

Article

Study of the Treatment of Organic Waste Gas Containing Benzene by a Low Temperature Plasma-Biological Degradation Method

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Abstract: Volatile organic compounds (VOCs) from the pharmaceutical and chemical industries have been a matter of concern for some years in China. Achieving efficient degradation of chlorobenzene (CB) in waste gas is difficult because of its high volatility and molecular stability. A DBD (dielectric barrier discharge) biological method was proposed to treat chlorobenzene, aiming to control high operating costs and prevent secondary pollution. In this investigation, a DBD biological method was introduced to deal with chlorobenzene by optimization of process parameters. The results showed that the degradation efficiency of chlorobenzene was close to 80% at a hydraulic retention time (HRT) of 85 s when the inlet concentration was 700 mg·m⁻³ for the biological method. The degradation efficiency of chlorobenzene reached 80% under a discharge voltage of 7 kV, an inlet concentration of 700 mg·m⁻³ and an HRT of 5.5 s. The degradation efficiency of an integrated system can be increased by 15–20% compared with that of a single biological system. Therefore, this method can be used as a new way to address chlorobenzene pollution in the pharmaceutical and chemical industries.

Keywords: biotrickling filter; dielectric barrier discharge; chlorobenzene; pharmaceutical and chemical industry



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1. Introduction

The atmosphere can influence vital human metabolic processes. With the acceleration of China's economic and industrial development, the problem of atmospheric environmental pollution has become increasingly prominent over the past two decades [1]. From 2003 to 2017, emissions of sulfur dioxide (SO₂), nitrogen oxide (NO_x) and particulate matter (PM) decreased by 14.93 MT (million tons), 5.61 MT and 4.08 MT, respectively. However, emissions of volatile organic pollutants (VOCs), which are precursors to PM_{2.5} and cause photochemical smog, rose from 0.15 MT to nearly 0.3 MT [2,3]. VOCs were produced mainly by emissions from the painting, petrochemistry, pharmaceutical and chemical industries. The total production value of the Chinese pharmaceutical and chemical industry in 2014 was less than 3% of China's GDP, but its VOC emissions accounted for 6% of China's total VOC emissions [4,5]. In 1990, 21 of the hazardous air pollutants mentioned in amendments to the Clean Air Act by the Environmental Protection Agency (EPA) were organic pollutants. A large number of organic compounds are used for pharmaceutical synthesis intermediates and as organic solvents [6]. Chlorobenzene and its derivatives are amongst the commonly occurring materials listed in a blacklist of exhaust gases by the European Union. Chlorobenzene has high volatility and molecular stability. Moreover, it is

difficult to biodegrade and readily accumulates in organisms [7,8]. As shown in Table 1, traditional VOC treatment technology (absorption, adsorption, etc.) has a poor treatment effect, is hard to operate for a long time, produces secondary pollution and so on [9,10].

Table 1. Comparison of main technologies for VOCs treatment.

Treatment Technology	Advantages	Disadvantages	Application Field
Adsorption	High removal efficiency Low investment cost	Expensive of adsorbent Regular replacement	Spraying, petroleum, chemical, packaging printing, oil and gas recovery, paint, leather, etc.
Absorption	Mature technology Low investment cost	High cost of maintenance Wastewater treatment problems	Petrochemical, surface coating, packaging and printing, Electronics, etc.
Catalytic Combustion	High concentration of VOCs treatment Wide range of application	Expensive of catalyst High investment cost The formation of toxic by-products	Spraying, chemical, electronic, pharmaceutical, etc.
Condensation	High concentration of VOCs treatment; Recovery of single component	High investment cost Low exhaust gas flow requirement	Petrochemical; chemical industry; oil and gas recovery; Pharmaceutical, etc.
Membrane Separation	Recyclable components High efficiency	High cost Membrane pollution Low flux	Chemical, environmental protection, food, medicine, electronics, etc.
Biodegradation	Low energy consumption Low operation cost	Susceptible for activity of microorganisms High requirements for substrates	Sewage waste gas treatment, Low concentration of waste gas treatment occasions
Plasma Discharge	Suitable for refractory pollutants and high exhaust gas flow	Incomplete of mineralization of pollutants	Biological fermentation, chemical industry, textile printing and dyeing, etc.

Deng [11] et al. studied the catalytic combustion effect of mixed cobalt-based oxide on chlorobenzene degradation at low temperature. The results showed that the addition of Cr or Fe promoted the apparent activity of the original Co_3O_4 at low temperature and inhibited the formation of polychlorinated by-products. The chlorobenzene conversion rate was greater than 90% at 300 °C for 50 h operation. Jin [12] et al. studied the removal of chlorobenzene by dielectric barrier discharge (DBD) combined with $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. The presence of a catalyst can significantly enhance the degradation and oxidation capacity of chlorobenzene in a DBD reactor [13]. However, DBD technology can not completely mineralize targeted pollutants, and some by-products can appear along with high energy consumption [14,15]. Biotechnology has good degradation capacity for low carbon organic matter with relatively good water solubility. In addition, it has the advantages of convenient operation, low secondary pollution and low energy consumption; however, high substrate concentrations inhibit the activity of microorganisms, which leads to low removal efficiency [16,17]. Therefore, it is feasible to use DBD as a pretreatment to a biological method to degrade chlorobenzene and other macromolecular VOCs, improving the water solubility and degradability of VOCs. This method would not only promote the removal of pollutants but would also reduce the generation of secondary pollutants. At present, the integrated method of the two processing technologies is being paid more and more attention to address the disadvantages of a single technology. There are few studies on VOC treatment by DBD-integrated biofilter [18,19]. Jiang [20] et al. found that a plasma biotrickling filter (BTF) integrated system was superior to a BTF system for the degradation of 1, 2-dichloroethane and n-hexane, and that the microbial community had higher biodiversity. As a pretreatment of BTF, a plasma-catalytic system can effectively remove pollutants which are hard to biodegrade. The combined system showed better

adaptability with fluctuation in the inlet concentration of pollutants and HRT (hydraulic retention time).

At present, domestic research on the treatment technology for typical chlorine-containing VOCs is still in its infancy [21], and the research on the combined treatment of VOCs by DBD and biological method is insufficient, with only a few engineering application cases; therefore, research into the combined treatment of VOCs by these two methods is of much significance [22].

This study investigated the optimal process parameters for the separate treatment of chlorobenzene by BTF and DBD [23]. It also explored the degradation effect of a DBD biologically integrated system on chlorobenzene derived from the pharmaceutical and chemical industries [24]. This technology is predicted to result in improved economic and social benefits and to become more widely used and applied.

2. Materials and Methods

2.1. Materials

The basic composition of the medium (per liter) was as follows: 0.1 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.04 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.004 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50.0 g $(\text{NH}_4)_2\text{SO}_4$, 0.02 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 2.0 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.008 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.002 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.004 g $\text{Na}_2\text{MoM}_4 \cdot 2\text{H}_2\text{O}$, 32.0 g K_2HPO_4 , 16.0 g $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. These reagents were obtained from Zhengzhou Yidore Reagent Co. (Zhengzhou, China) and China National Chemical Co., Ltd. (Beijing, China).

All standard gases (O_2 (99.999%), N_2 (99.999%) and CO_2 (dry ice)) were provided by Henan Yuancheng Science and Technology Development Co., Ltd. (Zhengzhou, China). Xylene and chlorobenzene were both analytically pure (obtained from Zhengzhou PAINI Chemical Reagent of Chemistry Co., Zhengzhou, China). The experimental water was oxygen-free distilled water.

2.2. Apparatus

Figure 1 shows the integrated DBD and BTF device. The gases were generated and controlled by gas cylinders, a mixing tank and a mass flowmeter. The DBD was constructed from a quartz tube (total diameter/height: 0.03 m/0.65 m). A stainless steel discharge electrode was installed inside the quartz tube and connected to the high voltage power. A cylindrical BTF was of a polymethylmethacrylate (PMMA) column (total volume/height: 4 L/0.8 m). Some Raschig-ring fillers were regularly filled up to half of the reactor volume. A tank for liquid storage was set up at the bottom of the BTF. The inlet and outlet of the liquid flow were connected by a circulating pump. The gas (1) and (2) passed through the gas flowmeter (3) and then entered the VOC generator (4). The VOCs entered the DBD reactor (5), and the treated exhaust gas was introduced into the BTF reactor (8) from the outlet (7). The exhaust gas was further treated by BTF and finally discharged. The black arrows in Figure 1 show the flow direction of the system. Gas analysis was mainly carried out by gas chromatography. Chlorobenzene is a typical simulated waste gas of chlorine-containing VOCs in the pharmaceutical and chemical industry.

2.3. Experimental Methods

It has been found that some process parameters are particularly important for the treatment of chlorobenzene by BTF and DBD, such as the hydraulic retention time (HRT for short), discharge voltage, gas flow, and the inlet concentration of chlorobenzene [25,26]. Therefore, this study mainly focused on the influence of these process parameters on the removal efficiency of chlorobenzene. The influence of the parameters on chlorobenzene removal efficiency by a single biological process was analyzed at ambient temperature. The optimal concentration range of chlorobenzene was found to be 400–700 $\text{mg} \cdot \text{m}^{-3}$. In general, the emission concentration of VOCs from the pharmaceutical and chemical industries is no more than 400 $\text{mg} \cdot \text{m}^{-3}$. However, the wider range of VOC concentrations was chosen to better understand the treatment capacity of the system and the feasibility of scale up in this study [27,28]. The effects of different HRT on the degradation efficiency

of chlorobenzene and the oxygen concentration of BTF were investigated. *Erythrococcus pyridine* LR (GDMCC No. 60677), which was cultured in our laboratory, were inoculated into the biotrickling filter. Further, the effects of HRT, input voltage and inlet concentration on degradation efficiency were investigated in a single DBD device [29,30]. Under the conditions of an oxygen concentration of 10% and an inlet chlorobenzene concentration of 300–1000 mg·m⁻³, the degradation efficiency for different HRT (5.5–11 s) and input voltages (1–9 kV) was studied. The degradation efficiency for different inlet chlorobenzene concentrations (100–1100 mg·m⁻³) was also studied. After the stable operation of the DBD-BTF integrated system was achieved, the concentration of inlet chlorobenzene gradually increased from 50 mg·m⁻³ to 1500 mg·m⁻³ under the conditions of a solution spray density of 10 L (m⁻³·s⁻¹), an oxygen concentration of 10%, and an input voltage of 7 kV [31,32]. The effect of chlorobenzene degradation was evaluated, and the treatment effect of the integrated system was compared with that of BTF.

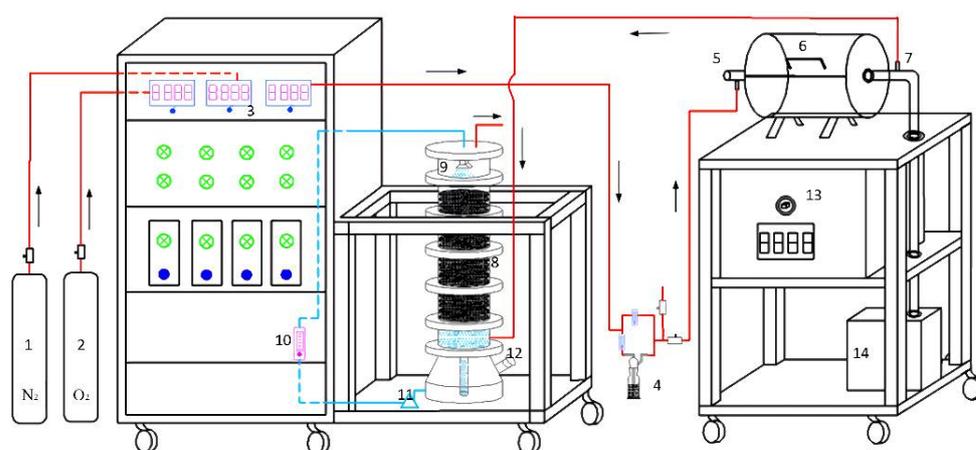


Figure 1. Integrated device of low temperature plasma biological BTF. 1. N₂; 2. O₂; 3. Gas flowmeter; 4. VOC generator; 5. Inlet of gas; 6. Safety device; 7. Outlet of gas; 8. Biotrickling filter; 9. Spray; 10. Liquid flowmeter; 11. Pump; 12. Liquid replacement; 13. Control panel on plasma reactor; 14. Power supply for plasma reactor.

2.4. Analysis Method

The concentrations of chlorobenzene and xylene were both determined by gas chromatography (Agilent HP-Innowax, column temperature 160 °C, FID detector, Santa Clara, CA, USA). The growth of microorganisms on the filler was observed by scanning electron microscopy (JEOL JSM-6490LV, Tokyo, Japan) [33]. A pH meter (Yimai IS128CP, Shanghai, China) was used for all pH measurements in this experiment.

3. Results and Discussion

3.1. Reactor Start-Up Stage

The experimental strains were all from the activated sludge at a sewage treatment plant. During the membrane-hanging period, the BTF was operated for 8 h, the density of circulating liquid was 5.17 m³·(m²·h)⁻¹, and the HRT was 96 s. The membrane was matured after 600 h. Scanning electron microscope images (Figure 2) of the filler showed that the biofilm was attached to the surface of the filler after membrane hanging [34].

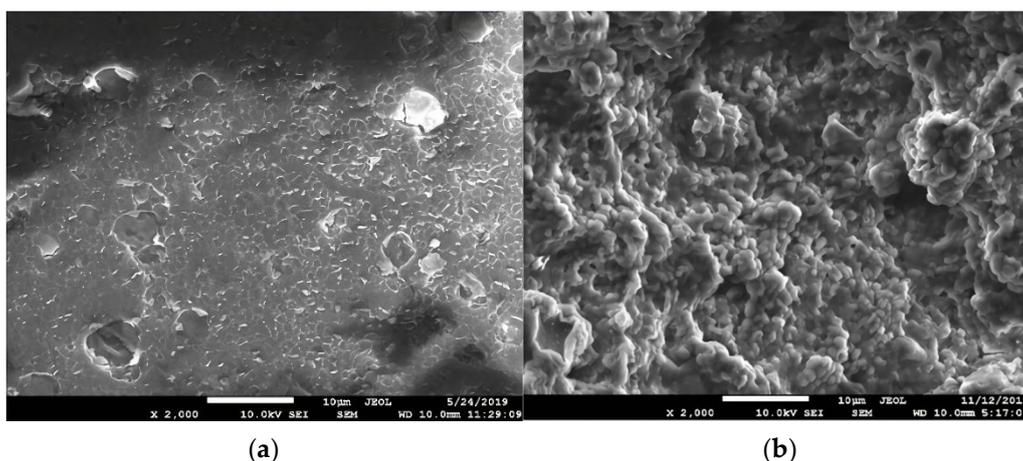


Figure 2. SEM of packing before and after membrane hanging in the biofilter. Original packing (a); Packing after hanging film (b).

3.2. Optimization of the Operating Parameters of the BTF

3.2.1. Influence of Inlet Concentration of Chlorobenzene on BTF

The inlet concentration is crucial for the degradation of organic waste gas. Padhi [35] et al. found that the higher the inlet concentration of VOCs, the lower the degradation efficiency of BTF. As is shown in Figure 3, with increasing concentration of chlorobenzene from $50 \text{ mg}\cdot\text{m}^{-3}$ to $1500 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency of BTF gradually decreased. When the inlet concentration of chlorobenzene was lower than $700 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency of BTF was close to 80% and remained stable. A suitable concentration of chlorobenzene provided the carbon source for normal growth of microorganisms. However, the treatment efficiency decreased significantly to below 70% at higher concentrations ($\geq 1300 \text{ mg}\cdot\text{m}^{-3}$), and the absolute degradation amounts of chlorobenzene increased with increase in the inlet concentration, which was consistent with Padhi's study. It was inferred that the excessively high concentration of chlorobenzene had a toxic effect on the activity of the microorganisms.

3.2.2. Influence of Hydraulic Retention Time on BTF

HRT has a significant influence on the degradation performance of BTF. Wang and Chen [36] found that HRT could improve the degradation efficiency of organic contaminants, since the mass transfer from gas to biomass was the main factor that limited the degradation of dichloromethane. As shown in Figure 4, the degradation efficiency and removal load of chlorobenzene increased with increasing HRT. At the initial HRT of 45 s, the degradation efficiency was $74 \pm 2\%$. When the HRT was 85 s, the degradation efficiency increased rapidly, but, after that, the growth rate decreased and gradually became stable. The maximum degradation rate reached $95 \pm 2\%$ when the HRT was increased to 165 s and the removal loading also increased from $30 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ to $41 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. However, the rate of removal loading slowed down and remained at about $40 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ with an HRT of 85 s. This was because the activity of the microorganisms was inhibited and the gas-liquid mass transfer decreased, which led to a reduction in the ability to degrade the chlorobenzene [37].

3.3. Optimization of the Operating Parameters of the DBD

3.3.1. Influence of HRT on Degradation Efficiency of DBD

Under the conditions of an oxygen concentration of 10% and a chlorobenzene inlet concentration of $300\text{--}1000 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency for different HRT is shown in Figure 5; the degradation effect of chlorobenzene was enhanced with increase in HRT. When the HRT was 5.5 s, the degradation efficiency reached 70%.

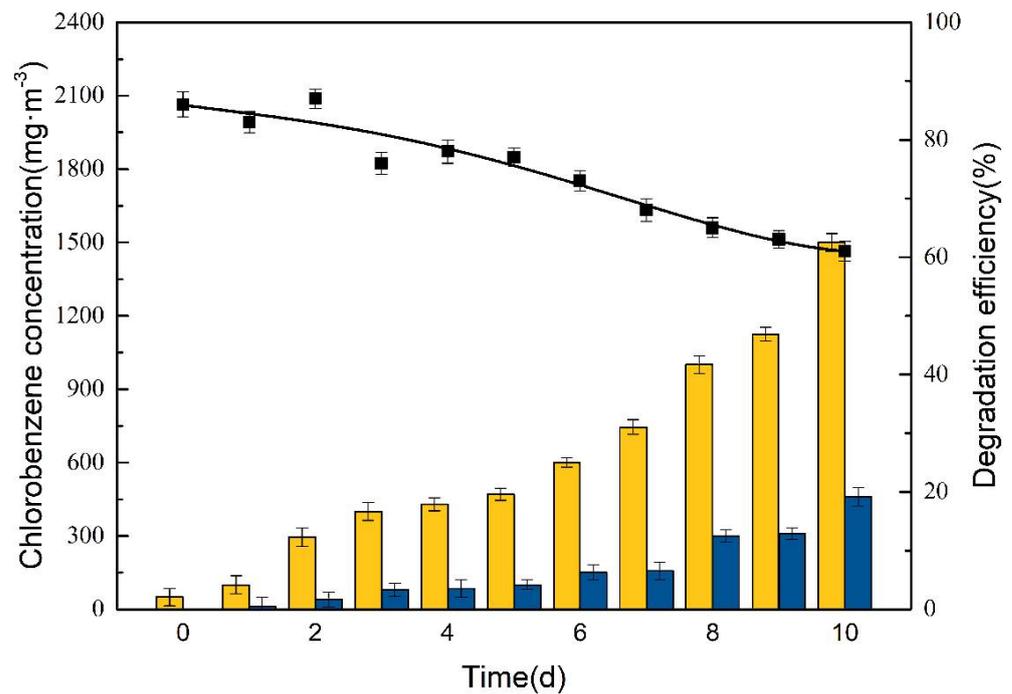


Figure 3. Influence of chlorobenzene concentration on degradation efficiency of BTF (■ Degradation efficiency, ■ Inlet concentration, ■ Outlet concentration) (air inlet gas flow = 2000 mL·min⁻¹, nutrient spray density = 5.17 L·(m⁻³·s⁻¹), oxygen concentration = 10%, empty tower dwell time = 48 s, pH = 6.5–7.0).

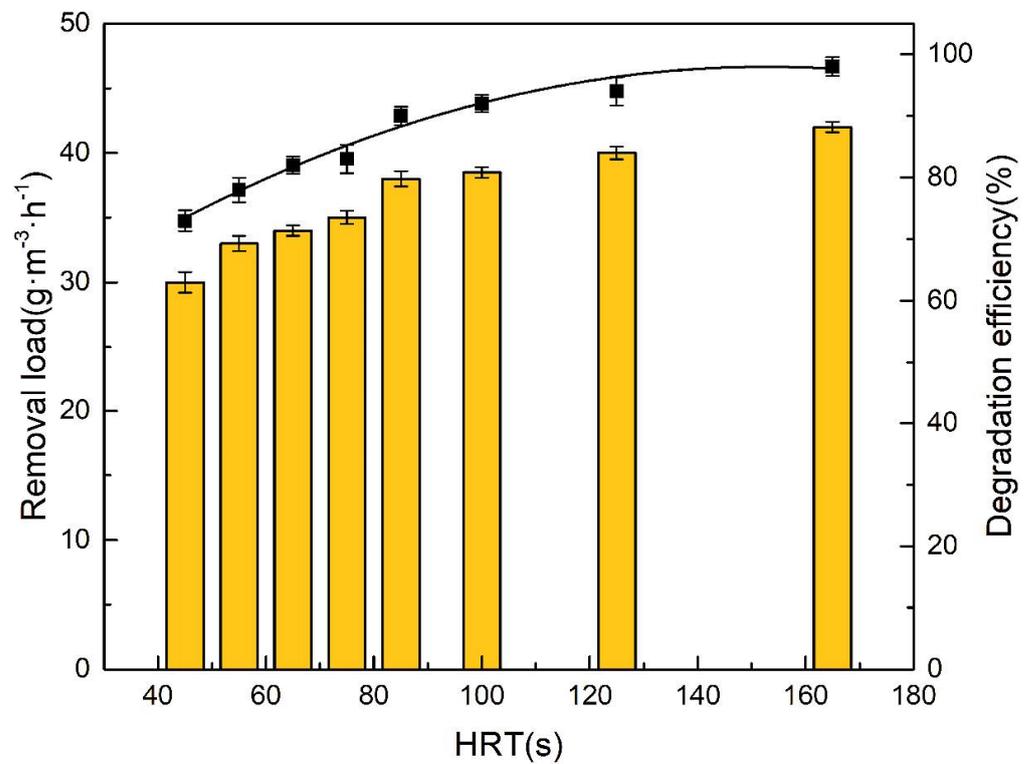


Figure 4. Influence of HRT on degradation efficiency and removal loadings of BTF. (■ Degradation efficiency, ■ Removal load) (Air inlet gas flow = 2000 mL·min⁻¹, nutrient spray density = 5.17 L·(m⁻³·s⁻¹), oxygen concentration = 10%, pH = 6.5–7.0).

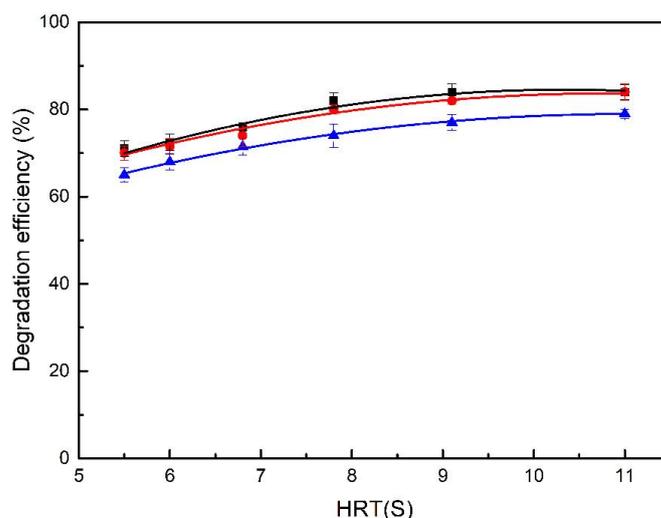


Figure 5. Influence of residence time on chlorobenzene degradation. (■ 300 mg·m⁻³, ● 600 mg·m⁻³, ▲ 1000 mg·m⁻³) (Oxygen concentration = 10%, chlorobenzene inlet concentration = 300–1000 mg·m⁻³).

3.3.2. Influence of Input Voltage on Degradation Efficiency of DBD

The degradation efficiency of different input voltages (1–9 kV) was studied under conditions of HRT of 5.5 s, oxygen concentration of 10%, and inlet concentrations of chlorobenzene of 300 mg·m⁻³, 600 mg·m⁻³ and 1000 mg·m⁻³. As shown in Figure 6, with increasing voltage, the degradation efficiency of chlorobenzene by plasma increased. When the inlet concentration was 300 mg·m⁻³ and the voltage was 1 kV, the degradation efficiency was only 15 ± 2%, and when the discharge voltage reached 9 kV, the degradation efficiency increased to 86 ± 2%. When the inlet concentration was 600 mg·m⁻³ and 1000 mg·m⁻³, the degradation efficiency increased for both concentrations by 72%. When the voltage exceeded 7 kV, the degradation efficiency of chlorobenzene increased slowly under the three different inlet concentrations. An increasing number of high energy electrons with increase in the discharge voltage of DBD would have increased the probability of collision between CB molecular and high-energy electrons. Moreover, O·, OH· and other active free radicals would be generated by the increasing discharge voltage of DBD, which is also crucial to the degradation of CB.

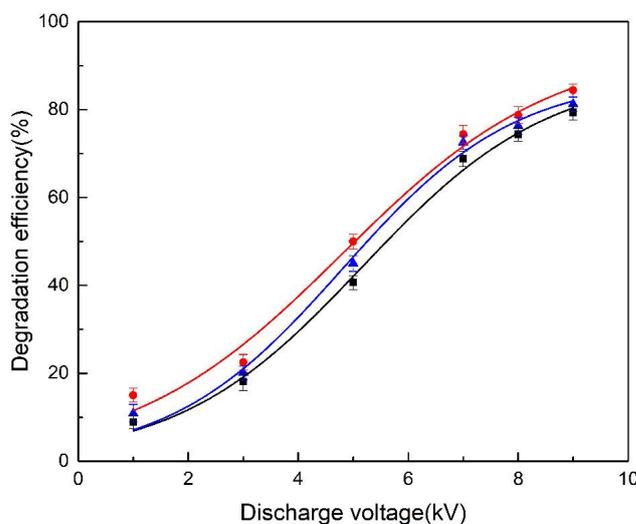


Figure 6. Effect of discharge voltage on chlorobenzene degradation (● 300 mg·m⁻³, ▲ 600 mg·m⁻³, ■ 1000 mg·m⁻³) (HRT = 5.5 s, oxygen concentration = 10%, chlorobenzene inlet concentration = 300 mg·m⁻³, 600 mg·m⁻³ and 1000 mg·m⁻³).

3.3.3. Influence of Inlet Concentration on Degradation Efficiency by DBD

The degradation efficiency of chlorobenzene inlet concentrations was studied under conditions of an HRT of 5.5 s, an oxygen concentration of 10%, a discharge voltage of 7 kV, and inlet concentrations of chlorobenzene of $100 \text{ mg}\cdot\text{m}^{-3}$, $300 \text{ mg}\cdot\text{m}^{-3}$, $500 \text{ mg}\cdot\text{m}^{-3}$, $700 \text{ mg}\cdot\text{m}^{-3}$, $900 \text{ mg}\cdot\text{m}^{-3}$ and $1100 \text{ mg}\cdot\text{m}^{-3}$. As shown in Figure 7, the degradation efficiency for chlorobenzene by DBD decreased with increase in the inlet concentration. When the inlet concentration of chlorobenzene was $100 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency reached $82 \pm 1\%$. When the inlet concentration was $1100 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency was only $41 \pm 2\%$. When the inlet concentration was higher than $700 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency began to decrease rapidly. Since chlorobenzene has poor biodegradability, Jiang et al. [38] studied the influence of DBD on chlorobenzene degradation by adjusting the technical parameters. The results showed that the chlorobenzene degradation was 40% when the inlet concentration was $500 \text{ mg}\cdot\text{m}^{-3}$ with a voltage of 8 kV. However, when the voltage was more than 12 kV, the HRT had little effect on chlorobenzene degradation. Moreover, with increase in the discharge voltage, the by-products became more biodegradable. The degradation of chlorobenzene was apparently positive at a voltage of more than 20 kV. It was found that the degradation efficiency of chlorobenzene in this system was 76% with an inlet concentration of $500 \text{ mg}\cdot\text{m}^{-3}$, and of 41% with an inlet concentration of $1100 \text{ mg}\cdot\text{m}^{-3}$, compared to 40% for an inlet concentration of $500 \text{ mg}\cdot\text{m}^{-3}$ observed by Jiang et al. Our study achieved higher degradation efficiency under the same conditions of concentration and voltage. It is clear that DBD and biological treatment have their own advantages and disadvantages for VOC treatment. The combination of the two technologies utilizes the advantages of both to improve the efficiency of VOC treatment. DBD technology can decompose macromolecular organic compounds, and it can reduce the toxicity of macromolecular organic matter to microorganisms as a pre-treatment method, thus improving the efficiency of subsequent biological treatment. In addition, the subsequent biological process can also remove the by-products of DBD treatment.

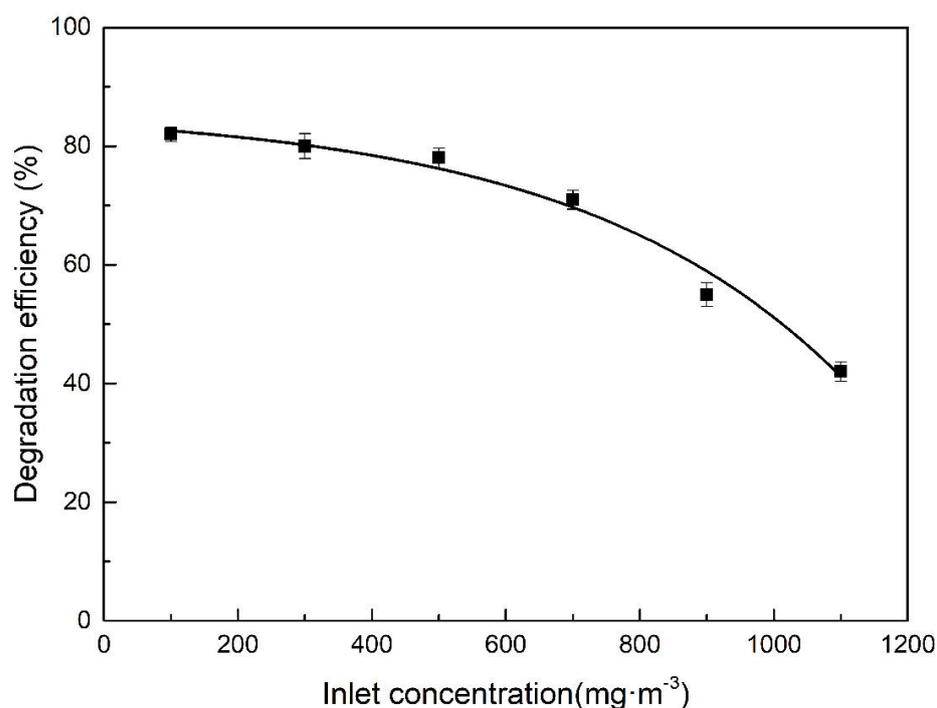


Figure 7. Influence of import concentration on chlorobenzene degradation (HRT = 5.5 s, oxygen concentration = 10%, discharge voltage = 7 kV, chlorobenzene inlet concentration = 100–1100 $\text{mg}\cdot\text{m}^{-3}$).

3.4. Analysis of Chlorobenzene Degradation by DBD-Biological Process

When the operation of the integrated system was stable, the concentration of chlorobenzene inlet was gradually increased from $50 \text{ mg}\cdot\text{m}^{-3}$ to $1500 \text{ mg}\cdot\text{m}^{-3}$ under the conditions of a cycling solution density of $10.36 \text{ L}(\text{m}^{-3}\cdot\text{s}^{-1})$, an oxygen concentration of 10% and an input voltage of 7 kV. The HRTs for BTF and DBD were 85 s and 5.5 s, respectively. The effect of the inlet concentration on chlorobenzene degradation is shown in Figures 8 and 9. When the inlet concentration increased from $50 \text{ mg}\cdot\text{m}^{-3}$ to $1500 \text{ mg}\cdot\text{m}^{-3}$, the degradation efficiency of BTF decreased from 85% to 61%, and that of the integrated system decreased from 100% to 72%. However, the degradation efficiency and the removal load of the integrated system was generally higher than that of BTF. When DBD was used as a pretreatment method, a large number of high-energy active substances were produced by the plasma, degrading part of the chlorobenzene and decomposing part of the chlorobenzene into other organic matter that could be more easily degraded, thus improving the degradation efficiency of the overall integrated system. Nie et al. [39] applied DBD with catalysis as a pretreatment technology for BTF. The results obtained by Nie et al. indicated that the removal efficiency of BTF was equivalent to that of the integrated system for treating a low inlet concentration of chlorobenzene at an HRT of 90 s. They found that the removal rate of chlorobenzene gradually decreased with gradual increase in inlet chlorobenzene concentration for an HRT of 90 s. In addition, the removal rate of chlorobenzene was maintained at about 87%, when the inlet concentration of chlorobenzene was $1200 \text{ mg}\cdot\text{m}^{-3}$. When the inlet concentration was more than $1200 \text{ mg}\cdot\text{m}^{-3}$, the removal efficiency of our integrated system achieved 82% at an HRT of only 90.5 s, while there was no catalysis reaction in our system.

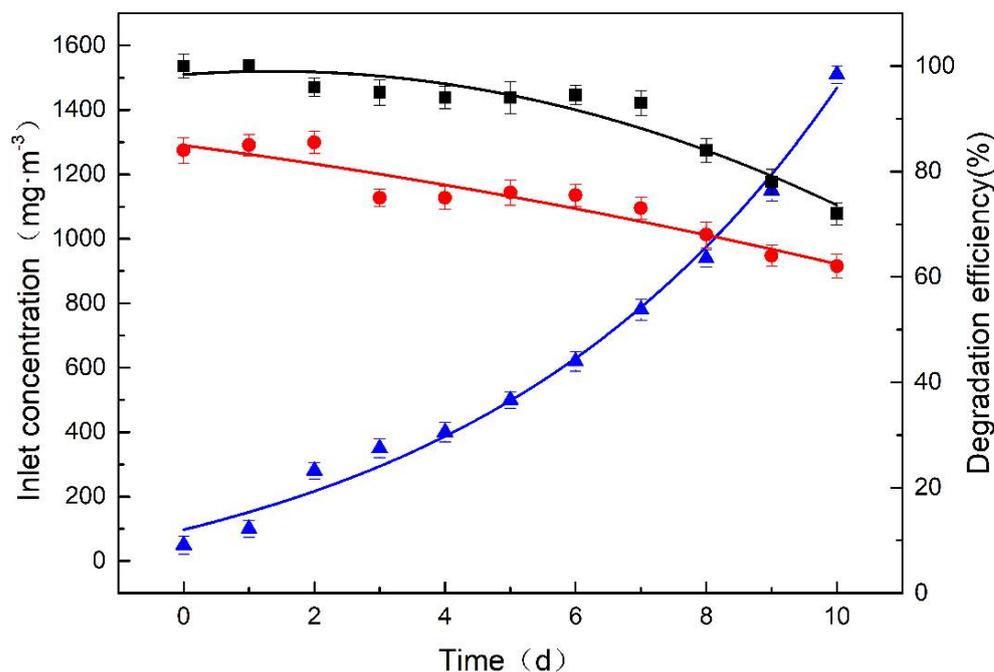


Figure 8. Comparison of chlorobenzene degradation between the integrated system and BTF only (● Degradation efficiency of a single biofilter system, ▲ Imported chlorobenzene concentration, ■ Degradation efficiency of integrated system) (cycling solution density = $10.36 \text{ L}(\text{m}^{-3}\cdot\text{s}^{-1})$, oxygen concentration = 10%, input voltage = 7 kV, HRT of the BTF = 85 s, HRT of the DBD = 5.5 s.).

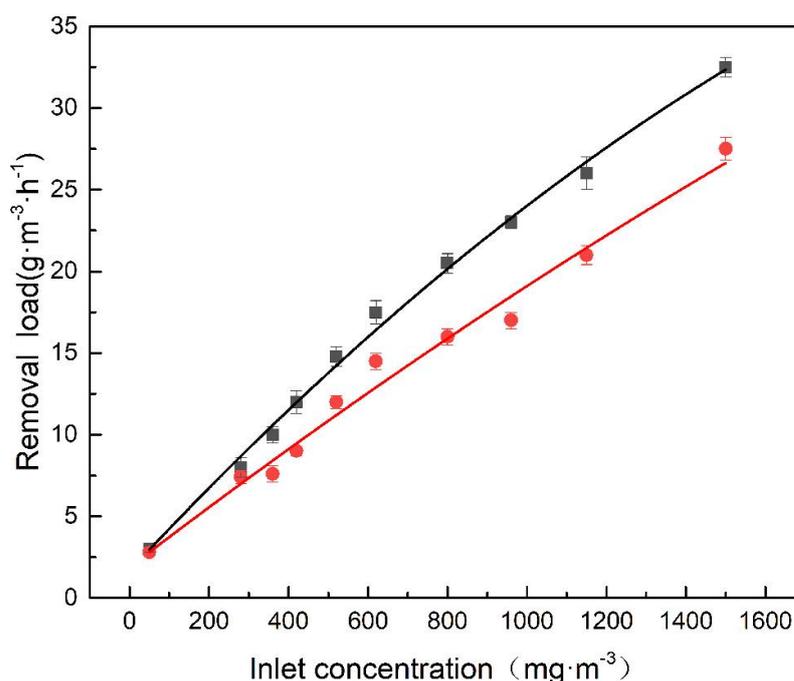


Figure 9. Comparison of chlorobenzene removal load between the integrated system and a separate biofiltration system (● Degradation efficiency of a single biofilter system, ■ Degradation efficiency of integrated system) (cycling solution density = $10.36 \text{ L} \cdot (\text{m}^{-3} \cdot \text{s}^{-1})$, oxygen concentration = 10%, input voltage = 7 kV, HRT of the BTF = 85 s, HRT of the DBD = 5.5 s.).

Taken together, the degradation efficiency of chlorobenzene and the removal load of the integrated system was evidently affected by the concentration of chlorobenzene. The higher the concentration of chlorobenzene, the greater the percentage of chlorobenzene per unit volume needed to be converted. However, higher concentrations of chlorobenzene produce an excess number of by-products in BTF, which is toxic to microorganisms. As a result, an excess number of by-products accumulated in BTF. The growth environment space for microorganisms deteriorated, which led to further restriction of microbial growth, thus reducing the degradation efficiency of chlorobenzene. Furthermore, the decrease in HRT resulted in an increasing number of chlorobenzene molecules passing through the reactor at the same time. The contact time and probability of collision between CB molecules and high-energy electrons were both reducing. Therefore, this study indicates that DBD, as a pretreatment method of BTF, can decompose chlorobenzene into by-products with smaller molecular weight (MW), thus benefiting the further process of microbial degradation and alleviating the effect of by-products with high MW on the activity of microorganism, even with reduction in HRT.

4. Conclusions

During the stable operation, the degradation efficiency of chlorobenzene reached $78 \pm 2\%$; the optimal operating conditions of the BTF, of those studied, were as follows: an inlet chlorobenzene concentration range of $400\text{--}700 \text{ mg} \cdot \text{m}^{-3}$, an oxygen concentration of about 10%, and an HRT of 85 s. The degradation efficiency of chlorobenzene by DBD reached $80 \pm 5\%$. The optimal operating conditions of DBD, of those studied, were as follows: an HRT of 5.5 s, an input voltage of 7 kV and an inlet chlorobenzene concentration of $700 \text{ mg} \cdot \text{m}^{-3}$. The degradation efficiency of chlorobenzene reached $98 \pm 2\%$ under the conditions of a spray density of $10.36 \text{ L} \cdot (\text{m}^{-3} \cdot \text{s}^{-1})$, an oxygen concentration of 10% and an input voltage of 7 kV.

Taking into account the fluctuation in inlet concentration in practical applications, the highest inlet chlorobenzene concentration in this study reached $700 \text{ mg} \cdot \text{m}^{-3}$, while VOC concentrations in the exhaust gas from pharmaceutical and chemical industry are commonly

no more than $400 \text{ mg}\cdot\text{m}^{-3}$. Thus, the DBD-BTF system in this study demonstrated good technical and practical feasibility for dealing with low concentration, high flows of a toxic exhaust gas. The degradation efficiency and removal load of the integrated system was superior to similar systems that have been reported. However, when any technology is applied in practice, the economic feasibility (such as the cost of discharging modes), the operational stability (such as the activities of microorganisms), and the safety of the device (such as being explosion-proof and anti-high pressure) are also key factors; we are currently studying these issues. It is believed that the DBD-BTF system has broad application prospects in sewage waste treatment, spraying, pharmaceutical and chemical applications, textile printing and dyeing, etc. once these problems are solved.

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