Supplementary Information

A Perspective of emerging trends in integrated PFAS detection and remediation technologies with data driven approaches

Samaneh Yaghoobian [a], Manuel A. Ramirez-Ubillus [b], Lei Zhai [b,*], Jae-Hoon Hwang [a,**]

[a] Department of Building, Civil and Environmental Engineering, Concordia University, Montreal, QC, H3G 1M8, Canada

[b] NanoScience Technology Center and Department of Chemistry, University of Central Florida, Florida, USA.

∗ Corresponding authors.

∗∗ Corresponding authors.

E-mail addresses: lzhai@ucf.edu (L. Zhai), Jaehoon.hwang@concordia.ca (J.-H. Hwang)

The electrochemical degradation mechanism of PFOA has been extensively explored and involves multiple steps. Initially, a direct electron transfer generates $C_7F_{15}COO\bullet$ radicals on the anode surface (Eq. 1). These radicals undergo Kolbe decarboxylation, releasing CO_2 (Eq. 2) and form $C_7F_{15}\bullet$ radicals. Subsequent hydrolysis leads to the formation of perfluoroheptanoic acid ($C_6F_{13}COOH$), formic acid and fluoride ions (Eq. 3).[1, 2]

$$C_7F_{15}COO^- \rightarrow C_7F_{15}COO^{\bullet} + e^- \quad (1)$$

$$C_7F_{15}COO^{\bullet} \rightarrow C_7F_{15}^{\bullet} + CO_2 \quad (2)$$

$$C_7F_{15}COO^{\bullet} + 3H_2O \rightarrow C_6F_{13}COOH + HCOOH + 2F^- + 2H^+ + OH^{\bullet} \quad (3)$$

After decarboxylation, $C_7F_{15}\bullet$ radicals react with O_2, H_2O, or OH• radicals. C7F15• radicals react with O_2 to form the $C_7F_{15}OO\bullet$ radicals (Eq. 4), which subsequently interact with perfluoro-heptylperoxy radicals to produce the intermediates $C_7F_{15}O\bullet$ (Eq. 5). These intermediates eventually break down into shorter-chain compounds and byproducts such as CO_2, COF_2, and HF (Eq. 6 and 7). These four steps (4-7) cycle until the initial 7-carbon chains break down into shorter chain products.[3, 4]

$$C_7F_{15}^{\bullet} + O_2 \rightarrow C_7F_{15}OO^{\bullet} \quad (4)$$

$$C_7F_{15}OO^{\bullet} + R'COO^{\bullet} \rightarrow C_7F_{15}O^{\bullet} + R'CO^{\bullet} + O_2 \quad (5)$$

$$C_7F_{15}O^{\bullet} \rightarrow C_6F_{13}^{\bullet} + COF_2 \quad (6)$$

$$COF_2 + H_2O \rightarrow CO_2 + 2HF \quad (7)$$

Hydrolysis pathways are also crucial for PFAS degradation. The oxidation of radicals like $C_7F_{15}\bullet$ on the anode produces carbocation intermediates $C_6F_{13}C^+F_2$ (eq. 8), which react

with water to form alcohols such as $C_6F_{13}CF_2$-OH (Eq. 9). These alcohols undergo anodic oxidation to generate acyl fluoride ($C_6F_{13}COF$) (Eq. 10), which can further oxidize and hydrolyze into shorter chain perfluoroalkyl carboxylic acids like $C_6F_{13}COOH$ (Eq. 11, 12 and 13). Finally, $C_6F_{13}COOH$ undergoes deprotonation (Eq. 14), forming radical $C_6F_{13}COO^{\bullet}$. The subsequent decomposition through Kolbe's decarboxylation reduces the initial carbon chain by a CF_2 unit.[5] This deprotonation process generates radicals that drive the Kolbe decarboxylation reaction forward, progressively shortening the PFAS carbon chain length.

$$C_7F_{15}^{\bullet} \rightarrow C_6F_{13}C^{+}F_2 + e^{-} \quad (8)$$

$$C_6F_{13}C^{+}F_2 + H_2O \rightarrow C_6F_{13}CF_2OH + H^{+} \quad (9)$$

$$C_6F_{13}CF_2OH \rightarrow C_6F_{13}COF + F^{\bullet} + H^{+} + e^{-} \quad (10)$$

$$C_6F_{13}COF \rightarrow C_6F_{13}C^{+}O^{\bullet}F + e^{-} \quad (11)$$

$$C_6F_{13}C^{+}O^{\bullet}F + H_2O \rightarrow C_6F_{13}CO^{-}F\text{-}O^{+}H + H^{+} \quad (12)$$

$$C_6F_{13}CO^{-}F\text{-}O^{+}H \rightarrow C_6F_{13}COO^{+}H + F^{-} \quad (13)$$

$$C_6F_{13}COO^{+}H \rightarrow C_6F_{13}COO^{\bullet} + H \quad (14)$$

Finally, when the hydroxyl radical $OH^{\bullet}$ is the main oxidative specie, the degradation mechanism comprises the following reactions. The addition of the hydroxyl radical to the species $C_7F_{15}^{\bullet}$ will produce an unstable alcohol $C_7F_{15}OH$ (eq. 15). This alcohol undergoes HF elimination to form $C_6F_{13}COF$ and release a fluoride anion F^- (eq. 16). The $C_6F_{13}COF$ specie will be hydrolyzed forming $C_6F_{13}COO^-$ along with the release of another fluoride anion (eq. 17). Finally, the perfluoroheptanoic acid in its anionic form can be oxidized (eq. 18) to produce the species $C_6F_{13}COO^{\bullet}$ and repeat the cycle until the initial carbon chain is

reduce by a CF_2 unit [1,6].

$C_7F_{15}^{\bullet} + OH^{\bullet} \rightarrow C_7F_{15}OH$ (15)

$C_7F_{15}OH \rightarrow C_6F_{13}COF + H + F^-$ (16)

$C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COO^- + 2H^+ + F^-$ (17)

$C_6F_{13}COO^- \rightarrow C_6F_{13}COO^{\bullet} + e^-$ (18)

Reference

1. A. Román Santiago, P. Baldaguez Medina and X. Su, *Electrochim. Acta*, 2022, **403,** 139635.
2. M.-K. Kim, T. Kim, T.-K. Kim, S.-W. Joo and K.-D. Zoh, *Sep. Purif. Technol.*, 2020, **247**.
3. S. Sharma, N. P. Shetti, S. Basu, M. N. Nadagouda and T. M. Aminabhavi, *Chem. Eng. J.*, 2022, **430**.
4. K. Sivagami, P. Sharma, A. V. Karim, G. Mohanakrishna, S. Karthika, G. Divyapriya, R. Saravanathamizhan and A. N. Kumar, *Sci. Total Environ.*, 2023, **861**, 160440.
5. D. Huang, K. Wang, J. Niu, C. Chu, S. Weon, Q. Zhu, J. Lu, E. Stavitski and J. H. Kim, *Environ. Sci. Technol.*, 2020, **54**, 10954-10963.
6. Q. Zhuo, S. Deng, B. Yang, J. Huang and G. Yu, *Environ Sci Technol*, 2011, **45**, 2973-2979.