

Treatment Trends and Hybrid Methods for the Removal of Poly- and Perfluoroalkyl Substances from Water—A Review

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Abstract: Poly- and perfluoroalkyl substances (PFASs) encompass a diverse group of engineered chemicals extensively manufactured and utilized in various facets of human life. They exhibit widespread distribution in aquatic environments due to their prevalent usage and resistance to degradation. Recognized for their toxicity to both humans and animals and a major public health concern, various techniques have been employed to eliminate them from water sources. However, these methods have shown limitations in efficiently and cost-effectively removing PFASs, particularly in the presence of other water contaminants, which are often present at much higher concentrations than PFASs. This review critically discusses these methods, presenting their respective advantages and limitations. This review illustrates that, rather than solely depending on individual methods as often presented in previous reviews, a combination of techniques has shown greater effectiveness in PFAS removal, owing to their synergistic effects. Hybrid methods capable of practical integration for efficient PFAS removal include adsorption coupled with oxidation, membrane separation combined with oxidation, and the integration of adsorption with membrane separation and incineration. In these hybrid approaches, one technique extracts PFASs from contaminated water and concentrates them, while the other degrades the extracted PFASs. The review presents strategies to enhance the performance of these hybrid methods.

Keywords: PFASs; treatment; adsorption; membrane separation; oxidation



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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) constitute a large group of persistent chemicals that have been extensively used in industrial processes and commercial products over the past few decades. These substances are characterized by fully or partially fluorinated carbon chains with varying lengths and functional groups [1,2] (Figure 1). The C–F bond in their structure is one of the strongest found in nature and becomes even stronger with increasing replacement of hydrogen atoms by fluorine at each carbon position [3].

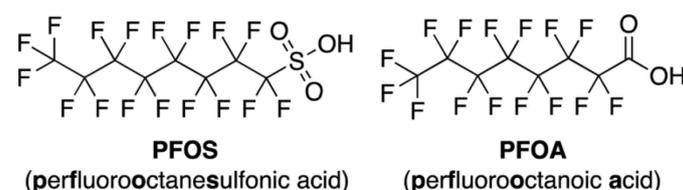


Figure 1. Structures of PFOS and PFOA.

Due to their stable chemical structure, high electronegativity, and the small size of the fluorine atom, PFASs are considered environmentally persistent substances with

long biological half-lives and a high potential for accumulation [3]. Consequently, these compounds are widely distributed in the environment due to their extensive use and resistance to degradation [4]. They have been extensively detected in various aquatic systems, including wastewater, surface water, groundwater, and drinking water. Their concentrations typically range from several picograms per litre (pg/L) to micrograms per litre ($\mu\text{g/L}$), with concentrations in the low nanograms per litre (ng/L) range being the most commonly observed [1]. They have been associated with significant human health risks, including cancer, infertility, low birth weight, and delayed puberty [2,3,5]. Recognizing these concerns, the US Environmental Protection Agency (EPA) established a lifetime health advisory level for combined perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in drinking water at 70 parts per trillion (70 ng/L or 70 ppt) [1,4,5]. In March 2023, the US EPA proposed Federal Maximum Contaminant Levels (MCLs) for six PFASs in drinking water. The proposed MCLs for PFOA and PFOS are 4 ppt. Additionally, a Hazard Index MCL was proposed for the combined concentration of four other PFAS compounds (perfluorononanoic acid (PFNA), GenX chemicals, perfluorohexane sulfonic acid (PEHxS), and perfluoro-butane sulfonic acid (PFBS)), reflecting their differing relative health risks [6,7].

PFAS compounds represent a diverse group of engineered chemicals, with the number of known compounds exceeding several thousand [1]. They can be classified into three categories: perfluoroalkyl acids (PFAAs), PFAA precursors, and other compounds such as fluoropolymers and perfluoropolyethers (PFPEs). Among the PFAAs, PFOA and PFOS are the most commonly encountered species in the environment that have been extensively studied [1]. Their structures are shown in Figure 1. These substances were previously produced in significant quantities worldwide but have since undergone a voluntary and gradual phase-out in the United States since 2000, driven by ecological and health concerns [1]. However, despite these efforts, PFOA and PFOS persist in the environment due to their inherent stability and ongoing imports from other countries [1].

Since the 1940s, PFASs have been extensively manufactured and utilized in various aspects of our lives [1]. These substances can be found in a wide range of products, including but not limited to aqueous film-forming foam, nonstick cookware, fast food wrappers, stain-resistant carpets and fabrics, cleaning products, and personal care items [1,8,9]. Major sources of PFOA and PFOS in municipal wastewater, as revealed by a survey, include fluoropolymer industrial wastewater, foam fire extinguishing agents, and chromium mist inhibitors [10]. Additionally, PFASs are commonly employed in the semiconductor and photolithography industries due to their excellent chemical resistance and thermal stability, and they can be found in fire extinguishers, firefighting foams, and fabric protectors [11]. Throughout the production and application processes of these products, PFASs have the potential to be released into the environment, subsequently being transported across different media, such as air, water, soil, and even food. As a result, aquatic organisms, plants, and humans can uptake these compounds, leading to their presence in various biological systems.

A comprehensive review by Kurwadkar et al. [12] examined PFAS concentrations reported in numerous countries. Between 2004 and 2010, surface water samples from 41 cities across 15 countries were analyzed, revealing the presence of PFOS and PFOA in all samples. The average concentrations ranged from non-detectable (ND) to 70.1 ng/L for PFOS and 0.2 to 1630.2 ng/L for PFOA [13]. Notably, the study found that rivers in the UK exhibited maximum mean concentrations of PFOS at 19 ng/L, while surface waters in Osaka, Japan, recorded maximum concentrations of PFOA at 1630.2 ng/L. The average PFOA concentrations in other cities included in the study area generally remained below 100 ng/L. In Eastern Spain, PFASs were detected in the Jucar River across different environmental compartments. Water samples exhibited concentrations ranging from 0.04 to 83.1 ng/L, sediments ranged from 0.22 to 11.5 ng/g, and biota concentrations spanned from 0.63 to 274 $\mu\text{g/kg}$ [14]. Vo et al. [15] reviewed the concentrations of PFASs in wastewater, surface water, groundwater, and drinking water across multiple countries and found

that the general order of concentration was wastewater > groundwater \geq surface water > drinking water. Among different types of wastewaters, domestic wastewaters, which originate from sources such as food packaging, dust, and household equipment, exhibited the lowest concentrations of PFASs (>100 ng/L). Wastewater from non-intensive industries, such as chrome plating and hospitals, had average PFAS concentrations ranging from 100 to 1000 ng/L. On the other hand, wastewaters from intensive industries involved in activities like water-proofing agents and aqueous film-forming foam showed average PFAS concentrations exceeding 1000 ng/L. This trend highlights the prevalence of short-chain PFASs in the manufacturing of PFAS products, as the concentration of short-chain PFASs was found to be at least 50 times greater than that of long-chain PFASs. Compared to wastewater, groundwater had much lower concentrations, ranging from 1 to 100 ng/L, surpassing the concentrations observed in surface water by more than two orders of magnitude. For drinking water, the mean concentrations of PFASs ranged from 0.1 to more than 1 ng/L.

However, other studies have consistently reported elevated concentrations of PFASs in drinking water across various regions in the United States, particularly in proximity to industrial sites involved in their production or use [4]. Investigations cited by Hu et al. [4] have revealed contamination of many civilian airports and military fire training areas due to the presence of PFASs in AFFFs, which are extensively utilized during firefighting training exercises. The groundwater and surface waters surrounding these sites had been found to contain PFAS concentrations that are three to four orders of magnitude higher than the drinking water health advisory level set by the US EPA at 70 ng/L.

Yadava et al. [9] have highlighted that epidemiological studies investigating the long-term effects of PFASs on human health have suggested potential reproductive and developmental impacts. These effects include conditions such as ADHD in children, disruptions to hormone systems leading to diabetes, increased cholesterol levels, thyroid function impairment, as well as the potential for cardiovascular and cerebrovascular diseases, and complications in liver, kidney, and immune system function. Additionally, studies examining both the general population and individuals occupationally exposed to PFOS and PFOA production have reported lower birth weights, increased postnatal mortality, and reduced postnatal growth. However, it is important to note that while these findings have been observed, Yadava et al. [9] also emphasize that the confirmation of these health outcomes and their relationship to PFAS exposure remains a subject of ongoing research and is a topic of debate within the scientific community. Additional research is necessary to establish definitive and universally accepted conclusions regarding the specific impact of PFASs on human health. Darlington et al. [16] have highlighted concerns regarding the potential toxic effects of PFASs on human health based on toxicology studies. These studies have raised alarm about possible developmental effects in fetuses and young children. Furthermore, other research has indicated potential links between PFAS exposure and conditions such as cancer, immune system disorders, and fertility problems. Epidemiological studies, as reported by Fenton et al. [17], have also indicated associations between exposure to specific PFASs and a range of health effects. These effects include altered immune and thyroid function, liver disease, dysregulation of lipids and insulin, kidney disease, adverse reproductive and developmental outcomes, as well as the potential for cancer. These findings collectively highlight the potential adverse health impacts of PFAS exposure, but further research is still needed to fully understand and establish the causal relationships between PFASs and these health outcomes.

In a review conducted by Xu et al. [18] on the toxic effects of PFASs in animals, adverse effects such as genotoxicity, immunotoxicity, neurotoxicity, and hepatotoxicity were observed due to the accumulation of PFOA *in vivo*. Hepatotoxicity, characterized by the presence of unusual fat deposits, liver enlargement, and hepatocarcinogenesis, was widely observed in vertebrate animals.

To assess the potential effects on humans, the majority of toxicology studies on PFOS have been conducted on animals. A comprehensive review by the US EPA [19] focused

on oral animal studies investigating PFOS over short-term and sub-chronic durations involving species such as monkeys, rats, and mice. The review revealed several possible effects on animals, including developmental impacts such as decreased body weight and survival, as well as increased serum glucose levels and insulin resistance in adult offspring. Reproductive effects were observed in terms of altered mating behaviour. Liver toxicity was evident through increased liver weight, decreased cholesterol levels, and the presence of hepatic steatosis. Furthermore, developmental neurotoxicity was indicated by alterations in spatial learning and memory. Immune effects and potential cancer risks, specifically thyroid and liver cancer, were also identified in these animals. Overall, the available toxicity studies on PFOS demonstrated that the developing foetus is particularly susceptible to PFOS-induced toxicity.

Due to the high toxicity of PFASs at elevated concentrations, safeguarding human and animal health necessitates their removal from all water bodies, including groundwater, surface water, and wastewater. This imperative presents a significant challenge to the water treatment industry. Numerous technologies, including adsorption, ion exchange, oxidation, and membrane processes, have been utilized to remove PFASs from water. However, these approaches often fall short in efficiently and cost-effectively eliminating PFASs, especially when other contaminants are present in the water. Detailed discussions of these challenges are presented later in the paper, segmented under individual technology sections.

This review explores the diverse methods employed for PFAS removal, examining their respective strengths and weaknesses. A central focus of this paper is placed on the combined or hybrid treatment processes for PFAS removal. These lead to improved effectiveness stemming from the synergistic interactions between processes with distinct removal mechanisms. A comprehensive review of such integrated PFAS removal methods is not available in the literature. This review also addresses the advantages of the hybrid process which have not been reported earlier.

1.1. Conventional Water Treatment Methods

There are various methods used for water treatment to remove contaminants, broadly categorized as separation and destructive methods. The separation process involves conventional techniques like flocculation, coagulation, sedimentation, aeration, disinfection, and filtration. It also includes non-conventional techniques such as sorption techniques using activated carbon, biomaterials, minerals, ion exchange resins, polymers, and nanomaterials. Additionally, non-conventional techniques that include more advanced techniques such as foam fractionation and ozofractionation, as well as membrane technologies like nanofiltration and reverse osmosis, are utilized for separation [17,20–23]. On the other hand, destructive methods involve advanced oxidation techniques, such as chemical, electrochemical, and photochemical processes, as well as ultrasonication and the conventional technique of biological remediation, aeration, and disinfection [17,20–23].

Numerous reviews of the existing literature on PFAS treatment have consistently found that conventional treatment processes are ineffective for PFAS degradation. This is primarily due to the recalcitrant behaviour of PFASs, resulting from their high chemical and thermal stability, which is a consequence of the strong covalent C–F bond in their molecular structure, as well as their high negativity in F^- , low water concentration, and pronounced amphiphilicity and lipophobicity [16,20,21,23–26]. Biological treatments, both aerobic and anaerobic, are capable of breaking the C–C bond in PFAS compounds, leading to the formation of short-chain PFASs. However, it has been observed that only polyfluorinated forms very slowly transform into extremely persistent perfluoroalkyl acids (PFAAs), with some intermediate forms still unidentified [24]. Crone et al. [25] also reported the ineffectiveness of both aerobic and anaerobic biological treatment, particularly when considering contact time constraints in drinking water facilities. When advanced treatment technologies are not utilized, biological wastewater treatment plants (WWTPs) can impact receiving water bodies, resulting in higher concentrations of PFASs detected in finished water compared to untreated water [26]. Under typical water treatment plant conditions, disinfection using

free chlorine or UV irradiation and biological treatment alone is ineffective in removing PFASs [27,28].

Crone et al. [25] reviewed the literature and found that conventional treatment technologies generally achieve PFAS removal rates of 0 to 5 percent. Rahman et al. [28] conducted a review on PFAS removal from water treatment plants in Japan, Australia, and other locations using conventional processes such as coagulation, flocculation, and sedimentation. They concluded that these techniques resulted in minimal removal of PFASs.

In their study, Appleman et al. [27] evaluated 15 full-scale treatment systems in water treatment utilities across the US for the removal of PFASs. They reported that water treatment techniques such as ferric or alum coagulation, granular/micro-/ultrafiltration, aeration, oxidation (i.e., permanganate, ultraviolet/hydrogen peroxide), and disinfection (i.e., ozonation, chlorine dioxide, chlorination, and chloramination) were mostly ineffective in removing PFASs.

Compared to conventional water treatment methods, advanced treatment approaches, such as high-pressure nanofiltration (NF) and reverse osmosis (RO), adsorption/anion exchange using specialized synthetic materials, and certain advanced oxidation methods, have shown better success in removing PFASs [8,17,20,21,23–30]. However, these advanced methods can be costly, may not always be applicable in plant-scale operations, and can generate toxic waste. These aspects are further discussed in the following sections, including steps that can be taken to address some of these challenges (e.g., combining two or more processes in a treatment train).

1.2. Membrane Processes

O'Connor et al. [31] conducted a review on PFAS remediation using membrane processes. Membranes were categorized into two groups: size-dependent and pressure-sensitive membranes. Low-pressure membranes, such as MF (100–400 nm) and UF (~10 nm), were capable of separating high-molecular-weight (MW) PFASs (e.g., PFNA, PFOS, and PFOA) but exhibited low efficiency in separating low MW PFAS (e.g., PFBS or PFHxS) from water. The literature values for PFOA and PFOS removal by low-pressure membranes ranged from 0 to 23 percent [25]. In the evaluation by Appleman et al. [27] of two full-scale treatment systems in the US for PFAS attenuation, it was found that MF and UF were mostly ineffective, resulting in only partial reductions in the concentrations of PFASs. Specifically, reductions of 24% for PFOS, 44% for PFD_oA, and 42% for FOSA were observed.

In their study, Olimattel et al. [32] employed a commercially available UF membrane (UA60, Trisep), with a pore size distribution in the range of 1000 Daltons. They also investigated the effects of modification by functionalizing the membrane with polyacrylic acid and polyallylamine hydrochloride for the removal of PFOS and PFOA. The results indicated that the unmodified UF membrane achieved only $21.8 \pm 11.6\%$ and $20.6 \pm 6.9\%$ removals of PFOS and PFOA, respectively. In contrast, the modified UF membrane exhibited improved removal, achieving $52.1 \pm 10.2\%$ and $50.4 \pm 9.5\%$ removals for PFOS and PFOA, respectively. This represents an increase of 30% in removal efficiency. The enhanced removal was attributed to an approximately 38% reduction in membrane MWCO (molecular weight cut-off) and a 9.2% reduction in membrane porosity due to the modifications. However, it is noteworthy that the removal efficiencies obtained by both the unmodified and modified UF membranes were not as high as those reported in other studies using NF and RO processes.

In contrast to low-pressure membranes, high-pressure membranes, such as NF and RO, have proven to be highly effective in separating both low-MW and high-MW PFASs from wastewater [31]. NF and RO processes have been found to efficiently remove various PFAS, including PFAA precursors, with size exclusion suggested as the primary mechanism in this filtration process. Additionally, other mechanisms like electrostatic repulsion, diffusion, and cake layer filtration may also play a role during the process. When comparing NF and RO, NF (especially the NF270) is recommended as a better option for PFAS removal due to its lower cost [25]. Boonya-atichart et al. [33] reported high PFOA removal efficiencies

using NF filtration (fully aromatic polyamide advanced composite membrane, membrane model 2540-ACM5-TSF, 2.5'' diameter) with 99.78–99.87% removal efficiency for spiked deionized water and 99.49–99.54% for spiked groundwater samples.

Crone et al. [25] conducted a comprehensive literature review and reported that RO is highly effective in removing PFASs (>99%) regardless of chain length, utilizing size exclusion and charge rejection mechanisms. However, the operation cost of RO is high due to the requirement for high pressure [27]. On the other hand, NF membranes with larger pores operate at lower pressures and employ mechanisms like electrostatic repulsion, hydrophobicity, and dipole moments to remove short-chain PFAS, which are too small to be solely rejected by size exclusion [23,28].

Despite the effectiveness of high-pressure membranes for PFAS removal, there are some limitations highlighted by Crone et al. [25] in their review. High recovery rates (typically around 80 percent for non-desalination systems) lead to the production of a concentrated retentate stream (20 percent of feed volume), which requires treatment before disposal. Dealing with this retentate stream poses significant challenges and costs due to its higher concentrations and volume. To optimize the cost efficiency of the membrane treatment, the residual stream treatment scheme should be carefully designed. Additionally, the impact of membrane fouling is a concern that needs to be addressed to maintain effective membrane performance.

1.3. Adsorption Processes

Adsorption is a highly effective method for remediating various pollutants in water, including PFASs, owing to its environmentally friendly nature, cost-effectiveness, low energy requirement, high efficiency, simple design, and ease of operation [31,34]. The mechanisms of adsorption encompass hydrophobic effects, self-aggregation (formation of micelles or hemimicelles), electrostatic interactions, hydrogen bonding, covalent bonding, ligand exchange, Van der Waals forces attraction, π - π bonding, and diffusion into adsorbent pores [9,15,22,26,31,34–36]. A schematic illustration of the various mechanisms of PFAS adsorption is presented in Figure 2. Adsorption can also occur through an ion exchange process where target pollutant ions in a solution replace exchangeable charged co-ions (e.g., Cl^- and Na^+) on the surface of a polymeric resin. These ion exchange resins are classified as cation exchange resins and anion exchange resins, with positively charged pollutants and negatively charged pollutants being exchanged, leading to the removal of these pollutants on the resins. Since PFASs are anionic in the pH range of natural water [28], they are typically removed by anion exchangers. An advantage of this process is its reversibility, as the resin can be regenerated and reused after saturation with PFASs using organic solvents like methanol, inorganic salts such as sodium chloride, bases like sodium hydroxide, or a combination of these regenerants [8].

Various materials, including ion-exchange resins, carbonaceous materials (e.g., granular activated carbon, biochar, and graphene oxide), natural and modified clays and clay minerals, renewable polymeric materials (e.g., chitosan and alginate), and inorganic and synthesized materials (e.g., layered double hydroxides, metal–organic frameworks, and nanomaterials), have been extensively investigated for their ability to adsorb PFASs from wastewater. In the past five years, several review articles have been published, focusing on the use of these materials for the remediation of PFASs [1,8,9,21–23,25,26,31,34,35,37].

Among various adsorbents and ion exchangers, activated carbon (AC) stands out as the most widely used for PFAS removal, owing to its exceptional adsorptive potential, primarily attributed to its unique porous structure [31]. Powdered activated carbon (PAC) exhibits higher adsorption capacity than granular activated carbon (GAC) due to its smaller pore size and larger surface area [37]. The reported adsorption capacity of GAC is in the range of 71.6–290 mg/g (for PFOS) and 41.3–120 mg/g (for PFOA), while PAC demonstrates a higher adsorption capacity of 560 mg/g (for PFOS) and 290–500 mg/g (for PFOA) [35]. However, PAC is not reusable, whereas GAC, despite being more expensive, can be regenerated and is better suited for column-based filtration in treatment plants. Considering the relatively long

equilibrium time and limited adsorption capacities of AC, anion exchange resins have been employed, with adsorptive capacities ranging from 200 to 2390 mg PFOS/g and 525–1500 mg PFOA/g [33]. Anion exchange resins have been shown to be particularly effective for removing PFOA, which exists as an anion at the environmental pH. The hydrophobicity of the exchange functional group of the anion exchange resin also plays a significant role in its adsorptive capacity for PFASs [38]. Highly hydrophobic resins exhibited higher adsorptive capacity (52.3–260.5 mg/g) for PFASs than nonhydrophobic (19.1–186.2 mg/g) and fairly hydrophobic (29.5–210.4 mg/g) resins [38]. This is because the hydrophobic resins have an affinity to the hydrophobic C–F chain part of the PFAS [22]. Ion exchange resins have also demonstrated high adsorption capacity for PFOS (210–2575 mg/g) and PFOA (1206 mg/g) [37]. Anion exchange resins have shown potential for removing short-chain PFASs like PFBA and PFBS, making them a preferable choice over GAC in such cases [31]. Metal–organic frameworks have also been investigated and have shown promise in terms of PFAS adsorption. For instance, Barpaga et al. [11] found that a mesoporous Cr–organic framework outperformed GAC in PFAS adsorption. Recently, Huang et al. [39] presented findings on the potential of covalent organic frameworks (COFs) characterized by structural regularity and task-specific functionality as highly promising materials for efficiently removing PFASs. In their study, they synthesized hollow COF nanospheres grafted with cystamine through a hard-template method. Subsequently, they functionalized these nanospheres using the thiolene “click” reaction. The results demonstrated the exceptional efficacy of these functionalized nanospheres in removing various anionic PFASs that included carboxylic, sulfonic, and phosphoric groups, as observed through batch and column-mode experiments. Remarkably, the Langmuir maximum adsorption capacities of the functionalized material towards three PFASs were nearly double those of powdered activated carbon (AC).

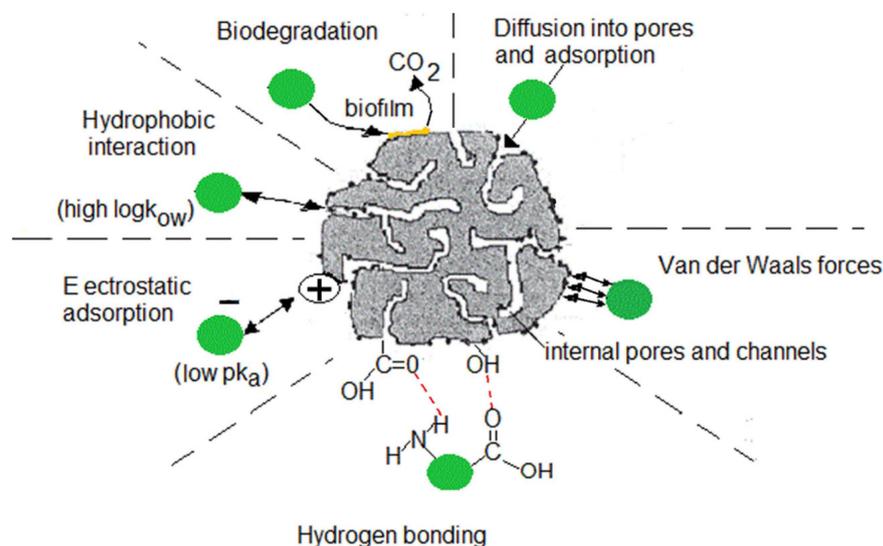


Figure 2. Possible mechanisms of PFAS adsorption. (Green colour = PFAS; large porous ball in the centre = adsorbent) (modified from [36]).

In summary, while AC remains widely used for PFAS removal, anion exchange resins and metal–organic frameworks offer promising alternatives with higher adsorptive capacities for specific PFAS compounds, particularly short-chain PFASs. GAC, though less effective in some cases, remains suitable for certain treatment processes, and its regeneration capability is advantageous in terms of cost-effectiveness.

While adsorption stands as a well-established method for removing PFASs from water, it presents certain limitations requiring attention. One challenge lies in the concentration of PFASs from the solution phase to the solid phase during adsorption, necessitating appropriate treatment for handling spent adsorbents [31]. The effective destruction of adsorbed PFASs, either through regeneration or safe disposal of spent adsorbents, is imperative in

this context. Moreover, the relatively low removal efficiency of short-chain PFASs and mixtures of PFAS compounds and their precursors poses another obstacle, prompting research efforts to develop novel adsorbent materials, enhance the removal capacity of existing materials, and improve the regeneration potential of adsorbents [31]. The widespread application of ion exchange resins and carbon nanotubes (CNTs) is hindered by their cost despite their promising efficiency as adsorbents [35]. Conversely, abundant biosorbent materials like plant wastes, wood chips, compost, manures, and sewage sludge offer inexpensive, renewable, and environmentally friendly alternatives to activated carbon and resins [22,34,35]. However, their adsorption capacities are relatively modest, necessitating research to modify them by functionalizing surfaces with cationic groups to increase adsorption capacities and identifying cost-effective regeneration or disposal methods for used adsorbents. For example, Zhang et al. [40] crosslinked chitosan beads and utilized them as efficient biosorbents to remove PFOS from aqueous solutions. This modified chitosan biosorbent exhibited a sorption capacity of up to 5.5 mmol/g for PFOS at an equilibrium concentration of 0.33 mmol/L, surpassing the capabilities of some conventional adsorbents. The authors identified the mechanisms of adsorption, including electrostatic and hydrophobic interactions, along with the contribution of hemi-micelles and micelles formed in the porous structure, which led to the high adsorption capacity.

In general, most of the research on PFAS adsorption has been conducted at the laboratory scale under ideal conditions and in short-term studies [21,31,34]. Therefore, it is crucial to validate the developed methodologies in real-world, large-scale applications through longer-term studies involving actual wastewater containing organic matter and other contaminants. These contaminants can compete for adsorption sites of PFASs, particularly considering their typically much higher concentrations in water (e.g., natural organic matter), which may diminish the adsorption capacities of PFASs. Additionally, factors such as pH, ionic strength, and other solution properties can influence adsorption behaviour [34]. These aspects also necessitate comprehensive investigation before implementing the adsorption process in full-scale treatment plants.

1.4. Oxidation

PFASs exhibit greater resistance to oxidation by ozone and hydroxyl radicals compared to other micro-contaminants, primarily due to the strong C–F bond and the electron-withdrawing nature of their functional groups [24]. Rahman et al. [28] highlighted that F is the most electronegative element, which hinders its oxidation and helps retain its electrons. Consequently, the powerful inorganic oxidant ozone faces thermodynamic challenges in oxidizing F. This, combined with the presence of the strong C–F bond and electron-withdrawing functional groups -COOH and -SO₃H in PFCAs and PFSA structures, indicates their likely resistance to oxidation, even when exposed to molecular ozone and hydroxyl radicals. Furthermore, Xu et al. [18] stated that many conventional approaches, such as thermal treatment, direct photolysis, and general hydroxyl-based chemical oxidation, are ineffective for removing aqueous PFASs. The review by Ross et al. [24] revealed that advanced oxidation processes, which have a higher oxidation potential compared to most physico-chemical and biological reactions, were also ineffective in degrading PFOSs at a concentration of 20 mg/L over a 120 min period using laboratory-scale experimentation with ozone, ozone hydrogen peroxide, ozone/UV, and Fenton's reagent. Moreover, other oxidants like dichromate and potassium permanganate had no significant effect on a wide range of PFAAs, including PFOS. The review also highlighted that perfluoroalkyl sulfonates seem to be considerably more recalcitrant to chemical oxidation compared to perfluoroalkyl carboxylates.

Advanced oxidation processes have also shown limited effectiveness for PFAS removal, even when applied at doses and contact times typical of drinking water treatment plants. These processes often result in the formation of non-selective hydroxyl radicals when combining technologies such as hydrogen peroxide plus iron (Fenton's reagent), ozone plus peroxide, UV plus titanium dioxide, UV plus ozone, UV plus chlorine, and

UV plus peroxide [31,41]. According to Crone et al. [25], removal rates typically range between 0 and 15 percent under conditions observed in drinking water treatment plants. Gagliano et al. [24] reported that advanced oxidation processes often lead to only the partial degradation of PFASs, resulting in the formation of PFASs with shorter perfluorinated alkyl chains. Even at a full-scale water reclamation plant in Queensland, Australia, multiple stages of ozonation with doses as high as 5 mg/L and a 15 min contact time did not satisfactorily remove PFASs [29].

1.5. Other Remedial Treatments

Other treatment techniques have also been researched and found to be somewhat successful in remediating most of the PFASs, particularly the long-chain ones, in water. These techniques include electrochemical oxidation, sono-chemical oxidation, foam fractionation, ozone fractionation, photocatalytic oxidation, plasma treatment, thermal treatment, and chemical reduction [9,15,17,21,23,31,37]. However, it is important to note that these methods are primarily confined to laboratory-scale batch studies using pure waters, and many of them may not directly translate to practical treatment plants operating under continuous flow conditions and dealing with wastewaters containing other pollutants [23]. Given that other pollutants, which are typically present in much higher concentrations in water, may strongly compete with PFASs, the removal of PFASs can be affected. Moreover, the cost of implementing these processes may be prohibitive, and therefore, the economic feasibility needs to be carefully assessed. Further research should be conducted at the field scale to demonstrate the practical capabilities and validate the effectiveness of these treatments under real-world conditions.

2. Hybrid Treatment Methods

A hybrid synergistic process amalgamates two or more distinct treatment methods into a coherent treatment regime. This approach has proven to surpass the efficacy of standalone individual treatments. The uniqueness lies in each method's specific mechanism of pollutant removal. When these distinct mechanisms collaborate within an integrated treatment, they synergize to heighten the elimination of diverse pollutants [39,40]. PFASs exist in various forms, each exhibiting its own distinct properties [1,8,15,21]. This inherent diversity poses a challenge when attempting to eliminate PFASs using a solitary treatment approach. Integrated treatment emerges as a solution to address diverse PFAS types and attain superior overall removal efficiency [9,23,30,42]. In separation procedures, one technique extracts PFASs from contaminated water, while another degrades the extracted PFASs. For instance, activated carbon can effectively extract PFASs from water. Subsequently, subjecting the activated carbon to heat or chemical treatments facilitates PFAS degradation. Furthermore, the simultaneous application of multiple degradation technologies can be harnessed through parallel treatment lines [42]. For instance, the combined utilization of electro-Fenton and electrochemical anodic oxidation, alongside hydrogen peroxide and activated persulfate oxidation, showcase effective PFAS degradation. The subsequent sections delve into amalgamated separation and degradation treatments, each grounded in distinctive mechanisms and processes. These approaches culminate in a cost-effective and efficient eradication of PFASs from the environment.

2.1. Adsorption/Oxidation Treatment

Liang et al. [43] showcased the efficacy of coupling ion-exchange resin with electrochemical (EO) oxidation in augmenting PFAS treatment within groundwater through a pilot plant field trial. The treatment sequence encompassed two pivotal steps:

- Ion exchange: This initial phase facilitated the separation and concentration of PFASs from groundwater. The ion exchange resin exhibited the capability to eliminate 18 distinct PFASs from the groundwater, encompassing PFHxS, PFOS, and 6:2 FTS. The resin effluent displayed PFAS concentrations below detectable limits, except for PFBA, PFPeA, and PFHxA. The resin was regenerated by leaching with methanol

and NaI solution, and the methanol in the leachate was removed via distillation. The resulting solution was treated using EO.

- Electrochemical oxidation (EO): subsequent to ion exchange, this stage annihilated the concentrated PFASs. The EO process manifested a notable reduction in PFAS precursor concentrations by 74.1–96.8% and four extended-chain PFAAs (namely PFHxS, PFHpS, PFOA, and PFOS) concentrations by 59.2–94.0%.

The amalgamated ion exchange/EO treatment train stands out compared to isolated EO treatment due to its energy efficiency. Notably, the heightened ionic strength of ion exchange effluent, a result of increased salt concentrations, obviates the necessity for electrolyte dosing to enhance electrical conductivity, a requirement in a standalone EO system.

Recently, Fang et al. [44] conducted a study on the extraction of four structurally different perfluoroalkyl ether carboxylic acids (PFECAs) from tap water (0.2 mg C/L TOC) and groundwater (7.3 mg C/L TOC). The PFECAs were removed using an ion exchange (column-based)/EO hybrid method. Their findings revealed that the ion exchange material A592E (a microporous resin) successfully adsorbed >92% of the PFECAs. Moreover, a solution comprising ammonium sulphate + methanol effectively desorbed 60–100% of the adsorbed PFECAs. Subsequently, EO treatment resulted in the removal of >99.9% of the PFECAs after distilling off >99.9% of methanol.

Crimi et al. [45] similarly deployed an adsorption/oxidation treatment train to address PFAS removal from simulated groundwater. Their approach entailed two sequential stages:

- Adsorption: Employing granular activated carbon (GAC), this phase concentrated and adsorbed PFASs from groundwater.
- Oxidation: GAC underwent activated persulfate oxidation to dismantle the adsorbed PFASs. PFOS was not transformed even with high oxidant doses, but PFOA degraded into shorter-chain compounds.

The GAC/oxidation treatment train's appeal stems from its relatively lower cost. However, a noteworthy consideration lies in the post-treatment disposal of GAC, potentially constituting a significant expense. In summary, both the ion exchange/EO and GAC/oxidation treatment trains exhibit efficacy in addressing PFASs within groundwater. The ion exchange/EO treatment train holds an advantage in energy efficiency and electrolyte-free operation, albeit at a higher cost. Conversely, the GAC/oxidation treatment train presents a more economical solution, albeit with the added cost of GAC disposal. The optimal treatment train selection hinges on specific site conditions and budgetary considerations.

Nanoscale materials exhibit significant potential as adsorbents for PFAS treatment due to their large surface area and corresponding reactivity, as demonstrated by Birch et al. [46]. Their adaptability allows for facile modifications, such as the incorporation of surface-bound metal catalysts and fluorine, effectively enhancing their PFAS removal capacities. Birch et al. [46] showcased multiple recent studies focusing on PFAS removal from aqueous samples utilizing various nano-enhanced adsorbents, along with strategies for subsequent targeted destruction of PFASs at or near the material's surface. Furthermore, the authors presented integrated methods that involved adsorption on nanoscale materials followed by directed PFAS destruction.

This “concentrate-and-degrade” strategy was recently applied to adsorb PFOA from a synthetic solution using a novel adsorptive photocatalyst called FeTNTs@AC, which consists of low-cost commercial activated carbon (AC) and nano TiO₂ (80% anatase and 20% rutile) doped with Fe [47]. This material effectively adsorbed PFOA within a few minutes, concentrating the contaminant on the photoactive sites. Subsequently, it was successfully degraded over 90% of the preconcentrated PFOA on the solid within 4 h under UV irradiation. In another study, where indium (In) was doped on AC-supported titanate nanotubes followed by photocatalytic oxidative destruction, excellent PFOA adsorption (>99% in 30 min) and photodegradation (>99% in 4 h) were achieved under optimal

conditions [48]. This adsorbent demonstrated the ability to be repeatedly used in four consecutive adsorption–photodegradation cycles.

2.2. Membrane Separation/Oxidation Treatment

Nanofiltration (NF) stands out as a highly efficient technology capable of eliminating over 99% of perfluorooctanoic acid (PFOA) from groundwater [33]. Nonetheless, an inherent drawback of employing membrane filtration lies in the accumulation of concentrated PFOA within the membrane reject. To achieve complete eradication of PFOA and other PFASs, it becomes imperative to neutralize them within the reject phase.

In a study conducted by Boonya-atichart et al. [49], a trial showcased the application of advanced oxidation for dismantling PFOA within NF reject through photocatalysis [Figure 3]. Nanoscale zero-valent iron was harnessed as the catalyst for this process. Subsequent to the photocatalysis, the nanoparticles were removed via ultrafiltration (UF) prior to discharging the treated water into the environment. The findings highlighted a remarkable 99.62% efficiency in PFOA removal by NF and an additional 59.64% degradation of the rejected portion through photocatalysis.

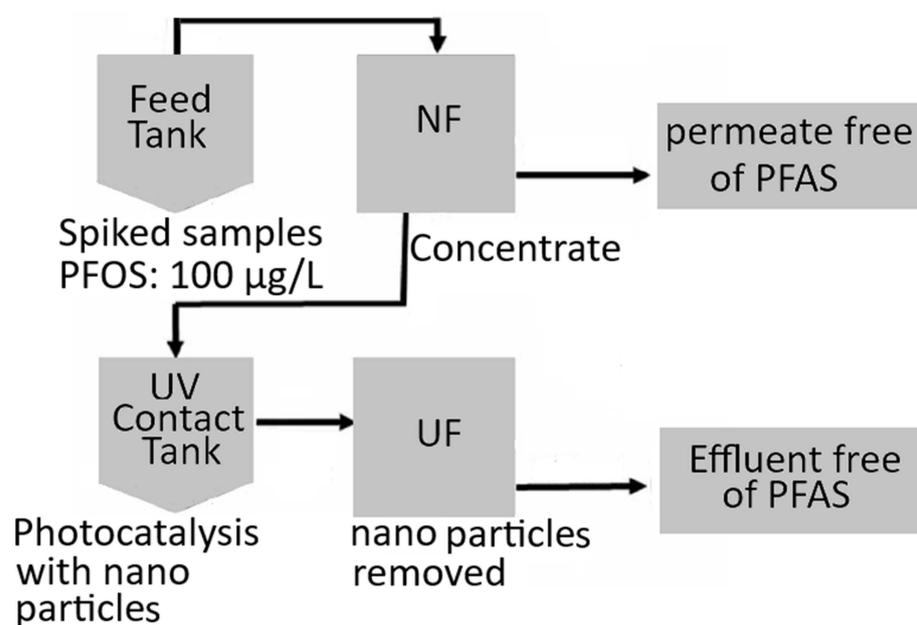


Figure 3. Removal of PFOA by NF followed by photocatalytic oxidation (modified from [49]).

In a parallel study by Pica et al. [30], an NF membrane (N90) was demonstrated to effectively eliminate 99.5% of hexafluoropropylene oxide dimer acid (HFPO-DA) from a synthetic contaminated water matrix. This was accomplished while working with background electrolytes of 500 mg/L Na_2SO_4 and 100 mg/L NaCl , alongside a 1 mg/L HFPO-DA solution. At a water recovery rate of 80%, the resulting concentrations were 4.98 mg/L in the reject and a mere 0.005 mg/L in the permeate. Electrochemical oxidation (EO) treatment of the NF reject facilitated the breakdown of HFPO-DA, leading to a substantial reduction in energy and electrode costs, surpassing the efficiency of EO treatment alone on raw water by over an order of magnitude. The role of electrochemically activated sulphate was identified as a catalyst for oxidation. The study concluded that the combination of NF and EO represents a viable and sustainable strategy for the cost-effective elimination of HFPO-DA and other PFASs from contaminated water. It was also recommended that measures be adopted to address the byproducts resulting from electrochemical oxidation, with options such as biological reduction within the NF reject. Impressively, the study showcased that the use of reverse osmosis coupled with under-vacuum evaporation can drastically curtail the volume of regeneration effluents requiring incineration for PFAS destruction by over 96.5%.

In summation, these investigations underscore the effectiveness of synergizing NF with advanced oxidation as a potent and economically viable approach for eradicating PFASs from polluted water. While the NF phase handles the bulk of PFAS removal, advanced oxidation effectively disposes of the residual compounds. This integrative approach not only achieves high removal efficiencies but also significantly mitigates the volume of PFAS-laden waste, necessitating proper disposal.

2.3. Adsorption/Membrane Separation Treatment

Adsorption is a commonly employed strategy to combat the presence of PFASs in contaminated water. However, reusing spent adsorbents requires effectively dealing with the adsorbed PFASs—typically by desorbing PFASs and incineration of the desorbed solution. The economic and safe viability of these approaches relies on minimizing the volume of desorbed PFAS solution. This is where membrane processes come into play, offering a practical way to reduce solution volumes.

In a study conducted by Zaggia et al. [38], three robust anion exchange resins (Purolite® A520E, A600E, and A532E) were utilized to remove trace levels of PFOA, PFOS, PFBA, and PFBS from drinking water-targeted groundwater (with concentrations in the hundreds of nanograms per litre range). Among these, A600E (non-hydrophobic) and A520E (moderately hydrophobic) exhibited lower sorption capacities compared to A532E (highly hydrophobic). They demonstrated that while A600E and A532E could be regenerated using solvent-free, dilute solutions of non-toxic NH_4Cl and NH_4OH . A532E required concentrated solutions of methanol or ethanol along with 1% NH_4Cl . Notably, they integrated reverse osmosis with under-vacuum evaporation, drastically reducing the volume of regeneration effluents requiring incineration by over 96.5% (Figure 4) [38]. In this setup, the reverse osmosis module operated at 20–22 bars with an average recovery rate of 65%. The volume of regeneration eluate was decreased by a factor of 2.9 (to 1.2 L) and subsequently concentrated in an under-vacuum evaporator operating at 35–38 °C until reaching a final volume of 0.11 L.

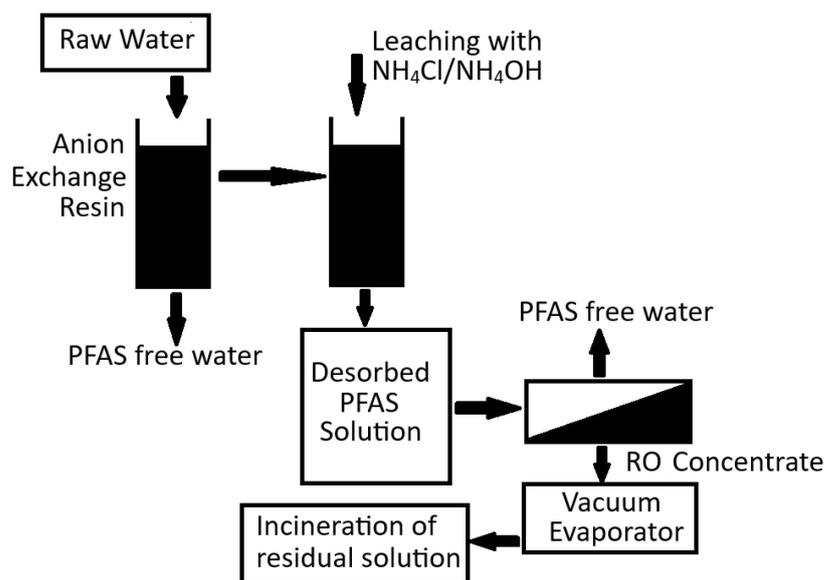


Figure 4. Use of anion exchange resins followed by reverse osmosis (RO) vacuum evaporation and incineration to remove PFAS (modified from [38]).

An alternative sequence involves employing membrane treatment followed by adsorption. In this scenario, the adsorbent must either be disposed of in specialized zones post-usage or destroyed. Alternatively, the adsorbed PFASs could be desorbed into small-volume solutions for subsequent disposal or destruction. Franke et al. [50] conducted a similar exploration in a Swedish NF pilot plant over a 6-month period, achieving over 98%

PFAS removal (Figure 5). After the pilot plant's concentration, the researchers subjected it to adsorption treatment in columns containing GAC materials and anion exchange resins. The latter outperformed the GACs in PFAS elimination based on the cumulative bed volumes each material could process before meeting predefined discharge targets. Previous observations have noted greater adsorption of PFAS on the anion exchanger, attributed to the presence of adsorption sites and functional groups that are more specific to PFAS adsorption compared to those of GAC [51,52].

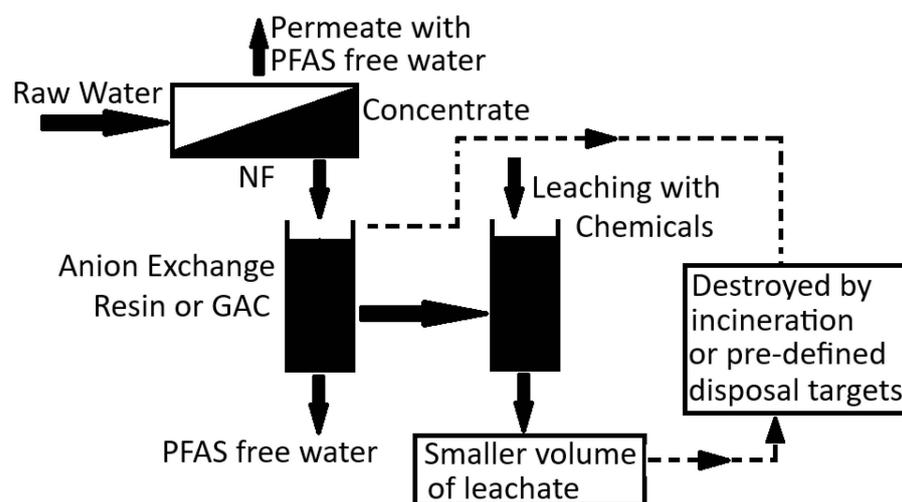


Figure 5. Removal of PFAS using nanofiltration followed by adsorption in a pilotplant study (modified from [50]).

Upon reaching bed volume limits, the GAC was regenerated and reused, while the resin was incinerated and replaced with new material. Cost considerations factored in the procurement of virgin GAC, its regeneration, and transportation to and from the treatment site. In contrast, anion exchange resin costs encompassed the procurement of new material, transportation, and the incineration of spent resin. An economic assessment for various concentrate discharge objectives revealed that using anion exchange resins for discharge goals was more economically viable than relying on GAC for concentrate treatment.

In conclusion, these investigations underscore that anion exchange resins offer a more cost-effective and efficient method for removing PFASs from polluted water compared to GAC utilization. The ability of anion exchange resins to be regenerated with non-toxic solutions, combined with the substantial reduction in regeneration effluent volumes through reverse osmosis with under-vacuum evaporation, further reinforces their advantage. Moreover, these resins can be disposed of in an environmentally safe and sustainable manner.

3. Conclusions

Poly- and perfluoroalkyl substances (PFASs) present a significant health concern at high concentrations in water, impacting both humans and animals. To address this issue, various treatment technologies have been applied to PFAS removal. Conventional techniques like ferric or alum coagulation, granular/micro-/ultrafiltration, aeration, oxidation (e.g., permanganate, ultraviolet/hydrogen peroxide), and disinfection (e.g., chlorine dioxide, chlorination, and chloramination) have proven mostly ineffective in PFAS removal. Advanced methods such as adsorption, ion exchange, ozone oxidation, and membrane processes also face challenges, particularly in the presence of other contaminants, mainly dissolved natural organic matter in water whose concentration is much higher than that of PFASs.

The primary hurdle lies in not only removing PFASs from water but also degrading the removed PFASs. In the adsorption process, the adsorbent must selectively remove

PFASs amidst other contaminants. Once removed, the adsorbed PFASs must be destroyed. This can be achieved by leaching the adsorbed PFASs into a smaller volume of solution, making it easier and less costly to handle during the incineration process for PFAS destruction. Furthermore, the adsorbent can be rejuvenated for repeated use. In membrane technology, ultrafiltration (UF) and microfiltration (MF) prove ineffective as their pores are larger than the molecular size of PFASs. Nanofiltration (NF) and reverse osmosis (RO) processes, employing higher pressures and smaller membrane pore sizes, effectively remove PFASs. However, these methods demand higher energy consumption and produce a concentrated retentate stream, requiring additional treatment before disposal. Membrane fouling presents an additional challenge, reducing the operational lifespan of the membrane. While oxidation processes are effective, they are typically expensive, time-consuming for complete PFAS degradation, and frequently yield undesirable byproducts.

Given the limitations of individual methods in completely and cost-effectively eliminating PFASs from water, hybrid treatment methods have emerged as a successful approach. Hybrid methods that integrate individual methods have a synergistic effect in removing PFASs. In hybrid methods, one technique extracts PFASs from contaminated water and concentrates them, while the other degrades the extracted PFASs. Examples such as adsorption + oxidation, membrane separation + oxidation, and adsorption + membrane separation + incineration are discussed in the review, highlighting their effectiveness in separating and destroying PFASs from water. However, the majority of studies on these hybrid methods have been conducted under short-term laboratory conditions using synthetic solutions. It is imperative to extend these studies to long-term pilot-scale levels using real wastewater containing PFASs.

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