Experimental Study on the Removal of Formaldehyde by Plasma-Catalyst

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Abstract. In this paper, a new type of indoor air purification device was designed. Corona discharge combined with catalysis and physical adsorption was used in this device. Formaldehyde (PA), a typical indoor air pollutant, was chosen as the model pollutant. The effects of MnO2 in degradation of PA by electrical discharge were discussed. The results showed that corona discharge can effectively remove PA, and the addition of MnO2 can not only accelerate the degradation rate, but also solve the problem of excessive ozone (O3). Besides, the corona discharge plasma also has the function of in-situ cleaning for MnO2. The new reactor has the characteristics of high efficiency, energy-saving, without secondary pollution.

1. Introduction

Indoor air quality often has substandard conditions due to the comprehensive influence of various factors such as decorative materials and furniture appliances. Common indoor pollutants mainly include formaldehyde (PA), benzene, particulate matter, bacteria, viruses and other substances can seriously damage human health [1]-[2]. Furthermore, PA is directly harmful to eyes and respiratory system, as well as the central nervous system, which could cause symptoms such as headache, dizziness, tearing, and nausea [3]. The hazards of PA have attracted lots of attention from the whole world. The national standard GB/IT6127-1995 [4] stipulates that the maximum allowable values of PA concentration in public places and living rooms are 0.12 mg/m3 and 0.08 mg/m3, respectively. Therefore, how to degrade and remove PA has become an important research problem.

Traditional methods for removing PA include adsorption, titanium dioxide photocatalysis, ozone (O3) oxidation, metal catalysis, and plant purification [5]. The above methods have the disadvantages of low efficiency, secondary pollution, high technical requirements, high maintenance cost, short service life and small application range. Faced with these conditions, new technology is urgently needed to remove PA. In this paper, a new type of indoor air purification device was designed, which combines corona discharge plasma method and adsorption method.

At present, the application of corona discharge plasma in gas purification is receiving more and more attention. Corona discharge is a way of generating non-thermal plasma, containing high energy electrons and various active substances such as H-, HO- and H2O2. Plasma-induced free radical
reaction can remove toxic gas pollutants with advantages unmatched by previous technologies. However, the problems of this method such as high energy consumption requirements and secondary pollution need to be solved [6].

2. Experimental

2.1. Corona discharge power supply
The voltage range of power supply is 3-15 kV. The frequency regulation range is 5-15 kHz. The speed range of high voltage rotating electrode is 0-1200 r/min. And the discharge power range is 100-300 W. The parameters are selected according to the stable and uniform corona discharge. Priority is given to the following table 1.

| Range                                      | Recommended choice |
|--------------------------------------------|--------------------|
| High voltage power supply voltage 3-15kV   | 5 kV               |
| Frequency 5-15kHz                          | 10 kHz             |
| High-voltage rotating electrode speed 0-1200 r/min | 600 r/min         |
| Discharge power 100-300W                   | Power switchable adjustment |

2.2. Corona discharge reactor
The self-made barrel reactor in this experiment is shown in figure 1 and figure 2. The cylindrical grounding electrode is made of metal plate and has a thickness of about 1 mm. The inner wall is closely attached with a layer of carbon felt with a thickness of 1 mm. The carbon felt can be used to adsorb the microorganisms and the harmful gases in the air effectively. It can ensure the contact probability and residence time. This carbon felt improve the air purification efficiency and making the discharge treatment more complete. Both the cylindrical grounding electrode and the carbon felt are processed in a hole array with a hole diameter of about 2 mm. The outer surface of the cylindrical grounding electrode is provided with an insulating outer casing which is structurally supported and insulated. And it is also processed by a hole array with a hole diameter of about 1 mm. The purified air by discharge was blowed through a cylindrical grounding electrode, a carbon felt, and a hole-shaped air outlet on the insulating casing.

![Figure 1. Reaction device](image1)

![Figure 2. Section diagram of the device](image2)

The middle part reaction O₃ was set with a high-voltage rotating electrode and a cylindrical grounding electrode and a plasma reaction region is formed between the high-voltage rotating electrode and the cylindrical grounding electrode. The high-voltage rotating electrode is composed of a metal rotating shaft and a serrated stainless steel plate. The metal rotating shaft and the lead-out wire
of the high-voltage power supply are electrically connected by a brush. The thickness of the serrated stainless steel plate is 0.5-1 mm. The plasma produced by corona discharge can react with MnO₂ photocatalysis synergistically [7]. Under the premise of maintaining a certain discharge power, it can enhance the efficiency of air purification by plasma and decompose O₃ which is the by-product of plasma. The contradiction between the efficiency of air purification by plasma and the concentration of O₃ exceeding the standard can be well solved.

2.3. experimental procedure
The volume of the sealing device was 0.058 m³. The chamber was filled with PA gas by evaporating the PA solution. The space was provided to a purification experiment with a self-developed air purifier. PA solution was placed in the sealing device. Then the fan was opening for 30 minutes to make the PA solution fully volatilized and evenly distributed in the sealing device. A detection device is arranged on the inner side of the sealing device. The reaction device was turned on for discharge treatment to investigate the effect of PA treatment under different influencing factors when the display of the detector is no longer changed. The experiment was carried out at room temperature.

3. Results and Discussions

3.1. The remove of PA by corona discharge
The change in PA concentration is shown in figure 3. The concentration of PA reduced from 1.02 mg/m³ which is 10 times of the national standard [4] to 0 within 13 minutes. However, the excess production of O₃ is a problem that should not be overlooked. Therefore, O₃ should be restricted within an appropriate range to accelerate the process of treatment and eliminate secondary pollution at the same time.

3.2. Effect of discharge power on O₃ production
In order to solve the problem of excessive O₃, it is necessary for us to have research on the effect of discharge power on O₃ production. Two different input power were set. There were 14 W and 29 W, respectively. As shown in figure 4, when the power was 29 W, a bright purple streamer corona can be seen between the plates which was not obvious in 14 W. Meanwhile, from the experimental data, 29 W produces more O₃ than 14 W.

3.3. Adsorption capacity of MnO₂
The with MnO₂ was introduced into the reaction system because of its certain absorption effect on O₃. Besides, MnO₂ could degradate PA as an effective catalyst [4,8]. Based on these characteristics, not only the reaction rate of PA increased, but also the production of O₃ was limited. Therefore, the adsorption capacity of MnO₂ became an important norm. Loaded with MnO₂ catalyst was installed in...
the unit and the unit did not start up. As shown in figure 5, the adsorption effect of PA and O₃ was studied when the device was not started. The concentration of PA and O₃ decreases very rapidly in the first 20 minutes. After 20 minutes, the adsorption rate of the MnO₂ was slowed down, and the O₃ was completely removed at nearly 50 minutes.

3.4. Corona discharge synergistic MnO₂ catalyzed adsorption degradation of PA

Figure 6 shows that MnO₂ catalyst was placed in the device at 14 W power to remove PA by discharge. Comparing the previous experimental data, the treatment effect of PA is obviously improved, and the O₃ amount produced by the experiment is also greatly reduced. It took 6 minutes and 30 seconds for PA to degrade to 0. Compared with experimental results without MnO₂, O₃ degradation speed up to four times. Compared with the three cases, this scheme has the best effect.

3.5. Reaction mechanism analysis

The mechanism of removal of gaseous pollutants by non-thermal plasma (NTP): Under the action of an applied electric field, a large number of energetic electrons bombard the pollutant molecules, causing them to ionize, dissociate and excite, and then trigger a series of complex physical and chemical reactions. Mineralize complex toxic macromolecular organic pollutants into simple non-toxic or low-toxic inorganic substances [9]-[12], so that pollutants can be degraded and removed. In addition, the generated O₃ can also be oxidatively decomposed. The mechanism for removing PA from exhaust gas can be divided into two parts, one of which is that electrons generated by an electric field directly collide with PA. In theory, the electrons generated during the discharge process can completely destroy the PA molecules. Thereby the PA molecules are ionized, dissociated and excited. The second is the chemical interaction between various reactive groups (•OH, HO₂ and O atoms) and O₃ and PA molecules, and a series of reactions between them and the destroyed PA molecules the physicochemical reaction. This reaction completely decomposes the PA molecules, and finally produces CO₂, CO and H₂O. Figure 7 shows the main path of PA molecular removal. The possible reaction process between PA and reactive groups in the gas is shown in the following formula [13].

\[
\begin{align*}
    \text{HCHO} + \text{OH} & \rightarrow \text{CHO} + \text{H}_2\text{O} \\
    \text{HCHO} + \text{O} & \rightarrow \text{CHO} + \text{OH} \\
    \text{CHO} + \text{H} & \rightarrow \text{CO} + \text{H}_2 \\
    \text{CHO} + \text{O}_2 & \rightarrow \text{CO} + \text{OH} \\
    \text{CHO} + \text{OH} & \rightarrow \text{CO} + \text{H}_2\text{O} \\
    \text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H}
\end{align*}
\]
Figure 7. The main approach of HCHO removal

When the MnO2 catalytically degrades PA, the highly reactive hydroxyl radicals and oxygen ions initiate the chain decomposition reaction of PA. And the oxidative decomposition of PA into carbon dioxide is the most common. The mechanism is as follows.

\[
\begin{align*}
\text{Mn}^{4+} + e & \rightarrow \text{Mn}^{3+} \\
\text{O}_2(g) & \rightarrow \text{O}_2(\text{ads}) \\
\text{O}_2(\text{ads}) + \text{Mn}^{3+} & \rightarrow \text{O}_2^{-}(\text{ads}) + \text{Mn}^{4+} \\
\text{O}_2^{-}(\text{ads}) + e & \rightarrow \text{O}_2^2^- + e \rightarrow \text{O}^- + \text{O}^2^- \\
\text{O}^- + \text{H}_2\text{O} + e & \rightarrow \bullet\text{OH} \\
\text{HCHO} + \bullet\text{OH} & \rightarrow \bullet\text{CHO} + \text{H}_2\text{O} \\
\bullet\text{CHO} + \text{O}_2^- & \rightarrow \text{HCOO}^- + \text{H}^+ \rightarrow \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

4. Conclusions

- The corona discharge method can effectively remove PA.
- MnO2 can not only play a catalytic role to accelerate the degradation rate, but also solve the problem of excessive O3 generation.
- As the discharge power increases, the removal efficiency of PA is higher.
- Corona discharge plasma has the function of in-situ cleaning of MnO2, and finally achieves the purpose of high efficiency, energy-saving, no pollution and long-term use.

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