Mechanism and Pathway of Nonylphenol Degradation in Aqueous Solution by Dielectric Barrier Discharge

Rongjie YI, Haijun YU, Qi ZHANG, Liu YANG and Chengwu YI¹

School of Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China

Abstract. Nonylphenol (NP) is a typical environmental endocrine disruptor with low concentration and high toxicity, $\mu\text{g/L}$ level of NP is enough to interfere with the sex differentiation of many aquatic organisms and affect the population dynamic balance. The mechanism and pathway of NP degradation in aqueous solution by strong ionization dielectric barrier discharge were studied. The results showed that the degradation rate of NP can reach 95.2% in 60 min when the flow rate of O_3 is 5 L/min and the input voltage is 3.8 kV. Based on the electron spin resonance (ESR) results and the detection of O_3 , a large amount of hydroxyl radical ($\cdot\text{OH}$) and O_3 were verified. In addition, the ability of DBD method to degrade NP was also tested. The intermediate products were analyzed by liquid chromatography-mass spectrometry (LC-MS), and the degradation pathway was speculated.

Keywords. Dielectric barrier discharge, nonylphenol, ozone, hydroxyl radical

1. Introduction

Nonylphenol (NP) is the main degradation product of nonylphenol polyoxyethylene ethers (NPEOs), which widely exists in the natural environment. At present, the NP concentration of natural water in China is about 30.05-288.75 ng/L [1], and that of some watersheds is as high as 33200 ng/L [2], which is far higher than the national standard (6.6 $\mu\text{g/L}$). NP structure is similar to estradiol, so it can simulate natural estrogen, affect sex differentiation and reproduction of organisms, and destroy liver, kidney and gonad tissue of organisms [3]. Studies have found that NP can induce apoptosis, autophagy and necrosis of cells, to a certain extent, it can induce the production of cancer cells [4]. At present, researchers have detected the presence of NP in decidua and early embryos of pregnant women, and found that it has obvious maternal transfer, which indicates that NP pollution can't be ignored [5].

Due to the high toxicity and stable structure of NP, it is difficult for microorganisms to degrade it [6, 7]. However, physical and chemical methods are mostly the transfer of pollutants and can't completed degrade NP. In this case, advanced oxidation technology (AOPs) has gradually become the focus of research on NP degradation. Fenton methods with catalysts have become the new favorite of AOPs,

¹ Corresponding Author, Chengwu YI, School of Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China; Email: yichengwu0943@163.com.

the new methods are indeed effective in the degradation of nonylphenol [8], but the problems of its service life and recovery are still difficult to solve [9]. In contrast, low temperature plasma technology does not need reagents or catalysts, and the degradation process is highly efficient and non-selective, which shows great prospects in the treatment of such refractory organic compounds.

Dielectric barrier discharge (DBD) is one of the most representative low temperature plasma technologies. Because of its simple reaction structure, stable discharge state and large amount of active substances, DBD has become one of the most widely used discharge forms. Compared with other plasma discharge methods [10, 11], DBD can produce uniform and stable streamer discharge [12], and the ionization degree of particles is stronger, and the energy of active particles produced by DBD is much higher than that of similar discharge methods [13]. In this experiment, the strong ionization discharge method is used to further optimize the conventional DBD, improve its energy efficiency, expand the processing scale, and achieve a processing scale of 1.8 t/h.

In this study, the performance of DBD device was explored, and NP was taken as the main research object. The degradation ability of DBD system to NP was determined by UV-Vis, TOC and other methods. The intermediate products and final products were analyzed by LC-MS and other analysis methods, and the possible degradation pathways of NP degradation were proposed.

2. Material and Methods

2.1. Experimental Materials

Nonylphenol (NP, 99%) was purchased from Aladdin Industrial Corporation Ltd. Acetonitrile and methanol were purchased from China Pharmaceutical Co., Ltd.

2.2. Experimental Apparatus

The experimental device mainly includes dielectric barrier discharge (DBD) reactor, high-voltage and high-frequency power, gas-liquid circulation system and electric monitoring system (figure 1). The power frequency voltage of 220 V/50 Hz is converted into high frequency voltage of 2.5~4 kV, 15 kHz~23 kHz by high-frequency high-voltage power supply, which is input to the DBD generator. The raw material O_2 and H_2O are ionized and excited to produce a large number of active particles, such as O_3 , $\cdot OH$, O_2^+ , O_2^- , etc. In order to achieve the purpose of purifying organic pollutants, active substances mainly composed of O_3 and $\cdot OH$ are formed to oxidize and degrade pollutants in water.

Figure 1. The flow-process diagram of water treatment systems of strong ionization discharge.

Figure 2. ESR spectrum of free radicals collected after different reaction times.

2.3. Analytical Methods

The concentration and the absorption wavelength of NP was measured by UV-visible spectrophotometer (UV22450, Shimadzu, Japan). The mineralization of the NP was detected using a TOC analyzer (TOC-VCPH/CPN, Shimadzu Corporation, Japan). High concentration ultraviolet dissolved water ozone analyser (CL-7685, B&C electzanice, Italy) and an electron paramagnetic resonance spectrometer (ESR) (Bruker, MicroESR, Germany) were used to measure the concentrations of O_3 and $\cdot OH$ generated during the process. The intermediate byproducts of NP were measured by high-performance liquid chromatography mass spectrometry (LC/MS/MS) (7890B-5977B, Agilent, USA).

3. Results and Discussion

3.1. Determination of Major Reactive Species in the Reaction Process

The type and quantity of active particles present are important parameters for evaluating the treatment effect of a large-volume strong ionization DBD water treatment system. DMPO was used as a spin-trapping reagent for the hydroxyl groups, and the free radicals in the strong ionization discharge DBD system were measured using an ESR spectrometer. In the ESR spectrometer (figure 2), the 1:2:2:1 quadruplet signal characteristic of DMPO- $\cdot OH$ adducts appeared. The concentration of $\cdot OH$ in the DBD reactor was 0.32 mmol/L (figure 3). Based on the signal in the ESR spectrometer, it can be seen that the concentration of the hydroxyl group increases with the reaction time. It is confirmed that $\cdot OH$ plays an important role in the degradation of quinoline. In this experiment, the concentration of O_3 in the outlet of DBD system and then dissolved in water was determined under the voltage of 2.1 kV, 2.8 kV, 3.0 kV, 3.3 kV and 3.8 kV, respectively. As illustrated in figure 4, with the increase of the input voltage, the content of O_3 produced by the DBD system also increases. When the applied voltage reaches 3.8 kV, the amount of O_3 produced reaches 56.9 mg/L and the dissolved amount in water reaches 14.22 mg/L.

Figure 3. A plot of calibration curve between different concentration and absorbance of DMPO.

Figure 4. The concentration of O₃ in water and in DBD.

3.2. Analysis of UV-Vis and TOC Results

As can be seen from figure 5, the maximum absorption wavelength of NP is at 274nm. The degradation rate of NP has reached about 95% in 30min, and the characteristic peak of NP can hardly be scanned in 60min. Besides, the peak intensity decreased significantly with increasing reaction time. This can be explained by the fact that the carbon ring in the NP structure was gradually disassembled under the conditions of the DBD, generating a large number of small molecular organic compounds.

As shown in figure 6, the TOC decreased from 15.6 to 8.3 mg/L in 60 min using the DBD system, and its degradation efficiency reached 46.7%, while the NP removal efficiency reached 95.2% under the same experimental conditions. It can be seen that many small molecule intermediates are not completely degraded into H₂O and CO₂.

Figure 5. UV-vis analysis of NP solutions of 0-60 min during NP degradation.

Figure 6. The TOC change in degradation process of NP.

3.3. Analysis of LC-MS Results

In order to further explore the mechanism of the OTC degradation via DBD system, LC-MS was used to determine the intermediate by-products formed during the NP degradation process. Due to the fact that the simulated wastewater itself is made by dissolving NP in tap water and contains certain impurities, and the treatment system is

an open system, and some instruments and equipment cannot be manipulated in the detection process, it is necessary to remove the impurity compounds in the degradation products in the mass spectrometry analysis.

According to the intermediate products, it is speculated that the degradation process of NP by the dielectric barrier discharge device is as shown in figure 7 below. It mainly goes through the following two ways: a part of the C-C bond on the alkyl chain of NP is attacked and broken by O₃, free radicals and other active particles, and the broken bond combines with hydrogen ions in water to produce alkylphenols. The same process continues to make the alkyl chain finally fall off and become phenol. The other part of NP was attacked by ·OH, the C-H bond of alkyl was broken, the hydrogen ion was replaced by hydroxyl to form nonylphenol hydroxyl compound, and then the C-C bond was broken and returned to the previous way. In addition, some literatures mentioned that benzoquinones would be produced in the process of NP degradation [14], but the presence of benzoquinones was not detected in this experiment. It is speculated that benzoquinone itself is not stable enough and it is easy to be converted into hydroquinone. The presence of hydroquinone was also found in LC-MS results, which verified this point. Finally, under the action of O₃ and ·OH, the benzene ring was opened and finally oxidized to small molecule carboxylic acids and CO₂. According to the detected mass spectra and the previous literature, the possible intermediate products are inferred as shown in table 1.

Figure 7. Proposed reaction pathway for the degradation of NP by DBD.

Table 1. NP intermediates via LC-MS analysis.

No.	Chemical formula	Molecular weight (m/z)
1	C ₁₅ H ₂₄ O	221.01
2	C ₁₅ H ₂₄ O ₂	239.05
3	C ₁₃ H ₂₀ O	192.90
4	C ₁₁ H ₁₆ O	165.01
5	C ₉ H ₁₂ O	137.00
6	C ₆ H ₆ O ₂	112.05
7	C ₆ H ₆ O	95

4. Conclusions

In this paper, the performance of dielectric barrier discharge (DBD) device was studied. The ozone and $\cdot\text{OH}$ produced in the process of wastewater degradation by strong ionization discharge were qualitatively and quantitatively analyzed. With the increase of voltage, the concentration of O_3 gradually increased and then tended to be stable. The change of $\cdot\text{OH}$ and other free radicals was basically the same as that of O_3 . After that, the mechanism and pathway of NP degradation by DBD were studied. It was found that the removal efficiency of NP in wastewater by DBD was 95.2%, but the removal rate of TOC was only 46.7%, indicating that many intermediate products could not be completely decomposed into CO_2 and H_2O . The intermediate products of NP degradation were detected by LC-MS. according to the detection results, it was speculated that the process of NP degradation was relatively simple. In the early stage, the main reason was the breaking of alkyl chain. NP removed different amounts of alkyl to form alkylphenols, and $\cdot\text{OH}$ attacked C-H bond to form nonylphenol hydroxylate. Phenol and hydroquinone were the important intermediate products, In the later stage, the benzene ring was attacked by O_3 and $\cdot\text{OH}$, and phenol and hydroquinone were oxidized to small molecule carboxylic acids and CO_2 .

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