

Plasma Degradation of Perfluoro Compounds in Water

水中有機フッ素化合物のプラズマ分解

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Environmentally harmful and persistent substances, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), have been successfully decomposed in solution using DC oxygen plasmas generated within small gas bubbles. After 180 min of operation, 99% of fluorine atoms were detached from the PFOA, and the energy efficiency of defluorination was 6.0 mg/kWh. Although almost 100% of PFOS was decomposed, only 68% of fluorine atoms were detected in the PFOS solution after 480 min of operation. The defluorination energy efficiency of PFOS was 2.2 mg/kWh. This lower efficiency seems to be caused by the reformation of perfluoroalkyl sulfonates with the detached sulfate ions.

1. Introduction

Perfluorocarbons (PFCs), such as PFOA and PFOS, are widely used owing to their chemical stability; however, unexpected toxicity of long-chain PFCs has raised environmental concerns [1]. Advanced oxidation technology utilizing OH radicals is unable to decompose PFCs. Methods developed for decomposing PFOA include UV-induced photochemical [2] and sonochemical [3] techniques, VUV irradiation [4], S₂O₈-added hot water treatment at 80°C [5], and a microwave hydrothermal technique [6]. PFOS is more persistent than PFOA; therefore, PFOS degradation has been reported in a limited number of studies, e.g., using zero-valent iron in subcritical water [7] and sonochemical methods [3,8].

We have found that DC plasmas generated within oxygen bubbles [9] can decompose PFOA/PFOS in solution. The decomposition rates and efficiencies were significantly higher than those of the aforementioned methods. In this paper, we will show the differences in the decomposition rates and mechanisms of PFOA and PFOS degradation.

2. Experimental Setup

A schematic diagram of the plasma reactor is shown in Fig. 1. The container was filled with 50 mL of 50 mg/L PFOA (C₇F₁₅COOH) or PFOS (C₈F₁₇SO₃H) solutions, for which the molecular weights are 414 and 500, respectively. Both are found in ionic states in the solution.

The electrode system consisted of a high-voltage electrode, a 1-mm-thick dielectric alumina spacer having a central hole (diameter,

0.2-mm), and a grounded 0.2-mm-thick annular metal plate immersed in the solution. Oxygen was fed into the solution through the hole at a flow rate of 100 sccm. Gas bubbles (diameter, 4 mm) formed and detached from the hole. The high-voltage electrode was connected to a DC power supply through a 200-kΩ ballast resistor. DC plasmas originated from the electrode and ended at the inner surface of the bubbles. The concentration of anions was measured with a pH/ion meter (Mettler-Toledo, S80) and an ion chromatograph (Metrohm, 861). The products in the solution were measured via liquid chromatography-mass spectrometry (LC-MS; Shimadzu, LCMS-2020).

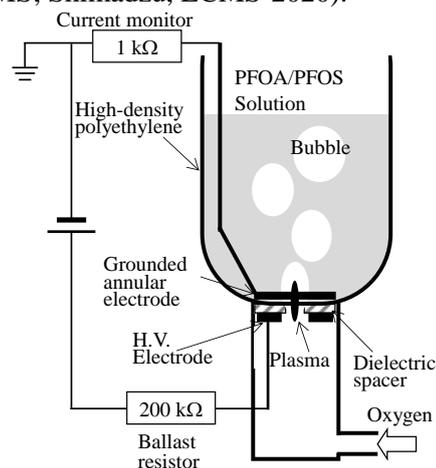


Fig. 1. Schematic diagram of plasma reactor

3. Results and Discussion

The initial conductivity of the PFOA and PFOS solutions were 26 and 29 μS/cm, respectively. The solution conductivity increased with the degradation of PFOA or PFOS, owing to the increase of detached fluorine ions in the solution.

The plasma current was maintained at 10 mA. Fig. 2 shows the PFOA/PFOS decomposition ratio as a function of input energy which included energy loss with the ballast resistor and the electric resistance of the solution. Ninety-seven percent of PFOA molecules were decomposed after 180 min of operation and 99% of fluorine atoms contained in PFOA were detached into the solution. The energy efficiency of defluorination was 6.0 mg/kWh. For PFOS degradation, however, complete decomposition required a longer time (480 min), and around 70% of fluorine atoms detached from PFOS. As shown in Fig. 2, the decomposition rate of PFOS changed at 11 Wh; 60% of PFOS was decomposed.

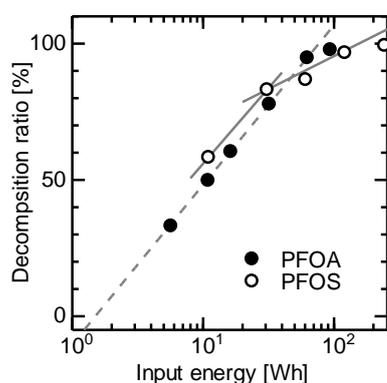
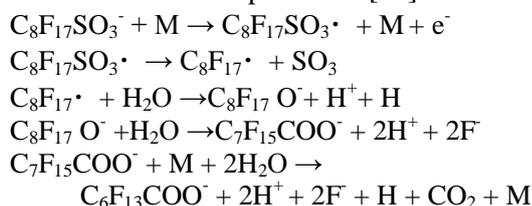


Fig. 2. Decomposition ratio vs. input energy

The degradation processes of PFOS were evaluated by measuring the concentration of F , SO_4^{2-} , $C_7F_{15}COOH$, $C_6F_{13}COOH$, $C_5F_{11}COOH$, C_4F_9COOH , C_3F_7COOH , C_2F_5COOH , CF_3COOH , $C_4F_9SO_3H$, PFOA, and PFOS.

The reaction processes for PFOA/PFOS degradation are not fully understood; nevertheless, a possible explanation for the plasma degradation processes is shown in the following equations that refer to atom-initiated processes [10].



PFOS molecules ionize in the solution and react with M, which represents the plasma effect at the bubble and solution interface. The generated radical, $C_8F_{17}SO_3^\bullet$, is unstable and dissociates to $C_8F_{17}^\bullet$ and sulfur trioxide, SO_3 . The sulfur trioxide molecule thus formed reacts with a water molecule and forms sulfuric acid, H_2SO_4 . The fluorinated radical $C_8F_{17}^\bullet$ reacts with H_2O to yield $C_8F_{17}OH$, which is unstable and dissociates to $C_8F_{17}COF$, and

then reacts with H_2O to yield a carboxyl substance: $C_7F_{15}COO^-$ (PFOA). In the same way, by-products with shorter carbon chains should be formed.

By-products with the sulfo group might be generated through the following reaction by the detached sulfur trioxide from PFOS. This reaction may reduce the decomposing rate at 11 Wh of input energy as shown in Fig. 2.



The energy consumption of PFOA decomposition was 58 mg/kWh to achieve 30% detachment of fluorine atoms from the PFOA. For PFOS decomposition, 26 mg/kWh was required to detach 54.8% of fluorine atoms. The energy efficiency was higher compared to the 0.61 mg/kWh requirement for PFOS photo degradation in two-propanol solution, or the 1.2 mg/kWh requirement under ultrasonic cavitation.

4. Conclusions

The degradation of PFOA/PFOS was successfully demonstrated by using DC plasmas generated inside oxygen bubbles, and the decomposition efficiency was higher than that of other methods. The lower decomposition rate for PFOS may be attributed to the reaction associated with sulfuric acid, which was a by-product of PFOS decomposition.

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