Destruction of Perfluorooctanoic acid (PFOA) in water by cold atmospheric plasma

Konstantia Papalexopoulou[1,2], Avner Ronen[3] and Christos A. Aggelopoulos[1]*

[1] Laboratory of Cold Plasma and Advanced Techniques for Improving Environmental Systems, Institute of Chemical Engineering Sciences, Foundation for Research and Technology Hellas (FORTH/ICE-HT), GR-26504 Patras, Greece

[2] Department of Chemistry, University of Patras, GR-26504, Patras, Greece

[3] Ben-Gurion University of the Negev, Department of Desalination & Water Treatment (DWT), POB 653, Beer-Sheva, Israel

*corresponding author: e-mail: caggelop@iceht.forth.gr

Abstract Cold atmospheric plasma was investigated as for the remediation of perfluorooctanoic acid (PFOA) contaminated water. The destruction of the highly toxic PFOA is a challenging task since it is a persistent and bioaccumulative chemical causing pollution in waterbodies. In this study, plasma experiments were conducted in a gas-liquid DBD (GLDBD) reactor, driven by high voltage microsecond pulsed generator. The effect of different critical parameters such as the treatment time and the plasma gas were investigated towards the degradation of PFOA in water. It was observed that air has a better performance compared to argon. In particular, a complete degradation of PFOA (>99.9%) was noticed with the air-GLDBD reactor after 30 min of treatment with the corresponding electrical energy per order (E_{EO}) being ~900 kWh/m^3.

Keywords: Per- and polyfluoroalkyl substances (PFAS), cold atmospheric plasma (CAP), wastewater treatment, dielectric barrier discharge (DBD), reactive oxygen and nitrogen species (RONS)

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals containing organo-fluorine compounds with stable C−F bonds. Perfluorooctanoic acid (PFOA) is considered as one of the most notorious PFAS, which is widely used in many industrial and commercial products (Raj Kamal Singh, et al., 2019). The large dissociation energy of C-F bond (485 kJ/mol) in the molecule of PFOA provides important properties (chemical and thermal stability, etc.), while on the other hand making its degradation very challenging. Recent studies have indicated its high persistence in the environment, being extensively found in waterbodies (Jiushan Cheng, et al., 2022). This leads to many potential effects on human health like congenital disabilities, infertility and reduced immune function. Many conventional water remediation methods have been applied so far for the degradation of PFOA in water, including biodegradation, membrane separation and photocatalysis (Dahai Zhu, et al., 2022). Nevertheless, there are several disadvantages in these methods such as limited PFOA removal, high energy consumption, extended treatment time and secondary pollution.

Currently, Cold Atmospheric Plasma (CAP) is regarded as a fast, cost-effective and environmentally friendly method, based on the production of highly reactive oxygen and nitrogen species (RONS), UV photons and hydrated electrons, able to successfully destruct organic pollutants present in water. In this study, PFOA contaminated water was treated by a gas-liquid dielectric barrier discharge (DBD) plasma reactor. The optimum operational conditions were identified by examining parameters like treatment time, plasma gas and energy consumption were explored.

2. Experimental section

2.1. Materials and chemicals

Perfluorooctanoic acid (PFOA, purity 95%, Sigma Aldrich) was used without any purification. Ultrapure water was used for the preparation of PFOA solution. Dry air and argon were purchased by Linde (Athens, Greece).

2.2 Experimental set up

The experimental-setup (Fig. 1) includes the plasma reactor, a microsecond pulsed high voltage power supply (Leap100, PlasmaLeap Technologies), the instrumentation for the electrical characterization and a

feeding gas setup. For the electrical characterization a digital oscilloscope (Rigol MSO2302A) was used which was connected with current and voltage probes (Pearson electronics 2877 and Tektronix P6015A, respectively). Experiments were conducted with a plane-to-plane gas-liquid dielectric barrier discharge (GLDBD) reactor (Fig. 2). The treated volume inside the GLDBD reactor was 15 mL. The plasma treated PFOA samples were analyzed by LC-MS-MS Agilent Infinity 1260 LC coupled to Ultivo MS-MSLC-MS/MS.
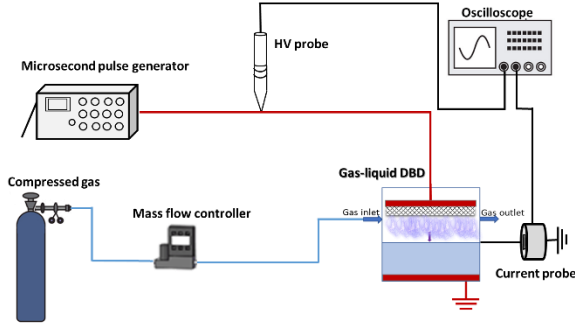

Figure 1: The general setup of the cold plasma-based treatment of PFOA.
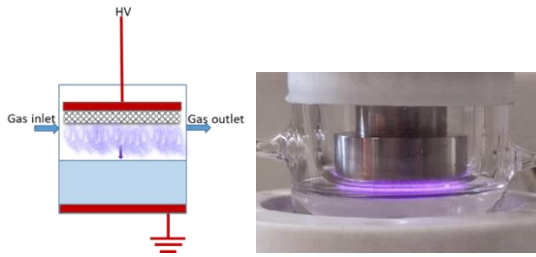

Figure 2: Sketch diagram (left) and real image (right) of the gas-liquid dielectric barrier discharge (GLDBD) reactor.

2.3 Treatment conditions

In each treatment, the initial PFOA concentration in distilled water was 10 mg/L and the gas (air and/or argon) flow rate was selected as 1.0 L min^{-1}, based on previous experience (C.A. Aggelopoulos, 2020). For this microsecond-pulsed system (MSP), the DBD experiments were performed at pulse voltage 20.0 kV and pulse frequency 1000 Hz whereas the treatment time varied from 5 to 30 min. For the calculation of the degradation efficiency, $D(\%)$, the following equation was used:

$$D(\%) = \left[\frac{C_0 - C_f}{C_0}\right] \times 100$$

where C_0 and C_f is the concentration of PFOA before and after plasma treatment, respectively.

3. Results and discussion

3.1 Electrical characterization and energy consumption of the pulsed microsecond DBD

Typical voltage and current high voltage micropulses recorded during the PFOA treatment inside the GLDBD reactor are presented in Fig. 3. It consists of multiple pulses with maximum amplitude of voltage and current being 20 kV and ~350 mA, respectively. The pulse energy (E_p) dissipated in the reactor was calculate by the equation.

$$E_p = \int_{pulse} P(t)dt = \int_{pulse} V(t)I(t)dt$$

By multiplying pulse repetition frequency f by the average pulse energy we calculate the mean discharge power P:

$$P = fE_p$$

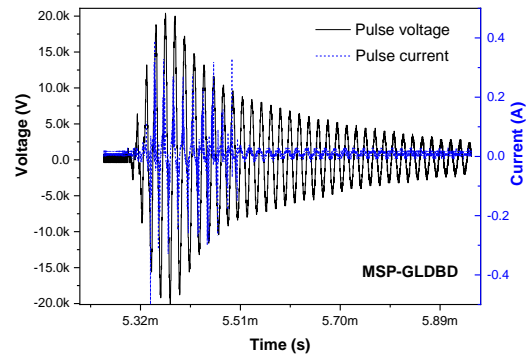For the GLDBD reactor a discharge power of ~60 W was calculated.

Figure 3: Instantaneous voltage and current waveforms of the microsecond pulsed-high voltage.

3.2 Effect of plasma gas on PFOA degradation in water

A crucial parameter that affects the plasma-based remediation approach is the plasma feeding gas. PFOA degradation was examined under air atmosphere where hydrated electrons e_{aq-} and a plethora of different plasma RONS is produced (e.g. $\cdot$OH, O_3, $^1O_2$, $O_2^{\cdot-}$, H_2O_2, NO_2^-/NO_3^-, $ONOO^-$) and then the results were compared to those obtained for PFOA degradation under argon atmosphere where mainly $\cdot$OH, H_2O_2 and e_{aq-} are generated. In Fig. 4 the degradation efficiency of PFOA is presented as a function of treatment time under air and argon atmospheres. Obviously, PFOA degradation was higher during air-GLDBD treatmemnt compared to that during argon-GLDBD treatment. After 15 min of plasma treatment, PFOA was degraded by ~92% and ~44% under air-GLDBD and argon-GLDBD, respectively. It is

noteworthy that after 30 min of treatment, PFOA was completely degraded (>99.9%) inside air-GLDBD reactor whereas a respectable PFOA degradation (~65%) was achieved for argon-GLDBD. These results highlight the important role of $\cdot$OH and e_{aq-} on PFOA degradation but also the significant contribution of other plasma RONS (e.g. NO_2^-/NO_3^-, $ONOO^-$) generated solely under air atmosphere.
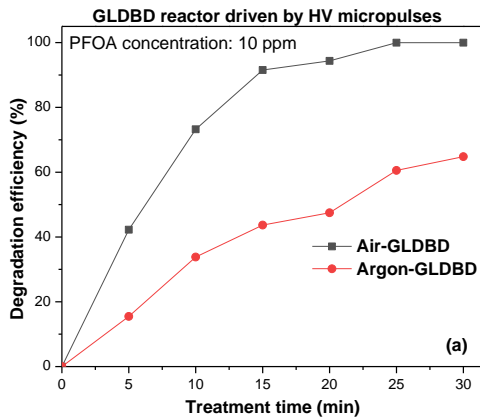

Figure 4: The PFOA degradation efficiency as a function of treatment time for different plasma gases (conditions: discharge frequency: 1000 Hz, pulse voltage: 20 kV, gas flow rate: 1.0 L/min, initial PFOA concentration: 10 ppm).

3.3 Electrical energy per order of GLDBD

The electrical energy per order (E_{EO}) expressed in kWh/m^3, is the electrical energy, that is needed for the contaminant degradation by one order of magnitude in 1 m^3 of contaminated water:

$$E_{EO} = \frac{Pt}{V log(\frac{C_0}{C})}$$

where P is the dissipated in the reactor power, V the solution volume, and t is the treatment time. The electrical energy per order (E_{EO}) for this air-GLDBD system was equal to ~900 kWh/m^3.

4. Conclusions

A gas-liquid DBD reactor driven by microsecond pulses, was examined for the removal of PFOA in water. Firstly, the electrical characteristics of the discharge were investigated and the energy consumption of the system was calculated (~60 W). Results have shown that a completely PFOA degradation (>99.9%) was achieved within 30 min under air-GLDBD. On the other hand, a sufficient PFOA degradation (~65%) was achieved for argon-GLDBD at the same treatment time. In this way the important role of $\cdot$OH, e_{aq}^- and other plasma RONS (e.g. NO_2^-/NO_3^-, $ONOO^-$) on PFOA degradation was demonstrated. Also, for the air-GLDBD system the electrical energy per order (E_{EO}) was estimated to ~900

kWh/m^3. This study is a preliminary effort to develop a competitive cold plasma remediation solution for PFAS contaminated water.

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