Research on the degradation mechanism of pyridine in drinking water by dielectric barrier discharge

Yang Li**, Rongjie Yi**, Chengwu Yi*, Biyun Zhou, Huijuan Wang

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

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ABSTRACT

Pyridine, an important chemical raw material, is widely used in industry, for example in textiles, leather, printing, dyeing, etc. In this research, a dielectric barrier discharge (DBD) system was developed to remove pyridine, as a representative type of nitrogen heterocyclic compound in drinking water. First, the influence of the active species inhibitors tertiary butanol alcohol (TBA), HCO$_3^-$, and CO$_3^{2-}$ on the degradation rate of pyridine was investigated to verify the existence of active species produced by the strong ionization discharge in the system. The intermediate and final products generated in the degradation process of pyridine were confirmed and analyzed through a series of analytical techniques, including liquid chromatography–mass spectrometry (LC–MS), high performance liquid chromatography (HPLC), ion chromatography (IC), total organic carbon (TOC) analysis, ultraviolet (UV) spectroscopy, etc. The results showed that the degradation of pyridine was mainly due to the strong oxidizing power of ozone and hydroxyl radical produced by the DBD system. Several intermediate products including 3-hydroxyl pyridine, fumaric acid, 2, 3-dihydroxypyridine, and oxalic acid were detected. Nitrogen was removed from the pyridine molecule to form nitrate. Through analysis of the degradation mechanism of pyridine, the oxidation pathway was deduced. The study provided a theoretical and experimental basis for the application of DBD strong ionization discharge in treatment of nitrogen heterocyclic compounds in drinking water.

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Introduction

Nitrogen heterocyclic compounds are common contaminants found widely in coking wastewater, pharmaceutical wastewater, pesticide wastewater and printing and dyeing wastewater (Zalat and Elsayed, 2013). Discharge of these contaminants into water bodies will cause serious pollution of the aquatic ecological environment. The compounds are classified as bio-refractory compounds and have carcinogenic, teratogenic and mutagenic characteristics, which are a serious threat to drinking water security (Singh and Chandra, 2005; Li et al., 2001). Pyridine is widely used in industry as a good organic solvent. Meanwhile, pyridine dissolves easily and can exist in natural water stably or infiltrate into groundwater through the soil. Long-term intake of drinking water containing pyridine will cause serious damage to human reproductive and nervous systems (Fetzner, 1998). Pyridine is also a major cause of stench in the air and the occurrence of odor problems in drinking water. Thus, pyridine is...
incorporated in the Surface Water Environmental Quality Standards as part of a drinking water source specific monitoring project in our country, and pyridine compounds are also listed as priority control pollutants by the United States Environmental Protection Agency.

At present, studies on methods for the degradation of pyridine mainly focus on the development of microorganisms, adsorption media, and microbial degradation and catalytic oxidation processes (Liu et al., 2015; Tian et al., 2013). Lataye et al. (2006) examined the bagasse fly ash from bagasse-fired boilers for the adsorption of pyridine. The maximum removal of pyridine was determined to be 99% at lower concentrations (<50 mg/dm³) and 95% at higher concentrations (600 mg/dm³), using a bagasse fly ash dosage of 25 kg/m³ at room temperature. Aki and Abraham (1999) applied catalytic supercritical water oxidation to treat pyridine, and the addition of a Pt/γ-Al₂O₃ catalyst was able to increase the reaction rate, and complete conversion of pyridine was achieved at 370°C. Shen et al. (2015) investigated nitrate as an electron acceptor to enhance pyridine biodegradation under anoxic conditions, and demonstrated that Paracoccus, Thioacillus and Paludibacter were the dominant species in their anoxic degradation system. Yao et al. (2011) used Lysinibacillus cresliivorans, a bacterium capable of phenol biodegradation, to study the substrate interactions of m-cresol and pyridine. The study showed that L. cresliivorans had good potential for degrading mixed substrates of m-cresol and pyridine. Li et al. (2009) found that a novel bacterium Streptomyces sp. HJ02 could grow using pyridine as its only carbon resource and had strong ability for pyridine degradation. The results suggested that the metabolism of pyridine involved cleaving the molecule between C-2 and C-3, and pyridine was hydrolyzed to succinate semialdehyde and formamide. Because of the strong toxicity of pyridine toward microbes, a high processing cost and long processing cycle are required to obtain satisfactory results by routine biological treatments. In addition, it was shown that the inhibition of microbial growth by nitrogen heterocyclic compounds can be weakened through destroying the ring structure (Zhang et al., 2014). Thus, developing a new type of treatment technology as a pre-treatment or deep treatment to destroy the structure of heterocyclic nitrogen compounds in drinking water treatment would have great significance.

The dielectric barrier discharge (DBD) apparatus is based on the use of a discharge electrode plate covered with a dielectric barrier of glass, quartz, ceramics, mica or alumina, etc., which can uniformly distribute the discharge over the entire electrode area. To prevent spark formation and eliminate electrode corrosion, the dielectric has strict requirements. A high frequency voltage is input between the plates so that a micro-discharge of filament-shaped pulses can be formed to excite background molecules and produce large quantities of active species such as ·OH, O₃, O₂⁺ and so on (Jiang et al., 2014; Hijosa-Valsero et al., 2013). These active species have strong activity and can induce chain reactions in pollutant molecules. As a result of its strong oxidizing capability, complex organic pollutants in drinking water could be degraded fully into CO₂ and H₂O, conforming to the principles of green oxidation technology (Wang et al., 2014). Compared with other discharge types such as corona discharge (Wan et al., 2011), glow discharge (Liu et al., 2016), microwave discharge (Shiyan et al., 2016), etc., the dielectric barrier strong ionization discharge can form a uniform, diffuse and stable discharge. The electric field intensity between the discharge plates is greater than 380 Td and even as high as 800 Td or more, and the electron average energy can reach more than 10 eV (Bai et al., 2005). Based on the theory of strong ionization discharge and the oxidizing properties of active chemical species, a strong ionization discharge system for use in drinking water treatment was developed in this study. Strong ionization discharge technology uses O₂ and H₂O as materials and generates no pollution, in accordance with the green treatment concept for environmental pollution (Zhang et al., 2002). Compared with other treatment processes, the technology has the advantages of short processing cycle, high processing efficiency, smaller footprint, no secondary pollution, etc. This work adopted dielectric barrier strong ionization discharge technology that was able to overcome the shortcomings of the existing technology, such as small water treatment volume due to the restrictions of plate clearance, discharge medium and energy consumption. This system can achieve 2 t/h water treatment volumes through improvements in structure and process parameters. The degradation characteristics of pyridine by DBD were researched in this study, and the results provide a valuable reference for the efficient treatment of nitrogen heterocyclic compounds in drinking water.

1. Experiments

1.1. Experimental apparatus

The experimental device mainly consisted of a generator producing active species by dielectric barrier strong ionization discharge, and a water circulation system. The generator operates by dielectric barrier strong ionization discharge technology. Using a high voltage high frequency power supply capable of producing high voltage/high frequency of 2.5–4 kV/15–23 kHz to input between the discharge electrode and the ground electrode, the O₂ molecules were strongly ionized to produce more active species such as O, O₃, O₂, and O₂. The discharge electrodes were made of sintered silver metal, and their outer surface was sprayed with a thin (330 μm) dielectric layer composed of dense insulating α-Al₂O₃ powder. A stainless steel plate was processed to form a cavity through which water or air could flow to regulate the temperature of the plasma reaction process and used as the ground electrode, as shown in Fig. 1. The structure of the discharge area was made up of three hollow grounding plates (plate size 19.5 cm × 10 cm × 1 cm) and two groups of discharge electrodes (plate size 19.5 cm × 10 cm × 1 mm). A grounding plate was placed in the bottom, with a discharge plate placed above it, and so on. Insulating tapes were placed between the discharge plate and the grounding plate to maintain plate clearance of 0.2 mm. After completion of assembly, glass cement was used to seal the shell to avoid leakage of O₂. Due to the outstanding characteristics of the dielectric, a large number of stable, uniform, micro-fine-filament pulse discharges could be formed in the discharge gap. The discharge intensity of electric field in the discharge gap can be described as follows (Zhang et al., 2013):

\[ E_g = \frac{V_{Ed}}{2\epsilon_d \epsilon_g + \frac{1}{2} \epsilon_d} \]
where, $E_g$ (kV/cm) refers to electric field intensity, and $l_g$ (cm), $l_d$ (cm), $\varepsilon$ are the thickness of plate clearance or medium and permittivity, respectively. The materials and processing technology level of the dielectric is the key to achieving stable dielectric barrier strong ionization discharge. The dielectric can be made from glass, quartz, ceramics, polymers or other materials of low dielectric loss and high breakdown strength (Tao et al., 2011). The $\alpha$-Al$_2$O$_3$ dielectric had these specific characteristics: volume density more than 3.8 g/cm$^3$, thermal conductivity more than 21 W/(m·K), volume resistivity greater than $10^{15}$ Ω·cm, dielectric breakdown electric field intensity greater than 400 kV/cm, and relative dielectric constant more than 10. Using this advanced homogeneous dielectric thin layer and the narrow discharge gap technology, strong ionization discharge was realized under atmospheric pressure. Almost all electronic energy from the applied electric field was passed to the heavy particles, and the electron energy ($\varepsilon$) could be expressed as follows:

$$T_e = \frac{\sigma m_e E_g^2}{9k_B n_e \nu_e} \tag{2}$$

where, $n_e$ (cm$^{-3}$) represents electron concentration, and $m_e$ (eV) and $m_h$ (eV) are the mass of electronic and heavy particles respectively, $k$, $\nu_e$ (sec$^{-1}$), $\sigma$ (μS/cm), $E_g$ (kV/cm) stand for the Boltzmann constant, electron collision frequency, plasma conductivity, and discharge intensity of the electric field, respectively.

During discharge, the discharge energy flow density can reach 2.1 W/cm$^2$, and the average electron energy can exceed 13 eV. So the system is classified as strong ionization discharge, which is far higher in energy intensity than other similar dielectric barrier discharge technologies, as shown in Table 1. Dielectric barrier micro-discharge can only produce a local glow or corona discharge and the discharge intensity is weak. Under atmospheric pressure, the form of this discharge is not uniform (Napartovich, 2001). In this study, the discharge characteristics of the generator could produce very stable discharge. Meanwhile the intensity of ionization is far higher than other atmospheric pressure discharges (Fridman et al., 2005). Strong ionization discharge occurred in the discharge gap, as shown in Fig. 2. When $O_2$ flows through the plate, the oxygen molecules will be excited and ionized into high-activity ions and atoms (Bauer et al., 2010). Meanwhile, a series of complex reactions including ionization, excitation, and synthesis reactions take place to produce a large number of active species such as $O_3$, $O_2^+$, $O_2^-$, etc. during the discharge process (Hu and Guo, 2011).

$$O_2 + e \rightarrow O^+ + UO + 2e$$

$$O_2 + UO \rightarrow O_3 \tag{3}$$

$$O_2 + e \rightarrow O_2^+ + 2e \tag{4}$$

$$O_2 + e \rightarrow O_2^- \tag{5}$$

The system used for removal of the pollutant pyridine in drinking water is shown in Fig. 3. In the system, an oxygen tank provided $O_2$ (99.99%, 5 L/min) and the device produced active species by strong ionization discharge. Between the discharge plates, the voltage of 2.5–4 kV/15–23 kHz was applied to the plates to ionize $O_2$, which produced a large number of high-energy species. The active species were injected and mixed with the drinking water containing pyridine through a venturi jet device, and then flowed into the gas–liquid mixing tank for both intensive mixing and reaction. When the water entered into the gas–liquid separation device, the residual gas and the treated water were separated; gas was discharged by the exhaust valve, and the water flowed into the sample barrel to be recirculated through the process by a pump (800 L/hr). The power parameters were monitored on an oscilloscope (Jet 354A, LeCroy Wave, USA) and an ammeter.

### 1.2. Experimental materials

Pyridine, 3-hydroxypyridine, fumaric acid, oxalic acid, formic acid, sodium thiosulfate, tertiary butanol alcohol (TBA), sodium carbonate, sodium bicarbonate, methyl alcohol (100%, Honeywell, B&J, USA). Before measurement by liquid chromatography–mass spectrometry, high performance liquid chromatography and ion chromatography, all the reaction samples

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**Table 1 – Main physical parameters of strong ionization discharge and micro-discharge.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DBD discharge</th>
<th>Strong ionization discharge</th>
<th>Micro-discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas pressure</td>
<td>≥0.1 MPa</td>
<td>0.1 MPa</td>
<td></td>
</tr>
<tr>
<td>Electric field intensity</td>
<td>100–320 kV/cm</td>
<td>0.1–100 kV/cm</td>
<td></td>
</tr>
<tr>
<td>Electron concentration</td>
<td>&gt;10$^9$ cm$^{-3}$</td>
<td>10$^8$–10$^9$ cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Electron average energy</td>
<td>&gt;10 eV</td>
<td>1–10 eV</td>
<td></td>
</tr>
<tr>
<td>Discharge energy</td>
<td>1–2.1 W/cm$^2$</td>
<td>&lt;1 W/cm$^2$</td>
<td></td>
</tr>
</tbody>
</table>

DBD: dielectric barrier discharge.
were filtered through 0.45 μm polyether sulfone (PES) membranes (W2545, JinTeng, China).

1.3. Analytical methods

In order to determine the concentrations of pyridine in drinking water, the samples were measured by a UV–visible spectrophotometer (UV-9600, Rayleigh, China) at 254 nm wavelength. During the pyridine decomposition process, the intermediate and final products were determined by quantitative and qualitative analysis by liquid chromatography–mass spectrometry (LC–MS) (ThermoLXQ, Thermo Corporation, USA) HPLC (LC-10AVP, Shimadzu Corporation, Japan) and IC (861 Advanced Compact IC, Metrohm limited, China). The detection conditions were flow rate of 0.7 mL/min, wavelength of 254 nm, and automatic injection volume 20 μL. The temperature of the chromatographic column (Symmetry®C18, Waters, Ireland, 5 μm × 4.6 mm × 250 mm) was 35°C and the maximal pressure of the pump was 20 MPa. The mobile phase composition was methanol and water (volume ratio: 70%:30%). For observing the degradation trends of pyridine and the change of pH value in the reaction process, UV wavelength scanning spectroscopy, a total organic carbon (TOC) survey meter (TOC-VCPH/CPN, Shimadzu Corporation, Japan) and pH meter (FE20, METTLER TOLEDO, China) were used. The desired concentration of pyridine solution was established in the 40 L sample barrel and stirred well. The drain valve and exhaust valve of the water treatment equipment were opened to empty the residual solution and gas. Then, the valves were closed. The oxygen flow was controlled at 5 L/min using a rotameter, and cooling water circulation was maintained during the process of equipment operation. Using the display parameters of the oscilloscope and ammeter to adjust the parameters of the strong ionization generator power supply, the voltage was maintained in the range 2.6–4.1 kV, the frequency was 15–23 kHz, and the current was 0.6–1.2 A. After the reading was stable, the outlet was connected to the venturi jet, and timing was started. 50 mL aliquots of solution were transferred into glass tubes after treatment for 0, 5, 10, 20, 30, 45 and 60 min, then 0.5 mL of 0.05 mol/L sodium thiosulfate was added immediately, and the solution was shaken well and left to stand for 5 min. Each sample was measured three times, and the average value was recorded. In the experiment, the concentrations of O₃ in water were determined by the iodometric method.

2. Results and discussion

2.1. The active species in the reaction process

The degradation efficiency of the organic pollutant pyridine depends on the amount of active species during the discharge process. Based on the theory of dielectric barrier strong ionization discharge, the main active species generated in the system are hydroxyl radical, ozone, negative oxygen ions and oxygen atoms. In this experiment, the existence of the active species O₃ and ·OH and their role in the reaction with pyridine were verified by investigating the impact of inhibitors including TBA, HCO₃⁻, and CO₃²⁻ on the pyridine degradation rate before and after treatment. A free radical inhibitor can block free radical chain reactions and help identify the oxidation functions of free radicals in their reaction with pyridine (Najjar et al., 2014; Kasprzyk-Hordern et al., 2007).

\[
\text{UOH} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{UCOH} \quad k = 1.9 \times 10^{10} \text{(mol/L)}^{-1}\text{sec}^{-1} \quad (7)
\]

\[
\text{UOH} + \text{HCO}_3^- \rightarrow \text{OH}^- + \text{UHCO}_3 \quad k_2 = 1.5 \times 10^7 \text{(mol/L)}^{-1}\text{sec}^{-1} \quad (8)
\]

\[
\text{UOH} + \text{CO}_3^{2-} \rightarrow \text{OH}^- + \text{UCO}_3^- \quad k_2 = 4.2 \times 10^8 \text{(mol/L)}^{-1}\text{sec}^{-1} \quad (9)
\]
The degradation rate of pyridine was found to increase with prolonging of treatment time, indicating that the pyridine could be decomposed by the active species produced by DBD. The original sample and samples with addition of free radical inhibitors at 30 mg/L TBA and 30 mg/L CO$_3^-$ or HCO$_3^-$ were compared, as shown in Fig. 4. Under the same conditions, the pyridine degradation rates were 94.85% and 60.41% respectively after treatment for 60 min without or with 30 mg/L TBA. The lower degradation rate indicated that the free radical inhibitor TBA could effectively restrain pyridine from being oxidized by active species. When the solutions containing 30 mg/L CO$_3^-$ or HCO$_3^-$, the degradation rate of pyridine was 86.84% and 58.54% respectively, indicating that the ions CO$_3^-$ and HCO$_3^-$ inhibited the generation of hydroxyl radicals, leading to the degradation rate of pyridine being decreased greatly. Therefore, the experiment confirmed that the species O$_3$ and ·OH played a major role in the pyridine oxidation process. The concentration of O$_3$ in water was 5.76 mg/L after discharge for 60 sec. Research has shown that the ozone oxidation function can be divided into direct oxidation and indirect oxidation, with direct oxidation corresponding to strong oxidation by O$_3$ itself (Wang et al., 2012). The oxidation potential of O$_3$ is 2.08 V, which is sufficient for direct oxidation of pyridine in drinking water. The indirect oxidation process is mainly produced through decomposition of O$_3$ to produce the active species ·OH, which has stronger oxidation ability (oxidation potential 2.80 V) (Lovato et al., 2009; Tang et al., 2013). Hydroxyl radical could enter into chain reactions with most organic pollutants rapidly so that they would be oxidized selectively to CO$_2$, H$_2$O or mineral salt, with no secondary pollution (Shinde et al., 2012). Meanwhile, hydroxyl radicals were also produced through the following routes:

\[ \text{O}_3^- + \text{H}_2\text{O} \rightarrow \text{O}_2^- (\text{H}_2\text{O}) \]  
\[ \text{O}_2^- (\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}_2 + \text{UOH} \]

\[ \text{O}_2^= (\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ (\text{OH}) + \text{O}_2 \]  
\[ \text{H}_3\text{O}^+ (\text{OH}) + \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{UOH} \]

\[ \text{O}_2^= (\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ (\text{OH}) + \text{O}_2 \]  
\[ \text{H}_3\text{O}^+ (\text{OH}) + \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{UOH} \]

\[ \text{O}_2^= (\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ (\text{OH}) + \text{O}_2 \]  
\[ \text{H}_3\text{O}^+ (\text{OH}) + \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{UOH} \]

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\[ \text{H}_3\text{O}^+ (\text{OH}) + \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{UOH} \]

2.2. Degradation mechanism of pyridine

2.2.1. Variation of UV–Vis spectra, TOC and pH

In order to investigate the initial formation and eventual degradation of intermediate products in the reaction with active species, the variation of UV–Vis spectra of pyridine solutions at different treatment times was monitored as shown in Fig. 6a. Pyridine is a heterocyclic compound, and the characteristic absorption bands of pyridine at 254 nm were observed. Meanwhile, another absorption band was observed around 200–220 nm due to the intermediate products generated during the degradation process, which have absorbance bands between 200–220 nm. With the extension of treatment time, the characteristic absorption wavelength of pyridine disappeared gradually, which illustrated that the nitrogen atom of pyridine was removed effectively, but the absorbance between 200–220 nm was still observed, indicating that other substances had been generated. After treatment for 120 min, the characteristic absorption bands of these substances had not disappeared completely. The result showed that a large number of refractory small-molecule organic compounds or inorganic ions had been formed. As shown in Fig. 6b, during the degradation process of pyridine, the decrease in pH value from 7.35 to 6.89 illustrated that a large number of acidic substances had been generated such as small-molecule organic acids, including oxalic acid and formic acid, etc. Additionally, the TOC decreased from 36 to 29.5 mg/L after treatment for 60 min. Pyridine and its intermediate products were transformed eventually into CO$_2$ and H$_2$O by O$_3$ and ·OH.

When a large number of active species including O$_3$, O$_2$, O$_3^-$, ·O, etc. produced by DBD entered into the water, the hydroxyl radical could be formed. The O$_3$ and ·OH species could attack high-charge-density positions of organic compounds to generate both easily oxidized and stable intermediate products. In order to capture the main intermediate products effectively in the degradation process of pyridine, the method of LC-MS
was used to detect the molecular weight of the products. Chromatography and mass spectral results for a sample containing 20 mg/L pyridine after treatment for 20 min are shown in Fig. 7. The spectrogram showed that the characteristic wavelength of pyridine at 255 nm could be seen as an obvious peak. At the same time, the appearance time of two peaks with absorbance wavelengths of 232 nm and 237 nm was 3.70–4.0 min. By analyzing mass spectra for the retention times 2.5–3.2 min and 3.7–4.0 min, the molecular weights 91, 96, 117 etc. of intermediate products could be attained respectively. Because the MS was carried out in the positive ion mode, the mass-to-charge ratio should be reduced by one on the basis of the original molecular weight to obtain 90, 95, and 116. Therefore, based on the results it could be speculated that the intermediate products might be oxalate, hydroxyl pyridine, fumaric acid or maleic acid.

### 2.2.2. HPLC analysis

In order to further delineate the molecular structures of intermediate products which the molecular weights of 90, 95, 116 as detected by LC-MS, the method of HPLC was used for analysis of the oxidized samples. Comparing the retention times and peak areas of the original samples and those of samples to which pure reagents had been added, the intermediate products were identified. As shown in Fig. 8a, in contrast to the sample with 3-hydroxy pyridine under the same conditions, it was found that the peak area for the retention time of 4 min increased sharply, illustrating that the degradation product obtained at the retention time of 4 min was 3-hydroxyl pyridine. Under the same conditions, a comparison of the liquid phase diagram of the original solution and that for a solution containing fumaric acid showed that the peak area changed obviously once fumaric acid was added to the solution. The analysis indicated that the chromatographic peak with the retention time of 3 min corresponded to fumaric acid (Fig. 8b). Under the same conditions, the retention time for 2, 3-dihydroxy pyridine was 3.573 min as determined by HPLC analysis (Fig. 9b). Meanwhile, a peak emerged at 6.731 min, which coincided well with the peak time of oxalate oxalic under the same conditions. Through monitoring and analyzing the results of HPLC and LC-MS, it was determined that there were three main intermediate products of 3-hydroxy pyridine, fumaric acid, 2,3-dihydroxy pyridine, and oxalic acid, in the reaction process of pyridine and active species produced by DBD (Fig. 9a).

### 2.2.3. Ion chromatography analysis

As shown in Fig. 10, the pyridine solution was analyzed by ion chromatography after treatment for 60 min. Because the retention time for the NO$_3^-$ peak was 500–700 sec, the change in the peak area was observed in the degradation process of pyridine for 60 min. When the treatment time was 0 min, the peak area of NO$_3^-$ was 825; 20 min later, the peak area reached 1056. The peak area reached 1056 after treatment for 60 min. An increase in the peak area of NO$_3^-$ was detected, indicating that the N atom of pyridine was oxidized into NO$_3^-$ (not NO$_2^-$) by O$_3$ and ·OH during the degradation process. With the extension of treatment time, the pyridine ring was opened continuously to denitrify the molecule, making the nitrate concentration increase observably in the solution.
2.3. Degradation path analysis

Based on the detection of intermediate and final products, a possible degradation mechanism for pyridine was analyzed and described as shown in Fig. 11. Pyridine is an aromatic heterocyclic compound and the nitrogen atoms have an electron withdrawing effect, which reduces the π charge density of the benzene ring, especially at the ortho and counter position in the pyridine ring. This structure leads to the passivation of the pyridine ring, so that electrophilic substitution is more difficult than for the benzene ring, and the electrophilic substitution reaction mainly takes place at the meta-position (Leyva et al., 2008). Active species could induce an electrophilic reaction in pyridine oxidation, which is based on attacking ring positions with high electron density by positively charged species (Huang et al., 2010). The effect of the nitrogen atom in pyridine was similar to that in nitrobenzene. Due to the lowering of the electron cloud density in the pyridine ring, the electron cloud density at the α and β positions had lower levels. Therefore, the electron cloud density of the β position was higher than that at the α or γ position, so that electrophilic reaction was more likely to occur at the β position (Li et al., 2016). The intermediate products were determined to include 3-hydroxy pyridine by analysis of HPLC results. Because the hydroxyl could activate the pyridine ring, the pyridine ring continued to be oxidized in the ortho-position or meta-position by hydroxyl (Aramendía et al., 2008). The 3-hydroxy pyridine intermediate could be oxidized to generate 2,3-dihydroxy pyridine, after which the hydroxyl group would be oxidized to the carbonyl group. The pyridine ring was damaged once the

Fig. 8 – High performance liquid chromatography of treated pyridine. (Voltage = 3.8 kV, frequency = 15 kHz, oxygen flow = 5 L/min, pump flow = 800 L/hr, pH = 7.35, pyridine concentration in Fig. 8a = 5 mg/L, pyridine concentration in Fig. 8b = 30 mg/L, detection wavelength = 254 nm, flow rate = 0.7 mL/min, injection volume = 20 μL, volume ratio of methanol and water = 70%:30%, injection temperature = 35°C).

Fig. 9 – Analysis of the intermediate products by high performance liquid chromatography. Voltage = 3.8 kV, frequency = 15 kHz, oxygen flow = 5 L/min, pump flow = 800 L/hr, pH = 7.35, pyridine concentration = 30 mg/L, detection wavelength = 254 nm, flow rate = 0.7 mL/min, injection volume = 20 μL, volume ratio of methanol and water = 70%:30%, injection temperature = 35°C.
carbonyl group continued to be oxidized. Then the $^6\text{C} - \text{N}$ bond was broken in the denitrification reaction, and oxidized to form nitrate as validated by ion chromatography. The carbon would be oxidized to generate formate and the remaining four carbons of the pyridine molecule generated fumaric acid as validated by HPLC. The carbon–carbon double bonds were broken to generate acetic acid, then the acetic acid was oxidized to generate formic acid. Finally, pyridine and the intermediate products were completely transformed into CO$_2$ and H$_2$O.

3. Conclusions

In this research, a DBD system for use in drinking water treatment was constructed to produce active species of O$_3$ and ·OH, and was shown to be effective in removing pyridine from water. In comparison and observation of the changes in pyridine degradation rates before and after adding active species inhibitors, the degradation rate of the sample with TBA was found to be reduced by 34%; and when 30 mg/L HCO$_3^-$ or 30 mg/L CO$_3^{2-}$ was added to the samples, the degradation rate of pyridine declined from 94.85% to 86.84% and 58.54%, respectively. These experiments revealed that the O$_3$ and ·OH generated by DBD played major roles during the degradation process of pyridine. The UV–Vis spectra, pH and TOC studies indicated that pyridine could be oxidized to produce some small-molecule organic acids in drinking water, and the final products were CO$_2$ and H$_2$O. Based on the results of analytical techniques including LC–MS, HPLC and IC, the degradation pathway and mechanism of the oxidation of pyridine by DBD were proposed. The DBD technology was shown to have promising application potential in treatment of nitrogen heterocyclic pollutants.

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