Research on the degradation mechanism of dimethyl phthalate in drinking water by strong ionization discharge

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Abstract
The degradation mechanism of dimethyl phthalate (DMP) in the drinking water was investigated using strong ionization discharge technology in this study. Under the optimized condition, the degradation efficiency of DMP in drinking water was up to 93% in 60 min. A series of analytical techniques including high-performance liquid chromatography, liquid chromatography mass spectrometry, total organic carbon analyzer and ultraviolet–visible spectroscopy were used in the study. It was found that a high concentration of ozone (O₃) produced by dielectric barrier discharge reactor was up to 74.4 mg l⁻¹ within 60 min. Tert-butanol, isopropyl alcohol, carbonate ions (CO₃²⁻) and bicarbonate ions (HCO₃⁻) was added to the sample solution to indirectly prove the presence and effect of hydroxyl radicals (·OH). These analytical findings indicate that mono-methyl phthalate, phthalic acid (PA) and methyl ester PA were detected as the major intermediates in the process of DMP degradation. Finally, DMP and all products were mineralized into carbon dioxide (CO₂) and water (H₂O) ultimately. Based on these analysis results, the degradation pathway of DMP by strong ionization discharge technology were proposed.

Keywords: strong ionization discharge, dimethyl phthalate, active particles

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

1. Introduction
Dimethyl phthalate (DMP) was mainly used in the manufacture of resins, paints, dyes, coatings, plastics, cleaning agents and lubricants. The World Health Organization stipulated that the maximum allowable concentration of DMP in drinking water is 18 μg l⁻¹ [1, 2]. However, researchers have found that DMP in surface water in different regions of the world exceeded the normal standard. For example, the average content of DMP detected in the surface water in different regions of China exceeded the national standard of surface water [3, 4]. The DMP residue was also detected in the effluent from European countries’ sewage treatment plants [5–7]. DMP was an environmental hormone substances and entered the human body through skin, mouth and nasal cavity. Additionally, it combined with the human body-related hormone receptors and interfered with the normal level of hormones in the blood, thus affected human reproductive and development behavior. At the same time, DMP was highly toxic to aquatic organisms. The systematic functioning of aquatic reproductive system or central nervous system of people around pollutant areas will be disrupted by sudden increase of DMP concentration in the drinking water. At present, physical method, chemical method, biological method and advanced oxidation technology were the commonly used degradation method to remove DMP from drinking water. A comparison of absorption ability of different activated carbon that were used to remove DMP from
The contaminated water was investigated by several researchers [8]. Some researchers have used the technology of hydrogen peroxide and ultraviolet radiation (H$_2$O$_2$/UV) to remove DMP, phthalic acid (PA) and 4-hydroxy-1,2-benzoic dicarboxylic acid, dimethyl ester were identified as the aromatic oxidation intermediates by gas chromatography mass spectrometer analysis [9]. Zhang et al [10] found that freshwater unicellular cyanobacteria can effectively repair contaminated drinking water. PA was detected to be an intermediate degradation product of DMP and accumulated in the culture solution. Wu et al [11] studied the bio-degradation of DMP under the fermentation conditions. Monomethyl phthalate (MMP) and PA were detected as the intermediates of DMP bio-degradation. Nowadays, there have little reports on the mechanism of degradation of DMP in the drinking water by advanced oxidation technology. This paper intends to find a new method to degradation of DMP in drinking water, hoping to achieve the target of efficiency, convenience and no secondary pollution.

The dielectric thin layer that have the high dielectric strength and high dielectric constant of glass, quartz, ceramics, mica and aluminum oxide (Al$_2$O$_3$) covered in the electrode surface constituted dielectric barrier discharge (DBD) reactor [12]. The strong ionization discharge can be achieved at atmospheric pressure or above atmospheric pressure. The obtained electric field strength was greater than 400 Td, the average energy of electrons were greater than 10 eV and electron density were higher than 10$^{15}$ cm$^{-3}$ [13, 14]. This was sufficient to ionize most of the gas molecules in the DBD reactor into electrons, photons, free radicals, excited atoms and molecules. When the strong ionization discharge occurs, the energy obtained by the electrons from the applied electric field was almost completely transferred to the gas molecules. At room temperature and atmosphere pressure, the strong electric field ionization discharge caused discharge in the discharge gap of DBD reactor, which could cause the excitation, super-excitation and ionization reaction of oxygen molecules and water molecules [15].

Compared with other treatment methods, the technology has the advantages of short processing cycle, high processing efficiency, no secondary pollution, etc. This study adopted strong ionization discharge technology that was able to overcome the shortcomings of traditional technology, such as small amount of treated water, low active particle concentration and large dielectric loss. This equipment can achieve 2 t h$^{-1}$ water treatment volumes through the improvement in structure parameters of DBD reactor. In summary, strong ionization discharge is a new type of advanced oxidation technology that can produce -OH, O$_3$ and other active particles with high concentration, large scale and low cost. It can be widely used in the field of drinking water disinfection, ship ballast water treatment and sewage pretreatment.

2. Materials and methods

2.1. Experimental apparatus

As shown in figure 1, the strong ionization discharge water treatment equipment was mainly consisted of high-frequency and high-voltage power supply, DBD reactor, discharge monitoring equipment and water circulation system, and the treated water reaches 1.6 th$^{-1}$. A 45 l sample solution was placed in the sample barrel and stirred well and it was recycled by the action of a pump (800 l h$^{-1}$). The oxygen flow was controlled at 51 min$^{-1}$ using a rotameter, and cooling water circulation was maintained during the process of equipment operation. The high frequency and high voltage power supply was used to convert common voltage 220 V/50 Hz into high frequency voltage of 2.1–4.5 kV/15–23 kHz. The raw material (O$_2$) were ionized, generating a large amount of active particles like O$_3$, oxygen radical (-O), oxygen cation (O$_2^+$), oxygen anion (O$_2^-$) [16]. Pollutants in the water can be oxidized rapidly by active particles, and the purpose of purifying the water will be achieved by strong ionization discharge. DBD reactor structure was shown.
of the DBD device spark electric or arc discharge, and improves the performance of strong ionization discharge were shown in table 1.

The parameter conditions of HPLC were as follows: the temperature of chromatographic column \(T\) was 30 °C, the mobile phase \(W\) was 80%:20% acetonitrile:water. The intermediates and final products was measured by HPLC (LC-10AVP, Shimadzu Corporation, Japan) and LC-MC (Thermo-LXQ, Thermo Corporation, USA). All the sample solution were filtered using a 0.3 \(\mu\)m polyether sulfone membranes (W2545, JinTeng, China). The parameter conditions of HPLC were as follows: the temperature of chromatographic column (Symmetry\textsuperscript{®}C18, Waters, Ireland, 5 \(\mu\)m \(\times\) 4.6 mm \(\times\) 250 mm) was 30 °C, the mobile phase was methanol and water (volume radio = 80%:20%), the flow rate was 1.0 ml min\(^{-1}\), the injection volume was 20 \(\mu\)l, the wavelength was set at 230 nm, and the retention time was 6 min.

In summary, each generation of 100 eV energy can produce 5.5 \(\cdot\)OH, a total of 8.25 or more free radicals. The number of \(\cdot\)OH was more than 10 times the weak ionization discharge, resulting in high concentration of \(O_3\) and \(\cdot\)OH [21, 22]. \(O_3\), \(O_2^+\), \(O_2^-\) and other active particles produced by the DBD reactor in the strong ionization discharge water treatment system entered the gas–liquid mixing device through the Venturi jet and reacted with the water molecules to produce the active substance. DMP and the intermediate products can be rapidly oxidized by the active substance in the water. After 60 min, the removal rate of DMP in water was more than 93%, and a small amount of intermediates was detected by high-performance liquid chromatography (HPLC) and LC-MC.

2.2. Experimental materials

DMP, Tert-butanol (TBA), isopropyl alcohol (IPA), and other analysis reagents were purchased from Shanghai Sinopharm Group Chemical Reagent Co., Ltd China, including methanol, ethanol, anhydrous sodium carbonate, sodium thiosulfate, sodium bicarbonate, sodium sulfate, sodium chloride, hydrochloric acid and sodium hydroxide. All experimental solutions were prepared with deionized water without other buffers. DMP was added to deionized water stirred for 8 h by magnetic stirrer until the initial oil in water drop disappeared, yielding a 1000 mg l\(^{-1}\) DMP stock solution. The stock solution was diluted with tap water to prepare into different initial concentrations according to specific requirement of the research.

2.3. Experimental methods

The initial concentration of DMP in the aqueous solution was up to 20 mg l\(^{-1}\). The concentration variation of DMP during the reaction was measured by a ultraviolet–visible (UV–vis) spectrophotometer (UV-9600, Rayleigh Corporation, China). During DMP degradation, the maximum absorption wavelength and peak variation of DMP were measured using an UV–vis (UV2450, Shimadzu Corporation, Japan). The intermediates and final products was measured by HPLC (LC-10AVP, Shimadzu Corporation, Japan) and LC-MC (Thermo-LXQ, Thermo Corporation, USA). All the sample solution were filtered using a 0.3 \(\mu\)m polyether sulfone membranes (W2545, JinTeng, China). The parameter conditions of HPLC were as follows: the temperature of chromatographic column (Symmetry\textsuperscript{®}C18, Waters, Ireland, 5 \(\mu\)m \(\times\) 4.6 mm \(\times\) 250 mm) was 30 °C, the mobile phase was methanol and water (volume radio = 80%:20%), the flow rate was 1.0 ml min\(^{-1}\), the injection volume was 20 \(\mu\)l, the wavelength was set at 230 nm, and the retention time was 6 min.

\[\begin{align*}
O_2 + e^- & \rightarrow O_2^+ + 2e^-, \\
O_2 + e^- & \rightarrow O^+ + O^+ + e^-, \\
O_2 + O^+ & \rightarrow O_3, \\
O_3 + e^- & \rightarrow O_3^-, \\
O_2 + e^- & \rightarrow O_2^-.
\end{align*}\]
The amount of active particles was the key factor affecting the degradation efficiency of DMP in the drinking water. Therefore, the concentration of active particles during the reaction was an important part of the mechanism research. In the study, CO$_3^-$, HCO$_3^-$, TBA and IPA were added to prove the existence of O$_3$ and -OH. Research has shown that the ozone oxidation can be divided into direct oxidation and indirect oxidation. In the process of DMP degradation, a large number of active particles produced by DBD reactor after entering the gas–liquid mixing device through the Venturi jet would react with the water molecules to produce the strong oxidizing properties of active substances (O$_3$, -OH, etc). The direct oxidation function is that the strong oxidation ability of O$_3$. And then, the indirect oxidation function was reflected through the decomposed of O$_3$. The produced O$_3$ was decomposed into strong oxidizing ability of the active group (-OH) in weak alkaline solution which can rapidly oxidize contaminants in water. The oxidation potential of -OH was 2.8 V and much higher than other oxidants of chlorine gas (1.36 V) and oxygen (1.23 V) [22, 23]. Pollutants would be oxidized to CO$_2$, H$_2$O or mineral salt under the attack of active substance, with no secondary pollution. Positive oxygen ions reacted with water to produce hydrated ions under the reaction of strong electric filed, and the decomposition reaction of hydrated ions is the main way of generating -OH, as shown in equation (7). The main reaction pathway of production of -OH by ionizing O$_2$ is the decomposition reaction of hydrated ions. The reaction formula is shown in equations (8)–(10).

\[
\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{O}_2^+ (\text{H}_2\text{O}), \quad (7)
\]

\[
\text{O}_2^+ (\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{O}_2 + \cdot \text{OH}, \quad (8)
\]

\[
\text{O}_2^+ (\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ (\text{OH}) + \text{O}_2, \quad (9)
\]

\[
\text{H}_2\text{O}^+ (\text{OH}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2\text{O} + \cdot \text{OH}. \quad (10)
\]

In this experiment, the concentration of -OH was proved indirectly by calculating variation of DMP degradation efficiency after adding free radical inhibitors. As shown in figure 3, there was a large difference in DMP degradation efficiency between the presence or absence of inhibitors under the same experimental conditions. After 60 min, the removal efficiency of DMP was 80.4%, 78.9%, 76.6% and 74.4% after addition of 30 mg l$^{-1}$ CO$_3^-$, HCO$_3^-$, TBA and IPA, but it was up to 93.6% in only DMP sample solution. It can be seen that the presence of -OH promotes the reaction process of DMP degradation, indicating that addition of free radical inhibitors slows down the chain reaction process, inhibiting the formation of -OH and degradation of DMP.
concentration of DMP solution decreased from 20 to 1.29 mg l$^{-1}$, the energy consumption per unit volume of wastewater was 507.9 kJ ($\text{mg l}^{-1}$)$^{-1}$ after 60 min, and electric energy consumption per unit volume wastewater was 0.21 kJ ml$^{-1}$ when the discharge voltage is 3.3 kV, initial concentration is 20 mg l$^{-1}$. In order to ensure better experimental results, the applied voltage in the experimental study is 3.3 kV.

$$E = U \cdot I \cdot t,$$
$$R = E / \Delta C,$$

where, $R$ (kJ (mg l$^{-1}$)$^{-1}$) refers to the energy consumed when degradation of unit concentration wastewater, $E$ (kJ) is the electric energy consumed in the unit time, $U$ (V), $I$ (A) and $t$ (s) represents the measured voltage, the measure current and the reaction time, respectively, and $\Delta C$ (mg l$^{-1}$) is reduced concentration of DMP in the unit time.

The removal efficiency of DMP was decreased from 93% to below 75% after addition of different free radical inhibitors, which revealed that O$_3$ play a key role in the oxidation process of DMP. Simultaneously, the maximum concentration of O$_3$ in this experiment is up to 74.4 mg l$^{-1}$. It also displayed that the oxidation process of DMP was influenced by the species of O$_3$. Therefore, the significant variation of DMP degradation efficiency after addition of free radical inhibitors and high concentration of O$_3$ produced both revealed that the oxidation reaction of DMP was carried out under the combined action of O$_3$ and -OH. In addition, the continuous improvement of DBD reactor structure to produce higher concentrations of O$_3$ was the major focus of future experimental research.

3.2. Degradation mechanism of DMP

3.2.1. Variation of TOC, COD and pH. The mineralization degree of organic matter in water is an important index to measure the removal effect of organic matter. In order to investigate the mineralization degree of DMP in the sample solution, the changes of TOC value during different reaction time was measured in the experiment of DMP degradation. As shown in figure 5(a), TOC decreased from 30.15 to 16.67 mg l$^{-1}$ after 60 min, and its removal rate reached 45%. It can be inferred that the TOC removal efficiency should be higher when the reaction time is prolonged. This indicates that most of DMP in the water was oxidized to CO$_2$, H$_2$O and other small molecules substance under the attack of O$_3$ and -OH. The TOC analyzer showed that TOC value of DMP solution decreased by 45% and the organic carbon (TC) decreased from 32.92 to 19.28 mg l$^{-1}$, which was 41.4%; the inorganic carbon (IC) decreased from 2.766 to 2.661 mg l$^{-1}$, a decrease of 3.8%. From the point of view of material balance, most of carbon in the solution was decomposed into organic carbon in the solution and the other was converted to IC.

In the process of DMP oxidation, the changes of pH and COD values was also studied. As shown in figure 5(b), pH rose from 6.97 to 7.54 within 60 min. Before 30 min, the change of pH was slower, probably because the intermediate products of DMP was rapidly oxidized by the active substance and accumulated to a certain amount at 30 min, and resulting in weak acid solution. The oxidizing ability of O$_3$ and -OH was very strong, all intermediate products
including some small molecular organic acid produced in the reaction were oxidized to CO\textsubscript{2} and H\textsubscript{2}O. Thus, pH of DMP solution during 40–60 min kept a slow down trend. The COD change of DMP solution was shown in figure 5(b), COD decreased from 40 to 23 mg\textsuperscript{-1} after 60 min, and the removal efficiency was 42.5%. The change of TOC, COD and pH of DMP solution in the study show that the degradation of DMP in the drinking water can achieve good effect by strong ionization discharge.

### 3.2.2. UV–vis analysis

The UV absorption spectra variation of DMP during different reaction time was shown as figure 6. As the reaction progresses, the characteristic peaks of DMP at 230 nm in the visible region were weakened faster. During 0–10 min, the characteristic peak disappearance velocity was the fastest at 230 nm. After 60 min, the absorption peak almost disappeared, indicating that the aromatic ring of DMP was destroyed and degraded to the straight chain. The absorption peak of DMP in range of 190–200 nm also weakened, but did not completely disappear. With the reaction time to continue, these absorption peaks gradually reduced. It can be seen from figure 6 that existing a product after 60 min, and the removal peak B was the smallest, and the intermediate product gradually increased with the reaction. After 60 min, the maximum peak B was the smallest, and the peak area of A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3} byproducts reached the maximum, which indicated that the degradation process of DMP continued to produce other different kinds of intermediates. Next, LC-MC was used to determine the possible intermediate products in the degradation of DMP. Additionally, some byproducts that maybe exist but not detected were not discussed in this study.

### 3.2.3. HPLC analysis

The variation of DMP chromatographic peak were shown as figure 7, the retention time of chromatographic peak was controlled within 6 min. A\textsubscript{1}, A\textsubscript{2}, A\textsubscript{3} and B chromatographic peak can be seen clearly. The maximum peak B had the obvious down trend and was determined to the area peak of DMP according to the peak time of 2.10 min. This indicated that DMP was progressively degraded by active substance during the reaction. The reason was that the aromatic ring and branched chain of DMP was more easily broken by the strong oxidizing performance of \( \cdot \text{OH} \) and O\textsubscript{3} produced in the strong ionization discharge water treatment equipment. At the same time, it can be seen that the intermediate product peaks A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3} continuously generated in the period of 1.28–2.80 min, and the peak area of the intermediate product gradually increased with the reaction. After 60 min, the maximum peak B was the smallest, and the peak area of A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3} byproducts reached the maximum, which indicated that the degradation process of DMP continued to produce other different kinds of intermediates. Next, LC-MC was used to determine the possible intermediate products in the degradation of DMP. Additionally, some byproducts that maybe exist but not detected were not discussed in this study.

### 3.2.4. LC-MC analysis

Under the influence of O\textsubscript{3} and \( \cdot \text{OH} \), the molecular structure of DMP was destroyed through two different forms \[24, 25]. (i) The side chain (ester group) of DMP was simultaneously hydrolyzed to form a monoester product. (ii) The aromatic ring was broken, the C–C bond linking the carbonyl and aromatic ring was opened. After reaction time of 20 min, it was evident that there were four noticeable peaks in the MS with retention time at 1.38 min, 1.74 min, 2.10 min and 2.78 min respectively (figure 8(a)). After 60 min, there have no any chromatographic peaks as shown in figure 8(b). DMP and all intermediate products have been degraded into other small molecular mater completely. As shown in figures 9(a) and (b), the mass ratio of different intermediates was detected by LC-MC. The damage of DMP molecular structure may yield four intermediate product with molecular ion peaks at 167.13 m/z, 181.27 m/z, 195.21 m/z and 225.33 m/z, other peaks also detected in the DMP profile as shown in figure 10. The molecular weight of 166, 180, 224
were MMP, PA and methyl ester PA (MEPA) according to the molecular structure of DMP.

In the mass spectrum (figure 9(a)), mass ratio of products at 2.10 min was 195.21 m/z (DMP + H). It has the same retention time with standard sample of DMP. Other detected peaks in the mass spectrum were 218.34 m/z (DMP + Na + H), 219.29 m/z (DMP + Na + 2H), corresponding to the addition of 24–25 mass units (figure 10(b)). The MS displayed molecular ion peak at 167.13 m/z (PA + H), it could be proposed to the standard sample of PA. As shown in figure 10(b), other discernible peaks were 241.14 m/z (PA + Ca + K – 3H), 245.25 m/z (PA + K + Ca). PA was further confirmed by comparing the LC-MC profiles of PA standard with this product.

For the peak at retention time of 1.74–2.10 min, the MS displayed molecular ion peak (MMP + H) at 181.27 m/z. It was similar to that for standard sample of MMP. Other major peaks with m/z of 261.23 (MMP + K + Ca + 2H), 279.13 (MMP + Ca + K + Na – 3H), 303.0 (MMP + 2Na + K + Ca – 2H) were identified as MMP (figures 9(c) and 10(a)).

Additionally, the MS displayed molecular ion peak at 225.33 m/z (MEPA + H), and other detected peaks in figure 10(b) were 241.23 m/z (MEPA + Na – 6H), 243.12 m/z (MEPA + Na – 4H), 245.31 m/z (MEPA + Na – 2H). These peaks indicated the presence of MEPA. There also have some small molecular organic as shown in figures 9(a), (b) and 10(b), it can be speculated that the following mass-to-charge ratios correspond to acetic acid (AA), oxalic acid (OA), maleic acid (MA), succinic acid (SA), adipic acid (ADA). The peaks in the mass spectrum were 99.0 m/z (AA + Na + 2H), 131.02 m/z (OA + Ca + H), 132.41 m/z (MA + 2H), 159.04 m/z (SA + Ca + H) and 187.27 m/z (ADA + Ca + H).

From the result of HPLC and LC-MC, it can be inferred that PA, MMP and MEP could be the major intermediates during the degradation of DMP. Some small molecular organic acid were produced including AA, OA, MA, SA, ADA. The research result is in agreement with most of previous study findings on degradation of DMP [8, 26, 27].

3.3. Pathway of DMP degradation

Based on the UV–vis, HPLC and LC-MC results of DMP, the degradation pathway of DMP by strong ionization discharge could be proposed as figure 11. The high concentration of ·OH and O₃ produced by strong ionization discharge technology played the key role in the DMP degradation. The attack of ·OH leads to the destruction of DMP molecular structure. The side chain (−COOCH₃) lost a methoxyl group (−OCH₃) and addition of one ·OH to formation of the product for 1 (MMP). Then, the side chain (−COOCH₃) of the product 1 was broken and one or two ·OH was added to form the isomer 3 or 4. Based on the study data, it was presumed that the product 3 and product 4 may be PA and TPA, respectively, depending on the ·OH position. The two side chains of DMP were simultaneously cleaved to form product 2. It was added ·OH to form products 5 (HADE) (it maybe exist but not detected) and product 6 (MEPA). In addition, product 2 did not detected by LC-MC analysis. The reason may be that the
Figure 9. The mass spectrum of main intermediate products during the degradation process of DMP (DMP concentration = 20 mg l$^{-1}$, voltage = 3.3 kV, oxygen flow = 5 l min$^{-1}$, pump flow = 800 l h$^{-1}$, pH = 6.97, detection wavelength = 230 nm, flow rate = 1 ml min$^{-1}$, injection volume = 20 μl, temperature = 30 °C, volume ratio of methanol and water = 80%:20%).
presence of product 2 was particularly short and was rapidly oxidized to product 5 and product 6 under the action of O$_3$ and ·OH. Finally, the aromatic ring of DMP and intermediate product were destroyed to produce various small molecule organic acids under the attack of O$_3$ and ·OH. According to the mass spectrum at 20 min and the reaction process, it was speculated that the organic acid may be product 7 (AA), product 8 (OA), product 9 (MA), product 10 (SA), product 11 (ADA), etc. After 60 min of reaction, all the products in the solution were decomposed into carbon dioxide, water and other inorganic salts, achieving the target of complete degradation.

4. Conclusion

In this study, the DBD reactor was constructed to produce high concentration of O$_3$, ·OH and other active particles that was used to efficiently remove DMP from the solution. The UV ozone detector displayed the content of O$_3$ was up to 74 mg l$^{-1}$ within 60 min when 30 mg l$^{-1}$ of CO$_3^-$, HCO$_3^-$, TBA and IPA was added to the samples, the degradation rate of DMP declined from 93.6% to 80.4%, 78.9%, 76.6% and 74.4%, respectively. The comparative experiment of DMP removal efficiency revealed that O$_3$ and ·OH generated by the DBD reactor played key roles in degradation of DMP from solution. The UV–vis spectra, pH, COD and TOC studies indicated that DMP and all the products were mineralized into CO$_2$ and H$_2$O. The intermediates from the degradation of DMP were determined by HPLC and LC–MC analysis including MMP, PA (TPA), MEPA and several small molecular organic acids (AA, MA, OA, SA, ADA, etc). As the reaction progresses, all the products in the solution were decomposed into carbon dioxide, water and other inorganic salts. Based on these analysis results, the degradation pathway of DMP were proposed. The study provided a theoretical and experimental basis for the removal of organic pollutants from drinking water by strong ionization discharge.

Figure 10. The mass spectrum of main intermediate products during the degradation process of DMP (voltage = 3.3 kV, pump flow = 800 l h$^{-1}$, oxygen flow = 5 l min$^{-1}$, DMP concentration = 20 mg l$^{-1}$, pH = 6.97, detection wavelength = 230 nm, flow rate = 1 ml min$^{-1}$, temperature = 30 °C, injection volume = 20 μl, volume ratio of methanol and water = 80%:20%).
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References

[16] Napartovich A P 2001 Plasmas Polym. 6 1
[18] Li Y et al 2017 J. Environ. Sci. 53 238

Figure 11. The proposed degradation pathway of DMP by strong ionization discharge.