Degradation and mineralization of ciprofloxacin by gas–liquid discharge non-thermal plasma

To cite this article: Shuheng HU et al 2019 Plasma Sci. Technol. 21 015501

View the article online for updates and enhancements.
Degradation and mineralization of ciprofloxacin by gas–liquid discharge non-thermal plasma

Shuheng HU (胡淑恒) 1,3, Xinghao LIU (刘行浩) 1,2,3, Zimu XU (许子牧) 1,3,4,5,6, Jiaquan WANG (汪家权) 1, Yunxia LI (李云霞) 1, Jie SHEN (沈洁) 2,4,5, Yan LAN (兰彦) 2,4,5 and Cheng CHENG (程诚) 2,4,5,6

1 School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, People’s Republic of China
2 Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, People’s Republic of China
3 Intelligent Manufacturing Technology Research Institute, Hefei University of Technology, Hefei 230088, People’s Republic of China
4 Center of Medical Physics and Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, People’s Republic of China
5 Anhui Province Key Laboratory of Medical Physics and Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, People’s Republic of China

E-mail: xzm666@hfut.edu.cn and chengcheng@ipp.ac.cn

Received 2 April 2018, revised 29 August 2018
Accepted for publication 30 August 2018
Published 13 November 2018

Abstract

A typical quinolones antibiotic ciprofloxacin (CIP) in aqueous solution was degraded by a gas–liquid discharge non-thermal plasma system. The discharge plasma power and the emission intensity of the excited reactive species (RS) generated in the gas phase were detected by the oscilloscope and the optical emission spectroscopy. The effects of various parameters on CIP degradation, i.e. input powers, initial concentrations addition of radical scavengers and pH values were investigated. With the increase of discharge power, the degradation efficiency increased but the energy efficiency significantly reduced. The degradation efficiency also reduced under high concentration of initial CIP conditions due to the competitive reactions between the plasma-induced RS with the degradation intermediates of CIP. Different radical scavengers (isopropanol and CCl4) on ·OH and H· were added into the reaction system and the oxidation effects of ·OH radicals have been proved with high degradation capacity on CIP. Moreover, the long-term degradation effect on CIP in the plasma-treated aqueous solution proved that the long-lived RS (H2O2 and O3, etc) might play key roles on the stay effect through multiple aqueous reactions leading to production of ·OH. The degradation intermediates were determined by the method of electrospray ionization (+)-mass spectroscopy, and the possible degradation mechanism were presented.

Keywords: gas–liquid plasma, ciprofloxacin, mineralization, degradation mechanism

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

1. Introduction

In recent years, the release of organic pollutants into the environment from municipal waste-water has gained worldwide attention. All of the organic contaminants, pharmaceuticals and personal care products (PPCPs) are of concern to us human beings because of their great variety and high consumption over the past years and their persistence in our natural environment. They mainly consist of drugs, hormones, food supplements, household chemicals, as well as their respective transformation
products [1]. The waste-water with PPCPs could enter the environment through many channels, which mainly include inadequate treatment of pharmaceutical waste-water and direct disposal of unused medicine primarily from the hospitals [2, 3]. A major following with interest about PPCPs has focused on antibiotics because a great deal of multiple antibiotics, which are commonly discovered in a wide range of places such as surface and ground water [4, 5] and soil, are abused [6].

Among antibiotics, fluoroquinolones are a group of broad-spectrum synthetic antibacterial agents that have been widely used in aquaculture, farming, human, and veterinary medicines since they were introduced in the 1980s [7, 8]. Ciprofloxacin (CIP), a third generation of fluoroquinolone agentia, is one of the most continually prescribed fluoroquinolones in the world. As an antibacterial agent, it is no surprise that fluoroquinolones are not effectively biodegradable in waste-water treatment plants (WWTPs) [8]. Unfortunately, more than 95% of the fluoroquinolones dose is excreted unmetabolized or as active metabolites and end up in municipal waste-water [9, 10]. The presence of CIP in the environment may pose serious threats to the ecosystem, human health, and the biological treatment process of waste-water treatment even at low concentrations. Since the elimination of CIP in conventional WWTP is ineffective, alternative effective physio-chemical technologies are being considered.

Advanced oxidation processes (AOPs) have been demonstrated to be effective for the removal of pharmaceuticals, herbicides, and other micro-pollutants. The main degradation mechanism of AOPs is based on the formation of reactive species (RS) (such as -OH, ·O, H2O2 and O3) through various channels and their attractive behavior on organic pollutant molecules [11]. The popular AOPs, including Fenton oxidation [12], ozonation [13], peroxymonosulfate oxidation [14] and photocatalysis [15], were all shown to be effective. However, ozone is not easy to store and transport while peroxymonosulfate oxidation operates more troublesome and expensive [16, 17]. Moreover, the mineralization rate was relatively low by UV treatment [18]. Therefore, there is still room for the improvement of the methods until they are available for removing CIP.

Plasma, one kind of AOPs, could generate a lot of oxidative chemical special during the discharge process in water, including oxygen free radicals (-O, -OH, etc) and active molecules (H2O2, O3, etc). Reactive oxidizing species are effective for the decomposition of targeted molecules and they can lead to high degradation efficiency of organic substances. Plasma produced electrical discharge has been widely used in wastewater (dye and pharmaceutical wastewater) treatment as a possible method. Miessner et al [19] used the dielectric barrier discharge (DBD)-plasma to degrade diclofenac and ibuprofen in aqueous solution. The result indicates that the highest total organic carbon (TOC) removal was obtained by DBD plasma in an Ar/O2 atmosphere. Magureanu et al [20] used a DBD in coaxial configuration to decompose pentoxifylline in water, and the result shows that after 60 min of O2 plasma treatment, 92.5% removal of pentoxifylline was achieved and the corresponding decomposition yield was 16 g kW⁻¹ h⁻¹. Reddy et al [21] utilized DBD at the gas water to degrade dye contaminated wastewater. They concluded that the high degradation yield is up to 67 g kW⁻¹ h⁻¹ and the mineralization of pollutant is better than conventional physical methods. As a very effective working method, plasma is definitely a promising treatment technology dealing with organic pollutants.

In this study, the degradation effect and mechanism on CIP in aqueous solution by a homemade gas–liquid phase discharge plasma was investigated. The main advantage of this kind of plasma source is its simple structure. Variety of gases’ discharge could be easily achieved which is free from external air interference. Moreover, although CIP was selected as the target pollution in some researches [22–24], few studies were carried out on the effect of the long-lived RS generated in the liquid phase induced by the plasma treatment as well as the degradation intermediates. The influences of input power, initial concentration, different radical scavengers and initial aqueous pH values on the degradation efficiency were studied. Variations on the TOC, UV–vis absorption spectra and the electrospay ionization (ESI) (+)-mass spectrometry (MS) of the plasma-treated aqueous solution were also analyzed. Notably, different radical scavengers have been applied to determine the degradation effect from the plasma-induced -OH radicals.

2. Materials and methods

2.1. Plasma source

Non-thermal atmospheric discharge plasma was generated by a ‘needle type’ reactor shown in schematic diagram in figure 1, and the experimental equipment was described in detail in our previous report [25]. This study gives a brief description of the reactor. It primarily consists of a hollow stainless steel needle surrounded by a quartz tube with an inner diameter of 4 mm mounted tightly on one end. As high voltage electrode, the needle was connected to high-DC power source and the gas inlet. The ground electrode is the solution of CIP. Wastewater container was made of a quartz cylinder (65 mm height and 27.5 mm inner diameter, 32.5 mm outer diameter) and capped with a PTFE sheet. The plasma was generated in the gas liquid and gas channel interface. Figure 1 is a typical photograph of the air discharge plasma and clearly shows a filamentary mode of discharge. The applied voltage and discharge current of the plasma were recorded by a Tektronix MSO 5104 digital oscilloscope equipped with a high voltage probe (Tektronix P6015A) and current probe (Tektronix P6021).

2.2. Analysis methods

The concentration of CIP was measured by using HPLC (Agilent 1200, USA) with a C18 column (4.6 × 150.0 mm, 5.0 μm, Agilent, USA) which was maintained at 30.0 °C, and the detection wavelength of UV detector was set in 277.0 nm. The mobile phase included 82.0%, 0.05 mol l⁻¹ citric acid
and 18.0% acetonitrile (Triethylamine regulates pH to 3.5) with a flow rate of 1.0 ml min$^{-1}$. The infection volume of degradation solution was 20.0 μl.

The concentration of TOC was measured with a TOC analyzer (TOC-V CPN, Shimadzu, Japan). The volume of the aqueous solution used in all tests is 30.0 ml.

The degradation efficiency of CIP for each sample was calculated using equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100.0\%.$$  \hspace{1cm} (1)

$\eta$ indicates the degradation rate of CIP (%), $C_0$ is the initial concentration of CIP (mg l$^{-1}$) and $C_t$ represents the residual CIP concentration after different treatment time (mg l$^{-1}$).

Energy yield (g kW$^{-1}$ h$^{-1}$) was considered as the quantity of CIP (g) removed per discharge power (kW h) consumed during the discharge treatment following equation:

$$Y = \frac{C_0 \times V \times \eta}{P \times T} \times \frac{1}{1000}.$$  \hspace{1cm} (2)

$Y$ represents the energy yield (g kW$^{-1}$ h$^{-1}$), $C_0$ is initial concentration of CIP (g l$^{-1}$), $V$ indicates the volume of the liquid (l), $P$ is discharge power (kW) and $T$ is the discharge processing time (h).

2.3. Optical emission spectroscopy (OES)

An AvaSpec-2048-8-RM spectrometer (gratings of 2400 grooves mm$^{-1}$) was used to record the optical emission spectra of the gas–liquid plasma. The fiber probe is about 10.0 mm apart from the plasma source and located at the exit of glass tube nozzle.

2.4. Measurement of long-lived RS in deionized water

RS are produced in liquid inevitably when the gas–liquid phase discharge plasma counteracts with water. However, the direct determinations of short-lived RS are very difficult because of short half-life and high reactivity. In this study, the concentrations of long-lived RS (H$_2$O$_2$, O$_3$, and -NO$_3$) in the gas–liquid phase plasma-treated liquid were measured with three kinds of relevant test kits 18789, 00607 and 09713 on a spectrophotometer (PhotoLab 6100, WTW, Germany), respectively. The measurement methods were operated in accordance with the manufacturer’s manual. Above reagents are with good specificity when they interact with specific substances (ions) in the plasma-treated aqueous solutions [25, 26].

2.5. ESI (+)-MS

To better understand the degradation mechanism of CIP, the major intermediates in the reaction solution after various treatment durations were investigated and the possible degradation pathways were analyzed by MS conducted in the positive mode with an ESI source. The parameters were listed below: fragmentation at 125.0 V, capillary voltage of 3.5 kV, desolation gas (nitrogen, 99.99% purity) flow of 10.01 min$^{-1}$, nebulizer pressure of 40.0 psi, temperature of 350.0 °C, scanned range of m/z 50–1000, and argon (99.99% purity) as the collision gas [24].

3. Results and discussion

3.1. Discharge characterization

Figure 2 shows the typical voltage and current waveform of the gas–liquid air plasma. Specifically, the power supply is homemade, which presents DC characteristics in voltage when unloaded. Noteworthy as the discharge current is relatively large (~A), a rapid drop in voltage could be caused when the power source is working, thereby leading to a pulsed and oscillated waveform. The plasma discharge powers are all determined by the discharge current and voltage waveforms at the same stable status (after 1 min of stable discharge).
The voltage waveform is repetitive with pulse duration at about 1.5 ms and a frequency of 670 Hz. In one period, the rise of the current correlates to the drop of the voltage leading to plasma generation. The discharge voltage and current obtained from the oscilloscope are used to calculate the average power of plasma discharge through integration based on the following formula where $T$ represents the discharge period.

$$ P = \frac{1}{T} \int_0^T u(t) i(t) \, dt. $$

In this work, the variation range of the discharge powers is from 9.8 to 32.6 W. The temperature of plasma treated liquid is measured and monitored by a thermometer. In order to avoid water over heating during discharge, a refrigerating system was added in the plasma treatment system to keep the temperature of solution at about 35.0 °C.

### 3.2. Optical emission spectroscopy (OES)

The OES is an ideal means to understand gas–liquid plasma states of a discharge. The optical emission intensity of the gas–liquid phase gas composition plasma between 200.0 and 950.0 nm is shown in figure 3. The spectrum is mainly composed of the bands of OH lines, various nitrogen species peaks observed in the range of 300.0–400.0 nm, atomic hydrogen lines: $H_\alpha$ (656.3 nm), $H_\beta$ (486.1 nm) and excited atomic oxygen lines (777.2 and 844.6 nm). Various nitrogen species peaks coming from high energy particles excite nitrogen in the air. Notably, very weak spectral lines of $N_2$ are displayed which might be caused by the filamentary discharge mode as well as the $H_2O$ (g) molecules [27]. The atomic hydrogen lines and part of atomic oxygen lines coming from high energy particles excite water molecules, and another part of atomic oxygen lines were generated by high energy particles exciting oxygen molecules. In the air gas–liquid discharge, the charged particles react with water molecules to produce more RS ($H_2O_2$, $O_3$ and $NO_3$). The detailed reactions are in the section 3.3 (concentration of RS in liquid induced by plasma).

### 3.3. Concentration of RS in liquid induced by plasma

The RS produced by the gas–liquid plasma possess high oxidizing potential to degrade organic pollutants. RS include long-lived RS ($H_2O_2$, $O_3$ and $NO_3$) and short-lived RS (·OH). However, it is difficult to determine the concentration of short-lived RS. The long-lived RS can indirectly reflect the short-lived RS, so this study only detects the concentration of long-lived RS ($H_2O_2$, $O_3$ and $NO_3$). Figure 4 shows the aqueous concentration of $H_2O_2$, $O_3$ and $NO_3$ induced by plasma treatment. With the increasing discharge period, $NO_3$ and $H_2O_2$ concentrations significantly enhanced while the $O_3$ concentration raised slightly. Specifically, it was about 72.0 mg l$^{-1}$ and 38.9 mg l$^{-1}$ for $NO_3$ and $H_2O_2$ respectively at exposure time of 24 min. Meanwhile, the concentration of $O_3$ was only 6.4 mg l$^{-1}$ due to decomposition into other possible species.
H₂O₂ and O₃ are the major RS in the gas–liquid process. H₂O₂ is formed by the following reaction [28–30]:

\[
\begin{align*}
H_2O + e^- & \rightarrow H + \cdot OH + e^- \\
\cdot OH + \cdot OH & \rightarrow H_2O_2 \\
H + \cdot O_2 & \rightarrow HO_2 \\
HO_2 + \cdot H & \rightarrow H_2O_2 \\
HO_2 + \cdot HO_2 & \rightarrow H_2O_2 + O_2.
\end{align*}
\]

O₃ is produced in the plasma by the interaction between atomic oxygen and oxygen in the gas phase, and it is a widely applied strong oxidizing agent dealing with wastewater and reacts with target compounds via molecular and radical reactions [31]. Simplified reaction mechanisms of O₃ can follow the below equations [32]:

\[
\begin{align*}
O + O_2 & \rightarrow O_3 \\
3O_3 + H_2O & \rightarrow 2 \cdot OH + 4O_2 \\
H_2O_2 + 2O_3 & \rightarrow 2 \cdot OH + 3O_2 \\
NO_2 + H_2O & \rightarrow HNO_3 + HNO_2 \\
H_2O_2 + O_3 & \rightarrow \cdot OH + O_2 + HO_2 \\
O_3 + \cdot OH & \rightarrow HO_2 + \cdot O_2.
\end{align*}
\]

During the air discharge, the system produces nitrogen oxides, which react with water to form nitrites and nitrates in the liquid and leads to the solution becoming strong acidity, which were followed by the reaction:

\[
\begin{align*}
N + O & \rightarrow NO \\
NO + O & \rightarrow NO_2 \\
NO + O_3 & \rightarrow NO_2 + O_2 \\
2NO_2 + H_2O & \rightarrow HNO_3 + HNO_2.
\end{align*}
\]

Specifically, the concentrations of O₃ and H₂O₂ were very low in the plasma-treated solution which were far less than the concentration of NO₃, while NO₃ do not react with the organic pollutant directly but react with H⁺ to form HNO₃ leading to enhancing aqueous acidity after plasma treatment, and even attenuate the CIP degradation efficiency as a certain amount of H₂O₂ and ·OH have been consumed due to reactions (14)–(17). High NO₃ concentration could effectively signify the reason for the variation on the aqueous pH after plasma treatment. Moreover, H₂O₂ and O₃ could not only react with the target pollutant CIP directly, but also possess long lifetimes even with very low concentrations. Consequently, ·OH may be produced from them by the following reactions (18) and (19) [30]. Certain concentrations of ·OH could thereby exist for a long time in the plasma-treated aqueous solution

\[
\begin{align*}
H_2O_2^{\text{(aq)}} + O_3^{\text{(aq)}} + OH^-^{\text{(aq)}} & \rightarrow \cdot OH^{\text{(aq)}} \\
+ \cdot HO_2^{\text{(aq)}} + O_2^{\text{(aq)}} + OH^{\text{(aq)}} \\
H_2O_2^{\text{(aq)}} & \rightarrow \cdot OH^{\text{(aq)}} + \cdot OH^{\text{(aq)}}.
\end{align*}
\]

3.4. Effects of discharge power on CIP degradation

Figure 5 shows the CIP degradation rates at different discharge powers (from 9.8 to 32.6 W) using gas–liquid plasma. The volume of the plasma-treated solution is 30.0 ml with initial CIP concentration at 10.0 mg l⁻¹ and the initial aqueous pH value is about 7.3. The discharge power had an obvious influence on the degradation of CIP, and the degradation efficiency of CIP increased when the discharge power increased. With regard to a discharge time of 24 min and discharge power of 9.8 W, 19.7 W and 32.6 W, the degradation of CIP was 84.1%, 91.2% and 93.4%, respectively. The discharge powers could directly affect the production of RS and UV irradiation [33]. With the increase of discharge power, more ultraviolet light will be produced, which could lead to the production of more ·OH [34].

In order to consider practical applications, we calculated the energy efficiency of degradation of CIP by the gas–liquid plasma. As shown in figure 6, it could be seen that the energy yield decreased as the discharge power increased. The degradation of CIP decreased from 7.3 mg kW⁻¹ h⁻¹ at 9.8 W to 0.2 mg kW⁻¹ h⁻¹ at 32.6 W after 20 min reaction in plasma system. The result indicated that it was hard to obtain both the best degradation efficiency and a higher energy yield at the same time [35], because the increased input power led to increased energy waste (e.g. more electrical energy was
converted into heat) [36]. For this reason, we selected discharge power of 19.7 W over the following experiments.

3.5. Effect of initial concentration on CIP degradation

Figure 7 shows the effect of initial concentration on CIP degradation by the gas–liquid plasma. The volume of the plasma-treated solution is 30.0 ml with initial CIP concentration from 10.0 to 40.0 mg l\(^{-1}\) and the initial aqueous pH value of is about 7.3. The discharge power is set at 19.7 W. After 24 min of treatment, the degradation efficiency was determined at initial CIP concentrations of 10.0, 20.0, 40.0 mg l\(^{-1}\). It could be observed from figure 7 that the removal efficiency of CIP decreased when initial concentration decreased from 40.0 to 10.0 mg l\(^{-1}\). The phenomenon was similar to other researches [37, 38]. The RS in water produced by plasma is a certain amount at certain discharge power. At high concentration of CIP, more molecules of CIP competition reacted with RS and the by-production also consumed a part of RS [39]. Therefore, the removal efficiency of CIP decreased under the high concentration condition.

3.6. Effect of initial pH value of the solution

The pH value of solution of CIP was examined during the discharge process, and the result is shown in figure 8. The volume of the plasma-treated solution is 30.0 ml with initial CIP concentration at 10.0 mg l\(^{-1}\) and the discharge power is set at 19.7 W. The initial aqueous pH value varies from 4.2 to 9.4. The pH of the solution decreased gradually with the increase of the discharge time. Consequently, we explored the effect of initial pH on degradation of CIP. As shown in figure 9, the degradation efficiency decreased with an increased initial pH value from 4.2 to 9.4, and this result was similar to that of Feng et al [40]. The initial pH value of solution will affect the solution properties as well as the RS formation in the discharge process [41]. At low pH value, more \(\cdot\)OH were produced, and simultaneously inhibit the decomposition of \(\text{H}_2\text{O}_2\) and \(\text{O}_3\). The RS produced by the plasma discharge is the main substance for the degradation of organic pollutants, additional \(\cdot\)OH, \(\text{H}_2\text{O}_2\), and \(\text{O}_3\) signified a higher degradation rate for CIP. However, under alkaline conditions, the generated \(\cdot\)OH in the gas–liquid discharge area reacted with carbonate ions and alkaline ions immediately, which consumed a number of \(\cdot\)OH and decreased the degradation rate of CIP [42].

3.7. Effect of different radical scavengers

A series of experiments analyzed the influence of different radical scavengers (isopropanol and carbon tetrachloride (CCl\(_4\))) during degradation of the CIP by plasma treatment, the result is shown in figure 10. The volume of the plasma-treated solution is 30.0 ml with initial CIP concentration at 10.0 mg l\(^{-1}\) and the initial aqueous pH value is about 7.3. The discharge power is set at 19.7 W. The isopropanol ((CH\(_3\))\(_2\)-CHOH) is a well-known kind of \(\cdot\)OH radicals scavenger, the reaction is followed by equilibrium [43, 44]:

\[
\text{(CH}_3\text{)}_2\text{CHOH} + \cdot\text{OH} \rightarrow \text{(CH}_3\text{)}_2\text{COH} + \text{H}_2\text{O} \\
k = 1.9 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}. 
\]
While CCl₄ is known to be an effective hydrogen atom scavenger \((k = 3.8 \times 10^7 \text{ M}^{-1} \text{s}^{-1})\) and hydrogen atoms generated by pyrolysis of water molecule (equation (21)) could be scavenged by CCl₄ in the cavity (equation (22))

\[
\text{H}_2\text{O} \rightarrow \cdot\text{H} + \cdot\text{OH} \quad (21)
\]

\[
\text{CCl}_4 + \cdot\text{H} \rightarrow \text{HCl} + \cdot\text{CCl}_3 \quad k = 3.8 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \quad (22)
\]

\[
\text{CCl}_4 + \cdot\text{OH} \rightarrow \text{HOCl} + \cdot\text{CCl}_3 \quad k < 6.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1} \quad (23)
\]

\[
\text{CCl}_4 + \text{OH}_2 \rightarrow \text{products} \quad (24)
\]

As shown from the reaction rate constants and the related reaction equations, CCl₄ could largely consume \(\cdot\text{H}\) which would easily react with \(\cdot\text{OH}\). The kinetics (Rate constants) of the CCl₄ reaction with hydroxyl radicals or hydroperoxyl radicals would be 2 orders of magnitude slower than hydrogen atoms [45–47].

In this study, the isopropyl alcohol ((CH₃)₂–CHOH) and carbon tetrachloride (CCl₄) were added into solution, which could scavenge \(\cdot\text{OH}\) and \(\cdot\text{H}\) in aqueous solution, respectively. With the 2.0 ml⁻¹ isopropanol, the degradation efficiency of CIP obviously dropped from 91.2% to 66.4%. This phenomenon can be explained as the fact that the majority of \(\cdot\text{OH}\) was rapidly captured by isopropanol, which prevented the reaction with CIP. Results show that \(\cdot\text{OH}\) play an important role in degrading CIP. With 0.03 ml CCl₄ [48] added to 30.0 ml CIP solution, the removal efficiency of CIP improved from 91.2% to 92.6%. Specifically, the chance of recombination of \(\cdot\text{H}\) and \(\cdot\text{OH}\) [49] was attenuated by CCl₄ [50], leading to subsequent increasing degradation efficiency on CIP.

3.8. Effect of storage time of the plasma-treated CIP solution

The purpose of this test is to investigate the long-term (stay) degradation effect on CIP by the plasma-induced aqueous RS. As shown in figure 11, the post-treatment storage time possesses a significant influence on the CIP degradation effect.
During the discharge process, various RS, such as short-lived RS (·OH etc) and long-lived RS (H₂O₂ and O₃, etc), were produced in the solution. The short-lived RS only exist in solution for a very short period of time after being discharged while the long-lived RS can exist in solution for a relatively long period. The degradation efficiency of CIP improved at the time point of 12.0 h compared with that at 0.0 h, which illustrated that the long-lived RS (i.e. H₂O₂) in the solution continued to react with CIP. Specifically, even the long-lived RS cannot exist for many hours, they (H₂O₂ and O₃) could produce ·OH by above-mentioned reactions (18) and (19) even with low concentrations [30]. A little amount of ·OH

### Table 1. Intermediate products identified using ESI (+)-MS during the degradation of CIP.

<table>
<thead>
<tr>
<th>Intermediate compounds</th>
<th>m/z</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIP</td>
<td>332.0</td>
<td><img src="image1" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Compound I</td>
<td>363.0</td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Compound II</td>
<td>307.0</td>
<td><img src="image3" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Compound III</td>
<td>263.0</td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Compound IV</td>
<td>261.0</td>
<td><img src="image5" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Compound V</td>
<td>347.0</td>
<td><img src="image6" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Compound VI</td>
<td>288.0</td>
<td><img src="image7" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>
could thereby exist for long periods in the plasma-treated aqueous solution, which serve as the main dynamics for CIP degradation as the oxidative reactions would continue to occur thus reduce the present organics leading to the high and long-term removal efficiency. After 12.0 h of storage, the degradation efficiency of CIP did not change much as the long-lived reactive substances might have been already fully consumed.

Figure 14. Analysis of the degradation path of CIP.
3.9. Spectrophotometry and TOC analysis of CIP degradation

The spectrophotometric analysis could indicate some characteristic peaks of organic compounds, and the spectrophotometric of the target CIP solution after different treatment times (from 0 to 24 min) were detected for illustrating the degradation process of the CIP. The volume of the plasma-treated solution is 30.0 ml with initial CIP concentration at 10.0 mg l⁻¹ and the initial aqueous pH value is about 7.3. The discharge power is set at 19.7 W. As shown in figure 12, there was one distinct characteristic adsorbing peak (about 277.0 nm) of the CIP solution in the ultraviolet and the visible light area. With the increase of treatment time in the gas–liquid plasma system, the characteristic adsorbing peak became weak, which could indicate that some of the corresponding structures were broken by the RS and other species came into being. The concentration of TOC was measured with a TOC analyzer (TOC-V CPN, Shimadzu, Japan).

As shown in figure 13, with the increase of treatment time, TOC decreased gradually, and the removal rate of TOC was 47.4% at 24 min. Boutamine et al [51] only used photocatalyst to degrade Basic Red 29, and the results showed that the mineralization of the dye is about 10.0%. In order to make sure the by-products were produced by the gas–liquid plasma, the possible degradation pathway of CIP in plasma was elucidated from the ESI (+)-MS.

3.10. Identification of reaction products and degradation pathway of CIP

The decomposition products of CIP by the gas–liquid plasma (power at 19.7 W) are mainly obtained by ESI (+)-MS measurement with some theoretical analysis. Table 1 presents the details of the identified intermediates (I–VI) of CIP. Seven main intermediate products of CIP are detected and the possible CIP degradation mechanism is illustrated in figure 14. Degradation process may be divided into two routes, one of which is that the plasma produced the hv, -OH and -O₂ oxidation of the open piperazine ring occurs to form compound I, and then two C=O groups are disassociated from the piperazine ring and compound II is produced. Abstraction of the piperazine ring may also occur upon the triplet formation to form compound III [52]. Lastly, the -NH₂ is oxidized to generate compound IV [53]. Similarly, the compound V is the result of the primary attack of -OH followed by its oxidation and elimination of HO₂-, and this further undergoes decarboxylation and water elimination leading to the formation of VI. The appearance and disappearance of various intermediates clearly demonstrate the multiple reaction ability of -OH. When the concentration of CIP declines during plasma treatment, -OH would react with intermediates leading to formation of various secondary products [53]. Through previous reports, it is known to all that the short chain carboxylic acid is generally known as the final product of the whole mineralization [54]. According to the results of TOC, oxidation, inorganic carbon and water constitutes are the last steps of mineralization.

4. Conclusion

Gas–liquid discharge plasma treatment was efficient for the removal of CIP. During the discharge, RS (+OH, H₂O₂, etc.) were produced to react with CIP. With regard to a discharge time of 24 min and discharge power of 9.8 W, 19.7 W or 32.6 W, the degradation of CIP was 84.1%, 91.2% or 93.4%, respectively. Initial concentration and initial pH value showed a negative effect on degradation CIP as they increased from 10.0 to 40.0 mg l⁻¹ and 4.2 to 9.4, respectively. The study on radical scavenger and storage time confirmed that the -OH play a key role in the degradation of CIP. Gas–liquid plasma degradation mechanism was proposed according to the determined degradation intermediates. All research results indicate that gas–liquid plasma is an attractive treatment technology for the degradation of CIP in aqueous solution.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (Nos. 51777206 and 51541807), Natural Science Foundation of Anhui Province (Nos. 1708085MB47 and 1708085MA13), Foundation of Anhui Province Key Laboratory of Medical Physics and Technology (No. LMP17Y7BP01U581), Doctoral Fund of Ministry of Education of China (No. 2017M612058), Specialized Research Fund for the Doctoral Program of Hefei University of Technology (Nos. JZ2016HGBZ0768, JZ2016HGBZ0769, and JZ2017HGBZ0944).

References

[22] Zhou Z et al 2015 Chemosphere 119 S95
[34] Olszewski P et al 2014 J. Hazard. Mater. 279 60
[37] Zhu D et al 2014 Chemosphere. 117 506
[44] Lu N et al 2013 Chemosphere. 91 1266
[47] Lee M and Oh J 2010 Ultrason. Sonochim. 17 207