Effect of subsurface gas supply on PFOS decomposition by plasma

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Abstract: Perfluorooctane sulfonic acid (PFOS: $C_8F_{17}SO_3H$) in water was treated by plasma generated over the water surface with a subsurface gas supply. This mechanism has been shown to be effective in improving the PFOS decomposition efficiency. The improved efficiency may be attributed to the presence of bubbles that enhance the transportation of PFOS molecules from the bulk liquid to the gas-liquid interface, allowing PFOS to be replenished.

Keywords: Plasma water treatment, PFOS.

1. Introduction

Perfluorooctane sulfonic acid (PFOS) has been used for numerous applications such as fire-extinguishing foam owing to its excellent properties as a surfactant and its high stability. However, the production and utilization of PFOS have been restricted because of high toxicity and resistance to environmental and biological degradations, and many research groups have investigated efficient decomposition methods for PFOS using various types of plasma [1].

Conventional wastewater treatment procedures such as coagulation, filtration, aeration, oxidation, and disinfection are not effective to remove PFOS. Granular activated carbon (GAC) is the chief option to capture perfluorinated compounds from aqueous sources followed by incineration [2]. In fact, although GAC has been shown to be effective in removing PFOS, it is not a degradation process, which might cause secondary pollution. Many other technologies can degrade PFOS that are being investigated, such as sonolysis [3][4], photocatalysis [5], mechanochemical [6], bioremediation [7][8], etc.

Water treatment using gas-liquid interface plasma has been the subject of much research. More recently, liquidphase electrical discharge reactors have been investigated, and are being developed, for several environmental applications, including drinking water and wastewater treatment, as well as potentially for environmentally benign chemical processes. Miichi et al. decomposed aqueous acetic acid solutions using needle-water surface oxygen corona discharges [9]. 8 needle electrodes were used as ground electrodes and aqueous acetic acid solutions as high-voltage electrodes, and corona discharges were generated near the needle electrodes to decompose acetic acid, resulting in a decrease in acetic acid concentration from 20 mg/L to 4 mg/L in 60 minutes. Raj Kamal Singh et al. used a plasma treatment process to decompose PFOS and PFOA, and determined the byproducts produced, they proposed a degradation pathway for PFOA and PFOS in plasma treatment [10].

Our previous study of decomposing PFOS by plasma generated in the gas bubbles found that the decomposition efficiency decreased while the input power increased by changing the frequency, capacitance, and the applied AC voltage. The decrease in efficiency might attribute to the generation of new surface-active products and the decrease in the concentration of PFOS at the gas–liquid interface. In this study, a subsurface bubble mechanism was built to enhance the transportation of PFOS from the liquid to the interface and improve the efficiency of PFOS decomposition. The main objective of this study was to investigate the effect of the subsurface bubble mechanism on PFOS decomposition, and this experiment involved two different diameters of bubbles.



Fig. 1. The sketch of the subsurface gas supply reactor (Fine bubble type).

2. Experiment Methods

Figure 1 shows the reactor for the subsurface gas supply reactor (Fine bubble type). To generate plasma over a PFOS solution, a tungsten H.V. needle electrode was placed several millimeters above the solution surface with the solution grounded. DC plasma was generated between the tip of the needle and the solution surface with and without the bubbling of argon gas inside the solution. Two types of diffusers were used to produce fine bubbles with a diameter of 100 μ m and normal bubbles of 1 mm. Argon gas was introduced through the submerged diffuser at a gas flow rate of 50 sccm, and argon gas was also introduced from the upper inlet at 200 sccm.

The initial PFOS concentration used in this experiment was 5 mg/L, and the solution volume was 300 mL.

The concentrations of PFOS and its by-products were measured with a liquid chromatography-mass spectrometer (LCMS) in negative ion mode, and the concentration of fluoride ion was measured with a fluoride ion meter. The mass balance of fluorine was calculated to check for the formation of unknown by-products.

3. Results and Discussions

Figure 2 shows the variations of PFOS concentration under two experimental conditions. Figure 3 shows the variations of fluoride ion concentration under two experimental conditions. The efficiency of PFOS decomposition under fine bubble condition and normal bubble condition was 0.047 mg/Wh and 0.035 mg/Wh, respectively, and the defluorination efficiency was 0.0090 mg/Wh and 0.0046 mg/Wh, respectively. The higher decomposition efficiency and defluorination efficiency were obtained by providing fine bubbles with a diameter of less than 100 μ m.



Fig. 2. Concentration profiles of PFOS.



Fig. 3. Concentration profiles of fluoride ion.



Fig. 4. Mass balance of fluorine (Fine bubble).

Figure 4 shows the mass balance of fluorine under the fine bubble condition. According to the results of LCMS, it appears that after 60 min of plasma treatment, the unknown fraction of the figure contains perfluorinated compounds consisting of 3 to 7 carbons.

The decomposition rate of PFOS was significantly increased by adding the submerged diffuser, and the decomposition rate under the fine bubble condition was higher than that under the normal bubble condition. We speculate that this could be attributed to the presence of bubbles creating a higher interfacial area between the gas– liquid phase, which could enhance the mass transfer process, and smaller diameter bubbles are more efficient for PFOS transport and maintain the PFOS concentration at the gas–liquid interface [11].

4. References

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