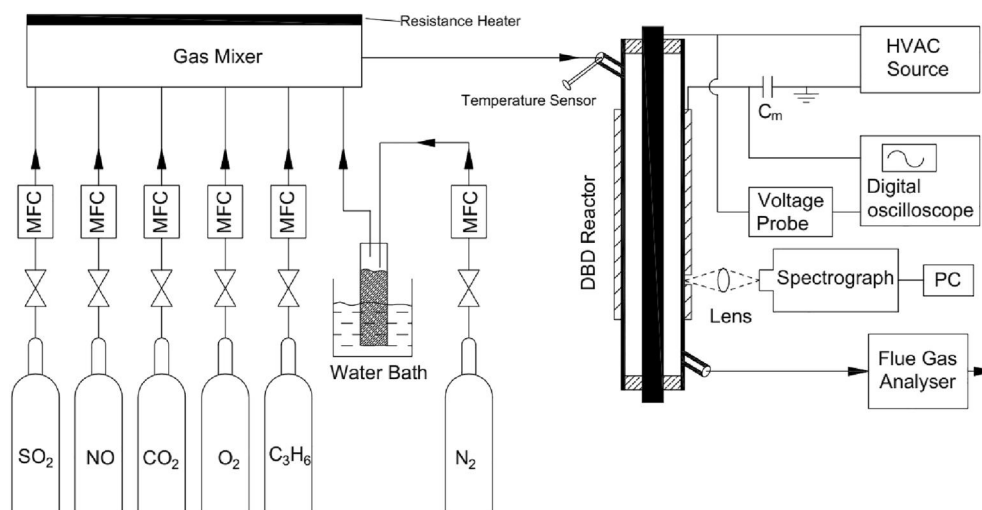


FIGURE 1 The schematic diagram of the experimental setup

TABLE 1 Emission characteristics of diesel engine YC6C

| Power/kW | SO <sub>2</sub> /ppm | THC/ppm | NO <sub>x</sub> /ppm | O <sub>2</sub> /(%) | CO <sub>2</sub> /(%) |
|----------|----------------------|---------|----------------------|---------------------|----------------------|
| 811.2    | 357.2                | 244.8   | 857.8                | 10.3                | 7.5                  |
| 606.6    | 319.3                | 172.5   | 377.6                | 11.3                | 6.7                  |
| 405.1    | 304.8                | 127.1   | 407.6                | 11.8                | 6.4                  |
| 203.6    | 285.1                | 122.3   | 476.6                | 12.3                | 5.9                  |

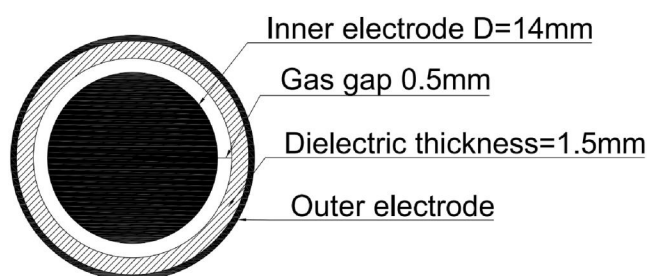


FIGURE 2 A cross-sectional view of the dielectric barrier discharge reactor

The experimental results were expressed in terms of NO and SO<sub>2</sub> removal efficiency by plasma, which were defined as follows:

$$\text{NO removal efficiency} = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\% \quad (1)$$

$$\text{SO}_2 \text{ removal efficiency} = \frac{[\text{SO}_2]_{\text{inlet}} - [\text{SO}_2]_{\text{outlet}}}{[\text{SO}_2]_{\text{inlet}}} \times 100\% \quad (2)$$

where  $[\text{NO}]_{\text{inlet}}$  and  $[\text{NO}]_{\text{outlet}}$  are the concentrations of NO (ppm) measured at the inlet and outlet of DBD reactor;

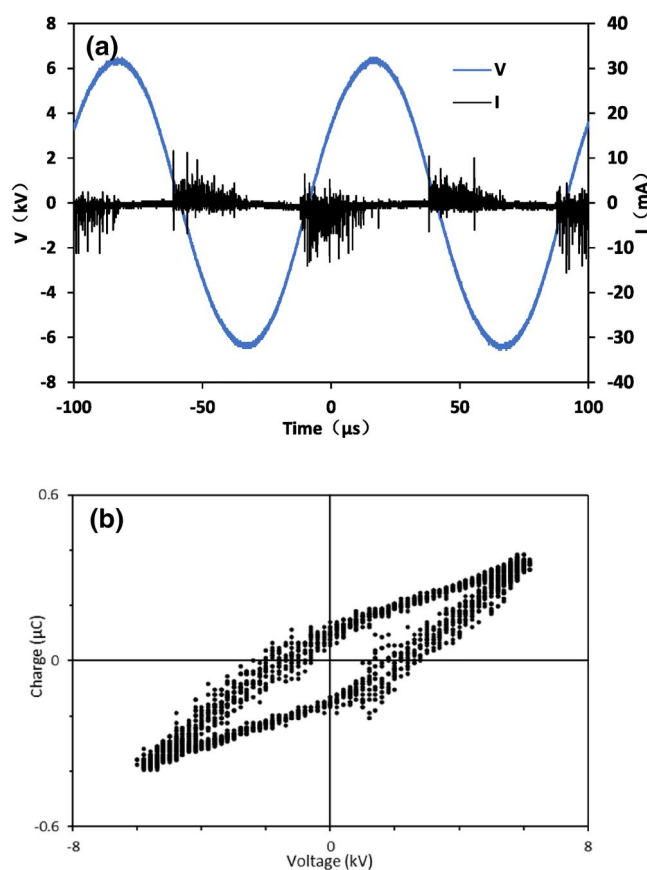


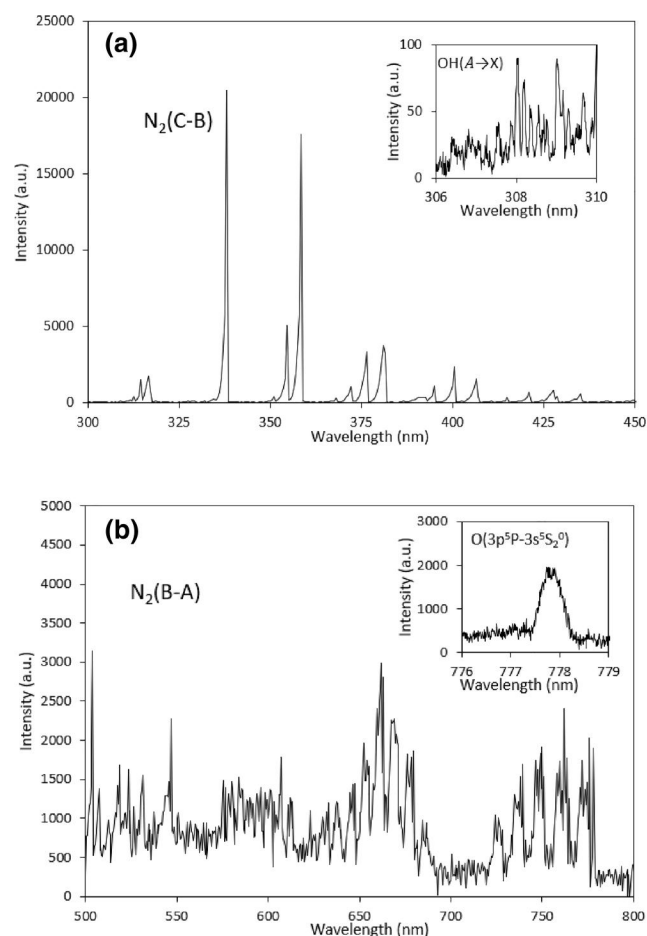
FIGURE 3 The current-voltage waveforms of dielectric barrier discharge reactor: (a) the voltage and current waveforms and (b) the Lissajous figure

$[\text{SO}_2]_{\text{inlet}}$  and  $[\text{SO}_2]_{\text{outlet}}$  are the concentrations of SO<sub>2</sub> (ppm) at the inlet and outlet of DBD reactor, respectively.

In order to study the energy efficiency of DBD reactor for NO and SO<sub>2</sub> removal, the removal energy per molecule is calculated by [21]:

**TABLE 2** Testo 350 gas analyser

| Sensor          | Range      | Accuracy                           |
|-----------------|------------|------------------------------------|
| O <sub>2</sub>  | 0–25 Vol%  | ±0.2 Vol%                          |
| CO <sub>2</sub> | 0–25 Vol%  | ±0.3 Vol%+1% of the measured value |
| NO              | 0–2000 ppm | ±5% of the measured value          |
| NO <sub>2</sub> | 0–500 ppm  | ±5% of the measured value          |
| SO <sub>2</sub> | 0–2000 ppm | ±5% of the measured value          |
| CO              | 0–500 ppm  | ±5% of the measured value          |

**FIGURE 4** Typical emission spectra generated by dielectric barrier discharge: (a) 350–450 nm and (b) 500–800 nm

$$\text{Energy per NO removed [eV/NO]} = 232 \times \frac{\text{SED [J/L]}}{\text{NO removal [ppm]}} \quad (3)$$

$$\text{Energy per SO}_2 \text{ removed [eV/SO}_2\text{]} = 232 \times \frac{\text{SED [J/L]}}{\text{SO}_2 \text{ removal [ppm]}} \quad (4)$$

where SED is the specific energy density, J/L.

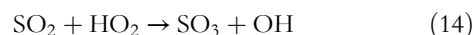
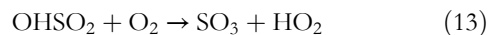
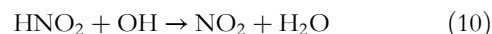
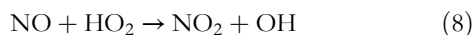
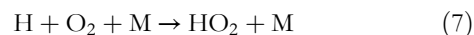
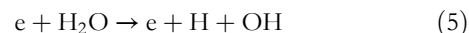
### 3 | RESULTS AND DISCUSSION

#### 3.1 | Effects of H<sub>2</sub>O vapour

The simulated diesel exhaust gas was composed of 10% O<sub>2</sub>, 7% CO<sub>2</sub>, 820 ppm NO, 320 ppm SO<sub>2</sub>, 200 ppm C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>O and N<sub>2</sub> (balance), and we added water vapour to the simulated gas, and changed the water vapour content of the gases to 0, 3.1%, 6.6% and 9.8%, respectively. The gas temperature at the inlet of DBD reactor is fixed at 115°C. The input discharge power of the DBD reactor is fixed at 25 W.

Effects of water vapour content on simultaneous desulfurization and denitrification are shown in Figure 5. In the process of water vapour content increasing from 0% to 9.8%, the removal efficiency of NO increased from 18.9% to 57.3%, and the removal efficiency of SO<sub>2</sub> increased from 4.8% to 35.3%. The energy per NO removed decreased from 449.0 to 148.1 eV/NO, and the energy per SO<sub>2</sub> removed decreased from 2784.0 to 582.9 eV/SO<sub>2</sub>, when water vapour content increased from 0% to 9.8%. The removal and energy efficiency of NO and SO<sub>2</sub> is improved significantly with the increase of water vapour, especially when the content of water vapour changes from 0% to 6.6%.

Water vapour is an important source of OH radicals, which play an important role in the removal of NO and SO<sub>2</sub> [14]. A lot of OH and HO<sub>2</sub> are produced via the reactions (5)–(7) [22]. NO is oxidized to NO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub> by OH radical and HO<sub>2</sub> radical via reactions (8)–(11) [15, 22]. Meanwhile, SO<sub>2</sub> is oxidized to SO<sub>3</sub> by OH radical and HO<sub>2</sub> radical via reactions (12)–(15), and then SO<sub>3</sub> reacts with H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub> [23].



The CO generated in DBD reactor mainly comes from the decomposition of CO<sub>2</sub> and the incomplete oxidation of C<sub>3</sub>H<sub>6</sub> via reactions (16)–(19) [20, 22]. As a kind of air pollutants, CO is an unwanted by-product in DBD reactor, which also needs attention. The effect of water vapour on CO concentration is shown in Figure 6. The experimental results show that the CO concentration at the outlet of DBD reactor decreases from 460 to 229 ppm, while the water content increases from 0% to 9.8%. Increasing the content of water vapour can effectively

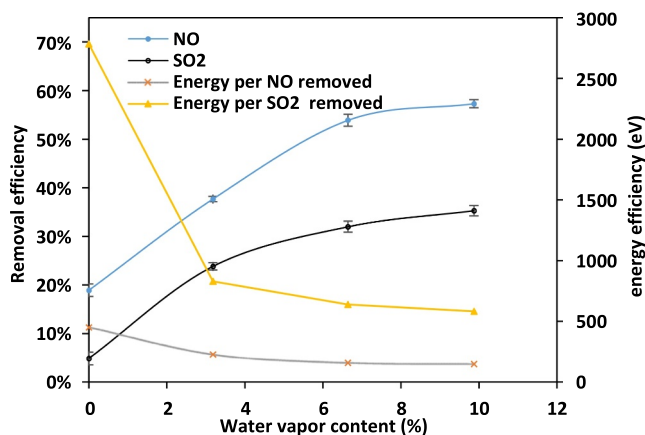


FIGURE 5 Effects of water vapour on NO and SO<sub>2</sub> removal efficiency

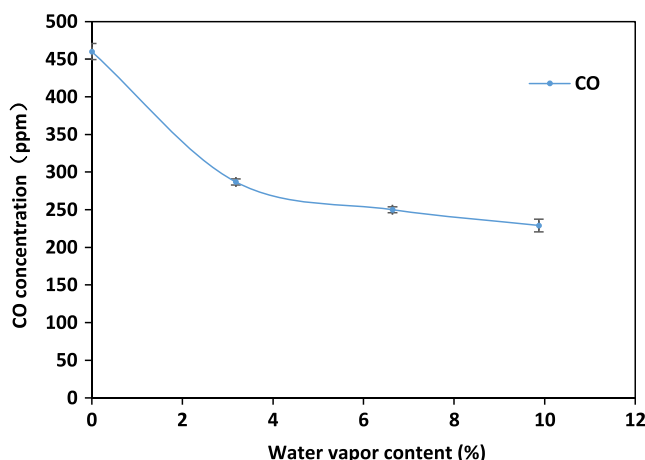
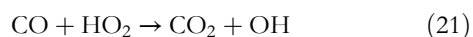
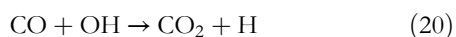
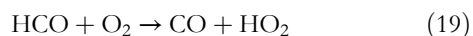
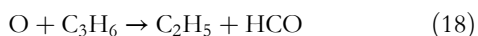
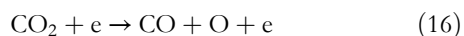


FIGURE 6 Effects of water vapour on CO concentration

reduce the generation of CO in DBD reactor. The increase of water vapour content promotes the formation of OH and HO<sub>2</sub>, which makes CO oxidized to CO<sub>2</sub> more easily via reactions (20)–(21) [22].



To analyse the effect of water vapour on NO removal, the concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> were measured during the change of water vapour content, as shown in Figure 7. It can be seen from the experimental results that the concentration of NO<sub>x</sub> (NO + NO<sub>2</sub>) decreased from 735 to 480 ppm, the concentration of NO decreased from 665

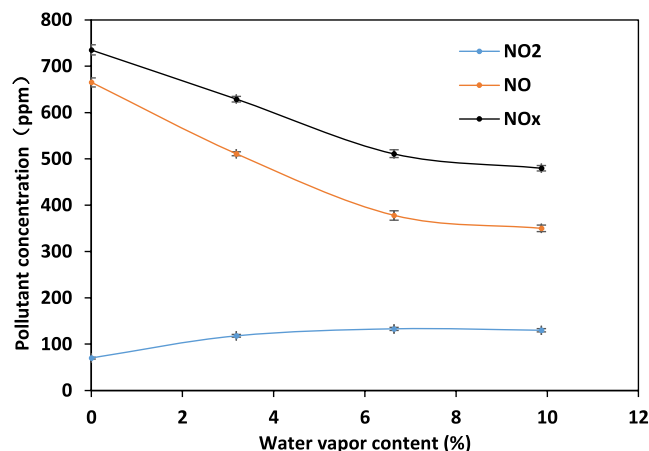
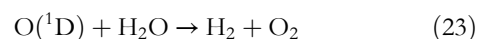


FIGURE 7 Effects of water vapour on NO, NO<sub>2</sub> and NO<sub>x</sub> concentration

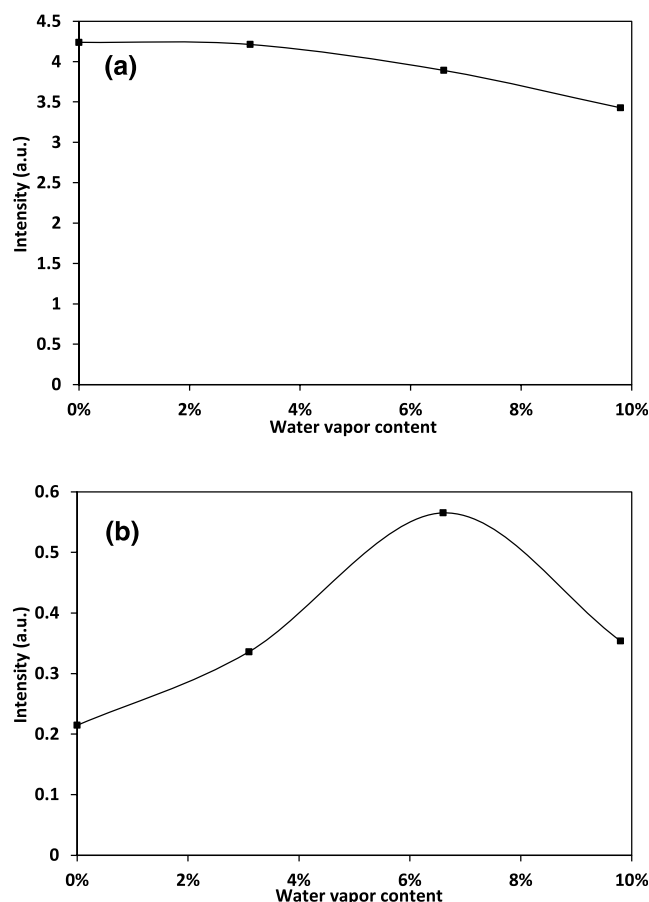
to 350 ppm, and the concentration of NO<sub>2</sub> increased from 70 to 130 ppm in the process of increasing the content of water vapour from 0% to 9.8%. Only about 19% of the removed NO was oxidized to NO<sub>2</sub>. It is speculated that most of NO is oxidized to NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub> and HNO<sub>2</sub> et al.

The influence of water vapour on the OES of O ( $3p^5P \rightarrow 3s^5S_2^0$ ) and OH ( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) in DBD reactor was measured by spectrometer. The experimental results are shown in Figure 8. It can be seen from Figure 8a that increasing the water vapour content reduces the emission intensity of O radicals. This is mainly due to the fact that water vapour will consume part of O radicals and generate OH radicals, H<sub>2</sub> and O<sub>2</sub> via reactions (22) and (23) [22]. Therefore, the increase of water vapour content will lead to the decrease of O radicals and emission intensity of O radicals.



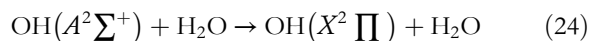
The experimental results in Figure 8b show that the increase of water vapour in the range of 0%~6.6% increases the emission intensity of OH radicals. It can be seen that the increase of water vapour promotes the generation of OH radicals. This experimental phenomenon can explain the results in Figures 5 and 6. The increase of water vapour content promotes the generation of OH radicals, thus significantly promoting the removal of NO and SO<sub>2</sub>, and reducing the generation of CO.

When water vapour content is in the range of 6.6%~9.8%, the emission intensity of OH ( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) decreased with the increase of water vapour. According to the experimental results in Figures 5 and 6, in the range of 6.6%~9.8%, the removal efficiency of NO, SO<sub>2</sub> and the concentration of CO have little change, so it is speculated that the generation amount of OH radical has little

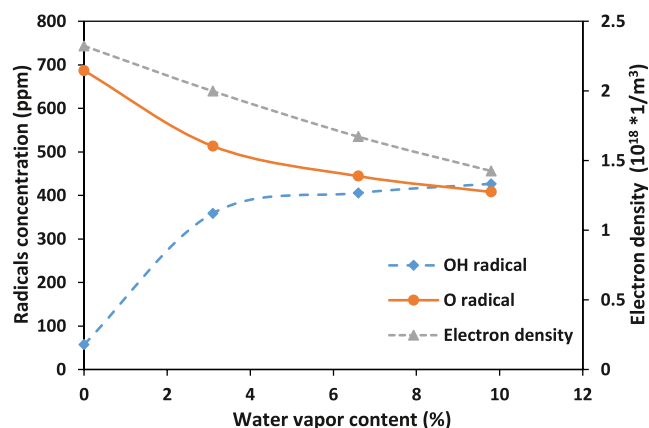


**FIGURE 8** Effects of water vapour on the OES of (a)  $O(3p^5P \rightarrow 3s^5S_2)$  and (b)  $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$

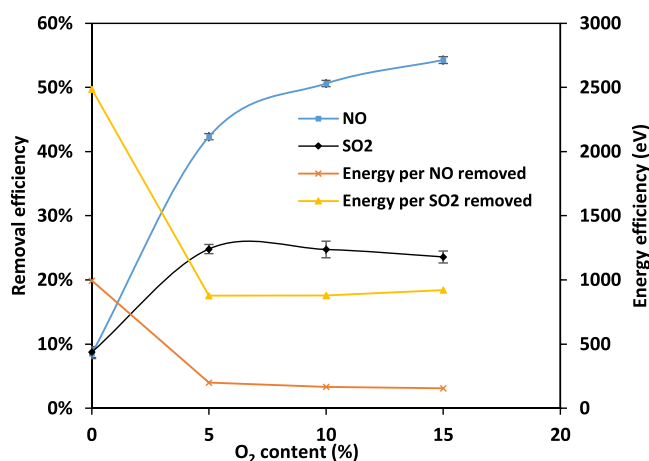
change. In the range of 6.6%–9.8%, the quenching effect of water vapour on  $OH(A^2\Sigma^+)$  is dominant via reaction (24) [24], which makes the emission spectral intensity of  $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$  decrease.



For study of the effect of  $H_2O$  vapour content, COMSOL Multiphysics was used to calculate the effect of water vapour content on electron density, OH radical and O radical formation in corona discharge reactor (inner electrode diameter 7 mm, outer electrode diameter 7.5 mm, discharge gap 0.5 mm). The applied voltage is 6.5kV, and the discharge duration is  $3 \times 10^{-5}$  s, as shown in Figure 3a. Table A1 lists the reactions considered in the model [22, 25–37]. The simulation results are shown in Figure 9. With the increase of water vapour content, the OH radical increased from 57 to 427 ppm, O radical decreased from 687 to 408 ppm, and electron density decreased from  $2.3 \times 10^{18} \text{ m}^{-3}$  to  $1.4 \times 10^{18} \text{ m}^{-3}$ . This indicates that water vapour is the main source of OH radical. Especially in the range of 0%–6.6%, OH radical increases from 57 to 406 ppm. In the range of 6.6%–9.8%, OH radical increases slowly, which is caused by the decrease



**FIGURE 9** Effects of water vapour content on OH, O radicals and electron concentration (calculated by COMSOL Multiphysics)



**FIGURE 10** Effects of  $O_2$  content on NO and  $SO_2$  removal efficiency

of electron density, the quenching effect of water vapour on  $OH(A^2\Sigma^+)$  may play an important role in the decrease of  $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$  emission intensity as shown in Figure 8b.

### 3.2 | Effects of $O_2$

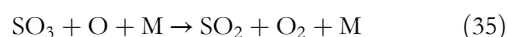
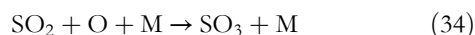
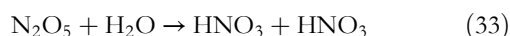
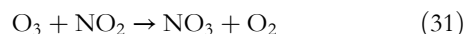
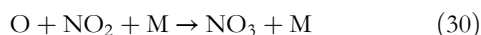
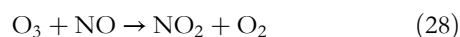
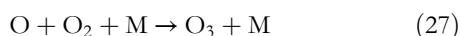
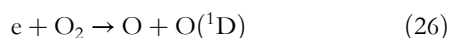
To study the effects of  $O_2$  on NO and  $SO_2$  removal efficiency in the 820 ppm NO/320 ppm  $SO_2$ /7%  $CO_2$ /200 ppm  $C_3H_6$ /3.1 %  $H_2O$ / $O_2$ / $N_2$  (balance) system, the  $O_2$  content of the gases was adjusted to 0, 5%, 10% and 15%, respectively. The gas temperature at the inlet of DBD reactor is fixed at 115°C. The input discharge power of DBD reactor is fixed at 25 W.

Figure 10 shows the effects of  $O_2$  content on NO and  $SO_2$  removal efficiency. According to the experimental results in Figure 8, the removal efficiency of NO increases from 8.5% to 54.2%, and the energy per NO removed decreased from 994.3 to 156.4 eV/NO when the  $O_2$  content increases from 0% to 15%. The removal efficiency of NO is significantly improved with the increase of oxygen content.

The effect of O<sub>2</sub> on SO<sub>2</sub> removal is different at different O<sub>2</sub> content. When O<sub>2</sub> content increases from 0% to 5%, the removal efficiency of SO<sub>2</sub> increases from 8.7% to 24.8%, and the energy per SO<sub>2</sub> removed decreases from 2485.7 to 876.6 eV/SO<sub>2</sub>. In the range of 5%–15%, increasing O<sub>2</sub> concentration reduces SO<sub>2</sub> removal efficiency from 24.8% to 23.5% and increases energy per SO<sub>2</sub> removed from 876.6 to 922.1 eV/SO<sub>2</sub>.

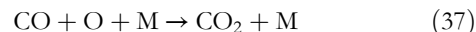
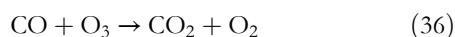
In NTP, O and O (<sup>1</sup>D) radicals can be produced by O<sub>2</sub> colliding with electrons via reactions (25) and (26) [38]. Moreover, O<sub>2</sub>, O and O(<sup>1</sup>D) can produce oxidizing substances such as HO<sub>2</sub>, OH, O<sub>3</sub> via reactions (7), (22) and (27) [22]. Then, NO is oxidized to NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>2</sub> and HNO<sub>3</sub> via reactions (8)–(11) and (28)–(33) [15, 22, 39]. Therefore, increasing O<sub>2</sub> content promotes NO removal efficiency.

The effect of O<sub>2</sub> on SO<sub>2</sub> removal is more complex. At a lower oxygen concentration (0%–5%), O<sub>2</sub> and O radicals oxidize SO<sub>2</sub> to SO<sub>3</sub> via reactions (13) and (34). In the range of 5%–15%, more O radicals are formed via the reactions (25) and (26). And SO<sub>3</sub> reacts with O to generate SO<sub>2</sub> via reaction (35), which is faster than reaction (28) [36]. Therefore, when the oxygen content is between 5% and 15%, SO<sub>2</sub> removal efficiency is inhibited.



The effect of O<sub>2</sub> content on CO concentration is shown in Figure 11. During the process of O<sub>2</sub> content increasing from 0% to 5%, the CO concentration at the outlet of DBD reactor increased from 200 to 350 ppm. In the process of increasing O<sub>2</sub> content from 5% to 15%, the concentration of CO gradually decreased from 350 to 311 ppm.

In the range of 0%–5%, due to the low oxygen content, C<sub>3</sub>H<sub>6</sub> cannot be completely oxidized, and CO is generated via reactions (18) and (19). In the range of 5% ~ 15%, the increase of O<sub>2</sub> content promotes the formation of O and O<sub>3</sub>, which makes CO oxidized to CO<sub>2</sub> via reactions (36) and (37) [2, 22]. Therefore, in the range of 5%–15%, increasing the content of O<sub>2</sub> can inhibit the formation of CO.



In order to analyse the specific effect of O<sub>2</sub> on NO removal, the concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> were measured during the change of O<sub>2</sub> content. The experimental results are shown in Figure 12. It can be seen from the experimental results that in the process of O<sub>2</sub> content increasing from 0% to 15%, the concentration of NO<sub>x</sub> (NO + NO<sub>2</sub>) decreased from 750 to 530 ppm, the concentration of NO decreased from 750 to 375 ppm, and the concentration of NO<sub>2</sub> increased from 0 to 155 ppm. About 41.3% of the removed NO was oxidized to NO<sub>2</sub>. The effect of O<sub>2</sub> on the transformation of NO to NO<sub>2</sub> is stronger than that of water vapour.

The influence of O<sub>2</sub> on the OES of O(3p<sup>5</sup>P → 3s<sup>5</sup>S<sub>2</sub><sup>0</sup>) and OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) was measured by spectrometer. The experimental results are shown in Figure 13. It can be seen from Figure 13a that in the range of 0%–15%, increasing the content of O<sub>2</sub> improves the emission intensity of O(3p<sup>5</sup>P → 3s<sup>5</sup>S<sub>2</sub><sup>0</sup>). The dissociation of O<sub>2</sub> promoted the

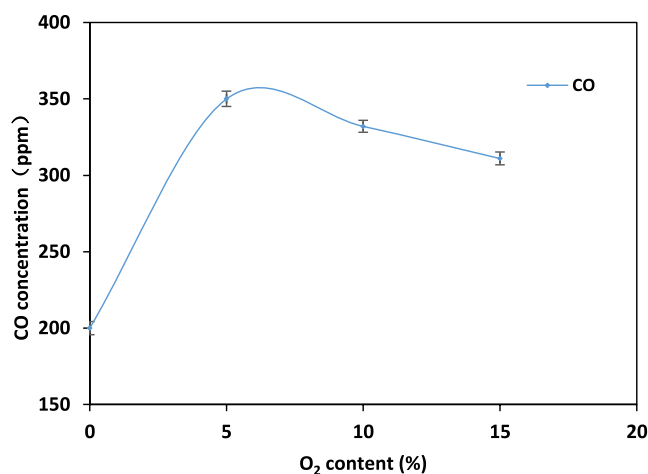


FIGURE 11 Effects of O<sub>2</sub> content on CO concentration

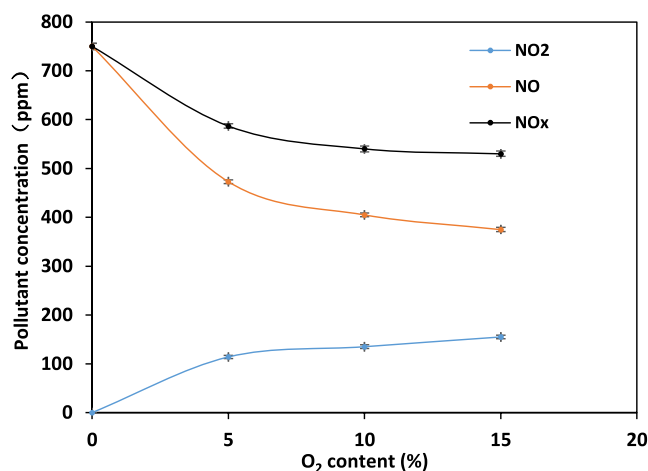
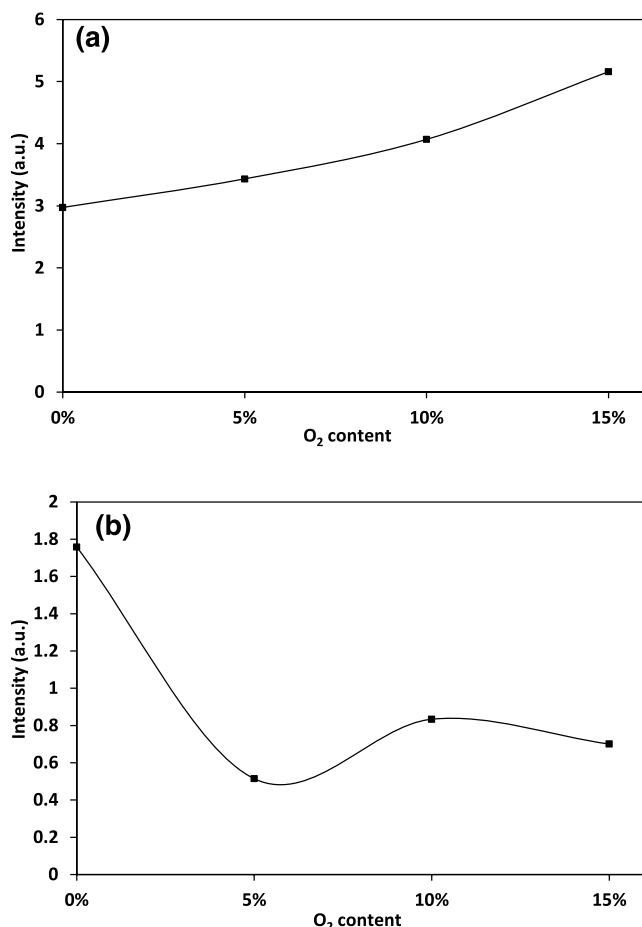


FIGURE 12 Effects of O<sub>2</sub> content on NO, NO<sub>2</sub> and NO<sub>x</sub> concentration

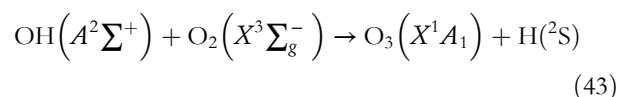
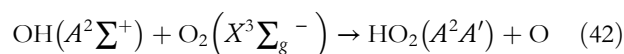
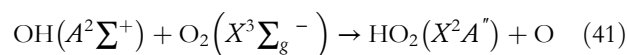
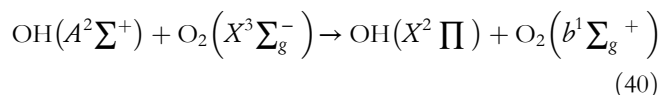
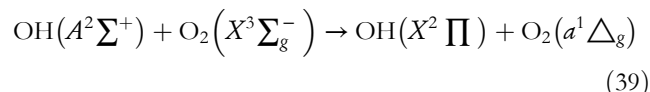
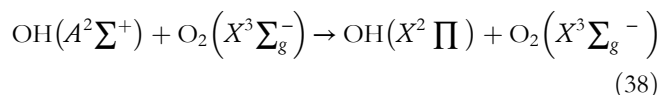


**FIGURE 13** Effects of O<sub>2</sub> content on the emission spectra of (a) O(3p<sup>5</sup>P → 3s<sup>5</sup>S<sub>2</sub>) and (b) OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π)

formation of O radicals via reactions (25) and (26). Therefore, the increase of O<sub>2</sub> content will lead to the increase of O radicals and emission intensity of O(3p<sup>5</sup>P → 3s<sup>5</sup>S<sub>2</sub>). This experimental phenomenon can explain the experimental results of Figures 10–12. In the range of 0%–15%, the increase of O<sub>2</sub> content promoted the formation of O radicals, which promoted the oxidation of NO to NO<sub>2</sub> via reactions (27)–(29). In the range of 0%–5%, the low O<sub>2</sub> content corresponds to the low O radicals, which promotes the removal of SO<sub>2</sub> via reaction (34) and the incomplete oxidation of C<sub>3</sub>H<sub>6</sub> into CO via reactions (18) and (19). In the range of 5%–15%, more O radicals were generated by increasing O<sub>2</sub> content, which inhibited SO<sub>2</sub> removal via reaction (35), and promoted CO oxidation to CO<sub>2</sub> via reactions (36) and (37).

The experimental results in Figure 13b show that the emission intensity of OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) is the highest when the content of O<sub>2</sub> is 0 in the range of 0%–15%. When O<sub>2</sub> is added into the gas mixture, the emission intensity of OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) decreases sharply due to the quenching of OH(A<sup>2</sup>Σ<sup>+</sup>) by O<sub>2</sub> via reactions (38)–(43) [40]. In the range of 5%–10%, the emission intensity of OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) increases with the increase of O<sub>2</sub> content. And the emission intensity of OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) decreased with the increase

of O<sub>2</sub> content in the range of 10%–15%. This indicates that although O<sub>2</sub> can promote the generation of OH radicals via reactions (26) and (22), the effect of O<sub>2</sub> on the generation of OH radicals is limited, and O<sub>2</sub> is mainly used for quenching OH(A<sup>2</sup>Σ<sup>+</sup>).



## 4 | CONCLUSIONS

In order to improve the removal efficiency of NO and SO<sub>2</sub> by NTP, the NO and SO<sub>2</sub> removal performance under different O<sub>2</sub>, H<sub>2</sub>O content were investigated. The effects of H<sub>2</sub>O vapour and O<sub>2</sub> on the emission intensity of O(3p<sup>5</sup>P → 3s<sup>5</sup>S<sub>2</sub>) and OH(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π) were detected. The effect mechanisms of H<sub>2</sub>O and O<sub>2</sub> on NO, SO<sub>2</sub> removal and CO generation in NTP system were discussed. In the end, we get the following conclusions:

- (1) When the water vapour content increasing from 0% to 9.8%, the removal efficiency of NO increased from 18.9% to 57.3%, the removal efficiency of SO<sub>2</sub> increased from 4.8% to 35.3%, the CO concentration at the outlet of DBD reactor decreases from 460 to 229 ppm, the energy per NO removed decreases from 449.0 to 148.1 eV/NO, and the energy per SO<sub>2</sub> removed decreases from 2784.0 to 582.9 eV/SO<sub>2</sub>, and only about 19% of the removed NO is oxidized to NO<sub>2</sub>, and most of NO is directly removed to form HNO<sub>2</sub> and HNO<sub>3</sub>, and so on.
- (2) The increase of water vapour content promotes the generation of OH radicals and decreases the generation of O radicals in H<sub>2</sub>O/O<sub>2</sub>/SO<sub>2</sub>/NO/C<sub>3</sub>H<sub>6</sub>/CO<sub>2</sub>/N<sub>2</sub> system. The increase of water vapour significantly promotes the removal of NO and SO<sub>2</sub>, decreases energy efficiency of NO and SO<sub>2</sub> removal, and reduces the generation of CO, especially in the range of 0%–6.6%.

- (3) When water vapour content is in the range of 6.6%–9.8%, the efficiency of desulfurization and denitrification and the generation of OH radical increases slowly with the increase of the water vapour content, which is caused by the decrease of electron density. The quenching effect of water vapour on  $\text{OH}(A^2\Sigma^+)$  may play an important role in the decrease of  $\text{OH}(A^2\Sigma^+ \rightarrow X^2\Pi)$  emission intensity.
- (4) In the process of  $\text{O}_2$  content increasing from 0% to 15%, the removal efficiency of NO increases from 8.5% to 54.2%, the energy per NO removed decreased from 994.3 to 156.4 eV/NO, and about 41.3% of the removed NO was oxidized to  $\text{NO}_2$ . The effect of  $\text{O}_2$  on the transformation of NO to  $\text{NO}_2$  is stronger than that of water vapour.
- (5) When  $\text{O}_2$  content is in the range of 0%–5%, the removal efficiency of  $\text{SO}_2$  increases from 8.7% to 24.8%, and the energy per  $\text{SO}_2$  removed decreased from 2485.7 to 876.6 eV/ $\text{SO}_2$  with the increase in  $\text{O}_2$  content. In the range of 5%–15%, increasing  $\text{O}_2$  concentration reduces  $\text{SO}_2$  removal efficiency from 24.8% to 23.5% and increases energy per  $\text{SO}_2$  removed from 876. to 922.1 eV/ $\text{SO}_2$ .
- (6) In the range of 0%–15%, increasing the content of  $\text{O}_2$  improves the emission intensity of  $\text{O}(3p^5P \rightarrow 3s^5S_2^0)$ . The dissociation of  $\text{O}_2$  promoted the generation of O radicals. However,  $\text{O}_2$  has limited effect on the generation of OH radicals, and is mainly used for quenching  $\text{OH}(A^2\Sigma^+)$ . When  $\text{O}_2$  content is in the range of 0% ~ 5%,  $\text{O}_2$  and O radicals oxidize  $\text{SO}_2$  to  $\text{SO}_3$ . In the range of 5%–15%, more O radicals are formed, and  $\text{SO}_3$  reacts with O to generate  $\text{SO}_2$ , which is faster. Therefore, when  $\text{O}_2$  content is between 5% and 15%,  $\text{SO}_2$  removal efficiency is inhibited.

In this article, the effects of two chemical additives ( $\text{H}_2\text{O}$  and  $\text{O}_2$ ) on the efficiency of NTP for desulfurization and denitrification were studied. Moreover, it is easy to change the content of  $\text{H}_2\text{O}$  and  $\text{O}_2$  in the exhaust pipe by spraying water or introducing air. The results of this paper are helpful for improving the efficiency of desulfurization and denitrification by NTP in practical application without increasing the discharge power.

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## APPENDIX

**TABLE A1** Considered reactions in the model

| No. | Reaction                                             | Rate constant ( $cm^3 s^{-1}$ or $cm^6 s^{-1}$ ) | References |
|-----|------------------------------------------------------|--------------------------------------------------|------------|
| R1  | $e + O_2 \rightarrow O + O^-$                        | $f(E/N)$                                         | [25]       |
| R2  | $e + O_2 \rightarrow O + O$                          | $f(E/N)$                                         | [25]       |
| R3  | $e + O_2 \rightarrow O + O(^1D)$                     | $f(E/N)$                                         | [25]       |
| R4  | $e + N_2 \rightarrow e + N_2(X, v \geq 13)$          | $f(E/N)$                                         | [26]       |
| R5  | $e + N_2 \rightarrow e + N_2(A^3\Sigma_u^+)$         | $f(E/N)$                                         | [26]       |
| R6  | $e + N_2 \rightarrow e + N_2(B^3\Sigma_g)$           | $f(E/N)$                                         | [26]       |
| R7  | $e + N_2 \rightarrow e + N_2(C^3\Sigma_u)$           | $f(E/N)$                                         | [26]       |
| R8  | $e + N_2 \rightarrow e + e + N_2^+$                  | $f(E/N)$                                         | [26]       |
| R9  | $e + N_2 \rightarrow e + N + N$                      | $f(E/N)$                                         | [26]       |
| R10 | $e + H_2O \rightarrow OH + H^-$                      | $f(E/N)$                                         | [25]       |
| R11 | $e + H_2O \rightarrow OH + H + e$                    | $f(E/N)$                                         | [25]       |
| R12 | $e + CO_2 \rightarrow CO + O + e$                    | $f(E/N)$                                         | [27]       |
| R13 | $e + CO_2 \rightarrow CO + O^-$                      | $f(E/N)$                                         | [27]       |
| R14 | $e + CO_2 \rightarrow e + e + CO_2^+$                | $f(E/N)$                                         | [27]       |
| R15 | $N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2 + O + O$   | $1.7 \times 10^{-12}$                            | [22]       |
| R16 | $N_2(A^3\Sigma_u^+) + H_2O \rightarrow N_2 + OH + H$ | $4.2 \times 10^{-11}$                            | [22]       |
| R17 | $N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2 + O_2$     | $7.5 \times 10^{-13}$                            | [28]       |
| R18 | $N_2(A^3\Sigma_u^+) + O \rightarrow N_2 + O(^1D)$    | $3.0 \times 10^{-11}$                            | [28]       |

(Continues)

TABLE A1 (Continued)

| No. | Reaction                                                                                                              | Rate constant ( $\text{cm}^3 \text{s}^{-1}$ or $\text{cm}^6 \text{s}^{-1}$ )                     | References |
|-----|-----------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|------------|
| R19 | $\text{N}_2(B^3\Sigma_g) + \text{O}_2 \rightarrow \text{N}_2 + \text{O} + \text{O}$                                   | $3.0 \times 10^{-10}$                                                                            | [28]       |
| R20 | $\text{N}_2(B^3\Sigma_g) + \text{N}_2 \rightarrow \text{N}_2 + \text{N}_2(A^3\Sigma_u^+)$                             | $3.0 \times 10^{-11}$                                                                            | [28]       |
| R21 | $\text{N}_2(C^3\Sigma_u) + \text{N}_2 \rightarrow \text{N}_2 + \text{N}_2(B^3\Sigma_g)$                               | $1.0 \times 10^{-11}$                                                                            | [28]       |
| R22 | $\text{N}_2(C^3\Sigma_u) + \text{O}_2 \rightarrow \text{N}_2(A^3\Sigma_u^+) + \text{O} + \text{O}$                    | $3.0 \times 10^{-10}$                                                                            | [28]       |
| R23 | $\text{N}_2(A^3\Sigma_u^+) + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{N}_2 + \text{N}_2(C^3\Sigma_u)$              | $1.6 \times 10^{-10}$                                                                            | [28]       |
| R24 | $\text{N}_2(A^3\Sigma_u^+) + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{N}_2 + \text{N}_2(B^3\Sigma_g)$              | $7.7 \times 10^{-11}$                                                                            | [28]       |
| R27 | $\text{N}_2(A^3\Sigma_u^+) + \text{O} \rightarrow \text{NO} + \text{N}(^2\text{D})$                                   | $7 \times 10^{-12}$                                                                              | [29]       |
| R28 | $\text{N}_2(B^3\Sigma_g) \rightarrow \text{N}_2(A^3\Sigma_u^+) + h\nu$                                                | $2 \times 10^5$                                                                                  | [29]       |
| R29 | $\text{N}_2(C^3\Sigma_u) \rightarrow \text{N}_2(B^3\Sigma_g) + h\nu$                                                  | $2.73 \times 10^7$                                                                               | [30]       |
| R30 | $\text{N}(^2\text{D}) + \text{O}_2 \rightarrow \text{NO} + \text{O}$                                                  | $1.5 \times 10^{-12} (T_g/300)^{0.5}$                                                            | [31]       |
| R31 | $\text{N}_2(A^3\Sigma_u^+) + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}$                                    | $7.8 \times 10^{-14}$                                                                            | [22]       |
| R32 | $\text{N}_2(X, v \geq 13) + \text{O} \rightarrow \text{NO} + \text{N}$                                                | $1 \times 10^{-13}$                                                                              | [32]       |
| R33 | $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$                                                              | $1.1 \times 10^{-14} T_g \times \exp(-3150/T_g)$                                                 | [33]       |
| R34 | $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$                                                              | $1.1 \times 10^{-12} (T_g)^{0.5}$                                                                | [33]       |
| R35 | $\text{N} + \text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N}_2$                                                 | $1.76 \times 10^{-31} \times T_g^{-0.5}$                                                         | [32]       |
| R36 | $\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$                                                            | $5 \times 10^{-16}$                                                                              | [32]       |
| R37 | $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{NO} + \text{NO}$                                         | $7.2 \times 10^{-11}$                                                                            | [33]       |
| R38 | $\text{N}_2\text{O} + \text{N}(^2\text{D}) \rightarrow \text{NO} + \text{N}_2$                                        | $2.2 \times 10^{-12}$                                                                            | [30]       |
| R39 | $\text{N}_2\text{O} + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{O} + \text{N}_2 + \text{N}_2$                       | $26.2 \times 10^{-12}$                                                                           | [30]       |
| R40 | $\text{N}(^2\text{D}) + \text{N}_2 \rightarrow \text{N} + \text{N}_2$                                                 | $2.2 \times 10^{-14}$                                                                            | [30]       |
| R41 | $\text{O} + \text{O}_2 + \text{N}_2 \rightarrow \text{O}_3 + \text{N}_2$                                              | $6.2 \times 10^{-34} \times (300/T_g)^2$                                                         | [34]       |
| R42 | $\text{O} + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_3 + \text{O}_2$                                              | $6.9 \times 10^{-34} \times (300/T_g)^{1.25}$                                                    | [34]       |
| R43 | $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$                                                         | $1.4 \times 10^{-12} \times \exp(-1310/T_g)$                                                     | [35]       |
| R44 | $\text{O} + \text{NO} + \text{N}_2 \rightarrow \text{NO}_2 + \text{N}_2$                                              | $1.03 \times 10^{-30} \left( \frac{T_g}{298} \right)^{-2.87} \exp\left( \frac{780}{T_g} \right)$ | [35]       |
| R45 | $\text{O} + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2$                                              | $1.03 \times 10^{-30} \left( \frac{T_g}{298} \right)^{-2.87} \exp\left( \frac{780}{T_g} \right)$ | [35]       |
| R46 | $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$                                                           | $1.7 \times 10^{-11} \exp(-300/T_g)$                                                             | [33]       |
| R47 | $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$                                                                        | $7.6 \times 10^{12} \exp(-12274/T_g)$                                                            | [35]       |
| R48 | $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$                                         | $2.3 \times 10^{-10}$                                                                            | [22]       |
| R49 | $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$                                       | $2.3 \times 10^{-12}$                                                                            | [22]       |
| R50 | $\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}$                                                | $k_M = 6.05 \times 10^{-14}$                                                                     | [36]       |
| R51 | $\text{SO}_3 + \text{O} + \text{M} \rightarrow \text{SO}_2 + \text{O}_2 + \text{M}$                                   | $k_M = 1.79 \times 10^{-10}$                                                                     | [36]       |
| R52 | $\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5 + \text{HCO}$                                       | $2.62 \times 10^{-17} (T_g)^{1.8} \exp(612/T_g)$                                                 | [37]       |
| R53 | $\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{CH}_2\text{CO} + \text{CH}_3 + \text{H}$                           | $8.31 \times 10^{-17} (T_g)^{1.8} \exp(-38/T_g)$                                                 | [37]       |
| R54 | $\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{HOC}_3\text{H}_6$                                                 | $4.85 \times 10^{-12} \exp(503/T_g)$                                                             | [37]       |
| R55 | $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$                                                         | $1.26 \times 10^{-11} \exp(206/T_g)$                                                             | [37]       |
| R56 | $\text{HOC}_3\text{H}_6 + \text{O}_2 \rightarrow \text{HOC}_3\text{H}_6\text{O}_2$                                    | $1.66 \times 10^{-12} \exp(554/T_g)$                                                             | [37]       |
| R57 | $\text{HOC}_3\text{H}_6\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{HCO} + \text{NO}_2$ | $4.2 \times 10^{-12} \exp(180/T_g)$                                                              | [37]       |
| R58 | $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2$                                        | $3.67 \times 10^{28} (T_g)^{-13.3} \exp(-4910/T_g)$                                              | [37]       |

TABLE A1 (Continued)

| No. | Reaction                                                                                              | Rate constant ( $\text{cm}^3 \text{s}^{-1}$ or $\text{cm}^6 \text{s}^{-1}$ )        | References |
|-----|-------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------|
| R59 | $\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{NO}_2$ | $4.2 \times 10^{-12} \exp(180/T_g)$                                                 | [37]       |
| R60 | $\text{CH}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{HCO} + \text{HO}_2$         | $6.64 \times 10^{-14} \exp(-554/T_g)$                                               | [37]       |
| R61 | $\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$                     | $1.2 \times 10^{-10} \exp(-1800/T_g)$                                               | [37]       |
| R62 | $\text{CH}_3\text{CH}_2\text{O} + \text{M} \rightarrow \text{CH}_3 + \text{CH}_2\text{O} + \text{M}$  | $2.24 \times 10^{14} (T_g)^{-7} \exp(-11978/T_g)$                                   | [37]       |
| R63 | $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$                                          | $1.5 \times 10^{35} (T_g)^{-15} \exp(-8567/T_g)$                                    | [37]       |
| R64 | $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$                     | $4.2 \times 10^{-12} \exp(180/T_g)$                                                 | [37]       |
| R65 | $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$                      | $8.52 \times 10^{-14} \exp(-1293/T_g)$                                              | [37]       |
| R66 | $\text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}$                               | $2.5 \times 10^{-11}$                                                               | [37]       |
| R67 | $\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$                               | $2.1 \times 10^{-11}$                                                               | [37]       |
| R68 | $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}$                                   | $3.6 \times 10^{-11} (T_g)^{-0.6}$                                                  | [35]       |
| R69 | $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$                                 | $5.9 \times 10^{-32}$                                                               | [22]       |
| R70 | $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$                                         | $3.5 \times 10^{-12} \exp(-241/T_g)$                                                | [35]       |
| R71 | $\text{NO} + \text{OH} \rightarrow \text{HNO}_2$                                                      | $3.2 \times 10^{-11}$                                                               | [35]       |
| R72 | $\text{HNO}_2 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$                               | $3.67 \times 10^{28} \left(\frac{T_g}{298}\right) \exp\left(-\frac{69}{T_g}\right)$ | [35]       |
| R73 | $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$                              | $2.2 \times 10^{-30}$                                                               | [22]       |
| R74 | $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$                                                    | $3.5 \times 10^{-11}$                                                               | [22]       |
| R75 | $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$                                            | $2.6 \times 10^{-13}$                                                               | [22]       |
| R76 | $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$                                  | $6.6 \times 10^{-33} \exp(-2173/T_g)$                                               | [22]       |
| R77 | $\text{O}_2 + \text{N}_2^+ \rightarrow \text{N}_2 + \text{O}_2^+$                                     | $4.7 \times 10^{-12}$                                                               | [22]       |
| R78 | $\text{O}_2^- + \text{O}_2^+ \rightarrow \text{O}_2 + \text{O}_2$                                     | $4.2 \times 10^{-7}$                                                                | [22]       |
| R79 | $\text{O}^- + \text{O}_2^+ \rightarrow \text{O} + \text{O}_2$                                         | $9.6 \times 10^{-8}$                                                                | [22]       |
| R80 | $\text{H}_2\text{O} + \text{N}_2^+ \rightarrow \text{N}_2 + \text{H}_2\text{O}^+$                     | $2 \times 10^{-9}$                                                                  | [22]       |
| R81 | $\text{O} + \text{H}_2\text{O}^+ \rightarrow \text{H}_2 + \text{O}_2^+$                               | $5.5 \times 10^{-11}$                                                               | [22]       |
| R82 | $5.5 \times 10^{-11}$                                                                                 | $2.6 \times 10^{-10}$                                                               | [22]       |
| R83 | $2.6 \times 10^{-10}$                                                                                 | $\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{NO}_3 + \text{M}$              | [22]       |
| R84 | $5 \times 10^{-32}$                                                                                   | $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$                     | [22]       |
| R85 | $1.7 \times 10^{-16}$                                                                                 | $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$                        | [22]       |
| R86 | $1.1 \times 10^{-12}$                                                                                 | $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3$ | [22]       |
| R87 | $5 \times 10^{-21}$                                                                                   | $\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2$                                 | [35]       |
| R88 | $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$                                    | $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$                  | [35]       |
| R89 | $1.3 \times 10^{-12} \exp(-2735/T_g)$                                                                 | $\text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH}$                     | [35]       |
| R90 | $2.01 \times 10^{-17}$                                                                                | $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$                | [35]       |
| R91 | $1.2 \times 10^{-15}$                                                                                 | $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$                            | [35]       |