

Biological Remediation of Polyfluorinated Compounds

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Polyfluorinated compounds (PFCs) are a class of anthropogenic emerging persistent organic pollutants that consist of a fully fluorinated hydrophobic alkyl chain attached to a hydrophilic chain end group. The PFCs' carbon–fluorine (C-F) bond, characterized by strong polarity and strength, make them possess peculiar physicochemical properties such as hydrophobicity and resistance to degradation by heat and acid. Their environmental occurrence particularly in drinking water samples and water receiving bodies, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) being the most detected PFCs is evident that they cannot be completely eradicated by conventional wastewater treatment plants (WWTPs). However, despite the PFCs' stable C-F bond, recent literature suggests that PFCs are susceptible to bioremediation by certain bacterial strain and plant species. A lot of work still needs to be done in the context of understanding the biodegradation pathway of PFOA and PFOS by both bacterial strain and plant species.

polyfluorinated compounds

microbial species

phytoremediation

1. Bacterial Biodegradation

Conventional wastewater treatment plants (WWTPs) use biological techniques to treat water and wastewater streams for reuse. During biological treatment of aqueous streams, biodegradable material consisting of organics in dissolved form, such as starches, alcohols, acids, aldehydes, and esters, are utilized for food by microorganisms, thus decontaminating aqueous streams. It is worth noting that microbial utilization of dissolved organics can be accompanied by oxidation, which is the deletion of hydrogen from elements of an organic molecule, or by reduction, which is the addition of hydrogen to elements of the organic molecule ^[1]. However, a number of previously performed studies suggests that the biodegradation pathways and fate of polyfluorinated compounds (PFCs) are unknown to a large extent. This is attributed to the general belief that the strength of the C–F bond is the limiting factor on PFC biodegradability. However, early evidence suggests that organohalogen compounds, including PFCs, are susceptible to microbial degradation, despite their high stability, as reported by Parsons et al. ^[2]. The biodegradation of organohalogen compounds and PFCs are relatively slow due to their kinetic stability because of the carbon–halogen bond, thus contributing significantly to their long-term environmental fate.

Hitherto, dehalogenation is the thermodynamically recognized reaction mechanism for the degradation of organohalogen compounds. Early studies ^{[2][3]} suggest that under aerobic conditions, organohalogen compounds are degraded by catabolic pathways similar to those for nonhalogenated analogues. There are a number of

dehalogenation mechanisms that are reported in the literature for both aliphatic and aromatic substrates, i.e., haloacid dehalogenation, halohydrin dehalogenation, haloalkane dehalogenation, and reductive dehalogenation [2]. However, there is very little information reported on the degradation of PFCs, particularly perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). This is attributed to the biodegradation mechanism of 8:2 fluorotelomer alcohol by OH radicals, which yields PFOA and other perfluorinated carboxylic acids as products [2]. Fluorotelomer alcohols have been reported to biodegrade under aerobic and anaerobic environments [2]. In an early study conducted by Meesters and Schröder [4], it was demonstrated that both PFOA and PFOS are xenobiotic under aerobic environments. Despite the observed removal of PFOA and PFOS under anaerobic environments, no fluoride ion concentration was detected, which results in the biodegradability mechanism of PFOA and PFOS in aquatic environments remaining difficult to understand. In the subsequent section, the biodegradation of PFOA and PFOS are explained, indicating that their xenobiotic characteristics are something of the past.

Despite the chemically challenging C–F bond cleavage, recently performed studies have demonstrated that PFCs, particularly PFOA and PFOS, can be defluorinated by strong chemical oxidants, as well as by microbial population [5][6][7]. Many researchers have reported limited microbial defluorination of PFCs. This is attributed to the displacement of C–F bonds, which yield a fluoride ion, F[−], that is toxic to microbial population at minute concentrations [8]. The fluoride ion, which is produced as a result of PFCs' biodegradation (i.e., defluorination), enters bacterial cells, thus poisoning them [7][8]. The poisoning of bacterial cells ceases or hinders metabolic activities, resulting in the nonbiodegradability of PFCs. Such a biological reaction mechanism explains why fluorine concentrations are not detected during biodegradation of PFCs. The revelation of the toxicity of the fluoride ion to bacterial cells explains why PFCs are characterized as xenobiotic compounds. Moreover, the biodegradation mechanism of PFCs suggests that their xenobiotic characteristics are not solely a result of the C–F bond, but it can be attributed to the toxicity of the fluoride ion which hinders microbial activities.

Due to the recalcitrance and high stability of PFCs, particularly PFOA and PFOS, researchers have continued to test various microbial species aimed at testing their ability to biodegrade the aforementioned model contaminants. Apart from *Acidimicrobium* sp. strain A6 [6][9], *Pseudomonas parafulva* strain YAB1 [10], *Pseudomonas aeruginosa* strain HJ4 [11], and *Pseudomonas plecoglossicida* 2.4-D [12] are the only microbial species reported to biodegrade PFOA and PFOS. Yi et al. [10] investigated the growth rate of strain YAB1 which was extracted from soil sediments near a PFC-producing plant. Yi et al. and co-workers conducted their investigation in an aerobic environment and PFOA was added as a carbon source for strain YAB1. Optimal bacteria growth rate and PFOA degradation were recorded for a PFOA concentration of 500 mg/L. Interestingly, Yi et al. [10] inferred that a PFOA concentration of 1000 mg/L inhibited the growth rate of strain YAB1; however, the strain demonstrated tolerance and growth adaptability but not as significant when compared to a PFOA concentration of 500 mg/L. The findings by Yi et al. [10] suggests that higher PFOA concentrations hinder microbial activities, consequently inhibiting the bacterial proliferation. This is congruent to the work reported by Huang and Jaffé [6] and Ruiz-Urigüen et al. [9] that higher PFOA concentrations become toxic to microbial species, thus hindering microbial activities. Yi et al. [10] reported a PFOA removal efficiency of 48%, which was achieved after adding yeast to promote bacterial growth rate.

The growing interest in the investigation of various microbial species to degrade PFCs has demonstrated that PFOS can be degraded by *Pseudomonas aeruginosa* strain HJ4 under an aerobic environment [11]. PFOS was added as a carbon source at an initial concentration ranging from 1400 µg/L to 1800 µg/L for the growth of strain HJ4. Kwon et al. [11] reported an overall PFOS biodegradation of 67%, which was recorded after adding glucose to enhance the growth rate of strain HJ4 for PFOS biodegradation. However, according to Kwon et al. [11], no defluorination was observed. Fluoride ion concentration remained constant during biodegradation of PFOS. On the other hand, Chetverikov et al. [12] reported 75% PFOS degradation as a carbon source for the growth of *Pseudomonas plecoglossicida* 2.4-D. A significant growth rate on the 2.4-D strain was observed after adding NaCl which was maintained at less than 5% to avoid any microbial inhibition. Chetverikov and co-workers reported a fluoride ion concentration of up to 150 mg/L in the culture medium to account for the fact that defluorination indeed took place.

2. Microbial Degradation Pathway of Perfluorooctanoic Acid and Perfluorooctane Sulfonic Acid

Despite the experimentally illustrated biodegradation of PFOA and PFOS by microbial species [6][9][10][11], there is no available literature confirming a precise biodegradation mechanism of PFOA and PFOS. In the few studies that have reported on PFC biodegradation, particularly PFOA and PFOS, the mechanism is based on the detection of intermediate metabolites. According to Zhang et al. [13], this is attributed to PFOA and PFOS having a low redox potential of about -450 mV. Typical microbial oxidizable growth substrates demonstrate redox potentials greater than -450 mV [5][13]; therefore, at a low redox potential, the transfer of an electron from a substrate for PFC reduction will not be thermodynamically attractive for microbial species. However, as indicated in the previous sections, studies have demonstrated that selected bacteria can degrade PFOA and PFOS under anaerobic [6] and aerobic [9][10][11] environments. Besides the redox potential, Wackett [7] reported that, in order for a microbe to degrade a PFC, it needs to transport the fluorinated compound into the cell, harbor a recently evolved enzyme to catalyze the C–F bond cleavage, detect the poisonous fluoride ion generated, and protect itself against the fluoride with a fluoride–proton antiporter. However, the disadvantage in C–F bond reduction is that it can be selected against an evolution on the basis that it provides no benefit to the microbial species but drains cellular energy [5]. Despite the shortcomings of C–F bond reduction, selected bacteria which have been exposed to environments with fluoride concentrations exceeding 1 ppm have developed systems to protect themselves against the toxic fluoride ion. Last et al. [14] reported that bacteria can resist the toxicity of environmental fluoride by expelling the fluoride ion from its cytoplasm by the aid of a proton-coupled fluoride ion antiporter, *E. casseliflavus* being the common antiporter. The microbial attributes necessary to biodegrade PFCs suggest that bacteria that are found near PFC-producing subjects or in PFC-contaminated environments can develop antiporters and survive the toxic fluoride ion. It is worth noting that in the available literature reporting on PFOA and PFOS degradation by novel microbial species, all reported bacteria were harvested from PFCs contaminated sites, which explains why the reported bacteria can biodegrade PFOA and PFOS.

The degradation of PFOA and PFOS by novel bacteria, as reported in the literature [6][9][10][11], can be attributed to certain enzymes cleaving the C–F bond through either oxidation by inserting oxygen atoms or reduction by adding extra electrons to the bond [13]. The dictation of fluoride ions during microbial degradation of PFCs indicates that microbes can break the C–F bond under control environments, which can be either aerobic or anaerobic. Yu et al. [15] reported that during microbial degradation of PFCs, C–F bond cleavage occurs at the sp^2 and sp^3 C–F bonds. However, Yu and co-workers reported that, despite the tertiary sp^3 C–F bond having the lowest bond dissociation energy for the model PFCs (i.e., perfluoro (4-methylpent-2-enoic acid) and 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-pentenoic acid), the sp^2 C–F bond was more microbially active. The production of fluoride ions [6] and intermediate products [9][10][11] during the biodegradation of PFOA and PFOS is an indication that the C–F bond was cleaved, despite having a bond dissociation energy of up to 130 kcal/mol [13]. There is no available literature reporting on the specific pathways for PFOA and PFOS biodegradation. It is worth noting that the extensively reported biodegradation of fluorotelomer alcohols and other PFCs, apart from PFOA and PFOS, is limited to the removal of non-fluorinated moieties rather than C–F bond cleavage.

Factors Affecting Perfluorooctanoic Acid and Perfluorooctane Sulfonic Acid Biodegradation

It is apparent that the microbial biodegradation of PFOA and PFOS can be affected by certain factors, such as the type of microbial species, initial concentration of model PFCs, and co-substrates. To date, *Acidimicrobium* sp. strain A6, *Pseudomonas parafulva* strain YAB1, *Pseudomonas aeruginosa* strain HJ4, and *Pseudomonas plecoglossicida* 2.4-D are the only reported microbial species in the literature that are capable of PFOA and PFOS biodegradation. This suggests that the type of microbial species plays a significant role in the biodegradation process of PFCs, which are characterized as xenobiotic during their bio-remediation process. Moreover, the available literature on the biodegradation of PFOS and PFOA have demonstrated that higher PFC concentrations, ranging between 100 mg/L and 1000 mg/L, can inhibit microbial growth rate depending on the microbe strain, thus compromising PFC degradation. Moreover, selected microbes use PFOA and PFOS as carbon sources and simultaneously perform bio-defluorination [6][13]. The presence of co-substrates can enhance microbial growth rate due to microbial preference [6][9][11].

3. Other Biological Remediation Processes of Perfluorooctanoic Acid and Perfluorooctane Sulfonic Acid

Previously conducted studies have reported on a number of effective remedial technologies of PFCs from aquatic environments, such as photocatalysis and electrochemical oxidation [16][17][18][19], plasma technology [20][21], and adsorption by granular-activated carbon [22]. However, the aforementioned treatment technologies are energy-intensive, consequently resulting in high operational costs [23]. Hence, the subsequent sub-section focuses on PFOA and PFOS remediation by phytoremediation, characterized as an environmentally green and cost-effective technology.

Phytoremediation of Perfluorooctanoic Acid and Perfluorooctane Sulfonic Acid

The removal of organic pollutants by plants is known as phytoremediation. The mechanism of the phytoremediation process consists of (1) phytofiltration, which is essentially the uptake of pollutants by the plant; (2) phytovolatilization, which is the conversion of pollutants to volatile form; and (3) phytodegradation, which involves the participation of root exudes and microbial population [23]. Early studies [24][25] have demonstrated that plants can absorb PFCs, where long-chain PFCs are likely to be accumulated in roots, and short chains are more likely to be accumulated in buds, fruits, and crops [22]. Gobelius et al. [24] investigated the uptake of PFCs by various plant species, and it was reported that high concentrations of short-chain PFCs were detected in leaves, with PFOA and PFOS being detected in roots. It is worth mentioning that Gobelius et al. [24] did not report on PFOA and PFOS phytovolatilization and phytodegradation. The findings suggest that only phytofiltration was observed for PFOA and PFOS phytoremediation mechanisms.

Colomer-Vidal et al. [25] investigated the sorption of PFCs in the water-sediment-plant system along the Dongzhulong and Xiaoqing rivers by floating and rooted plant species. The average PFC concentration in water was reported to be 84,000 ng/L and 2300 ng/L in sediments, respectively, with PFOA accounting for up to 97% in both water and sediment. It was reported that PFOA demonstrated high sorption affinity with floating plant species absorbing a higher concentration of PFCs as compared to rooted plants. The high uptake capacity by floating plants is attributed to large proliferation rates. Higher PFOA concentrations were detected in the roots of plant species for both floating and rooted plant species, suggesting that phytofiltration took place. The PFCs distribution analysis within the model plant species for the work reported by Colomer-Vidal et al. [25] demonstrated that short-chain PFCs were concentrated more in the shoots than in the roots, congruent to the work reported by Gobelius et al. [24]. Short-chain PFC uptake is attributed to the water potential gradient resulting from plant transpiration, consequently promoting the upward uptake of PFCs through the xylem [25]. On the other hand, the accumulation of long-chain PFCs in plant roots can be attributed to the proteinphilic-linked sorption. Previously undertaken studies on the phytoremediation of PFOA and PFOS suggest that long-chain PFCs are bound strongly to the roots' surface due to a positive correlation with protein content as opposed to short-chain PFCs [25][26].

The phytoremediation of PFOA and PFOS is strongly dependent on plant species. Wen et al. [26] investigated the role of proteins and lipids in the accumulation of PFOA and PFOS by different plant species, i.e., alfalfa, lettuce, maize, mung bean, radish, ryegrass, and soyabeans. It was reported that the concentration of PFOA and PFOS in the roots of the aforementioned model plant species did not follow the same trend, with ryegrass, maize, and radish roots recording the lowest PFOA and PFOS concentrations. The observed behavior was attributed to the low protein content in the roots of ryegrass, maize, and radish, as reported by Wen et al. [26]. Moreover, it was reported that the binding of PFOS to roots was stronger than that of PFOA; therefore, the transfer potential of PFOA from roots to shoots is more favorable compared to PFOS [26]. The observed behavior could be attributed to the relatively large molecular structure and lipophilicity of PFOS when compared to PFOA.

Based on the available literature, it is evident that PFCs can be eradicated from the environment by phytoremediation. However, the detection of PFCs in plant leaves suggests that nonedible plant species should be considered for phytoremediation of PFCs to avoid human exposure to PFCs. Moreover, the reported literature on

phytoremediation focuses on the translocation of PFCs in plant species. There is no available literature reporting on the degradation of PFCs in plant tissues.

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