The degradation mechanisms of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) by different chemical methods: A critical review

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) are a class of artificial compounds comprised of a perfluoroalkyl main chain and a terminal functional group. With them being applied in a wide range of applications, PFASs have drawn increasing regulatory attention and research interests on their reductions and treatments due to their harmful effects on environment and human beings. Among numerous studies, chemical treatments (e.g., photochemical, electrochemical, and thermal technologies) have been proved to be important methods to degradation PFASs. However, the pathways and mechanisms for the degradation of PFASs through these chemical methods still have not been well documented. This article therefore provides a comprehensive review on the degradation mechanisms of two important PFASs (perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)) with photochemical, electrochemical and thermal methods. Different decomposition mechanisms of PFOA and PFOS are reviewed and discussed. Overall, the degradation pathways of PFASs are associated closely with their head groups and chain lengths, and H/F exchange and chain shortening were found to be predominant degradation mechanisms. The clear study on the degradation mechanisms of PFOA and PFOS should be very useful for the complete degradation or mineralization of PFASs in the future.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been extensively used in a wide range of applications, (including fluoropolymers, liquid repellants for paper, packaging, textile, leather, and carpet goods, industrial surfactants, additives, and coatings, etc.) due to its unique physicochemical characteristics (Wang et al., 2015; Ateia et al., 2019; Bentel et al., 2019; Pelch et al., 2019; Johnson et al., 2020; Poothong et al., 2020). However, there are growing concerns regarding PFAS exposures because human PFASs exposure is positively linked to cancer, obesity, elevated cholesterol, immune suppression, and endocrine disruption (Behr et al., 2018; Caron-Beaudoin et al., 2019; Sunderland et al., 2019; Anderko and Pennea, 2020; Spratlen et al., 2020). Meanwhile, significant potential health risks could come from the regulatory determination. In 2016, US Environmental Protection Agency (EPA) issued a Lifetime Health Advisory for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) at 70 ng L⁻¹ in drinking water (Boone et al., 2019; Pontius, 2019). In November 2018, the EPA published Draft Human Health Toxicity Assessments for PFASs, which emphasized the apprehensions about these short-chain PFASs that have been widely detected in various environmental media. In February 2019, EPA published a comprehensive Action Plan that described the approaches to address current PFASs contamination, preventing future contamination, and effectively communicating with the public about PFASs (Boone et al., 2019). Therefore, the aim of human health and requirement of regulatory pressure motivate industries to seek more effective and efficient treatment technologies for PFASs.

Until now, effective degradation methods have been incorporated as physical, chemical and biological treatments for PFASs (Song et al., 2013; Lin et al., 2018; Watanabe et al., 2018; Chen et al., 2020a; Xu et al., 2020b).
et al., 2020). But the biological method (e.g., cometabolic biotransformation) generally behaves relatively low degradation ratio, while the physical technology (e.g., carbon adsorption and membrane filtration) merely make PFASs removal and the enriched PFASs in physical separation wastes often require be further treated using chemical methods (Tenorio et al., 2020b). The chemical decomposition have shown good prospects because it can not only strongly destruct highly stable C-F bonds of PFASs, but also is more efficient than the other two methods (Merino et al., 2016a). The chemical technologies for PFASs degradation mainly include photochemical, electrochemical, and thermal process (Wang et al., 2015; Kucharyzk et al., 2017; Li et al., 2020b). UV radiation has been used to destroy highly stable C-F bonds of PFASs (Vellanki et al., 2013b; Chen et al., 2020b). In electrochemical decomposition, complete mineralization of perfluorooalkyl acids (PFAs) has been achieved by electro-oxidation via direct electron transfer on “non-active” anodes, and boron-doped diamond (BDD), SnO2-Sb, and Ti/SnO2-Sb have usually been used as electrode (Lin et al., 2018). PFOA and PFOS can be quickly decomposed and mineralized under appropriate thermal conditions, and this technology usually is assisted by inorganic calcium such as calcium hydroxide (Ca(OH)2), calcium oxide (CaO), calcium carbonate (CaCO3) (Wang et al., 2015). Although these methods have shown some advantages and beneficial effects for PFASs (e.g., PFOA and PFOS) treatment (shown in Table 1), there are inevitably a few limitations such as generation of harmful side products. Further improvement and optimization of these technologies for PFASs degradation are therefore urgently needed.

Although there has been extensive research work on the occurrence, fate, and transformation of PFASs, the destruction mechanisms of PFASs, special for PFOA and PFOS, have been significantly underexplored in the literature. In the review, findings from literatures on PFOA and PFOS degradation using the chemical technologies including photochemical, electrochemical, and thermal process are reviewed and discussed. The aim was to provide a state-of-the-art review on the systematic mechanisms and pathways of PFASs decomposition in the process.

2. Photochemical degradation

Photochemical reductive destruction with assistance of photocatalytic materials can produce various free reducing radicals (e.g., \( \text{OH, } \text{H}^\bullet \) and \( \text{O}_2^\bullet^- \)) in solution, such as photoreduction of sulfite (\( \text{SO}_4^{2-} \)), iodide (\( \Gamma^- \)), dithionite (S\( \text{O}_4^{2-} \)), ferrocyanide (Fe(CN)\( \text{S}^\bullet^- \)), which facilitate the effective decomposition of PFASs in the liquid phase (Huang et al., 2007; Vellanki et al., 2013a; Merino et al., 2016b; Bao et al., 2019; Tenorio et al., 2020a). In fact, the effective degradation of PFASs via the photochemical treatment is predominantly attributed to the generation of \( \text{e}_\text{aq}^- \) instead of other reducing agents produced (e.g., \( \text{OH, } \text{O}_2^\bullet^- \) and \( \text{H}_2\text{O}_2 \)), evidenced by scavenging experiments (Lyu et al., 2015; Tian et al., 2016; Gu et al., 2017b; Sun et al., 2018; Rao et al., 2020). \( \text{e}_\text{aq}^- \) is a powerful reducing agent with a standard reduction potential of \(-2.9 \text{ V}\), and it has a high tendency to react with PFASs via a one-electron transfer mechanism (Schwarz, 1981; Park et al., 2011; Gu et al., 2017a). Rate constants of the reactions vary from \(-10 \text{ M}^{-1} \text{ s}^{-1}\) to a diffusion-control limit but the activation energies are in the range 6–30 kJ mol\(^{-1}\), implying that the reactive kinetics is restricted via the accessibility of a vacant orbital over target species (Huang et al., 2007; Yamamoto and Suzuki, 2020; Zheng et al., 2020).

2.1. Photochemical degradation of PFOA

H/F exchange and chain shortening are mainly reactive mechanisms (see Fig. 1), which have been extensively related to the PFOA degradation with \( \text{e}_\text{aq}^- \) (Qu et al., 2010; Li et al., 2012; Song et al., 2013; Yamamoto and Suzuki, 2020). In the PFOA molecule, the \( \alpha \)-location \(-\text{CF}_7\text{F}_7\text{OH}^- \) at the carboxyl group exhibits a high chemical reactivity, which may be linked to the induction of the head group, which provides a preferential reaction center (Qu et al., 2010; Bentel et al., 2019a). Density Functional Theory (DFT) calculations show that the \( \alpha \)-position C-F bonds of perfluorocarboxylic acids (PFacas) radical anions will spontaneously stretch when additional electrons attack the PFacas, which subsequently promotes bonds breaking (Biotegovil et al., 2018; Bentel et al., 2019a; Wang et al., 2020c). The subsequent cleavage of the C-F bonds results in production of fewer-fluorine radical anions, removal of \( \text{F}^- \) (Eq. (1)), and addition of H (Eq. (2)) to complete the H/F exchange process (Qu et al., 2010; Ahmed et al., 2020; Li et al., 2020c).

\[
\begin{align*}
\text{C}_2\text{F}_7\text{O}_2^\bullet^- + \text{e}_\text{aq}^- & \rightarrow \text{C}_2\text{F}_7\text{COO}^- + \text{F}^- \quad (1) \\
\text{C}_2\text{F}_7\text{COO}^- + \text{H}_2\text{O} & \rightarrow \text{C}_2\text{F}_7\text{HCOO}^- + \cdot\text{OH} \quad (2)
\end{align*}
\]

In the first degradation pathway, the photochemical treatment is deemed to trigger PFOA decomposition to generate \( \text{C}_2\text{F}_7\text{COO}^- \), and CH carbens (i.e., \( \text{CH}_2 \)) (Eq. (3)) after two aforementioned H/F exchanges (\( \text{C}_2\text{F}_3\text{H}_2\text{COO}^- \)) (Wang et al., 2017a; Bentel et al., 2019b). The produced \( \text{C}_2\text{F}_3\text{H}_2\text{COO}^- \) can be recombined to form \( \text{C}_2\text{F}_5\text{COO}^- \), which has a fewer \( \text{CF}_3 \) than PFOA anions (Eq. (4)) (Huang et al., 2007; Wang and Zhang, 2011; Gu et al., 2017b; Bentel et al., 2019a; Liu et al., 2020).

\[
\begin{align*}
\text{C}_2\text{F}_7\text{H}_2\text{COO}^- + \cdot\text{H}_2\text{O} & \rightarrow \text{C}_2\text{F}_7\text{COO}^- + \cdot\text{CH}_2 \quad (3) \\
\text{C}_2\text{F}_7\text{COO}^- + \cdot\text{H}_2\text{O} & \rightarrow \text{C}_2\text{F}_7\text{HCOO}^- \quad (4)
\end{align*}
\]

The second route involves four consecutive steps which are composed of decarboxylation (Eq. (5)), induced by \( \text{e}_\text{aq}^- \), hydroxylation (Eq. (6)), F elimination (Eq. (7)) and hydrolysis (Eq. (8)) (Chen et al., 2019; Yang et al., 2020a). This degradation pathway is commonly named as the decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) mechanism (Ahmed et al., 2020).

\[
\begin{align*}
\text{C}_2\text{F}_7\text{COO}^- + \cdot\text{H}_2\text{O} & \rightarrow \text{C}_2\text{F}_7\text{COO}^- \quad (5) \\
\text{C}_2\text{F}_7\text{COO}^- + \cdot\text{H}_2\text{O} & \rightarrow \text{C}_2\text{F}_7\text{HCOO}^- + \text{H}^+ \quad (6) \\
\text{C}_2\text{F}_7\text{H}_2\text{OH} & \rightarrow \text{C}_2\text{F}_7\text{COOH} + \cdot\text{H}^+ + \text{F}^- \quad (7) \\
\text{C}_2\text{F}_7\text{COOH} + \cdot\text{H}_2\text{O} & \rightarrow \text{C}_2\text{F}_7\text{COO}^- + 2\text{H}^+ + \text{F}^- \quad (8)
\end{align*}
\]

Since the formed \( \text{C}_2\text{F}_7\text{COOH} \) can be further degraded in the similar manner as above mentioned, several \( \text{CF}_2 \) units can be stepwise eliminated through the DHEH mechanism (Wang et al., 2017b; Chen et al., 2020).

<table>
<thead>
<tr>
<th>Chemical methods</th>
<th>PFAs</th>
<th>Conditions</th>
<th>Degradation ration (%)</th>
<th>Defluorination ration (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photochemical treatment</td>
<td>PFOA</td>
<td>0.02 mM, pH = 9, 6 h</td>
<td>&gt;99</td>
<td>&gt;80</td>
<td>Zhang et al. (2015)</td>
</tr>
<tr>
<td></td>
<td>PFOS</td>
<td>0.20 μM, pH = 2.5 h</td>
<td>&lt;35</td>
<td>17</td>
<td>Park et al. (2009b)</td>
</tr>
<tr>
<td>Electrochemical treatment</td>
<td>PFOA</td>
<td>0.012 mM, pH = 6.7</td>
<td>&gt;90</td>
<td>58</td>
<td>Schaefer et al. (2017)</td>
</tr>
<tr>
<td></td>
<td>PFOS</td>
<td>0.40 mM, pH = 4.0, 30 h</td>
<td>&gt;90</td>
<td>100</td>
<td>Carter and Farrell (2000)</td>
</tr>
<tr>
<td></td>
<td>PFOA</td>
<td>300–900 °C, 15 min</td>
<td>–</td>
<td>–</td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td></td>
<td>PFOS</td>
<td>300–900 °C, 1–30 min</td>
<td>–</td>
<td>–</td>
<td>Wang et al. (2013)</td>
</tr>
</tbody>
</table>

Table 1: Efficient methods of chemical degradation for PFOA and PFOS.
et al., 2019; Liu et al., 2020).

In fact, both the reactive mechanisms for PFOA photochemical degradation have been proposed to have their deficiencies in the literature. As for the direct photolysis hypothesis of C–C bonds breakage on PFOA, studies show that a limited defluorination efficiency could be present, but that is not sufficient to support direct UV photolysis of PFOA (Song et al., 2013; Li et al., 2020b). Although another study advocating the DHEH mechanism, it was not clear how eaq triggers decarboxylation (Bentel et al., 2019a). In summary, the DHEH decomposition route seems more plausible than the H/F exchange in the two chain shortening mechanisms (e.g., Eq. (1)–(4), Eq. (5)–(8)), but the in-depth studies are needed to explore how eaq is involved in the C–C scission of PFOA.

2.2. Photochemical degradation of PFOS

As shown in Fig. 2, four reaction pathways including desulfonation, H/F exchange and two types of chain shortening by the photochemical technology have been proposed to explain the reductive destruction of PFOS with eaq (Park et al., 2011; Jin and Zhang, 2015; Gu et al., 2016; Trojanowicz et al., 2020). In the desulfonation process, the breaking of C–S bonds on PFOS initially occurs after the attachment of eaq (Yamamoto et al., 2007; Gu et al., 2017a; Yang et al., 2020b). Since C–S band (272 kJ mol⁻¹) of PFOS has a lower bond energy than C–C band (346 kJ mol⁻¹), and the distance between C and S atoms (4.463 Å) is longer than that of C–C (1.529–1.727 Å) or S–O (1.651 Å) on PFOS, so that C–S separation is relatively easy to happen (Eq. (9)–(10)) (Filho and de Souza, 2020; Khan et al., 2020). Furthermore, the DFT calculation also shows that the C-S bond will stretch after the production of ‘CF2SO3⁻’ radical anions, which indicates the removal of sulfate group from the fluorocarbon chain (Bentel et al., 2019a). However, there are two reactive directions for the following C–S scission of ‘CF2SO3⁻’. On the one hand, the ‘CF2SO3⁻’ will decompose into CF3I, followed by the production of CF2OH, which is subsequently converted to PFOA by Eqs. (7) and (8) (Gu et al., 2016). On the other hand, ‘CF3I’ may be formed in the desulfonation reaction (Eq. (11)), before being transformed to PFOA via Eq. (6)–(8) (Bentel et al., 2019a).

\[ \text{C}_8\text{F}_{17}\text{SO}_3^- + e_{aq} \rightarrow \text{C}_8\text{F}_{17}\text{SO}_2^- \]  
(9)  
\[ \text{C}_8\text{F}_{17}\text{SO}_2^- \rightarrow \text{C}_8\text{F}_{17} + \text{SO}_4^- \]  
(10)

\[ \text{C}_8\text{F}_{17}\text{SO}_3^- \rightarrow \text{C}_8\text{F}_{17} + \text{SO}_4^- \]  
(11)

H/F exchange is the second degradation pathway, the removal of F could happen after eaq attacks on PFOS, resulting in the formation of PFOS radicals (Sun et al., 2018; Gu et al., 2020). The generation of PFOS radicals is result from the eaq preferentially attaches the centermost C–F bonds on PFOS depending on the lowest bond dissociation energy (446.31 kJ mol⁻¹) (Jin and Zhang, 2015; Gu et al., 2016; Cui et al., 2020). The F elimination is successively finished through the reactions (Eq. (12) and (13)), which like the H/F exchange of PFOA (Eq. (1) and (2)) but taking the place of C–F positions.

\[ \text{C}_8\text{F}_{17}\text{SO}_3^- + e_{aq} \rightarrow \text{C}_8\text{F}_{17}\text{SO}_2^- \rightarrow \text{C}_8\text{F}_{17}\text{SO}_2^- + F^- \]  
(12)  
\[ \text{C}_8\text{F}_{17}\text{SO}_2^- + \text{H}_2 \rightarrow \text{C}_8\text{F}_{17}\text{HSO}_3^- + \text{OH}^- \]  
(13)

Chain shorting is the third degradation pathway for PFOS. The C4–C8 atom of the perfluoroalkane chain on PFOS possess the lowest molecular orbitals unoccupied, thus the positions have sigma antibonding abilities (Park et al., 2009a; Gu et al., 2016). The binding between the carbon atoms is weak when eaq is attached to the intermediate –CF2– units, which promotes the fracture of the C–C bonds. As a result, the first C–C scission mechanism occurs after the attachment of eaq on the middle –CF2– to produce ‘CF2(CF2)2CF2–’ (CF2)2SO3⁻, which subsequently recombines with protons to finish the C-C bond breaking via intramolecular electron transfer fracture (Eq. (14)) (Park et al., 2009a).

\[ \text{C}_8\text{F}_{17}\text{SO}_2^-+ \text{CF}_2(\text{CF}_2)\text{SO}_3^- + \text{H}^- \rightarrow \text{C}_8\text{F}_{17}\text{SO}_2^-+ \text{CHF}_2 + \text{CF}_2(\text{CF}_2)\text{SO}_3^- \]  
(14)

The final C–C division pathway produces ‘CF8F16SO3⁻’ after undergoing reaction Eq. (12), which is subsequently converted into carbanion ‘CF8F16SO3⁻’ after reacting with eaq (Eq. (15)) (Park et al., 2009a; Jin and Zhang, 2015).

\[ \text{C}_8\text{F}_{17}\text{SO}_2^- + e_{aq} \rightarrow \text{C}_8\text{F}_{16}\text{SO}_3^- \]  
(15)

Furthermore, the perfluoroalkane anion (‘CF8F16SO3⁻’) could be further dissociated into the shorter-chain ‘CF3I’ and the alkene due to the reductive cleavage of C–C (Eq. (16)) (Park et al., 2009a; Gu et al., 2016). The carbanion ‘CF3I’ would react with ‘COOH from the PFOA degradation to generate perfluorobutanoic acid (PFBA) (Cui et al., 2020).

\[ \text{C}_8\text{F}_{17}\text{SO}_2^-+ \text{CF}(\text{CF}_2)\text{SO}_3^- + \text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2 + \text{CF}_{17} = \text{CF}(\text{CF}_2)\text{SO}_3^- \]  
(16)
3. Electrochemical degradation

Oxidation electrochemical technology can degrade the toxic or difficult biodegradable organic pollutants because of its advantages including high oxidation efficiency, fast reaction rate, easy operation, environmental compatibility, and cost-effectiveness (Chen et al., 2003; Trautmann et al., 2015; Li et al., 2020a; Mousset and Doudrick, 2020; Wang et al., 2020b). Electrochemical oxidation has also been shown to significantly destroy PFASs through the function of reactive oxygen species (e.g., *OH, H2O2, O3*) (Sires et al., 2006; Chaplin, 2014). The reaction process is generally initiated by non-active anodes (e.g., BDD, PbO2, SnO2, and Magnéli phase Ti6O7) (Sires et al., 2006; Niu et al., 2012; Yang et al., 2017; Wang et al., 2020b; Witt et al., 2020). Both long-chain PFASs and short-chain analogues can be degraded effectively in electrochemical reactors (Schaefer et al., 2017, 2018; Schaefer et al., 2018; Pierpaoli et al., 2020).

The degradation of PFASs on surface of the electrodes is associated closely with electron transfer reactions (Soriano et al., 2017; Liang et al., 2018). A brief mechanism of degradation for PFASs by anodes is described in the following chemical reactions. Under the influence of an electric field, an electron is initially transferred from the head group of PFASs to the anode to form PFASs radicals (Eq. (17) and Eq. (18)), which are then decomposed into *CnF2n+1* (Eq. (19) and Eq. (20)), and the formed *CnF2n+1* would combine with *OH* to undergo the subsequent stepwise elimination of −CF2− units (Lin et al., 2013; Fang et al., 2017; Le et al., 2019; Su et al., 2019).

\[
\begin{align*}
C_2F_5COO^- & \rightarrow C_2F_5COO^- + e^- \quad (17) \\
C_2F_5SO_3^- & \rightarrow C_2F_5SO_3^- + e^- \quad (18) \\
*C_2F_5COO & \rightarrow C_2F_5COO^- + CO_2 \quad (19) \\
*C_2F_5SO_3 & + H_2O \rightarrow C_2F_5COO^- + SO_4^{2-} + 2H^+ \quad (20)
\end{align*}
\]

3.1. Electrochemical degradation of PFOA

Two kinds of carbon chain shortening pathways are involved in the electrochemical degradation mechanism of PFOA (shown in Fig. 3). The first is a route from PFOA to perfluorohexanoic acid (PFHxA, a fewer −CF2− than PFOA) (Zhuo et al., 2011). As shown in Eq. (21), a degradation mechanism initiated by *OH* is proposed, because the amount of *OH* is abundant, resulting in high chemical reactivity in the electrolysis process (Ahmed et al., 2020). Then HF will be eliminated from C2F5OH to generate acyl fluoride C2F5COF (Eq. (22)). The C2F5COF generated subsequently react with H2O through hydrolysis to produce C2F5COOH (Eq. (23)) (Xiao et al., 2011; Zhuo et al., 2012; Liu et al., 2019; Pierpaoli et al., 2020).

\[
\begin{align*}
*C_2F_5 + *OH & \rightarrow C_2F_5OH \\
C_2F_5OH & \rightarrow C_2F_5COF + HF \quad (22) \\
C_2F_5COF + H_2O & \rightarrow C_2F_5COOH + F^- \quad (23)
\end{align*}
\]

Another degradation pathway is a process in which the *CnF2n* radicals firstly react with oxygen produced from water electrolysis to generate the C2F5O* radicals (Eq. (24)) (Lin et al., 2012). Then, the C2F5O* radical would combine with another RCOO* radical to form a C2F5O* radical (Eq. (25)) (Panchangam et al., 2009; Zhuo et al., 2011). As shown in Eqs. (26) and (27), the C2F5O* radicals subsequently follow two reaction pathways, namely 1) reaction with HO* to form C2F5OH; and 2) decomposition to form perfluoroalkane radicals (*CnF2n*) and carboxyl fluoride (COF2). The produced COF2 will be completely decomposed (Eq. (28)) (Hori et al., 2008; Zhuo et al., 2011; Wang et al., 2020a). For these pathways, the generated CnF2nCOOH intermediate would undergo the same −CF2− extraction process like as PFOA and transfer to perfluorohexanoic acid (PFHxA, C2F5COOH).

\[
\begin{align*}
*C_2F_5 + O_2 & \rightarrow C_2F_5OO* \quad (24) \\
C_2F_5O* + RCOO* & \rightarrow C_2F_5O* + RCOO* + O_2 \quad (25) \\
C_2F_5O* + HO* & \rightarrow C_2F_5OH + O_2 \quad (26) \\
C_2F_5O* & \rightarrow *C_2F_13 + COF_2 \quad (27) \\
COF_2 & \rightarrow CO_2 + 2HF \quad (28)
\end{align*}
\]

3.2. Electrochemical degradation of PFOS

There are two main decomposition mechanisms for PFOS via electrochemical degradation (Fig. 4). Under one decomposition pathway, C6F15SO3 initially undergoes chemical reactions Eq. (18) and Eq. (20) to form C6F15*, resulting from the transfer of an electron from the head-group of C6F15SO3 to an anode (Lin et al., 2012; Yang et al., 2017). Then the formed C6F15* will react with OH* from electrolysis of H2O to generate C6F15OH (Eq. (29)) (Niu et al., 2016; Duan et al., 2020). It is evident that the C6F15OH generated decompose into C6F15COF as shown in Eq. (30), and then rapidly hydrolyze to C7F15COO− (Eq. (31)) (Ma et al., 2015; Pica et al., 2019). C7F15COO− could further go through the decarboxylation cycle stepwise, resulting in the elimination of the CF2 units until complete mineralization, this process is usually reported as the degradation of PFCAs during advanced oxidation (Lin et al., 2013).

\[
\begin{align*}
*C_6F_{15} & \rightarrow C_6F_{15}OH \quad (29) \\
C_6F_{15}OH & \rightarrow C_6F_{14}COF + HF \quad (30) \\
C_6F_{15}OH & \rightarrow C_6F_{15}COOH + 2H^+ + HF \quad (31)
\end{align*}
\]
In another mechanism, the \( \text{C}_8\text{F}_{17} \) radical is firstly produced in the manners shown in Eq. (18) and Eq. (20). The formed \( \text{C}_8\text{F}_{17} \) can go through a reaction from \( \text{C}_8\text{F}_{17} \) to \( \text{C}_8\text{F}_{17}\text{OO} \) in the presence of a large amount of oxygen produced from water hydrolysis, which would consequently combine with \( \text{RFOO} \) to form \( \text{C}_8\text{F}_{17} \text{O} \) (Eq. (32) and Eq. (33)) (Zhuo et al., 2011, 2016; Zhuo et al., 2016). The \( \text{C}_8\text{F}_{17}\text{O} \) then decompose to \( \text{C}_7\text{F}_{15} \) and \( \text{COF}_2 \) due to its instability, and the \( \text{COF}_2 \) subsequently react with \( \text{H}_2\text{O} \) to produce \( \text{CO}_2 \) and \( \text{HF} \) (Eq. (34)) (Pehkonen et al., 1995; Kutsuna and Hori, 2007). By recycling the process, PFOS may be decomposed to \( \text{CO}_2 \) and \( \text{F}^- \).

\[
\begin{align*}
\text{C}_8\text{F}_{17} + \text{O}_2 & \rightarrow \text{C}_8\text{F}_{17}\text{OO} \quad (32) \\
\text{C}_8\text{F}_{17}\text{OO} + \text{RFOO} & \rightarrow \text{C}_8\text{F}_{17}\text{O} + \text{RFO} + \text{O}_2 \quad (33) \\
\text{C}_8\text{F}_{17}\text{O} & \rightarrow \text{C}_7\text{F}_{15} + \text{COF}_2 \quad (34)
\end{align*}
\]

4. Thermal degradation

Thermal treatment is an effective strategy to destruct PFASs because it can efficiently breakdown the strong halogen-carbon bonds on PFASs, such as C–F bonds (Yamada et al., 2005; Zhang et al., 2008; Ahmed et al., 2020). However, very few studies have explored the fate and pathways of PFASs during thermal process. PFASs could be decomposed under heat treatment, releasing fluorocarbon gases if these gases do not react with other materials such as calcification (FABEL and SWADD, 1975; Krusic and Roe, 2004; Ellis et al., 2005).

While calcium compounds (e.g., \( \text{CaO} \), \( \text{Ca(OH)}_2 \) and \( \text{CaCO}_3 \)) are commonly applied in sludge thermal conditions, the potential reactions between PFASs and these calcium-containing chemicals under thermal conditions have not been studied in detail (Wang et al., 2011, 2013; Wang et al., 2013; Song et al., 2013). Alkaline earth metal oxides such as \( \text{CaO} \) would form a cubic crystal structure, and activation of their surfaces by irradiation or thermal
treatment can provide strong reducing sites for the molecules in contacted, including PFASs (Klabunde et al., 1978; Chiesa et al., 2001; Valvekens et al., 2014). Moreover, the splitting of CaO crystals caused via heating continues to supply new surfaces for PFASs contact (Ikoma et al., 2001). At the same time, PFASs molecules would decompose into short-chain fluorinated radicals that are more reactive than PFASs molecules (Wang et al., 2015). Overall, mineralization of fluorine by calcium compounds is a promising strategy for PFAS treatment, and Fig. 5 shows thermal degradation mechanisms of PFOA and PFOS under the function of Ca(OH)2 (Wang et al., 2011, 2013, 2015bib_Wang_et_al_2011bib_Wang_et_al_2013bib_Wang_et_al_2015).

4.1. Thermal degradation of PFOA

PFOA is thermally stable at temperatures below 100 °C, while the thermogravimetric analyses (TGA) of previous studies indicates that PFOA could occur self-decomposition (decarboxylation reaction) when the temperature reached around 150 °C (Eq. (35)) (Wang et al., 2015; Xiao et al., 2020). Happening of the decarboxylation reaction for PFOA results from facilitation of the heating condition, like the decarboxylation reaction triggered by $\varepsilon_{\text{eq}}$ in the photochemical degradation (Wang et al., 2015). On the other hand, PFOA would decompose into many ion fractions ($\text{C}_x\text{F}_y\text{H}_z\text{O}_w$) such as $\text{CF}_x\text{F}_y\text{H}_z$ and $\text{CF}_x\text{H}_z$ in together function of high temperature and Ca(OH)2 (Eq. (36)), but the detailed reaction mechanism between PFOA and Ca(OH)2 is not clear until now due to the limited studies (Wang et al., 2015; Xiao et al., 2020).

$$\text{C}_2\text{F}_3\text{COOH} \rightarrow \text{C}_2\text{F}_3\text{H} + \text{CO}_2$$

$$\text{C}_2\text{F}_3\text{COOH} + \text{Ca(OH)}_2 \rightarrow \text{C}_2\text{F}_3\text{H} + \text{CaF}_2$$

4.2. Thermal degradation of PFOS

One possible reaction happening between PFOS and Ca(OH)2 is the replacement of fluorine on the perfluoroalkyl chain by a hydrogen atom from Ca(OH)2, which is defined as a hydrofluorination reaction, a type of organic reaction in which C–F bonds are replaced by C–H bonds in a matrix (Wang et al., 2013; Sedgwick et al., 2018; Kervarec et al., 2020; Webb et al., 2020). It is proposed that the substitution reaction occurs at the c-location C–F bonds adjacent to the sulfonic headgroup (Eq. (37)), because a-location –CF2 – performs higher activity, which may be due to the induction of the head group, similar to photochemical degradation of PFOA above discussed (Wang et al., 2015). The generated CaF2 subsequently react with H2O from the Ca(OH)2 to produce HF (Eq. (38)) (Wang et al., 2013; Olsen et al., 2017). As shown in Eq. (39), Ca(OH)2 also can trigger the decomposition of PFOS to generate many ion fractions including $\text{C}_x\text{F}_y\text{H}_z\text{O}_w$, $\text{C}_x\text{F}_y\text{O}_z\text{K}$ and $\text{C}_x\text{F}_y\text{O}_z\text{SO}_3\text{K}$ at a temperature lower than its gasification temperature (425 °C) (Wang et al., 2013, 2015bib_Wang_et_al_2013bib_Wang_et_al_2015). Although the thermal treatment is an effective and convenient method for the organic pollutants including PFASs, there are very little studies about the thermal degradation mechanisms of PFASs. As large amounts of PFASs existed in waste for incinerations, more studies are needed to show the thermal behavior, fate and transports of PFASs during waste incinerations.

$$\text{C}_2\text{F}_3\text{SO}_3\text{K} + \text{Ca(OH)}_2 \rightarrow \text{C}_2\text{F}_3\text{H}_z\text{SO}_3\text{K} + \text{CaF}_2$$

$$\text{CaF}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + \text{HF}$$

$$\text{C}_2\text{F}_3\text{SO}_3\text{K} + \text{Ca(OH)}_2 \rightarrow \text{C}_2\text{F}_3\text{H}_z\text{O}_w\text{K}$$

5. Conclusions

This review outlined degradation pathways of PFOA and PFOS via three common chemical methods (photocatalytic, electrochemical and thermal treatments), and H/F exchange and chain shortening were found to be the predominant degradation mechanisms. However, there are some different degradation mechanisms were also figured out between PFOA and PFOS and among different methods. For example, the sulfonate group in PFOS caused a desulfonation reaction during its degradation, and different chain-length PFASs and F− would be formed under the synergistic reactions of H/F exchange, chain shortening and desulfonation. For different methods, besides the similar H/F exchange and chain shortening mechanisms, thermal treatment also behaves the decarboxylation reaction for PFOA. Furthermore, it is worthy to note that calcium compounds can effectively facilitate the degradation of PFASs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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