



## Review

# Microbial and thermal treatment techniques for degradation of PFAS in biosolids: A focus on degradation mechanisms and pathways

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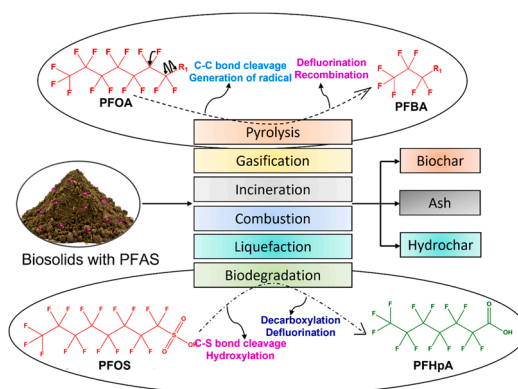
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## HIGHLIGHTS

- Thermal degradation of PFAS follows a 3-step random chain-scission pathway.
- Microbial degradation involves C-S bond cleavage, hydroxylation, decarboxylation.
- Nucleophilic substitution and decarboxylation are favoured in liquefaction.
- Catalysts and basic solvents promote PFAS mineralization.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

Editor: Jörg Rinklebe

**Keywords:**

Biosolids  
Pyrolysis  
Per-and polyfluoroalkyl substances  
Incineration  
Hydrothermal liquefaction  
Gasification

## ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are persistent organic chemicals detected in biosolids worldwide, which have become a significant concern for biosolids applications due to their increasing environmental risks. Hence, it is pivotal to understand the magnitude of PFAS contamination in biosolids and implement effective technologies to reduce their contamination and prevent hazardous aftermaths. Thermal techniques such as pyrolysis, incineration and gasification, and biodegradation have been regarded as impactful solutions to degrade PFAS and transform biosolids into value-added products like biochar. These techniques can mineralize PFAS compounds under specific operating parameters, which can lead to unique degradation mechanisms and pathways. Understanding PFAS degradation mechanisms can pave the way to design the technology and to optimize the process conditions. Therefore, in this review, we aim to review and compare PFAS degradation mechanisms in thermal treatment like pyrolysis, incineration, gasification, smouldering combustion, hydrothermal liquefaction (HTL), and biodegradation. For instance, in biodegradation of perfluorooctane sulfonic acid (PFOS), firstly C–S bond cleavage occurs which is followed by hydroxylation, decarboxylation and defluorination re-

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<https://doi.org/10.1016/j.jhazmat.2023.131212>

Received 2 February 2023; Received in revised form 9 March 2023; Accepted 13 March 2023

Available online 15 March 2023

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actions to form perfluoroheptanoic acid. In HTL, PFOS degradation is carried through OH<sup>-</sup> catalyzed series of nucleophilic substitution and decarboxylation reactions. In contrast, thermal PFOS degradation involves a three-step random-chain scission pathway. The first step includes C–S bond cleavage, followed by defluorination of perfluoroalkyl radical, and radical chain propagation reactions. Finally, the termination of chain propagation reactions produces very short-fluorinated units. We also highlighted important policies and strategies employed worldwide to curb PFAS contamination in biosolids.

## 1. Introduction

Sewage sludge is the by-product of wastewater treatment, which is often treated with processes like anaerobic digestion and lime treatment to meet the standard guidelines for its acceptable usage [1]. This treated sewage sludge is called biosolids. Biosolids are often enriched with essential nutrients like P and N and other essential metals such as Zn, Cu, Co, and Ni for plant growth [2,3]. As a result, biosolids are widely used for agriculture and land rehabilitation applications. Evidently, some European countries, such as Germany and Australia, utilize > 60% of their biosolids for agriculture, while in the USA, approximately 50–55% of biosolids are applied for land applications [4]. The usage of biosolids is expected to increase governments' move toward circular and sustainable economies. Biosolids are considered eco-friendly and sustainable; thus, a circular economy around biosolids could be developed. Biosolids' employment in agriculture can replace inorganic fertilizers that can reduce the greenhouse gas (GHG) emissions related to their production. Approximately 192.5 kg of CO<sub>2e</sub> can be avoided by replacing 1 tonne of inorganic fertilizers with dry biosolids [4]. The carbon content of biosolids which is nearly 20%, can be converted to renewable energy, energy products, and value-added chemicals using thermochemical techniques such as pyrolysis, hydrothermal liquefaction, and anaerobic digestion. Producing green electricity from biosolids can attract Renewable Energy Credits, which could be valued at around US \$100/tonne of dry biosolids [4]. Considering all applications of biosolids, currently, the total biosolids economy is valued at US\$1.6 billion [2]. Since the usage of biosolids is expected to increase in agriculture, the biosolids economy is also projected to rise by 4.2% in the next decade [2].

Biosolids offer several advantages as nutrients for plant growth and as raw materials to produce green energy, but there are also certain challenges associated with emerging contaminants (ECs) that need to be addressed. For instance, wastewater treatment facilities are not designed to reduce ECs that finally end up in biosolids. Several ECs, including per- and polyfluoroalkyl substances (PFAS), have been identified in biosolids [5,6]. PFAS are considered of significant concern due to their persistent and ubiquitous nature and associated environmental risks [7]. PFAS are synthetic fluorinated chemicals made up of strong C–F bonds, which are characterized by extreme resistance to degradation and increase bioaccumulation and mobility potential. Consequently, elevated concentrations of PFAS have been reported in biosolids as well as effluents and influents in wastewater treatment plants. PFAS contamination also increases the cost of biosolids management [8–10]. A survey in the USA revealed that the average cost of biosolids management increased nearly 37% after PFAS regulations to reduce contamination were introduced [2]. Despite such costs, the ecological risks and the toxicological effects of PFAS, it is pivotal to reduce PFAS in biosolids so that they can be converted into a safe product for niche applications.

The application of cost-effective and sustainable technologies is highly desirable to manage PFAS-contaminated biosolids by reducing their environmental risks while maintaining or improving the important physicochemical characteristics of biosolids for advantageous applications [8,11]. Thermochemical techniques such as pyrolysis and gasification have been proved successful to destruct PFAS in biosolids while maintaining the carbon and nutrients contents [12]. Consequently, these techniques have been implemented on the commercial level. For instance, gasification of biosolids at 600 °C has shown to reduce PFAS

below the detection limit, producing biochar as the by-product free of PFAS [13]. Similarly, pyrolysis of biosolids at 650 °C has demonstrated to reduce PFAS of varying chain-lengths below the detection limit and produced high-quality biochar with fixed carbon and phosphorous contents [14]. More importantly, these technologies could be self-sustainable and do not require an external energy supply since the syngas produced during the processes could be used to generate energy [13,15].

Several studies have been carried out in recent years that demonstrate the presence of PFAS in biosolids (and other mediums like soil, wastewater and other aquatic systems) and suggest possible technologies to mitigate PFAS and transform biosolids into value-added products [16–18]. A few review articles have been published in recent years, focusing on treatment technologies to destruct PFAS in various wastes including biosolids [19–21]. For example, Garg et al. [22] recently published a review article on various PFAS destruction technologies such as incineration, hydrothermal liquefaction, pyrolysis, thermal hydrolysis, and supercritical water oxidation. Another article by Longendyke et al. [23] reviewed the thermal degradation of PFAS in different mediums like water, sewage sludge, soil and municipal solid waste. These articles have discussed important parameters of thermal technologies and provided valuable information on their role in PFAS degradation. However, less attention has been paid to review PFAS-degradation mechanisms in these treatment technologies and to the best of our knowledge, only one review paper has been published focusing on degradation mechanisms of PFAS in thermal techniques (mainly focusing on pyrolysis and incineration) [24], while no article has critically discussed PFAS-degradation mechanisms in hydrothermal liquefaction and biodegradation. Therefore, the primary objective of the article was to provide and compare critical information about PFAS-degradation mechanisms in biological and thermochemical techniques including hydrothermal liquefaction. Another main objective of the article was to identify the most suitable and efficient technique to mitigate PFAS in biosolids and understand the influence of biosolids composition (presence of metals like Ca and Mg) and the operating parameters of the techniques on PFAS destruction. The article also aimed to review the existing policies and regulations to restrain PFAS contamination in biosolids worldwide. In addition, the critical challenges that limit the understanding of PFAS degradation mechanisms were identified in the article, which could be taken as potential objectives for future studies. The literature for this review article was searched from different databases like Scopus and Google Scholar using individual and collective keywords such as PFAS, biosolids, pyrolysis of biosolids, thermal treatment of biosolids, biodegradation of PFAS, incineration of biosolids, and techniques for PFAS degradation. A special attention was given to include the recent five years publications.

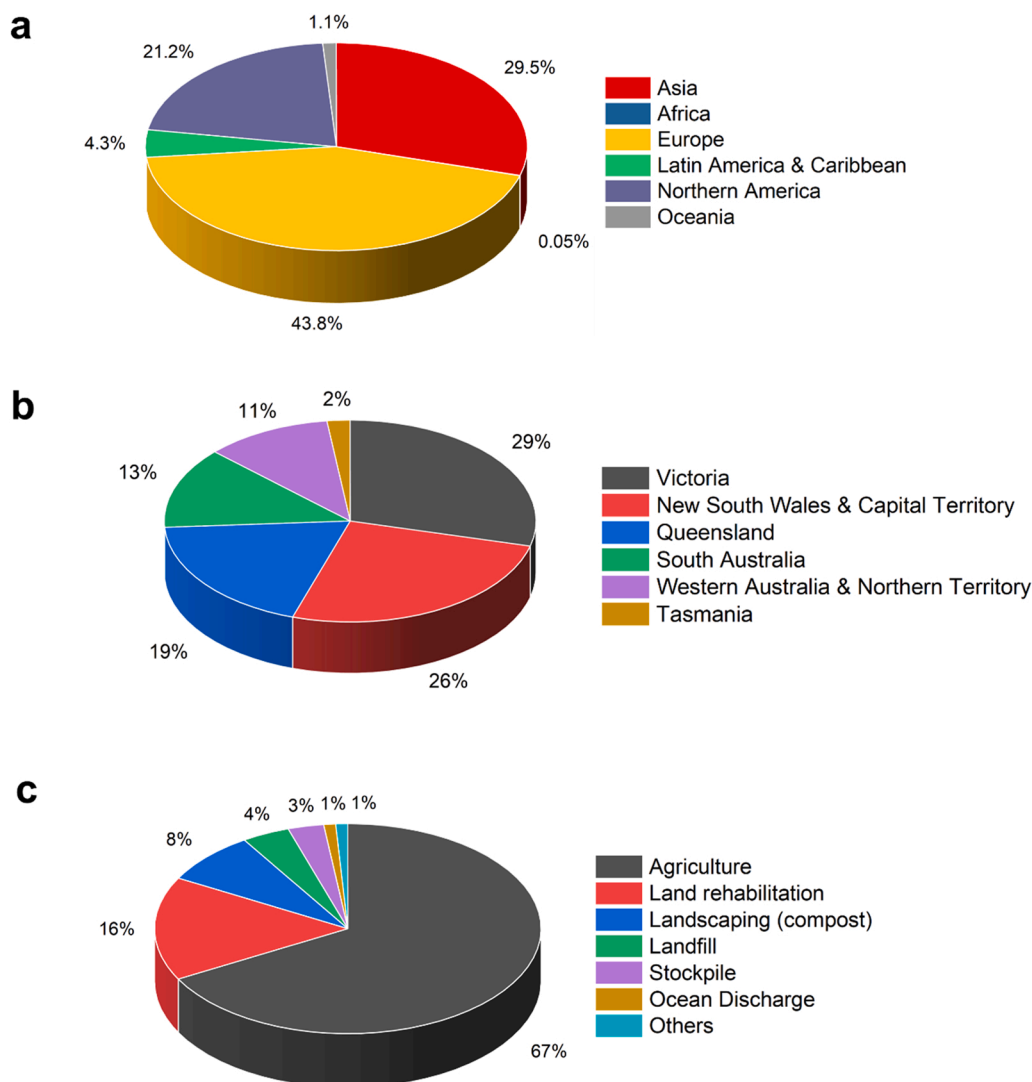
## 2. Biosolids production and market value

Fig. 1a shows biosolids production by region based on the 2015 population size. It was estimated from data that more than 33 million tonnes of dry biosolids were produced worldwide in 2015. Europe produced the highest amount of biosolids, 14.7 million dry tonnes, which is 43.8% of the total biosolids around the globe [2]. Asia is the second largest biosolids producer, accounts 29.5% of the overall proportion. Biosolids production has been observed the least in the African continent, at only 0.05% [2]. In the same year, Australia reported to

produce 310,000 dry tonnes of biosolids which increased to 349,000 dry tonnes in 2021 [25]. Fig. 1b shows the Australian state-wise production of biosolids in 2019, and Fig. 1c presents the percentage usage of biosolids across Australia, suggesting Victoria is the leading state to produce the maximum amount of biosolids [25]. The major application of biosolids in Australia is agriculture. Some countries around the world utilise 50–60% of biosolids for agriculture [2,26]. Australia has been setting a benchmark for other countries for biosolids applications, it employs 67% biosolids for agriculture, 16% for land rehabilitation, and 8% for landscaping [4]. This is primarily because biosolids contain essential nutrients like N and P and other micronutrients that are readily available for plant uptake [25]. In 2021, the biosolids market around the globe was projected to be valued at around US\$1.6 Bn [27]. The usage of biosolids is expected to increase in agricultural application and revegetation of mine sites [28,29]. In addition, biosolids can also be used as a potential feedstock for several processes like pyrolysis and hydrothermal liquefaction to produce energy and value-added products like biochar [30]. Other biosolids applications that include landscaping and minor horticulture, cement, and brick making also contribute to biosolids' economy [4]. Thus, expecting an increase in the widespread usage of biosolids, its overall market is projected to surge by 4.2% in the next decade, from US\$ 1.6 Bn to US\$2.4 Bn by 2031 [27]. In Australia, total biosolids production was assessed at 371,000 tonnes in 2019 (Fig. 1b). Each tonne of dry biosolids is valued at around US\$100 for agriculture, US\$40 for land rehabilitation and landscaping, and US\$80 for energy

production [4]. Based on applications of biosolids, according to Fig. 1, the market value of biosolids in Australia can be estimated at US\$30.97 million. Since agriculture is the primary market for biosolids, it could be valued at US\$24.8 million, while land rehabilitation and landscaping may contribute up to US\$3.50 million to the economy [4]. If diverting the remaining biosolids (9%) for energy production, US\$2.67 million can be further added to the economy.

Biosolids' usage contributes to a clean and sustainable economy, and it can reduce GHG emissions in two primary ways. Firstly, the organic content present in biosolids can be successfully converted to produce high-density energy products like biochar and bio-oil via thermochemical processes such as pyrolysis, gasification and hydrothermal liquefaction, and bioenergy using anaerobic digestion (AD). The AD process can produce 600–900 kWhr net energy per tonne of 90% dry biosolids, equating to around 0.6–0.9 tonne of carbon dioxide equivalents (CO<sub>2e</sub>) if generating the same energy using a coal-fired power plant [4]. Since biosolids can replace non-renewable fuels to generate electricity, they can attract Renewable Energy Credits, which could be valued at around US\$100/tonne of dry biosolids [4]. Secondly, biosolids are enriched with macro and micronutrients and other organic and inorganic matter, they can replace inorganic fertilizers. Therefore, GHG emissions related to the production of fertilizers can be significantly reduced. It has been estimated that approximately 192.5 kg of CO<sub>2e</sub> can be avoided by replacing 1 tonne of inorganic fertilizers with dry biosolids. In addition, diverting 1-tonne dry biosolids from landfilling for energy production



**Fig. 1.** (a) Biosolids production distribution in the world in 2015. Total biosolids production was estimated at 33,690,725 dry tonnes in 2015. (b) Biosolids production in all states and territories of Australia in 2018/19. Approximately 371,000 tonnes of dry biosolids were estimated to be produced across Australia. Victoria state contributed the highest at 29% (107,590 tonnes), while Tasmania produced only 2% (7420 tonnes) of the total biosolids. (c) Biosolids end-use in Australia in 2018/19. Data suggest that 91% of the biosolids are productively used for advantageous applications such as agriculture, land rehabilitation, and landscaping, while only 9% of biosolids are not sustainably managed. (a) Data taken from reference [2]. Source: Australian Biosolids Statistics 2018/19 [25].

can avoid 5 tonnes of CO<sub>2e</sub> [4].

Nonetheless, biosolids contain essential nutrients, and their usage for different applications could be considered highly advantageous and sustainable; however, biosolids are often adulterated with various categories of emerging contaminants, such as per- and polyfluoroalkyl substances (PFAS), pharmaceutical and personal care products, endocrine-disrupting chemicals, surfactants, flame retardants, and many other potentially toxic elements [6]. The implications of these contaminants in biosolids are challenging, but PFAS are the most profound concern among all pollutants due to their recalcitrant nature and toxic effects on ecosystems and human health [20,31]. Therefore, finding additional technologies to remove the pollutants of concern and make biosolids safe to use for further applications is a priority. The fate of PFAS in biosolids and mitigation regulations/policies, and technologies have been discussed in detail in following sections.

### 3. Per- and polyfluoroalkyl substances in biosolids

PFAS are also known as 'forever chemicals' due to the presence of highly stable carbon-fluorine (C–F) bonds. The dissociation energy required for C–F is around 120 kcal/mol, higher than other carbon-halide bonds like C–Cl and C–Br that possess bond dissociation energies of 81 and 46 kcal/mol, respectively [32]. Other bonds like C–C and C–H also require less dissociation energy compared to C–F. In addition, the C–F bond dissociation energy in CF<sub>3</sub> moiety is higher than CF<sub>2</sub> and increases with an increase in surrounding F atoms [33]. For example, Bentel et al. [34] calculated bond dissociation energies for C–F of selected PFAS molecules and revealed that it requires higher energy (117.7–122.7 kJ mol<sup>-1</sup>) to break C–F in CF<sub>3</sub> compared to CF<sub>2</sub> moiety present in the fluorinated tail (106.8–110.9 kJ mol<sup>-1</sup>). Consequently, different rates of degradation and defluorination have been reported for different categories of PFAS compounds [34–36]. In PFAS, generally, the atomic radius of a C–F bond shields the perfluorinated carbon atom and C–C bonds along the perfluoroalkyl chain without steric stress. This shielding of the C–C bond by much stronger C–F bonds is one of the primary reasons for greater stability of PFAS compounds and their perseverance in the environment including biosolids or sewage sludge [33]. Fig. 2 shows a general structure of non-polymeric, perfluorinated PFAS substances, comprising hydrophobic tail and hydrophilic head, and dissociation energies required to break C–F bond.

PFAS compounds enter wastewater treatment plants (WWTPs) through many sources such as industries dealing with manufacturing and processing PFAS compounds, municipal wastewater contaminated with PFAS compounds, leachate from landfills containing PFAS-laden wastes, and PFAS-contaminated rainwater [18,37]. The majority of

PFAS compounds, including long-chain and short-chain compounds, enter the treatment facilities from external sources. However, a small proportion of long-chain PFAS compounds can be degraded to generate small-chain PFAS or new intermediate PFAS compounds; their fate and presence primarily depend on the type of treatment process [33,38]. For instance, Schultz et al. [38] determined the concentrations of various PFAS compounds in a wastewater treatment plant, analysing the mass flow of PFAS compounds after each treatment step. The results revealed substantial decreases and increases in some PFAS compounds while others were not affected by the treatment processes. The study reported that the conventional treatment was ineffective in removing 6:2 fluoroelomer sulfonate (6:2FtS) and perfluorooctanoate (PFOA), as the mass flows of these compounds were nearly similar after each step of the treatment [38]. Alternatively, a 2.5 times increase in mass flow for perfluorooctanesulfonate (PFOS), a 2 times increase for perfluorodecanesulfonate (PFDS), and a 4-fold increase in perfluorononanoate (PFNA) was observed after activated sludge treatment, ascribing their generation from the degradation of precursors molecules [38]. If PFAS are not removed in WWTPs with a target technology, there is a high tendency for PFAS to end up in recycled water as well as biosolids.

The removal of PFAS during wastewater treatment and their presence in biosolids primarily depends on their sorption behaviour. Since each PFAS compound exhibits unique physical and chemical properties, its adsorption behaviour onto solid particles is also different [39]. In addition, there are several other factors, such as the pH of biosolids, biosolids composition (total organic carbon, metals, minerals, and other organic and inorganic contaminants), cation and anion exchange capacity, and interaction forces that affect the adsorption of PFAS on biosolids, which ultimately impact their final concentrations in biosolids [39–41]. Fig. S1 represents primary interactions that influence the accumulation of PFAS on biosolids. The probability of PFAS translocation to sludge/biosolids rises with increasing perfluoroalkyl chain lengths, attributing to increasing sorption capacity validated by sorption isotherms, such as Freundlich and Langmuir [42]. Zhang et al. [41] showed that long-chain PFAS, PFOA and PFOS achieved K<sub>f</sub> values of 1.13–2.28 and 1.52–3.58, respectively. On the other hand, short-chain PFAS, like PFBA, exhibited lower K<sub>f</sub> values in the range of 0.84–1.14 and PFBS in 1.13–1.34, confirming stronger sorption for long-chain PFAS compared to short-chain PFAS [41]. The higher sorption capacity of long-chain PFAS can be attributed to the enhanced hydrophobic and oleophilic character arising from the additional number of carbon-fluorine atoms [39,40]. Low pH and abundance of divalent cations such as Mg<sup>2+</sup> and Ca<sup>2+</sup> are known to enhance PFAS adsorption on biosolids [43]. The change in pH greatly influences the organic

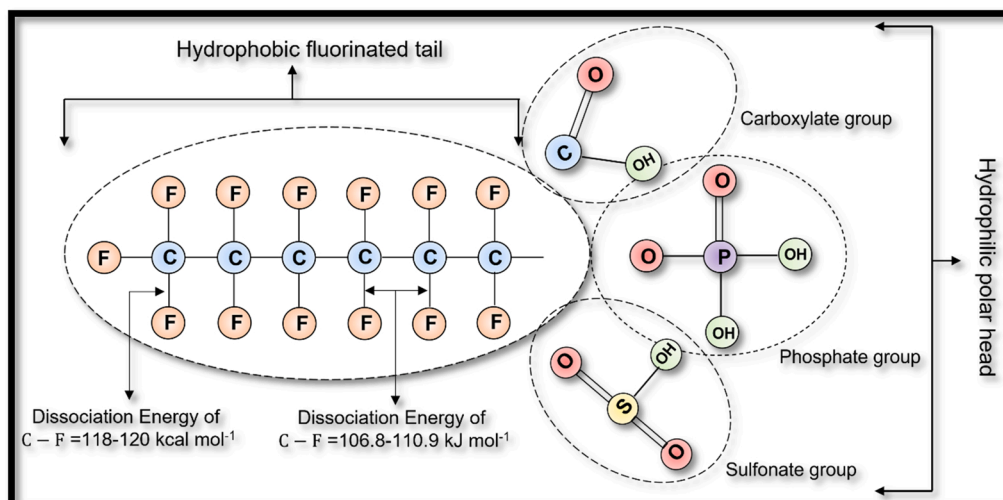


Fig. 2. A general structure of non-polymeric, perfluorinated PFAS substances. A PFAS compound is generally comprised of two components. Firstly, a hydrophobic tail comprises centrally located C–C bonds, which are surrounded by C–F bonds. This hydrophobic tail may contain a variable number of carbon and fluorine atoms. The second is the hydrophilic head that has polar groups like carboxylate and sulfonate group, providing a PFAS compound in a special category, perfluorocarboxylates and perfluorosulfonates, respectively.

**Table 1**  
Quantification of different PFAS detected in biosolids worldwide.

PFAS type	Average PFAS concentration in biosolids ( $\mu\text{g}/\text{kg}$ )														
	Johnson et al. [18], USA	Pepper et al. [5], USA	Gallen et al. [16], Australia	Navarro et al. [26], Spain	Schultz et al. [38], USA	Moodie et al. [45], Australia	Venkatesan et al. [55], USA	Loganathan et al. [46], USA	Kundu et al. [14], Australia	Kim et al. [56], USA	Gallen et al. [57], Australia	Letcher et al. [58], Canada	Guerra et al. [59], Canada	Campo et al. [47], Spain	Armstrong et al. [60], USA
<b>Perfluorinated sulfonic acids</b>															
PFBS	3.40	1.90	NA	7.72	NA	2.30	3.40	NA	2.20	1.10	7.40	3.07	NA	0.78	NA
PFPeS	NA	NA	NA	NA	NA	0.20	NA	NA	NA	NA	NA	NA	NA	NA	NA
PFHxS	5.90	3.70	0.11	7.78	NA	1.80	5.90	< 2.50	0.60	< LOD	NA	NA	NA	0.01	NA
PFOS	403.00	34.00	25.00	23.7	100.00	23.00	403.00	95.00	14.80	13.40	67.00	50.40	16.20	41.4	22.50
PFDS	NA	NA	NA	NA	91.00	< LOD	NA	NA	NA	3.20	NA	NA	NA	0.01	5.61
PFOSA	NA	NA	NA	NA	NA	NA	20.70	21.00	NA	NA	NA	NA	NA	0.67	NA
<b>Perfluorinated carboxylic acids</b>															
PFBA	NA	NA	NA	NA	NA	0.80	2.00	NA	2.00	0.60	NA	NA	NA	399.00	NA
PFPeA	3.50	NA	NA	5.47	NA	2.00	3.50	NA	2.30	NA	NA	NA	NA	193.00	8.27
PFHxA	6.20	4.20	0.50	18.4	NA	2.80	6.20	NA	3.70	2.30	2.60	NA	NA	1.33	7.71
PFHpA	3.40	1.40	0.26	NA	NA	0.90	3.40	NA	1.30	< LOD	NA	NA	NA	6.41	5.12
PFOA	3.40	4.30	6.50	6.23	< 3	8.30	34.00	219.00	8.60	1.90	11.00	NA	2.90	21.7	23.5
PFNA	9.20	1.80	1.10	3.34	9.90	0.90	9.20	< 2.50	NA	3.90	1.20	NA	5.00	27.2	25.10
PFDA	26.10	12.00	17.00	5.67	5.90	14.00	26.1	34.00	NA	1.40	29.00	NA	1.35	160.00	NA
PFUnDA	11.70	2.30	1.20	NA	6.80	0.60	11.70	5.90	NA	2.10	1.60	NA	4.10	8.68	NA
PFDoDA	10.90	8.00	5.70	NA	3.80	5.90	10.90	7.20	NA	1.90	9.90	NA	7.50	0.10	NA

Note: NA-not available; LOD-limit of detection; PFBA: Perfluorobutyric acid; PFBS: Perfluorobutanesulfonate; PFDA: Perfluorodecanoic acid; PFDS: Perfluorodecanesulfonate; PFOSA: Perfluorooctane sulfonamide; PFHpA: Perfluoroheptanoic acid; PFHxA: Perfluorohexanoic acid; PFHxS: Perfluorohexanesulfonate; PFNA: Perfluorononanoic acid; PFOA: Perfluorooctanoic acid; PFOA: Perfluorooctanoic acid; PFOS: Perfluorooctane sulfonate; PFPeA: Perfluoropentanoic acid; PFPeS: Perfluoropentanesulfonate; PFDoDA: Perfluorododecanoate; PFUnDA: Perfluoroundecanoate

matter surface charge of biosolids. At low pH, the overall surface charge is positive, and the quantity of cationic chemical species increases that can interact with anionic polar head groups of PFAS [42]. The results from different studies have shown that polyvalent cations compared to monovalent cations like  $\text{Na}^+$  exhibit stronger attraction with interfacial layer and thus can increase adsorption of PFAS on biosolids [39,43,44].

A number of studies (however, limited in many countries) demonstrated the presence of various types of PFAS in biosolids across the world, reporting a concentration between 0.11 and 403  $\mu\text{g}/\text{kg}^{-1}$  [5,16,18,26,45]. Table 1 summarizes the worldwide distribution of selected PFAS in biosolids. It was observed from these studies (in Table 1) that the quantities of long-chain PFAS, such as PFOS, PFDS, PFOA, and PFDA were consistently higher in the majority of biosolids compared to other counterparts. For example, Venkatesan and Halden [46] found 403  $\mu\text{g}/\text{kg}^{-1}$  of PFOS and 34  $\mu\text{g}/\text{kg}^{-1}$  of PFOA in biosolids, while the concentrations of PFBS and PFBA were reported to be 3.4 and 2  $\mu\text{g}/\text{kg}^{-1}$ , respectively. Similarly, Loganathan et al. [46] achieved 95  $\mu\text{g}/\text{kg}^{-1}$  PFOS and 219  $\mu\text{g}/\text{kg}^{-1}$  PFOA in biosolids that were several times higher than PFNA, PFDA, and PFOSA. Though PFOS (in 2009) and PFOA (in 2019), their salts and related compounds were added to the Stockholm Convention's list of persistent organic pollutants, and their production is restricted in European Union, but some countries still produce these PFAS [47]. PFOS and PFOA can also be generated from precursor compounds during wastewater treatment and accumulate in biosolids. Since primary applications of biosolids are agriculture and land rehabilitation, PFAS contaminated biosolids constitute a significant source of PFAS for soil contamination and are highly prone to be taken up by roots and other parts of plants [48,49]. There are several pieces of evidence of PFAS uptake by plants in biosolids amended soil, which has been discussed in detail by Ghisi et al. [20] and Mei et al. [50]. Once PFAS accumulate in plants, they can translocate to corresponding food chains and ultimately to humans. The toxic effects of PFAS exposure on human health are well known and have been linked to kidney and testicular cancers, endocrine dysfunction, liver malfunction, immunotoxicity, hypothyroidism, and many other diseases [51–53].

Despite being aware of the toxic effects of PFAS, very less attention has been paid to implement strict regulations and policies to limit PFAS contamination in biosolids. A few countries from Europe, such as Germany, Denmark, Netherlands, Sweden, the USA, and Australia have taken some critical steps to restrict PFAS concentration in biosolids. For instance, Germany has set a PFAS limit of 100  $\mu\text{g}/\text{kg}^{-1}$  in biosolids as well as in soil. Denmark has set a PFAS limit of 400  $\mu\text{g}/\text{kg}^{-1}$  in soil, while Sweden set the PFAS limit of 3  $\mu\text{g}/\text{kg}^{-1}$  for sensitive land use (gardens and residential) and 20  $\mu\text{g}/\text{kg}^{-1}$  for less sensitive land use (offices and industrial). On the other hand, the Netherlands adopted a unique approach to PFAS regulation, limiting the use of only PFOS and PFOA in soil by 0.9 and 0.8  $\mu\text{g}/\text{kg}^{-1}$ , respectively. The USA has set the PFAS limit of 70  $\text{ng}/\text{L}^{-1}$  for drinking water but has been carrying out risk assessment analyzing the effects of PFAS in biosolids-amended soil, so might bring new regulations in the near future. In 2017, Canada restricted the use of agricultural soil containing PFAS above 10  $\mu\text{g}/\text{kg}^{-1}$ . In Australia, though biosolids do not have an upper limit, the environment authority has recommended considering ecological direct (for PFOS-1000  $\mu\text{g}/\text{kg}^{-1}$ , for PFOA-10000  $\mu\text{g}/\text{kg}^{-1}$ ) and indirect exposure values (for PFOS-10  $\text{ng}/\text{g}^{-1}$ ) when performing the risk assessment for the land applications of biosolids [54]. In addition, Queensland state of Australia took further steps to limit PFAS and issued PFAS trigger values in soils in the range of 1–10  $\mu\text{g}/\text{kg}^{-1}$ , which need to be evaluated after biosolids application.

The guidelines and policies presented above can be considered effective in evaluating PFAS contamination and regulating the usage of contaminated biosolids. However, additional imperative actions are required to prevent PFAS accumulation in biosolids and cost-effective and sustainable technologies to eradicate PFAS from biosolids. The most inexpensive and impactful approach could be the reduction or prohibition of primary PFAS sources, which can be achieved either by restricting the production of PFAS and seeking feasible alternative

chemicals or setting a PFAS limit on industrial discharge points to prevent/reduce their occurrence in WWTPs. Another efficient solution to mitigate PFAS involves the application of advanced thermochemical technologies such as incineration, gasification, hydrothermal liquefaction, pyrolysis, and microbial degradation. The potential of these techniques to destroy PFAS in biosolids has been discussed in the next section.

#### 4. Technologies for PFAS removal from biosolids

Several technologies, including thermochemical processes, electrochemical, water oxidation, adsorption, membrane filtration, photolytic and photocatalytic degradation, and biological treatment, have been used to mitigate PFAS compounds from various waste streams. However, mainly thermochemical techniques such as incineration, gasification, combustion, hydrothermal liquefaction (HTL), pyrolysis, and biodegradation have been reported to remove PFAS from biosolids

**Table 2**  
Operating characteristics, advantages and disadvantages of technologies employed for PFAS-biosolids treatment.

Technique	Operating parameters	Advantages	Disadvantages
Biodegradation	-time: 1–150 days -room temperature -additives like Fe (III) -anaerobic or aerobic bacteria	-cost-effective -degrades 50–60% PFAS -does not require pre-drying of biosolids -low environmental risks	-takes a long time to degrade PFAS -lower PFAS degradation efficiency -low availability of microbes
Hydrothermal liquefaction	-temperature: 150–350 °C -time: 30 min–6 h -pressure: 5–20 MPa -inert gas	-does not require pre-drying of biosolids -low temperature -suitable to degrade PFCA	-energy-intensive -expensive post-treatment -requirement of special reactors -does not degrade PFSA
Smouldering Combustion	-temperature: 200–1200 °C -oxygen (5–20%) -air flux: 0.1–4 cm/min -porous medium required	-low cost -requires less energy input -effective for PFAS destruction (>99%)	-requires pre-drying of biosolids -releases toxic gases
Incineration	-temperature: 800–1000 °C -time: 30 min -oxygen or air -atmospheric pressure	-biosolids volume reduction -potential energy recovery -highly efficient for PFAS degradation (>99%) -generation of stable ash	-high capital investment -high operating costs -toxic gases and hazardous emissions -requires pre-drying of biosolids
Gasification	-temperature: > 600 °C -time: > 30 min -gasifying agent, CO <sub>2</sub> or steam -atmospheric pressure	-suitable to degrade all types of PFAS -> 99% degradation efficiency -biosolids volume reduction	-formation of volatile PFAS -energy-intensive -high capital investment -requires mechanical dewatering and pre-drying of biosolids
Pyrolysis	-temperature: 200–700 °C -time: 30 min–6 h -inert gas -atmospheric pressure	-suitable to degrade all types of PFAS -highly efficient for PFAS degradation (>99%) -low environmental risks, such as GHG emissions -biosolids volume reduction	-energy-intensive -high capital investment -requires mechanical dewatering and pre-drying of biosolids

[61–63]. Table 2 shows the operating conditions, advantages, and disadvantages of these technologies for PFAS-biosolids treatment, whereas Table 3 presents the performance of different techniques for PFAS destruction in various matric conditions.

##### 4.1. Biological degradation of PFAS-biosolids

Biodegradation is one of the ecofriendly and cost-effective techniques to degrade PFAS present in biosolids. Biodegradation of PFAS primarily depends on the structural complexity of PFAS, the composition of microbes and operating conditions. Biotransformation of PFAS either in aerobic or anaerobic conditions using bacterial species like *Pseudomonas* and *Acidimicrobium* and fungal species such as *Phanerochaete chrysosporium* have been reported in previous studies [73,74]. Microbes generally use PFAS compounds as the carbon source and can promote their defluorination when applied for iron reduction using  $\text{NH}_4^+$  or  $\text{H}_2$  as electron donors. A study demonstrated PFAS degradation (PFOA and PFOS) using pure *Acidimicrobium* sp. strain A6 and mixed culture (*Ralstonia*, *Bacillus*, *Acidimicrobium*, *Aciditerrimonas*, and *Desulfosporosinus*), Fe (III) as electron acceptor and  $\text{NH}_4^+$  as electron donor over 100 days of incubation [62]. The results showed 50% PFOA removal using mixed culture and 33% with pure culture. It was further noticed that the pure culture and enrichment culture showed different mechanisms of PFOA degradation since, in the former scenario, only one intermediate product that is perfluorohexanoic acid (PFHxA), was detected, while in the latter case, four intermediate compounds, perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA) were observed. No PFOA degradation was observed in the absence of  $\text{NH}_4^+$ . Similarly, the mixed culture showed higher degradation of PFOS compared to the pure culture, which was 47% and 23%, respectively [62]. In a separate study, Huang et al. [73] carried out anaerobic degradation of PFOA-biosolids using *Acidimicrobium* sp. strain A6 enrichment culture and Fe (III)- $\text{NH}_4^+$  enrichment medium with an incubation period of 150 days. The results showed a significant reduction in PFOA between 60 and 150 days, while the concentration of short-chain PFCAs like PFBA, PFPeA, PFHxA and PFHpA, as well as total fluorine content, consistently increased, indicating the successful microbial degradation of PFOA in biosolids [73]. Another study demonstrated the biotransformation of PFOA and PFOSAmS with incubation of soil microcosms for 142 days and observed slow but noticeable degradation of PFOA into PFOA (30%) and the conversion of PFOSAmS into PFOS (3%), FOSA (<0.005%), and perfluorooctanesulfonamidoamide (PFOSAm)– 10% [75].

For PFAS biodegradation, a microbe requires to transport PFAS into the cell; needs to produce an active enzyme to catalyze C–F bond cleavage; requires sensing the toxic fluoride ion; a fluoride-proton antiporter to eliminate fluoride ion from the cell. While these components are vital for PFAS biodegradation, a physiological barrier makes PFAS biodegradation an unfavorable process. For instance, polychlorinated compounds can act as preferable electron acceptors because of the positive redox potential for dechlorination that usually ranges between + 250 and + 600 mV, making it favorable to accept electrons via an electron transport chain [76]. On the other hand, polyfluorinated compounds exhibit negative redox potential for their reduction, making them unable to serve as final electron acceptors [77]. However, PFAS can be microbially degraded in cometabolism with the addition of potential electron donors and acceptors. In such conditions, microbes are known to degrade PFAS, mainly via defluorination process that releases fluoride anion. High-level of defluorination may result in high intracellular fluoride concentrations. Fluoride shows intrinsic cellular toxicity, it can bind to critical enzymes (such as ATPases and pyrophosphatase) even at a low concentration of 0.1 mM and inhibits cellular metabolism [78]. Therefore, it is important for a microbe to develop a high tolerance to fluoride. Generally, bacteria like *Pseudomonas* sp. are known to contain two types of proteins, fluoride/protein

**Table 3**  
Performance of different techniques for PFAS destruction in various waste.

Technique	Operating parameters	Matrix conditions	Target PFAS type	Concentration	Major products	Conversion Efficiency	Reference
Biodegradation	<i>Acidimicrobium sp. strain A6</i> , 100 days	Anaerobic	PFOA	100 mg/kg	HFBA; PFPeA; PFHxA; PFHpA	50%	[62]
Biodegradation	<i>Acidimicrobium sp. strain A6</i> , 100 days	Anaerobic	PFOS	100 mg/kg	HFBA; PFBS	47%	[62]
Biodegradation	<i>Pseudomonas plecoglossicida</i> 2.4-D, 90 days	Aerobic soil	PFOS	1000 mg/kg	NA	75%	[64]
Biodegradation	<i>Pseudomonas plecoglossicida</i> 2.4-D, 6 days	Aerobic mineral	PFOS	1000 mg/kg	PFHpA	100%	[64]
Biodegradation	Mixed culture, 180 days	Aerobic soil	6:2 FTOH	2.9 mg/kg	PFPeA; 5:3 Acid; PFHxA; 5:2 sFTOH; 6:2 FTOH; PFBA	67%	[65]
Biodegradation	Mixed culture, 180 days	Aerobic sludge	6:2 FTOH	2.8 mg/kg	6:2 FTUA; 5:2 sFTOH; 6:2 FTCA; 5:3 Acid; PFHxA	60%	[65]
Hydrothermal liquefaction	Batch reactor, T-350 °C, P-16.5 MPa, t-1.5 h, 2.5 M NaOH	NR	PFOS	50 mg/L	NA	100%	[66]
Hydrothermal liquefaction	Batch reactor, T-350 °C, P-16.5 MPa, t-1.5 h, 1 M NaOH	NR	PFOS	50 mg/L	NA	80%	[66]
Hydrothermal liquefaction	Batch reactor, T-350 °C, P-21.9 MPa, t-6 h, 9.61 mM Fe	NR	PFHpS	1.46 µM	NA	100%	[67]
Hydrothermal liquefaction	Batch reactor, T-500 °C, P-35 MPa, t-1 h, H <sub>2</sub> O <sub>2</sub> , NaF	NR	PFOS	28.6 mg/L	NA	70%	[68]
Hydrothermal liquefaction	Batch reactor, T-500 °C, P-35 MPa, t-1 h, H <sub>2</sub> O <sub>2</sub> , NaF	NR	PFHpS	0.31 mg/L	NA	55%	[68]
Hydrothermal liquefaction	Batch reactor, T-300 °C, P-35 MPa, t-1 h	Sewage sludge	PFOA	20 ng	NA	100%	[69]
Hydrothermal liquefaction	Batch reactor, T-300 °C, P-35 MPa, t-1 h	Sewage sludge	PFHpA	20 ng	NA	100%	[69]
Hydrothermal liquefaction	Batch reactor, T-300 °C, P-35 MPa, t-1 h	Sewage sludge	PFHxA	20 ng	NA	100%	[69]
Pyrolysis	Pilot-scale reactor (63.6 kg/h), T-650 °C	Biosolids	PFOA	86.70 ng/g	NA	100%	[17]
Pyrolysis	Pilot-scale reactor (63.6 kg/h), T-650 °C	Biosolids	PFOS	25.10 ng/g	NA	100%	[17,70]
Pyrolysis	Batch reactor, T-700 °C, 10 min, Granular activated carbon	Sewage sludge	PFOA	49.4 mg/g	NA	> 99%	[70]
Pyrolysis	Batch reactor, T-700 °C, 10 min, Granular activated carbon	Sewage sludge	PFOS	10 mg/g	NA	> 99%	[70]
Pyrolysis	Batch reactor, T-700 °C, 10 min, Granular activated carbon	Sewage sludge	PFHxA	47.3 mg/g	NA	> 99%	[70]
Pyrolysis	Semi-pilot plant, T-600 °C, Granular activated carbon	Biosolids	PFBS	2.20 ng/g	NA	74%	[14]
Pyrolysis	Semi-pilot plant, T-600 °C, Granular activated carbon	Biosolids	PFOS	14.78 ng/g	NA	98%	[14]
Pyrolysis	Semi-pilot plant, T-600 °C, Granular activated carbon	Biosolids	PFHxA	3.65 ng/g	NA	84%	[14]
Pyrolysis	Semi-pilot plant, T-600 °C, Granular activated carbon	Biosolids	PFOA	8.63 ng/g	NA	96%	[14]
Smouldering Combustion	T- > 900 °C, air flux-5 cm/s, velocity-0.24–0.71 cm/min	Soil	PFBA	0.003 mg/kg	NA	> 99%	[71]
Smouldering Combustion	T- > 900 °C, air flux-5 cm/s, velocity-0.24–0.71 cm/min	Soil	PFHxS	0.009 mg/kg	NA	> 99%	[71]
Smouldering Combustion	T- > 900 °C, air flux-5 cm/s, velocity-0.24–0.71 cm/min	Soil	PFOA	0.0003 mg/kg	NA	> 99%	[71]
Incineration	Tube furnace, air, T-500 °C, Granular activated carbon	NR	PFBA	NR	NA	> 99%	[72]
Incineration	Tube furnace, air, T-500 °C, Granular activated carbon	NR	PFOA	NR	NA	> 99%	[72]
Incineration	Tube furnace, air, T-500 °C, Granular activated carbon	NR	PFOS	NR	NA	> 99%	[72]

Note: NA-not analyzed; NR-not reported

antiporter and CrcB-type that help to transport fluoride from the inside to the outside of the cell [79].

Microbial degradation of PFAS may involve a series of reductive defluorination, decarboxylation, hydroxylation, and hydrogenation reactions. PFAS compounds also contain C–S (sulfonate) and C–C (carboxylate) bonds which are considered weaker than the C–F bond and may undergo one-electron reduction or oxidation to generate a carbon-centered radical, followed by hydroxylation. Fig. 3a presents PFOS and PFOA degradation by *Ensifer adhaerens*. As shown in this figure, PFOS firstly undergoes C–S (sulfonate) bond cleavage and releases SO<sub>3</sub> to produce perfluorooctane, followed by hydroxylation,

decarboxylation and defluorination reactions to form per-fluoroheptanoic acid. On the other hand, PFOA firstly undergoes decarboxylation reaction to form perfluoroheptane which further undergoes hydroxylation and defluorination reactions to generate per-fluoroheptanoic acid. Following this pathway, PFAS is degraded one-carbon short compared to the initial PFAS and the carbon is lost in the form of CO<sub>2</sub>. Fig. 3b shows a proposed mechanism of PFOA defluorination. In this pathway, the first microbial enzymatic cleavage occurs at the C<sub>1</sub>-C<sub>2</sub> bond to form a carbon-centered radical, followed by radical quenching to produce a C<sub>7</sub> perfluorinated alcohol. Then the alcoholic compound undergoes non-enzymatic and rapid defluorination and





#### 4.2. Hydrothermal liquefaction treatment of PFAS-biosolids

Hydrothermal liquefaction (HTL) is a well-known technology utilised to recover energy from biomass feedstocks at a temperature range of 250–350 °C and pressure of 10–25 MPa [83]. HTL generally utilizes a solvent like water and methanol that influences the decomposition of the feedstock significantly, and thus the final products depend primarily on the operating parameters and the solvent used. A number of studies have been carried out to demonstrate the potential of the HTL process for bio-oil production using different types of biomass feedstocks, including sewage sludge and biosolids [84–86]. HTL is conducted in the presence of a solvent and is thus considered more suitable and economical for wet feedstocks like biosolids. Biosolids contain a high amount of moisture (80–85%) and can be directly used in HTL without drying [87]. The primary product of HTL of biosolids or sewage sludge is biocrude oil, and the PFAS present in the feedstock are depolymerised during the process, and most of them end up in the biocrude oil. Operating parameters like temperature and residence time play an important role in the destruction of a specific class of PFAS. For instance, Yu et al. [88] demonstrated the effect of temperature and residence time on PFAS degradation in the HTL process. The results showed that low temperatures of 260 and 300 °C and residence time of 30 min were capable to achieve > 99% degradation of PFOA and 8:2 FTUCA, but no degradation was detected for PFOS. However, increasing the temperature to 350 °C and residence time to 90 min could achieve a maximum degradation of 34% for PFOS and 67% for 8:2 FTS [88]. The main pathway for the degradation of PFOA was attributed to defluorination, while the presence of metal ions like  $\text{Ca}^{2+}$  might promote the cleavage of the C–F bond and form stable inorganic fluoride minerals such as  $\text{CaF}_2(\text{s})$  [88]. Another study reported similar results for PFAS destruction in HTL, which showed that PFCAs were completely degraded at 300 °C; however, an increase in the concentration of PFSA compounds was noticed [69].

During the HTL process, PFAS are expected to degrade through  $\text{OH}^-$  catalyzed series of nucleophilic substitution and decarboxylation reactions. The highly electronegative fluorine atom creates a strong dipole

when bonded to carbon creating an affinity for the solvated electron to attack the relative positive charge ( $\delta^+$ ) of the carbon atom presenting a viable mechanism for the reductive attack which can potentially overcome the bond dissociation energy of the C–F bond and the associated shielding to other forms of a chemical attack. The small size of a solvated electron may be the reason for its propensity to access the C–F bond as a nucleophile without being repelled by the helix of fluorine atoms shielding the C–F and C–C bonds in the perfluoroalkyl chain [66]. The proposed mechanism of PFOS degradation is shown in Fig. 4. In PFOS hydrothermal degradation, the first step involves  $\text{OH}^-$  substitution with a sulfonate headgroup, forming an unstable perfluorinated alcohol compound. In the second step, the unstable alcohol intermediate undergoes rapid HF elimination to generate a ketonic intermediate compound. Further, the ketonic compound undergoes a hydration reaction and eliminates another  $\text{F}^-$  to form PFOA. In subsequent reactions, PFOA undergoes decarboxylation reactions, releasing 2 F<sup>-</sup> in each reaction and forming short-chain perfluorocarboxylates like PFPeA. In PFOS degradation, the first reaction involving the cleavage of the sulfonate group is the rate-limiting step. The reactivity of PFOS is lower compared to the reactions initiated with PFOA since decarboxylation reactions were found to occur more frequently compared to the cleavage of the sulfonate group [66].

The results discussed above suggest that the HTL process is highly advantageous to destruct PFCA compounds in biosolids but has shown less efficacy in degrading PFSA compounds. Therefore, advancement in HTL is inevitable to accomplish the complete destruction of PFAS in biosolids that generally contain a mixture of PFCA and PFSA species. This can be achieved by employing alkaline HTL, such as NaOH [66,86]. Wu et al. [66] conducted HTL of PFOS in the presence of 1 M NaOH, a temperature range of 200–350 °C, and pressure between 2 and 16.5 MPa. The results revealed up to 80% of PFOS defluorination after 90 min at 350 °C. The addition of strong basic solvents like NaOH and dimethyl sulfoxide (DMSO) promotes the decomposition of PFAS in near-critical and supercritical water conditions. Interestingly, NaOH catalyzes the decarboxylation of long-chain PFAS like PFOS and PFOA as well as short-chain PFAS such as PFPeA. A recent study published in the

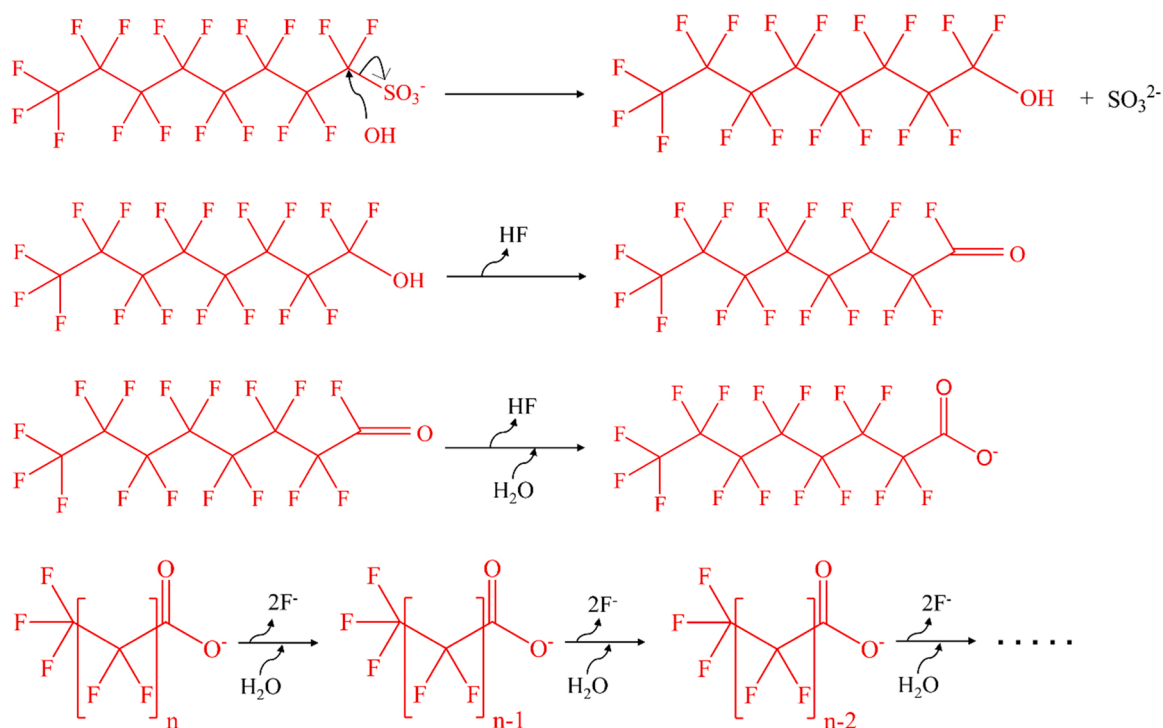


Fig. 4. Proposed mechanism of PFOS degradation in the hydrothermal liquefaction process. Adapted with permission [66]. Copyright (2019) American Chemical Society.

journal Science revealed that decarboxylation is the key first step of the defluorination of PFCAs like PFOA, and the fluorine atoms originating from the PFOA destruction are recovered as fluoride ions [89]. The fluoride ions content increases proportionally to the decrease in PFOA concentration, indicating that most of the perfluoroalkyl fluorines are defluorinated and mineralized rather than being transformed to smaller-chain PFAS or being lost as volatile fluorocarbons. The destruction of short-chain PFCAs (C=2–3) like trifluoroacetate (C=2) is slower compared to long-chain PFCAs like PFOA. It is possibly because of the instability of the  $\text{CF}_3$  anion that hinders decarboxylation reaction which either slows down the degradation or directs it towards a different degradation mechanism. Where the degradation of long-chain PFCAs is shortened by one carbon each and generates volatile  $\text{CF}_3\text{CF}_2\text{H}$ , the degradation of trifluoroacetate takes place by a different, non-single-carbon shortening mechanism [89].

In PFOA degradation, decarboxylation is the rate-limiting step and a series of defluorination reactions are low-barrier reactions. Fig. 5 shows the proposed PFCA degradation mechanism under basic conditions like in the presence of DMSO or NaOH. Density functional theory (DFT) results showed that the initial decarboxylation of PFOA requires an activation energy of 28 kcal/mol to produce an intermediate anion (INT1 in the figure) compound which releases a fluoride ion to form perfluoroalkene (INT2) like perfluoro-1-heptene [89]. This perfluoroalkene undergoes hydroxylation under no enthalpic barriers ( $\Delta G = -44.3$  kcal/mol) to produce an enol intermediate product (INT3), taking place especially on the terminal position because hydroxylation on the internal side of the alkene has an enthalpy barrier of 8.9 kcal/mol [89]. The enol product undergoes fluoride elimination to form  $\alpha, \beta$ -unsaturated acyl fluoride (INT4) through retro 1,4-conjugate addition, followed by an enthalpically barrierless fluoride elimination to form 1,3-diketone compound (INT5). Hydroxide again adds INT5 on the ketone carbonyl side to generate an intermediate product that further

undergoes fragmentation to form an equivalent of PFCA three carbons shorter than the initial PFCA. For example, if eight-carbon PFOA undergoes this degradation cycle, it will degrade to PFPeA by losing one carbon as  $\text{CO}_2$  and two carbons as fluoroacetic acid.

HTL might be the most suitable process for sustainable biosolids management since does not require the pre-drying of biosolids. However, HTL might not be the best process to mitigate PFAS completely from biosolids. Alkaline HTL has shown promising results for PFOS removal, but primary studies have been conducted using aqueous mediums and soil, thus demanding future studies on PFAS mitigation from biosolids. In addition, the short-chain PFAS compounds generated during the HTL process finally end up in the biocrude oil. Therefore, extraction of PFAS from biocrude oil and their safe disposal is another substantial challenge and might need additional technology, which can make biosolids management more expensive. Moreover, PFAS destruction pathways in HTL are not very clear; therefore, a thorough corroboration should be conducted to understand the destruction mechanism, which can open doors to develop innovative strategies to enhance PFAS destruction and make the HTL process highly efficient.

#### 4.3. Thermal degradation of PFAS-biosolids

Smouldering combustion (SC) is a developing process for biosolids management. SC is a slow, flameless and self-sustained thermal technique operated by the heat generated from the fuel's oxidation [90]. SC generally requires a porous material that allows a high surface area for reaction and permeability for oxygen/air. The main products of biosolids SC are gases (primarily CO and  $\text{CO}_2$ ) and solid residue (char), while the parameters such as sand/biosolids ratio, biosolids moisture content, and forced air flux play a critical role in the process [90]. This process has not been extensively explored for biosolids management, and very few studies have been published. For example, Rashwan et al.

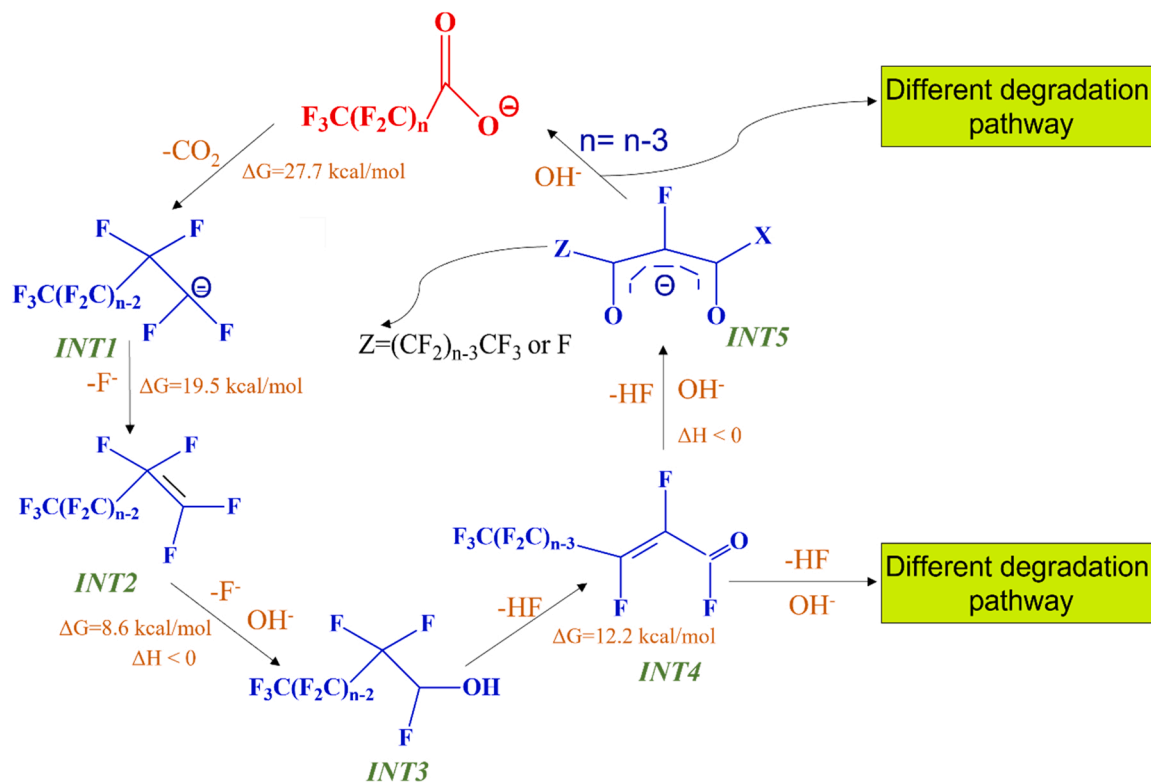


Fig. 5. Proposed PFCA degradation mechanism under a basic condition like in the presence of DMSO or NaOH. The cycle showing a three-carbon shortening of the original PFCA of  $n$  carbons, with one carbon lost as  $\text{CO}_2$  (converted to  $\text{CO}_3^{2-}$ ) and two carbons lost to fluoroacetic acid, which readily degrades under these reaction conditions.

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[91] carried out SC of biosolids (with a moisture content of 71–84%) mixed with sand in a fixed bed stainless steel column at a preheating temperature of 200 °C (preheating phase was varied from 1 to 4 h) and an air flux rate of 1.6–8.1 cm/s. The oxygen introduction started the smouldering process and increased the temperature up to 650 °C, and further combustion was sustained by the energy released by biosolids. The results showed that sand/biosolids mass ratios from 1.7 to 11 g/g that provided the lowest energy content up to 0.28 kJ/g of the mixtures were capable to achieve a self-sustainable SC process. In addition, increasing the air flux rate and energy content of the mixtures improved smouldering robustness [91]. However, emissions and the char left from the process were not quantified and characterized.

SC of biosolids containing PFAS has not been reported so far; however, destruction of PFAS-contaminated soil and granular activated carbon (GAC) has been reported during the SC process. For instance, Duchesne et al. [71] successfully demonstrated PFAS destruction in soil and GAC during the SC. The authors prepared the samples using 175 mg PFAS/kg GAC-sand and 4 mg PFAS/kg soil and conducted SC in a stainless-steel column (height of 21–28 cm and diameter of 16 cm) at a preheating temperature of 260 °C and an air flux rate of 5 cm/s [71]. The results showed > 99% of PFAS destruction in both samples after the SC, whereas a small quantity of PFAS was also observed in emissions. PFAS destruction starts in the preheating phase since short-chain PFAS compounds start generating before reaching the peak temperature (e.g., 900 °C), suggesting there is sufficient energy to break down the sulfonate headgroup and volatilize a small fraction of PFAS [71]. A similar study was carried out by Major [92] to examine the PFAS-GAC and PFAS-soil destruction during SC in a stainless-steel column (height of 60 cm and diameter of 16 cm) at a preheating temperature of 260 °C and an air flux rate of 5 cm/s and achieved excellent results for PFAS removal. Three PFAS compounds, namely PFOA, PFOS and PFHxS, with initial concentrations of 590, 140 and 240 mg/kg, respectively, were present in the sample mixtures, while after the SC process, no PFAS was detected in the solid residue but noticeable quantities of PFAS were observed in the emissions. PFAS compounds in smoldering combustion can be degraded via several pathways including H/F exchange and dissociation of the functional groups, PFOS desulfonation and defluorination. During smoldering combustion, PFOS can transform into PFOA and shorter-chain perfluorinated carboxylic acids can break down the C4-C9 compounds to C2 and C3 chain lengths. The analysis confirmed the occurrence of H/F exchanges on PFBA, PFPA and PFPeA. The detection of 6:2 fluorotelomer sulfonate also indicated that PFOS underwent four consecutive H/F exchanges [71].

However, the technology is still in its infancy, and more research is required to determine the optimum parameters to obtain the maximum PFAS removal at the minimum cost and environmental risks. The technology could prove expensive if it requires a long period of ignition/preheating phase, which consumes more energy. Therefore, efforts should be made to reduce the ignition time. Alternative porous materials that provide a suitable energy balance can make the SC process self-sustainable and reduce the total cost of biosolids management. As mentioned earlier, PFAS destruction could be started in the preheating phase, and a comprehensive study should be conducted to understand the fate of different types of PFAS under varying preheating temperatures. In addition, more attention should be paid to examine the environmental risks associated with the emissions and quantify the total mass loss in the process. The technology has shown promising results at the laboratory scale; hence, it would be interesting to determine its feasibility at the pilot scale.

**Gasification** is also a commercialized technology used for biosolids management. The technology has been successfully used in Germany, Japan, the USA and Australia to convert biosolids into syngas and biochar and simultaneously mitigate emerging organic contaminants [17]. Similar to pyrolysis and incineration, gasification is an energy-intensive technology that requires high temperatures of around 600–900 °C, pre-drying of biosolids and a limited supply of oxygen. Gasification of

biosolids has been used to generate biochar at a large scale, but the fate of PFAS has not been explored thoroughly during the process. A study showed that 200 °C was an adequate temperature to initiate the gasification of PFOA, while a range of 400–600 °C is required to gasify PFOS compounds, owing to the stability of sulfonic compounds over carboxylic acids [24]. Gasification of PFAS-biosolids has been demonstrated at a pilot-scale in the Queensland state of Australia. Logan City Council has been operating a gasifier at 600 °C in a low oxygen environment to convert biosolids (-PFAS) into biogas and biochar [7]. The gasification plant also utilizes the energy recovered from syngas for drying and heating processes. It can recover and reuse almost 70% of the energy in biosolids, while the rest of the energy required is provided by an onsite solar array, making the facility energy neutral. Thermal treatment at high temperatures in the gasification of PFAS-biosolids followed by combustion of the hydrogen-rich syngas stream in a thermal oxidizer could potentially destroy PFAS by mineralizing them into shorter PFAS molecules or less recalcitrant constituents. The reports suggest that gasification of PFAS-biosolids destructs nearly all PFAS compounds since the produced biochar showed PFAS quantities below the detection limit [7]. However, it is a challenging task to understand the PFAS degradation mechanism and evaluate potential products of incomplete destruction due to the complex composition of PFAS and biosolids. Hence, experimental and computational studies using sole PFAS molecules can be conducted to estimate destruction mechanisms and pathways under varying parameters. Because gasification also involves thermal treatment and oxygen, PFAS are supposed to follow similar degradation pathways of pyrolysis and incineration which are discussed in the following sections.

**Incineration** is a renowned thermochemical waste-to-energy technology that involves the combustion of feedstocks into heat, gas and ash [93]. It is one of the prominent approaches employed for waste management, including biosolids. Incineration is an energy-intensive technology and generally requires a high temperature (800–1000 °C) to destruct PFAS-biosolids [23]. For instance, the Tahuna wastewater treatment plant in Dunedin city council of New Zealand operates biosolids incineration at 830 °C [94], and over 200 plants are used in the incineration of sewage sludge in the USA [23]. However, employing PFAS-contaminated sludge or biosolids in incineration has rarely been studied. Since biosolids contain high moisture content of up to 85%, it requires pre-drying prior to incineration. The composition of resultant products depends mainly on the incineration conditions like temperature, oxygen content and moisture. However, the presence of PFAS in biosolids may result in extra hazardous emissions of volatile or mobile products [95]. Incineration of polytetrafluoroethylene (PTFE) between the temperature range of 750 and 1050 °C has been shown to produce major products like CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, CHF<sub>3</sub>, tetrafluoroethene, hexafluoropropene [93]. In addition, it has been argued that greenhouse gases produced during the incineration of PTFE contain C–F bonds, which absorb electromagnetic radiations in the range of 1000–1400 cm<sup>-1</sup>, indicating its significant potential for global warming [93]. Yamada et al. [96] investigated the incineration of a polyester/cellulose fabric substrate treated with a fluorotelomer-based acrylic polymer at 1000 °C and 2 s residence time. The study aimed to examine the release of PFOA from the incineration of the fluorotelomer polymer. The results revealed that the fluorotelomer polymer was completely degraded at the studied incineration conditions, and no PFOA was detected [96]. A similar study was performed by Taylor et al. [97] to determine the fate of fluorotelomer-based polymers in incineration at 1000 °C, 2 s residence time, a varying amount of hydrogen fluoride (3.2–6.6 mg dscm<sup>-1</sup>) and 7% of oxygen. At all operating parameters studied, fluorotelomer-based polymers were completely destroyed, and no PFOA was detected [97].

PFAS-biosolids mineralisation pathways in incineration are less explored so far. Garcia et al. [98] carried out thermal degradation of PTFE at 850 °C in the presence and absence of oxygen and the results revealed the occurrence of C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> in the gases, while numerous

fluorinated semi-volatiles such as benzoyl fluoride were noticed in oxygen-free thermal degradation and benzenepentafluoro was observed in the presence of oxygen [98]. Fig. S2 shows the possible mechanism of PTFE destruction. The thermal degradation of PTFE begins slowly at around 250 °C, consisting of random chain cleavage, followed by depolymerisation. The formation of fluorinated and perfluorocarbon compounds can be attributed to the cleavage of C–C bonds in PTFE. C<sub>3</sub>F<sub>6</sub> was found to be the major product between 750 °C and 1050 °C temperatures of PTFE incineration, mainly because the monomer C<sub>2</sub>F<sub>4</sub> could react to generate C<sub>3</sub>F<sub>6</sub> [98]. It was further noticed that oxygen-free conditions favored the formation of C<sub>3</sub>F<sub>6</sub>, whereas, in the presence of oxygen, C<sub>3</sub>F<sub>6</sub> decomposed to C<sub>2</sub>F<sub>6</sub>. This was evident from the results that indicated a decrease in the concentration of C<sub>3</sub>F<sub>6</sub> in oxygen-dominant conditions, meanwhile, the quantities of C<sub>2</sub>F<sub>6</sub> and CH<sub>4</sub> were found to be increased and no C<sub>2</sub>F<sub>4</sub> was detected, primarily attributing to the reaction of C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> with oxygen. C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> after reacting with oxygen can also form CF<sub>4</sub> and CO<sub>2</sub> [98]. In addition, the thermal degradation of PTFE also releases perfluorocarbon compounds and fluorinated semi-volatiles, toluene, 2-hexanol, 3-penten-2-one, and 3-penten-2-ol. Thermal destruction can completely transform PTFE into F (as HF), CO<sub>2</sub> and H<sub>2</sub>O [99].

Since thermal destruction of PFAS can result in a number of smaller to larger end products, it is essential to measure the treatment efficacy and understand the degree of PFAS mineralization. To enhance the efficacy, surrogates like HF or CF<sub>4</sub>, and C<sub>2</sub>F<sub>4</sub> can be used to indicate the mineralization extent of PFAS since these are dominant end products of PFAS thermal degradation. However, there are some challenges associated with these surrogates. The application of HF can be complicated because it is reactive to the silica-based lining of the reactor and could form SiF<sub>4</sub>. On the other hand, if CF<sub>4</sub> is used individually as a surrogate, it might be unsuitable to understand complete PFAS defluorination for inert thermal degradation because no CF<sub>4</sub> was detected, and the primary short-chain product was C<sub>2</sub>F<sub>4</sub>. The challenge with C<sub>2</sub>F<sub>4</sub> as a surrogate arises in the presence of oxygen because it can react with oxygen and produce CF. Therefore, to avoid the underestimation of PFAS mineralization, a mixture of surrogates with the most common end products (compounds) including HF or CF<sub>4</sub>, and C<sub>2</sub>F<sub>4</sub> should be considered in the targeted analysis [93].

**Pyrolysis** is a well-known thermochemical process to convert biomass/biosolids into value-added products like biochar and bio-oil [83,100,101]. Pyrolysis operating parameters such as feedstock composition, temperature, heating rate, and residence time play a decisive role in the fate of PFAS destruction. Studies have shown that pyrolysis at temperatures ranging from 250° to 800°C can effectively degrade various PFAS compounds, including PFOA and PFOS [17,23]. At temperatures above 650 °C, most PFAS are completely demineralized [14].

Pyrolysis of PFAS-biosolids and sewage sludge has been thoroughly studied and has achieved excellent results in removing all types of PFAS compounds. For instance, Thoma et al. [17] carried out pyrolysis of PFAS-biosolids around 650 °C and a residence time of 19 min. The results showed that the pyrolysis system achieved 99.9% PFAS removal, and no PFAS compound was detected in the biochar. The gas-phase analysis confirmed the presence of fluorine-containing gases like hydrogen fluoride, hydrogen chloride, and other carbon-fluorine compounds [17]. The distribution of PFAS in bio-oil was not estimated in the study; therefore, it would be interesting in the future to examine the fate of PFAS in bio-oil as well. Another study performed pyrolysis of PFAS-biosolids at 500–600 °C and obtained more than 90% removal of PFOA and PFOS [14].

The mechanisms involved in the thermal decomposition of PFAS are mainly: cleavage of intramolecular bonds, hydrolysis, radical reactions, homolytic cleavage, and oxidation [23]. In pyrolysis, PFAS compounds are generally pyrolyzed in organofluorine products distributed in pyrolytic products. Since pyrolysis is a temperature-dependent technique, less stable bonds in PFAS compounds require lower temperatures

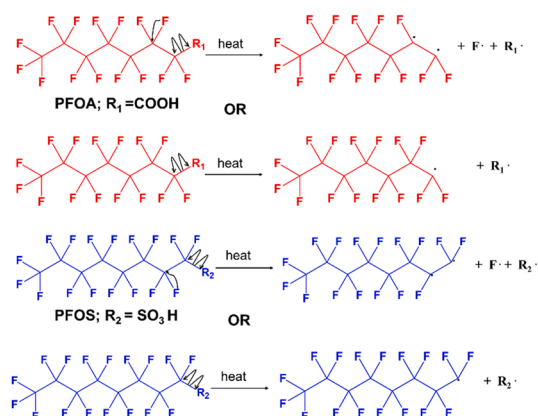
(200–500 °C) to degrade, while strong bonds require high temperatures (500–900 °C) to initiate the degradation. For example, perfluoroether carboxylic acids need a lower temperature (200–300 °C) to decompose than PFCAs with the same number of fluorinated carbons, demonstrating that the presence of ether bonds makes the molecule weaker [24]. Similarly, PFCA compounds are considered less stable than PFSA and thus require 200 °C for the former and 450 °C for the latter category to initiate the decomposition.

The destruction of any PFAS compound is completely dependent on the strength and types of chemical bonds in the PFAS structure and the bond dissociation energies (BDE) required to break them. Recently, Alinezhad et al. compared PFAS degradation of several polyfluorinated compounds (N-MeFOSAA, 8:2 FTS, PFOAB, PFOAaMS, PFOSB, and PFOSAms), perfluoroalkyl compounds (PFOS, PFOA) and fluorinated ether compounds (HFPO-DA and 6:2 Cl-PFAES) in the presence of air and inert environment [102]. The results reported nearly complete degradation (>99%) for all PFAS compounds at 500 °C under both conditions. The minimum temperature required to decompose more than 30% of PFOA and PFOS alternatives was found to be 200 °C. The authors further revealed that among all the studied PFAS compounds, polyfluorinated compounds were thermally most unstable compounds (compared to fluorinated ether compounds and perfluoroalkyl compounds) because of the presence of a nonfluorinated moiety that can readily undergo side-chain stripping. Thermal degradation of PFAS compounds (for example, PFOA and PFOS) has been recommended to follow a three-step random-chain scission pathway [103]. The possible degradation mechanism is shown in Fig. 6.

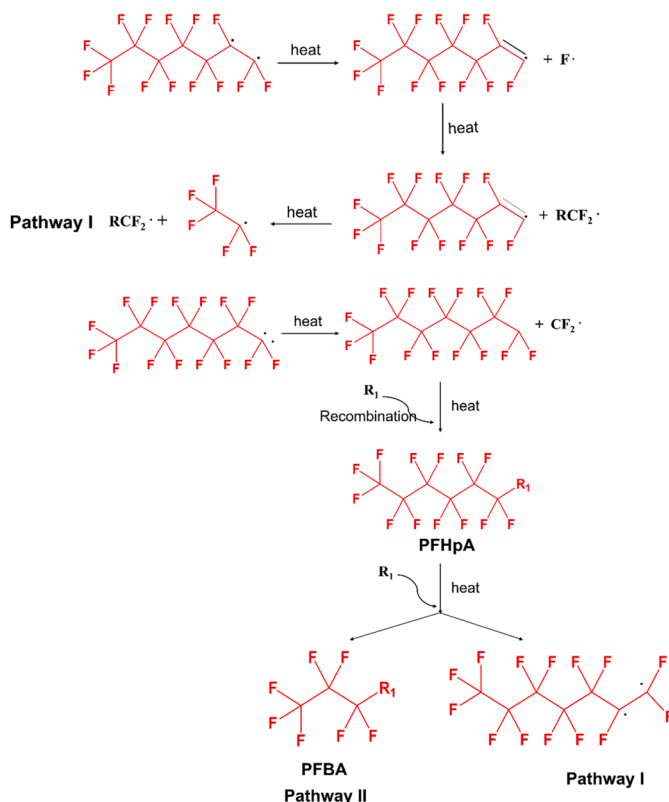
Thermal degradation of PFOA can be initiated with a homolytic cleavage of weaker C–C bond, while in PFOS, the C–S bond next to the sulfonate group could be a preferable target since it has less BDE compared to the C–F bond [104]. This first step of degradation initiation with C–C bond cleavage in PFOA generates a nonfluorinated moiety and a perfluoroalkyl biradical C<sub>7</sub>F<sub>14</sub>; and C–S bond cleavage in PFOS forms a nonfluorinated moiety and a perfluoroalkyl biradical C<sub>8</sub>F<sub>16</sub>. The second step is called chain propagation which involves the defluorination of perfluoroalkyl radical and radical chain propagation reactions, resulting in the formation of shorter-chained perfluoroalkyl radicals. Subsequently, the perfluoroalkyl radicals can recombine with carbonyl groups to generate PFCA intermediates. The last step is called termination which comprises the termination of chain propagation reactions to produce very short fluorinated units as the end products [104]. The pyrolysis of PFOA and PFOS at 500 °C produces a similar type of fluorinated products such as perfluoro-1-heptene (C<sub>7</sub>F<sub>14</sub>), 1 H-perfluorohexane (C<sub>6</sub>HF<sub>13</sub>), perfluoro-1-hexene (C<sub>6</sub>F<sub>12</sub>), perfluoro-1-butene (C<sub>4</sub>F<sub>8</sub>), hexafluoropropene (C<sub>3</sub>F<sub>6</sub>), and tetrafluoroethylene (C<sub>2</sub>F<sub>4</sub>). The compounds can be generated following a random chain scission mechanism as explained previously. In addition, the pyrolysis of PFOS produced long-chain perfluoroalkanes, including perfluorooctane (C<sub>8</sub>F<sub>18</sub>) and perfluoroheptane (C<sub>7</sub>F<sub>16</sub>), following a chain-scission and recombination mechanism [102].

Thermal degradation of cationic (PFOAaMS) and zwitterionic (PFOSB) PFAS compounds has been found to yield PFOA and PFOS [103]. Fig. 7 presents two thermal decomposition mechanisms of polyfluoroalkyl sulfonamides: (i) a radical-mediated mechanism involving end-chain scission and random-chain scission to form PFOA and homologues and (ii) a chain-stripping mechanism where the nonfluorinated moiety is eliminated. In the first pathway, the thermal decomposition of PFOSB follows multistep radical chain reactions similar to PFOS which include initiation, chain propagation, and termination reactions. However, compared to PFOS, in PFOSB, two types of initiation reactions can be favored; (a) end-chain scission: where PFAS are cleaved from the bond between the nonfluorinated side chain and perfluoroalkyl chain, producing a perfluoroalkyl radical that further undergoes C radical oxidation to form PFOA [105]. The second initiation reaction is random-chain scission that involves a C–C bond cleavage at apparently random locations on the perfluoroalkyl chain.

## a) Initiation



## b) Chain propagation



## c) Termination



Fig. 6. Possible “unzip” decomposition pathways of perfluoroalkyl substances during thermal treatment. Reproduced with permission [102]. Copyright (2022) American Chemical Society.

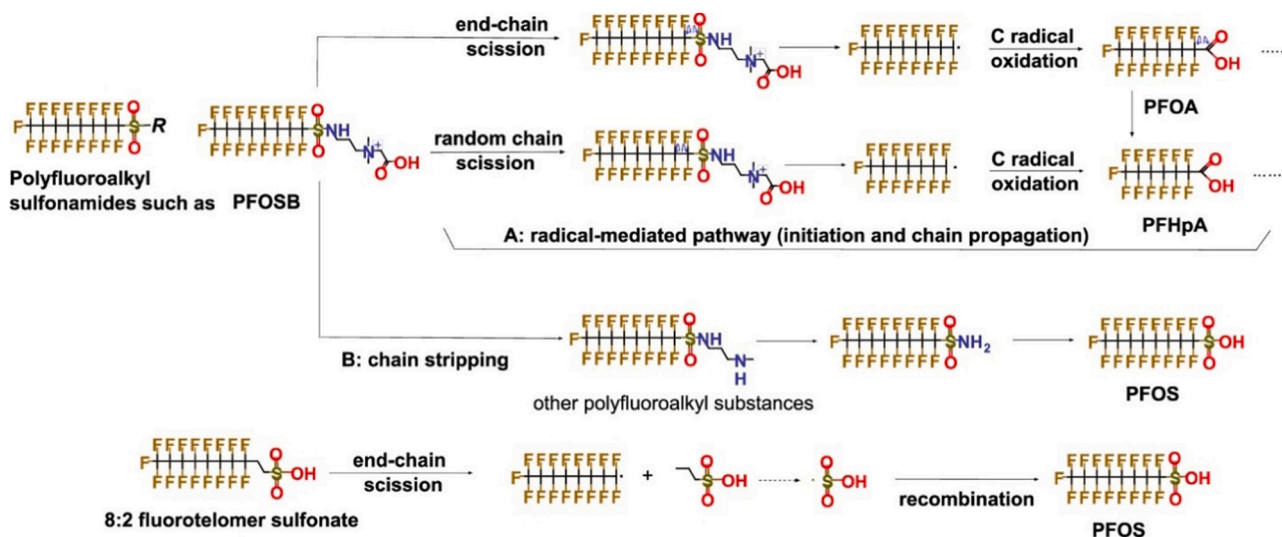


Fig. 7. Thermal decomposition pathways of polyfluoroalkyl sulfonamides. Reproduced with permission [103]. Copyright (2021) American Chemical Society.

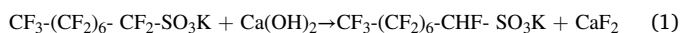
The resultant perfluoroalkyl radicals also undergo C radical oxidation to form perfluoroalkyl carboxylic acids of different chain lengths, such as PFHpA and PFHxA [103].

The second thermal decomposition mechanism of polyfluoroalkyl sulfonamides involves the degradation of the nonfluorinated moiety which produces PFOS and other polyfluoroalkyl substances, as shown in Fig. 7. A similar thermal decomposition mechanism has been suggested for anionic polyfluoroalkyl substances, namely, N-MeFOSAA and 8:2

FTS [103]. The thermal degradation of 8:2 FTS also starts with the end-chain scission step, followed by the recombination step where the perfluoroalkyl radical recombines with the sulfonate group and transforms into PFOS [103].

In addition, the concentration of metal ions (such as  $\text{Ca}^{2+}$ , which may act as catalysts) in biosolids significantly influences PFAS degradation [106].  $\text{Ca}(\text{OH})_2$  has been demonstrated to mineralize PFAS compounds such as PFOS and PTFE and produce  $\text{CaF}_2$  [107,108]. The

application of  $\text{Ca}(\text{OH})_2$  also reduces the pollution of acidic gases during the thermal degradation of PFAS compounds [107]. Fig. S3 shows the possible mechanism of mineralization for PFOS during the thermal treatment of  $\text{Ca}(\text{OH})_2$ -containing sludge. Results have shown that temperature and heating play a pivotal role in the mineralization of PFAS. At a lower temperature ( $400^\circ\text{C}$ ),  $\text{CaF}_2$  was found after 3 min of thermal treatment and reached 50% of transformation efficiency. The total fluorine content was increased when the temperature varied from  $300^\circ$  to  $600^\circ\text{C}$ . This is mainly because this temperature range may enhance the diffusion process of fluoride into Ca-containing reactants to form  $\text{CaF}_2$  (pathway (III) in Fig. S3) and promote the capture of gas products by the Ca-reactant (pathway V in Fig. S3). But at temperatures of 600 and  $900^\circ\text{C}$ ,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  was also observed in addition to  $\text{CaF}_2$  after 1 min of the treatment, reaching 71% and 68% of transformation efficiency, respectively. This could be attributed to the reduction in the concentration of  $\text{CaF}_2$  at higher temperatures.  $\text{Ca}(\text{OH})_2$  molecule contains two hydrogen and previous studies have shown that C–F bonds can be converted to C–H bonds via a hydrodefluorination reaction [66]. Hence, there is a possibility of a hydrodefluorination reaction between PFOS and  $\text{Ca}(\text{OH})_2$  where each fluorine of the perfluoroalkyl chain can be replaced by hydrogen of  $\text{Ca}(\text{OH})_2$ . Hydrodefluorination reaction may initiate at alpha carbon, proximate to the sulfonic headgroup and may continue through the perfluoroalkyl chain to the terminal trifluoromethyl moiety, as shown in Eq. (1).



On the other hand, metal oxide like CaO forms a face-centered cubic crystal structure and the heat treatment induces cleavage of CaO crystal structure and creates reducing sites for contacting molecules such as PFOS [107]. The constant heat treatment continues to generate more reducing sites for PFOS molecules. Subsequently, PFOS would degrade to produce fluorinated carbon radicals which are considered more reactive than PFOS molecules and therefore, react with CaO to form  $\text{CaF}_2$ . Mineralization of PTFE, PFOA and FOSA is also considered to occur in a similar way to PFOS; however, the temperature range can have a different influence. For instance, PTFE was readily mineralized in the presence of  $\text{Ca}(\text{OH})_2$  at  $400^\circ\text{C}$ , achieving an 80% of fluorine transformation ratio which is higher than PFOS and PFOA [108].

Liming (the addition of calcium hydroxide) of biosolids is a common treatment aimed at reducing odor and immobilizing potentially toxic elements. The addition of lime to biosolids can help to increase the pH of biosolids, which in turn, can promote the stabilization of organic matter and the reduction of pathogens. The occurrence of lime in biosolids can further enhance the decomposition or destruction of PFAS during the pyrolysis process, following the different destruction pathways discussed above [107,108]. Therefore, pyrolysis could be a preferred solution to mitigate PFAS contamination in limed-biosolids.

Apart from the solid waste stream like biosolids, it is important to understand PFAS degradation in liquid waste streams like groundwater and wastewater. In this regard, photo-induced processes have a substantial tendency to enhance PFAS degradation, which mainly targets C–F bond breakage and has no effect on the surrounding  $\text{H}_2\text{O}$  molecules [109]. PFAS degradation mechanisms under photo-induced processes usually occur on electronic-excited surfaces [109]. Real-time time-dependent density functional theory (RT-TDDFT) calculations are highly advantageous to examine the reaction dynamics of photo-induced PFAS degradation. A recent study demonstrated RT-TDDFT calculations for photo-induced PFOA degradation under a variety of optical fields and observed unique dissociation dynamics of different C–F bonds as a function of time [109]. For instance, before the irradiation, all C–F bonds in PFOA had an initial length of  $\sim 1.35 \text{ \AA}$  but after the irradiation, C–F bonds showed minor to major oscillations [109]. Particularly, the C3–F14 bond initially contracted up to the time of 12 fs but rises constantly thereafter, whereas other C–F bonds showed continuous oscillation from the beginning (1 fs) to the end (35 fs) before the

breakage of C3–F14 and C1–F10 bonds [109]. Overall, the study revealed that photo-induced PFAS degradation is quite selective for C–F bond cleavage without affecting the surrounding  $\text{H}_2\text{O}$  molecules.

Another promising approach for PFAS remediation is through the use of hydrated electrons. Hydrated electrons are highly reactive species that can reduce the C–F bonds in PFAS, leading to their degradation [110,111]. Hydrated electrons can be generated through various means, such as the radiolysis of water or the use of chemical reducing agents. In the presence of PFAS, hydrated electrons can selectively attack the C–F bonds, breaking them down into smaller, less toxic compounds. The initial degradation stage requires the conversion of a C–C bond resembling an alkane into a C=C bond resembling an alkene within the PFAS molecule [111]. This process is triggered by the trans elimination of F atoms bonded to C atoms located next to each other [111]. A recent study explored the degradation mechanism of PFOS and PFOA with hydrated electrons in water using ab initio molecular dynamics (AIMD) simulations and revealed that the activation barrier for C–F bond dissociation in PFOS is three times greater than that in PFOA [110]. Before reacting with PFAS, the hydrated electron undergoes the transition from a localized state to a delocalized state several times [110]. In the beginning, the hydrated electron delocalizes over C3 and C4 atoms of a PFOS molecule and then the spin density localizes at the C3 centre (the dissociation site) and cleaves the C–F bond [110]. To get more information on the comparative degradation of PFOS and PFOA, C–F bond distances were calculated from pre-created cavity simulations for the hydrated electron. The results revealed that in the start, the C–F bond fluctuated around  $1.35 \text{ \AA}$  but at the end of the simulation, the distance of the C–F bond was stretched to  $3 \text{ \AA}$ , indicating the complete dissociation. The degradation of PFOA with the hydrated electron is carried out by two primary reaction pathways that involve H/F exchange and chain shortening [110]. On the other hand, the presence of a sulfonic functional group in PFOS leads to the C3 and C4 carbon centres having the lowest bond dissociation energy among all C–F bonds, resulting in a distinct degradation process that differs significantly from PFOA degradation [110].

## 5. Conclusions and the way forward

This article reviews and compares the primary technologies used for PFAS destruction in biosolids. Among all the techniques, thermochemical processes like pyrolysis and gasification have emerged as efficient solutions to mitigate PFAS and convert biosolids into a sustainable product called biochar that can be applied for agricultural applications. On the other hand, smouldering combustion and biodegradation cannot degrade all PFAS completely but are highly economical compared to pyrolysis and gasification. Moreover, each technique follows a unique pathway for PFAS degradation. Thermal degradation of PFOS involves a three-step random-chain scission pathway that includes C–S bond cleavage, followed by defluorination of perfluoroalkyl radical, radical chain propagation reactions, and finally the termination of chain propagation reactions to produce very short-fluorinated units. The presence of oxygen could influence the end-products in the emissions. For example, the thermal degradation of PTFE in oxygen-free conditions favors the formation of  $\text{C}_3\text{F}_6$  whereas, in the presence of oxygen,  $\text{C}_3\text{F}_6$  is transformed to  $\text{C}_2\text{F}_6$ . The addition of catalysts like  $\text{Ca}(\text{OH})_2$  promotes hydrodefluorination reactions and enhances PFAS degradation. In HTL, PFOS degradation is carried through  $\text{OH}^-$  catalyzed series of nucleophilic substitution and decarboxylation reactions whereas microbial PFAS degradation firstly involves C–S bond cleavage followed by hydroxylation, decarboxylation and defluorination reactions to form perfluoroheptanoic acid (PFHpA). Basic solvents like NaOH and DMSO promote decarboxylation reactions and improve the degradation of PFAS in the HTL process.

Destruction of PFAS-biosolids in thermochemical techniques especially pyrolysis and gasification is remarkable that can remove up to 99% of PFAS and its understanding has been progressing in an upright

direction. However, there is still a large scope to further understand the fate of PFAS in these thermochemical techniques. For instance, biosolids are usually contaminated with a mixture of varying proportions of PFAS compounds and may require different temperature ranges to destroy long-chain PFAS compounds, such as PFDA and PFUnDA. Therefore, more studies are required to optimize the operating conditions of thermochemical techniques considering the mixtures of diverse PFAS compounds. In addition to this, the composition of biosolids, especially, the presence of divalent cations like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  enhances the thermal degradation of PFAS. Hence, more studies can be designed to study the effect of other mono or divalent cations, or other contaminants present in biosolids since considerable concentrations of contaminants like PPCPs have been reported in biosolids. Moreover, the addition of certain catalysts targeting the dissociation of C–F bonds can be highly advantageous to enhance the thermal degradation of PFAS. Currently, non-catalytic pyrolysis has been widely studied for PFAS destruction and less attention has been paid to employ the catalysts. Bentel et al. [34] revealed that it requires higher energy (117.7–122.7 kJ mol<sup>-1</sup>) to break the C–F bond in the CF<sub>3</sub> moiety of PFAS compared to the CF<sub>2</sub> moiety present in the fluorinated tail (106.8–110.9 kJ mol<sup>-1</sup>). Hence, catalysts can be designed to break the C–F bond in CF<sub>2</sub> moiety to further reduce the activation energy and increase the PFAS destruction rate. Employing catalysts in pyrolysis can decrease the required temperature for the process, reducing the energy input demand.

The formation of undesirable by-products or intermediate PFAS products is not completely known in biological and thermochemical techniques. Thus, future studies should focus on the identification of by-products or intermediate PFAS products, which can also help to completely understand the mechanism of PFAS destruction. Meanwhile, studies should also emphasize the characterization and identification of the incomplete combustion products of PFAS under different operating parameters since the understanding of the generation of incomplete combustion by-products is almost completely unknown. The outcomes of these studies could be crucial to estimate the associated environmental risks of the emissions generated from these technologies and developing possible measures to mitigate them.

The analysis of intermediate PFAS compounds during pyrolysis or gasification causes a substantial barrier to understand their degradation mechanism. For example, quantifying PFAS in bio-oil or gases in real-time is a great challenge. Hence, more advanced sampling and analytical methods are required to develop the accurate measurement and identification of incomplete combustion by-products or intermediate PFAS products. Particularly, at the pilot-scale, there is a lack of knowledge about the efficiency of treatment processes for thermal degradation products of PFAS. Evaluation of total fluorine measurements in ash and gaseous emissions in PFAS treatment processes would be a key which would require analytical techniques that can close the fluorine mass balance. Analysis of trace amounts of PFAS in ash is a major challenge since the instrumentation detection limits for total fluorine are high. Therefore, to detect the trace level of PFAS in ash, concentration methods are required for the sample preparation.

#### 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.

#### Data Availability

No data was used for the research described in the article.

#### Acknowledgements

The authors thank the Queensland Government (The Advance Queensland Industry Research Fellowships program) Queensland Water

Regional Alliance Program, Queensland Water and the regional councils of Northern Queensland for funding this research. The regional councils include Townsville City Council, Burdekin Shire Council, Cairns Regional Council, Mackay Regional Council, Whitsundays Regional Council, and Isaac Regional Council.

#### Environmental Implications

Per- and polyfluoroalkyl substances (PFAS) are persistent organic chemicals and are considered one of the most hazardous pollutants on earth. They possess high environmental risks to human health, plants, and terrestrial and aquatic animals. In this manuscript, we have reported PFAS contamination in biosolids and the physicochemical properties of PFAS and biosolids responsible for PFAS accumulation in biosolids. We reviewed thermochemical and biological processes for PFAS degradation and critically discussed PFAS degradation mechanisms for each technology. We also highlighted the major challenges of these technologies and suggested possible solutions to improve them. We believe this manuscript could be of high interest if published in the Journal of Hazardous Materials.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2023.131212](https://doi.org/10.1016/j.jhazmat.2023.131212).

#### References

- [1] Englande, A.J., Reimers, R.S., 2001. Biosolids management - sustainable development status and future direction. *Water Sci Technol* 44 (10), 41–46.
- [2] Goh, C.H., et al., 2018. Chapter 4 biosolids: the growing potential for use. In: Crocker, R., et al. (Eds.), *Unmaking Waste in Production and Consumption: Towards the Circular Economy*. Emerald Publishing Limited, pp. 67–88.
- [3] Antunes, E., et al., 2018. Microwave pyrolysis of sewage biosolids: dielectric properties, microwave susceptor role and its impact on biochar properties. *J Anal Appl Pyrolysis* 129, 93–100.
- [4] P. Darvodelsky. *Biosolids Snapshot* 2012; 1 38.
- [5] Pepper, L.L., et al., 2021. Incidence of Pfas in soil following long-term application of class B biosolids. *Sci Total Environ* 793, 148449.
- [6] Kumar, R., et al., 2022. Emerging contaminants in biosolids: Presence, fate and analytical techniques. *Emerg Contam* 8, 162–194.
- [7] Ankley, G.T., et al., 2021. Assessing the ecological risks of per- and polyfluoroalkyl substances: current state-of-the science and a proposed path forward. *Environ Toxicol Chem* 40 (3), 564–605.
- [8] Bolan, N., et al., 2021. Remediation of poly- and perfluoroalkyl substances (PFAS) contaminated soils – to mobilize or to immobilize or to degrade? *J Hazard Mater* 401, 123892.
- [9] O'Connor, J., et al., 2022. Distribution, transformation and remediation of poly- and per-fluoroalkyl substances (PFAS) in wastewater sources. *Process Saf Environ Prot* 164, 91–108.
- [10] Bolan, N., et al., 2021. Distribution, behaviour, bioavailability and remediation of poly- and per-fluoroalkyl substances (PFAS) in solid biowastes and biowaste-treated soil. *Environ Int* 155, 106600.
- [11] Mukhopadhyay, R., et al., 2021. Natural and engineered clays and clay minerals for the removal of poly- and perfluoroalkyl substances from water: state-of-the-art and future perspectives. *Adv Colloid Interface Sci* 297, 102537.
- [12] Hoang, S.A., et al., 2022. Treatment processes to eliminate potential environmental hazards and restore agronomic value of sewage sludge: a review. *Environ Pollut* 293, 118564.
- [13] Loganholme Wastewater Treatment Plant: *Biosolids Gasification Demonstration Plant*. 2021.
- [14] Kundu, S., et al., 2021. Removal of PFASs from biosolids using a semi-pilot scale pyrolysis reactor and the application of biosolids derived biochar for the removal of PFASs from contaminated water. *Environ. Sci.: Water Res. Technol.* 7 (3), 638–649.
- [15] Patel, S., et al., 2019. Transformation of biosolids to biochar: a case study. *Environ Prog Sustain Energy* 38 (4), 13113.
- [16] Gallen, C., et al., 2018. A mass estimate of perfluoroalkyl substance (PFAS) release from Australian wastewater treatment plants. *Chemosphere* 208, 975–983.
- [17] Thoma, E.D., et al., 2022. Pyrolysis processing of PFAS-impacted biosolids, a pilot study. *J Air Waste Manag Assoc* 1–10.
- [18] Johnson, G.R., 2022. PFAS in soil and groundwater following historical land application of biosolids. *Water Res* 211, 118035.
- [19] Ross, I., et al., 2018. A review of emerging technologies for remediation of PFASs. *Remediat J* 28 (2), 101–126.

- [20] Ghisi, R., Vamerali, T., Manzetti, S., 2019. Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: a review. *Environ Res* 169, 326–341.
- [21] Banayan Esfahani, E., et al., 2022. Photo-chemical/catalytic oxidative/reductive decomposition of per- and poly-fluoroalkyl substances (PFAS), decomposition mechanisms and effects of key factors: a review. *Environ Sci: Water Res Technol* 8 (4), 698–728.
- [22] Garg, A., et al., 2023. Treatment technologies for removal of per- and polyfluoroalkyl substances (PFAS) in biosolids. *Chem Eng J* 453.
- [23] Longendyke, G.K., Katel, S., Wang, Y., 2022. PFAS fate and destruction mechanisms during thermal treatment: a comprehensive review. *Environ Sci: Process Impacts* 24 (2), 196–208.
- [24] Wang, J., et al., 2022. Critical review of thermal decomposition of per- and polyfluoroalkyl substances: mechanisms and implications for thermal treatment processes. *Environ Sci Technol* 56 (9), 5355–5370.
- [25] Australian Biosolids Statistics. 2021.
- [26] Navarro, I., et al., 2016. Bioaccumulation of emerging organic compounds (perfluoroalkyl substances and halogenated flame retardants) by earthworm in biosolid amended soils. *Environ Res* 149, 32–39.
- [27] Biosolids Market Size, Share, Growth Trends. 2021.
- [28] Wijesekara, H., et al., 2021. Carbon sequestration value of biosolids applied to soil: a global meta-analysis. *J Environ Manag* 284, 112008.
- [29] Wijesekara, H., et al., 2016. Utilization of biowaste for mine spoil. *Rehabilitation* 97–173.
- [30] Paz-Ferreiro, J., et al., 2018. Biochar from biosolids pyrolysis: a review. *Int J Environ Res Public Health* 15 (5), 956.
- [31] Panieri, E., et al., 2022. PFAS molecules: a major concern for the human health and the environment. *Toxics* 10 (2), 44.
- [32] Shahsavari, E., et al., 2021. Challenges and current status of the biological treatment of PFAS-contaminated soils. *Front Bioeng Biotechnol* 8, 602040.
- [33] Horst, J., et al., 2020. Understanding and managing the potential by-products of PFAS destruction. *Groundw Monit Remediat* 40 (2), 17–27.
- [34] Bentel, M.J., et al., 2019. Defluorination of per- and polyfluoroalkyl substances (PFASs) with hydrated electrons: structural dependence and implications to PFAS remediation and management. *Environ Sci Technol* 53 (7), 3718–3728.
- [35] Yu, Y., et al., 2020. Microbial cleavage of C-F Bonds in Two C 6 Per- and polyfluorinated compounds via reductive defluorination. *Environ Sci Technol* 54 (22), 14393–14402.
- [36] Che, S., et al., 2021. Structure-specific aerobic defluorination of short-chain fluorinated carboxylic acids by activated sludge communities. *Environ Sci Technol Lett* 8 (8), 668–674.
- [37] Abunada, Z., Alazaiza, M.Y.D., Bashir, M.J.K., 2020. An overview of per- and polyfluoroalkyl substances (PFAS) in the environment: source, fate, risk and regulations. *Water* 12 (12), 3590.
- [38] Schultz, M.M., et al., 2006. Fluorochemical mass flows in a municipal wastewater treatment facility. *Environ Sci Technol* 40 (23), 7350–7357.
- [39] Arvaniti, O.S., et al., 2012. Occurrence of different classes of perfluorinated compounds in Greek wastewater treatment plants and determination of their solid-water distribution coefficients. *J Hazard Mater* 239–240, 24–31.
- [40] Sun, H., et al., 2011. Long-chain perfluorinated chemicals in digested sewage sludges in Switzerland. *Environ Pollut* 159 (2), 654–662.
- [41] Zhang, C., et al., 2013. Sorption of short- and long-chain perfluoroalkyl surfactants on sewage sludges. *J Hazard Mater* 260, 689–699.
- [42] Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. *Environ Sci Technol* 40 (23), 7251–7256.
- [43] Arvaniti, O.S., et al., 2014. Sorption of perfluorinated compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment. *Chemosphere* 111, 405–411.
- [44] Cai, W., et al., 2022. Increasing ionic strength and valency of cations enhance sorption through hydrophobic interactions of PFAS with soil surfaces. *Sci Total Environ* 817, 152975.
- [45] Moodie, D., et al., 2021. Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Australian biosolids. *Chemosphere* 270, 129143.
- [46] Loganathan, B.G., et al., 2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Water Res* 41 (20), 4611–4620.
- [47] Campo, J., et al., 2014. Distribution and fate of perfluoroalkyl substances in Mediterranean Spanish sewage treatment plants. *Sci Total Environ* 472, 912–922.
- [48] Blaine, A.C., et al., 2013. Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: field and greenhouse studies. *Environ Sci Technol* 47 (24), 14062–14069.
- [49] Lee, H., et al., 2014. Fate of polyfluoroalkyl phosphate diesters and their metabolites in biosolids-applied soil: biodegradation and plant uptake in greenhouse and field experiments. *Environ Sci Technol* 48 (1), 340–349.
- [50] Mei, W., et al., 2021. Per- and polyfluoroalkyl substances (PFASs) in the soil-plant system: sorption, root uptake, and translocation. *Environ Int* 156, 106642.
- [51] Barry, V., Winquist, A., Steenland, K., 2013. Perfluorooctanoic acid (PFOA) exposures and incident cancers among adults living near a chemical plant. *Environ Health Perspect* 121 (11–12), 1313–1318.
- [52] Foresta, C., Tescari, S., Di Nisio, A., 2018. Impact of perfluorochemicals on human health and reproduction: a male's perspective. *J Endocrinol Invest* 41 (6), 639–645.
- [53] Pierozan, P., Jermeren, F., Karlsson, O., 2018. Perfluorooctanoic acid (PFOA) exposure promotes proliferation, migration and invasion potential in human breast epithelial cells. *Arch Toxicol* 92 (5), 1729–1739.
- [54] PFAS National Environmental Management Plan Version 2.0. p. 134.
- [55] Venkatesan, A.K., Halden, R.U., 2013. National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. *J Hazard Mater* (252–253), 413–418.
- [56] Kim Lazcano, R., et al., 2020. Characterizing and comparing per- and polyfluoroalkyl substances in commercially available biosolid and organic non-biosolid-based products. *Environ Sci Technol* 54 (14), 8640–8648.
- [57] Gallen, C., et al., 2016. Occurrence and distribution of brominated flame retardants and perfluoroalkyl substances in Australian landfill leachate and biosolids. *J Hazard Mater* 312, 55–64.
- [58] Letcher, R.J., Chu, S., Smyth, S.-A., 2020. Side-chain fluorinated polymer surfactants in biosolids from wastewater treatment plants. *J Hazard Mater* 388, 122044.
- [59] Guerra, P., et al., 2014. Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment. *J Hazard Mater* 272, 148–154.
- [60] Armstrong, D.L., et al., 2016. Temporal trends of perfluoroalkyl substances in limed biosolids from a large municipal water resource recovery facility. *J Environ Manag* 165, 88–95.
- [61] Wei, Z., Xu, T., Zhao, D., 2019. Treatment of per- and polyfluoroalkyl substances in landfill leachate: status, chemistry and prospects. *Environ Sci: Water Res Technol* 5 (11), 1814–1835.
- [62] Huang, S., Jaffé, P.R., 2019. Defluorination of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) by Acidimicrobium sp. Strain A6. *Environ Sci Technol* 53 (19), 11410–11419.
- [63] Berg, C., et al., 2022. Developing innovative treatment technologies for PFAS-containing wastes. *J Air Waste Manag Assoc* 1–16.
- [64] Chetverikov, S.P., et al., 2017. Degradation of perfluorooctanyl sulfonate by strain *Pseudomonas plecoglossicida* 2.4-D. *Appl Biochem Microbiol* 53 (5), 533–538.
- [65] Liou, J.S., et al., 2010. Investigating the biodegradability of perfluorooctanoic acid. *Chemosphere* 80 (2), 176–183.
- [66] Wu, B., et al., 2019. Rapid destruction and defluorination of perfluorooctanesulfonate by alkaline hydrothermal reaction. *Environ Sci Technol Lett* 6 (10), 630–636.
- [67] Hori, H., et al., 2008. Iron-induced decomposition of perfluorohexanesulfonate in sub- and supercritical water. *Chemosphere* 70 (5), 800–806.
- [68] Pinkard, B.R., et al., 2021. Destruction of perfluorooctanesulfonate (PFOS) in a batch supercritical water oxidation reactor. *Chemosphere* 279, 130834.
- [69] Zhang, W., Liang, Y., 2021. Effects of hydrothermal treatments on destruction of per- and polyfluoroalkyl substances in sewage sludge. *Environ Pollut* 285, 117276.
- [70] Watanabe, N., et al., 2018. Thermal mineralization behavior of PFOA, PFHxA, and PFOS during reactivation of granular activated carbon (GAC) in nitrogen atmosphere. *Environ Sci Pollut Res Int* 25 (8), 7200–7205.
- [71] Duchesne, A.L., et al., 2020. Remediation of PFAS-contaminated soil and granular activated carbon by smoldering combustion. *Environ Sci Technol* 54 (19), 12631–12640.
- [72] Xiao, F., et al., 2020. Thermal stability and decomposition of perfluoroalkyl substances on spent granular activated carbon. *Environ Sci Technol Lett* 7 (5), 343–350.
- [73] Huang, S., et al., 2022. Anaerobic degradation of perfluorooctanoic acid (PFOA) in biosolids by Acidimicrobium sp. strain A6. *J Hazard Mater* 424, 127699.
- [74] Zhang, Z., et al., 2022. Biodegradation of per- and polyfluoroalkyl substances (PFAS): a review. *Bioresour Technol* 344, 126223.
- [75] Mejia-Avendaño, S., et al., 2016. Generation of perfluoroalkyl acids from aerobic biotransformation of quaternary ammonium polyfluoroalkyl surfactants. *Environ Sci Technol* 50 (18), 9923–9932.
- [76] Levar, C.E., et al., 2017. Redox potential as a master variable controlling pathways of metal reduction by *Geobacter sulfurreducens*. *ISME J* 11 (3), 741–752.
- [77] Sun, Z., et al., 2021. Vitamin B12 (CoII) initiates the reductive defluorination of branched perfluorooctane sulfonate (br-PFOS) in the presence of sulfide. *Chem Eng J* 423.
- [78] Wackett, L.P., 2022. Nothing lasts forever: understanding microbial biodegradation of polyfluorinated compounds and perfluorinated alkyl substances. *Micro Biotechnol* 15 (3), 773–792.
- [79] Wackett, L.P., 2022. *Pseudomonas*: versatile biocatalysts for PFAS. *Environ Microbiol* 24 (7), 2882–2889.
- [80] Chetverikov, S.P., Loginov, O.N., 2019. A new ensifer adhaerens strain M1 is capable of transformation of perfluorocarboxylic acids. *Microbiology* 88 (1), 115–117.
- [81] Luo, Q., et al., 2018. Perfluorooctanesulfonate degrades in a laccase-mediator system. *Environ Sci Technol* 52 (18), 10617–10626.
- [82] Luo, Q., et al., 2015. Laccase-catalyzed degradation of perfluorooctanoic acid. *Environ Sci Technol Lett* 2 (7), 198–203.
- [83] Kumar, R., Strezov, V., 2021. Thermochemical production of bio-oil: a review of downstream processing technologies for bio-oil upgrading, production of hydrogen and high value-added products. *Renew Sustain Energy Rev* 135.
- [84] Xiu, S., Shahbazi, A., 2012. Bio-oil production and upgrading research: a review. *Renew Sustain Energy Rev* 16 (7), 4406–4414.
- [85] Chen, W.-T., et al., 2020. A perspective on hydrothermal processing of sewage sludge. *Curr Opin Environ Sci Health* 14, 63–73.
- [86] Hao, S., et al., 2022. Application of hydrothermal alkaline treatment for destruction of per- and polyfluoroalkyl substances in contaminated groundwater and soil. *Environ Sci Technol* 56 (10), 6647–6657.



- [87] Antunes, E., et al., 2017. Biochar produced from biosolids using a single-mode microwave: characterisation and its potential for phosphorus removal. *J Environ Manag* 196, 119–126.
- [88] Yu, J., et al., 2020. Fate of per- and polyfluoroalkyl substances (PFAS) during hydrothermal liquefaction of municipal wastewater treatment sludge. *Environ Sci: Water Res Technol* 6 (5), 1388–1399.
- [89] Trang, B., et al., 2022. Low-temperature mineralization of perfluorocarboxylic acids. *Science* 377 (6608), 839–845.
- [90] Wang, J., *Smouldering Combustion of Biosolids from Wastewater Treatment Plants (WWTPs)*. p. 46.
- [91] Rashwan, T.L., Gerhard, J.I., Grant, G.P., 2016. Application of self-sustaining smouldering combustion for the destruction of wastewater biosolids. *Waste Manag* 50, 201–212.
- [92] David, M., SERDP Project ER18–1593, *Demonstration of Smoldering Combustion Treatment of PFAS-impacted Investigation-Derived Waste*. 2019.
- [93] Aleksandrov, K., et al., 2019. Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas. *Chemosphere* 226, 898–906.
- [94] Drew, S., M.B. Ltd, and C. Henderson, *BIOSOLIDS INCINERATION AT TAHUNA WWTP – FUELLING A \$10 MILLION CAPITAL SAVING*. p. 12.
- [95] Wang, H., et al., 2008. Technological options for the management of biosolids. *Environ Sci Pollut Res - Int* 15 (4), 308–317.
- [96] Yamada, T., et al., 2005. Thermal degradation of fluorotelomer treated articles and related materials. *Chemosphere* 61 (7), 974–984.
- [97] Taylor, P.H., et al., 2014. Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment. *Chemosphere* 110, 17–22.
- [98] García, A.N., Viciano, N., Font, R., 2007. Products obtained in the fuel-rich combustion of PTFE at high temperature. *J Anal Appl Pyrolysis* 80 (1), 85–91.
- [99] Altarawneh, M., Almatarneh, M.H., Dlugogorski, B.Z., 2022. Thermal decomposition of perfluorinated carboxylic acids: kinetic model and theoretical requirements for PFAS incineration. *Chemosphere* 286, 131685.
- [100] Kumar, R., et al., 2020. Lignocellulose biomass pyrolysis for bio-oil production: a review of biomass pre-treatment methods for production of drop-in fuels. *Renew Sustain Energy Rev* 123.
- [101] Antunes, E., et al., 2018. Isotherms, kinetics and mechanism analysis of phosphorus recovery from aqueous solution by calcium-rich biochar produced from biosolids via microwave pyrolysis. *J Environ Chem Eng* 6 (1), 395–403.
- [102] Alinezhad, A., et al., 2022. An investigation of thermal air degradation and pyrolysis of per- and polyfluoroalkyl substances and aqueous film-forming foams in soil. *ACS EST Eng* 2 (2), 198–209.
- [103] Xiao, F., et al., 2021. Thermal decomposition of anionic, zwitterionic, and cationic polyfluoroalkyl substances in aqueous film-forming foams. *Environ Sci Technol* 55 (14), 9885–9894.
- [104] Sasi, P.C., et al., 2021. Effect of granular activated carbon and other porous materials on thermal decomposition of per- and polyfluoroalkyl substances: mechanisms and implications for water purification. *Water Res* 200, 117271.
- [105] Xiao, F., et al., 2018. PFOA and PFOS are generated from zwitterionic and cationic precursor compounds during water disinfection with chlorine or ozone. *Environ Sci Technol Lett* 5 (6), 382–388.
- [106] Ebrahimi, F., et al., 2021. Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes. *Chemosphere* 271, 129530.
- [107] Wang, F., et al., 2015. Effectiveness and mechanisms of defluorination of perfluorinated alkyl substances by calcium compounds during waste thermal treatment. *Environ Sci Technol* 49 (9), 5672–5680.
- [108] Wang, F., et al., 2013. Mineralization behavior of fluorine in perfluorooctanesulfonate (PFOS) during thermal treatment of lime-conditioned sludge. *Environ Sci Technol* 47 (6), 2621–2627.
- [109] Yamijala, S., et al., 2022. Photo-induced degradation of PFASs: excited-state mechanisms from real-time time-dependent density functional theory. *J Hazard Mater* 423 (Pt A), 127026.
- [110] Biswas, S., Yamijala, S., Wong, B.M., 2022. Degradation of per- and polyfluoroalkyl substances with hydrated electrons: a new mechanism from first-principles calculations. *Environ Sci Technol* 56 (12), 8167–8175.
- [111] Yamijala, S., Shinde, R., Wong, B.M., 2020. Real-time degradation dynamics of hydrated per- and polyfluoroalkyl substances (PFASs) in the presence of excess electrons. *Phys Chem Chem Phys* 22 (13), 6804–6808.