Design of a MT-DBD reactor for H$_2$S control

Xu CAO (曹栩), Weixuan ZHAO (赵玮璇), Renxi ZHANG (张仁熙), Huiqi HOU (侯惠奇), Shanping CHEN (陈善平) and Ruina ZHANG (张瑞娜)

Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP$^3$), Institute of Environmental Science, Fudan University, Shanghai 200433, People’s Republic of China
Shanghai Institute for Design & Research on Environmental Engineering, Shanghai 200232, People’s Republic of China

E-mail: zrx@fudan.edu.cn

Received 8 September 2016, revised 6 December 2016
Accepted for publication 9 December 2016
Published 9 March 2017

Abstract
This study aimed to discuss the removal of hydrogen sulfide (H$_2$S) with non-thermal plasma produced by a multilayer tubular dielectric barrier discharge reactor, which is useful in the field of plasma environmental applications. We explored the influence of various factors upon H$_2$S removal efficiency ($\eta_{H_2S}$) and energy yield (Ey), such as specific energy density (SED), initial concentration, gas flow velocity and the reactor configuration. The study showed that we can achieve $\eta_{H_2S}$ of 91% and the best Ey of 3100 mg kWh$^{-1}$ when we set the SED, gas flow velocity, initial H$_2$S concentration and layers of quartz tubes at 33.2 J l$^{-1}$, 8.0 m s$^{-1}$, 30 mg m$^{-3}$ and five layers, respectively. The average rate constant for the decomposition of hydrogen sulfide was 0.206 g m$^{-3}$ s$^{-1}$. In addition, we also presented the optimized working conditions, by-product analysis and decomposition mechanism.

Keywords: dielectric barrier discharge (DBD), odor pollution, low temperature plasma, H$_2$S

(Some figures may appear in colour only in the online journal)

1. Introduction

H$_2$S odor gas, which has strong toxicity and corrosiveness, has recently been the focus of increasing global concern [1–4]. Traditional methods of H$_2$S treatment consist of combustion, catalytic oxidation, absorption, activated carbon adsorption and biological method [5–8]. The dielectric barrier discharge (DBD) reactor, proposed as a simple, cheap and efficient method to produce non-thermal plasma in atmospheric pressure, is considered to be a very attractive approach for gas pollutant removal [9–13].

A coaxial sleeve-type dielectric barrier discharge (CS-DBD) reactor composed of two coaxial quartz tubes was employed in our previous study [14–16], and the results showed high odor removal efficiency. However, this kind of DBD reactor encountered many difficulties in further industrial applications because of its limited processing capacity. A multilayer tubular dielectric barrier discharge (MT-DBD) reactor was used to produce non-thermal plasma in this work to overcome the shortcomings of the CS-DBD reactor. The dielectric barrier of the reactor was composed of five layers of quartz tubes arranged in a row with an equal distance gap between each other. The electrodes placed in the quartz tubes were made of stainless steel and led out from the tube ends. The discharge process occurred between adjacent tubes where gas streams flow through.

According to the processing requirements, we can easily change the layers of quartz tubes arranged in a row to achieve higher efficiency. Comparing with the CS-DBD reactor previously used in our group [17, 18], this new MT-DBD reactor has a high exploitation of space, lower system resistance, stronger adaptability with no electrode corrosion and lower energy consumption.

In this paper, we focus on the $\eta_{H_2S}$ and the Ey versus different specific energy densities (SED), initial gas concentrations, gas flow velocities and reactor configurations utilized MT-DBD. The mechanisms and optimum conditions were also given for the MT-DBD reactor to be better employed in the field of pollution control. Experimental
The MT-DBD reactor used in our experiment has several quartz tubes through only one power supply, which could dramatically reduce the volume of the instrument. Figure 3(b) shows the true picture of the quartz tube arrangement and the real status of discharge in the reactor.

2. Experimental section

2.1. Experimental setup and reagents

The schematic of the experimental apparatus is displayed in figure 1. The removal of H2S consists of three steps: gas generation and mixing, decomposition reaction, and detection. H2S was generated from a compressed cylinder (H2S purity >99.999%). After mixing and diluting with air, the reaction gas flowed into the MT-DBD reactor under a tunable air blower (CZR, China) with a certain concentration and gas flow velocity. A self-made HV generator was employed with the applied voltage varying from 5000 to 20 000 V, and the frequency varying from 20 to 100 kHz. The initial concentration ranged from 20 to 80 mg m\(^{-3}\). The initial H2S concentration of 40 mg m\(^{-3}\) was inserted into the quartz tubes. The stainless steel electrode was inserted into the quartz tubes with 2 mm tube wall thickness, 20 mm outer diameter, and 400 mm length. The stainless steel electrode was inserted into the quartz tubes. The current was fixed from 0.1 to 5.0 A. In this research, the energy acting on the reactor was assumed to be equal to the power supplied by the power source.

Figure 3(a) shows that the gas discharge process occurred between adjacent tubes where gas streams flow through. To obtain a high-efficiency DBD, the quartz tubes with odd numbers (①,③,⑤,⑦) were connected to the negative electrode of the power supply, while the quartz numbers with even numbers (②,④,⑥) were connected together to the positive electrode. The stainless steel electrode was inserted into the quartz tubes, which could effectively avoid the electrode corrosion. Meanwhile, the MT-DBD reactor could connect several quartz tubes through only one power supply, which could dramatically reduce the volume of the instrument. Figure 3(b) shows the true picture of the quartz tube arrangement and the real status of discharge in the reactor.

2.2. MT-DBD reactor

The MT-DBD reactor used in our experiment has five layers of tubes arranged in a row, and each layer consists of seven quartz tubes with 2 mm tube wall thickness, 20 mm outer diameter, and 400 mm length. The stainless steel electrode was inserted into the quartz tubes. The current was fixed from 0.1 to 5.0 A. In this research, the energy acting on the reactor was assumed to be equal to the power supplied by the power source.

Figure 3(a) shows that the gas discharge process occurred between adjacent tubes where gas streams flow through. To obtain a high-efficiency DBD, the quartz tubes with odd numbers (①,③,⑤,⑦) were connected to the negative electrode of the power supply, while the quartz numbers with even numbers (②,④,⑥) were connected together to the positive electrode. The stainless steel electrode was inserted into the quartz tubes, which could effectively avoid the electrode corrosion. Meanwhile, the MT-DBD reactor could connect several quartz tubes through only one power supply, which could dramatically reduce the volume of the instrument. Figure 3(b) shows the true picture of the quartz tube arrangement and the real status of discharge in the reactor.

2.3. Analysis methods

The removal efficiency (\(\eta_{\text{H}_2\text{S}}\)), absolute removal amount (ARA) and energy yield (Ey) were defined in our previous research [17].

3. Results and discussions

3.1. Influence of SED

Figure 4 shows the influence of SED upon removal efficiency (\(\eta_{\text{H}_2\text{S}}\)) and Ey in the MT-DBD reactor with the initial H2S concentration of 40 mg m\(^{-3}\), gas flow velocity of 8.0 m s\(^{-1}\), and five quartz tube layers.

Figure 4 shows that the removal efficiency of H2S and Ey enhanced as SED increased in the MT-DBD reactor. The removal efficiency of H2S changed more obviously than Ey. When the SED is 33.2 J l\(^{-1}\), the removal efficiency of H2S reached 71\%, and Ey could be up to 3080 mg kWh\(^{-1}\).

With the increase in SED, the electric field would increase, which improved the electron attraction and quantity, and thus greatly strengthened the collision possibility between H2S molecules and electrons.

However, with the increase of SED, the energy consumption and cost are also increased. The results showed that the appropriate SED was essential to obtain acceptable H2S removal efficiency and energy yield. Therefore, we should consider the removal efficiency and Ey for the purpose of making the appropriate choice in practical industrial applications.

3.2. Influence of the gas flow velocity

The experimental conditions were set at the SED of 33.2 J l\(^{-1}\), the initial H2S concentration of 40 mg m\(^{-3}\) and five layers of quartz tubes arranged in a row. Figure 5 shows the relationship between the removal efficiency of H2S or Ey and the gas flow velocity.

Figure 5 shows that with the increase in gas flow velocity, the removal efficiency of H2S decreased stably, whereas
Figure 2. (a) Voltage waveforms measured at the discharge electrode. (b) Corresponding charge–voltage Lissajous figure.

Figure 3. (a) Sketch map of the electrodes 1—quartz tube, 2—stainless steel electrode, 3—the discharge area. (b) True picture of discharge in the MT-DBD reactor.

Figure 4. $\eta_{H_2S}$ and $E_y$ as a function of SED in the MT-DBD reactor (voltage varied from 6 to 13.2 kV, corresponding frequency of 25–30 kHz).

Figure 5. $\eta_{H_2S}$ and $E_y$ as a function of the gas flow velocity in the MT-DBD reactor (voltage fixed at 13.2 kV, corresponding frequency of 26.7 kHz).
Ey first initially increased and then decreased slowly. When the gas flow velocity was 8 m s$^{-1}$, the removal efficiency of H$_2$S could be up to 71% with the best Ey of 3080 mg kWh$^{-1}$.

The gas residence time decreases when the gas flow velocity increases, which determined the collision probability of the H$_2$S molecules with the energetic electrons in the plasma reactor, resulting in the decrease in H$_2$S removal efficiency. By contrast, with higher gas flow velocity initially, more H$_2$S molecules were introduced into the DBD reactor under the same H$_2$S concentration, which results in more H$_2$S molecules colliding with the active particles under the same applied voltage. Consequently, the ARA of H$_2$S and Ey are increased. However, the number of high-energy active particles in the reactor is limited, such that Ey initially increased and then decreased gradually when the gas flow velocity further increased.

Figure 6 shows the relationship between the outlet concentration (C$_{out}$) and gas residence time. The transient rate constant was 0.237 g m$^{-3}$ s$^{-1}$ when the residence time was 0.075 s, while the average rate constant was 0.206 g m$^{-3}$ s$^{-1}$. With the increase in residence time, the decomposition reaction rate constants would decrease. It is an effective way to choose the appropriate reactor size and gas flow velocity in industrial applications.

3.3. Influence of the initial H$_2$S concentration

Figure 7 shows that the initial H$_2$S concentration has an influence on the removal efficiency of H$_2$S and Ey at the SED of 33.2 J l$^{-1}$, the gas flow velocity of 8.0 m s$^{-1}$ and with five quartz tube layers.

Figure 7 shows that, with the increase in initial H$_2$S concentration, the removal efficiency of H$_2$S decreased quickly but Ey initially increased and then decreased slowly. Though H$_2$S could be removed completely when the initial H$_2$S concentration was 20 mg m$^{-3}$, the energy yield was as low as 2100 mg kWh$^{-1}$. At the preferable initial concentration of 30 mg m$^{-3}$, removal efficiency reached 91% with the best Ey of 3100 mg kWh$^{-1}$.

The removal of H$_2$S depended on the ratio of active particles to H$_2$S molecules. Under the same input energy, the number and energy magnitude of electrons would not vary significantly. Therefore Ey, defined as ARA to the input energy of the DBD reactor, depends on the changes of ARA at a given applied voltage.

With a higher initial concentration, the total quantity of collision particles increased, and therefore, ARA correspondingly increased initially. But for each H$_2$S molecule, the collision probability decreased, resulting in the decrease of removal efficiency of H$_2$S. When the initial concentration was more than 30 mg m$^{-3}$, the number of high energy active particles in the MT-DBD reactor would not be sufficient, thus the ARA decreased eventually. Therefore, in practical applications, we could increase the H$_2$S initial concentration of H$_2$S appropriately to ensure higher energy efficiency.

3.4. Influence of the tube layer number

The influences of the tube layer number on removal efficiency of H$_2$S and Ey is shown in figure 8. The results were obtained at the SED of 33.2 J l$^{-1}$, the initial H$_2$S concentration of 30 mg m$^{-3}$ and the gas flow velocity of 8.0 m s$^{-1}$.

The data showed that the removal efficiency of H$_2$S increased gradually with the increase in discharge layers of quartz tubes arranged in row. Meanwhile, Ey improved significantly. With the layer number changing from one to five, the removal efficiency of H$_2$S increased from 34% to 91%, and Ey increased from 2350 to 3100 mg kWh$^{-1}$.

The increase in the number of discharge layers of quartz tubes arranged in row is beneficial to the degradation of H$_2$S because H$_2$S molecules could be removed through multistage degradation reactions. Meanwhile, the collision probability between H$_2$S and high-energy electrons or active groups was relatively higher, which could lead to an increase in $\eta_{H_2S}$ and Ey.
3.5. Decomposition mechanism

The nitrogen emission spectrum under atmosphere pressure was displayed to underpin a clear understanding of the electrical field in the MT-DBD reactor using a fiber optic spectrometer (AvaSpec-ULS, CN). We choose the second positive system \((\text{C}\,^3\Pi_u \rightarrow \text{B}\,^3\Pi_g)\) as the characteristic spectrum of \(\text{N}_2\). The main emission spectra ranged from 316 to 406 nm, such as \(\text{N}_2(0–0, 337\,\text{nm})\), \(\text{N}_2(0–1, 357\,\text{nm})\), \(\text{N}_2(1–0, 316\,\text{nm})\), \(\text{N}_2(1–2, 353\,\text{nm})\), \(\text{N}_2(1–3, 375\,\text{nm})\) and so on [19].

The transition of \(\text{N}_2\) molecules of the second positive system were because of the collision between high energy electrons between \(\text{N}_2\) molecules. The mechanism can be listed as follows [20]:

\[
\begin{align*}
\text{e} + \text{N}_2 & \rightarrow \text{N}_2(\text{C}\,^3\Pi_u) + \text{e} \quad E = 11.05\,\text{eV} \quad \text{R1} \\
\text{e} + \text{N}_2 & \rightarrow \text{N}_2(\text{B}\,^3\Pi_g) + \text{e} \quad E = 7.391\,\text{eV} \quad \text{R2} \\
\text{N}_2(\text{C}\,^3\Pi_u) & \rightarrow \text{N}_2(\text{B}\,^3\Pi_g) + \text{h}\nu \quad \lambda = 337\,\text{nm} \quad \text{R3}
\end{align*}
\]

The spectrum of 337 nm was observed in our experiment, as shown in figure 9. We can conclude from R3 that there were \(\text{N}_2(\text{C}\,^3\Pi_u)\) particles in the discharge area, and therefore, R1 also existed in DBD and the energy of the electrons could be at least 11.05 eV. So in our MT-DBD, the energy of the electrons was sufficient to break the \(\text{HS}–\text{H}\) bond, \(\text{O}–\text{O}\) bond and \(\text{HO}–\text{H}\) bond.

The decomposition of \(\text{H}_2\text{S}\) could be considered as primary initiated reactions and secondary reactions. The primary initiated reactions involve the process of the attack of energy electrons on \(\text{H}_2\text{S}\), \(\text{O}_2\) and \(\text{H}_2\text{O}\) molecules. The secondary reactions consist of four parts of reactions between \(\text{H}_2\text{S}\) molecules, oxidation radicals, induced and intermediate particles.

The basic principle of chemical kinetics in the \(\text{H}_2\text{S}\) removal process in the MT-DBD reactor is shown in figure 10 (table 1).

The sulfate ion, as a by-product, was identified by means of IC. The result further indicated that the aforementioned mechanism was reasonable. In conclusion, the decomposition of \(\text{H}_2\text{S}\) included the processes of direct attack of energy electrons on \(\text{H}_2\text{S}\) and oxidation of oxidative radicals on \(\text{H}_2\text{S}\) in the MT-DBD reactor.
### 4. Conclusions

This experiment mainly investigated H₂S removal applied using a MT-DBD technology, and examined the influences of applied voltage, gas flow velocity, initial H₂S concentration and layers of quartz tubes on H₂S removal efficiency and energy yield. The voltage and the number of quartz tube layers are positively related to the removal efficiency of H₂S. By contrast, the gas flow velocity and initial concentration show opposite results. Under the preferable condition of the SED of 32.3 J l⁻¹, the gas flow velocity of 8 m s⁻¹, the H₂S initial concentration of 30 mg m⁻³, and five layers of quartz tubes, the removal efficiency of H₂S will reach 91% with the best Ey of 3100 mg kWh⁻¹. The average energy yield constant for the decomposition reaction of H₂S is 0.206 g m⁻³ s⁻¹.

Compared with a CS-DBD reactor, the MT-DBD reactor has a more compact structure, wider adaptability, and superior industrial application prospects. In practical industrial applications, higher voltage, suitable initial concentration, reasonable gas flow velocity and more layers of quartz tubes would be better. The efficiency of energy utilization should be considered. In addition, advanced treatment is essential to prevent secondary pollution.

### Acknowledgments

The financial support for this research was provided by National Natural Science Foundation of China (Nos. 21577023), and the Key Project supported by the Science and Technology Commission of Shanghai Municipality (No. 15DZ1205904). The authors thank Hong Zhang and Jianyuan Hou for their help in the research work.

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