

# Effects of pH and coexisting chemicals on photolysis of perfluorooctane sulfonate using an excited xenon dimer lamp

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## ABSTRACT

Vacuum ultraviolet (VUV) photolysis at the wavelength of 172 nm in a sulfate solution was introduced as a more efficient process for perfluorooctane sulfonate (PFOS) degradation than ultraviolet (UV) photolysis at 254 nm. The effects of pH and coexisting chemicals on VUV photolysis under the coexistence of 100 mM sulfate were investigated. VUV irradiation successfully degraded PFOS, and the degradation rate was 5.5 times higher than by UV photolysis. Direct VUV photolysis was inferred to mainly contribute to PFOS degradation. PFOS degradation by VUV irradiation was enhanced at pH less than 2 due to sulfate radicals generated via VUV photolysis of sulfate ions. Consequently, VUV photolysis was superior to UV photolysis for PFOS removal on both the removal rate and energy efficiency. However, the inorganic chemicals phosphoric acid and nitric acid strongly inhibited PFOS degradation, probably by masking PFOS from VUV rays by their VUV absorption. Accordingly, PFOS separation from inorganic materials such as phosphate and nitrate will be recommended for the application of VUV techniques for PFOS removal. In this research, organic solvent abstraction was inferred to be one of candidates for PFOS separation.

**Key words** | excimer lamp, perfluorooctane sulfonate, photolysis, sulfate radical, ultraviolet ray, vacuum ultraviolet ray

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## INTRODUCTION

Perfluorooctane sulfonate (PFOS) is a fully fluorinated organic compound with a hydrophobic perfluoroalkyl group and a hydrophilic sulfo group. Accordingly, it acts as a chemically stable surfactant, and has been widely used for surface treatments in textile mills, leather tanneries, etc., as well as paper protection in food and nonfood contact applications, performance chemicals for fire-fighting forms, electronic chemicals, etc. (Lim *et al.* 2011). Although it is a very useful chemical for industrial activities, it accumulates in the environment and bioaccumulates due to its chemical and biochemical stability (Fujii *et al.* 2007). Therefore, the negative health effects of PFOS are known, and it was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in 2009 to restrict its production and use. PFOS is a human-made compound and is not substantially decomposed in the natural environment (half-life in water:  $\geq 41$  years (Beach *et al.* 2006)). Accordingly, PFOS removal

from industrial water streams is strongly required when PFOS is used in industrial activities.

Many researchers have tried to treat PFOS in water streams using chemical oxidation, photolysis, sonolysis, filtration, adsorption, and so on (Vecitis *et al.* 2009; Yu *et al.* 2009; Chen *et al.* 2012). Among these techniques, nanofiltration, reverse osmosis, and activated carbon adsorption are applicable to industrial wastewater treatment from the point of view of the treatment time required. However, these processes generate concentrated wastes such as PFOS-concentrated effluent or PFOS-contaminated activated carbon. Consequently, incineration of the concentrated wastes would be required for the complete destruction of PFOS (Vecitis *et al.* 2009). Chemical oxidation, photolysis, and sonolysis are destruction techniques, which are more advantageous than the separation techniques such as filtration and adsorption because they do not generate concentrated wastes. Various

destruction techniques have been discussed for the treatment of perfluorinated chemicals like PFOS. Conventional advanced oxidation processes (AOPs) at normal pressure and temperature conditions can successfully destroy various persistent compounds using the strong oxidation ability of hydroxyl radicals ( $\cdot\text{OH}$ ) (Ikehata *et al.* 2008). However, PFOS cannot be destroyed by AOPs (Schröder & Meesters 2005), because  $\cdot\text{OH}$  is less reactive with perhalogenated aliphatic compounds (von Sonntag 2008). There are some reports of the successful degradation of PFOS, for example, subcritical water treatment with iron powders (Hori *et al.* 2006), heat-activated permanganate oxidation (Liu *et al.* 2012), and sonolysis (Cheng *et al.* 2008). Ultraviolet (UV) ray irradiation is another candidate for PFOS degradation. Although a single application of UV irradiation is not effective in destroying PFOS, UV irradiation with the addition of 2-propanol can degrade PFOS (Yamamoto *et al.* 2007). However, the long treatment time (10 days' UV irradiation for a degradation efficiency of 80%) keeps this technique from practical application. It is natural that UV irradiation at 254 nm is ineffective in destroying PFOS, because the C–F bond typically has a bond energy of 120–125 kcal/mol (503–524 kJ/mol) (Burdeniuc *et al.* 1997), which is higher than the photon energy of UV light at 254 nm (471 kJ/mol). By comparison with conventional UV, vacuum ultraviolet (VUV) rays have higher photon energies (for example, 695 kJ/mol at 172 nm) than the C–F bond energy. Therefore, VUV irradiation is expected to enhance the photochemical degradation of PFOS. It has been reported that the photodegradation of perfluorooctanoic acid (PFOA), which is one of perfluorocarbons similar to PFOS, is enhanced by VUV irradiation (Chen & Zhang 2006). However, simple VUV irradiation was not effective in PFOS destruction (Yang *et al.* 2013), though the combination of VUV photolysis with ultrasound irradiation (Yang *et al.* 2013) or with nitrogen gas bubbling under alkaline conditions (Jin & Zhang 2015) enhanced PFOS destruction. Thus, some additional process is required for an efficient VUV photolysis of PFOS.

In this study, the effects of pH and coexisting chemicals on the VUV photolysis of PFOS in a sulfate solution are discussed. In VUV photolysis  $\cdot\text{OH}$  can be generated by the direct photolysis of water as follows (Heit *et al.* 1998):



Although  $\cdot\text{OH}$  is less reactive with PFOS,  $\cdot\text{OH}$  can react with hydrogen sulfate ions ( $\text{HSO}_4^-$ ) and produce sulfate radicals ( $\cdot\text{SO}_4^-$ ) as shown in reaction (3) (Neta *et al.* 1988).



Therefore, it is expected that  $\cdot\text{SO}_4^-$  production is enhanced in acidic conditions. Since  $\cdot\text{SO}_4^-$  enhanced PFOA degradation (Chen & Zhang 2006), the enhancement of PFOS degradation was also expected by VUV photolysis in an acidic sulfate solution in this study.

## MATERIAL AND METHODS

### Photochemical reactor

The photochemical reactor used in this research was similar to the one previously reported (Kishimoto *et al.* 2015b), though a 2 L tall beaker was used as a reactor instead of the 3 L tall beaker. An excited xenon dimer lamp (excimer lamp; 172/120Z, Heraeus, Germany) was used in this research; it consumed 20 W of electric power and mainly emitted a VUV light at 172 nm with the irradiance of 5.7 W. The 1.4 L of PFOS-contaminated water was treated in this reactor for 7 hours, and it was continuously mixed with a magnetic stirrer during the photolysis.

### Contaminated water

Potassium heptadecafluoro-1-octanesulfonate (Tokyo Chemical Industry, Japan) was used as a source of PFOS. The stock PFOS solution was prepared by dissolving the reagent into ion-exchanged water at the final concentration of 186  $\mu\text{M}$ . Then, the stock solution was diluted 10 times with ion-exchanged water for the experiments. The contaminated water pH was adjusted by adding sulfuric acid (Nacalai Tesque, Japan). The final concentration of sulfate ions was set at 100 mM by adding an adequate amount of sodium sulfate (Nacalai Tesque, Japan).

When the effects of coexisting chemicals were discussed, phosphoric acid (Sigma-Aldrich Japan, Japan), nitric acid, ethanol, or acetonitrile (Nacalai Tesque, Japan) were added to the contaminated water at the final concentration of 101, 190, 853, and 951 mM, respectively. The

contaminated water pH was set at  $1.3 \pm 0.2$  by the addition of sulfuric acid, and the final sulfate concentration was adjusted to 100 mM by the addition of an adequate amount of sodium sulfate.

### Photochemical production of sulfate radicals

To clarify the influence of sulfate radicals produced during VUV photolysis, VUV and UV photolysis of contaminated water containing 5 g/L of potassium persulfate without sulfates was performed. The contaminated water pH was 2. A low-pressure mercury vapor lamp (UVL20PH-6, Sen Lights, Japan) was used for the UV photolysis; it consumed 20 W of electric power and mainly emitted UV light at 254 nm with the irradiance of 4.3 W.

### Determination of molar absorption coefficient

The molar absorption coefficients of coexisting chemicals at 172 nm were evaluated as follows: A quartz optical cell with an optical path of 1 cm was set on the surface of the VUV lamp. A VUV light sensor at 172 nm (VUV-S172, Ushio, Japan) was glued to the opposite side of the optical cell. Then, pure water was poured into the cell, and the VUV irradiance transmitted ( $i_{t0}$ ) was measured with the sensor. Next, an aqueous solution with an adequate concentration of a coexisting chemical was poured into the cell, and the VUV irradiance transmitted ( $i_t$ ) was measured again. The molar absorption coefficient ( $\epsilon$ ) was calculated using the following equation.

$$\epsilon = \frac{\log i_{t0} - \log i_t}{CL} \quad (5)$$

where  $C$  is the concentration of coexisting chemical [M], and  $L$  is the optical path of the cell (=1 cm).

### Chemical analysis

The concentration of PFOS was determined using a liquid chromatography system (1100, Agilent Technologies Japan, Japan) coupled with a quadrupole mass spectrometer (G1956B, Agilent Technologies Japan, Japan). Analytical conditions followed the previous report (Kishimoto & Kobayashi 2016). The concentration of fluoride ions ( $F^-$ ) produced through the photochemical degradation of PFOS was determined with an ion chromatography system (DX-500, Dionex, USA). Analytical conditions were the same as in the previous report (Kishimoto *et al.* 2015a).

## RESULTS AND DISCUSSION

### Photochemical degradation curve of PFOS

Figure 1 shows changes in PFOS concentration and  $F^-$  concentration during VUV photolysis at pH 5.8. The photochemical degradation curve of PFOS followed zero-order reaction kinetics in all experimental runs as shown in Figure 1. Therefore, the photochemical degradation performance in each of the conditions can be compared using the following normalized degradation rate.

$$k_N = \frac{kV}{I} \quad (6)$$

where  $k_N$  is the normalized degradation rate [ $\mu\text{mol}/\text{Wh}$ ],  $k$  is the zero-order degradation rate evaluated from the slope of the regression line [ $\mu\text{M}/\text{h}$ ],  $V$  is the volume of contaminated water (=1.4 L), and  $I$  is the total irradiance at 172 nm (=5.7 W) for VUV photolysis or at 254 nm (=4.3 W) for UV photolysis.

As is shown in Figure 1, the increment of  $F^-$  in the early stage is smaller than the decrement of PFOS. This means that defluorination would occur after the cleavage of C–S bonds in PFOS as Yamamoto *et al.* (2007) reported. The enhancement of  $F^-$  production rate over time in Figure 1 also supports this assumption.

### Effect of pH on VUV photolysis

Figure 2 summarizes the  $k_N$  observed during VUV photolysis under various pHs. The degradation rate was significantly enhanced at pH less than 2. The production of  $\cdot\text{SO}_4^-$  (reaction (3)) would be enhanced at pH less than 2, because the pKa

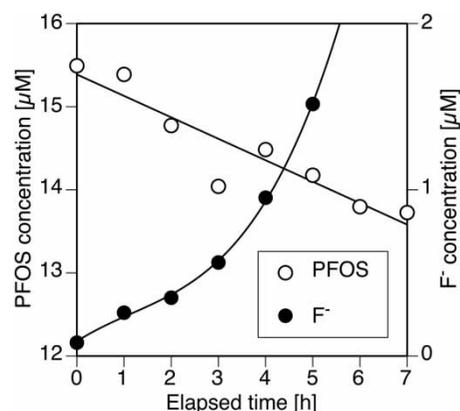
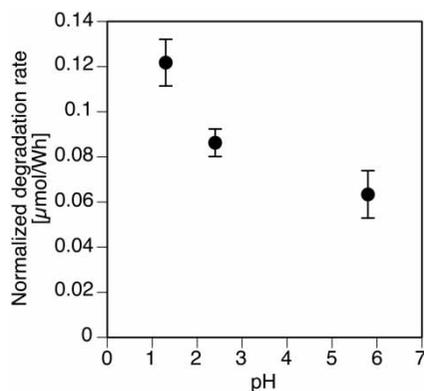


Figure 1 | Changes in PFOS and  $F^-$  concentrations during VUV photolysis at pH 5.8.



**Figure 2** | Dependency of normalized PFOS degradation rate ( $k_N$ ) by VUV photolysis on pH. Error bars show the standard error.

of  $\text{HSO}_4^-$  (reaction (4)) is 1.99 (Wu & Feng 1995). Accordingly, the enhancement of PFOS degradation at pH less than 2 in Figure 2 suggests the contribution of  $\bullet\text{SO}_4^-$  to the degradation of PFOS. Jin & Zhang (2015) reported that the photodegradation of PFOS by VUV at 185 nm emitted from a low-pressure mercury lamp was enhanced in an anoxic alkaline solution because of the contribution of hydrated electrons. The normalized degradation rate ( $k_N$ ) estimated from their data was  $0.127 \mu\text{mol/Wh}$  at the optimal conditions of pH 12.5 with continuous nitrogen-gas bubbling (see Supplementary material, available with the online version of this paper), which was nearly equal to  $k_N$  observed at pH 1.3 ( $0.122 \pm 0.010 \mu\text{mol/Wh}$ ). Thus, the contribution of  $\bullet\text{SO}_4^-$  to the degradation of PFOS in this study was thought to be similar to that of hydrated electrons in the study by Jin & Zhang (2015).

Vecitis *et al.* (2009) summarized the energy efficiencies of various PFOS degradation technologies reported. The observed energy efficiencies were in the range of 11–4,500 kJ/ $\mu\text{mol}$ . In this study, the energy efficiency at pH 1.3 in Figure 2 was calculated to be 30 kJ/ $\mu\text{mol}$  based on total irradiance at 172 nm and 104 kJ/ $\mu\text{mol}$  based on the consumed power of the VUV lamp. Thus, VUV photolysis in the acidic sulfate solution showed excellent energy efficiency, though the sub-critical treatment with iron powders (Hori *et al.* 2006) was more energy efficient (11 kJ/ $\mu\text{mol}$ ) than the VUV photolysis in this study.

### Contribution of $\bullet\text{SO}_4^-$ to PFOS degradation

The contribution of  $\bullet\text{SO}_4^-$  to PFOS degradation was explored by three photochemical experiments: UV photolysis of the  $\text{SO}_4^{2-}$ -containing water, and UV or VUV photolysis of

persulfate ion ( $\text{S}_2\text{O}_8^{2-}$ )-containing and  $\text{SO}_4^{2-}$ -free water. Table 1 summarizes the normalized degradation rate of each experiment. When UV photolysis was applied to the  $\text{SO}_4^{2-}$ -containing water, the PFOS degradation rate was much lower than that of the VUV photolysis shown in Figure 2. Thus, PFOS was not substantially decomposed by direct UV photolysis. When  $\text{S}_2\text{O}_8^{2-}$  was irradiated with UV rays,  $\bullet\text{SO}_4^-$  was generated by the UV photolysis of  $\text{S}_2\text{O}_8^{2-}$  (Dogliotti & Hayon 1967). As the result, the normalized PFOS degradation rate was enhanced by the UV irradiation of the  $\text{S}_2\text{O}_8^{2-}$ -containing water. However, the observed PFOS degradation rate was still lower than that observed in VUV photolysis shown in Figure 2. Thus,  $\bullet\text{SO}_4^-$  enhanced PFOS degradation, but its contribution to PFOS degradation was not so large. Compared with UV photolysis, VUV irradiation on the  $\text{S}_2\text{O}_8^{2-}$ -containing water remarkably enhanced the PFOS degradation rate, which was about 2.5 times higher than that of the UV photolysis of the  $\text{S}_2\text{O}_8^{2-}$ -containing water. This means that VUV rays are essential to the PFOS degradation. Consequently, it was inferred that direct VUV photolysis mainly contributed to the PFOS degradation with the assistance of  $\bullet\text{SO}_4^-$ .

In comparison with the UV photolysis of  $\text{SO}_4^{2-}$ -containing water in Table 1 and the VUV photolysis of  $\text{SO}_4^{2-}$ -containing water in Figure 2, the PFOS degradation rate by VUV photolysis ( $0.0863 \pm 0.0061 \mu\text{mol/Wh}$  at pH 2.4) was 5.5 times higher than that by UV photolysis. Thus, VUV photolysis was concluded to be more effective in PFOS degradation than UV photolysis.

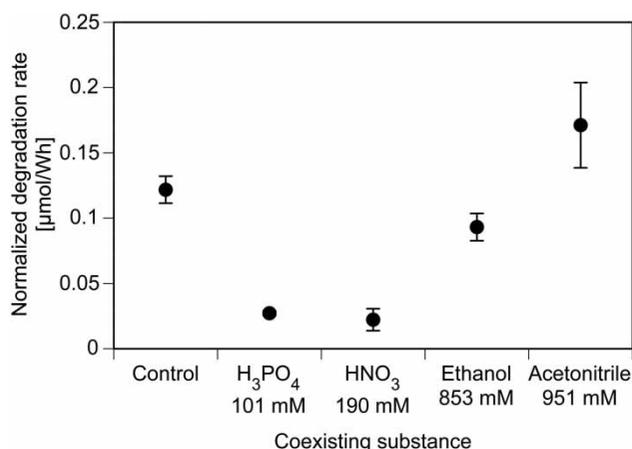
### Effects of coexisting chemicals on VUV photolysis

Figure 3 summarizes the  $k_N$  observed during the VUV photolysis of PFOS-contaminated water with single addition of various coexisting chemicals. In the comparison with the control, inorganic chemicals of phosphoric acid and nitric acid strongly inhibited PFOS degradation, whereas the organic chemicals ethanol and acetonitrile showed less

**Table 1** | Experimental conditions and observed degradation rate

Light source	Coexisting ion	pH	$\bullet\text{SO}_4^-$ generation	Normalized PFOS degradation rate ( $k_N$ ) [ $\mu\text{mol/Wh}$ ]
UV	100 mM- $\text{SO}_4^{2-}$	2.4	not generated	$0.0156 \pm 0.0091^a$
UV	18.5 mM- $\text{S}_2\text{O}_8^{2-}$	2.0	generated	$0.0269 \pm 0.0096^a$
VUV	18.5 mM- $\text{S}_2\text{O}_8^{2-}$	2.1	generated	$0.0512 \pm 0.0105^a$

<sup>a</sup>The range stands for the standard error.



**Figure 3** | Influences of coexisting chemicals on the normalized PFOS degradation rate ( $k_n$ ). Sulfate concentration and pH were 100 mM and  $1.3 \pm 0.2$ , respectively. Control means no addition of coexisting chemical. Error bars show the standard error.

inhibition effect or enhancement effect. Molar absorption coefficients of coexisting chemicals are summarized in Table 2. The molar absorption coefficients of phosphoric acid and nitric acid are much higher than those of ethanol and acetonitrile. Therefore, phosphoric acid and nitric acid mask PFOS from VUV rays by their VUV absorption. This may be one of possible reasons why phosphoric acid and nitric acid showed strong inhibition effects. However, ethanol and acetonitrile concentrations were higher than phosphoric acid and nitric acid concentrations in this study. Accordingly, there was no big difference among the VUV absorbances of the four chemicals in our experiments. Therefore, the masking effect was also expected in the VUV photolysis with ethanol or acetonitrile addition, but the inhibition effect of the PFOS degradation by organic chemical addition was smaller than that expected. Yamamoto *et al.* (2007) reported that 2-propanol could enhance the UV photolysis of PFOS by 9.5 times, probably due to defluorination by photochemically produced organic radicals. The similar radical defluorination mechanism might work in this study, especially in the case of acetonitrile addition.

**Table 2** | Molar absorption coefficient at 172 nm

Substance	$\epsilon$ [ $\text{L mol}^{-1} \text{cm}^{-1}$ ]
H <sub>3</sub> PO <sub>4</sub>	2.93
HNO <sub>3</sub>	1.92
Ethanol	0.398
Acetonitrile	0.383

The strong inhibition effects of phosphoric acid and nitric acid implied that VUV photolysis should be applied to PFOS degradation after the separation of PFOS from inorganic ions. The abstraction of PFOS by organic solvents may be an alternative technique for PFOS separation from water streams. But further studies will be required for the selection of a good solvent for the abstraction.

## CONCLUSIONS

The effects of pH and coexisting chemicals on VUV photolysis of PFOS-contaminated water with 100 mM of sulfate were investigated in this research. An excited xenon dimer lamp mainly emitting 172 nm was used as a VUV light source. The VUV irradiation successfully degraded PFOS according to zero-order reaction kinetics. The lag of defluorination compared with PFOS degradation suggested that the cleavage of C-S bonds in PFOS was an initial step of PFOS degradation.

As the result of VUV photolysis under different pHs, VUV photolysis of PFOS was enhanced at pH less than 2. Sulfate radicals produced from VUV photolysis were thought to contribute to PFOS degradation at the low pH conditions with sulfuric acid. However, the comparison of VUV photolysis with UV photolysis revealed that  $\cdot\text{SO}_4^-$  could enhance PFOS degradation, but the enhancement effect of  $\cdot\text{SO}_4^-$  alone was not significant. Consequently, the PFOS degradation by VUV irradiation was mainly caused by direct VUV photolysis, and  $\cdot\text{SO}_4^-$  was thought to assist the photodegradation of PFOS.

The effects of four coexisting chemicals: phosphoric acid, nitric acid, ethanol, and acetonitrile, were investigated. Inorganic chemicals of phosphoric acid and nitric acid strongly inhibited the photodegradation of PFOS, probably due to the masking of PFOS from VUV light by their strong VUV absorption. However, the inhibition effects of organic chemicals were much smaller than those of phosphoric acid and nitric acid, and acetonitrile inversely enhanced the photodegradation of PFOS.

In conclusion, VUV photolysis was superior to UV photolysis, because the PFOS degradation rate by VUV irradiation was 5.5 times higher than that by UV irradiation. However, inorganic chemicals of phosphoric acid and nitric acid strongly inhibited PFOS degradation. Therefore, it is recommended that VUV photolysis is applied to PFOS degradation after abstraction from water streams by organic solvents, though further studies will be required for the selection of a good solvent for abstraction.

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