

An efficient process for decomposing perfluorinated compounds by reactive species during microwave discharge in liquid

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Abstract

Microwave discharge plasma in liquid (MDPL) is a new type of water purification technology with a high mass transfer efficiency. It is a kind of low-temperature plasma technology. The reactive species produced by the discharge can efficiently act on the pollutants. To clarify the application prospects of MDPL in water treatment, the discharge performance, practical application, and pollutant degradation mechanism of MDPL were studied in this work. The effects of power, conductivity, pH, and Fe^{2+} concentration on the amount of reactive species produced by the discharge were explored. The most common and refractory perfluorinated compounds (perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in water environments are degraded by MDPL technology. The highest defluorination of PFOA was 98.8% and the highest defluorination of PFOS was 92.7%. The energy consumption efficiency of 50% defluorination ($G_{50,F}$) of PFOA degraded by MDPL is 78.43 mg/kWh, PFOS is 42.19 mg/kWh. The results show that the MDPL technology is more efficient and cleaner for the degradation of perfluorinated compounds. Finally, the reaction path and pollutant degradation mechanisms of MDPL production were analyzed. The results showed that MDPL technology can produce a variety of reactive species and has a good treatment effect for refractory perfluorinated pollutants.

Keywords: microwave discharge, plasma in liquid, reactive species, purification

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

1. Introduction

Plasma technology has been widely used in the field of environmental pollution, particularly in the treatment of environmental pollution [1, 2]. Some organic pollutants are difficult to degrade using traditional water treatment technologies, such as perfluorinated compounds (PFC), antibiotics, and

pesticides. However, plasma technology can degrade these efficiently [3–6]. Moreover, plasma technology has the advantages of simple operation, low cost, absence of secondary pollution, and high energy efficiency. Therefore, in recent years, plasma technology for the treatment of refractory organic pollutants in aquatic environments has become a research hotspot.

Hao *et al* [7] used a pulsed dielectric barrier discharge (DBD) plasma reactor with coaxial configuration and a

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spiral high-voltage electrode to treat tetracycline in an aqueous solution. When the initial concentration was 50 mg/L, the tetracycline degradation rate was 92.3%. The TOC (Total organic carbon) removal rate is 65.01%, and the energy efficiency was 20.24 g/kWh. Saleem *et al* [8] used a new type of radius plasma (RAP) discharge reactor to treat water polluted by a PFAS (Perfluoroalkyl Substances) surfactant, and the effect was remarkable. In particular, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have been studied. The removal rates of PFOA solutions with initial concentrations of 41 $\mu\text{g/L}$ and 41 mg/L reached 99% or higher in less than 2.5 min and 30 min, respectively. Singh *et al* [9] used a pilot-scale plasma reactor to degrade PFAS from liquid investigation-derived wastes. After less than 1 min, both PFOS and PFOA were removed to concentrations below the recommended concentration level (HAL) of the U.S. Environmental Protection Agency (USEPA). Stratton *et al* [10] used a high-voltage pulse power supply and laminar flow jet reactor with bubbles and a gas-liquid two-phase discharge to produce plasma to remove PFOA. During the treatment process of 30 min, the removal rate of PFOA (8.28 mg/L) reached 90% using a 76.5 W input power. From the above literature, it can be confirmed that plasma technology has a considerable effect on the removal of refractory organic pollutants.

Microwave discharge plasma-in-liquid (MDPL) technology is a new type of plasma water treatment technology. This technology discharges in the liquid phase to produce plasma. In terms of water treatment applications, compared with gas-phase discharge plasma technology, liquid-phase discharge plasma technology does not require additional gas or other conditions. Therefore, the operation of liquid-phase discharge plasma is simpler, and the actual cost of wastewater treatment is lower. A microwave discharge is generated by an electromagnetic wave with a frequency of over 2.45 GHz (wavelength $\lambda = 12$ cm). Electromagnetic energy is introduced into the plasma in the discharge electrode using coaxial waveguides [11–13]. The microwave discharge generates an alternating electric field. The transport of reactive species produced by traditional discharge plasma water treatment technology needs to be from gas to liquid, which leads to the loss of some short-lived reactive species during transport. However, MDPL technology has the advantage of a high mass transfer efficiency, and the reactive species produced in the discharge process do not require gas-liquid mass transfer. They can act directly on pollutants in the liquid phase. Therefore, MDPL technology is advantageous for the treatment of pollutants in water.

To clarify the application prospects of MDPL in water treatment, the discharge performance, practical application, and pollutant degradation mechanism of MDPL were studied in this work. The effects of microwave power, solution conductivity, solution pH, and Fe^{2+} on the amount of reactive species during the MDPL water treatment are discussed. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are typical refractory perfluorinated compounds (PFC) found in water pollution. In this study,

they were treated by MDPL, and the contribution of reactive species to the degradation of these pollutants was explored. Finally, the possible pathways and mechanisms of the MDPL degradation of pollutants were analyzed.

2. Analytical methods and calculation

The MDPL device is illustrated in figure 1. The microwave generator was an industrial microwave power supply (1 kW) with a microwave discharge frequency of 2.45 GHz. Electrodes were mounted at the bottom of the stainless-steel reactor, and the total volume of the reactor was 2.5 L. The top of the reactor was equipped with a transparent lid and an observation window on the right side. After the reactor was closed, a vacuum pump was connected to maintain a negative pressure in the reactor. The pressure inside the reactor was measured using a pressure gauge. After the power supply was connected, the microwave was transmitted to the electrode through the waveguide assembly and coaxial cable for discharge. The discharge process was monitored using emission spectrometers, computers, and high-definition cameras.

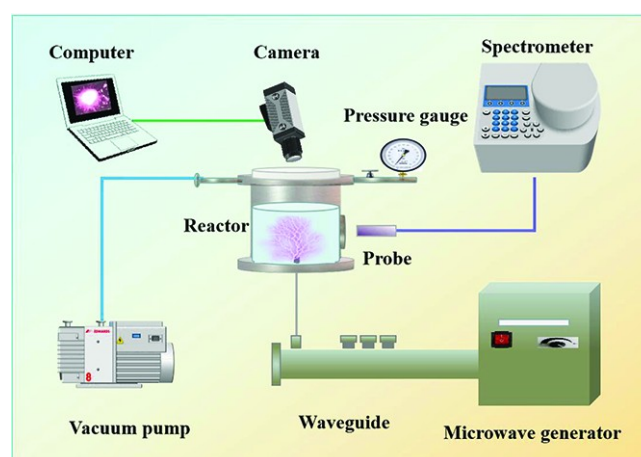


Figure 1. Schematic diagram of the MDPL system.

When the MDPL treats pollutants, the organic solution is poured into the reactor, which is then covered with a lid. When the reactor was in an airtight state, the vacuum pump was turned on. Finally, the power supply was turned on, the power was adjusted after ignition, and discharge was observed through the observation window. The camera recorded the experimental discharge-flame conditions. The probe of the spectrometer was placed in the visual area to detect the active material produced by discharge. After sampling, the concentration of the treated product was analyzed using liquid chromatography, liquid chromatography-mass spectrometry, and other detection equipment.

Fluoride ion concentration was detected by fluoride-ion-selective electrodes. Detection range is 1×10^{-1} – 1×10^{-6} mol/L. Ag/AgCl was used as the internal reference electrode. The concentrations of PFOA and PFOS were determined by liquid chromatography-mass spectrometry (Thermo Scientific, US). Chromatograph is Dinonex Ulti-

mate 3000 UHPLC. The type of chromatographic column is C_{18} (100 mm×4.6 mm, 3.5 μ m), and column temperature is 30 °C. The concentration of H_2O_2 was determined using titanium sulfate spectrophotometry (UV-5500PC). The samples to be tested were matched with the titanium sulfate reserve solution in proportion, and the absorbance at 410 nm was determined using an ultraviolet spectrophotometer after coloration [14].

2.1. Calculation formular

Defluorination

$$\text{Def} = \frac{C_{F^-}}{C_0 \times N_F} \times 100\%, \quad (1)$$

Def—Defluorination of PFC (%).

C_0 —Initial concentration of PFC (mg/L).

C_{F^-} —Concentration of F^- after treatment (mg/L).

N_F —Number of fluorine atoms in PFC.

Pseudo-first-order kinetic model.

$$\ln(C_t/C_0) = -kt, \quad (2)$$

C_0 —Initial concentration of PFC (mg/L).

C_t —Concentration of PFC after the treatment (mg/L).

2.2. Energy consumption efficiency of defluorination

$$G_{50-F} = \frac{\frac{1}{2}C_{F_0}(\text{mg/L}) \times V(\text{L})}{P(\text{kW}) \times t(\text{h})}, \quad (3)$$

G_{50-F} —Energy consumption efficiency of 50% defluorination (mg/kWh).

C_{F_0} —Initial concentration of fluorine (mg/L).

V —Volume of PFC solution (L).

P —Microwave input power (kW).

t —Treatment time required to achieve 50% defluorination (h).

2.3. Contribution rate

$$R_r = \frac{k_p - k_i}{k_p}, \quad (4)$$

R_r —Contribution ratio of reactive species (%).

k_p —Degradation kinetic constants of pollutant (min^{-1}).

k_i —Degradation kinetic constants of pollutant with inhibitor (min^{-1}).

3. Results and discussion

3.1. Discharge characteristics of MDPL

Figure 2 shows the spatiotemporal evolution of plasma excitation from a macro point of view. As shown in the figure, the bubble rises intermittently toward the liquid interface until it breaks. With the passage of time, in the process of continuous injection of microwave power into the reactor,

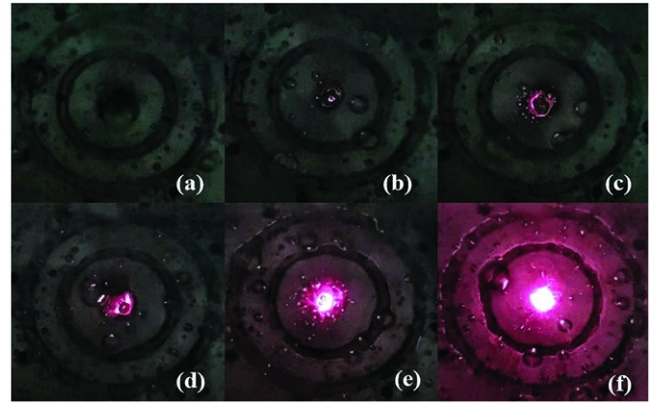


Figure 2. Spatiotemporal characteristics of plasma excitation process.

energy is continuously input, and the liquid medium in the reactor is heated and vaporized because of the absorbing energy. The volume of the bubbles in the reactor gradually decreased, and the number of bubbles increased significantly. The resulting bubbles will continue to rise owing to buoyancy and quickly become multiple small bubbles when they rise to a certain height, until they reach the liquid level and burst. Continuing to increase the microwave power until at some point, when the bubble passes through the tip of the electrode, the bubble is broken down and plasma is produced at the tip of the electrode. In other words, there is a so-called spark state when the plasma exhibits a magenta glow. With the continuous increase in microwave energy, the solution temperature in the reactor continues to rise, the liquid vaporization phenomenon gradually intensifies, and the solution in the whole reactor shows a state of rolling up and down, the water temperature rises from 20 °C to 47 °C. At this time, the frequency of the bubble passing through the electrode tip increased, which increased the probability of the bubble being broken down, and the discharge gradually changed from an unstable state to a steady state. The volume of the spark increased, and the color of the plasma became increasingly brighter. This is a change from figures 2(a)–(f).

3.2. Reactive species produced by MDPL

The treatment of organic pollutants mainly depends on reactive species with strong oxidation and reducibility, such as high energy electrons (e^*), hydrated electrons (e_{aq}^-), free radicals, H_2O_2 and so on [14, 15]. Therefore, to study the main reactive species produced by MDPL, an emission spectrometer (Hamamatsu Photonics Trading Co., model C7473) was used to detect free radicals produced by pure water during MDPL water treatment. An ultraviolet spectrophotometer was used to detect the concentration of H_2O_2 produced during the discharge. The microwave power was 100 W, and the aqueous solution volume was 400 mL. As shown in figure 3(a), $\bullet OH$, $\bullet H$, and $\bullet O$ are produced during the discharge process of the MDPL technology. These reactive species are produced because high-energy electrons (e^*) are produced during liquid-phase plasma discharge. It collides with the surrounding water to form a large number

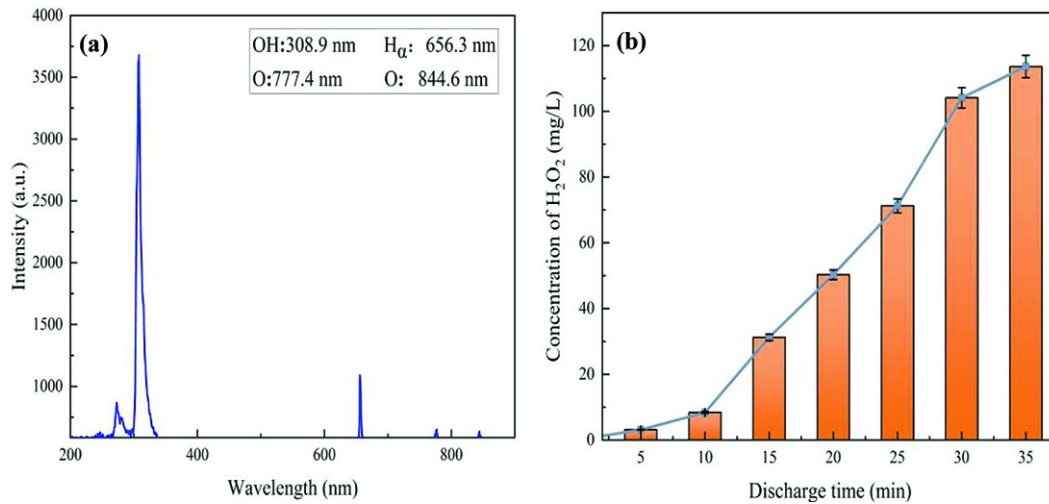
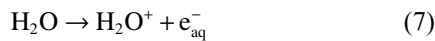
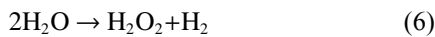
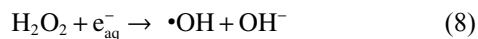


Figure 3. The main reactive species produced by MDPL. Detection of free radical (a) and H₂O₂ (b).

of reactive species, such as $\cdot\text{OH}$, $\cdot\text{H}$, $\cdot\text{O}$, H₂O₂, e_{aq}⁻ [16]. The main reactions are as follows (reactions (5)–(7)).



The emission spectrum of hydroxyl radical is a transition from the first excited state to the ground state $\text{A}^2\Sigma(\nu'=0) \rightarrow \text{X}^2\Pi(\nu'=0)$. The corresponding zero-order vibration spectrum had the strongest emission wavelength of 308.9 nm. The emission spectrum of the $\cdot\text{H}$ originated from the transition from the third excited state to the second excited state, and the corresponding wavelength of H α (3P \rightarrow 2S) was 656.3 nm. The emission spectrum of $\cdot\text{O}$ came from two excited state transitions, namely 3p³P \rightarrow 3s³S⁰ transition, wavelength of 844.6 nm and 3p³P \rightarrow 3s⁵S₂⁰ transition, wavelength of 777.4 nm [17, 18]. As shown in figure 3(b), H₂O₂ was produced during the discharge process. With increasing discharge time, the concentration of H₂O₂ increased. The H₂O₂ concentration reached 113.6 mg/L after 35 min of discharge. The slow increase in the H₂O₂ concentration after discharge for 30 min may be due to the reaction of H₂O₂ with water and electrons to form $\cdot\text{OH}$ and OH⁻. The main reaction is as follows:



3.3. Effect of microwave power

To explore the effect of the microwave power on the discharge of the MDPL. Discharge was carried out at 65 W, 75 W, 85 W and 100 W respectively. The amount of reactive species was then determined. The light intensity I_{ij} emitted by the transition from energy state i to state j is proportional to the number of atoms in excited state i [19]. The

formula is as follows:

$$I_{ij} = \alpha \cdot \nu_{ij} \cdot h \cdot c \cdot A_{ij} \cdot N_i, \quad (9)$$

where $\nu_{ij} \cdot h \cdot c$ is the energy of each quantum of light released by a particle with wavenumber ν_{ij} during transition. A_{ij} is the transition probability from energy state i to energy state j . N_i is the number of atoms (molecules) in energy state i . h is Planck's constant. c is the speed of light. α is the collection coefficient. In other words, the luminous intensity is proportional to the number of particles in energy state i , that is, proportional to the particle density. In our study, the α coefficient for each group of experiments was maintained at a certain level. The emission intensity is the number of free radicals that can be indirectly reflected. The volume of the aqueous solution used was 400 mL. From the detection results of figures 4(a) and (b), it can be seen that the contents of $\cdot\text{OH}$, $\cdot\text{H}$, $\cdot\text{O}$, and H₂O₂ all increase linearly with increasing microwave power. The magenta flame produced by the discharge becomes brighter with increasing microwave power, as shown in figure 4(c). The concentration of H₂O₂ also increases with increasing microwave power. After discharging for 30 min, the concentration of H₂O₂ was approximately 108 mg/L. This is because the increase in microwave power can increase the intensity of the plasma and accelerate the collision between high-energy electrons and water molecules, thus increasing the concentration of reactive species ($\cdot\text{OH}$, $\cdot\text{H}$, $\cdot\text{O}$, H₂O₂, e_{aq}⁻, etc.) [17]. In other words, a higher microwave power can promote the degradation of pollutants. However, the problem of energy consumption should also be considered in practical applications, and appropriate power should be used according to the degradation of pollutants.

3.4. Effect of conductivity

Electrical conductivity is an important parameter that affects discharge. To explore the effect of electrical conductivity on the reactive species in the process of MDPL discharge, the power constant was 100 W, and the conductivity were

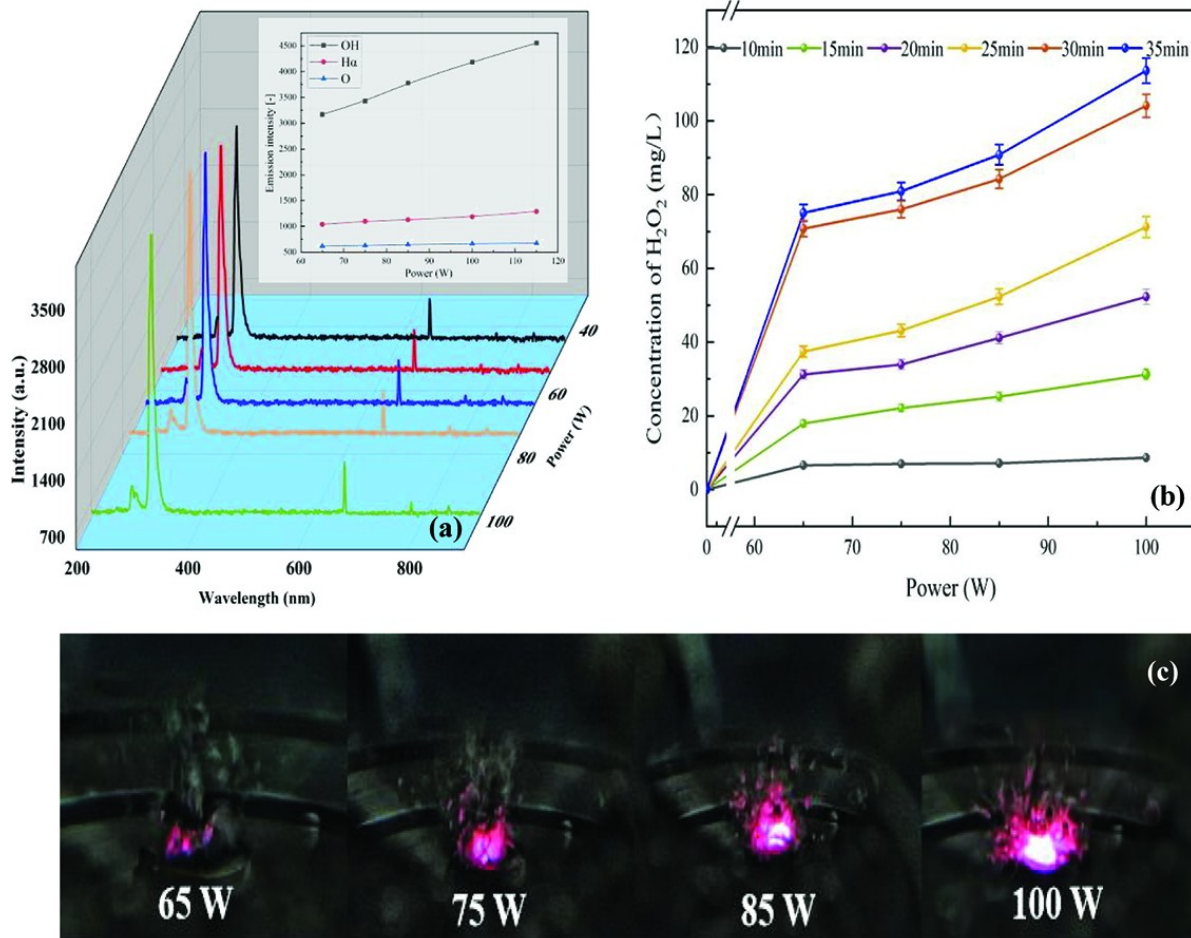


Figure 4. Effect of power on the reactive species of MDPL. Detection of free radical (a) and H₂O₂ (b). Effect of power on discharge morphology (c).

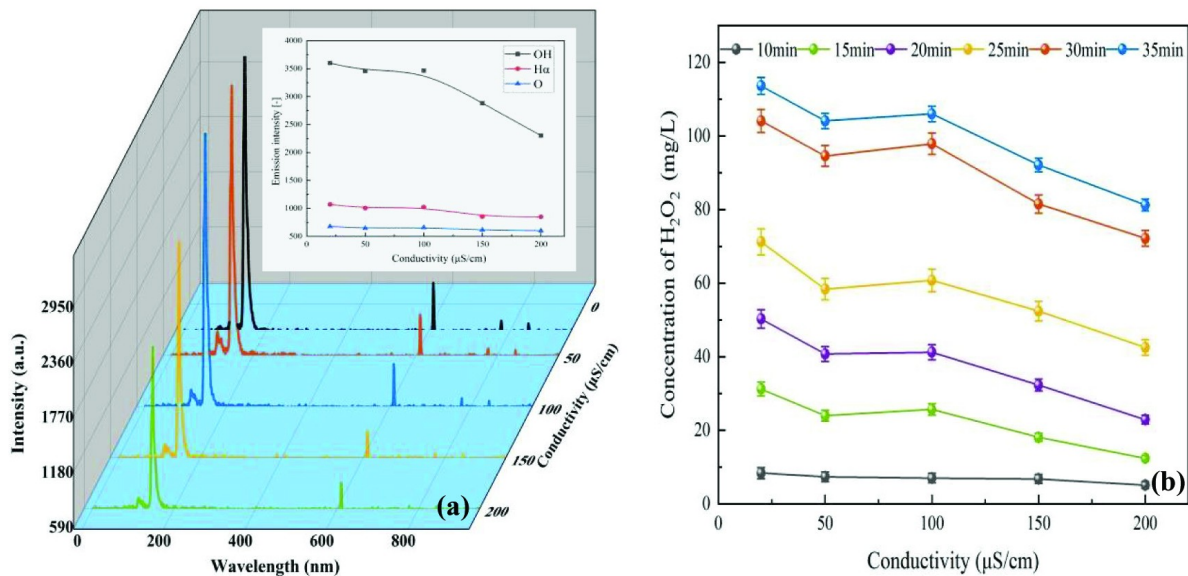


Figure 5. Effect of conductivity on reactive species of MDPL. Detection of free radical (a) and H₂O₂ (b). •OH: 308.9 nm, •H: 656.3 nm, •O: 777.4 nm, •O: 844.6 nm.

adjusted to 20, 50, 100, 150, and 200 μS/cm, respectively. The volume of the aqueous solution used was 400 mL. It can be seen from figure 5(a) that a conductivity of less than 100 μS/cm has little effect on the number of free radicals.

When the conductivity of the solution is more than 100 μS/cm, the amount of free radicals decreases, and the higher the conductivity, the more disadvantageous the production of free radicals. The same trend was observed in

figure 5(b). Although the yield of H_2O_2 fluctuated when the electrical conductivity was less than $100 \mu\text{S}/\text{cm}$, it changed slightly overall. When the conductivity of the solution was greater than $100 \mu\text{S}/\text{cm}$, the production rate of hydrogen peroxide was significantly lower than that when the conductivity was less than $100 \mu\text{S}/\text{cm}$. The higher the conductivity, the more disadvantageous the production of H_2O_2 . From the above experimental results, it can be seen that when the electrical conductivity of the solution exceeded $100 \mu\text{S}/\text{cm}$, the amount of reactive species decreased with an increase in electrical conductivity. This is because it is difficult to establish a strong electric field owing to the conductive effect of ionic current in highly conductive liquids. Moreover, the discharge intensity weakens again [20]. As the discharge intensity decreased, the plasma density decreased and the number of reactive species decreased. Combined with the influence of microwave power on the amount of reactive species in the previous section, an appropriate increase in microwave power can be considered to control the water environment with high conductivity to achieve the desired treatment effect.

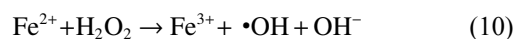
3.5. Effect of pH

The solution pH is an important parameter that affects the discharge. To explore the effect of acidity and basicity on the amount of reactive species in the MDPL discharge process, the power constant was 100 W, and the pH was adjusted to 4.0, 7.0, and 8.5. The volume of the aqueous solution used was 400 mL, all the conductivity was less than $100 \mu\text{S}/\text{cm}$. As shown in figure 6(a), the amount of the three free radicals did not change significantly under acidic and neutral conditions. Under alkaline conditions, the number of free radicals decreased, especially $\bullet\text{OH}$. Similarly, the production of H_2O_2 was similar under acidic and neutral conditions

(figure 6(b)), but lower under alkaline conditions. This is because H_2O_2 is acidic; therefore, it is consumed by a large amount of decomposition under alkaline conditions. In the discharge process, H_2O_2 reacts with hydrated electrons to form $\bullet\text{OH}$ (equation (8)). Therefore, when H_2O_2 decreased, $\bullet\text{OH}$ decreased. Similarly, H_2O_2 is relatively stable under acidic conditions and is more conducive to the formation of $\bullet\text{OH}$. Therefore, there was a greater mass of reactive species under acidic conditions. In other words, MDPL prioritizes the treatment of organic wastewater under acidic conditions.

3.6. Effect of Fe^{2+}

From the above studies, it is clear that H_2O_2 is produced during MDPL. In particular, under acidic conditions, the H_2O_2 content is higher. Under acidic conditions, the simultaneous presence of H_2O_2 and Fe^{2+} can result in a Fenton reaction. The Fenton process is an advanced oxidation technology that has unique advantages for the treatment of refractory organic pollutants [21, 22]. Thus, this is a promising wastewater treatment technology. Therefore, Fe^{2+} was added to the discharge system to introduce a Fenton reaction to further promote the removal of refractory pollutants. The Fenton reaction is as follows:



During the reaction, the discharge power was 100 W, the initial pH of the solution was 4.0 and the conductivity was $20 \mu\text{S}/\text{cm}$. The solution volume was 400 mL. As shown in figure 7(a), the $\bullet\text{OH}$ content increased significantly after adding Fe^{2+} (5 mg/L). This is because Fe^{2+} reacted with H_2O_2 to form $\bullet\text{OH}$, as shown in equation (10). Figure 7(b) shows that the H_2O_2 content in the reaction system with Fe^{2+} is significantly lower than that in the reaction system without Fe^{2+} . It is because H_2O_2 is removed during the Fenton

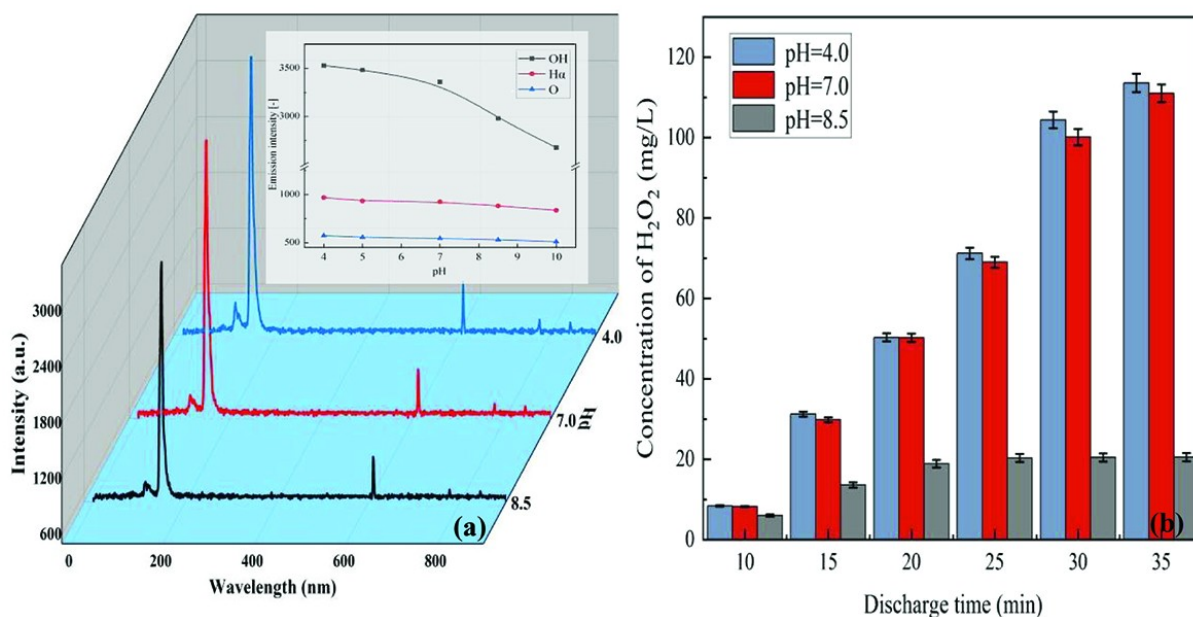


Figure 6. Effect of pH on reactive species of MDPL. Detection of free radical (a) and H_2O_2 (b). $\bullet\text{OH}$: 308.9 nm, $\text{H}\alpha$: 656.3 nm, $\bullet\text{O}$: 777.4 nm, $\bullet\text{O}$: 844.6 nm.

reaction to form •OH. Because the Fenton reaction produces a large number of •OH, which is very effective for the removal of organic pollutants; therefore, the introduction of the Fenton reaction can be considered in the process of MDPL water treatment to improve the removal rate of pollutants.

4. Treatment effect of MDPL on refractory organic matter wastewater

4.1. Degradation of PFOA and PFOS by MDPL

Per-fluorinated compounds (PFC) are persistent and refractory organic pollutants that have received significant attention in recent years. PFOA and PFOS are the most widely detected perfluorinated pollutants in aquatic environments [23]. PFOA and PFOS have high thermal and chemical stabilities. Both include C–F bonds, which are the strongest

covalent bonds in organic compounds [24]. Traditional water treatment technologies have a poor effect on the defluorination of PFOA and PFOS, which may lead to secondary pollution. The PFOA and PFOS solutions were discharged using the MDPL technology. MDPL was treated with different concentrations of PFOA and PFOS. The volume of the solution was 200 mL and the discharge power was 60 W. According to the best experimental parameters, the pH of the adjusted solution was always 4.0 and the electrical conductivity was always less than 100 μS/cm. As shown in figure 8 (a), low concentrations of PFOA and PFOS were more likely to be decomposed. After 100 min of discharge, the defluorination rates of PFOA and PFOS at an initial concentration of 4 mg/L were 96.8% and 88.6%, respectively. The defluorination rates of PFOA and PFOS at an initial concentration of 40 mg/L were 58.4% and 26.8%, respectively. This is because the amount of reactive species produced by discharge is certain, and the number of molecules that can effectively degrade pollutants is also certain; therefore, the

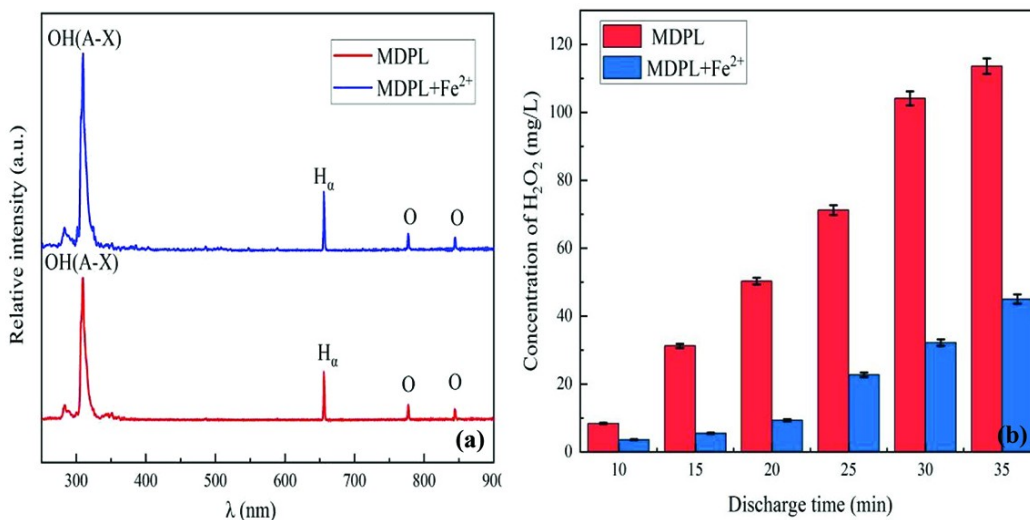


Figure 7. Effect of Fe²⁺ on reactive species of MDPL. Detection of free radical (a) and H₂O₂ (b)

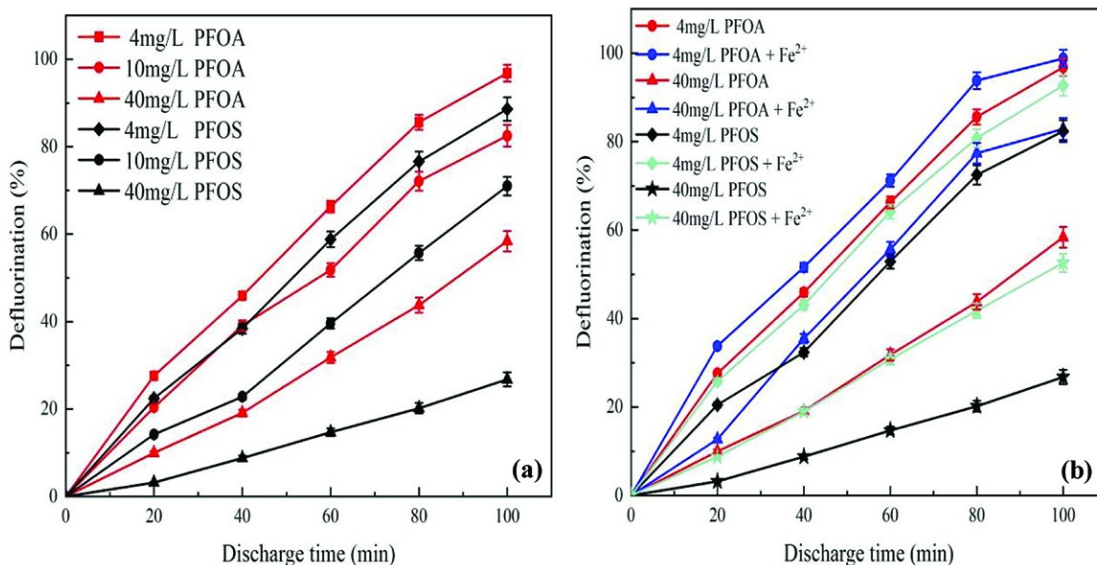


Figure 8. Defluorination rates of PFOA and PFOS by MDPL (a). Effect of Fe²⁺ on defluorination (b).

degradation effect of high-concentration pollutants is worse than that of low-concentration pollutants.

Previous studies have found that the amount of reactive species produced by the MDPL system increases after the introduction of Fe^{2+} . Thus, Fe^{2+} was added to the PFOA and PFOS discharge treatment. Figure 8(b) shows that with the addition of Fe^{2+} , the defluorination of both high and low concentrations of perfluorinated compounds significantly increased. After 100 min of discharge, the defluorination rates of PFOA and PFOS at an initial concentration of 4 mg/L were 98.8% and 92.7%, respectively. The defluorination rates of PFOA and PFOS at an initial concentration of 40 mg/L were 82.9% and 52.6%, respectively.

Table 1 compares the important parameters of degradation of the two types of PFC using different methods. The actual defluorination energy efficiency is not the removal energy efficiency but refers to the removal of F atoms in PFOA and PFOS. For perfluorinated compounds, the defluorination of PFOA and PFOS is much more difficult than their removal, but it is also more meaningful. Only thorough defluorination can reduce the secondary pollution of harmful fluorine-containing pollutants. According to formula 3, the energy consumption efficiency of 50% defluorination (G_{50-F}) of PFOA degraded by MDPL is 78.43 mg/kWh, PFOS is 42.19 mg/kWh. The results showed that MDPL technology has more advantages than other technologies in terms of defluorination and defluorination energy efficiency. This shows that the treatment effect of MDPL technology on the two types of PFC is more thorough, cleaner, and more efficient than other technologies.

4.2. Contribution rate of reactive species

To explore the main reactive species in the degradation of the two perfluorinated compounds using MDPL technology, inhibitor experiments were carried out. Tert-Butanol (TBA) was used as the trapping agent for $\bullet\text{OH}$. $\bullet\text{H}$ used ethanol (EtOH) as the trapping agent. $^1\text{O}_2$ uses furfuryl alcohol (FFA) as trapping agent. e_{aq}^- used NaNO_3 as the trapping agent [30]. As shown in figures 9(a) and (b), e_{aq}^- has the greatest influence on the defluorination of PFOA and PFOS, followed by $\bullet\text{OH}$, $\bullet\text{H}$, and $^1\text{O}_2$.

To determine the specific contribution rates of several reactive species, we calculated using formula 4 [31], and the results are shown in figures 9(c) and (d). For PFOA defluorination, the contribution rates of e_{aq}^- , $\bullet\text{OH}$, $\bullet\text{H}$, and $^1\text{O}_2$ are 56.9%, 20.7%, 12.1% and 6.9%, respectively. For PFOS defluorination, the contribution rates of e_{aq}^- , $\bullet\text{OH}$, $\bullet\text{H}$, and $^1\text{O}_2$ are 56.7%, 23.8%, 13.3% and 4.1%, respectively. This shows that e_{aq}^- has the greatest contribution to the degradation of the two kinds of PFC, followed by $\bullet\text{OH}$, and finally $\bullet\text{H}$ and $\bullet\text{O}$. This is consistent with previous studies showing that e_{aq}^- is indeed the key reactive species for the defluorination of the PFC [32]. From the results, it can be seen that in addition to the above four reactive species, there are other reactive species that contribute 3.4% to PFOA defluorination and 2.3% to PFOS. According to relevant literature, it is speculated that it may be defluorinated by the direct collision of high-energy electrons (e^*) with pollutant molecules.

5. Mechanism of contaminant removal by MDPL

Based on previous studies of liquid-phase discharge and the characteristics of reactive species produced by MDPL, the mechanism of MDPL removal of organic pollutants was speculated (figure 10(a)). First, the liquid-phase plasma method produces high-energy electrons (e^*) in the discharge process, and the high-energy electrons can directly collide with the pollutant molecules to decompose part of them. Simultaneously, e^* collides with surrounding water molecules to form a large number of reactive species, such as $\bullet\text{OH}$, $\bullet\text{H}$, $\bullet\text{O}$, and e_{aq}^- [33, 34]. As can be seen from the above experiments, the degradation and defluorination of PFOA and PFOS mainly depend on e_{aq}^- but also require $\bullet\text{OH}$. In addition to the above path, MDPL is accompanied by ultraviolet radiation, which acts on H_2O_2 to produce $\bullet\text{OH}$. $\bullet\text{OH}$ may act on the pollutant to decompose it. The MDPL discharge is also accompanied by photolysis, which leads to the decomposition of organic pollutants.

Figure 10(b) shows the mechanism of MDPL degradation of PFOS and PFOA. According to the characteristics of the reactive species produced by MDPL and the contribution rates of several reactive species to the degradation of

Table 1. The comparison of the important parameters of degradation of PFC by different technologies.

Method	Concentration (mg/L)	Volume (mL)	Defluorination rate (%)	G_{50-F} (mg/kWh)	Reference
Photocatalytic	5 mg/L PFOA	50	50% in 4.2 h	1.31	[25]
Photocatalytic	50 mg/L PFOA	1000	19% in 12 h	-	[26]
Electrochemical	3.39 mg/L PFOA	1000	50% in 4.3 h	7.11	[27]
Ultrasonic	2.9 mg/L PFOS	1000	50% in 3 h	1.24	[28]
Pulsed plasma	30 mg/L PFOA	300	50% in 2 h	57.71	[9]
DC plasma	41.4 mg/L PFOA	20	50% in 0.5 h	25.96	[29]
MDPL	4 mg/L PFOA	200	50% in 0.65 h	10.25	This work
MDPL	4 mg/L PFOS	200	50% in 0.77 h	8.65	This work
MDPL	40 mg/L PFOA	200	50% in 0.85 h	78.43	This work
MDPL	40 mg/L PFOS	200	50% in 1.58 h	42.19	This work

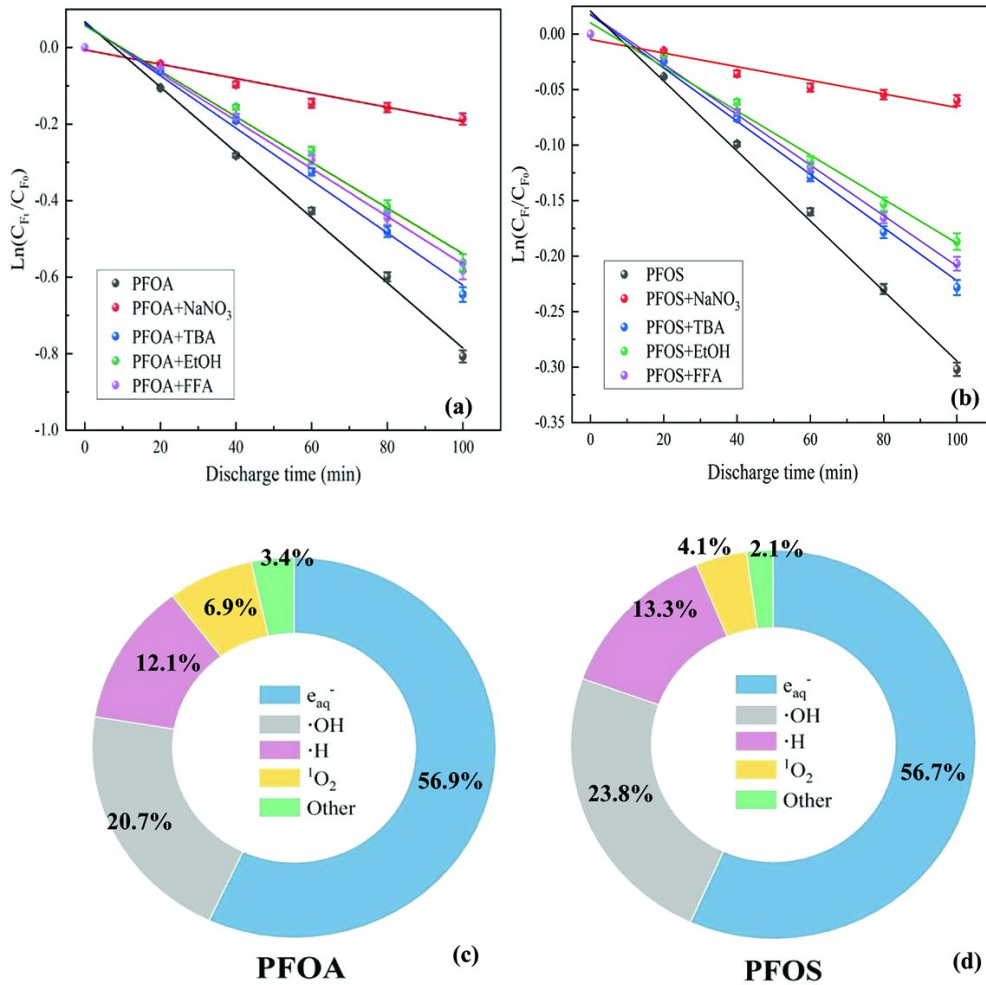


Figure 9. Reactive species trapping experiments of PFOA (a) and PFOS (b). Reactive species contribution rate of PFOA (c) and PFOS (d).

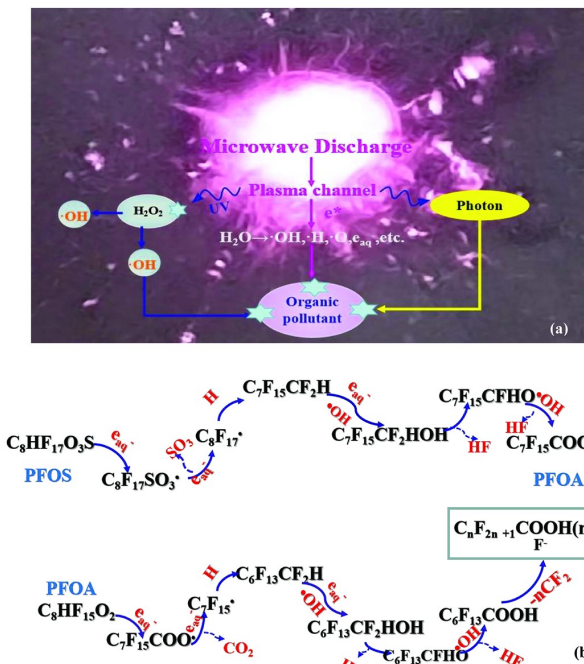


Figure 10. Generation of reactive species (a) and the degradation mechanism of PFOA and PFOS (b).

PFOA and PFOS, e_{aq}^- is the key reactive species for the defluorination of these two perfluorinated compounds. Previous studies have shown that e_{aq}^- is the first to destroy the stable structures of PFOS and PFOA [33]. It removes sulfonic groups from PFOS and carboxyl groups from PFOA. PFOS evolves into PFOA in the subsequent process. e_{aq}^- attacks the carboxyl group of PFOA, causing it to lose its stable structure, and then $\cdot OH$ plays a role in the subsequent defluorination process. CF_2 successively decreased to form short-chain carboxylic acids.

6. Conclusion

A recent review of related technical studies on refractory organic pollutants found that reactive species produced during treatment are crucial for the degradation of pollutants. In this study, the discharge characteristics of a new water treatment technology (MDPL) were studied. It is clear that several reactive species are produced in the process of discharge, such as $\cdot OH$ and e_{aq}^- . Under the optimal conditions, the defluorination of PFOA and PFOS achieved good results, and the defluorination efficiency was also outstanding. The defluorination of PFOA was 98.8%. The defluorina-

tion of PFOS was 92.7%. Through emission spectrometry and free-radical capture experiments, e_{aq}^- was found to be the key reaction species for the decomposition and defluorination of PFOA and PFOS, with contribution rates of 56.9% and 56.7%, respectively, and the contribution rates of \bullet OH reached 20.7% and 23.8%, respectively. Considering the discharge characteristics of reactive species and their effect on refractory perfluorinated compounds, MDPL has certain advantages as a new type of water treatment technology.

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