PFAS Degradation Techniques – A Road towards Alleviating Organic Pollution

Onkar Lotlikar¹, Dhwani Kapadia², Sreela Dasgupta³
¹,²,³ Jai Hind College Autonomous, 23-24 Backbay Reclamation, Churchgate, Mumbai - 400020, India

ABSTRACT: PFAS are commonly found pollutants in soil and water bodies. Of all the PFAS that are found, PFOA and PFOS are the most hazardous ones. The review focuses upon Adsorption, Sonochemical Degradation, Photocatalysts, and Bio-remediation as techniques for the removal and degradation of PFA.

KEYWORDS: Adsorption, Bio-remediation, Photocatalyst, Sonochemical Degradation.

INTRODUCTION
PFAS are human-made chemicals that are used on a large scale due to their long-lasting nature and a wide range of applications. Additionally, the presence of strong carbon-fluorine bonds makes PFASs highly stable, both chemically and thermally [1]. The presence of such a strong bond complicates its degradation. Due to their strong C-F bonds, perfluoro alkylated substances persist for a longer time in the environment and are difficult to remediate. Their resistance towards grease, oil, water, and heat enables its use in a variety of fields which include fire-fighting foams, water-resistant fabrics, furniture, carpeting, cleaning products, non-stick cook-wares, and paints [2,3]. PFAS accumulate in the environment leading to an increased risk of bioaccumulation, causing health hazards [1,3,4]. The presence of such a strong bond complicates its degradation [5,6].

PFAS are immensely difficult to degrade and pose a great risk to the environment [6]. Among all the PFAS chemicals, the most studied are PFOS and PFOA as they are the most hazardous ones [4,5]. Humans are indirectly exposed to these toxic PFAS through soil and water bodies and can cause serious effects on one’s reproductive system, and other immunological disorders [6]. The use of PFAS in commercially-treated products are to make them stain and water-repellent. This is how there is an increase in human exposure to PFAS. Drinking water can also act as a source of exposure in certain communities where water supplies are contaminated with PFAS. These alkylated substances were also found to cause hormonal disruption, and an increase in levels of cholesterol. Bioaccumulation and toxicity of such substances increases health risks [7]. All these reasons highlight the importance of degradation of PFAS.

PFOA and PFOS, are types of PFAS which contain saturated carbon chain with fluorine atoms, a long hydrophobic side, and a hydrophilic polar functional group. The term ‘surfactant’ or ‘surface active agent’ describes the tendency of this class of compounds to adsorb at the interface between two immiscible fluid phases. The structure of PFOS and PFOA is such that they are quite strong, water-soluble, long-chain acids that exist in equilibrium between the neutral and the anionic form [8-10]. Their solubility in water is largely influenced by the anionic forms which are significantly more water-soluble than their neutral forms [11]. Due to their amphiphilic property, these substances have a wide range of applications in surfactants [9,11]. At environmental pH values, both PFOA and PFOS exist primarily as anions (for PFOA pKa ranges from < 0 to 3.8). They are termed as forever chemicals [12].

Studies indicate that these chemicals are highly persistent in the environment, are bio-accumulative, and have been termed as forever chemicals as they persist in the environment for a very long time. There is a certain concentration up to which PFOA levels can be tolerated. The limit for the presence of the pollutants is 40 ng/L [13], after which the compounds can get highly concentrated in the body and pose a risk to all those consuming contaminated waters. As claimed by many researchers, long-chain PFAS cause more harm than the short ones but it is necessary to clean off the environment not just with PFOA and PFOS, but all the PFAS that persist in the environment. However, an in-depth study and the degradation pathway of all the compounds is difficult [13,14]. An array of techniques are emerging that study and bring about the degradation of PFAS. The current study reviews some of the promising techniques for the degradation of PFAS. The techniques discussed are as follows:
Adsorption: Adsorption is an age-old technique in which hydrophobicity of the chain plays an important role. The adsorption of PFAS depends upon the hydrophobicity and hydrophilicity of the groups attached to such compounds [15].

Sonochemical Degradation: Sonolysis is an emerging technique and most widely used for PFAS degradation. The mechanism of sonolysis depends upon high-temperature pyrolysis and surface reaction site. The degradation of the compounds depends upon the ultrasound frequency and the chains get degraded based on their chain lengths and frequency supplied to them [16].

Photocatalysts: Photocatalytic techniques have developed recently and proven to be cost-effective. A variety of materials are used as photocatalysts for adsorption of the compounds and thus can be irradiated through ultraviolet radiation for their complete degradation [17]. The influence on the photocatalysts is caused due to factors such as temperature, pH, light source, the presence of oxygen in the solution and they affect the degradation of PFAS.

Bioremediation: Bioremediation is an eco-friendly technique which is used to understand the interaction between the PFAS and the micro-organisms. By understanding their interaction many microorganisms can be used for the degradation of PFAS [18].

RESULTS AND DISCUSSION

This review focuses on four major methods of PFAS removal – Adsorption, Sonochemical Degradation, Use of Photocatalysts, and Bioremediation for degradation of PFAS. The methods are described as follows:

1. Adsorption:
The adsorption of PFAS relies on the hydrophobicity and hydrophilicity of the groups attached. The most widely and commonly used materials for the adsorption of PFAS are GAC, NF, AIX, and Polymers. In a pilot-scale study, a continuous source of groundwater contaminated with 10 types of PFAS was treated for 7 months with 4 activated carbons; Calgon F400 and F600, Norit GAC400, and GCN1240. The two models studied based on which its adsorbance efficiency was calculated were the equilibrium model and the intra-partition diffusion model. Longer chain compounds such as PFOA, PFHxS, PFHpS, and PFOS were found to be strongly adsorbing and followed the equilibrium as well as the intra-partition model. The transport of contaminants on the adsorbing material was due to the four steps followed. The steps followed were; Bulk solution transport, Film resistance to transport, Intraparticle transport and Adsorption. For longer chain compounds, carbon adsorbent type F400 and GAC400 performed 40–50% better than F600 and GCN1240. Their better adsorption efficiency could be
due to the high volume of transport pores in F400 and GAC400 as compared to F600 and GCN1240. Of the two models studied, the equilibrium model was found to be a better fitting model for breakthrough study [19].

In another type of study, different materials were modified for the adsorption of PFOS. GAC with enlarged pores was synthesized for better adsorption. Due to the granular adsorbent of bamboo derived GAC, the diffusion and adsorption of PFOS and PFOA was facilitated. It was found that the adsorption capacity of bamboo-derived GAC was much higher about 2.32 mmol/g for PFOS and 1.15 mmol/g for PFOA at pH 5 [5]. As the solution pH increased, the adsorption of PFOS and PFOA decreased. When the pH was lowered i.e. below 4.0, decrease in adsorption was observed for PFOS and pH below 6.0 for PFOA. GAC can be extensively used as they are also very effective against removing a large array of dissolved organic contaminants. Since products such as pesticides are found to contain PFAS in dissolved form, GAC was extensively able to remove the dissolved contaminants [5, 20].

An extensive body of literature has shown strong conviction in NF membranes accompanied by GAC and AIX. The promising results was given by this combination, were a removal efficiency of more than 99% was observed [21,22]. When GAC or AIX was combined with nanofiltration, it proved to be the most beneficial in adsorbing PFAS as compared to individual GAC or AIX filters. The study mainly focused on the adsorption of long-chain PFAS compounds. Longer chains were adsorbed more efficiently due to their hydrophobic effects for both GAC as well as AIX [21]. A study showed that adsorption on AC accompanied by aeration, helped in adsorption and removal of PFAAs up to 80%. Thus, aeration was proven to be more effective in the removal of long carbon chain alkylated substances as compared to short-chain substances. This can be accounted as aeration improved the efficiency of AC during treatment in water [23].

A new method of adsorption was studied for PFOS using Red Mud Modified Sawdust (RMSDN600) and Unmodified Sawdust (SDN600). The adsorption capacity of PFOS was attributed to both hydrophobic as well as electrostatic interactions. Of the two types of sawdust used, red sawdust showed more efficiency in the adsorption of the fluorinated substances as it contained certain minerals like Fe, Al, Ti, Si, and Ca. These minerals are proved to be a good source of OH\(^{-}\) functional group which in turn are beneficial for the adsorption of PFOS. Red sawdust had a better efficiency in adsorption which was due to a large number of metal-based functional groups and highly ordered graphitic carbon framework. pH greatly influenced the process of adsorption and was found to be inversely proportional to adsorption. Thus, the pH of solution was maintained at 3.1. The adsorption was also studied using help of Langmuir and Freundlich isotherm model. One more factor contributed to adsorption was surface area of adsorbent, lesser the particle size of the adsorbent, more adsorption of PFOS was observed [24].

Novel adsorbents such as molecularly imprinted polymers are continuously being studied in laboratories. Some PFOS at pH 3 could be adsorbed by cross-linked chitosan beads due to their greater adsorption capacity. Over 99.4% protonation of the amino groups of the chitosan beads was observed, due to which the negatively charged PFOS were easily adsorbed, this occurred when the pH of the solution was maintained at 3 resulting in increased removal of PFOS. The final sorption capacity of optimized chitosan sorbent was studied and reported at up to 5.5 mmol/g for PFOS which was found to be higher than the conventional absorbents. A very important role was played by electrostatic attraction in removing the targeted compounds in the sorption process. After successful adsorption of the compounds, they can be incinerated at high temperatures. The temperature for incineration depends upon the carbon chain lengths of PFAS [25].

2. Sonochemical Degradation:
In the sonochemical method of degradation, a frequency greater than 20kHz is used to degrade the PFAS [26, 27]. Ultrasound wave generates in an aqueous solution, and two types of effects result: compression and rarefaction. A pressure is exerted on compression which exerts a positive pressure on the liquid by pushing the molecules together and the molecules are pulled apart by rarefaction. Microbubbles are formed in the rarefaction region due to the large negative pressure. Microbubbles continue to grow in successive cycles, after a stage, they reach an unstable diameter and collapse violently, producing shock waves. Such a process is known as cavitation. Cavitation leads to an intense collapse of the bubbles adiabatically and generates pressures in the order of several hundred atmospheres, vapor temperatures range between 4,000 and 10,000 K, and bubble interface temperatures lie in the range of 1,000–1,500 K. Thus, PFAS can be pyrolyzed using high pressure and temperature conditions [26-28].

In research to degrade PFAS through the sonochemical method, the effect of various power densities, ultrasonic frequencies, pH and the temperature was studied. Power densities such as 83, 167, 250, and 330 W L\(^{-1}\) were studied at frequencies, 202 kHz, 358 kHz, and 610 kHz were found to be most effective in the degradation of PFHxS, PFOA, and PFOS. Studies have proven that rate of degradation increased with an increase in power densities except for PFBA and PFBS. The exception was caused due to the low
surface activities. On the other hand, the ultrasonic frequency of 358 kHz was proven to be most effective. For the degradation of short chains, US frequency of 610 kHz was required. The highest decomposition and defluorination rates of PFOA were reported in the range of 25-40 °C. pH too plays an important role while carrying out sonochemical degradation. Acidic pH as found to be the most effective as it generated hydroxyl anions which aided in PFAS degradation while ultrasound frequencies were passed. The defluorination capacity was decreased due to decrease in the surface tension of PFOA when the temperature was increased [29,30].

In a study that was carried out, US frequencies were combined with PS for synergistic degradation of PFAS. Degradation of PFAS was carried out using dual frequency US/PS to get the best degradation result of 100 ± 1.2% as compared to using the high-frequency US or low-frequency US alone [31]. PS played a crucial role as it gives out sulphate and hydroxide radicals which aid in the degradation of PFAS. Of the two radicals, sulphate radicals are more dominant in carrying out the degradation. Ultrasound frequency alone at 550 W and 250kHz could degrade only up to 14.6% [31]. Whereas, degradation was enhanced by 33.7% in the presence of PS. Defluorination occurs well under low pH, between 3-6 [30]. Alleviated temperature conditions were used to activate PS. As compared to PFOA; PFOS degraded better and its removal efficiency was faster by this method.

Another approach was studied to degrade PFOA using various surfactants along with US. For this study, anionic, non-ionic and cationic surfactant were selected. SDS is a surfactant that is anionic in nature, showed inhibition properties in the decomposition and defluorination of PFOA [29, 32]. The inhibition was caused due to the competitive adsorption observed at the bubble-water interface. Octyl phenol ethoxylate (Triton X-100), is a non-ionic surfactant, was found to improve the degradation of PFOA along with US. But the most efficient was Hexadecyl trimethyl ammonium bromide, a cationic surfactant, which reported a decomposition efficiency of 79% [29, 32]. This was because of their easy adsorption at the air-bubble interface.

A new method was developed where sulphate and persulphate radical were found to have removed more than 99% of PFOA. The radicals had higher selectivity and efficiency in the removal of PFOA. When sulphate radicals were present during the decomposition of PFOA accompanied by Ultra-Sound radiation, over 99% of the PFOA were removed in 120 minutes of US radiation [29].

3. Photocatalysts:
A variety of adsorbing materials were used with photocatalysts for adsorption of the PFAS which were irradiated through ultraviolet radiation for their complete degradation.

When Titanium Dioxide (TiO₂) was combined along with reduced Graphene Oxide (rGO), it was used as photocatalyst which showed promising results. The use of this composite photocatalyst, TiO₂ with graphene materials was reported to increase the lifetime of electron-hole pairs. This was due to the reduction of charge recombination and excellent electron trapping and electrical conductivity properties of graphene. Graphene aids in the photo response capacity by extending the wavelength if compared to plain TiO₂. This enhanced the photocatalytic activity in the degradation process of PFAS – mainly PFOS. The degradation efficiency went up to 93 ± 7% after 12 h of UV–vis irradiation using a medium pressure mercury lamp. Direct photolysis degradation efficiency was 58 ± 9% [33]. These findings proved that the combination of TiO₂ and rGO gave the best results to carry out the degradation of fluorinated substances.

In another study, an adsorbive catalyst referred to as Fe/TNTs@AC was prepared from activated carbon and TiO₂. The adsorptive catalyst degraded more than 90% of PFOA in water by irradiating for 4 hrs. Even after using for a longer duration, no significant loss was found in the efficiency of the photocatalyst. Such efficient photocatalytic and adsorptive efficiency was seen due to the narrow size of the adsorbent. Various characteristics of the above catalyst led to such a high efficiency. Few of the many properties are discussed; the micro-carbon particles on TNTs with the size range of 5-10 nm enhanced its adsorbing capacity. The micro-carbon particles also helped in enhancing the photoactivity. The adsorption and degradation on PFAS can be covered over a long range of pH such as 4.0 – 11.0. However, alkaline pH was found to be less favourable while using the above photocatalyst. On repeated cycles of adsorption and irradiation on this catalyst, the efficiency of degradation of PFAS remained unchanged [34].

In another study, an enhanced photocatalytic degradation was brought about by using a carbon-modified bismuth phosphate composite as a photocatalyst. Since PFAS are recalcitrant towards wastewater treatments, a novel catalyst was synthesized where carbon sphere modified Bismuth Phosphate (BiOHPCS) was prepared. BiOHPCS removed more than 99% of PFOA in 2 h with dosage values 1.0 g/L, at a particular pH that was 7.0. It also subsequently, in situ, decomposed the adsorbed PFOA in 4 h of UV irradiation. This rate of PFOA degradation was approximately 18 times greater than that by neat BiOHPCS. This was due to the carbon modifications which not only enhanced the adsorption capacity of PFOA but also enhanced side on adsorption configuration of
PFOA. It is known from studies that carbonaceous materials, e.g., AC, carbon nanotubes, and carbon spheres (CS) hold some unique properties such as high specific surface area (SSA), hydrophobic surface, and abundant π electrons, and are proven to be effective in the adsorption of PFOS through anion-π interactions [35]. Thus, a composite catalyst was prepared.

In a new method was introduced in which a microwave-assisted ceramic membrane filter was used. The PFOA removal was enhanced due to the catalytic coating onto the membrane. But the degradation by this method did not went to completion and a significant amount of PFAS were detected in the water body. Under microwave irradiation, only 65.9% of the PFOA was degraded [36].

4. Bioremediation:
Another field of study that was explored to study the degradation of PFAS was bioremediation. In bioremediation, microorganisms were used in breaking down PFAS. Those microorganisms were studied which could utilize PFAS in their life cycles. These microorganisms were found to be grown in places where the pollutants were found. The microorganisms were studied because the organisms degraded the longer chains of PFAS to shorter chains such as PFCA and PFSA [37].

![Fig 2: Micro-organisms used for the purpose of bioremediation](image)

In research, a bacterial strain that was studied to check its potential to degrade PFAS was *Pseudomonas plecoglossicida* 2.4-D. The strain used was extracted from the soil where the pollutants were found. This strain actively degraded PFOS as a source of carbon and energy. The dimensions of the bacterium under study were 1.0 μm diameter and a length of 2.5-3.0 μm. The optimal pH under which the results were obtained where 6.8-7.2. When the strain was developed under a liquid medium, it completely utilized the substances within 6 days. The substance, PFHpA was degraded and free fluorine atoms were found in the medium. When the strain was grown in soil, the strain degraded the substance up to 75% [38].

A study showed that *Pseudomonas* with the strain D2 degraded PFAS under aerobic conditions. The strain partially degraded sulfonate with hydrogen such as H-PFOS and 2,2,2-trifluoroethane by defluorination. The six products that were yielded, each of them contained oxygen but no sulfur. *Pseudomonas butanova*, another kind of bacteria fully degraded 6,2 Fluorotelomer alcohols (6-2 FTOH) effectively. Biotic transformation is a field where more light needs to be thrown upon and more research is needed to be done [39].

Research was carried out by using *Acidimicrobium* sp. strain A6. This strain is an autotroph that oxidizes ammonium to nitrite by reducing ferric to ferrous ions. For each ammonium oxidized a single reduction of Fe (III) was observed. This pathway in the nitrogen cycle for the bacterium is indeed beneficial and quite new that goes by the name Feammox process. In this process the ammonium ions undergo oxidation to nitrite ions under conditions that reduce iron. Results showed removal of up to 60% of PFOA and PFOS during 100 days incubation, while total fluorine content (organic plus fluoride) remained constant throughout the incubations. The pH under which testing was carried out was maintained acidic throughout to obtain better conditions. Incubation was carried out over 100 days, where a 50% decrease of PFOA was found in A6 enriched culture. Whereas, a 33% decrease was found in pure A6 culture. Studies suggest that as long as the pH solution is acidic and soils are iron-rich, the Feammox process can be proven to be successful in the degradation of PFAS in contaminated sediments [40].
CONCLUSION

There are a variety of techniques that have emerged to degrade a few of the most hazardous PFAS. However, the most promising ones were discussed in the review. Various factors play a role in the degradation of PFAS depending on their structure, chain length, pH, functional groups.

Adsorption is a technique used on a large scale due to its great efficiency in adsorbing PFAS. In this technique of adsorption, the pores present on the adsorbing material played a very crucial role to bring about adsorption. Further studies are on their way to develop an ideal adsorbate which could adsorb PFAS efficiently.

The sonochemical degradation technique has been proven to be very advantageous, due to its ease of operation and causes no secondary pollution to the environment.

Photocatalysts are one of the newly emerging techniques and has proven to be promising. The technique works best when composite catalysts are used instead of a plain one. This can be taken as a very good example of a concentrate and destroy technique where the PFAS are adsorbed onto the adsorbing material and then irradiated to destroy it.

Bioremediation was an eco-friendly method that used micro-organisms in the breaking down of PFAS into shorter chains which are believed to be less toxic than the longer ones. However, the micro-organisms that were useful for the degradation of PFAS, whether are beneficial to the soil and water bodies are yet to be studied and determined.

In the review, the author has tried to discuss the best techniques and their efficiencies in the degradation of PFAS. Future research can be done on photocatalysts as they sound promising and more combination of photocatalysts can be tried and tested to obtain better results. Novel photocatalysts and their combinations can be searched upon which can be re-used several times with the same level of efficiency. Photocatalysts sound very promising and cause minimalistic harm to the environment with close to 100% efficiency.

Acknowledgement: The authors wish to thank Jai Hind College Autonomous for providing the necessary support in carrying out this review study.

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**Fig 3**: Techniques and Materials used for PFAS degradation

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<tr>
<th>Techniques</th>
<th>Material used</th>
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<tbody>
<tr>
<td>Adsorption</td>
<td>Adsorptive Catalysts, Granular Activated Carbon, GAC + AIX + NF, Sawdust, Chitosan Beads (Polymers)</td>
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<tr>
<td>Sonochemical</td>
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<td>Degradation</td>
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<tr>
<td>Photocatalysis</td>
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<tr>
<td>Bioremediation</td>
<td><em>Pseudomonas plecoglossicida</em>, <em>Pseudomonas butanova</em>, <em>Acidimicrobium sp Strain A6</em></td>
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*Corresponding Author: Sreela Dasgupta*
Fig 4: List of Abbreviations and their full-forms

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<thead>
<tr>
<th>Abbreviation</th>
<th>Full-form</th>
<th>Abbreviation</th>
<th>Full-form</th>
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<tbody>
<tr>
<td>PFAS</td>
<td>Per-Fluoro Alkylated Substance</td>
<td>GAC</td>
<td>Granular Activated Carbon</td>
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<tr>
<td>PFOA</td>
<td>Per-Fluoro Octanoic Acid</td>
<td>NF</td>
<td>Nano Filtration</td>
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<tr>
<td>PFOS</td>
<td>Per-Fluoro Octanoic Acid</td>
<td>AIX</td>
<td>Anion Exchange Resin</td>
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<td>Per-Fluoro Hexane Sulphonic Acid</td>
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<td>Per-Fluoro Butyric Acid</td>
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<td>Per-Fluoro Carboxylic Acid</td>
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REFERENCES


