Detection and treatment strategies of Per- and polyfluoroalkyl substances (PFAS): Fate of PFAS through DPSIR Framework analysis

Juliana John¹, Frederic Coulon², Padmanaban Velayudhaperumal Chellam³*

¹ - Department of Civil Engineering,
National Institute of Technology - Tiruchirappalli, Tamilnadu, India.

² - School of Water, Energy and Environment,
Cranfield University, Cranfield, MK43 0AL, United Kingdom.

³ - Department of Biotechnology,
National Institute of Technology – Andhra Pradesh, India.

* Corresponding author:
V.C.Padmanaban vcpadmanaban88@gmail.com
Abstract:

Per/ Poly Fluoro Alkyl Substances (PFAS), regarded as "forever chemicals," are a class of emerging contaminants occurring worldwide that pose many serious environmental issues to water quality and human health. The presence of strong carbon-fluorine bonds in their backbone and their physicochemical properties offer them resistance and restrict them from breaking down into simple compounds in the environment. There are many challenges to be addressed in the detection and removal from the environment. In this comprehensive review, a Driver-Pressure-State-Impact-Response (DPSIR) framework has been proposed to understand PFAS from the source of emission and their impacts on the environment. We reviewed the various detection methodologies for monitoring PFAS levels and analytical techniques for their quantification to know their environmental levels. The challenges and scope of various treatment technologies developed and implemented have also been critically discussed. The future perspectives of PFAS, including their source reduction and framing regulatory policies and the challenges faced when moving towards a sustainable future, are focused.

**Keywords:** PFAS; DPSIR Framework; Sensors; Optimization; Treatment technologies; Regulatory standards.
1 Introduction

Per/Poly Fluoro Alkyl Substances (PFAS) are a class of anthropogenic chemicals that are recently receiving increased research interest due to their difficulty in detection and adverse environmental effects [1]. This class of chemicals comprises more than 4000 fluorinated compounds having fluoroalkyl backbones and are produced majorly by sources like aqueous film-forming foams (AFFF), nonstick cookware products, stain-resistant fabrics, fast food wrappers, and other chemical manufacturing plants [2]. Due to high electronegativities and bond dissociation energies (544 KJ/mol) of the Carbon-Fluorine backbone present in the PFAS structure, they exhibit high strength bonds and persist as a recalcitrant in the environment. The fate and transport of PFAS compounds mainly depend on their chain length and the functional groups attached to them. Their classification based on their chain lengths is that Long-chain PFAS compounds include the PFCAs and PFOS, which contain 8 to 12 carbon atoms and Short-chain PFAS compounds include the PFCAs and PFBS that contain 4 to 7 carbon atoms in their chemical structures [3]. Substances like per-fluoro octane sulfonic acid (PFOS) and per-fluoro octanoic acid (PFOA) belong to the long-chain PFAS, whereas per-fluorobutyric acid (PFBA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS) belong to the short-chain groups. The physicochemical properties of some prevalent PFAS are discussed in Table 1. These PFAS class of chemicals exhibits dual lipophobic and hydrophobic characteristics, are chemically stable, remain persistent in the environment and contaminate soil, surface water, groundwater, etc. [4][5][6][7]. Their solubility ranges above 300mgL$^{-1}$ and low log $K_{OW}$ values indicate their high-water solubility capacities and hydrophilic nature in freshwater, whereas its low polarizabilities, higher electronegativities, etc., confers them its lipophobic characteristics. Due to their highly electronegative C-F bonds and dissociation capacities, many PFAS compounds have lower pK$_a$ values in aquatic ecosystems exhibiting a highly acidic nature [8]. They have half-lives of more than 92 years in water and about 1 to 3 years in agricultural soils [5][9]. Two important PFAS
chemicals widely used in industrial applications are PFOA and PFOS are their chemical structures are shown in Fig.1.

Table 1 Physicochemical properties of different compounds belonging to PFAS class [10]

<table>
<thead>
<tr>
<th>Property</th>
<th>PFDA</th>
<th>PFOS</th>
<th>PFOA</th>
<th>PFHxA</th>
<th>PFBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{10}HF_{19}O_2</td>
<td>C_{8}HF_{17}O_3S</td>
<td>C_{8}HF_{15}O_2</td>
<td>C_{6}HF_{11}O_2</td>
<td>C_{4}HF_{9}O_3S</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>514.09</td>
<td>500.13</td>
<td>414.07</td>
<td>314.05</td>
<td>300.1</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>218</td>
<td>249</td>
<td>188 - 192</td>
<td>157</td>
<td>211</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>77-88</td>
<td>54</td>
<td>40-50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solubility in water (mgL⁻¹)</td>
<td>-</td>
<td>680</td>
<td>3300</td>
<td>15700</td>
<td>344</td>
</tr>
<tr>
<td>at 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pKa</td>
<td>-0.17</td>
<td>-6 to -2.6</td>
<td>-0.16 to 3.8</td>
<td>-0.16</td>
<td>-3.31</td>
</tr>
<tr>
<td>Log Kow</td>
<td>-</td>
<td>4.49</td>
<td>4.81</td>
<td>3.48</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Fig.1 The Chemical structure of two important compounds of PFAS class that are PFOA and PFOS, showing their strong Carbon-Fluorine backbone
Many countries have recently detected the occurrence of PFAS in environmental samples due to the development in detection technologies. Due to their adverse effects, countries have started refining their testing protocols and exploring their PFAS pollution sources to develop proper regulation policies. Higher levels of hazardous short-chain PFAS were found in tap water samples in India [11]. Most of the Bangkok region's rivers and tap water sources were found contaminated with PFOS based PFAS chemicals with concentrations ranging above 6 ng/L [12]. Under rainy conditions, these PFAS can penetrate through the soil and subsoil surface and get introduced into groundwater or dissolve with run-offs and reach water bodies, creating severe aquatic and marine life issues. Analysis of concentrations of PFAS substances in agricultural soils applied with sludges generated from wastewater treatment plants (WWTPs) of Alabama for over a decade showed that higher concentrations of PFAS substances were found in the range of ≤ 990ng/g of PFDA, ≤530ng/g of PFDoA, ≤ 410ng/g of PFOS and ≤ 320ng/g of PFOA [9]. Due to their hydrophilic nature, they are quickly taken up by the roots of plants and remain accumulated within them. When such contaminated plants are consumed for food, they lead to toxic effects in higher-level organisms. The detection of PFAS and its residues in many terrestrial organisms, including pigs, horses, cattle, etc., in the Middle East and Asian countries, confirms their bio accumulative potential even within the food web [13]. Measuring the concentration of PFAS in pigs inhabiting in an open dumpsite in South India and studying their toxicokinetic effects revealed that PFAS concentrations were higher (71 ± 70 ng/g wet weight liver) in female pigs found in the dumping sites than male pigs (9.0 ± 1.9 ng/g wet weight liver) when compared with the reference sites [14]. Analysis of the fecal excretion of pets for PFAS in the United States also showed that 13 different PFAS at a mean average concentration of 85.4 ± 94.5 ng/g of dry weight was found in the dog feces [15]. Many water streams in Vietnam had contaminations with high concentrations of PFAS, and the seafood obtained from such water sources is highly contaminated [16]. Analyzing the samples of Indian breast milk to monitor their bioaccumulation levels unveiled that the highest
PFOA contaminations were 16 times higher than drinking water limits [11]. These PFAS chemicals remain in the blood for a half-life of about 4.8 years, and their level of clearance of PFAS from the human body is generally low, leading to increased levels of accumulation. This can also cause severe health impacts like developmental abnormalities and cancer and reduce the effectiveness of vaccines in the human body [17]. As PFAS accumulation is observed in living beings in almost all parts of the world, it is necessary to analyze their toxicity on different levels so that their adverse health impacts in the future can be reduced.

A proper understanding of these PFAS compounds would be helpful to develop or opt for the best treatment technologies. Such understanding can be obtained by forming an easy framework through which all sorts of interactions of PFAS with the environment can be known. The Driver-Pressure-State-Impact-Response (DPSIR) framework is one of the popular frameworks used for Integrated Environmental Assessment and assessing water-related issues [18]. In this review, a DPSIR model has been used to discuss the fate of PFAS and its association with the environment. This review also provides a complete discussion on various detection methods of two important PFAS, PFOA and PFOS, and different treatment technologies that can be used to remove them from the environment.

2 DPSIR framework for PFAS (Drivers-Pressures-State-Impacts-Response Assessment)

DPSIR framework is a conceptual model used to describe, analyze, and understand environmental problems. This framework has been used to address problems faced by marine and coastal ecosystems and water quality issues that are caused due to natural or anthropogenic activities [18]. It is a widely opted framework because it helps to understand a problem simplified from its source to its impacts, and know-how regulation policies should be framed to mitigate their future impacts. They act as an important risk assessment tool for analyzing the critical sources or risks posed to the environment and exploring the interlinks between various components that benefit managers
and policymakers [19]. Any environmental problem can be formulated in a structured way from their detection to treatment using the DPSIR method. A DPSIR model has been developed for PFAS and shown in Fig.2.

![DPSIR Framework](image)

**Fig.2** Representation of a DPSIR (Drivers, Pressures, State, Impact, and Response) Framework showing the fate of PFAS from their source of production till its future impacts and a highlight on their regulatory policies.

### 2.1 Drivers – From the view of needs

The main "drivers" are the sources that directly or indirectly introduce increased concentrations of PFAS into the environment. Some of the point sources by which PFAS are released into the environment are using the aqueous film-forming foam (AFFF), wastewaters of industrial processes that produce PFAS based consumer products (water-resistant clothing, food wrappers, cleaning products), and landfills. The main application of AFFFs is to extinguish class B fires in
fire-fighting operations, and they majorly consist of a mixture of hydrocarbons and fluorinated PFAS containing surfactants. The firefighters are constantly being exposed to this mixture, and their risks are not known yet. The fate of PFAS compounds produced from AFFFs testing laboratory was investigated in a wastewater treatment plant receiving large quantities of contaminated inputs by Burgher et al. (2018) [20]. It was found that 15 classes of PFAS compounds were present in the effluent. The trickling filter system present in the treatment operation led to a 1.7% conversion of total PFAS compounds resulting in a higher yield of short-chain compounds. Other non-point sources are run-offs or infiltrations during heavy rains that may contribute as important drivers that introduce PFAS into the environment [21]. Two potential sources by which humans are directly exposed to this chemical daily are greaseproof coatings in food wrappers and nonstick cook wares [22]. People in developing countries are now shifting towards home-cooked foods to maintain a healthy lifestyle, so there is a massive demand for nonstick cookware products [23]. A graph showing their increased global value in the market has been shown in Fig.3. Although they are easy to handle, prolonged usage of these utensils may release large amounts of PFAS compounds into the environment and lead to adverse health effects. However, many companies claim that their products are Teflon free or PFAS free. Possibly, they may use other toxic polymeric coatings to provide a nonstick surface, which may be toxic to health. Other materials like carpets, stain-resistant fabrics, hydraulic fluids used in aviation indirectly contribute to the introduction of PFAS and their associated precursors into the environment. [24][2]. As sorption is one of the major techniques for removing PFAS from water, the remediation of spent adsorbents should also be taken care of, as these spent adsorbents act as a secondary source for reintroducing PFAS into the environment [25].
Fig.3 The forecast of Global Non-stick Cookware Market (2017 - 2025) by Maximize Research Private Ltd representing the global increase in usage of non-stick cookware and their values in a million US dollars [26]

2.2 Pressures – From the view of point source or non – point source

Environmental "pressures" are generally the stress applied to the drivers that induce them to release PFAS into the environment [27]. Considering point sources such as industrial and municipal wastewater treatment effluents, due to the hydrophobic partitioning of long-chain PFAS onto solid matrix in treatment plants and by degradation of precursor compounds, high concentrations of untreated short-chain PFAS remains in the effluents, and when discharged into water bodies or applied as biosolids on agricultural land, they readily contaminate them [28]. Disposing PFAS containing consumer products onto landfills or incinerating them is another form of threat caused due to human-induced emissions leading to pollution as their leachate can penetrate deep and contaminate groundwater and their toxic byproducts contaminate air [29]. As humans continuously use nonstick cookware, overheating them to a high temperature above 660°C can release PFAS into the air faster [30]. Cookware with damaged surfaces or scratches can release PFAS faster than usual, so proper replacement should be done once in five years. Using
high smoke point oils may also provoke PFAS emissions as they reach high temperatures very quickly.

2.3 State – From the view of quality assessment

"State" generally refers to the environment's condition after getting affected by different environmental pressures.

Soil quality: The functional groups present in these compounds decide the ionic state (anionic, cationic, zwitterionic, non-ionic) of the PFAS compound and govern their fate and transport in the environment. Two main mechanisms which govern their transport through the soil are sorption and infiltration [31]. Across the globe, soil acts as an important reservoir for PFAS in the environment. Their retention is found higher in the vadose zone, after which they leach through and reach the zone of saturation [7]. During their retention in the vadose zone, they remain an important contamination source and affect the quality of groundwater, surface water, and biota inhabiting them. The release, transport, and retention of PFOS in the vadose zone of a fire training site were mathematically modeled by Guo et al., and the study found that air-water interfacial adsorption had a significant impact on the sorption of PFOA onto soil and aided in low retardation factors before it reached ground water [32]. PFAS maintains its high sorption capacities with soil organic matter (SOM) through hydrophobic and electrostatic interactions and remains within the soil longer. Comparing the chain length of PFAS with their depth distribution in soil, long-chain PFAS predominate in shorter depths and short-chain PFAS in deeper depths. Under high saline conditions, their sorption onto clay particles was found to increase, indicating that organisms in benthic zones are more prone to potential risks caused by them [33]. Immobilizing the soil by sorbent amendment technique using different sorbents or performing Stabilization / Solidification are a few valuable methods to contain contaminated soil sites and reduce their mobility [34][35].
**Water quality:** Due to their widespread contamination, PFAS are detected in different concentrations worldwide in aquatic environments. As these PFAS compounds are highly soluble in water, they get easily transported by ground and surface water bodies to longer distances from where they are released. Their surfactant properties play a significant role in aqueous film-forming foams (AFFF) used in firefighting operations and produce large PFAS contaminated waters. The release of PFAS containing run-offs or industrial waters that have not undergone pre-treatment also affects the surface water quality as they remain in aquatic systems longer. When persisting in aqueous waters due to their chemical properties, these PFAS increase the toxicity levels and make it unfit for inhabitation and domestic and commercial purposes. The presence of strong C-F bonds in their chemical structure makes them difficult to remove using simpler technologies. Therefore, they require a complex or sequential treatment system to remove them from water [36].

**Air quality:** As incineration is one of the disposal methods opted during waste management, incomplete combustion of PFAS containing products may release fluorinated greenhouse gases and ozone-depleting substances into the air and affect the air quality. When PFAS containing consumer products are landfilled or dumped, their leachates contain PFAS compounds, and volatile ones may enter the air. Application of biosolids obtained from water treatment plants containing PFAS compounds onto agricultural lands may also lead to the release of volatile substances into the air [29]. Overheating of nonstick cookware, leakages from AFFF are also other ways by which air quality is getting affected. Julia et al. (2020) studied the release of PFAS substances from AFFFs into the air, and when analyzed, 16 different PFAS were detected in the headspace, and the predominant ones among them were PFOA at concentrations of about 13670 µg/m$^3$ in air [37]. Wind dispersion is one of the critical means by which PFAS gets easily transported to a greater distance. So, opting for proper disposal methods for PFAS containing wastes can reduce their persistence and cyclical problems in nature.
2.4 Impacts – From the view of toxicological consequences

"Impacts" are mainly the effects observed when the environment's original state gets disturbed due to various drivers and pressures. As the environment is getting contaminated by these PFAS, they pose many severe impacts on human health and other living beings that thrive in that area [38]. Humans get exposed to PFAS through different ways such as diet, drinking water, air, dust, etc., and they get absorbed through the skin and leading to bioaccumulation. Many immunological, reproductive, endocrine, and cardiovascular effects are observed in humans due to high PFAS accumulations in the body [39]. They show varied toxicokinetic and toxicodynamic profiles in different organisms and have a greater affinity towards proteins in the human body. Their precursors do not get metabolized within the human body and disturb the levels of various hormones and intermediates formed during metabolic pathways. Animal exposure to PFAS for a more extended period caused many neurobehavioral effects, hematological effects, and developmental effects [40]. Evaluating toxicity by exposing zebrafish to PFAS compounds for 5 days post fertilization showed that their exposure led to hyperactivity and defects in their swim bladder and unique toxicological effects that varied with their chemical structures [41]. Studying their level of toxicity and health effects using sentinel and non-traditional laboratory models also showed that PFAS disturbed the level of neurotransmitters and their metabolism in all levels of model organisms [42]. Northern leopard frogs exposed to higher PFAS concentrations of more than 100ppb showed accumulation in their brain with changes in levels of neurotransmitters such as acetylcholine [43]. PFAS are found to be associated with natural menopause in women, and higher PFAS concentrations lead to earlier natural menopause and act as a risk factor to women’s lives [44].

2.5 Response – From the view of framing regulation

As PFOS and PFOA contamination has increased to a greater extent, regulations are available only for a few or small groups of PFAS classes, and more stringent regulatory frameworks are
needed to control their environmental levels. In 2009, an international treaty of Stockholm Convention for PFAS was initiated. PFOS and their salts were added to the Persistent Organic Pollutants list to protect humans and the environment from these chemicals. Till 2018, strict regulations were not followed or mandated by industries of many companies. Since then, due to the emerging research in this field, many US companies that acted as the greatest commercial producers of PFAS have started their voluntary phaseout from PFAS production and started adopting modified PFAS substances having similar chemical properties. But these chemically modified PFAS were also toxic as PFOA and PFOA to the environment [45]. From 2019, the United States Environmental Protection Agency has framed and set the standards on the advisory levels for PFOA and PFOS in the drinking water supplies as 70 ng/L [46]. These compounds have also been added to the Contaminant Candidate List (CCL) 4 that US EPA has announced. As this standard limits covered only the regulation of two compounds, PFOA and PFOS, many other organizations such as the Michigan Department of Environmental Quality, American Water Works Association, and other few environmental and health organizations are also focusing more on the need and implementation of specific rules for PFAS compounds in the environment [17]. The list of various standards opted by various agencies has been shown in Table 2. Still, there is a lack of regulation on toxicity standards for the discharge of PFAS into the environment that could lead to environmental health risks. Monitoring PFAS using the “cradle to grave” approach can act as a risk assessment tool to understand their toxicity levels from production till their disposal and provide a stringent monitoring assessment. Nowadays, before setting up strict regulations for the existing PFAS compounds, many new PFAS compounds are being introduced into use day by day without proper or little regulatory policies, and more focus is needed in this regulatory area [45].
Table 2 The regulatory standards for PFAS compounds in soil and water set by different organizations of various countries all over the world [47] [48][46]

<table>
<thead>
<tr>
<th>Country</th>
<th>Compound</th>
<th>Regulatory standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alaska</td>
<td>PFOA</td>
<td>400 ng/L in groundwaters</td>
</tr>
<tr>
<td>Alaska</td>
<td>PFOS</td>
<td>400 ng/L in groundwaters</td>
</tr>
<tr>
<td>Maine</td>
<td>PFOA</td>
<td>130 ng/L in drinking waters as Noncancer health-based level</td>
</tr>
<tr>
<td>Maine</td>
<td>PFOS</td>
<td>560 ng/L in drinking waters as a Noncancer health-based level</td>
</tr>
<tr>
<td>Minnesota</td>
<td>PFOA</td>
<td>35 ng/L in drinking waters as Maximum Contaminant Level</td>
</tr>
<tr>
<td>Minnesota</td>
<td>PFOS</td>
<td>15 ng/L in drinking waters as Maximum Contaminant Level</td>
</tr>
<tr>
<td>New Jersey</td>
<td>PFOA</td>
<td>14 ng/L in drinking waters</td>
</tr>
<tr>
<td>New Jersey</td>
<td>PFOS</td>
<td>13 ng/L in drinking waters</td>
</tr>
<tr>
<td>North Carolina</td>
<td>PFOA</td>
<td>1000 ng/L in drinking waters as protective concentration levels</td>
</tr>
<tr>
<td>North Carolina</td>
<td>PFOS</td>
<td>560 ng/L in drinking waters as protective concentration levels</td>
</tr>
<tr>
<td>Texas</td>
<td>PFOA</td>
<td>290 ng/L of PFOA in drinking waters as maximum allowable concentrations</td>
</tr>
<tr>
<td>Texas</td>
<td>PFOS</td>
<td>560 ng/L of PFOA in drinking waters as maximum allowable concentrations</td>
</tr>
<tr>
<td>Vermont</td>
<td>PFOA</td>
<td>20 ng/L in groundwater</td>
</tr>
<tr>
<td>Vermont</td>
<td>PFOS</td>
<td>20 ng/L in groundwater</td>
</tr>
<tr>
<td>Sweden</td>
<td>PFAS</td>
<td>90 g/L of PFAS in drinking waters</td>
</tr>
<tr>
<td>Sweden</td>
<td>PFOS</td>
<td>0.003 mgkg⁻¹ dry weight in sensitive soils</td>
</tr>
<tr>
<td>Sweden</td>
<td>PFOS</td>
<td>0.020 mgkg⁻¹ dry weight in non-sensitive soils</td>
</tr>
</tbody>
</table>
## Detection of PFAS in environmental samples

### 3.1 Sensors based detection

Though conventional detection technologies using analytical instruments like Liquid Chromatography-Mass Spectrometry (LC-MS), Gas Chromatography-Mass Spectrometry (GC-MS) detect ionic, volatile, and semi-volatile PFAS compounds, they are expensive, time-consuming, and cannot be performed in situ. In such cases, sensor-based detection of PFAS may provide easy monitoring and accurate detection [49]. While developing a sensor, a few important challenges such as higher sensitivity, selectivity, easy portability, and instant results should be focused on to achieve a more accessible application. Considering the molecular characteristics of different PFAS compounds, the type of environmental sample in which they occur, and the interferences present with them in the complex matrix, appropriate sensors are being developed using advanced technologies. A comprehensive review of different types of sensors that have been developed until now for PFAS detection has been discussed here.
3.1.1. Nanoparticle-based sensors:

Due to high accuracy and sensitivity characteristics at nanoscale levels, nanoparticle-based sensors are one of the most widely preferred types of sensors. Because of their selective nature, these sensors can be applied successfully to detect PFAS and PFOS despite their anionic natures. One crucial nanoparticle sensor is the gold nanoparticle sensor, as they have many exciting properties like large surface area, stability, selectivity, adsorption capacities, recognition, and limit of detection of about 2.5ng / L. They are one of the most preferred materials for developing sensors. Modifying nanoparticles using chemical modifications or Quantum dots of good optical properties can enhance the properties of nanoparticles [50]. Ruth et al., had reported that quantum dots made of carbon quenched using berberine chloride hydrate (BH) were applied for sensing PFOS in water. The electrostatic interaction between PFOS and BH restored the fluorescence property during the application, and the change in fluorescence to PFOS concentration was quantified [51]. Nanoparticle-based sensors can be surface functionalized or tuned using other chemicals and confer a very accurate detection range [52]. The fluorescence and optical properties of nanoparticle-based sensors make them easily detected by different analytical types of equipment.

3.1.2. Electrochemical sensors:

Using electrochemical sensors of high sensitivity and lower detection times is preferred for PFAS detection. Different electrochemical sensors with varied detection methods such as potentiometric, voltammetric, impedimetric, and conductimetric types are usually suggested for the easy detection and sensing of PFAS in the environment [49]. As electrodes are an important part of these sensors, micromachining their surfaces using molecularly imprinted polymers or miniaturizing them in the form of screen-printed electrodes can provide good detections. The bubble nucleation-based method of the electrochemical sensor monitored the change in electrochemical signal during quantification of PFAS and had a Limit of Detection of about 30µg/L [53]. Another novel photoelectrochemical sensor fabricated by modifying TiO$_2$ nanotube arrays using molecularly
imprinted polymer was highly selective towards PFOS and had a LOD of about 86 ngmL\(^{-1}\) [54]. These sensors generally have higher selectivity and reusability characteristics and work stably at different environmental conditions. Interference due to small molecules other than analyte in water samples may be a problem during detection, affecting their level of sensitivity and detection times.

3.1.3. **Fluorescence sensors:**

Fluorescence-based sensors are another critical type of sensor which are being applied nowadays. Tagging fluorescent dyes as a recognition element for sensing PFAS in these sensors emits fluorescence in response to the quenching. The emitted light is related to the amount of PFAS present in the sample and is quantified using a fluorescence spectrophotometer. A rapidly detecting fluorescence sensor developed using Cadmium Sulfide quantum dots emitted strong fluorescence once they were quenched by PFOA and had a detection limit up to 0.3 \(\mu\)mol L\(^{-1}\) [55]. The selection of appropriate complexation molecules for detecting analytes can help develop sensors with high sensitivity and specificity [51]. Many optical sensors are also being opted for easy detection in which colorimetric reactions occur when ionic reactions occur between the target molecule and the recognition element, and their detection can be viewed with naked eyes. An optical sensor made using polystyrene modified nanoparticles for detecting PFOA quantified the color change from red to blue when PFOA addition took place [56]. These sensors are not cost-effective, and their selectivity may be affected by parameters such as pH.

3.1.4. **Smartphone-based sensors:**

Smartphone-based sensors are handy and easy to use, even by non-professionals in water research, and can provide more accurate results than many other detection sensors. In this sensor, reactions between PFAS and the recognition elements are read and captured through high-resolution cameras in smartphones and are analyzed using built-in systems. The intensity of the color observed is usually correlated and compared to quantify the amount of PFOA present in the
sample using software programs [50]. By linking such innovative technology sensors to other extensive databases such as the Internet of Things (IOTs), analysis and detection of a wide range of PFAS compounds can be carried out within a short time in the future [57].

3.2 Analytical methods

After detecting these PFAS using different methods, the critical part is the quantification using analytical instruments. As PFAS compounds do not have any chromophore groups and are non-volatile, their detection is difficult compared to other organic compounds [49]. During analysis, any background contamination caused by polymeric substances present in sample materials and sampling equipment should be avoided by proper rinsing and avoiding fluoropolymers. Some analytical methods by which PFAS can be quantified are:

3.2.1. Total oxidizable precursor assay (TOP Assay):

Some important precursor compounds of PFAS are perfluoroalkyl acids (PFAAs), fluorotelomer alcohols (FTOHs), fluoro octane sulfonamides (FOSAs), and fluoro octane sulfoethanols (FOSEs), and their indirect quantification in water or soil samples can be determined using this method. Due to their stable nature, these precursors can travel longer distances in the atmosphere by attaching to environmental particles [58]. The baseline PFAA levels in the sample should be noted before starting the assay so that the increased concentrations can be compared and measured after the assay [59]. In this assay, the precursor molecules undergo oxidative digestion to perfluoroalkyl acids (PFAA) end products under high temperatures and alkaline conditions. The increase in PFAAs concentration after the assay is quantified using analytical instruments such as LC-MS/MS. The sample aliquots are first exposed to a persulfate solution and maintained at elevated temperatures and in basic conditions. At these conditions, the thermolysis reactions promote the conversion of persulfate ($S_{2}O_{8}^{2-}$) to sulfate radicals ($SO_{4}^{2-}$). And as the basic conditions prevail, the hydroxide ions scavenge these sulfate radicals and result in hydroxyl radicals. The so formed hydroxyl radicals then oxidize these precursor compounds and produce
increased PFAAs concentrations, which are then analyzed [60] [61]. The chemical reactions are
given below in equations 1 and 2:

$$\text{SO}_4^{2-} \rightarrow \text{SO}_4^-$$ (At elevated temperatures)  \hspace{1cm} (1)

$$\text{SO}_4^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \cdot \text{OH}$$ (At basic pH conditions) \hspace{1cm} (2)

3.2.2. Total fluorine content determination (TF):

The total fluorine content could be studied based on total organofluorine and inorganic fluorine
content. The total organofluorine assay is an important method for PFAS analysis in which the
amount of organofluorine is quantified and compared to find the amount of PFAS in the sample.
This can be performed using combustion ion chromatography (CIC). The sample to be analyzed in
CIC is placed in ceramic boats and combusted in an oxygen-rich environment at high temperatures
of about 900 to 1000°C. During this combustion, the C-F bonds of organic fluorine break down,
and the hydrogen fluorides released dissociate into $H^+$ and $F^-$ ions in the absorbing solution of
sodium hydroxide. These absorbed solutions are then analyzed by ion chromatography, and the
fluoride contents are measured [62]. In extractable organofluorine (EOF) detection, sample
extracts obtained using different extraction methods such as solid-phase extraction, liquid-liquid
extraction, etc., are placed in ceramic boats. After the combustion process, they would be analyzed
to measure the amount of EOF. The adsorbable organofluorine (AOF) present in water samples
can also be separately determined by following a similar method. The water samples are eluted
through solid-phase extraction cartridges or activated carbon columns. The extract obtained after
eluting these columns with methanol should be analyzed using Combustion ion chromatography
[63]. The experimental procedures of these methods have been explained diagrammatically in
Fig.4. By analyzing the residues of EOF and AOF, the amount of non-extractable and the
inorganic fluorine content of the sample can be found. All unknown precursors present in the
sample cannot be found using these methods but analyzing different fluorine forms may help
understand the fate and transport of PFAS in the environment.
3.2.3. Fluorine Analysis by HPLC and GC:

Previously, fluorinated compounds were analyzed by quantifying their elemental fluorine or by Fluorine 19-Nuclear Magnetic Resonance spectroscopy. Due to the advances in the instrumentation field, Liquid or gas chromatography coupled with mass spectrometry is one of the predominant methods used for quantitative PFAS analysis. These methods perform the separation of compounds based on their boiling points as well as mobilities. Proper analyte derivatization and extraction are very important when analysing using such high-end chromatographic methods. Coupling these chromatography techniques with other selective separation methods may separate them with high selectivity and speed within limited detention times. Limit of detection (LOD) is an important parameter as it represents the lowest concentration of PFAS that can be detected using analytical equipment. The application of different chromatographic systems such as HPLC,
UHPLC, CLC to MS was compared. It was found that the UHPLC system had the best LOD for many analytes and performed analysis within a short time [64]. Mass analyzers such as Time Of Flight (TOF), Ion trap, Quadrapol alone, or combination are generally adopted in other literature to achieve higher resolution and sensitivity. An efficient quantification and identification of the target analytes of PFAS in the samples were observed when liquid chromatography was coupled with tandem mass spectrometry (LC-ESI-MS-MS) [65]. Coupling Ion Mass Spectrometry (IMS) to LC-MS for an adequate molecular description of PFAS from water samples showed trendlines obtained from the Mass-to-charge ratio and the Collision Cross Section relationship and led to a precise analysis of various subgroups of PFAS compounds based on their structural characteristics [66]. HPLC system coupled with electrospray triple-quadrupole mass spectrometer showed detection of around 10 PFAS compounds and 20 pharmaceuticals out of 14 PFAS compounds and 46 pharmaceuticals in raw and treated samples and helped in studying efficiencies of treatment plants [67]. During the air sample analysis in Northern Europe, Gas Chromatography-Positive Chemical Ionization-Mass Spectrometry(GC-PCI-MS) was useful for analysing volatile PFAS, whereas Liquid Chromatography-Time Of Flight-Mass Spectrometry (LC-TOF-MS) was useful for analysing Ionic PFAS [58].

4 Treatment strategies – Aquatic Systems:

It can be found that PFAS is leading to widespread pollution, and there is a need for proper treatment technologies so that their concentrations in the environment can be reduced. Different countries are developing novel technologies that could control their PFAS levels within standards based on their observed contamination levels. As the usage of PFAS based surfactants, non-sticking cookware, and water-resistant consumer products are increasing day by day, there is a need to control PFAS contamination in groundwater, surface water, wastewater, leachate, etc. Due to their stable nature and unique properties, only novel treatments can help complete removal or destruction. The treatment technologies should consider a wide range of factors such as the target
properties, the effect of other co-contaminants on the treatment process, cost of set up, operation, level of removal efficiency, residual contamination, etc. Many passive and active treatment methods that can be applied in situ or ex-situ are being adopted worldwide to control their levels. Some of the passive and active treatment methods are discussed below. The passive removal method is only a phase transfer of PFAS and is performed by non-destructive technologies. These treatment methods are usually combined and performed with other methods for effective removal. Proper disposal strategies should be adopted to avoid cross-contamination or the return of PFAS back into the environment.

4.1 Adsorption – Passive removal:

Removal of PFAS from waters by sorption is one of the most conventional treatment methods. To date, this kind of treatment is being performed as a "pump and treat system,"- which is in an ex-situ manner wherein the contaminated waters are passed through various sorbents to ensure their removal. During sorption processes, many factors such as pH, the concentration of contaminants, ionic strength, organic and inorganic competitive species present in PFAS contaminated waters may affect the efficiency or performance of the media used to perform sorption. Hence, considering these factors is also essential when opting for sorption. Different kinds of sorbents such as granular activated carbon (GAC), ion exchange resins (IEX), mineral clays, polymeric materials, carbon nanotubes, biopolymers, etc., are being preferred for their high surface areas and cost-effectiveness [68]. Sorbents such as GAC and IEX resins show greater sorption towards long-chain PFAS compounds due to their micellar and aggregate formation, whereas short-chain PFAS gets desorbed faster [69]. In a study conducted by Zaggia et al, PFAS contaminated waters were passed through resins of different hydrophobic properties during which ionic interactions and aggregate formation were dominant mechanisms for their removal [70]. The resin had functional groups of higher hydrophobicity showed higher sorption of PFAS compounds. By arranging more than one media or ion exchange resins in a series, continuous treatment can also increase removal
efficiencies. After their removal by appropriate media, managing the proper disposal of PFAS containing media is also essential as they could again cyclically contaminate the environment. [71] Wu et al., compared the performance of activated carbon and cyclodextrin polymer adsorbents for PFAS removal and found that in real water matrices, cyclodextrin polymers outperformed ACs, and two main parameters that affected their performance are pH and inorganic ions. Using Granular activated carbon for PFAS removal was found effective in selective removal of linear structured PFAS from the waters. Focusing more on operating conditions can avoid unwanted desorption of short-chain PFAS from GACs [69]. Therefore, the operational considerations and mechanisms should be well understood to increase the removal efficiencies. Regenerating or reactivating the media using chemicals could be a solution to manage them properly.

4.2. Membrane Filtration – Passive removal:

Membrane filtration is an important treatment technique for removing PFAS in massive scale levels. Modified filtration membranes by chemical techniques or new polymer chemistries would be more beneficial as they can produce membranes of a low-pressure drop, low cost, and high removal efficiencies [72]. Combining the filtration process with other treatment systems such as adsorption for PFAS removal is more efficient than performing filtration alone. Performing a combined treatment method of super fine powder of activated carbon (SPAC) and ceramic membrane filtration for PFAS removal showed minimum fouling and greater adsorption efficiencies(2990 µg/g), proving that such combined systems had adsorption capacities that were 480 times effective than GAC systems [73]. Using high-pressure membranes such as Reverse osmosis (RO) and Nanofiltration (NF) may help remove short-chain PFAS compounds. The most used systems are spiral wound and hollow fiber membrane configuration. Guo et al. (2017) opted for a nano porous filtration membrane operated by a gravity-driven filtration system to remove PFOS from water and found that low pH and high ionic strength increased their removal efficiencies and were reusable for over 20 regeneration cycles [74]. These pressure-driven systems
can even remove unidentified contaminants of the PFAS family and comparatively be cost-effective for implementation. When influent waters are passed through RO membranes, PFAS compounds are retained as concentrates within the filter media, whereas other compounds present in treated waters pass through as permeate across the media. As membrane flux is affected by fouling and temperature conditions, opting for proper pre-treatment methods can prevent the extent of fouling in membranes [75]. After PFAS removal by RO process, as the effluents obtained have lower alkalinity levels and corrosion inhibitors, discharge of these effluents into water bodies may not affect their quality. Proper disposal of these RO membranes and the contaminated concentrates should be regulated appropriately and disposed of according to the state or country standards.

4.3 Foam fractionation – Passive removal:
Foam fractionation is one of the effective technologies applied to remove contaminants of bio or chemical surfactant nature. As PFAS compounds are of this nature, purging high-pressure air into the contaminated waters may help separate them at the surface interface and aid in removal by stripping them out from the waters. A water treatment plant at the former fire station of Army Aviation Centre Oakey, Queensland, had employed foam fractionation technology to treat their PFAS contaminated groundwaters. More than 66000 gpd is being treated using this technology. More advances and developments in this technology by operating them as series and parallel columns may improve their future efficiencies.

4.4 Advanced oxidation process - Active destruction:
As conventional technologies require the regeneration of resins or adsorbents and have very short breakthrough times, opting AOPs can be a promising way to treat contaminated waters. AOPs are beneficial treatment technologies in which the reactive species formed by oxidizing agents readily destroy the contaminants' molecular structure. The carboxyl and sulfonyl groups in the PFAS compounds are more prone to redox reactions, whereas fluorine atoms are more resistant to
oxidation reactions due to their electronegativity characteristics and thermodynamically unfavourable reactions. To overcome this, combining two or three different methods of oxidation processes may help in the complete mineralization of PFAS and their precursor compounds, such as PFAAs and PFCAs. Some AOP processes which are being applied for PFAS removal are as follows:

**4.4.1 Electrochemical oxidation:**

In the past few decades, electrochemical oxidation has been a successful treatment technology for removing a wide range of micropollutants from waters and is now being tried for PFAS removal. As anodic oxidation is the primary mechanism in this process, employing different anode materials during oxidation and optimizing the critical process parameters may improve the destruction of PFAS to a greater extent. Considering these aspects, many bench-scale and pilot-scale studies are being carried out nowadays. During this process, the formation of many other per fluorinated compounds and their precursors are also observed because of the resistant nature of fluorine atoms, so adopting proper methods can help achieve complete mineralization. Due to the unique properties of Boron Doped Diamond (BDD) electrodes, using these electrodes for electrochemical oxidation of PFAS compounds in landfill leachates removed them at higher efficiencies of 80% and 78% for PFOA and PFOS at high current densities (75 mA/cm$^2$). The removal efficiencies were halved when low current densities (25 mA/cm$^2$) were maintained, concluding that current density is an important factor in degradation [76]. Using an anode of Ti$_4$O$_7$ reactive electrochemical membrane for electrochemical oxidation, found that at a residence time of 3.8s and a flux of 720 L m$^{-2}$ h$^{-1}$, maximum removal of 3415±203 µmol m$^{-2}$ h$^{-1}$ of PFOA and 2436±106 µmol m$^{-2}$ h$^{-1}$ of PFOS was achieved [77]. An economic anode material of PbO$_2$ panels from industrial lead-acid batteries was used for electrochemical oxidation, and after doping the electrodes and optimizing the process parameters, >99% of PFOA removal was observed during the reaction with the release of a few secondary contaminants [78]. PFOA and PFOS
sequentially undergo degradation during these oxidation reactions, and the equations of PFOA
degradation are given below [77]. This method is considered advantageous because it is energy
efficient, can be easily scaled up, and discontinuous operation under optimized conditions can be
carried out while performing this method.

\[
C_{7}F_{15}COO^{-} \rightarrow C_{7}F_{15}COO^{-} + e^{-} \tag{3}
\]

\[
C_{7}F_{15}COO^{-} \rightarrow C_{7}F_{15}^{\cdot} + CO_{2} \tag{4}
\]

\[
C_{7}F_{15}^{\cdot} + OH^{\cdot} \rightarrow C_{7}F_{15}OH \tag{5}
\]

\[
C_{7}F_{15}OH \rightarrow C_{7}F_{15}OF + HF \tag{6}
\]

\[
C_{7}F_{15}OF + H_{2}O \rightarrow C_{6}F_{14}COO^{-} + HF + H^{+} \tag{7}
\]

4.4.2. Photochemical oxidation:

Due to the nature of its chemical structure, PFAS do not absorb light at a wavelength greater than
220nm, so they do not undergo effective photolysis under these conditions [68]. This is because, at
a higher wavelength around 254nm, UV light’s energy would be 471kJ/mol, whereas the bond
dissociation energy of PFAS would be 544kJ/mol, so destruction cannot be achieved. The
validation was done by performing different UV experiments with and without shorter
wavelengths of 185nm and using combined wavelengths of 254nm and 185nm. High PFOA
photolysis took place with the release of certain intermediate compounds [79]. Coupling these
photolysis reactions with heterogeneous catalysts such as \( TiO_{2} \), \( In_{2}O_{3} \), \( Go_{2}O_{3} \) generate more
\( e^{-}\hat{h}^{\cdot} \) pairs when irradiated with a light source. The free-formed \( e^{-}\hat{h}^{\cdot} \) pairs result in \( e^{-\omega_{U}} \)
(hydrated electrons) by reacting with the adsorbed water molecules on the catalyst surface,
whereas the \( \hat{h}^{\cdot} \) generates °OH radicals by reacting with water molecules, and both promote the
degradation of PFAS compounds [80]. An iron oxide/ carbon sphere composite was synthesized to
perform photocatalysis in which FeO provided the complexing ability of PFOA, whereas CS
provided selective adsorption of it, and 95.2% degradation was achieved when the electron
transfer took place between them [81]. The energy difference between the valence and conduction
bands of photocatalyst and its oxidation-reduction ability plays a significant role in degradation during photocatalysis. Modifying these photocatalysts into composite form by coupling them with carbon nanotubes or other polymers may improve their properties and degradation efficiencies. Many important factors such as pH, reaction temperature, the light source, type of catalyst used, and dissolved organic matter can significantly affect photocatalytic reactions' degradation efficiency. Analyzing the PFAS samples receiving more intense solar radiation at higher altitudes of a mountain unveiled that natural photodegradation of PFAS compounds occurs at these altitudes, with the release of many short-chain PFAS, showing that natural environmental conditions are also a cause for the introduction of short-chain PFAS into the environment [82].

4.4.3. Ozone-based oxidation:

Until now, ozone-based systems alone are not effective for PFOS or PFOA removal from contaminated waters. Pre-treating them or combining these systems with the addition of hydrogen peroxide or other oxidizing agents generally promote their level of destruction. Performing alkaline ozonation led to the destruction of many long-chain PFAS and a few short-chain PFAS. Using air stripping systems can later remove the volatile unionized compounds formed during the process. Performing pre-treatment before ozonation increased the degradation rates by 56% for PFOA and 42% for PFOS under alkaline conditions [83]. A comparative analysis of different systems found that ozonated fractionation performed best due to high \( \cdot \text{OH} \) radicals and showed 95% removal of PFAS from waters, whereas other systems such as air fractionation, UV/ozone combined treatment, and UV alone showed 81%, 73%, and 17% at HRT of 20 min and removing short-chain PFAS remained as a challenge in all these systems [84]. A heterogeneously catalyzed ozonation process carried out in lab-scale and pilot-scale levels for removing PFAS from tap waters removed 98% having chain lengths of \( C_7 \) to \( C_{11} \), and while observing, the electrostatic interactions and hydrophobicity of PFAS towards the catalysts played a major role, whereas the degradation was independent of the chain length [85]. Thus, focussing future research on
combining ozone-based systems with other treatment technologies may help enhance degradations cost-effectively.

4.4.4. Hyperoxide and persulfate systems \( (\text{S}_2\text{O}_8^{2-}) \):

When oxidant like hydrogen peroxide is used to degrade PFAS, the hydroxyl radicals generated during the reactions readily destroy their alkyl groups but do not destroy their fluoroalkyl bonds leading to many short-chain precursors. Instead, as sulfate radicals have high oxidation capacities, the high redox potential of about 2.5-3.1V, and long half-lives in the range of 30 to 40 µs, they can effectively interact with various functional groups and degrade PFAS compounds to a greater extent. Using the micro-wave induced persulfate method to remove PFOA from aqueous solutions promoted 1.1-7.4 times increased mineralization and decomposition when maintained in acidic conditions [86].

4.4.5 Sonochemical method:

In the ultrasonication method, ultrasonic waves having frequencies greater than 20Hz are generally applied within solutions during which a sequence of compression and rarefaction occurs in the solutions. Due to the developed temperature and pressure difference, the bubble collapse due to cavitation and readily pyrolyze different PFAS compounds. The acoustic cavitation process produces hydroxyl radicals to enhance the degradation of PFAS compounds [87]. Here the PFAS remains stable at the bubble interfacial surface and gets exposed to different radical-mediated reactions to undergo degradation. Various parameters such as frequency, temperature, power density, etc., may affect sonication and efficiency. Adding other additives such as sulfates, salt ions, permanganates, periodates, and surfactants within this sonication system may influence the time taken for the process and may affect the removal rate of these compounds. The degradation pathway of PFOA has been explained, and it is given below [88]. Using a large scale sonochemical reactor for degrading PFAS in AFFF samples showed high mineralization and defluorination with the release of 102.2±0.2µM of fluorides and 76.6±0.1µM sulfates after 240
minutes of degradation [89]. Future research should focus more on their scalability aspects and the intermediates generated during this process.

\[ H_2O )) \rightarrow \text{cavitation bubbles} \] (8)
\[ H_2O )) \rightarrow OH^r + H^r \] (9)
\[ OH^r + SO_4^{2-} )) \rightarrow OH^- + SO_4^- \] (10)
\[ PFOA + SO_4^{2-} )) \rightarrow F^- + SO_4^{2-} + CO_2 \] (11)

4.4.6 Plasma technology:

Plasma technology is an advanced destruction technology for degrading a wide range of PFAS compounds. Thermal plasma and non-thermal plasma are the two groups of plasma produced using plasma technology. As non-thermal plasma technology is more selective and requires less energy comparatively, it is mainly preferred. The plasmas are generally generated in bubbles when electric discharge and gas are applied between two electrodes within contaminated waters in a reactor. The plasma composition mainly contains reactive oxygen species, reactive nitrogen species, aqueous electrons, free radicals, etc. [90]. The aqueous electrons are the predominant ones that directly destroy the PFAS compounds, whereas other ions perform indirect destruction. A submerged reverse vortex flow gliding arc plasmatron was used as a discharge system in a non-equilibrium plasma method during PFAS treatment, and it was found to be advantageous because this system showed very active mineralization of PFAS compounds at low energy costs [91]. A pilot-scale plasma reactor used for treating PFAS contaminated Investigation Derived Waste (IDW) removed long-chain PFAS compounds at faster rates than short-chain PFAS, and 36 to 99% of total precursors concentration was found to be removed while using this reactor, proving it as a viable technology to treat PFAS compounds [92]. By changing the arrangement of different electrodes within reactors and choosing different discharge systems for producing plasma, more reactive species get generated, and varieties of contaminants and emerging pollutants in water can be destroyed and degraded. Comparing the capabilities of three different plasma reactors which
used Alternative Current discharge, Direct Current discharge, and Self Pulsing plasma Discharge streamer as discharge systems, Self-Pulsing plasma Discharge showed improved mineralization of PFOA within a shorter duration of time, caused due to the extended interaction of PFOA with plasma at the liquid interface and high concentrations of reactive species generated during reactions at large surface areas [93].

4.5 Advanced reduction process:

The advanced reduction process (ARP) generates highly reactive free radicals like hydrogen radicals and hydrated electrons when combining reducing agents or reductants with activation methods and can successfully degrade the PFAS compounds [94]. The hydrated or solvated electrons are predominant during PFAS destruction, and they follow two pathways of destruction: chain shortening and hydrogen/fluoride elimination. Sulfites, sulfates, iodide, ferrous ions, and dithionate are important reducing agents. They can be activated by UV irradiation, microwave radiation, ultrasonic radiation, and electron beams. The UV radiation mechanism activating these reductants to generate hydrated electrons and other free radicals has been explained below [95].

Using sulfate mediated UV photochemical system, PFOA reduction showed 100% removal after 1 hr and 88.5% defluorination after 24 hours as hydrated electrons came into play and enhanced their mineralization [96]. During defluorination and the C-S bond decomposition, many short-chain intermediate compounds are found to be produced. Other constituents and coexisting species are also found to affect their mechanism of action, and so taking into account such factors may help in reducing the cost as well as the energy being spent [97]. Before employing ARPs, knowing more about pollutants’ molecular structure is vital to understanding their complete degradation mechanism. Nowadays, many researchers are moving towards ARPs and are using other strong reductants like Zero Valant Iron, Alkali metals, etc., to check their efficiencies towards PFAS removal.

\[
SO_3^{2-} + hv \rightarrow SO_2^{-} + e^{-} \tag{12}
\]
4.5.1 Radiation-induced degradation:

Irradiation of contaminated waters using high energy radiation is one of the advanced redox technology which generates free radicals, such as $\text{OH}^\cdot$, $\text{H}^\cdot$, $\text{e}^-\text{aq}$ for the destruction of pollutants in water. When irradiated, the water molecules degrade in the following way, as shown in the below equation [98]. As these reactions do not entail chemicals, this technology does not produce much secondary intermediate during mineralization and defluorination compared to other AOPs. Treating PFOA in synthetic waters using electron beam treatment effectively defluorinated PFOA by aqueous electrons and other free radicals, and the presence of oxygen greatly affected the efficiency of degradation of PFOA [99]. In another study, using this electron beam for treating PFOS and PFOA in aqueous solutions showed defluorination of 85.9% of PFOS and 95.7% of PFOA during which the role of radical scavengers, hydroxyl radical, and hydrated electrons were found to play a predominant role [98]. The degradation of PFOA using $\gamma$-radiation was carried out, in which $\text{OH}^\circ$ and hydrated electrons promoted complete mineralization of PFOA by cleaving C-C and C-F bonds and proved them as an efficient technique for removing persistent pollutants like PFOA [100].

\[
\text{H}_2\text{O} \rightarrow (0.28)\text{e}^-\text{aq} + (0.06)\text{H}^\cdot + (0.27)\text{OH}^\cdot + (0.27)\text{H}_2\text{O}^\cdot + (0.05)\text{H}_2 + (0.07)\text{H}_2\text{O}_2
\]  

(13)

4.6 Bioremediation:

Due to the strong C-F bonds in their chemical structures, PFAS compounds resist microbial biodegradation. More research needs to be done to project a clear explanation of their mechanism. PFAS compounds remain in the effluents and sludges of municipal treatment systems and act as a major source for introducing these compounds into the environment [101]. Even after prolonged incubation, no degradation was observed for most PFAS compounds, showing their high resistance towards microbial degradation [102]. A \textit{Pseudomonas aeruginosa} strain was used for degrading PFOS, and when incubated for 48 hours, 67% removal of PFOS was observed with no
change in fluorine content, indicating that only partial mineralization of PFOS compounds would have taken place during this degradation and no breakdown of C-F bonds was achieved [103]. Evaluating the results of biodegradation under both aerobic and anaerobic conditions in a lab-scale closed-loop reactor proved that the removal of PFAS compounds was found to be more during anaerobic conditions, whereas only lesser degradation was found under aerobic conditions, but in both cases, no increase in fluorine ion concentration was observed showing their resistant nature [104]. As it is an environment-friendly option, knowing more about their mechanisms may help perform more detailed works related to microbial degradation in the future. The fate of different PFAS compounds when degraded by microbes under aerobic and anaerobic conditions also needs to focus on their direct and indirect contributions of PFAS into the environment, and their reintroduction in a cyclical manner must be known.

Hence PFAS in aquatic systems can be passively removed by technologies like adsorption, membrane filtration, foam fractionation, etc. or can be actively destructed by advanced treatment systems like redox reactions, microbial systems, etc.

5 Treatment strategies – Land / Soil Systems:

Due to many direct and indirect sources, PFAS gets deposited as sediments in soil and groundwater. There is a need to encounter this issue and develop novel treatment technologies to tackle these contaminated sites. Some of their contamination sources are sludges of WWTP, biosolids, landfill leachate, infiltrated rainwaters, run-off from urban areas and military bases, etc. In the olden days, "dig and dump strategies" were used to treat them, but nowadays, many advanced mobilization and immobilization approaches are being followed to contain or destruct the PFAS from contaminated soils. Some of those approaches are discussed below:

5.1 Soil washing:

Soil washing is one of the most commonly used in situ techniques in which flushing solutions are injected into the soil, and the PFAS present in the soil gets desorbed from them according to the
functional groups present on them. Employing different cationic and anionic surfactants for soil flushings such as Cetrimonium bromide, Steartrimonium bromide, Sodium Dodecyl Sulfate, and other acidic and basic solvents such as ethyl acetate, tetrahydrofuran, dimethylformamide, etc. were found to enhance the desorption of PFAS compounds [105][106]. Injecting these flushing solutions can desorb PFAS and concentrate them within these solutions. Various ex-situ treatment technologies can then treat these concentrated solutions for further removal of PFAS. Opting for natural greener sorbents in place of chemical solvents would be an environment-friendly approach and help move towards a sustainable future.

### 5.2. Soil sorption & Stabilization:

Sorption using adsorbents and amendments is an effective stabilization technology that can be performed in situ and ex-situ to treat PFAS contaminated soils. Performing stabilization using stabilizers such as pozzolans, cement, fly ash can contain and restrain them within specific areas by blocking their mobility and can prevent them from leaching groundwaters and contaminating other nearby surfaces. Stabilizing them cannot help destroying entire PFAS compounds but can help control their level of contamination by forming them as a matrix within the soil surface. Soil mixing with different sorbents like activated carbon, molecularly imprinted polymers, biochar, and minerals can be applied on-site, and the contaminants can be transformed from the soils onto the adsorbent surface for removal. Evaluating the efficiency of three different amendments of mixed wood biochar (MW), paper mill waste biochar (PMW), and activated carbon for treating PFAS contaminated sites found that due to high sorption sites, surface area, and carbonization potentials, AC showed very good sorption towards PFOS, PFAS, PFHxS, etc., with sorption efficiencies in the order of AC>MW>PMW [107]. Different sorbents such as compost soil activated carbon and montmorillonite were applied as amendments and PFAS contaminated soil for immobilization; 99% stabilization was achieved when activated carbon was used, whereas compost soil and montmorillonite stabilized 35% of PFAS within the site [34]. Some disadvantages of using this
method are that prolonged usage may change the frictional properties of soil, the soil may become toxic, and maybe costly when applied for larger areas.

5.3 Bioremediation:

Different bioremediation approaches such as microbial, fungal, and phytoremediation are being opted for removing PFAS from contaminated soils. PFAS remediation using microorganisms is still not widely understood, and different literary works have observed many conflicting outcomes. During this, the complete degradation of PFAS compounds by oxygenase enzymes was not achieved; instead, many precursors led to increased release of shorter chain PFAS from them during the degradation process. Characterization of AFFF amended microcosms for carrying out aerobic degradation of 4:2, 6:2, and 8:2 fluorotelomer thioether amido sulfonate (FtTAoS) showed that during biotransformation, they released various intermediates such as FHS, FCA, PFCA compounds, and due to their slow degradation rates, they may remain in the environment and act as precursors for introducing PFAS into the environment [20]. When the *Anabaena* strain was pre-exposed to PFOS and PFOA compounds to evaluate their toxic effects, it was observed that higher toxicity levels indirectly affected them and greatly affected their properties of membrane potential and integrity [108]. Compared to bacteria, fungal degradation showed promising results and was a potential candidate for PFAS degradation. Phytoremediation is another sustainable technology that uses plants for treating contaminated soils. Due to their hydrophilic groups, PFAS gets easily transported through the plant's transpiration stream and accumulates within its vegetative part. Applying biosolids amended soils containing PFAAs for growing edible plants promoted high bioaccumulation factors of about 56.8 for PFBAs in lettuce and 17.1 for PFPeAs in tomatoes within these edible plants short-chain compounds accumulated in a higher amount than long-chain compounds [109]. Evaluating the phytoremediation potential of different plant species which were present in a fire fighting facility found that high concentrations of a sum of 29 PFAS compounds were found accumulated at levels of about 97ng$^{-1}$ and 94 ng$^{-1}$ in leaves and needles of the plant.
species showing that they can uptake and accumulate high levels of pollutants within them [110]. Using these plants for bio accumulating PFAS by remediating them from contaminated soils could be a sustainable and cost-effective solution for treating pollutants. Many factors, such as soil properties, plant type, and concentration of pollutants present in the soil, may affect the bioaccumulation factor, and so all these factors need to be taken into this account while focusing on their remediation.

5.4. Thermal treatment:

In this treatment method, extreme temperatures are applied to the contaminated site, and organic contaminants vaporize from them, and captured gas is then treated and converted to steam and carbon dioxide. Regular thermal treatments do not treat PFAS entirely due to their high melting points, so more advanced thermal treatments are required to degrade them. Application of thermal temperatures of about 550° C in PFAS contaminated soils removed 71 to 99% of different PFAS compounds by active destruction [111]. Crownover et al. performed thermal treatment by maintaining optimal temperatures at 350° C and 400° C, observed that 99.91% and 99.998% of PFAS compounds were removed. It was found that carboxylate-based PFAS volatilized faster than sulfonate-based PFAS [112]. Pretreating PFAS contaminated soils using activated Carbon before thermal treatment may also help in the complete volatilization of PFAS compounds when subjected to thermal destruction. Cost of initial investment, energy costs, very high temperatures, and high energy requirement are some of the disadvantages due to which its usage in large-scale applications is limited. This treatment is not a sustainable solution for destroying PFAS because they largely affect the properties of soil and microorganisms inhabiting them.

5.5 Ball milling:

Ball milling is one of the mechanochemical processes for treating PFAS contaminated soils in which high temperatures are generated when high energy mechanical force and co-milling agents are applied together. Due to these temperatures, a chemical reaction occurs at the surface to
destructor the pollutants, and it is an effective non-combustion technique for PFAS removal. The ball milling process's reaction pathway by which PFOS gets destroyed is given below [113]. During degradation of PFOS and PFAS using planetary ball mills, KOH served as an excellent co-milling agent for destructing CF bonds. An increase in fluoride and sulfate ions was observed when the degradation products were analyzed [113]. Ball milling with KOH was also performed for destroying fluorocarbon surfactants such as 6:2 FTS (6:2 fluorotelomer sulfonate), and when the mineralized products were analyzed, increased concentrations of fluoride was observed without any byproduct formation [114]. Co-milling fluorinated compounds with $La_2O_3$ during ball milling activated $La_2O_3$ and when the mechanochemical reactions took place, the defluorination of fluorinated compounds took place by undergoing different mechanisms such as carbonization and oxidation [115].

$$C_6F_{17}SO_3 + 18KOH \rightarrow 17KF + K_2SO_4 + 8CO + 9H_2O$$ (14)

$$C_6F_{17}SO_3K + 26KOH \rightarrow 17KF + K_2SO_4 + 4K_2SO_3 + 4C + 13H_2O$$ (15)

Hence PFAS contamination in soils can be treated using technologies like soil flushing, soil sorption and stabilization, thermal treatment, bioremediation, ball milling, etc.

6 Future Perspectives:

As the persistence and contamination level of PFAS is increasing in the environment to a greater extent, there is an urgent need to control their levels. Though many developed processes are in line, 100% destruction is not achieved anywhere, and the by-product formation is problematic to manage during the destruction of PFAS compounds. Future research needs to focus more on reducing them at the source level and controlling their cyclical contamination back into the environment. Some of the ways they can be managed are shown in Fig.5 and are discussed here.
Fig. 5 Future perspectives on managing PFAS contamination in environmental samples and steps to mitigate their future impacts

6.1 Source reduction:
In the waste management context, source reduction is one of the important ways by which future contamination can be controlled. The same can be done during PFAS management because controlling their generation levels at the source may control their future contamination levels to a greater extent. This can be done by reducing the usage of PFAS containing products like non-stick cookware and replacing them with other green cookware such as ceramic coated cookware, metal-based pans, cast iron pans, etc., As Aqueous Film Forming Foams are the primary cause for contaminating water by PFAS, opting PFAS-free foams for fire-fighting operations such as Forafac 1157N developed by DuPont can be an environmentally friendly option to control water as well soil contamination [116]. Avoiding fluoropolymer coatings on textiles, metals, food packaging and replacing them with alternatives such as perfluoro butyl iodide can control their levels in industrial discharges, contaminating water sources and the aquatic organisms residing in them [117].

6.2 Regulation:
As no strict standards are available in developing countries, different countries' regulatory bodies have started setting their standards to avoid an alarming future. Regulatory bodies should properly
assess a complete risk management approach, including the complete list of PFAS compounds observed in a particular country, their source, usage, contamination levels, and their release into the environment. The checking of PFAS at various levels from source to disposal need to be managed; only then can proper standards be formulated and followed by various communities. Addressing the exposure levels in such a manner can help understand toxicity levels among communities, help develop action plans for controlling their risk communication, and characterize the health impact of different PFAS compounds on human health. Hence, developing proper standards and performing risk assessments can help know their future effects and control them properly.

6.3 Synergistic treatment approaches:

As individual treatment processes cannot offer complete removal, treatment train processes or a synergistic approach are being tried nowadays. Combining different treatment processes in a sequential process can aid in destruction. As byproduct formation and release of a greater number of short-chain PFAS is a significant problem, performing synergistic approaches can aid incomplete removal and cost-effectively perform them. Coupling different oxidation systems with bioremediation processes, combining constructed wetland systems with microbial fuel cell approaches, and combining passive separation techniques such as adsorption and filtration with other active destruction technologies are some of the hybrid systems that may help in effective destruction. Such hybrid systems can provide overall process integration in water treatment plants and help destruct PFAS compounds. They can also help remove PFAS at high efficiencies and reduce the material and energy consumption, which would be high during individual treatment processes. More pilot studies should be conducted using such newly developed approaches to assess their suitability in large-scale applications.
6.4. Sustainable future:

Developing novel technologies using greener approaches can help in moving towards a sustainable future. In photo remediation, synthesizing functionalized low-cost catalysts can reduce the treatment cost and improve their treatment efficiencies. Recycling or immobilizing these catalysts for photodegradation can help perform them as a continuous process at low costs. Focusing more on phytoremediation and improved microbial degradations can be an excellent option for reducing system cost and byproduct formations. More focus is on treating only a few PFAS family compounds such as PFOS and PFOA, but the after-effects of other compounds belonging to this family also need to be monitored when moving towards sustainability consistently. When disposed of in landfills, capturing the leachate and treating them on site may also help prevent their future effects on soil and ground waters.

7. Conclusion:

This review elucidates the applications of the DPSIR framework for environmental problems and explicitly deals with emerging pollutants such as PFAS. The toxicological studies carried out in model organisms, and the bio accumulative potential of PFAS in different trophic levels have also been discussed. The regulatory policies and advisory limits set by organizations of various countries for the benefit of policymakers and researchers have been explained briefly. A brief review of currently available and emerging treatment technologies for PFAS removal in the environment samples have been discussed, along with their advantages and limitations considering the field scale and diffuse pollution issue. Future perspectives on source reduction, regulations, synergistic approaches, and sustainability have been described to provide valuable illustrations for upcoming research.
8. **Conflicts of interests:**

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.

9. **References:**


Ren, B. Wang, H. Sun, A.C. Alder, K. Kannan, D. Zhao, J. Cheng, C.D. Vecitis, M.R.
Hoffmann, J.P. Benskin, M.G. Ikonomou, F.A.P.C. Gobas, M.B. Woudneh, J.R. Cosgrove,
He, L. Liu, Q. Chai, M. Mumtaz, J. Huang, G. Cagnetta, G. Yu, Z. Wang, J.C. DeWitt, C.P.
Schaider, P. Grandjean, R. Lohmann, C.C. Carignan, A. Blum, S.A. Balan, C.P. Higgins,
Sarvajayakesavalu, A.J. Sweetman, J.E. Zenobio, M. Modiri-Gharehveran, C.D. Perre,
Chloe deVecitis, L.S. Lee, T. Xu, Q. Xiang, G. Shan, W. Wu, L. Zhu, M. Ateia, M.
Arifuzzaman, S. Pellizzeri, M.F. Attia, N. Tharayil, J.N. Anker, T. Karanfil, S.A. Sassman,
Kiatagawa, R. Arakawa, Z. Du, S.S. Deng, Y. Bei, Q. Huang, B. Wang, J. Huang, G. Yu,
X. Song, R. Vestergren, Y. Shi, J. Huang, Y. Cai, W.A. Gebbink, L. van Asseldonk, S.P.J.
van Leeuwen, L. Zhang, J. Niu, Y. Li, Y.Y. Wang, D. Sun, A.M. Trautmann, H. Schell,
K.R. Schmidt, K.-M. Mangold, A. Tiehm, Aerobic Biotransformation of Fluorotelomer
Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms., Environ. Sci.

https://doi.org/10.1007/978-3-319-15518-0_4.


[23] P. market Research, Global Market Study on Non-stick Cookware: Celebrity Endorsements
Offering Significant Impetus, (2019).

Sunderland, Can profiles of poly- and Perfluoroalkyl substances (PFASs) in human serum


[38] M.S. Johnson, R.C. Buck, I.T. Cousins, C.P. Weis, S.E. Fenton, Estimating Environmental Hazard and Risks from Exposure to Per- and Polyfluoroalkyl Substances (PFASs):
https://doi.org/10.1002/etc.4784.


https://doi.org/10.1016/j.trac.2016.10.008.


https://doi.org/10.1109/IWMN.2019.8805049.


https://doi.org/10.1021/es302274g.

[60] Y. Yang, J. Jiang, X. Lu, J. Ma, Y. Liu, Production of Sulfate Radical and Hydroxyl Radical by Reaction of Ozone with Peroxymonosulfate: A Novel Advanced Oxidation


Z. Song, H. Tang, N. Wang, L. Zhu, Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system, J. Hazard. Mater. 262


