Perfluorohexane Sulfonate Decomposition In a High Photon Flux UV/sulfite System: Kinetics and Influential factors

Yurong Gu¹, Jia Zhu¹*, Zijun Dong¹ and Xi Zhang¹
¹School of Construction and Environmental Engineering, Shenzhen Polytechnic, Shenzhen, Guangdong, 518055, P. R. China
*Corresponding author’s e-mail: zhujia@szpt.edu.cn

Abstract. Hydrated electron (e\textsubscript{aq}⁻) is a strong reductant, and is reported promising for recalcitrant organic pollutants decomposition. In this study, e\textsubscript{aq}⁻ based decomposition of one representative short chain perfluorinated compounds, perfluorohexane sulfonate (PFHxS) in a high photon flux UV/sulfite system was investigated. The observed rate constant (k\textsubscript{obs}) of PFHxS was 0.028 min⁻¹, which was one order of magnitude faster than that in previously studied UV/iodide system. UV intensity played an important role in the decomposition, when UV intensity was adjusted from 25% I\textsubscript{0} to 100% I\textsubscript{0}, k\textsubscript{obs} of PFHxS decomposition increased from 0.010 min⁻¹ to 0.028 min⁻¹. PFHxS decomposition efficiency was greatly enhanced in alkaline solution compared to that in the acidic solution.

1. Introduction

Due to the high chemical and thermal stability, low surface tension, perfluorinated compounds (PFCs) were widely used in many industrial activities [1]. The extensive usage of PFCs inevitably resulted in their existence in various environmental medium, especially in wastewater. Production of perfluorooctane sulfonate (PFOS), one dominant PFCs, has been restricted in most countries since 2009, considering their toxicities towards living organisms [2]. Short chain PFCs, such as perfluorohexane sulfonate (PFHxS) was introduced as an alternative of PFOS. Correspondingly, PFHxS has been frequently detected in water environment nearby fluorochemical manufacturing industries [3]. PFHxS has a similar chemical structure with PFHxS, and its biotoxicity has been recognized in recent years [4]. Thus, effective decomposition methods for PFHxS are very important for remediation of PFCs contaminated water environment.

Hydrated electron (e\textsubscript{aq}⁻) based process was promising for halogenated organic compounds decomposition, and UV/sulfite system was an eco-friendly and efficient way for e\textsubscript{aq}⁻ production [5]. e\textsubscript{aq}⁻ induced PFOS decomposition has been investigated by some researchers [6], whereas little attention was paid to the decomposition of short chain PFCs like PFHxS. In our previous study [7], a high photon flux UV/sulfite system was built and abundant e\textsubscript{aq}⁻ generation was achieved in this system. In this study, PFHxS was chosen as the representative short chain PFCs, the effects of UV intensity and initial solution pH on its decomposition was investigated. The findings can strengthen the understanding of e\textsubscript{aq}⁻ induced decomposition of recalcitrant organic pollutants

2. Materials and Methods

2.1. Chemicals

PFHxS (C\textsubscript{6}F\textsubscript{13}SO\textsubscript{3}K, 95%), sodium sulfite (Na\textsubscript{2}SO\textsubscript{3}, 98%), sodium hydroxide (NaOH, 96%), and
sulfuric acid (H$_2$SO$_4$, 98%) were purchased from Sigma-Aldrich and Aladdin Co., Ltd.

2.2. UV irradiation experiments
A high pressure mercury lamp (250W, Ushio, Japan) was used as the irradiation source, and its emission spectrum was mainly ranging from 200 nm to 600 nm. The maximum UV intensity (100% $I_0$) of this lamp was $6.6 \times 10^{-7}$ einstein cm$^{-2}$ s$^{-1}$ determined following the potassium ferrioxalate method [8], and UV intensity can be adjusted by transmission filters.

PFHxS decomposition experiments were carried out in a 50 mL opened glass cylinder. 25 mL reaction solution containing 16 mg/L PFHxS and 10 mM sulfite was pour into the reactor. The initial solution pH was 9.2 unless otherwise specified. The reaction temperature was maintained at 25 °C by a water cooling jacket. UV intensity was adjusted from 25% $I_0$ to 100% $I_0$ when investigating the effect of UV intensity on PFHxS decomposition. When investigating the effect of initial solution pH, pH was changed from 6.0 to 10.0 by adding hydroxide or sulfuric acid dropwise into the reaction solution.

2.3. Analysis
A UPLC/MS-MS analyser (Waters, USA) was used for PFHxS concentration determination. A mixture of acetonitrile and ammonium acetate (2 mM) was used as the mobile phase, and its flow rate was 0.3 mL/min. PFHxS was 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.

3. Results and discussion

3.1. Decomposition kinetics of PFHxS
PFHxS decomposition experiments in different photochemical systems were carried out, and results were shown in Figure 1. As shown in Figure 1, efficient PFHxS decomposition in the high photon flux UV/sulfite system was obtained. By using the same high pressure mercury lamp, PFHxS decomposition efficiencies in sole UV, UV/iodide, UV/sulfite systems after 30 min reaction were 1.37%, 12.75% and 52.45%, respectively. Pseudo first order model can be used to depict decomposition kinetics of PFHxS in the above three systems. The observed rate constants ($k_{obs}$) for PFHxS in sole UV, UV/iodide, UV/sulfite systems were 0.0005, 0.003 and 0.028 min$^{-1}$, respectively. Park et al reported $k_{obs}$ of PFHxS decomposition in UV/iodide system by a normal low pressure mercury lamp as irradiation source was 0.0012 min$^{-1}$ [9], which was one order of magnitude slower than that in the studied system, indicating the high pressure mercury lamp was very important for efficient PFHxS decomposition.

3.2. Effect of UV intensity
The effect of UV intensity on PFHxS decomposition were investigated where initial solution pH was kept at 9.2, and results were shown in Figure 2 and Table 1. PFHxS decomposition followed a pseudo first order model well, and higher UV intensity apparently enhanced PFHxS decomposition. For example, $k_{obs}$ increased from 0.010 min$^{-1}$ to 0.028 min$^{-1}$ when UV intensity was adjusted from 25% $I_0$ to 100% $I_0$. These results suggested higher UV intensity could lead to promoted $e_{aq}$ production, and hence benefit PFHxS decomposition. UV intensity in the present study provided by a high pressure mercury lamp was determined as $6.6 \times 10^{-7}$ einstein cm$^{-2}$ s$^{-1}$, and it was at least 20 folds higher than that provided by reportedly low-pressure mercury lamps [10]. A supplementary experiment further attested the employing of high pressure UV lamp was essential for the efficient decomposition of PFHxS, where the irradiation source was changed to a 10 W low pressure mercury lamp with other reaction conditions kept unchanged. After 300 min reaction, 79% PFHxS was decomposed at initial concentration of 16 mg/L, and the obtained $k_{obs}$ decreased to 0.005 min$^{-1}$.
3.3. Effects of initial solution pH

Decomposition of PFHxS at initial solution pH ranging from 6.0 to 10.0 was shown in Figure 3. The decomposition rate of PFHxS was strongly dependent on initial solution pH, with the increasing order of pH 6.0 ≈ pH 7.0 < pH 8.0 < pH 9.2 < pH 10.0. When initial solution pH was greater than 7.0, PFHxS decomposition could be fitted with pseudo first order kinetics (Table 1). It’s apparent that rate constant increased with an increase of initial solution pH. For example, the rate constant at initial solution pH 10.0 was 0.032 min⁻¹, which was 2.1 times higher than that at pH 8.0.

In the UV/sulfite system, sulfite can dissociate into an \( \text{e}_{aq}^- \) and sulfite radical under UV irradiation (Eq (1)). \( \text{e}_{aq}^- \) was a strong reductant, which could quickly react with PFCs [9]. The observed decomposition rate of PFHxS increased with the increase of initial solution pH indicated \( \text{e}_{aq}^- \) production in the present system increased with the increasing initial solution pH. Two main reasons accounted for this conclusion. Firstly, it’s believed higher pH values, especially above pH 7.0, can promote the generation of \( \text{SO}_3^{2-} \) in the testing solution, which governed \( \text{e}_{aq}^- \) production [11]. For example, the fraction of \( \text{SO}_3^{2-} \) at pH 9.0 was nearly 2.5 folds higher than that at pH 7.0 in 0.2 mM sulfite solution [12]. \( \text{SO}_3^{2-} \) fraction keeps increasing from pH 7.0 to 10.0, but when pH >9.0, more than 99% sulfite species was in the form of \( \text{SO}_3^{2-} \), thus further increase of pH led to less enhancement of \( \text{e}_{aq}^- \) production and PFHxS treatment efficiency. Secondly, the presence of \( \text{H}^+ \) under lower pH values would quickly converted \( \text{e}_{aq}^- \) to \( \cdot \text{H} \) with rate constant of \( 2.3 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) (Eq (3)), whereas at higher pH values, \( \cdot \text{H} \) was transformed to \( \text{e}_{aq}^- \) with rate constant of \( 2.2 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \) and thus increased \( \text{e}_{aq}^- \) quantum yield (Eq (4)).

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\begin{align*}
\text{SO}_3^{2-} + h\nu & \rightarrow \text{e}_{aq}^- + \text{SO}_3^- \quad \text{(1)} \\
\text{CH}_2\text{ClCOO}^- + \text{e}_{aq}^- & \rightarrow \cdot \text{CH}_2\text{COO}^- + \text{Cl}^- \quad \text{(2)} \\
\text{e}_{aq}^- + \text{H}^+ & \rightarrow \cdot \text{H} \quad \text{(3)} \\
\text{OH}^- + \cdot \text{H} & \rightarrow \text{e}_{aq}^- + \text{H}_2\text{O} \quad \text{(4)}
\end{align*}
\]

![Figure 1. PFHxS decomposition in different photochemical systems](image-url)
Figure 2. PFHxS decomposition at different UV intensity

Table 1. Pseudo first order rate constants of PFHxS at varied UV intensity and initial solution pH

| UV intensity (% I₀) | kₖobs  | R²       | Initial solution pH | kₖobs | R²       |
|---------------------|---------|----------|---------------------|--------|----------|
| 100                 | 0.028   | 0.9518   | 10.0                | 0.032  | 0.9730   |
| 75                  | 0.019   | 0.9668   | 9.2                 | 0.028  | 0.9518   |
| 50                  | 0.013   | 0.9815   | 8.0                 | 0.015  | 0.9065   |
| 25                  | 0.010   | 0.9803   | 7.0                 | na     | na       |
| -                   | -       | -        | 6.0                 | na     | na       |

Figure 3. PFHxS decomposition at different initial solution pH

Table 1. Pseudo first order rate constants of PFHxS at varied UV intensity and initial solution pH
4. Conclusion
Efficient PFHxS decomposition was achieved in the high photon flux UV/sulfite system with $k_{obs}$ of 0.028 min$^{-1}$, which was one order of magnitude faster than that in previously studied UV/iodide system. UV intensity played an important role in PFHxS decomposition, when UV intensity was adjusted from 25% $I_0$ to 100% $I_0$, $k_{obs}$ of PFHxS decomposition increased from 0.010 min$^{-1}$ to 0.028 min$^{-1}$. PFHxS decomposition efficiency was greatly enhanced in alkaline solution compared to that in the acidic solution.

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References
[1] Jin, H.B., Zhang, Y.F., Zhu, L.Y., Martin, J.W. (2015). Isomer profiles of perfluoroalkyl substances in water and soil surrounding a Chinese fluorochemical manufacturing park. Environ. Sci. Technol., 49: 4946-4954.
[2] Zhang, R.J., Ye, J.F., Wei, Q.Z., Li, M.J., Xu, K.H., Li, Z.H., Lin, W.T., Liu, P.S., Chen, R.P., Ma, A.D., Zhou, Z.F. (2018). Plasma concentration of 14 perfluoroalkyl acids (PFAAs) among children from seven cities in Guangdong, China. Sci. Total. Environ., 616: 1469-1476.
[3] Zhou, J., Li, Z., Guo, X.T., Li, Y., Wu, Z.H., Zhu, L.Y. (2019). Evidences for replacing legacy per- and polyfluoroalkyl substances with emerging ones in Fen and Wei River basins in central and western China. J. Hazard. Mater., 377: 78-87.
[4] Chen, F.J., Wei, C.Y., Chen, Q.Y., Zhang, J., Wang, L., Zhou, Z., Chen, M.J., Liang, Y. (2018). Internal concentrations of perfluorobutane sulfonate (PFBS) comparable to those of perfluoroocatane sulfonate (PFOS) induce reproductive toxicity in Caenorhabditis elegans. Ecotox. Environ. Safe., 158: 223-229.
[5] Merino, N., Qu, Y., Deeb, R.A., Hawley, E.L., Hoffmann, M.R., Mahendra, S. (2016). Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water. Environ. Eng. Sci., 33: 615-649.
[6] Tian, H.T., Guo, Y., Pan, B., Gu, C., Li, Hui., Boyd, S.A.. (2015). Enhanced photo reaction of nitro-aromatic comounds by hydrated electrons derived from indole on natural montmorillonite. Environ. Sci. Technol., 49: 7784-7792.
[7] Gu, Y.R., Dong, W.Y., Luo, C., Liu, T.Z. (2016). Efficient reductive decomposition of perfluoroocatanesulphonate in a high photon flux UV/sulfite system. Environ. Sci. Technol., 50: 10554-10561.
[8] Hatchard, C.G., Parker, C.A. (1956). A new sensitive chemical actinometer II potassium ferroxalate as a standard chemical actinometer[J]. Proceedings of the Royal Society A., 235: 518-536.
[9] Park, H., Vecitis, C. D., Cheng, J., Chio, W. Y., Mader, B. T., Hoffmann, M. R. (2009). Reductive defluorination of aqueous perfluorinated alkyl surfactants: Effects of inorganic group and chain length. J. Phys., Chem. 113: 690-696.
[10] Song, Z., Tang, H.Q., Wang, N., Zhu, L.H. (2013). Reductive defluorination of perfluoroocatanic acid by hydrated electrons in a sulfite-mediated UV photochemical system. J. Hazard. Mater., 262: 332-338.
[11] Fischer, M., Warneck, P. (1996). Photodecomposition and photooxidation of hydrogen sulfite in aqueous solution. J. Phys. Chem., 100: 15111-15117.
[12] Liu, X., Vellanki, B.P., Batchelor, B., Abdel-Wahab, A. (2014). Degradation of 1,2-dichloroethane with advanced reduction processes (ARPs): Effects of process variables and mechanisms. Chem. Eng. J., 237: 300-307.