Efficient Decomposition of Perfluorinated Compounds In a High Photon Flux UV/sulfite system

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Abstract. Perfluorinated compounds (PFCs) have attracted increasing attention due to their global distribution, high chemical stability and persistence. Hydrated electron (eaq-) is a strong reductant, and is reported promising for recalcitrant organic pollutants decomposition. In this study, eaq- based photodecomposition of several PFCs in a high photon flux UV/sulfite system was investigated. Perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) decomposition in the studied system were 1~2 orders of magnitude faster than that in previously studied BDD electrooxidation and UV/KI photoreduction systems. Kinetic study revealed the observed rate constant (kobs) of both PFSAs and PFCAs increased with the increase of carbon chain length. In mixed PFCAs or PFSAs solution, decomposition of each PFCAs or PFSAs was suppressed due to the competition of eaq-.

1. Introduction
Perfluorinated compounds (PFCs), especially perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs), are widely applied in industrial commodities [1]. Due to their extensive usage, PFCs were ubiquitously detected in various environmental medium [2]. Risks of PFCs toward living organisms have been gradually recognized, and thus production of two dominant PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), have been legally restricted in most developed countries since 2009. Nevertheless, PFOS and PFOA involved production in developing countries, such as China, have sharply increased [3]. Recently, some short-chain compounds (e.g. PFHxS, PFBS, PFHxA, PFBA), which are considered less bioaccumulative than PFOS and PFOA, have been introduced as alternatives [4]. As a consequence, PFOS, PFOA and their short-chain homologs are frequently detected in water environment nearby fluorochemical manufacturing industries [1], and short-chain homologs even exhibited higher concentration level than PFOS or PFOA in some cases [5]. Thus, effective decomposition methods for PFOS, PFOA and their short-chain homologs are of vital importance for remediation of PFCs contaminated water environment.

The high chemical stability of C-F bond makes PFCs inert to traditional AOPs oxidation and biological decomposition methods. With a high standard reduction potential of -2.9 V, hydrated electron (eaq-) based decomposition methods have received increasing attention in halogenated organic compounds remediation [6]. Ultraviolet photolysis (UV) of inorganic anions, such as sulfite and iodide, was an efficient way to generate eaq-. The potential insalubrious effect of iodide has been reported previously, thus the UV/sulfite system was an eco-friendly way for eaq- production and subsequent PFCs decomposition. eaq- induced PFOA and PFOS decomposition have been investigated by some researchers [7,8], whereas little attention was paid to the decomposition of short-chain PFCAs and
PFSAs. In our previous study [9], a high photon flux UV/sulfite system was built and abundant $e_{aq}$-generation was achieved in this system. In this study, a systematic study on the reductive decomposition of several PFCs with different carbon chain length and headgroups in the high photon flux UV/sulfite system was carried out. The outcomes would extend our understanding towards $e_{aq}$-based decomposition process.

2. Materials and Methods

2.1. Chemicals
Several PFCAs and PFSAs, including PFBA (C$_3$F$_7$COOH, 98%), PFHxA (C$_5$F$_{11}$COOH, 98%), PFOA (C$_7$F$_{15}$COOH, 96%), PFBS (C$_4$F$_9$SO$_3$K, 98%), PFHxS (C$_6$F$_{13}$SO$_3$K, 95%), and PFOS (C$_8$F$_{17}$SO$_3$K, 98%) were obtained from Sigma-Aldrich and Aladdin. Sodium sulfite (Na$_2$SO$_3$, 98%), sodium hydroxide (NaOH, 96%), and sulfuric acid (H$_2$SO$_4$, 98%) were purchased from Guoyao Co Ltd.

2.2. UV decomposition procedures
UV decomposition experiments were performed in an opened glass cylinder with volume of 50 mL. A 250 W (Ushio, Japan) high pressure mercury lamp was used as the irradiation source, and it mainly emits UV light ranging from 200 to 600 nm. Our previous study showed the maximum UV intensity of this lamp was $6.6 \times 10^{-7}$ einstein cm$^{-2}$ s$^{-1}$ [9]. The reaction temperature was maintained around 25 ℃ by a water cooling jacket.

25 mL reaction solution containing 16 mg/L single PFCAs (or PFSAs) and 10 mM sulfite was filled into the above reactor, and each of their molar concentrations was 74.8, 51.0, 38.6, 47.3, 36.5, 29.7 μM for PFBA, PFHxA, PFOA, PFBS, PFHxS, PFOS, respectively. Besides, mixed PFCAs or PFSAs solution was decomposed in this system to investigate the competitive relationship between each PFCAs or PFSAs, and each of their concentrations was the same as stated. Sulfite dosage and initial solution pH were 10 mM and 9.2.

2.3. Analysis
A UPLC/MS-MS analyser (Waters, USA) was used to determine PFCAs and PFSAs concentration, and the mobile phase was a mixture of 2 mM ammonium acetate and methanol with flow rate of 0.3 mL/min. PFCAs and PFSAs were detected by a gradient elution program, the elution was started at 5% methanol, which was held for 1 min, followed by a linear increase to 95% methanol at 7 min, held for 1 min, and then returned to the original conditions at 10 min. Fluoride ion concentration was detected using a fluoride ion selective electrode (INESA, Shanghai) with detection limit of 0.02 mg/L.

The bond order and bond length analyses were carried out by means of Multiwfn 3.3.8 program [10] for the C-C α bonds in PFCAs and the C-S bonds in PFSAs with different carbon chain length. Mayer bond order and Fuzzy bond order were both chosen in the calculations [11], since the former always performs better than Mulliken bond order for quantifying bonding strength, while the latter usually provides results close to the former in magnitude but is much more insensitive to basis set selection in the quantum chemistry calculation.

3. Results and discussion

3.1. Photoreductive kinetics of different PFCs
Single PFCAs (e.g. PFBA, PFHxA and PFOA) and PFSAs (e.g. PFBS, PFHxS and PFOS ) were decomposed in the high photon flux UV/sulfite system, and results were shown in Figure 1. For both PFCAs and PFSAs, their decomposition efficiencies and defluorination efficiencies were dependent on carbon chain length. After 30 min reaction, the decomposition efficiencies of PFBA, PFHxA and PFOA were 89.3%, 99.2% and 100%, and their defluorination efficiencies were 39.2%, 51.5% and 56.8%, respectively. As for PFSAs, the differences between decomposition efficiencies and defluorination efficiencies became larger. As shown in Figure 1(b), PFBS couldn’t be decomposed
after 30 min reaction, while 97.7% PFOS were decomposed at the same initial concentration. Except for PFBS, pseudo first order model can be used to depict decomposition kinetics of other PFCAs and PFSAs. The observed rate constants ($k_{obs}$) for PFBA, PFHxA, PFOA, PFHxS and PFOS were 0.139, 0.287, 0.455, 0.028 and 0.118 min$^{-1}$, respectively. Compared with BDD electrooxidation process and UV/KI photoreduction process, decomposition rate of PFCAs and PFSAs in the studied process showed considerable promotion, which was at least one order of magnitude faster (Table 1), indicating the high photon flux UV/sulfite system was promising for PFCs containing wastewater treatment.

3.2. Decomposition of mixed PFCAs and PFSAs

Decomposition of mixed PFCAs or PFSAs solution was also studied, and results were shown in Figure 2. Compared with single PFCAs or PFSAs solution, decomposition of each PFCAs or PFSAs was suppressed with different level in the mixed system. Furthermore, difference of decomposition rate between each PFCAs or PFSAs became smaller. For example, decomposition rate of PFBA and PFOA were almost equal in the mixed system, whereas in single PFBA or PFOA solution, $k_{obs}$ of PFOA decomposition was 2.27 times faster than that of PFBA decomposition. These results suggested decomposition of PFCAs and PFSAs homologs had inhibition effect on each other in the mixed system, which was mainly due to the competition on $e_{aq}^-$. When sulfite dosage and UV intensity was fixed, the generation rate of $e_{aq}^-$ was constant, whereas PFCAs and PFSAs with different chain length had different electron affinity towards $e_{aq}^-$, hence leading to distinct decomposition kinetics.

3.3. Effects of carbon chain length

Decomposition rate of PFCAs and PFSAs was highly correlated with their physicochemical properties. As shown in Table 2, log$k_{obs}$ of both PFCAs and PFSAs increased with the increase of carbon chain length, which means their hydrophobicity also increased with the increase of carbon chain length, thus longer-chain PFCAs and PFSAs would more likely assemble at the gas/liquid interface within the range of UV irradiation and lead to higher rate constants. Polarizability indicates the extent of covalent bond can be influenced by external electric field, and is closely related to the activity of chemical reagents. Generally, chemical activity of specific chemical reagent increases with the increase of its polarizability. As for PFCAs and PFSAs, their polarizability increased by 84.8% and 60.6%, respectively, when carbon chain length increased from 4 to 8 (Table 2). Therefore, the covalent bond between functional group and perfluoroalkyl group, was more likely impacted by external electric field and thus causing cleavage in longer-chain PFCAs and PFSAs, which resulted in faster decomposition kinetics. In addition, the bond order and bond length of covalent bond between functional group and perfluoroalkyl group in PFCAs and PFSAs were calculated by Multiwfn 3.3.8 program, and results were shown in Table 3. Bond order of C-C bond in PFCAs (or C-S bond in PFSAs) decreased with the increase of carbon chain length, whereas bond length showed the opposite trend, both of which suggested C-C bond in PFCAs (or C-S bond in PFSAs) became weaker and more easily attacked by nucleophile when carbon chain length increased.
Figure 1. Decomposition efficiency of (a) PFCAs and (b) PFSAs and defluorination efficiency of (c) PFCAs and (d) PFSAs in the high photon flux UV/sulfite system.

Figure 2. $k_{\text{obs}}$ of PFCAs and PFSAs decomposition in single and mixed solution.
Table 1. A summary of different treatment approaches for PFCs decomposition.

| Treatment methods                  | Reaction conditions                                                                 | \( k_{\text{obs}} \) (min\(^{-1}\)) | PFBA | PFHxA | PFOA | PFHxS | PFOS | Ref.   |
|------------------------------------|--------------------------------------------------------------------------------------|-------------------------------------|------|-------|------|-------|------|--------|
| BDD electrooxidation               | I=23.24 mA cm\(^{-2}\) T=32 \(^\circ\)C electrolyte=1.4 g/L NaClO\(_4\) [PFCs]\(_0\)=0.114 mM | 0.0332 0.0335 0.0428 0.0223 0.0357 | [12] |
| UV/KI reduction                    | \( \lambda=254 \text{ nm} \) [KI]\(_0\)=10 mM [PFCs]\(_0\)=10 mg/L                  | 0.0013 0.0013 0.0013 0.0012 0.003  | [13] |
| High photon flux UV/sulfite reduction | \( \lambda=200-600 \text{ nm} \) [Na\(_2\)SO\(_3\)]\(_0\)=10 mM [PFCs]\(_0\)=16 mg/L    | 0.139 0.287 0.455 0.028 0.118 This work |

Table 2. Physicochemical property of PFCs used in this study.

| PFCs    | \( \log K_{\text{OW}} \) | \( \log K_{\text{OA}} \) | Polarizability | Solubility (mol/L) | \( k_{\text{obs}} \) (min\(^{-1}\)) |
|---------|-----------------|-----------------|----------------|--------------------|-------------------------------------|
| PFBA    | 2.66            | 3.46            | 9.2            | 0.35               | 0.139                               |
| PFHxA   | 4.10            | 3.83            | 13.1           | 0.30               | 0.287                               |
| PFOA    | 5.68            | 4.16            | 17.0           | 0.28               | 0.455                               |
| PFBS    | 2.03            | 4.16            | 12.7           | 0.36               | -                                   |
| PFHxS   | 3.29            | 4.27            | 16.6           | 0.14               | 0.028                               |
| PFOS    | 4.29            | 4.75            | 20.4           | 0.0023             | 0.118                               |

Table 3. Bond order and bond length of C-C bond between the carboxyl group and perfluoroalkyl group in PFCAs and C-S bond between the sulfonic acid group and perfluoroalkyl group in PFSAs.

| PFCs   | Carbon chain length | Bond order | Bond length (Å) |
|--------|---------------------|------------|-----------------|
|        | Mayer method        | Fuzzy method |                  |
| PFBA   | 4                   | 0.8360     | 0.8473          | 1.5653          |
| PFHxA  | 6                   | 0.8040     | 0.8460          | 1.5655          |
| PFOA   | 8                   | 0.7979     | 0.8455          | 1.5662          |
| PFBS   | 4                   | 1.0113     | 0.8143          | 1.8649          |
| PFHxS  | 6                   | 0.9959     | 0.8141          | 1.8650          |
| PFOS   | 8                   | 0.9738     | 0.8139          | 1.8709          |

4. Conclusion

\( e_{\text{aq}} \) based reduction is efficient for recalcitrant organic pollutants decomposition, such as PFCs. PFSAs and PFCAs decomposition kinetics in the high photon flux UV/sulfite system were 1~2 orders of
magnitude faster than that in previously studied BDD electrooxidation and UV/KI photoreduction systems. $k_{obs}$ of both PFSAs and PFCAs increased with the increase of carbon chain length. In mixed PFCAs or PFSAs solution, decomposition of each PFCAs or PFSAs was suppressed due to the competition of $e_{aq}^-$. 

Acknowledgements
This research was financially supported by Guangdong Basic and Applied Basic Research Foundation (Grant No. 2020A1515011545), Shenzhen Water Group Program (Grant No. 2019-131-F) and Shenzhen Polytechnic Program (Grant No. 6019310013K0).

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