Reductive and Oxidative UV Degradation of PFAS

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Contributor: Muhammad Umar

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) consist of a group of environmentally persistent, toxic and bio-accumulative organic compounds of industrial origin that are widely present in water and wastewater. Despite restricted use due to current regulations on their use, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) remain the most commonly detected long-chain PFAS.

PFAS UV VUV oxidation water

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) (C5–C18) are widely used in different industrial applications (clothing, paper packing, non-stick cookware, food packaging, pesticide formulations, waterproof fabrics, fume suppressants, photographic films, masking tape, firefighting foams) due to their unique properties [1][2]. These special properties of PFASs are associated with characteristics such as: (1) the hydrogen atoms on the alkyl chain are replaced by fluorine atoms [3], and (2) the presence of both long hydrophobic perfluorinated (C_nH_{2n+1}) carbon chain and hydrophilic functional group ($-SO_3^-$, $-COO^-$), i.e., in PFOS and PFOA [4]. PFAS have been found in both influent and effluent of wastewater treatment plants which are considered as one of the major sources for their occurrence in surface and groundwater [5][6][7]. Like several other micropollutants, PFAS are found at very low concentrations [8], but their refractory nature and unique physicochemical properties (**Table 1**) exacerbates the challenge of their degradation and/or removal.

Table 1. Physicochemical properties of various PFASs (adapted from Espana et al. [9]).

Property	PFOA (Free Acid)	PFOS (Potassium Salt)
* Physical description	White powder/waxy white solid	White powder PFOA
Molecular formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3S$
Molecular weight (g mol^{-1})	414	538
Water solubility at 25 °C (mg L^{-1})	9.5×10^3	680
Melting Point (°C)	45–50	>400
Boiling point (°C)	189–192	Not measurable

Property	PFOA (Free Acid)	PFOS (Potassium Salt)
Vapour pressure at 25 °C (Pa)	4.2	2.48×10^{-8}
Organic–carbon partition coefficient (log K_{oc})	2.06	** 2.57
Henry's law constant (atm-m^3 mol^{-1})	Not measurable	3.05×10^{-9}
Half-Life	*** 90 days, **** >92 years (at 25 °C)	*** 114 days, **** >41 years (at 25 °C)

* At room temperature and atmospheric pressure, ** Value estimated based on anion and not the salt, *** Atmospheric, **** In water.

2. Photolysis and Photochemical Decomposition Using UVC/VUV

2.1. Direct Photolysis (UV/VUV)

UV irradiation is divided into four regions: UVA (315–400 nm), UVB (280–315 nm), UVC (200–280 nm) and vacuum UV (VUV, 100–200 nm) [10]. Low pressure (LP) mercury lamps emitting UVC irradiation primarily at 254 nm have been investigated for the degradation of various contaminants including PFAS. While it is an efficient process for a range of compounds, conventional direct photolysis is known to be inefficient for the degradation PFAS as demonstrated by several investigations [11][12][13][14]. Little to no degradation during direct UV photolysis is attributed to insufficient breakdown of the C-F bond by photo-energy generated during UV irradiation [15]. Giri et al. [15] corroborated these results and found negligible degradation of PFOA after 5 h of irradiation at 254 nm. The absorption of UV light at wavelength higher than 220 nm is very low resulting in direct photolysis being ineffective for PFAS degradation [16]. Similarly, Chen et al. [12] observed that the UV absorbance of PFOA from 190 to 280 nm (UVC) and reported a much stronger UV absorption in the VUV region below 200 nm.

Giri et al. [15] calculated the photon energy for both UVC (471.1 kJ mol^{-1}) and VUV (185 nm) (646.8 kJ mol^{-1}) and considering the C-C bond energy (347 kJ mol^{-1}), PFOA is prone to breakage by both wavelengths. However, C-F bond with the higher bond energy (552 kJ mol^{-1}) is unlikely to be cleaved by 254 nm. It is therefore established that direct UV photolysis at 254 nm is not a suitable process for the degradation of these compounds. Considering the higher photon energy generated during VUV photolysis, direct photolysis by VUV is more promising.

Although there are limited studies using VUV irradiation, the findings suggest that the process has the potential to degrade PFAS. Considering stronger UV absorption below 200 nm, the application of VUV photolysis requires to be investigated further using specially designed system emitting most irradiation at 185 nm such as in the case of Giri et al. [15] who reported 97% VUV emission when used a synthetic fused silica glass tube. It is worth noting that the VUV process generates ozone that could also lead to the degradation of PFAS. However, none of the studies have looked at the generation and potential degradation of PFAS related to ozone produced during VUV process.

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2.2. Photochemical Oxidation Using UVC/VUV

2.2.1. UV/H_2O_2

One of the most commonly used UV-based advanced oxidation processes (AOPs) that has been investigated for the degradation of recalcitrant organic contaminants is UV/H_2O_2. However, the addition of H_2O_2 is found to be unfavorable for the degradation of PFOA due to competitive absorption of photons [20]. The upper limit for the second-order rate constant of OH reaction with PFOA ($k_{•OH+PFOA}$) is $\leq 10^5$ L mol^{-1} s^{-1}, which is several orders of magnitude slower than the •OH reaction with most hydrocarbons [21]. The reaction of •OH with organic compounds principally involves three mechanisms: (1) hydrogen abstraction yielding carbon-centered radicals, (2) electrophilic addition of •OH to unsaturated carbon–carbon bonds, and (3) electron transfer in which case the •OH receives an electron from the organic substituent [22]. Reaction of •OH with saturated organic compounds occurs through hydrogen abstraction and unsaturated organic compounds via radical addition. Since PFOA and PFOS has no hydrogen for abstraction, •OH can only react via direct electron transfer pathway leading to formation of much less thermodynamically favored HO^- (E^0 = 1.9 V). The perfluorination or substitution of organic hydrogen atoms for fluorines make the PFASs inert to •OH oxidation [23]. Conventional UV/H_2O_2 process is therefore not considered efficient for the degradation of PFOA and PFOS. This has promoted research into using other oxidative agents in combination with UV irradiation.

2.2.2. UV/VUV/Sulfite

A comparison between VUV alone and in combination with $K_2S_2O_8$ and Na_2S under oxygen and nitrogen atmosphere, respectively, was made for the degradation of perfluorodecanoic acid (PFDeA) [24]. The degradation of PFDeA was ~60% after 5 h irradiation (light intensity of 62–69 mW cm^{-2}) but a much lower defluorination ratio of ~16% was achieved using VUV alone. However, in the presence of $K_2S_2O_8$ under oxygen atmosphere, the concentration of PFDeA was below the detection limit (not given) with 86% defluorination after 5 h. Increasing the $K_2S_2O_8$ concentration from 0.1 mM to 5 mM did not improve the PFDeA degradation and the formation of F^- that ranged between 0.41 and 0.43 mg L^{-1} min^{-1}. The trend of PFDeA degradation in the presence of 0.1–5 mM Na_2S under nitrogen atmosphere was fairly similar to VUV/$K_2S_2O_8$ system and the concentration of PFDeA was below the detection limit for both 0.1 and 0.5 mM Na_2S. Both direct photolysis of PFDeA by VUV and photochemical decomposition by $SO_4^{•-}$ was proposed during VUV/$K_2S_2O_8$ process with $SO_4^{•-}$ playing a significant role in the oxidative degradation of PFDeA. During VUV/Na_2S treatment, however, both oxidative and reductive (by e^-_{aq}) degradation occurred but no conclusion regarding which mechanism was most prevalent was made requiring this system to be investigated further. The PFOA degradation pathway during UV-based AOPs including $SO_4^{•-}$ is given

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in Figure 1 [25]. Typically, PFAS separation is conducted using chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry.

Figure 1. Degradation pathways of PFOA during UV-based AOPs (adapted from Wang et al. [25].

2.3. Reaction by-Products during UV/VUV Photodegradation

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Investigating PFOA degradation using VUV/Fe^{3+}, Cheng et al. [26] identified intermediate by-products containing C_2–C_7 perfluoroalkyl groups in agreement with previous investigations [12][20]. The longer chain intermediates including PFHpA (C_7) and perfluorohexanoic acid (PFHxA) (C_6) reached maximum concentration after 1.5 h and 3 h, respectively, followed by decreased concentration with increasing irradiation time. The remaining intermediates (C_2–C_5) increased throughout the 4 h irradiation period. The order of concentration followed PFPeA > PFBA > perfluoropropionic acid (PFPA) > trifluoroacetic acid (TFA) demonstrating the longer chain intermediates appeared at the start of the reaction followed by decomposition to shorter chain products. Investigating PFOA degradation using 254 nm UV during UV/H_2O_2/Fe^{2+} process, Tang et al. [27] found that the degradation intermediates included the short chain perfluorocarboxylic acids containing 2, 3 4, 5 and 6 carbon atoms and fluoride ions which is in agreement with others [15][28]. Liang et al. [29] also identified perfluoronated carboxylic acids with 2–7 carbon atoms during VUV/Fe^{3+} degradation of PFOA. It was further noted that the shorter chain degradation products were higher in concentration, i.e., PFPA > PFBA > PFPeA > PFHxA > PFHA [29]. Jin et al. [30] while investigating the degradation of PFOS using UV/Fe^{3+} found C_2–C_8 PFCAs in addition to sulphate and fluoride as degradation by-products. Theses intermediates are similar to that reported in earlier studies using UV/Fenton [27] and VUV/Fe^{3+} [29].

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2.4. Photochemical Oxidation Using MP UV—Impact of Experimental Conditions

Some studies have investigated the degradation of PFAS using medium pressure UV lamps. For example, Hori et al. [16] investigated photochemical degradation using MP UV lamp (220–460 nm) of PFCAs containing 3–5 carbon atoms (PFPrA, PFBA, or PFPeA). They reported that the absorption of UV light was much higher for deep-UV region to 220 nm but was much lower for 220–270 nm. After 24 h of direct photolysis, 24.3% of PFPeA was degraded yielding 12.1% F^-. The other two PFCAs (PFPrA, PFBA) showed lower but comparable degradation and F^- yield of about 16% and <10%, respectively. Degradation of these short chain PFAS enhanced when 5 mM Fe^{3+} was used such that the degradation of PFPeA, PFBA and PFPrA was about 2.7-, 3- and 3.8-fold greater when compared with UV alone after 24 h. Similarly, the amount of F^- yield was greater although it did not follow the trend of degradation. The degradation followed pseudo-first-order kinetics with increasing rate of degradation with increasing initial concentration of PFPeA demonstrating that the complexes formed between Fe^{3+} and PFPeA resulted in photo-redox reactions that led to the formation of Fe^{2+} and oxidized PFPeA. The degradation of PFPeA was markedly higher in the presence of oxygen (64.5%) than argon (35.6%) and so was the conversion of Fe^{3+} to Fe^{2+}, i.e., 93.3% and 0.70%, respectively. It was concluded that oxygen was required for re-oxidation step of Fe^{2+} conversion to Fe^{3+} since the presence of oxygen could increase the formation of HO_2 that can expedite the re-oxidation process.