

## Article

# Mechanism and Reactive Species in a Fountain-Strip DBD Plasma for Degrading Perfluorooctanoic Acid (PFOA)

Jiushan Cheng <sup>1,\*</sup>, Yangyang Fan <sup>1</sup>, Xueyun Pei <sup>1</sup>, Di Tian <sup>1</sup>, Zhongwei Liu <sup>1</sup>, Zachary Z. Wei <sup>2</sup>, Hai-feng Ji <sup>2</sup>  and Qiang Chen <sup>1</sup> 

<sup>1</sup> Laboratory of Plasma Physics, Beijing Institute of Graphic Communication, Beijing 102600, China

<sup>2</sup> Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA

\* Correspondence: jscheng@bigc.edu.cn

**Abstract:** Perfluorooctanoic acid (PFOA) is an artificially synthesized perfluorinated chemical widely used in industries. It is often released into the environment without treatment, which causes pollution in groundwater. Recently, we have reported a rapid and efficient removal of PFOA in aqueous solution by using a fountain-strip dielectric barrier discharge reactor (SF-DBD). This design allows for the gaseous–liquid interaction to happen in a large space at atmospheric pressure, so it is a promising method to efficiently remove PFOA from water. Recently, we reported the effects of the process parameters, including power mode, pulse time, sinusoidal wave discharge, the discharge gas, initial concentration, pH, conductivity, and positive and negative discharges, on the efficiency of this method for PFOA degradation. Understanding the reaction mechanism is key to further improve the efficiency of the system. In this work, we reported the decomposition mechanism of the SF-DBD for PFOA degradation. The mass spectrum (MS) showed that PFOA was degraded to perfluoroheptanoic acid, perfluorohexanoic acid, perfluoropentanoic acid, perfluorobutanoic acid, perfluoropropionic acid, and trifluoroacetic acid after the plasma treatment. The optical emission spectroscopy (OES) and the radical scavenger experiments indicated that the excited argon atoms and hydroxyl radicals played a major role in PFOA degradation, while the contributions from the solvated electrons ( $e^-_{aq}$ ), superoxide anion radical ( $\cdot O_2^-$ ), and singlet oxygen ( $^1O_2$ ) were negligible in initiating the cleavage reaction.

**Keywords:** mechanism; DBD; plasma; degrade; PFOA; reactive species



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## 1. Introduction

Perfluorooctanoic acid (PFOA) is an artificially synthesized, highly stable perfluorinated compound (PFC) [1,2], which is commonly used as a surfactant in industries to produce firefighting coating, soap, shampoo [3,4], etc. It does not degrade naturally [5,6] and is highly persistent in the environment [7], which can cause potential harm to the ecological system [8]. Hence, it is necessary to degrade PFOA before releasing PFOA as waste [9,10].

Current methods that degrade PFOA generally have low efficiency. These methods include ozone and hydrogen peroxide [11], photocatalysis [12], sonolysis [13], activated persulfate [14], electrolysis [15], ionizing radiation [16], etc. In the last decade, the non-thermal dielectric barrier discharge (DBD) plasma technique rose in popularity as a new method to degrade hydrocarbon organic pollutants. DBD contains a huge number of highly active species ( $\cdot OH$ ,  $\cdot H$ ,  $\cdot O$ ,  $H_2O_2$ ,  $\cdot O_2$ ,  $e^-_{aq}$ , etc.), high-energy electrons, UV radiation, and shock waves [17] that can degrade organic chemicals. Apart from hydrocarbons, it has also been reported that PFOA could be removed by DBD [18,19]. However, the efficiency of the reported DBD method for PFOA degradation is still not high enough for commercialization.

Recently, we have reported a plasma method for the rapid and efficient removal of PFOA in aqueous solutions by using a novel plasma source: a fountain-strip DBD

reactor (SF-DBD) [20]. This design allows a gaseous–liquid interaction in a large space at atmospheric pressure so it is a promising technique to efficiently remove PFOA from water. The effects of the process parameters, including power mode, pulse time, sinusoidal wave discharge, the discharge gas, initial concentration, pH, conductivity, and positive and negative discharges, on the efficiency of this method for PFOA degradation have been discussed. In this work, we report the decomposition mechanism of the SF-DBD for PFOA degradation, which is important because, for a new DBD system, the chemical species in the plasma can be different, albeit the difference may be small, from other DBD systems. Thus, understanding the reaction mechanism is needed to further improve the efficiency of the system. This study is crucial particularly for DBD since it is controversial which active species in a plasma degrade PFOA. Singh et al. [17] reported that hydroxyl radicals played an essential role in the degradation of PFOA, but N Takeuchi et al. [21] believed that hydroxyl radicals could not effectively degrade PFOA. Raj Kamal Singh et al. [17] concluded that the solvated electrons were the main active species for degradation. The by-products found in the plasma treatment process of PFOA in water are mainly produced by the gradual reduction of PFAS molecules to linear chain pfca, PFPA, short-chain organic acids and F. A small amount of gas-phase by-products, including cyclic perfluoroalkanes, are also produced and then degraded. Cheng-fang Lin [22] summarized the following four important steps of decomposition: ionization, electron transfer, decarboxylation, and perfluoroalkyl radical oxidation. These decomposition reactions complete several cycles until the quantity of perfluorocarbons in PFCA is equal to the decarboxylations. Satoshi Horikoshi [23] assumed that a continuous loss of the  $\text{CF}_2$  unit of perfluoric acid and decarboxylation intermediate was generated during PFOA treatment. The loss of  $\text{CF}_2$  unit after the first decarboxylation may occur through the oxidation of the protonated terminal carbon and the formation of  $\text{F}^-$  ions and  $\text{CO}_2$ . In order to understand the degradation mechanism of PFOA in this novel DBD plasma source, we first identify the degradation intermediates and products by liquid chromatography–mass spectrometry (LC-MS) that leads to the most plausible degradation pathway of PFOA, then use optical emission spectroscopy (OES) and the radical scavenger experiments to conclude the main active species for the degradation of PFOA.

## 2. Experiments

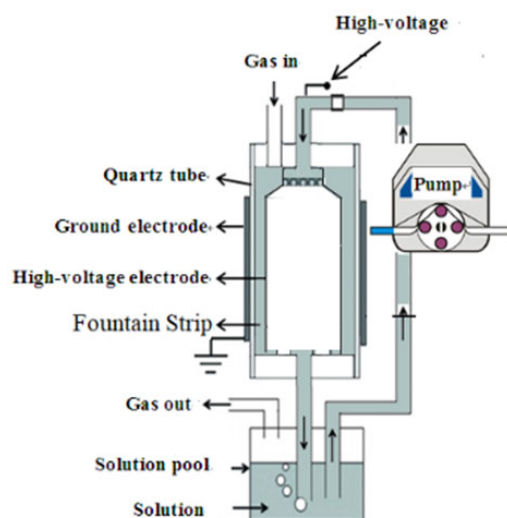
### 2.1. Materials

PFOA (purity > 95%) was purchased from Alfa Aesar. Other agents, such as isopropanol ( $\text{C}_3\text{H}_8\text{O}$ ; analytical grade), sodium nitrite ( $\text{NaNO}_2$ ; analytical grade), benzoquinone ( $\text{C}_6\text{H}_4\text{O}_2$ ; analytical grade), 2, 2, 6, 6-tetramethylpiperidine ( $\text{C}_9\text{H}_{19}\text{N}$ ; analytical grade), ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ; HPLC grade), methanol ( $\text{CH}_3\text{OH}$ ; HPLC grade), and acetonitrile ( $\text{C}_2\text{H}_3\text{N}$ ; HPLC grade) were purchased from Aladdin reagent (Shanghai) Co. LTD. All agents were not further purified before use. Ar gas (purity > 99.999%) was bought from Praxair technologies, Beijing, China. PFOA-polluted simulated wastewater was prepared in deionized water.

### 2.2. Experimental Setup

The schematics of the SF-DBD plasma system used in our experiment are shown in Figure 1 [20]. A waterfall was released from a fountain strip at a constant rate and passed through an electric field generated from a high-voltage power supply. The waterfall looked like a thin film, which allowed a maximum contact of the plasma in the gas phase with species in the water. A quartz tube (48 mm in outer diameter, 44 mm in inner diameter, 200 mm in height) was used as a dielectric layer, which was covered by a grounded 10 mm-long stainless-steel net. A stainless-steel tube acted as the high-voltage electrode and the discharge gap was 2–3 mm. Argon was used as the discharge gas to produce the DBD plasma. When the solution was released from the fountain strip, a 1 mm-thick water film flew to a pool at the bottom of the tube. A cooling tank was added to keep the temperature of the solution in the pool at around 297 K during the whole process. The volume of all

processed PFOA solutions was 200 mL, the initial concentration was 75 mg/L, the initial pH of the solution was around 4.3, the conductivity was around  $65 \text{ S}\cdot\text{m}^{-1}$ , and the duration between the treatment and analysis of the sample was 10 min. The Ar gas flow rate was  $3 \text{ L min}^{-1}$  and the liquid flow rate was  $280 \text{ mL}\cdot\text{min}^{-1}$ .



**Figure 1.** Schematic diagram of the SF-DBD system used in PFOA-polluted water treatment [20].

A negative pulse power supply (SY6515, Chengdu Senyuan technology Co., Ltd., Chengdu, China) was used to provide a high voltage of up to 16 kV with a frequency in the range of 0–15 kHz. The pulse width was 0.5–0.8  $\mu\text{s}$ , and the pulse rising edge period was in the range of 104–112 ns.

### 2.3. Analytical Methods

The by-products of the treated PFOA were analyzed using the Sciex QTRAP 5500 ultraperformance liquid chromatography/mass spectrometry (UPLC-MS/MS) system. The UPLC was equipped with an ACQUITY UPLC CSH C18 column, and the column temperature was set at 30 °C. A hybrid solution of 5 mM ammonium acetate aqueous solution and the methanol were used as the mobile phase, while the gradient flow rate was set at 0.2 mL/min. The mass spectrometry (MS) was also equipped with a water triple quadrupole LC/MS/MS ion source with jet technology. The ionization mode and scan mode were set to the ESI negative ion mode and multiple-reaction monitoring (MRM), respectively. The Flame-S-XR1-ES emission spectrometer was used in this study, which can monitor the wavelength range from 200 nm to 1000 nm. During the monitoring of the gaseous plasma, the optical fiber probe was placed near the discharge area outside the quartz tube.

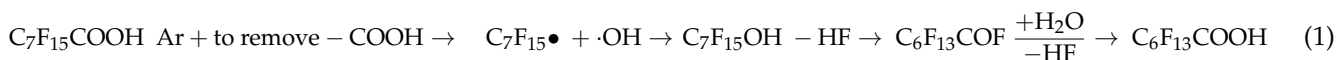
The experiments conditions consisted of a negative pulsed peak voltage of 15 kV, a frequency of 6 kHz, a pulse width of 500 ns, and an average power of 43 W. All experiments were conducted in duplicate.

### 3. Results and Discussion

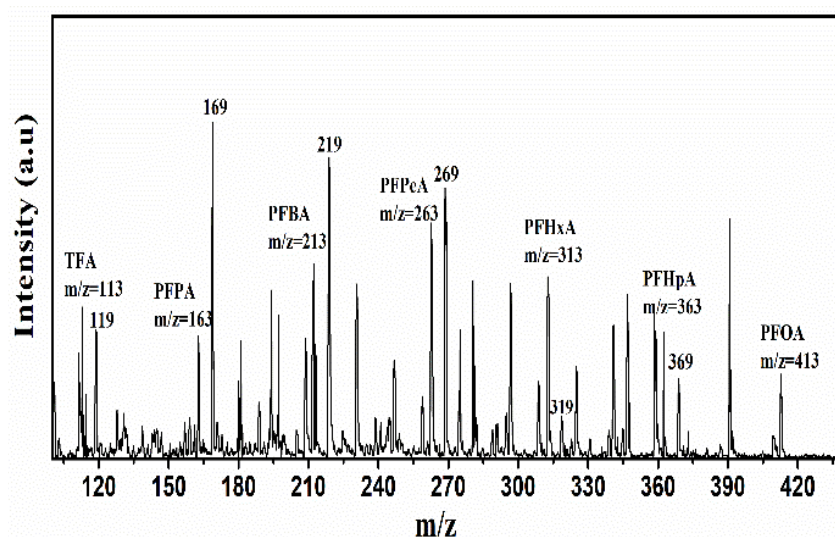
In our previous experiments, we observed that the Ar SF-DBD plasma was the most efficient when degrading PFOA compared to air and  $\text{O}_2$  plasma, so we paid attention to the reaction mechanism in an Ar plasma. Although Ar was used as the discharge gas, a small amount of reactive oxygen species (ROS) [24] and reactive nitrogen species (RNS) [11,19,25] were observed due to dissolved air in the aqueous solution.

### Decomposition Mechanism Analyzed from the Intermediates/Products

Singh et al. [17] reported a detailed study on the decomposition mechanism of PFOA by a plate-to-plate Ar DBD plasma, which was summarized in the following stepwise reactions (1):



The process above repeated several times to produce smaller perfluorinated acids. Several other reports showed a similar reaction mechanism [5,22,23,26,27]. Since our plasma system was different from Singh's [17] system, it was critical to understand whether the decomposition of PFOA followed the same mechanism mentioned above. The observation of a series of smaller perfluorinated acids would be direct evidence to support the above mechanism. To verify this, the intermediates and products of PFOA degradation after an Ar plasma treatment for 60 min were identified using MS in a negative ion mode. As shown in Figure 2, in the negative ion mode six smaller perfluorinated acids,  $\text{C}_6\text{F}_{13}\text{COO}^-$  ( $M/z = 363$ ),  $\text{C}_5\text{F}_{11}\text{COO}^-$  ( $M/z = 313$ ),  $\text{C}_4\text{F}_9\text{COO}^-$  ( $M/z = 263$ ),  $\text{C}_3\text{F}_7\text{COO}^-$  ( $M/z = 213$ ),  $\text{C}_2\text{F}_5\text{COO}^-$  ( $M/z = 163$ ),  $\text{CF}_3\text{COO}^-$  ( $M/z = 113$ ), were indeed formed. Table 1 summarizes the names and molecular weight of these corresponding acids.



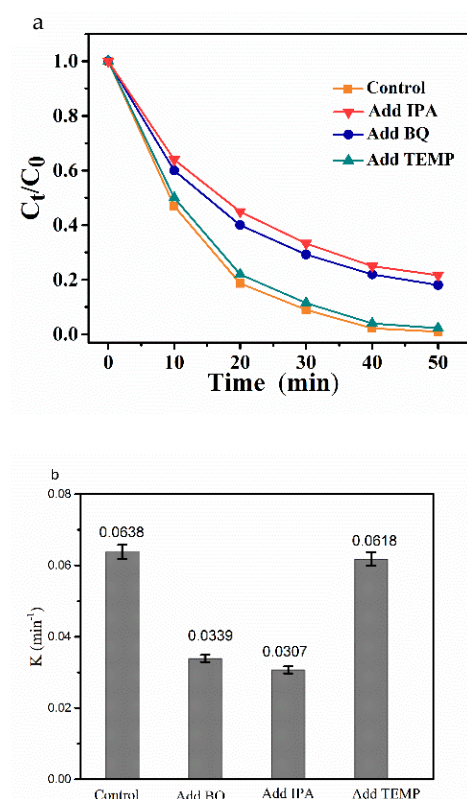
**Figure 2.** Electrospray mass spectrum of the PFOA decomposition by DBD plasma after 60 min treatment. The ionization mode and scan mode were set to ESI negative ion mode.

**Table 1.** Intermediates and products in Ar-plasma-treated PFOA solution.

C Number	Compound	Chemical Formula
6	Perfluoroheptanoic acid	$\text{C}_6\text{F}_{13}\text{COOH}$
5	Perfluorohexanoic acid,	$\text{C}_5\text{F}_{11}\text{COOH}$
4	Perfluoropentanoic acid	$\text{C}_4\text{F}_9\text{COOH}$
3	Perfluorobutanoic acid	$\text{C}_3\text{F}_7\text{COOH}$
2	Perfluoropropionic acid	$\text{C}_2\text{F}_5\text{COOH}$
1	Trifluoroacetic acid	$\text{CF}_3\text{COOH}$

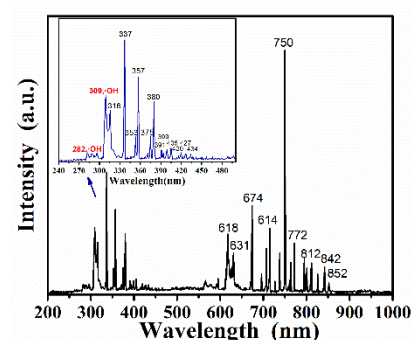
The mechanism suggested that  $\bullet\text{OH}$  played a major role in the formation of the degradation products. It is commonly known that  $\bullet\text{OH}$  can be mass-produced in the plasma when water is excited by the plasma ( $\text{H}_2\text{O}^* \rightarrow \bullet\text{OH} + \text{H}$ ). However, it is also likely other reactive oxygen species (ROS) such as the singlet oxygen ( $^1\text{O}_2$ ) or superoxide anion radical ( $\bullet\text{O}_2^-$ ) in plasma were also the source of  $\bullet\text{OH}$  in the formation of  $\text{C}_7\text{F}_{15}\text{OH}$  and other alcohols in the reactions. To confirm the source of the  $\bullet\text{OH}$  group, the scavenger effect on the degradation rate was studied. Isopropanol (IPA), 2, 2, 6, 6-tetramethylpiperidine (TMPA), and benzoquinone (BQ) were used as scavengers of hydroxyl radical ( $\bullet\text{OH}$ ), singlet oxygen ( $^1\text{O}_2$ ), and superoxide anion radical ( $\bullet\text{O}_2^-$ ), respectively [28,29]. Figure 3 shows the kinetic reaction constants decreased from  $0.064 \text{ min}^{-1}$  in pure PFOA solution to  $0.0307 \text{ min}^{-1}$ ,  $0.0618 \text{ min}^{-1}$ , and  $0.0339 \text{ min}^{-1}$ , for the addition of IPA, TEMP, and BQ, respectively. The results

suggested that both the hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide anion radical ( $\cdot\text{O}_2^-$ ) could be the source of the  $-\text{OH}$  group that was involved in PFOA degradation, while the effect of singlet oxygen ( $^1\text{O}_2$ ) was ruled out.



**Figure 3.** (a) Effect of radical scavengers on PFOA degradation; (b) kinetic constants under different treatment processes in Ar plasma ([IPA] = 10 mM; [BQ] = 5 mM; [TMPA] = 15 mM).

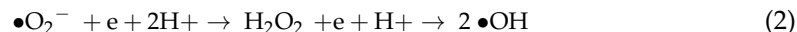
To further identify whether or not hydroxyl radicals ( $\cdot\text{OH}$ ) or superoxide anion radicals ( $\cdot\text{O}_2^-$ ) could possibly be a major source of  $-\text{OH}$  involved in PFOA degradation, the optical emission spectrum (OES) of the Ar plasma at the plasma/waterfall interface was collected. OES diagnosis is one of the most essential approaches to identifying gaseous components in plasma, which includes the chemical reactions between the long-lived active species and the short-lived charged species, as well as the physical reactions caused by electron collision, ultraviolet light, and shock waves [30]. Figure 4 shows the OES in Ar discharges from a 200 to 900 nm wavelength. The main excited argon atoms were located at 650–900 nm [31]. The lines located at 282 nm and 309 nm were from hydroxyl radical ( $\cdot\text{OH}$ ) [32]. It is known  $\cdot\text{OH}$  can be formed when the metastable argon atoms ( $\text{Ar}^*$ ) in plasma-dissociated water [31]. The peak of superoxide anion radical ( $\cdot\text{O}_2^-$ ) at around 245 nm, on the other hand, was not observed [32].



**Figure 4.** The optical emission spectrum in Ar discharge in the range of 240–900 nm (the inset is magnified in 240–500 nm).

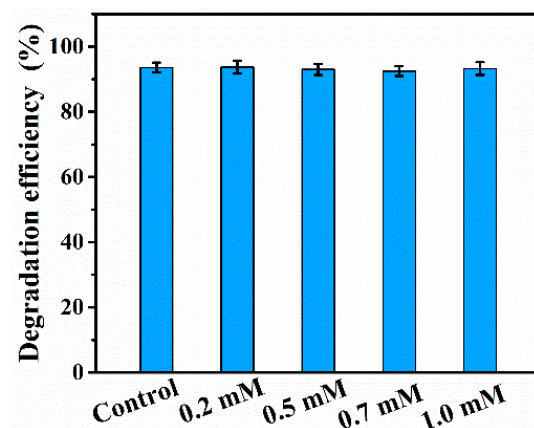


The absence of the OES peak of  $\cdot\text{O}_2^-$  indicated that the  $\cdot\text{O}_2^-$  did not contribute to the degradation of PFOA. However, it was also likely  $\cdot\text{O}_2^-$  would play such a role in the degradation by (1) fast reacting with  $\text{C}_7\text{F}_{15}\bullet$  to  $\text{C}_7\text{F}_{15}\text{OO}^-$  and (2) converting to  $\cdot\text{OH}$  according to the following known reaction (2) [33] in acidic conditions.



The absence of the  $\text{C}_7\text{F}_{15}\text{OO}^-$  peak ( $M/z = 401$ ) in the MS spectrum (Figure 2) excluded the reaction of  $\cdot\text{O}_2^-$  with  $\text{C}_7\text{F}_{15}\bullet$ . Thus, we paid attention to whether  $\cdot\text{O}_2^-$  was rapidly converted to  $\cdot\text{OH}$ , which is involved in the degradation of PFOA. To do so, the roles of proton and electron in the solution were studied since both are needed to convert  $\cdot\text{O}_2^-$  to  $\cdot\text{OH}$  as shown in reaction (2) above. As for the acidity of the solution, the solution pH decreased to 2.69 after the 60 min plasma treatment and the solution conductivity increased linearly along the 60 min exposure to the Ar plasma, suggesting the formation of protons and ionic species in the solution [34,35].

It is known that solvated electrons [36] are generated when a solution is treated by a plasma. These solvated electrons may excite, dissociate, or ionize the water molecules to degrade organic molecules in the solution. Gunnar R Stratton et al. [19] reported that the solvated electron quench agents could significantly slow down PFOA degradation. It has also been recognized as one of the most dominant species for PFOA degradation in a previous study [37] in a UV photochemical system. To confirm whether the solvated electrons played a role to convert  $\cdot\text{O}_2^-$  to  $\cdot\text{OH}$  and/or directly impacted water to degrade PFOA, we added  $\text{NaNO}_2$ , which is known as an effective quenching agent for the solvated electrons [37–39]. Figure 5 shows that the degradation efficiency did not change with or without  $\text{NaNO}_2$  in the PFOA solution, indicating the insignificance of solvated electrons in the PFOA decomposition in our system. The result may be due to the fact that the average penetration depth of the electrons into the water was as small as  $(2.5 \pm 1.0)$  nm [40], so the solvated electrons only reacted with PFOA molecules at the air/water interface. The absence of effect from the solvated electrons excluded the conversion of  $\cdot\text{O}_2^-$  to  $\cdot\text{OH}$  and/or the involvement in the degradation of PFOA.



**Figure 5.** Degradation efficiency of PFOA under different doses of  $\text{NaNO}_2$  (the initial conductivity was set near  $1358 \text{ S}\cdot\text{m}^{-1}$  using  $1 \text{ mol}\cdot\text{L}^{-1}$   $\text{NaCl}$ ).

The above OES and scavenger analysis suggested that  $\cdot\text{O}_2^-$  and the solvated electrons did not play a critical role in PFOA degradation, neither directly nor indirectly.

It is noteworthy that the lines of the second positive systems of  $\text{N}^+$  were also observed in the range of 300–500 nm. The strongest and most stable spectral band in this range was generated by the transition from the  $\text{N}_2$  ( $\text{C}^3\Pi_u$ ) level to the  $\text{N}_2$  ( $\text{B}^3\Pi_g$ ) level [41]. Another evidence of N species was the line at 674 nm, which belongs to the first positive systems of the excited  $\text{N}_2$  for the transition of the  $\text{N}_2$  ( $\text{B}^3\Pi_g$ ) energy level to the  $\text{N}_2$  ( $\text{A}^3\Sigma_u^+$ ) energy level [32]. The observation of the lines of N species in the Ar plasma was due to the trace amount of dissolved air in the solution. Although reactive nitrogen species (RNS) may play a role in PFOA degradation, the lack of those nitrogen-containing species in the MS spectra did not support their involvement in PFOA degradation.

#### 4. Conclusions

Recently, we reported a high-energy yield method for PFOA degradation by an FS-DBD system. In this work, the degradation intermediates and products were identified, and we proposed a degradation pathway. We concluded that the excited argon atoms and hydroxyl radicals played a major role in PFOA degradation. These studies will help improve the efficiency of the SF-DBD in the degradation of perfluorinated compounds, which proved a promising method for the efficient degradation of PFOA with reduced energy consumption.

**Author Contributions:** Conceptualization, Q.C. and H.-f.J.; methodology, J.C.; software, Y.F.; data curation, X.P. and D.T.; validation, Z.L.; writing—original draft preparation, Y.F.; writing—review and editing, J.C.; writing—English editing, Z.Z.W. All authors have read and agreed to the published version of the manuscript.

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