

Decomposition of Perfluorooctanesulfonate (PFOS) by Multiple Alternating Argon Plasmas in Bubbles with Gas Circulation

H. Obo, N. Takeuchi, and K. Yasuoka

Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, Japan

Abstract—Perfluorooctanesulfonate (PFOS) is used in a wide range of industrial applications, owing to its superior characteristics; however, its environmental persistence and biopersistence have become matters of concern, leading to the demand for decomposition treatments for industrial effluent containing PFOS. Although it is possible to decompose PFOS using direct current plasma generated within bubbles in water, low time and energy efficiencies arising from ballast resistance losses are major issues. This paper reports on the development of a reactor for generating plasma, with the number of treatment holes increased from one (in previous studies) to 21. Decomposition of 1 L of PFOS in 1200 min was successfully completed using this reactor, with a mass balance of fluorine reaching 90% or more over time. Furthermore, loss of ballast elements, which are used to stably generate electrical discharge, was significantly reduced by switching from resistors to capacitors. The exhaust gas from the reactor was recirculated through the treatment holes to successfully reduce the gas consumption flow rate to approximately 10% that of conventional systems.

Keywords—Perfluorooctanesulfonates (PFOS), plasma, water treatment, organic fluorine

I. INTRODUCTION

Perfluorooctanesulfonates (PFCs), exemplified by perfluorooctanesulfonate (PFOS) ($C_8F_{17}SO_3H$), have been used in a variety of industrial applications such as surface treatment agents for lenses and resistors on semiconductors owing to their chemical stability and favorable surface activity. However, PFCs, which have long chains with long spans of carbon gaps, have been confirmed to be environmentally [1, 2] and biologically persistent [3, 4]. In addition, their toxicity and carcinogenicity [8] are matters of concern.

PFCs have been detected in ocean fish and in rivers that are used as sources of drinking water in various regions in Europe [5] and Asia [6, 7], and attempts have been made to remove them from the effluent produced by semiconductor manufacturing plants and similar plants. However, although the PFOS contained in effluent can be collected and removed by ion exchange membranes [9] or reverse osmosis membranes [10], it is necessary to remove the separated PFOS molecules by decomposition through some other means.

Decomposition methods such as photochemical decomposition [11, 12], ultrasonic cavitation decomposition [13], vacuum ultraviolet decomposition [14], persulfate chemical decomposition [15], and microwave discharge decomposition [16, 17] have been proposed; however, they have issues such as low decomposition energy efficiencies and low processing capacities.

We succeeded in performing highly efficient decomposition of PFOS using plasmas generated within bubbles in water [18-20]. It is possible to generate these plasmas by applying a high-voltage direct current at

several kilovolts across the bubbles. Because organic fluorine compounds such as PFOS have high surface activity and adhere to air bubbles, it is possible for plasmas within bubbles to selectively decompose organic fluorine compounds [21]. Plasmas are in contact with air-liquid interfaces within bubbles [22] and are believed to decompose PFOS in water; however, because plasmas are generated within bubbles with diameters of approximately 4 mm, the contact surface of the plasmas is extremely small, which requires more time for the decomposition of the PFOS in larger amounts of effluent.

Furthermore, the problem of low energy efficiency exists for the entire circuit, because it is necessary to add a ballast resistance of several hundred kilohms to the circuit to generate plasmas using direct current in a stable manner; but the loss arising from this ballast resistance is several times that of the plasma electricity. Generating multiple plasmas in water is another method for accelerating the decomposition, but simply multiplying the current method only increases the amount of gas consumed when generating bubbles. It is therefore necessary to reduce the amount of gas consumed, while also improving time and energy efficiencies so as to improve the performance of PFOS decomposition.

We developed a reactor that circulates exhaust gas and is capable of generating 21 individual plasmas to decompose 1 L of PFOS in our study. The reactor developed utilizes capacitors instead of resistors (which are used in conventional systems) as ballast elements for generating plasmas in individual treatment holes in a stable manner. This method significantly reduces the modular loss of the ballast elements. The gas consumption flow rate is also reduced by approximately 10% by circulating the exhaust gas compared to not circulating it.

II. EXPERIMENTAL APPARATUS

A. Experimental Apparatus for PFOS Decomposition

The configuration of the system used for PFOS decomposition is shown in Fig. 1. The system comprised a plasma reactor, a high-voltage inverter power source, and a gas circulating mechanism. The plasma reactor was a cylindrical acrylic container, with a rated water processing volume of 1 L. The plasma reactor was equipped with a 1 mm-thick ceramic plate with 21 individual treatment holes (diameter 0.3 mm) installed on the bottom surface.

An overview of the ceramic plate is given in Fig. 2. Eight grounded electrodes made of stainless steel were installed in such a manner that they surrounded the 21 treatment holes. A discharge electrode and a capacitor were then placed at the lower section of the ceramic plate, as shown in Fig. 3. Stainless steel (SUS304) was used to make the discharge electrodes, which were positioned at a spacing of 0.5 mm from the ceramic plate. Furthermore, a 100 pF capacitor was connected between each discharge electrode and a high-voltage inverter. The electric current would then pass through the inverter, capacitor, discharge electrode, plasma, treated solution, grounded electrode, and then returned to the inverter.

A circuit diagram of the high-voltage inverter that applied voltage to the reactor is shown in Fig. 4. The inverter performed switching at a frequency of 20 kHz, outputting a high voltage via a transformer with a voltage-boosting ratio of 1:85. A MOSFET (FDA69N25) was used as the switching element for the inverter, with the dead time of the inverter at 1 μ s. The secondary leakage inductance of the transformer was 5 mH. A stabilized DC power supply (KIKUSUI, PWR400L) was used as the direct current power supply.

The gas circulating mechanism of the PFOS decomposition system consisted of a pump, a needle valve, and a flow-switching valve, which recirculated the exhaust gas from the upper section of the reactor through the treatment holes. The circulating flow rate of the gas was set at 1 L/min. To purge the flow channel of the reactor, 1 L/min of argon gas was supplied to the reactor from an argon cylinder and then released into the atmosphere during a 10 min interval prior to the generation of plasmas. The flow rate of the gas from the cylinder was then reduced from 1 L/min to 0.1 L/min, while the flow past the needle valve was switched to the side of the treatment holes to circulate the gas. To prevent the introduction of impurities (such as nitrogen in the air) into the flow channel during the experiment, 0.1 L/min of gas was supplied by the cylinder at all times. This gas was released using the safety valve located at the top of the reactor. To prevent evaporation of the solution during the experiment, the temperature of the solution was regulated by a cooling tube in the solution at a temperature of approximately 40°C.

Determination of the plasma electric power was accomplished by calculation using the secondary side voltage-ampere waveforms of the step-up transformer in the inverter circuit, the high-voltage probe (Tektronix

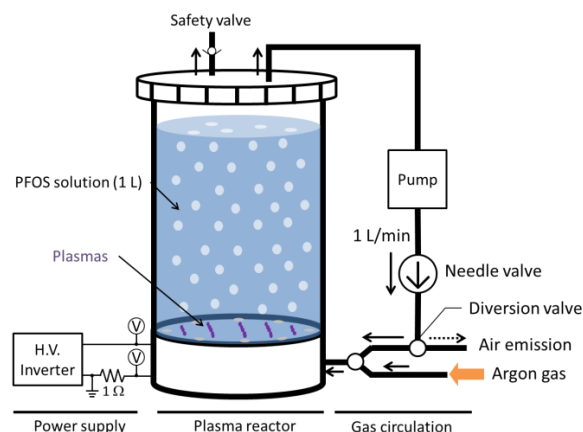


Fig. 1. Experimental setup used for PFOS decomposition.

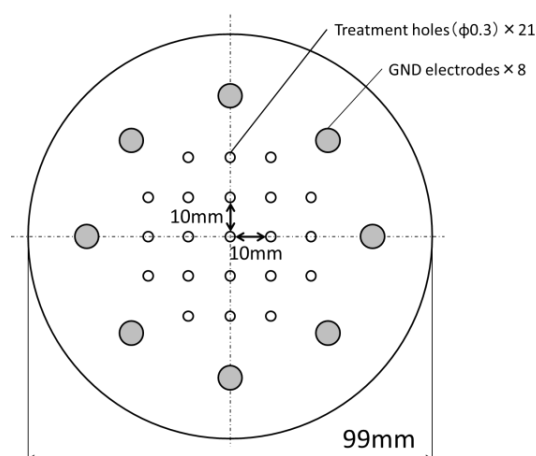


Fig. 2. Ceramic plate with 21 treatment holes and grounded electrodes.

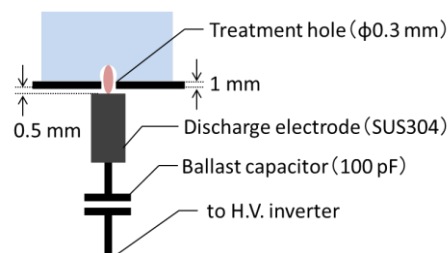


Fig. 3. Electrode configuration of each treatment hole.

P6015A) to measure the voltage at the inverter output, and the voltage probe (Tektronix P2220) to measure the voltage of the current-measurement resistor (1 Ω), and by taking the average of the respective products.

B. Experimental Conditions for PFOS Decomposition

The experimental conditions used in PFOS decomposition are displayed in Table I. The PFOS solution was regulated to ensure that the initial concentration was 50 mg/L using ultra-purified water (Milli-Q) and a PFOS specimen (Wako 515-28821). One liter of the PFOS solution was used. The treatment times were set to 1200 min, with a sampling of 1 mL performed at 120 min, 240 min, 360 min, and 1200 min

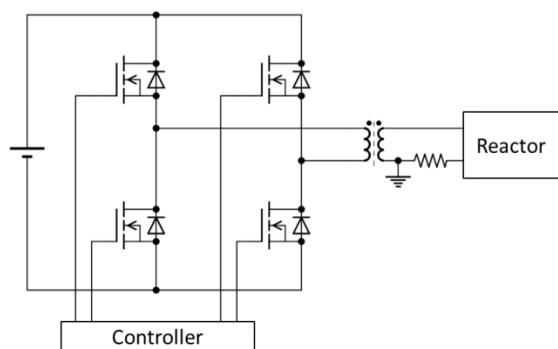


Fig. 4. Inverter circuit with step-up transformer.

TABLE I
EXPERIMENTAL CONDITIONS USED IN PFOS DECOMPOSITION

Parameters	Quantity
Solution	PFOS
Treatment quantity	1 L
Initial concentration	50.0 mg/L, 0.1 mmol/L
Initial conductivity	35 μ S/cm
Treatment time	1200 min
Circulation gas	Argon, 1 L/min
Average power	120 W
Switching frequency	20 kHz

TABLE II
MEASUREMENTS OF PFOS AND PFCAS BY LC/MS

Target	Formula	m/z
PFOS	$C_8F_{17}SO_3^-$	499
PFOA	$C_7F_{15}COO^-$	413
PFHpA	$C_6F_{13}COO^-$	363
PFHxA	$C_5F_{11}COO^-$	313
PFPeA	$C_4F_9COO^-$	263
PFBA	$C_3F_7COO^-$	213
PFPrA	$C_2F_5COO^-$	163
TFA	CF_3COO^-	113

into the treatment process. The discharge gas used was argon. The average electric power of the plasma during the experiment was 120 W.

Table II shows the formulas and mass-to-charge ratio (m/z) of PFOS ($C_8F_{17}SO_3^-$) and PFCAs ($C_nF_{2n+1}COO^-$, $n = 1-7$) as well as their by-products. The concentrations of PFOS and its by-products were measured using a liquid chromatography mass spectrometer (Shimadzu, LCMS-2020) with an RSpac JJ50-2D column. The mobile phase was a mixture of methanol, aqueous CH_3COONH_3 (50 mM), and ammonia (70 mM) with a flow rate of 0.2 mL/min. An electrospray ionization (ESI) mass spectrometry system was used to identify the intermediates in the treated solutions. Analyses were

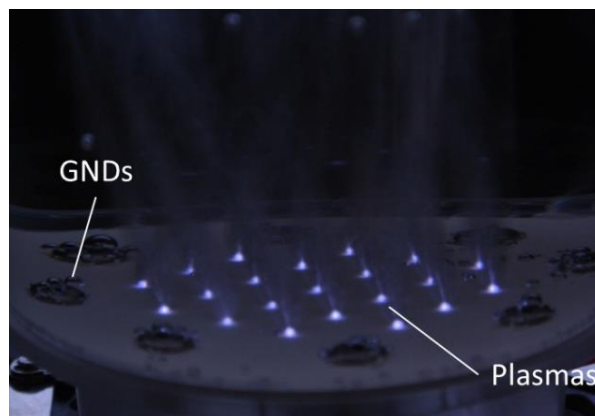


Fig. 5. Photograph of the 21 plasmas on the treatment holes (exposure time: 1 s).

carried out in negative-ion mode at an electrospray probe voltage of 1.2 kV.

C. Measurements of PFCs and Fluorine Ions

The concentrations of fluoride ions (F^-) were measured using ion chromatography (Metrohm, 861) with an SI-90 4E column. The mobile phase was an aqueous solution containing Na_2CO_3 (1.8 mM) and $NaHCO_3$ (1.7 mM) at a flow rate of 0.7 mL/min. For quantification of F^- concentrations, a standard solution (Wako, 133-11891) was used. After the predefined treatment time, the solution was removed from the reactor to be measured and treatment was restarted using the same solution.

III. EXPERIMENTAL RESULTS

A. Generation of 21 Plasmas with Gas Circulation

A photograph of the reactor during argon gas circulation is depicted in Fig. 5. It is clear that plasma is being generated at all of the 21 treatment holes. All of the generated plasmas were stable during all treatment time intervals. The flow rate of the argon gas consumed (to prevent the entry of nitrogen from the air, etc.) was 0.1 L/min. It was possible to reduce the gas flow rate consumed by approximately 10% of the gas flow rate necessary to generate bubbles using a gas circulation mechanism.

The voltage and the current waveforms of the inverter at treatment time intervals of 0 min and 300 min are shown in Figs. 6 and 7, respectively. Plasma generation began when the inverter voltage reached approximately 0 V. The average plasma electric power during the 1200 min of treatment was 120 W. Assuming that the electric power is distributed evenly over all treatment holes, then the plasma electric power at a single treatment hole can be assumed to have been approximately 5.7 W.

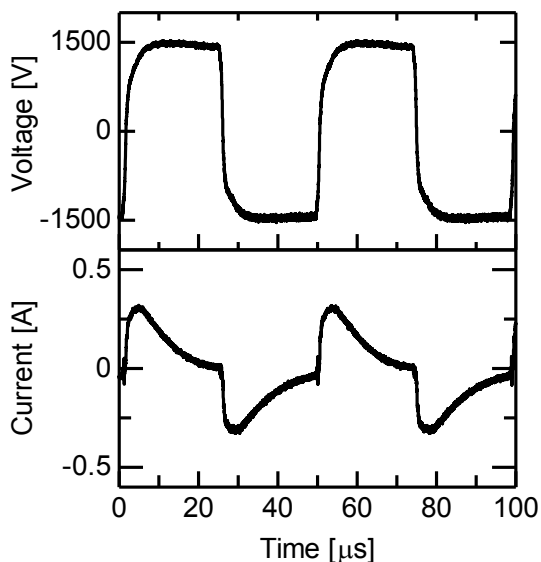


Fig. 6. Typical waveforms of the inverter voltage and current at 0 min.

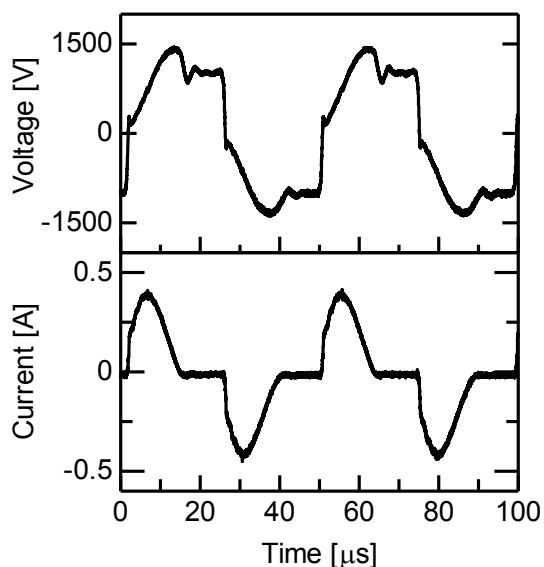


Fig. 7. Typical waveforms of the inverter voltage and current at 300 min.

B. Decomposition of PFOS by 21 Plasmas

The concentrations of PFOS and fluorine ions at different treatment times are shown in Fig.. Further, the concentrations of PFOS and fluorine ion in relation to the amount of electric power input to the reactor are shown in Fig.. The PFOS concentration decreased exponentially with the elapsed treatment time during plasma decomposition; the figure also shows a simultaneous increase in fluorine ion concentration.

The concentrations of PFOS and PFCAs in the treatment solution after 1200 min (2400 Wh) of treatment are listed in Table III. The concentration of PFOS decreased to 0.91 mg/L after 1200 min of treatment, indicating that 96% of the PFOS had successfully decomposed (relative to the initial concentration). Furthermore, the concentration of fluorine ions reached

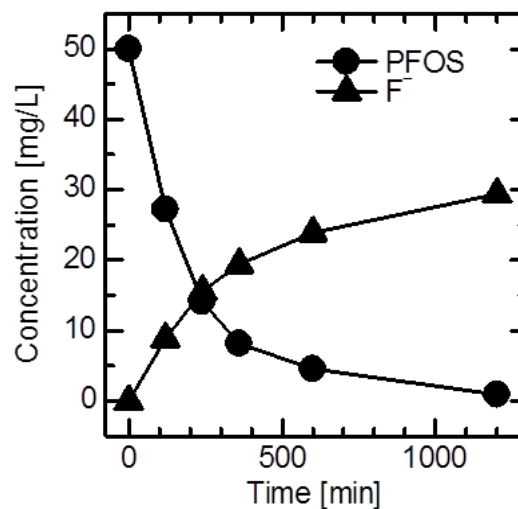


Fig. 8. Concentration of PFOS and fluoride ions as a function of treatment time for a 1 L PFOS solution treated with plasmas at 120 W.

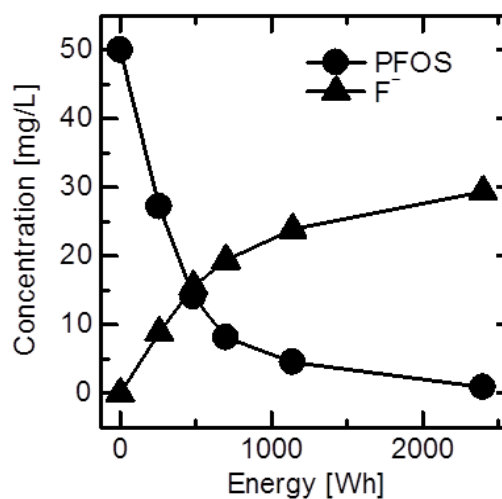


Fig. 9. Concentration of PFOS and fluoride ions as a function of plasma energy for a 1 L PFOS solution treated with plasmas at 120 W.

TABLE III
CONCENTRATION OF PFOS AND PFCAS AT 1200 MIN OF TREATMENT

Target	Concentration [$\mu\text{g/L}$]
PFOS	911.60
PFOA	23.70
PFHpA	10.60
PFHxA	8.55
PFPeA	1.25
PFBA	3.04
PFPrA	2.47
TFA	4.70

29.4 mg/L at 1200 min into the treatment. The concentrations of the various PFCAs were 0.5 mg/L or lower at all sampling times.

IV. DISCUSSION

A. Equivalent Circuit of the Plasma Reactor

The equivalent circuit of a single treatment hole in the plasma reactor is shown in Fig. 10. Each phase can be expressed in terms of both the plasma approximated using the ballast capacitor and Zener diode and the water resistance. A ballast capacitor was used at all treatment holes to generate plasma in a stable manner and to prevent losses, such as those due to the conventional resistance ballast, from occurring. The plasma inside the bubbles in water can be approximated using Zener diodes because the sustained voltage of the electric discharge is approximately 500 V when the electric current flows.

Following plasma generation, the circuit can be expressed as an LCR circuit, where L, C, and R are the leakage inductance (5 mH) of the transformer, the ballast capacitance, and the water resistance of the PFOS solution, respectively. The resonance condition of the circuit depends on the discriminant of the LCR circuit found using the following formula:

$$R < \sqrt{\frac{4L}{C}}$$

The voltage and current resonate if R is less than $\sqrt{4L/C}$. $\sqrt{4L/C}$ can be calculated as 3 k Ω when leakage inductance is 5 mH and total ballast capacitance is 2100 pF.

The water resistance represents the resistive component of water; thus, the water resistance was higher than 10⁴ Ω before the treatment because the electrical conductivity was low, only 35 $\mu\text{S}/\text{cm}$. The voltage and current of the inverter did not resonate, owing to high water resistance. However, as decomposition progressed and the fluorine and sulfate ions were released into the treated solution, the electrical conductivity of the treated solution reached approximately 420 $\mu\text{S}/\text{cm}$; the value of the water resistance was therefore less than 10³ Ω . The voltage in Fig. 7 changes slowly from 0 V because of the resonance between the leakage inductance of the transformer and the ballast capacitor.

B. Mass Balance of Fluorine

The mass balance of fluorine versus the treatment time is shown in Fig. 11. The mass balance of fluorine can be calculated using the following equation:

$$\text{M.B. (F)} = \frac{\text{Number of F moles in PFOS, PFCAs and F}^-}{\text{Number of F moles in PFOS before treatment}}$$

The mass balance continued to decrease until 300 min into the treatment, after which it began increasing again, finally reaching 92% at 1200 min. A potential

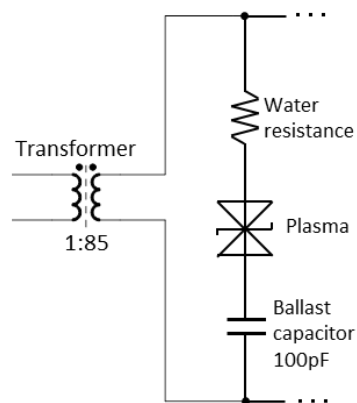


Fig. 10. Equivalent circuit of the plasma reactor.

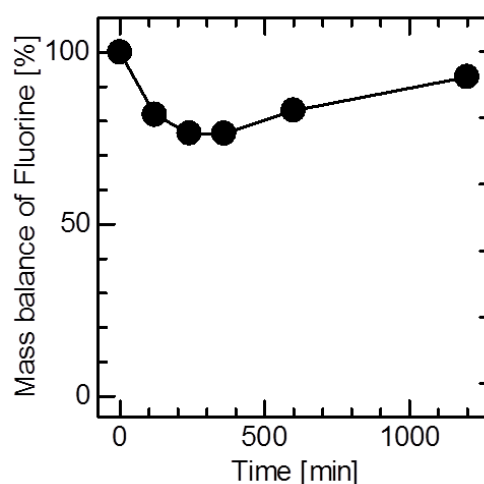


Fig. 11. Mass balance of fluorine as a function of treatment time.

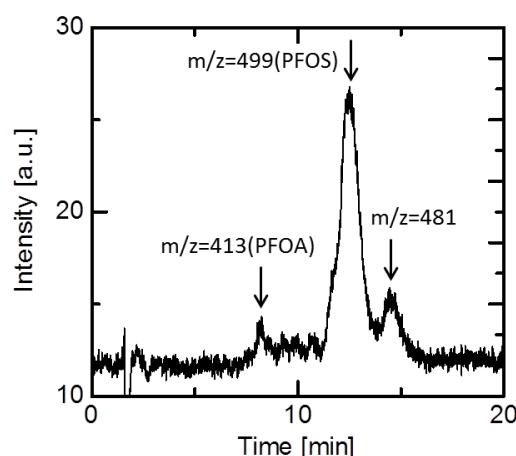


Fig. 12. TIC as a function of retention time.

cause for the increase in the mass balance of fluorine is the existence of a substance (which gradually decomposed to become fluorine ions) that had not been quantified in the treatment solution. Further, because the increasing mass balance trend from 300 min was

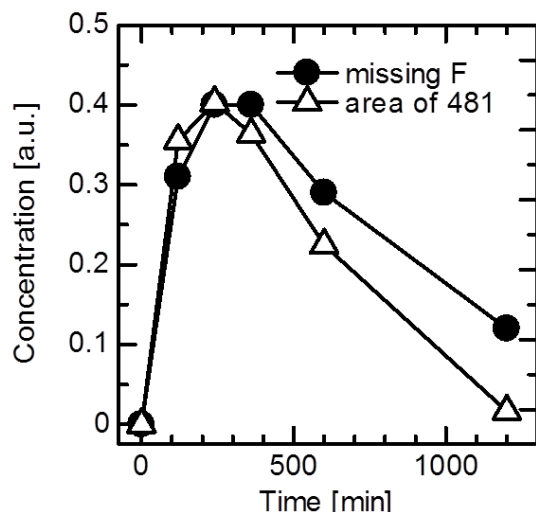


Fig. 13. Time evolution of the peak corresponding to $m/z = 481$.

smoother than the decreasing trend prior to 300 min, the unknown decomposition byproduct evidently had a lower decomposition velocity than PFOS. Therefore, at 360 min the treated solution was scanned in the range 10–500 m/z in an attempt to identify the unknown substances.

The total ion chromatogram (TIC) of the treated solution at 360 min into the treatment time is shown in Fig. 12. Peaks representing perfluorooctanoate (PFOA) at a retention time of 8 min ($m/z = 413$) and that of PFOS ($m/z = 499$) at a retention time of 12.4 min are confirmed. Furthermore, a relatively high peak ($m/z = 481$) is confirmed at a retention time of 14.5 min. These peaks clearly indicate that substances other than PFCAs, which have already been noted as a decomposition byproduct in the past, existed and the mass balance drops temporarily while these substances exist as intermediaries. Because their m/z is 481, these intermediaries are believed to be molecules with one of the carbon-fluorine bonds in a PFOS ($m/z = 499$) replaced by a hydrogen bond ($C_8F_{16}HSO_3^-$). Fig. 13 shows the time evolution of the peak area of $m/z = 481$. However, the concentration of $C_8F_{16}HSO_3^-$ cannot be measured quantitatively because there is no $C_8F_{16}HSO_3^-$ reagent; $C_8F_{16}HSO_3^-$ should be an intermediate product because the peak area changed in the same manner as the unknown amount of fluorine.

V. CONCLUSION

This paper reported on the development of an exhaust gas circulating type reactor with the number of treatment holes increased from one to 21 in order to accelerate the decomposition of PFOS. In the reactor developed, the conventional ballast resistors used to generate stable electrical discharges are replaced by capacitors to successfully generate 21 alternating current plasmas without introducing any ballast losses. Further,

these plasmas were used to decompose 1 L of PFOS, a representative organic fluorine compound. Ninety-six percent of the PFOS was successfully decomposed 1200 min into the treatment, with fluorine ion concentration at the point of 29.4 mg/L. The mass balance of the fluorine decreased temporarily, but increased again with increasing treatment time and converged to nearly 100%. The cause of this decrease in the mass balance is associated with intermediaries other than PFCAs that have already been suggested as a decomposition byproduct in the past. We believe that it is highly likely that these intermediary products are substances with $m/z = 481$ based on the chromatogram of the treated solution at 360 min into the treatment.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for JSPS Fellows Grant Number 10277.

REFERENCES

- [1] S. K. Kim, J. K. Im, Y. M. Kang, S. Y. Jung, Y. L. Kho, and K. D. Zoh, "Wastewater treatment plants (WWTPs)-derived national discharge loads of perfluorinated compounds (PFCs)," *Journal of Hazardous Materials*, vol. 201, pp. 82-91, 2012.
- [2] A. Pistocchi and R. Loos, "A map of European emissions and concentrations of PFOS and PFOA," *Environmental Science & Technology*, vol. 43, pp. 9237-9244, 2009.
- [3] M. G. de Vos, M. A. J. Huijbregts, M. J. van den Heuvel-Greve, A. D. Vethaak, K. I. V. de Vijver, P. E. G. Leonards, S. P. J. van Leeuwen, P. de Voogt, and A. J. Hendriks, "Accumulation of perfluorooctane sulfonate (PFOS) in the food chain of the Western Scheldt estuary: Comparing field measurements with kinetic modeling," *Chemosphere*, vol. 70, pp. 1766-1773, 2008.
- [4] K. Kannan, J. Koistinen, K. Beckmen, T. Evans, J. F. Gorzelany, K. J. Hansen, P. D. Jones, E. Helle, M. Nymen, and J. P. Giesy, "Accumulation of perfluorooctane sulfonate in marine mammals," *Environmental Science & Technology*, vol. 35, pp. 1593-1598, 2001.
- [5] R. Loos, J. Wollgast, T. Huber, and G. Hanke, "Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy," *Analytical and Bioanalytical Chemistry*, vol. 387, pp. 1469-1478, 2007.
- [6] A. Lin, S. Panchangam, and C. Lo, "The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers," *Environmental Pollution*, vol. 157, pp. 1365-1372, 2009.
- [7] B. R. Shivakoti, S. Tanaka, S. Fujii, P. H. L. Nguyen, M. Nozoe, C. Kunacheva, R. Okamoto, S. T. M. L. D. Seneviratne, and H. Tanaka, "Perfluorinated compounds (PFCs) in Yodo River system, Japan," *Water Science and Technology*, vol. 63, pp. 115-123, 2011.
- [8] I. Vassiliadou, D. Costopoulou, A. Ferderigou, and L. Leondiadis, "Levels of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in blood samples from different groups of adults living in Greece," *Chemosphere*, vol. 80, pp. 1199-1206, 2010.
- [9] D. J. Lampert, M. A. Frisch, and G. E. Speitel Jr, "Removal of perfluorooctanoic acid and perfluorooctane sulfonate from wastewater by ion exchange," *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, vol. 11, pp. 60-68, 2007.
- [10] C. Tang, Q. Fu, A. Robertson, C. Criddle, and J. Leckie, "Use of reverse osmosis membranes to remove perfluorooctane sulfonate

- (PFOS) from semiconductor wastewater," *Environmental Science & Technology*, vol. 40, pp. 7343-7349, 2006.
- [11] H. Hori, E. Hayakawa, H. Einaga, S. Kutsuna, K. Koike, T. Ibusuki, H. Kiatagawa, and R. Arakawa, "Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches," *Environmental Science & Technology*, vol. 38, pp. 6118-6124, 2004.
- [12] H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, and S. Kutsuna, "Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant," *Environmental Science & Technology*, vol. 39, pp. 2383-2388, 2005.
- [13] H. Moriwaki, Y. Takagi, M. Tanaka, K. Tsuruho, K. Okitsu, and Y. Maeda, "Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid," *Environmental Science & Technology*, vol. 39, pp. 3388-3392, 2005.
- [14] J. Chen and P. Zhang, "Photodegradation of perfluorooctanoic acid in water under irradiation of 254 nm and 185 nm light by use of persulfate," *Water Science and Technology*, vol. 54, pp. 317-325, 2006.
- [15] H. Hori, Y. Nagaoka, M. Murayama, and S. Kutsuna, "Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water," *Environmental Science & Technology*, vol. 42, pp. 7438-7443, 2008.
- [16] Y. C. Lee, S. L. Lo, P. T. Chiueh, Y. H. Liou, and M. L. Chen, "Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation," *Water Research*, vol. 44, pp. 886-892, 2010.
- [17] S. Horikoshi, S. Sato, M. Abe, and N. Serpone, "A novel liquid plasma AOP device integrating microwaves and ultrasounds and its evaluation in defluorinating perfluorooctanoic acid in aqueous media," *Ultrasonics Sonochemistry*, vol. 18, pp. 938-942, 2011.
- [18] K. Yasuoka and K. Sato, "Development of repetitive pulsed plasmas in gas bubbles for water treatment," *International Journal of Plasma Environmental Science and Technology*, vol. 3, pp. 22-27, 2009.
- [19] R. Hayashi, H. Obo, N. Takeuchi, and K. Yasuoka, "Decomposition of perfluorinated compounds in water by DC plasma within oxygen bubbles" (in Japanese), *IEEJ Transactions on Fundamentals and Materials*, vol. 132, pp. 767-772, 2012.
- [20] K. Yasuoka, K. Sasaki, and R. Hayashi, "An energy-efficient process for decomposing perfluorooctanoic and perfluorooctane sulfonic acids using dc plasmas generated within gas bubbles," *Plasma Sources Science & Technology*, vol. 20, 034009, 2011.
- [21] Y. Matsuya, N. Takeuchi, and K. Yasuoka, "Relationship between reaction rate of perfluorocarboxylic acids decomposition at the interface of plasma-liquid and adsorbed amount" (in Japanese), *IEEJ Transactions on Fundamentals and Materials*, vol. 132, pp. 1027-1032, 2012.
- [22] N. Takeuchi, R. Oishi, Y. Kitagawa, and K. Yasuoka, "Adsorption and efficient decomposition of perfluoro compounds at plasma-water interface," *IEEE Transactions on Plasma Science*, vol. 39, pp. 3358-3363, 2011.