Comparative Analysis of Treatment Technologies for Per- and Polyfluorinated Substances in Water

A Major Qualifying Project Report

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By

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Abstract

Many per- and polyfluoroalkyl substances (PFAS), which are characterized by fluorinated carbon chains, have been identified as chemicals of concern due to their toxicity, widespread distribution, and persistence in the environment. This study analyzes the conventional and novel treatment technologies of activated carbon, anion exchange resin, high-pressure membranes, electrocoagulation, foam fraction, ozonation, molecular imprinted polymer adsorbents, bioremediation, electrolysis, photolysis, and sonochemical degradation in regard to PFAS removal. Discussion of each treatment technology, including mechanism, advances, and effectiveness is presented. Further optimization of conventional and novel treatment technologies to remove PFAS from water is necessary. Future research will continue the development of treatment trains, in which multiple synergistic technologies are incorporated into one treatment process, to enhance removal efficiency and cost-effectiveness.

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1. Introduction to PFAS

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals consisting of a molecule with a carbon chain "backbone" with attached fluorines. As the shortest and strongest chemical bond in nature, the C-F bond can hold a dissociation bond energy of up to 547 kJ/mol (Simmie and Curran, 2009). The C-F bond is responsible for the unique characteristics of the 5,000 chemicals that make up the PFAS group, which are categorized as depicted in Figure 1. Due to their distinctive properties, PFAS have been used in hundreds of manufacturing and industrial applications (EPA, 2020B).

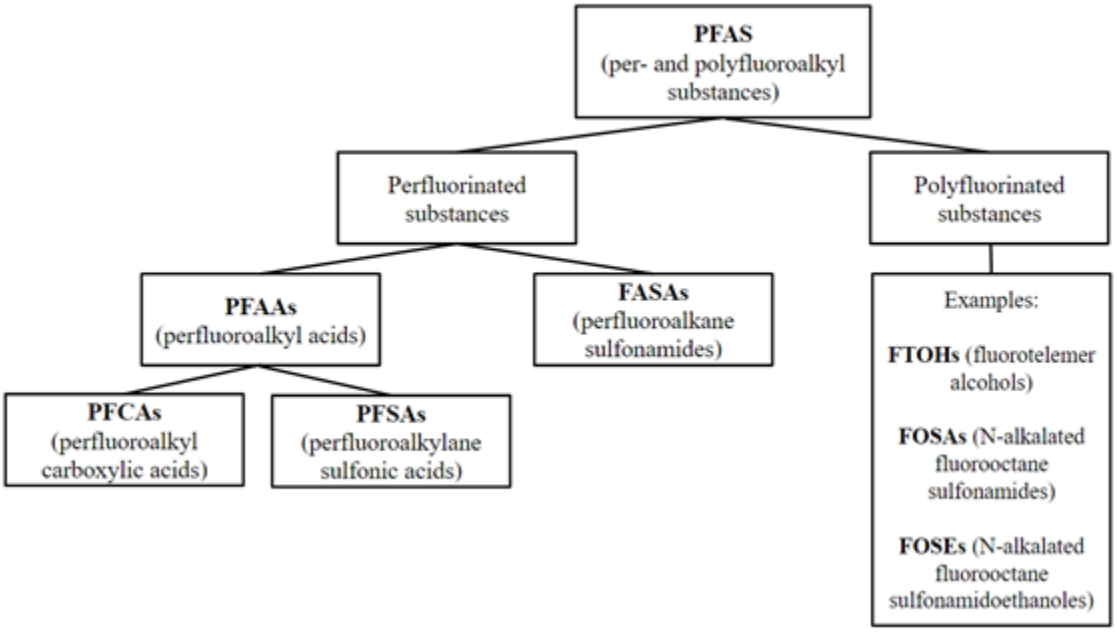


Figure 1: *Categorization of PFAS Types*

Perfluoroalkyl substances are compounds in which all hydrogens on all carbons (except for those associated with functional groups) are replaced with fluorine atoms. In polyfluoroalkyl substances, only some hydrogens on the carbon atoms are replaced by fluorines. The two most predominant and well-studied PFAS, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic

acid (PFOA), are both considered long-chain perfluoroalkyl acids. Chemical structures of PFOS and PFOA are depicted in Figure 2.

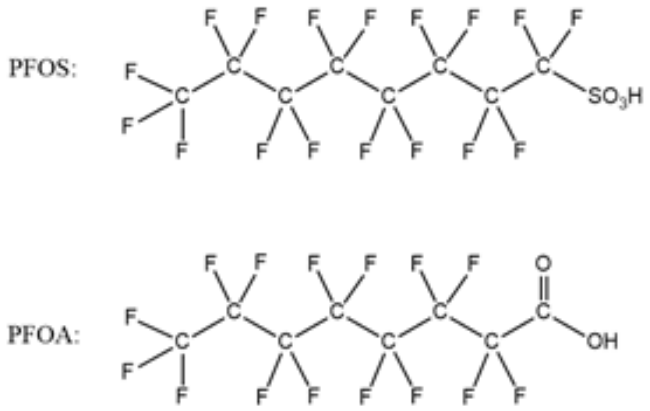


Figure 2: *Chemical Structures of PFOS and PFOA*

Following extensive study and analysis of PFOS and PFOA, EPA established a health advisory level of 70 parts per trillion (ppt) for the two compounds either separately or combined (EPA, 2019). Chemical manufacturing companies have thus phased these chemicals out of their processes. Instead, shorter-chain perfluoroalkyl acids, such as perfluorononanoic acid (PFNA), perfluorobutanesulfonic acid (PFBS), and perfluorohexanoic acid (PFHxA), serve as their key replacement chemicals. Manufacturers claim that these next-generation chemicals are less hazardous due to their chain of six or fewer carbon atoms rather than eight (Walker and Rundquist, 2017). Ongoing studies are evaluating the risks associated with these shorter-chain PFAS chemicals.

1.1. Physical and Chemical Properties

PFAS consist of chains of carbon atoms of varying lengths (typically C4 to C16) strongly bonded to fluorine atoms, as seen in Figure 3 (Alexander *et al.*, 2008). The unique chemistry of C-F bonds yields extraordinarily recalcitrant chemicals, which serves as the foundation for the distinct characteristics and environmental impact of PFAS (Environmental Working Group, 2003).

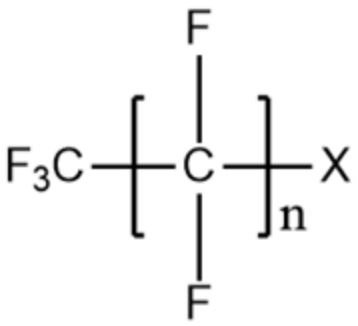


Figure 3: *General Chemical Structure of PFAS*

These chemicals are very persistent, soluble, and nonvolatile. As PFAS are hydrophobic, lipophobic and oleophobic, they experience resistance to heat, water, and oil (Alexander *et al.*, 2008). Furthermore, PFAS resist thermal, chemical, and biological degradation. The combination of these properties with their tendency to bioaccumulate leads to high toxicity at very low concentrations.

Key physical and chemical properties of PFOS and PFOA are summarized in Table 1.

Table 1: *Physical and Chemical Properties of PFOS and PFOA*

Property	PFOS	PFOA
Chemical Formula	$C_8HF_{17}O_3S$	$C_8HF_{15}O_2$
Molecular Weight (g/mol)	500.13	414.09
Boiling Point (°C)	259	192.4
Vapor Pressure (mm HG at 25°C)	~0.002	0.525
Solubility in Water (mg/L)	680	~9,500

1.2. Historical Contamination

In 1949, DuPont introduced an impressive advancement in cookware: Teflon coatings. Teflon is the tradename for polytetrafluoroethylene, a type of PFAS. While Teflon proves very successful as a non-stick surface, it also provides a plethora of environmental and health risks.

As production of Teflon increased at DuPont's Parkersburg, WV plant, various illnesses within the community increased as well. Pregnant female employees of the respective DuPont plant as well as animals on nearby farms began to give birth to offspring with birth defects such as facial deformities (ABC, 2010). DuPont released fifty women workers in order to avert risk, acknowledging that such high-level exposure may cause birth defects in pregnant women, but the company continued to claim that the chemical was safe to use within the home at normal cooking temperatures. However, when the chemical became overheated during cooking, ultrafine particles were released into the air, which could be inhaled by anyone nearby. Eventually, sickness due to such scenarios became known as the two-day "Teflon flu" (ABC, 2010). Various other illnesses appeared throughout Parkersburg, including the blackening of teeth, tumors in dogs, and cases of testicular cancer (Soechtig, 2018).

DuPont and 3M, the only manufacturers of PFOS in the United States at the time, had already been selling the chemical to other companies for a wide variety of applications for some time. By the 1970s, the chemicals were being incorporated into floss, popcorn bags, clothing, furniture materials, and many other industrial and consumer products. Production of PFAS increased dramatically as their use significantly expanded into several different industries (EPA, 2019). The lipid- and water-repellency of PFAS makes them suitable as surface-active agents in different applications, such as stain- and water-resistant coatings for fabrics and carpets, which are particularly useful in apparel and construction industries (Alexander *et al.*, 2008). Many coatings for paper products such as wrappers, bags and boxes approved for food contact also

contain perfluorinated chemicals (Walker and Rundquist, 2017). Due to the extreme persistence of C-F bonds, PFAS are also suitable for applications involving high temperatures as well as contact with strong acids and bases (Alexander *et al.*, 2008), and found useful in aerospace, chemical pharmaceutical, electronics, energy, oil and gas, and semiconductor industries. PFAS are also commonly used within the firefighting industry. With the ability to reduce surface tension, perfluorinated chemicals can create stable foams (Codling *et al.*, 2014) and are therefore a major component of aqueous film forming foam (AFFF) used for controlling fires.

As a result, these sources along with other industries such as healthcare, textile mills, and wastewater treatment plants are all contributors to PFAS releases into the air, soil, and water (EPA, 2019). Global annual production of PFOS-based compounds eventually increased from 500 tons in the 1970s to 4,500 tons by the 1990s (Codling *et al.*, 2014).

In a study of human blood, it was found that nearly everyone in the developed world had some detectable level of PFAS within their bloodstream. Since the main sources of contamination were industrial waste and consumer products that each spread the material over time, exposure to PFAS was involuntary. 3M pledged to phase out PFOA by the end of 2002, while DuPont merely replaced the original Teflon chemical with GenX compounds, which show similar test results.

1.3. Adverse Health Effects

Human exposure to PFAS can occur through several routes such as ingestion, dermal contact, and inhalation. For instance, PFOA in microwave popcorn paper bags has been found at concentrations as high as 300 ng/g (Alexander *et al.*, 2008). Upon heating in a microwave, these paper bags release traces of PFOA to the oil that coats the popcorn kernels. PFAS contamination has also been found in the tap water supplies of 15 million Americans in twenty-seven states (Walker and Rundquist, 2017). One study revealed that the estimated average intake of PFOS

with drinking water of the general adult populations of Italy, the Netherlands, Sweden, and the United Kingdom is 0.24 ng/kg body weight per day (Alexander *et al.*, 2008).

Human exposure is also largely affected by circumstantial factors, such as place of residence. With such strong chemical and biological stability, PFAS are not expected to degrade in the environment (Alexander *et al.*, 2008). Therefore, it can be expected that those residing in close proximity to a facility that either uses or produces PFAS will experience higher levels of exposure.

Due to their persistence, certain PFAS bioaccumulate and remain in the body for extended periods of time (EPA, 2020B), leading to adverse health effects in animals, including humans. One study of over 70,000 volunteers proved that PFAS are linked to six different diseases: kidney cancer, testicular cancer, ulcerative colitis, thyroid disease, preeclampsia, and high cholesterol (Soechtig, 2018). Ingestion of PFAS is also associated with liver toxicity, developmental toxicity, and immunotoxicity.

1.4. Ongoing Regulations

In 2006, the United States Environmental Protection Agency (EPA) invited eight major companies of the PFAS industry, including 3M, Arkema, Asahi, BASF Corporation, Clariant, Daikin, DuPont, and Solvay Solexis, to join the 2010/2015 PFOA Stewardship Program (EPA, 2018A). Their objectives were two-fold: 1) to achieve a 95% reduction in facility emissions to all media of PFOA and precursor chemicals that can break down to PFOA by 2010; and 2) to work toward the elimination of these chemicals from emissions and products by 2015. Most participating companies stopped the manufacture and import of long-chain PFAS by replacing them with alternative chemicals, while other companies exited the PFAS industry entirely.

In response to immense public concern, EPA established a drinking water health advisory level of 70 ppt for PFOS and PFOA either separately or combined in 2016. However, in 2018,

the Centers for Disease Control and Prevention estimated a safe level of exposure nearly ten times smaller than that established by EPA. Nineteen states also have independent, stricter standards. In Massachusetts, as of December 2019, the maximum contaminant level (MCL) is 20 ppt for the total of PFOA, PFOS, PFNA, PFHpA, PFHxS, and PFDA compounds.

EPA has taken further regulatory actions to address PFAS in manufacturing and consumer products. Under the New Chemicals program, EPA reviews alternatives for PFOS and PFOA and determines the concern associated with the toxicity, fate, and bioaccumulation present (EPA Feb 2020). EPA also frequently publishes regulations known as Significant New Use Rules (SNURs), which require manufacturers and processors of these chemicals to notify EPA of new uses before they are commercialized. These SNURs have impacted several hundred PFAS chemicals.

2. Conventional Treatment Technologies

Conventional technologies for PFAS removal from water include activated carbon adsorption, anion exchange on resins, and separation with high-pressure membranes. While these treatment technologies are considered to be established technologies and have wide applications, including point-of entry (POE) and point-of-use (POU) locations within homes, performance can vary greatly with site-specific conditions (EPA, 2018B). However, these treatment technologies are each based on separation and concentration, so their PFAS-contaminated products must be furthered managed via additional treatment or destruction. With high cost and low removal efficiency for shorter-chain PFAS, these conventional technologies must be further explored through bench-scale optimization testing in order to confirm their viability in regard to long-term operating cost and standardized system design parameters (Chiang and Im, 2019).

2.1. Activated Carbon Adsorption

Activated carbon is the most common treatment technology for PFAS removal. As water flows through activated carbon, contaminants sorb to the surface of the carbon and are removed from the water (EPA, 2018B). This sorption mechanism occurs due to both electrostatic and hydrophobic interactions.

As a highly porous material with strong heterogeneous surfaces, activated carbon provides a large surface area to which contaminants can adsorb (Merino *et al.*, 2016; EPA, 2018B). Since adsorption is both a physical and chemical process of accumulating a substance, contaminant chemicals such as PFAS “stick” to the carbon, specifically at the interface between liquid and solid phases, as the water passes through the system as seen in Figure 4 (EPA, 2018B). However, activated carbon must be replaced when all available surface area has been taken up by contaminants because additional contaminants will no longer be able to sorb onto the carbon.

Spent media may be replaced with fresh media or regenerated to remove the sorbed contaminants (EPA, 2018B).

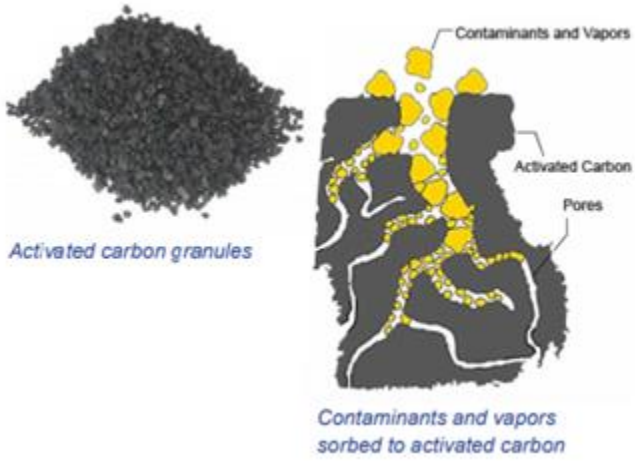


Figure 4: *Activated Carbon Schematic (adapted from EPA, 2012)*

The two most studied activated carbon forms are granular activated carbon (GAC) and powdered activated carbon (PAC). The fundamental difference between GAC and PAC is the size, and the cost of manufacture for the difference in particle size (Greenbank and Knepper, 2002). In particular, GAC has proven efficient in removing PFAS from water as a filter medium (Environmental Information System, 2020). It can be 100% effective for a relatively short period of time, but that time largely depends on a multitude of factors, such as the type of carbon used, carbon bed depth, influent water flow rate, PFAS structure, solution pH, temperature, and co-contaminants present in the water (EPA, 2018B). For instance, solution pH affects the adsorbent's charge, which in turn affects the electrostatic interactions and ultimately, the removal efficiency. PFAS structure also contributes to removal efficiency because additions of CF_2 moieties increase the hydrophobic character of the PFAS and therefore increase the hydrophobic interactions between the perfluoroalkyl tail and the hydrophobic surfaces of the sorbent (Merino *et al.*, 2016).

PAC is significantly smaller than GAC, with a typical diameter of less than 0.1 mm. The higher surface areas and larger micropores of GAC enable more advantageous diffusion of PFAS (Merino *et al.*, 2016). Further, PAC must be used only through direct addition to water followed by removal within the clarification stage (Environmental Information System, 2020; EPA, 2018B). However, such operation results in less efficiency and less cost-effectiveness on a long-term operational basis when compared to GAC (Environmental Information System, 2020). Even with high PAC dosages, it will not likely remove a significant amount of PFAS.

Proven disadvantages of activated carbon include its low removal efficiency for shorter-chain PFAS, likely due to their lower hydrophobic character, as well as its potential competitive adsorption with co-contaminants present in water, such as natural organic matter (Chiang and Im, 2019; American Water Works Association, 2019). Additionally, slow GAC adsorption rates may increase operating time, spent media requires regeneration via heating processes, and waste residuals must be disposed of properly for further treatment (American Water Works Association, 2019). Rather than investing in the equipment to regenerate activated carbon properly, many facilities simply replace the GAC instead (Environmental Information System, 2020).

Many manufacturers are enhancing their activated carbon filters to maintain their relevance and use. For instance, upon recognizing the lack of efficient GAC regeneration options, Battelle developed a regenerant solution to reduce operation and maintenance (O&M) costs and increase the system lifetime (Battelle, 2019). Such a solution allows for on-site recycling of spent GAC media. Preliminary studies have shown that regenerated GAC sorbs PFOS and PFOA with nearly the same efficiency as the original GAC (Battelle, 2019). Another manufacturer, Calgon Carbon, has enhanced their FILTRASORB® technology, which features reagglomerated bituminous

coal-based GAC, to retain carbon bed segregation after repeated backwashing and hydraulic transport and to treat typical levels of PFOS, PFOA, and GenX compounds to non-detect levels (Calgon Carbon, 2020). However, typical contact times may need to be extended to achieve practical breakthroughs for the shorter-chain PFAS.

Several case studies have reported high capital and O&M costs for activated carbon treatment systems. One plant in Oakdale, Minnesota with ten filters cost approximately $3 million to construct and requires approximately $25,000 for annual O&M costs (Cummings *et al.*, 2015). Additionally, the carbon must be replaced every eighteen months, costing approximately $250,000 each time (Cummings *et al.*, 2015). However, these costs vary significantly across different case studies. For instance, another report of plant upgrades including eight new filters in Wilmington, North Carolina cost approximately $46 million to install with annual O&M costs of $2.9 million for 4.4 MGD capacity of water to be treated (Stoiber *et al.*, 2020).

To enhance overall cost-effectiveness, the operating cost of GAC must be reduced and the spent media must be recycled in a beneficial manner (Chiang and Im, 2019). Further research should also determine the influence of environmental matrices and co-contaminants on PFAS removal efficiency within activated carbon treatment.

2.2. Anion Exchange Resin

Ion exchange resins serve as a medium for ionic contaminant removal and have proven effective for PFAS. Ion exchange is defined as the physical-chemical process in which ions are swapped between a solution phase and a solid resin phase (EPA, 2007). The insoluble matrix of an ion exchange resin usually consists of small microbeads, made from hydrocarbons, that are highly porous, insoluble to acid, base, and water, and act like magnets for ions (EPA, 2018B). Contaminant chemicals are attracted to these microbeads, become associated with ionic

functional groups on the resin, and are removed as the water passes through the system. The hydrophobic character of PFAS favors the conversion of PFAS molecules from the fully hydrated state to the sorbed state so strongly that the passage from solution to resin is still favored even in mildly hydrophobic and non-hydrophobic resin (Zaggia *et al.*, 2016).

There are two broad kinds of ion exchange resin: anionic and cationic. Although less extensively studied than GAC, anion exchange resins are particularly effective at removing long-chain PFAS. Anionic resins are positively charged, so they attract negatively charged contaminants, such as PFAS, onto the exchange sites of the resin beds (EPA, 2018B; Chiang and Im, 2019).

The effects of influent PFAS concentration, PFAS structure, treatment design parameters (including resin type, resin dosage, bed depth, and flow rate), competing co-contaminants, and the hydrophobicity of the resin functional group on the anion exchange resin performance have been explored (Chiang and Im, 2019; Zaggia *et al.*, 2016; EPA, 2018B). Studies have demonstrated that resin functional groups with higher hydrophobicity have higher sorption capacity for PFAS (Zaggia *et al.*, 2016). Sulfonic PFAS functional groups result in the highest resin sorption capacity, followed by carboxylic groups, and shorter-chain PFAS tend to correspond with lower sorption capacity (Zaggia *et al.*, 2016).

Resins must be regenerated upon exhaustion, which can be accomplished by a small amount of NaCl or NaOH and methanol. Regeneration could also be leveraged upon by running ion exchange columns in series with regeneration occurring every other column (Merino *et al.*, 2016). The successful in-situ regeneration of resin to near-original conditions as well as its ability to achieve complete PFAS removal with simultaneous removal of co-contaminants make anion exchange resin a promising technology for PFAS removal (Dixit *et al.*, 2019; Woodard *et*

al., 2017). However, anion exchange resins are typically more expensive than GAC, so both their benefits and limitations must be taken into consideration (EPA, 2018B).

Based on information provided by GAC and resin manufacturers, including Calgon Carbon, Cabot Norit, Emerging Contaminant Treatment Technologies, Evoqua, and Purolite, Merrimack Village District directly compared PFAS treatment options including both GAC and ion exchange resin. While GAC held an approximate capital cost of $3.95 million and an O&M cost ranging $130,000-$265,000 per year, ion exchange resin were significantly more expensive with an approximate capital cost of $4.75 million and an O&M cost ranging $320,000-$920,000 per year (Metcalf *et al.*, 2018).

2.3. High-Pressure Membranes

High-pressure membranes, which include both nanofiltration and reverse osmosis, have demonstrated effective removal of PFAS from water. These processes largely depend on membrane permeability as water is pushed through a membrane with very small pores that acts like a barrier to prevent contaminants from entering the water (EPA, 2018B; Franke *et al.*, 2019A). Both technologies are used to remove highly recalcitrant organic materials from water.

Since nanofiltration membranes have a thin selective layer with pores varying from 1-10 nanometers in size, PFAS separation via nanofiltration is primarily controlled by size-exclusion and electrostatic interactions (TetraTech, 2013; Boo *et al.*, 2018). However, reverse osmosis membranes are much tighter than nanofiltration membranes, with pores varying from 0.1-1 nanometers in size. Therefore, while nanofiltration rejects hardness efficiently but allows sodium chloride to pass through, reverse osmosis rejects all salts equally (TetraTech, 2013; EPA, 2018B; Boo *et al.*, 2018).

Efficacy of high-pressure membrane filtration can be greatly influenced by PFAS structure and water matrix characteristics. One study found that membrane treatment achieved higher

removal efficiencies of >95% for longer-chain PFAS compared to the short-chain homologues, likely due to the more hydrophobic character (Franke *et al.*, 2019A). Another study explored the effect of water matrix characteristics on the removal of PFOS and PFOA from various water sources. Natural water matrices achieved approximately 38% higher PFAS rejections than laboratory-prepared water, which was attributed to the dissolved organic matter and cations that are naturally present in water (Toure and Sadmani, 2019). High-pressure membrane filtration can remove this organic matter, as well as other co-contaminants, since it allows incorporation of multiple treatment goals into one treatment process (Toure and Sadmani, 2019). Another distinct benefit of high-pressure membrane filtration is long operation lifetime with control of membrane fouling (Franke *et al.*, 2019A).

High-pressure membranes for PFAS removal have been implemented in many water treatment facilities. The installation cost of reverse osmosis upgrades in a Brunswick County, North Carolina plant was estimated at $137 million with annual O&M costs of $4.7 million for a flow of 16 MGD (Stoiber *et al.*, 2020). However, costs can greatly vary due to diverse environmental conditions. A new reverse osmosis plant treating 10 MGD in Decatur, Alabama experienced much lower installation and annual O&M costs of $30 million and $1 million, respectively (Stoiber *et al.*, 2020).

Even though studies demonstrate >90% removal efficiency via high-pressure membrane filtration for a wide range of PFAS, including shorter-chain compounds, treatment and/or disposal of PFAS-contaminated products remains a challenge (Toure and Sadmani, 2019; Franke *et al.*, 2019A). Therefore, proper management of the membrane reject water and enhancement of the overall systems will be focal points of research moving forward. For instance, utilization of larger pore diameters than those commonly incorporated in commercial nanofiltration

membranes may reduce cost and environmental impact of the waste management (Boo *et al.*, 2018).

3. Novel Treatment Technologies via Separation

Novel treatment technologies via separation discussed herein include electrocoagulation, fractionation, and molecular imprinted polymer adsorbents. These treatment technologies follow the same general separation-based mechanisms of conventional treatment technologies, but they have potential to provide higher efficacy, reduced cost, and shorter residence time for PFAS removal from water. Similarly to conventional treatment technologies which are also based in separation, these treatment technologies also ultimately relocate the contamination issue as they require further treatment and/or destruction of their PFAS-contaminated end products.

3.1. Electrocoagulation

Electrocoagulation, a coagulation process enhanced by the passing of electrical current through a liquid which eventually changes to a solid or semi-solid state, has proven effective in the removal of PFAS from water with high sorption capacities (Lin *et al.*, 2015). The process typically consists of a rapid mixing stage, in which chemicals are quickly added to the water to promote contact between the hydrolyzed chemicals and contaminants in the water, and a subsequent slow mixing stage, in which contaminants and precipitated chemical species clump together into amorphous flocs (Xiao *et al.*, 2013). Therefore, the primary mechanism of PFAS removal via electrocoagulation is the hydrophobic interactions of fine floc adsorption as the metal hydroxide flocs strongly sorb pollutants and remove them from the water as seen in Figure 5 (Lin *et al.*, 2015; Xiao *et al.*, 2013). The large surface area of these flocs enables effective and rapid adsorption, but similarly to other sorption-based treatment technologies, electrostatic and hydrophobic interactions ultimately determine sorption efficiency (Lin *et al.*, 2015; Xiao *et al.*, 2013).

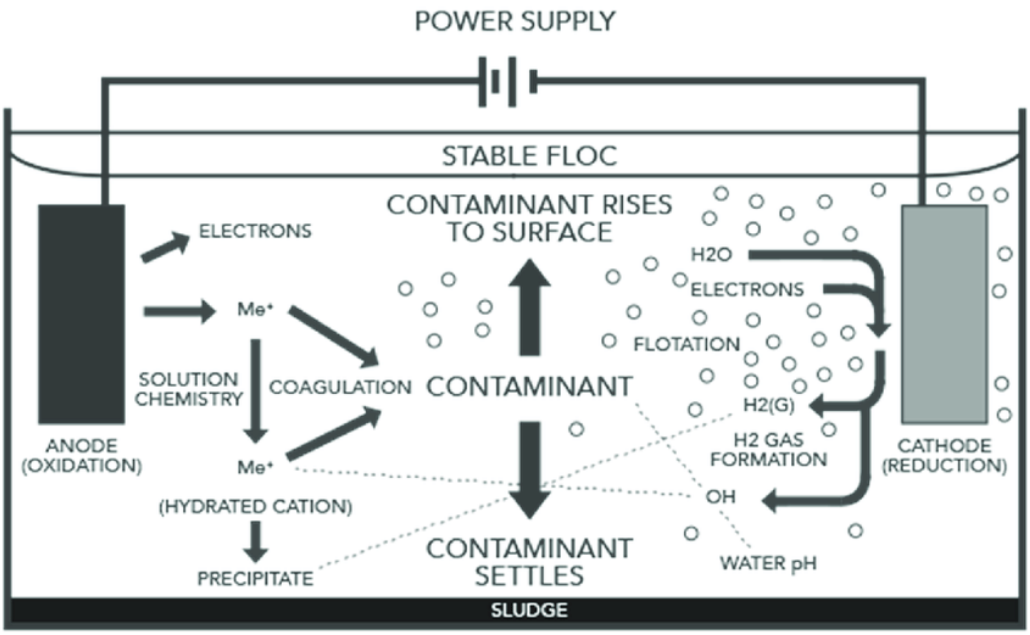


Figure 5: *Electrocoagulation Schematic (adapted from Posavic et al., 2019)*

One study demonstrated 96.7% PFAS removal efficiency using zinc hydroxide flocs with a wide range of PFAS concentrations after 10 minutes of electrocoagulation (Lin *et al.*, 2015). Another study presented a 99.6% conversion rate of PFOA onto flocs when treated with Al-Zn electrodes (Liu *et al.*, 2018). Since zinc is an essential semi trace element with a US EPA drinking water ordinance limit of 5 mg/L, it serves as a feasible coagulant option (Lin *et al.*, 2015). Furthermore, increase in coagulant dosage results in more surface area and lower pH, which both increase the number of adsorption sites available (Xiao *et al.*, 2013). Lower pH allows the surface charge of flocs to shift in a positive direction, effectively increasing PFOS and PFOA removal (Xiao *et al.*, 2013). PFAS structure is another dominant factor influencing its removal rate from water (Xiao *et al.*, 2013). Electrocoagulation achieved a higher removal rate for PFOS rather than PFOA, likely due to the tendency of sulfonate groups to readily adsorb on oxidized surfaces as well as the slightly smaller molecular size of PFOA, which contributes to slightly higher hydrophobicity (Xiao *et al.*, 2013).

Electrocoagulation holds several advantages, including operational simplicity, low energy consumption, and high conversion efficiency of pollutants onto flocs (Liu *et al.*, 2018). This process also has flexibility in set-up requirements, allowing it to be coupled with other treatment technologies, such as membrane separation or electrolysis, in order to achieve superior cost-effectiveness (Lin *et al.*, 2015). As an innovative technology, electrocoagulation must be further researched and characterized to potentially become a competitive treatment technology for PFAS removal from water.

3.2. Fractionation

Fractionation, which includes a set of emerging treatment technologies for PFAS removal from water, is a separation process which occurs because of a phase transition, causing a mixture to divide into smaller quantities of varying composition. Researchers have taken advantage of certain PFAS characteristics to demonstrate the potential efficacy of fractionation, specifically foam fractionation and ozonation, in removing PFAS from contaminated water.

3.2.1. Foam Fractionation

Foam fractionation, in which hydrophobic molecules are separated from liquid through rising columns of foam, can leverage the physicochemical characteristics of PFAS for its removal from water (Philips, 2017). Specifically, in downhole foam fractionation, PFAS are removed as a foam, then eventually extracted as a liquid concentrate (Niven *et al.*, 2019). In a downhole foam fractionation process being developed by OPEC systems, PFAS are isolated and removed from affected groundwater (Philips, 2017). Once compressed air is introduced to a well, air bubbles carry PFAS as a foam to the surface and the PFAS concentrate receives further treatment. Preliminary results for this system suggest 99% PFAS removal efficiency within minutes (Philips, 2017).

Foam fractionation serves as an operationally simplistic and cost-effective treatment technology with no evident environmental harm. Ongoing research continues, especially for the development of column testing methods for foam fractionation (Niven *et al.*, 2019).

3.2.2. Ozonation

Preliminary experiments with ozonation, a chemical water treatment technology based on the infusion of ozone into water, have proven the technique to be effective in treating PFAS-contaminated water. The gas termed ozone is composed of three oxygen atoms (O_3), making it a strong oxidant with an oxidation potential of 2.07 V (Franke *et al.*, 2019B). Ozone is commonly used to create micro-nano-bubbles with large available surface area and high zeta potential, which results in successful mitigation of bubble coalescence and stability improvement (McDonough, 2019).

Specific manufacturers, namely Arcadis and Evocra, have developed systems of multistage ozonation columns which remove 95% of PFAS from the influent water (Evocra, 2016; Ross *et al.*, n.d.). Inside of the columns, ozone creates bubbles whose high surface area allows for effective extraction of concentrated PFAS (Ross *et al.*, n.d.; Evocra, 2016). This concentrated form of the residual PFAS, which represents only a small fraction (0.5-2.0%) of the initial volume, is later passed through traditional polishing processes, such as nanofiltration (Evocra, 2016; McDonough, 2019). Pilot test data demonstrate 99.96% PFAS removal after ozonation and its corresponding polishing process (McDonough, 2019).

Ozonation consistently and efficiently removes PFOS, PFOA, and other PFAS precursors to meet the EPA-established health advisory level of 70 ppt. It also generates no spent media, produces minimal waste, and addresses co-contaminants such as organics, metals, and nutrients without requiring any pre-treatment stages (McDonough, 2019; Evocra, 2016).

Furthermore, the technology developed by Evocra, OCRA, is extremely versatile in its application and installation (Evocra, 2016). The system can be installed either as a stand-alone process or coupled with existing equipment as a pre- or post-treatment system. Its design results in very low energy and reagent consumption (Evocra, 2016). Technology standards will be challenging to establish as different ozone dosages are required for different pH levels. However, since ozone has proven to be successful through fractionation, the efficacy of other gases in fractionation for PFAS removal are also being explored (McDonough, 2019).

3.3. Molecular Imprinted Polymer Adsorbents

Molecular imprinted polymers (MIPs) are polymers that have been processed via molecular imprinting, which results in cavities within the polymer matrix with an affinity for a particular template molecule. As adsorbents for PFAS removal, MIPs have shown potential for outperforming conventional treatment processes with uptake percentages of PFAS as high as 90% (Barin, 2018; Zhang *et al.*, 2019). For selective adsorption of PFAS, MIPs are usually synthesized by the precipitation polymerization method as seen in Figure 6 (Zhang *et al.*, 2019).

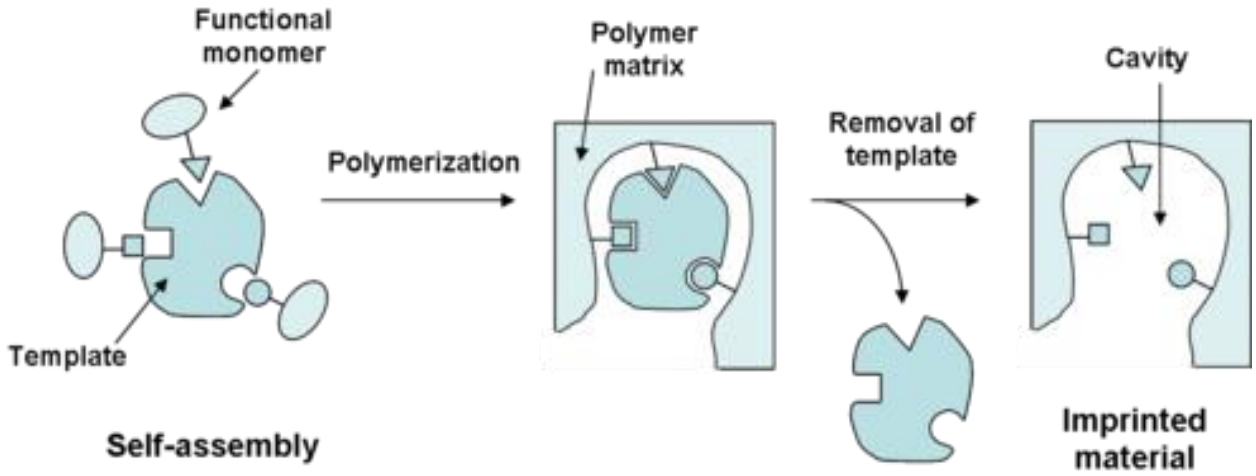


Figure 6: *Imprinted Material Polymerization (adapted from Mlunguza et al., 2019)*

MIPs can achieve fast sorption equilibrium largely due to the surface sorption of the anionic PFAS onto the electrostatic surface of the fine adsorbents (Deng *et al.*, 2009). Since MIPs can create specific binding sites complementary to its target molecules, key advantages of MIPs include this selectivity toward respective targets as well as its high affinity (Zhang *et al.*, 2019). Furthermore, the unique structure of innovative sorbents such as cationic polyaniline and polypyrrole allows for both the strong electrostatic interactions with PFAS functional head groups as well as the hydrophobic interactions with the PFAS fluorinated tails to occur, causing higher selectivity and wider application than conventional treatment technologies (Sierra-Alvarez, 2020). These benefits could result in reduction of cost and waste production; however, there exists a significant range of adsorptive capacity of MIP adsorbents for PFAS (Sierra-Alvarez, 2020; Barin, 2018). Similar to activated carbon and other adsorbent materials, MIP adsorbents must be replaced or regenerated when their capacity is reached or when breakthrough of contamination occurs.

As MIP adsorbents are considered emerging technology for PFAS treatment, much more research must be completed before MIP adsorbents can be cost-effectively produced large-scale. Future work will likely focus on the characterization of adsorption parameters for specific polymers as well as the optimization of reaction parameters (Barin, 2018).

4. Novel Treatment Technologies via Destruction

Novel treatment technologies via destruction discussed in this chapter include bioremediation, advanced oxidation and reduction processes, specifically electrolysis and photolysis, and sonochemical degradation. To offer a permanent solution, these methods often feature cleavage of the C-F bond, which initiates degradation (as seen in Appendix A), enabling mineralization of the PFAS compounds instead of merely concentrating the contaminant as separation-based technologies do (Merino *et al.*, 2016). However, these treatment technologies are often preceded by a separation-based technology to increase efficacy and cost efficiency of the overall water treatment system.

4.1. Bioremediation

The potential for bioremediation, the use of microorganisms to consume or break down environmental contaminants, to remove PFAS from water has also been explored. These microorganisms generally digest contaminants, altering them into small amounts of water and harmless gases such as carbon dioxide. The scarce amount of waste products, as well as its low requirements of both equipment and energy, prove bioremediation to be advantageous.

Many studies employ this emerging technology by using extracellular enzymes directly, since they hold less stringent growth requirements, such as temperature and nutrient availability, than many other potentially useful microbes (Mahendra, 2016). However, these preliminary experiments demonstrate low efficacy. Packaging active enzymes such as MnP in vault nanoparticles proved unsuccessful in transforming PFOA, likely due to lack of mediators. Another study demonstrated up to 60% removal of PFOS and PFOA during 100-day incubations of *Acidimicrobium sp.* Strain A6 (A6) cultures (Huang and Jaffe, 2019). A6 was proven to achieve defluorination of PFOS and PFOA as the concentrations of fluoride, sulfate, and shorter-chain PFAS products increased with reaction time (Huang and Jaffe, 2019).

With great variability of success in removing PFAS from water via bioremediation, more research must be completed before claiming it as a feasible option. Since bioremediation using microbial whole cells is greatly constrained by concerns of biofouling, longer incubation times and higher enzyme concentrations in future enzyme-catalyzed solutions may be explored in such work (Mahendra, 2016).

4.2. Advanced Oxidation and Reduction Processes

Advanced oxidation and reduction processes are a set of chemical treatment techniques that remove organic materials from water through oxidation and reduction and are considered a promising method for destruction of PFAS in water (Cui *et al.*, 2020). These processes are largely dependent on the presence of nonselective free radicals, which are species with an unpaired electron that have a strong tendency to either give up the unpaired electron or accept another electron to form a pair, therefore serving as very effective reductants and oxidants (Vellanki *et al.*, 2013).

Advanced oxidation processes (AOPs) are based on generation of strong oxidizing agents, such as hydroxyl radicals ($^{\bullet}OH$), which interact with organic pollutants to add onto unsaturated C-C bonds, remove a hydrogen atom from its target molecule, or substitute into aromatic rings (Trojanowicz *et al.*, 2018). Similarly, advanced reduction processes (ARPs) have demonstrated efficacy in destroying PFAS through generation of highly reductive hydrated electrons (e_{aq}^-) (Cui *et al.*, 2020; Vellanki *et al.*, 2013). Only a small fraction of e_{aq}^- is dedicated to PFAS degradation since they also target several co-contaminants (Cui *et al.*, 2020).

Factors with significant impact on AOPs and ARPs include solution pH, temperature, and solute dosage. Degradation tends to improve with both increasing solution pH and increasing temperature (Cui *et al.*, 2020). Degradation improves with increasing solute dosage only until a critical level, beyond which degradation efficiencies decrease (Cui *et al.*, 2020).

Most AOPs and ARPs for PFAS treatment have not yet been explored within real water matrices, so much research remains to be done for their successful development, including investigation of the impact of co-contaminants and operating conditions on PFAS degradation (Vellanki *et al.*, 2013; Cui *et al.*, 2020).

The specific advanced oxidation and reduction processes of electrolytic and photolytic methods will be presented.

4.2.1. Electrolysis

Electrolysis, also known as electrochemical oxidation, is an advanced oxidation process that consists of the chemical decomposition which results from an electric current passing through an ionic solution. The fundamental system consists of two electrodes (an anode and a cathode) connected to a power source.

The surface of the anode experiences generation of strongly oxidizing $^{\bullet}OH$, so surface coating holds significant influence over the contamination degradation rate (Trojanowicz *et al.*, 2018). With sufficient voltage between the anode and the cathode, PFAS molecules give up an electron to the cathode, which begins a continuously repeated electron transfer reaction, removing carbon through decarboxylation pathways, that results in sulfate and fluoride ions as final products (Merino *et al.*, 2016).

Many manufacturers have leveraged upon the high durability and cost-effectiveness of these electrodes. For instance, AECOM has begun developing an emerging treatment technology called DEFLUORO, which operates upon electrochemical oxidation and reduction (AECOM, 2018). Several studies have explored the effect of reactor configuration and electrode material on the degradation efficiency of PFAS. Two-sided reactors have significantly enhanced degradation efficiency to 98.9% for PFOS and 96% for PFOA after only three hours of electrolysis, which can be attributed to the larger anode area available for the reactions (Liang *et al.*, 2018).

Regarding electrode material, research has developed requirements for the metal oxide being used, including chemical inactivity to prevent passivation, long lifespan, low fabrication cost, and robustness during operation (Trojanowicz *et al.*, 2018). Titanium and tin are the most commonly used electrodes; however, they have significant shortcomings, such as the slow PFAS degradation associated with titanium and high fabrication cost associated with tin (Wang *et al.*, 2020). Many studies agree that boron-doped diamond outperforms other electrode material options due to its strong oxidation capacity (Schaefer *et al.*, 2019; Trojanowicz *et al.*, 2018). Within experiments utilizing boron-doped diamond as the electrode material, treatment occurred through direct electron transfer and $^{\bullet}OH$ generation had no notable impact on the PFAS removal rate (Schaefer *et al.*, 2019). Several degradation trends appeared, such as the slower degradation of PFOA than PFOS, of shorter-chain PFAS than long-chain PFAS, and of branched PFAS than linear PFAS (Liang *et al.*, 2018; Schaefer *et al.*, 2019).

As a research technology, successful electrolysis performance is much more challenging in the natural environment than in the laboratory, largely due to limited electroactive surface area of electrodes for practical application. Further development of the process, including optimization, design, and scaling, will be accompanied by several potential benefits (Trojanowicz *et al.*, 2018; Wang *et al.*, 2020). For instance, solar panels, which can last several years if maintained properly, could likely serve as the source of electricity for this treatment technology and significantly reduce costs associated with energy consumption. To exploit these benefits, future efforts in electrolysis for PFAS treatment must focus on the treatability of precursor compounds as well as the longevity of the boron-doped diamond anode (Schaefer *et al.*, 2019).

4.2.2. Photolysis

Photolysis, which involves the decomposition or separation of molecules by light, serves as a potential destructive PFAS treatment technology. Heterogeneous photocatalysis in particular is an advanced technology with relatively high efficacy in PFAS removal (Xu *et al.*, 2017).

Heterogeneous photocatalysis occurs because of energy difference between the valence and conduction bands with light exposure, which enables oxidation-reduction reactions to occur (Merino *et al.*, 2016). The mechanism behind heterogeneous photocatalysis involves the generation of electrons and corresponding positively charged holes that react with adsorbed contaminants to decompose them on the surface of the photocatalyst particles (Xu *et al.*, 2017). Process efficacy depends largely on this structure-reactivity relationship centered around the photo-generated electrons and holes (Bentel *et al.*, 2019; Xu *et al.*, 2017). The e_{aq}^- are considered to be the reductive species responsible for PFAS photodegradation as they cleave C-F bonds efficiently (Lyu *et al.*, 2015; Bentel *et al.*, 2019). Several studies have observed increasing concentrations of fluoride and sulfate ions coupled with declining PFAS concentrations, confirming that the original C-F and C-S bonds were destroyed by irradiation (Yamamoto *et al.*, 2007; Xu *et al.*, 2017; Lyu *et al.*, 2015). Multiple reaction pathways, such as H/F exchange and dissociation of terminal functional groups, lead to the formation of various defluorinated intermediate products, such as formic acid and acetic acid, which are further mineralized to degradation products such as shorter-chain perfluorinated compounds (Bentel *et al.*, 2019; Giri *et al.*, 2011; Lyu *et al.*, 2015).

Studies of PFAS degradation via photolysis have not yet been standardized. One study found PFOA degradation to be greatly enhanced to almost 100% removal in a 4-hour reaction period with combined wavelengths of 254 nm and 185 nm (Giri *et al.*, 2011). Another study demonstrated 50-90% degradation of PFOS, PFOA, and other emerging PFAS compounds with

low-pressure mercury lamps at ambient temperature and within a slightly basic solution (Bentel *et al.*, 2019). Other studies performed experiments over ten-day periods with nearly complete PFOS degradation (Yamamoto *et al.*, 2007; Lyu *et al.*, 2015).

While standardized protocols have not been established for these studies, the influence of certain factors that affect the degradation efficiency has been demonstrated. The extent of decay and defluorination, which represents the ratio of fluoride concentration to the total fluorine content in the sample before oxidation, are largely impacted by PFAS concentration and structure (Giri *et al.*, 2011; Bentel *et al.*, 2019). The oxidizing-reducing ability of the photo-generated electron-hole pairs is also affected by catalysts and various environmental conditions such as temperature, pH, and wavelength (Xu *et al.*, 2017; Lyu *et al.*, 2015). With decreasing initial PFAS concentrations, removal efficiencies slightly decreased, but defluorination significantly increased, potentially due to accelerated decomposition of the reaction's fluorinated intermediates (Giri *et al.*, 2011). Regarding PFAS structure, PFOA degrades approximately twice as fast as PFOS, likely due to the presence of an ionic headgroup in PFOS (Yamamoto *et al.*, 2007; Lyu *et al.*, 2015). Similarly, studies found that PFOS degraded 68% in water, but 92% in alkaline 2-propanol after the same amount of irradiation, while addition of t-BuOH in another study also significantly increased the degradation rate (Yamamoto *et al.*, 2007; Lyu *et al.*, 2015). Catalysts, especially In_2O_3, which can complete 100% PFOA removal within 30 minutes with only few modifications to its morphology, have been proven to enhance PFAS degradation efficiency in water (Xu *et al.*, 2017). Overall, PFAS degradation improves with increasing solution temperature but only to a certain extent since high temperatures increases the generation of hydrated electrons, but too high temperature could lead to inactivation of the catalyst (Xu *et al.*, 2017, Lyu *et al.*, 2015). However, the impact of pH on photocatalytic degradation is still

unclear. Some studies claim that increasing initial pH leads to decreasing photocatalytic degradation due to its impact on the photocatalytic performance of the ionizable compounds, while others demonstrated that PFOS decomposition rates decrease at lower pH (Xu *et al.*, 2017; Lyu *et al.*, 2015). It has also been proposed that catalysts need to absorb relatively shorter wavelengths of light to successfully facilitate the electronic transition and cleave C-F bonds (Xu *et al.*, 2017).

Photodegradation is a promising PFAS treatment technology due to its operational simplicity, but it must be both standardized and enhanced for maximum efficiency (Lyu *et al.*, 2015). While catalysts increase the PFAS degradation efficiency, they come with increased costs and potential environmental concerns (Lyu *et al.*, 2015). As an innovative technology, photolysis must be further researched and characterized to potentially become a competitive treatment technology for PFAS removal from water. Future work will likely focus on proper design of UV jacket and reactor, synthesis of high-performing, low-cost catalysts, and establishment of recycling methods for catalysts to make the process continuous (Giri *et al.*, 2011; Xu *et al.*, 2017). Potential methods could include the utilization of solar energy and natural contaminants to strengthen the generation of e_{aq}^- (Lyu *et al.*, 2015).

4.3. Sonochemical Degradation

As sound waves have been studied extensively for the degradation of many organic contaminants, sonochemical degradation, which consists of the breaking of chemical bonds and the formation of radicals using high-frequency ultrasound, has been identified as a promising PFAS treatment technology (Shende *et al.*, 2019).

Acoustic irradiation of the aqueous solution induces cavitation, which involves the formation, growth, and collapse of bubbles within a liquid due to the changing pressure field created by the sound waves (Moriwaki *et al.*, 2005; Fernandez *et al.*, 2016). Pyrolysis inside and

in the vicinity of the collapsing cavities creates a microenvironment characterized by extremely high temperature, near 5,000 K (Moriwaki *et al.*, 2005; Shende *et al.*, 2019; Fernandez *et al.*, 2016). The heat energy released in these collapsed cavity areas breaks down nearby chemicals, thus releasing highly reactive radicals into the aqueous solution where they oxidize further chemicals (Shende *et al.*, 2019). In particular, the sonolytic degradation of PFAS follows sequential pyrolytic steps as the PFAS first forms volatile fluorinated intermediate byproducts at the interfacial region between the cavities and the bulk aqueous solution (Moriwaki *et al.*, 2005). These intermediate byproducts then get thermally mineralized into organic components, such as fluoride and sulfate ions, which indicates successful cleavage of the original C-F and C-S bonds (Shende *et al.*, 2019; Fernandez *et al.*, 2016).

As adsorption of non-volatile compounds at the interior cavity-water interface leads to PFAS degradation, the first step of sonolytic degradation largely depends on PFAS structure at the time of adsorption (Shende *et al.*, 2019). This first step is considered the rate-limiting step as the reaction rate is contingent upon the number of active cavities present as well as the diffusion of contaminants into the cavities (Shende *et al.*, 2019). One study, which was performed with ultrasonic waves of 575 kHz and initial concentration between 1 mg/L and 20 mg/L PFOS or PFOA, showed higher sonolytic degradation for PFOA than PFOS at lower concentrations; however, at higher concentrations, PFOS showed slightly higher sonolytic degradation than PFOA (Shende *et al.*, 2019). The discrepancy is likely due to the significantly greater amount of cavity sites participating in PFOS degradation as well as the tendency for sulfonate groups to thermally degrade at temperatures higher than those at which corresponding carboxylic groups thermally degrade (Shende *et al.*, 2019). In another study, which investigated sonochemical degradation of different PFAS at 500 kHz, PFOS and PFOA defluorinated at comparable rates

(Fernandez *et al.*, 2016). However, the degradation rate increased significantly with increasing perfluoroalkyl chain length, which can be attributed to increasing compound hydrophobicity and therefore the concentration at the cavity-water interface (Fernandez *et al.*, 2016). Chemical structure, especially the hydrophilic functional group, had a weak, but notable correlation with degradation rate, as the carboxylates degraded slightly faster than the sulfonates of the same perfluorocarbon chain length under corresponding conditions (Fernandez *et al.*, 2016). This higher defluorination rate can be attributed to the lower thermal activation energies of carboxylates (Fernandez *et al.*, 2016). Shorter-chain PFAS are less likely to degrade efficiently via sonochemical degradation due to their less hydrophobic character (Fernandez *et al.*, 2016).

RemWell has developed the InSRT reactor, which destroys PFAS through sonolysis after collecting the PFAS-contaminated groundwater within a horizontal well (Laramay, 2020). One study achieved half-life times of 22 min and 43 min for PFOS and PFOA, respectively, and the specific InSRT reactor technology can reduce O&M costs by approximately 40% by avoiding the expensive energy costs associated with pumping and incineration. As a research technology, the scalability and strong performance of sonochemical degradation depends largely on further research of the effects of parameters such as initial concentration (which can impact saturation kinetics), power density, solution temperature, and frequency (Laramay, 2020; Moriwaki *et al.*, 2005; Fernandez *et al.*, 2016; Shende *et al.*, 2019).

5. Comparative Analysis of Treatment Technologies

The comparative analysis presented in Table 2 evaluates each discussed conventional and novel PFAS treatment technology in terms of stage of development, relative cost, PFOS and PFOA removal efficiencies, potential to remove shorter-chain PFAS, and material and energy consumption. Potential benefits and limitations are also discussed at the end of the chapter.

Table 2: *Comparative Analysis of Treatment Technologies*

Treatment Technology	Relative Cost	PFOS/PFOA Removal Efficiencies	Potential to Remove Shorter-Chain PFAS	State of Development	Material Lifetime Expectancy	Energy
Activated Carbon	$$	≥90%	-	I, M	-	-
Anion Exchange Resin	$$	≥90%	-	I, M	-	+
High-Pressure Membranes	$$	≥90%	+	I, M	+	-
Electrocoagulation	$$	>95%	+/-	P	+	+
Foam Fractionation	$	>95%	+/-	P	+	+/-
Ozonation	$$$	95%	+	P	+	+
MIP Adsorbents	$$	90%	+/-	B	+/-	+/-
Bioremediation	$$	60%	+/-	B	+/-	+
Electrolysis	$$	>95%	-	P	+	+
Photolysis	$$$	>90%	+	P	+	+
Sonochemical Degradation	$$	>95%	-	P	+	-

5.1. Stage of Development

The state of development of a treatment technology is determined by the extent to which the technology has been applied in various settings. EPA established the following four categories

for the stage of development of treatment technologies: established, research, innovative, and emerging.

Established technologies are defined as those which are implemented within more than 1% full-scale facilities in North America. Research technologies include those which have been tested at laboratory or bench scale. Innovative technologies consist of those which have been studied in a full-scale demonstration, have been implemented within North America for less than five years, have some degree of initial use, or are considered to be established technologies in other countries (Tetra Tech, 2013). Emerging technologies are defined as those which have been tested at a pilot or demonstration scale, or that have been implemented at full-scale in three or fewer installations for less than a year (Tetra Tech, 2013).

As conventional PFAS treatment technologies, activated carbon, anion exchange resin, and high-pressure membranes, including nanofiltration and reverse osmosis, were each categorized as established technologies. Relevant research treatment technologies include electrolysis and sonochemical degradation, attributed to the significant amount of studies which employ these technologies and demonstrate effective PFAS removal. Since electrocoagulation and photolysis have been studied in full-scale demonstrations, they were classified as innovative technologies (Liu *et al.*, 2018; Xu *et al.*, 2017). With significantly less proven success, foam fractionation, ozonation, MIP adsorbents, and bioremediation were marked as emerging technologies (Franke *et al.*, 2019B).

EPA further classifies the stage of development of treatment technologies with the following adapted descriptive labels based on the current implementation of each treatment technology.

- Bench scale (denoted as “B”);

- Pilot scale (denoted as “P”);
- Full-scale industrial applications (denoted as “I”); and
- Full-scale municipal applications (denoted as “M”).

Activated carbon, anion exchange resin, and high-pressure membranes are all implemented within both full-scale industrial and municipal applications and were therefore awarded both the I and M designations. Treatment technologies in the pilot scale phase, including electrocoagulation, foam fractionation, ozonation, electrolysis, photolysis, and sonochemical degradation, were given the P designation. Treatment technologies in the bench scale phase, including MIP adsorbents and bioremediation, were identified with the B designation.

5.2. Relative Cost

Relative cost of each treatment technology is represented by one of the following designations:

- $, which represents relatively low cost;
- $$, which represents relatively medium cost; and
- $$$, which represents relatively high cost.

Both capital and annual O&M costs contribute to the ultimate relative cost of each treatment technology. Capital costs include aspects such as equipment, buildings, add-on costs, and indirect costs. Annual O&M costs include aspects such as labor, materials and supplies, residual management, and energy consumption (EPA, 2020A).

The most cost-effective treatment technology with the lowest relative cost was foam fractionation. Activated carbon, anion exchange resin, high-pressure membranes, electrocoagulation, MIP adsorbents, bioremediation, electrolysis, and sonochemical degradation all had comparable relatively medium cost. Ozonation and photolysis hold the highest relative

cost, attributed to materialistic costs of ozone and catalysts, such as In_2O_3, that these treatment technologies depend on.

5.3. Removal Efficiencies

Removal efficiencies, specifically of PFOS and PFOA, for each treatment technology are represented within the comparative analysis as percentages as previously cited in Chapters 2, 3, and 4. Every treatment technology, with the exception of bioremediation, has demonstrated the ability to achieve at least 90% PFAS removal efficiency. Electrocoagulation, foam fractionation, electrolysis, and sonochemical degradation even achieve >95% PFAS removal efficiency under optimized conditions.

The ability of treatment technologies to remove shorter-chain PFAS was evaluated on a positive, neutral/mixed, and negative scale. A positive evaluation confirms that the treatment technology can remove shorter-chain PFAS, while a negative evaluation indicates incapability. A neutral/mixed evaluation indicates conflicting research outcomes or insufficient information available for accurate evaluation.

Only high-pressure membranes, ozonation, and photolysis have demonstrated significant removal efficiencies for shorter-chain PFAS, notably PFHxA, perfluoro-n-butyric acid (PFBA), and perfluoropentanoic acid (PFPeA) (Franke *et al.*, 2019A). Activated carbon, anion exchange resin, electrolysis, and sonochemical degradation have performed ineffectively for shorter-chain PFAS removal. Further research efforts must be completed to accurately evaluate the potential shorter-chain PFAS removal efficiencies for electrocoagulation, foam fractionation, MIP adsorbents, and bioremediation.

5.4. Material and Energy Consumption

Material and energy consumption were evaluated on a positive, neutral/mixed, and negative scale as established by EPA (with slight modifications for simplification purposes) (Tetra Tech, 2013).

5.4.1. Material Lifetime Expectancy

Material lifetime expectancy considers both the longevity and potential reuse of the necessary materials within the treatment technology. A positive evaluation confirms that the treatment technology holds a long material lifetime expectancy and/or is capable of reusing materials. A negative evaluation indicates that the treatment technology holds a short material lifetime expectancy and/or is incapable of reusing materials. A neutral/mixed evaluation indicates conflicting research outcomes or insufficient information available for accurate evaluation.

A large majority of the treatment technologies, namely high-pressure membranes, electrocoagulation, foam fractionation, ozonation, electrolysis, photolysis, and sonochemical degradation, hold long material lifetime expectancy and/or are capable of material reuse. As activated carbon and anion exchange resin require frequent and expensive regeneration of media, they were given negative evaluations for material lifetime expectancy. Notably, many facilities prefer to replace activated carbon instead of investing the time and money required for regeneration (Environmental Information System, 2020). MIP adsorbents and bioremediation require additional research regarding their material consumption before an accurate evaluation can be given.

5.4.2. Energy

The energy evaluation considered the amount of energy required to maintain the process. A positive evaluation confirms that the treatment technology consumes a low amount of energy and a negative evaluation indicates that the treatment technology consumes a significant amount of

energy. A neutral/mixed evaluation indicates conflicting research outcomes or insufficient information available for accurate evaluation.

The least energy-intensive treatment technologies include anion exchange resin, electrocoagulation, ozonation, bioremediation, electrolysis, and photolysis. With slight modifications, some of these treatment technologies may even assist in reducing energy consumption of their overall respective water treatment systems.

The most energy-intensive treatment technologies include activated carbon, high-pressure membranes, and sonochemical degradation. Foam fractionation and MIP adsorbents require additional research regarding their energy consumption before an accurate evaluation can be given.

5.5. Potential Benefits and Limitations

Beyond the evaluated criteria presented in the comparative analysis, notable potential benefits and limitations of treatment technologies should be taken into consideration. For instance, many treatment technologies, such as activated carbon, high-pressure membranes, electrocoagulation, foam fractionation, and photolysis, hold very simplistic operations. This ease of operation often enables flexibility in set-up requirements and therefore versatility in application, such as inclusion in residential POE or POU systems (Lin *et al.*, 2015; Evocra, 2016). Additionally, a significant portion of the treatment technologies address multiple treatment goals through their singular respective process. These technologies, which include activated carbon, anion exchange resin, high-pressure membranes, electrocoagulation, and advanced oxidation processes such as electrolysis and photolysis, can remove many co-contaminants found in natural water.

However, these treatment technologies often suffer from competitive adsorption of the co-contaminants present in solution with PFAS. These co-contaminants can even clog anion

exchange resin and high-pressure membranes, so pretreatment may be required to reduce potential fouling. Further, though they produce high PFAS removal efficiencies, novel treatment technologies via destruction are often both more challenging to demonstrate in the natural environment and more expensive to operate due to incorporated catalysts which may cause potential environmental concerns (Lyu *et al.*, 2015).

It should also be noted that all separation-based treatment technologies consistently require further treatment and/or destruction of their PFAS-contaminated end products.

6. Results and Discussion

With six distinct evaluation criteria, each treatment technology performs uniquely in the comparative analysis. With lower PFAS removal efficiencies and significant necessary further research, MIP adsorbents and bioremediation are not competitive treatment technologies. Although activated carbon is currently the most widely used treatment technology, its lower PFAS removal efficiency coupled with low potential to remove shorter-chain PFAS as well as high material and energy consumption make it a less favorable option.

Anion exchange resin, high-pressure membranes, photolysis, and sonochemical degradation performed neutrally. The most notable advantages of anion exchange resin and high-pressure membranes are their energy efficiency and potential to remove shorter-chain PFAS, respectively. The high cost of photolysis and energy consumption of sonochemical degradation currently inhibit them from becoming truly competitive treatment technologies.

The most viable treatment technologies include electrocoagulation, foam fractionation, ozonation, and electrolysis. Electrocoagulation achieves high PFAS removal efficiencies with low material and energy consumption. However, its potential to remove shorter-chain PFAS must be further researched throughout its development to potentially become a conventional treatment technology. Similarly, though foam fractionation achieves high PFAS removal efficiencies with relatively low cost and low material consumption, further research must be completed to evaluate its potential to remove shorter-chain PFAS and to determine its energy consumption.

Though ozonation holds relatively high cost, it also demonstrates high PFAS removal efficiency and potential to remove shorter-chain PFAS with low material and energy consumption. If its cost-effectiveness can be enhanced through process modifications, ozonation has potential to become a conventional treatment technology. Electrolysis also demonstrates

potential to become a conventional treatment technology as it achieves high PFAS removal efficiency with low material and energy consumption but would require process modifications to gain potential for removing shorter-chain PFAS.

While electrocoagulation, foam fractionation, ozonation, and electrolysis may be viable PFAS treatment technologies, their stage of development is critical to consider. As emerging and innovative technologies, these treatment technologies have only been performed within bench-scale or pilot testing. To further develop the limited number of competitive PFAS treatment technologies, future efforts will likely focus on performing further pilot testing before moving onto field implementation and establishment of commercially available products (Lu *et al.*, 2020). Notably, many of these treatment technologies require additional research specifically to confirm their ability to treat PFAS to below the EPA's established health advisory level of 70 ppt for PFOS and PFOA.

6.1. Treatment Trains

Though successful in destroying PFAS, novel destruction-based treatment technologies often require extreme operating conditions, such as high operating temperature or material or energy consumption, leading to higher overall costs (Lu *et al.*, 2020). To improve effectiveness, enhance practical feasibility, and maximize economic and environmental benefits of PFAS treatment technologies, many researchers have begun merging multiple treatment technologies together into one cohesive process, termed treatment trains. Incorporation of multiple technologies into the same process can refine the PFAS removal efficiency, diminish total cost, decrease energy consumption, and reduce harmful byproducts (Lu *et al.*, 2020). The most viable treatment trains will include at least one destruction-based treatment technology to fully mineralize any PFAS directly from the environment or from a concentrated product stream of a separation-based treatment technology acting as an earlier step of the treatment train.

6.2. Site-Specific Conditions

When evaluating and comparing treatment technologies, fully understanding the source of the contaminant is critical. Doing so will provide answers regarding which types of co-contaminants are present and to what extent. Performance of treatment technologies will vary as conditions vary both spatially and temporally. Ultimately, the most promising PFAS treatment technology depends on the magnitude of contamination, present co-contaminants, and local environmental factors.

7. Conclusions and Recommendations

Though activated carbon, anion exchange resin, and high-pressure membranes are established as conventional PFAS treatment technologies, their low removal efficiencies and high material and energy consumption have fostered interest in developing novel treatment technologies. Several novel separation-based and destruction-based treatment technologies have demonstrated success in PFAS removal from water in preliminary studies. Due to their associated early stages of development, further research and characterization must be completed to consider any to be potentially competitive. Many of these treatment technologies have effectively removed select PFAS from water only under idealized laboratory conditions. To evaluate their performance with real water matrices, future research efforts are required to determine degradation parameters and decomposition products of each treatment technology. Development of a design basis for confidently employing PFAS treatment technologies, including optimized conventional treatment technologies, is critical.

In the meantime, treatment trains of multiple PFAS treatment technologies, selected based on site-specific conditions, are an emerging trend to effectively remove PFAS from water. Due to their compiled performance in the comparative analysis, the following treatment trains prove most viable:

- Anion exchange resin with electrolysis;
- Nanofiltration with electrocoagulation; or
- Nanofiltration with ozonation.

These treatment trains would enhance removal efficiency and cost-effectiveness of PFAS removal from water. Economic and environmental benefits may also be strengthened through the

implementation of these treatment trains. However, the novel technologies involved must first be further developed to confirm their success in PFAS treatment.

References

ABC. 2010. The Truth About Teflon. ABC's 20/20. Available from: https://www.youtube.com/watch?time_continue=2&v=b3IDF_px4AY.

AECOM. 2018. AECOM's Promising New PFAS Treatment Technology DE-FLUORO™ Shows Complete Destruction of PFAS. AECOM. Available from: https://www.aecom.com/wp-content/uploads/2018/10/PFAS-Info-Sheet.pdf.

American Water Works Association. 2019. Perfluorinated Compounds: Treatment and Removal. American Water Works Association. Available from: https://www.awwa.org/Portals/0/AWWA/Programs/AWWAPFCFactSheetTreatmentandRemoval.pdf.

Alexander J, Auounsson G, Benford D, Cockburn A, Cravedi J, Dogliotti E, Di Domenico A, Fernandez-Cruz M, Fink-Gremmels J, Furst P, Galli C, Grandjean P, Gyzl J, Heinemeyer G, Johansseon N, Mutti A, Schlatter J, van Leeuwen R, van Peteghem C, and Verger P. 2008. European Food Safety Authority;653:1-131. Available from: https://efsa.onlinelibrary.wiley.com/doi/pdf/10.2903/j.efsa.2008.653.

Barin G. 2018. Remediation of Perfluorinated Chemicals in Water Using Novel High-Affinity Polymer Adsorbents. CycloPure. Available from: https://grantome.com/grant/NIH/R43-ES029401-01.

Battelle. 2019. Granular Activated Carbon Regeneration. Battelle. Available from: https://www.battelle.org/government-offerings/energy-environment/environmental-services/pfas-assessment-mitigation/granular-activated-carbon-regeneration.

Bentel M, Yu Y, Li Z, Yong B, Men Y, and Liu J. 2019. Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. Environmental Science and Technology;53(7):3718-3728. Available from: https://pubs.acs.org/doi/full/10.1021/acs.est.8b06648.

Boo C, Wang Y, Zucker I, Choo Y, Osuji C, and Elimelech M. 2018. High Performance Nanofiltration Membrane for Effective Removal of Perfluoroalkyl Substances at High Water Recovery. Environmental Science and Tehcnology;52(13):7279-7288. Available from: https://pubs.acs.org/doi/full/10.1021/acs.est.8b01040.

Calgon Carbon. 2020. PFAS: FILTRASORB® Granular Activated Carbon and Calgon Carbon's equipment line are proven treatment solutions for PFAS removal. Calgon Carbon, a Kuraray Company. Available from: https://www.calgoncarbon.com/pfas/.

Chiang D and Im J. 2019. PFAS Cleanup Approaches – GAC vs Anion Exchange Resin. CDM Smith. Available from: https://www.cdmsmith.com/-/media/Insights/PFAS-Treatment-Options/PFAS-March-Newsletterdocx.pdf.

Codling G, Vogt A, Jones P, Wang T, Wang P, Lu Y-L, Corcoran M, Bonina S, Li A, Sturchio N, Rockne K, Ji K, Khim J, Naile J, and Giesy J. 2014. Historical trends of inorganic and organic fluorine in sediments of Lake Michigan. Chemosphere;114:203-209. Available from: https://www.sciencedirect.com/science/article/pii/S0045653514004317.

Cui J, Gao P, and Deng Y. 2020. Destruction of Per- and Polyfluoroalkyl Substances (PFAS) with Advanced Reduction Processes (ARPs): A Critical Review. Environmental Science and Technology;54(7):3752-3766. Available from: https://pubs.acs.org/doi/10.1021/acs.est.9b05565.

Cummings L, Matarazzo A, Nelson N, Sickels F, and Storms C. 2015. Recommendation on Perfluorinated Compound Treatment Options for Drinking Water. New Jersey Drinking Water Quality Institute Treatment Subcommittee. Available from: https://www.nj.gov/dep/watersupply/pdf/pfna-pfc-treatment.pdf.

Deng S, Shuai D, Yu Q, Huang J, and Yu G. 2009. Selective sorption of perfluorooctane sulfonate on molecular imprinted polymer adsorbents. Frontiers of Environmental Science and Engineering in China;3:171-177. Available from: https://link.springer.com/article/10.1007/s11783-009-0017-4.

Dixit F, Barbeau B, Mostafavi S, and Mohseni M. 2019. PFOA and PFOS removal by ion exchange for water reuse and drinking applications: role of organic matter characteristics. Environmental Science: Water Research and Technology;10. Available from: https://pubs.rsc.org/en/content/articlelanding/2019/ew/c9ew00409b#!divAbstract.

Environmental Information System. 2020. Difference between PAC and GAC. Environmental Information System. Available from: http://www.envis.org/technology/water-treatment/687-difference-between-pac-and-gac.

Environmental Working Group. 2003. PFCs: Global Contaminants. Environmental Working Group. Available from: https://www.ewg.org/research/pfcs-global-contaminants.

EPA. 2007. Removing Multiple Contaminants from Drinking Water: Issues to Consider. United States Environmental Protection Agency. Available from: https://nepis.epa.gov/Exe/ZyPDF.cgi/P1009V6Q.PDF?Dockey=P1009V6Q.PDF.

EPA. 2012. A Citizen's Guide to Activated Carbon Treatment. United States Environmental Protection Agency. Available from: https://clu-in.org/download/Citizens/a_citizens_guide_to_activated_carbon_treatment.pdf.

EPA. 2018A. Fact Sheet: 2010/2015 PFOA Stewardship Program. United States Environmental Protection Agency. Available from: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program.

EPA. 2018B. Reducing PFAS in Drinking Water with Treatment Technologies. United States Environmental Protection Agency. Available from: https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies.

EPA. 2019. Technical Brief for Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS). United States Environmental Protection Agency. Available from: https://www.epa.gov/water-research/pfas-methods-and-guidance-sampling-and-analyzing-water-and-other-environmental-media.

EPA. 2020A. Drinking Water Treatment Technology Unit Cost Models and Overview of Technologies. United States Environmental Protection Agency. Available from: https://www.epa.gov/sdwa/drinking-water-treatment-technology-unit-cost-models-and-overview-technologies.

EPA. 2020B. Risk Management for Per-and Polyfluoroalkyl Substances (PFAS) under TSCA. United States Environmental Protection Agency. Available from: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas#tab-3.

Evocra. 2016. OCRA removes PFAS from contaminated water to below USA EPA drinking water criteria. Evocra. Available from: https://evocra.com.au/source-assets/images/pdf/evocra-pfas-removal-case-study_v3.pdf.

Fernandez N, Rodriguez-Freire L, Keswani M, and Sierra-Alvarez R. 2016. Effect of chemical structure on the sonochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs). Environmental Science: Water Research & Technology;2:975-983. Available from: https://pubs.rsc.org/en/content/articlehtml/2016/ew/c6ew00150e.

Franke V, McCleaf P, Lindegren K, and Ahrens L. 2019A. Efficient removal of per- and polyfluoroalkyl substances (PFASs) in drinking water treatment: nanofiltration combined with active carbon or anion exchange. Environmental Science: Water Research and Technology;11. Available from: https://pubs.rsc.org/en/content/articlelanding/2019/ew/c9ew00286c#!divAbstract.

Franke V, Schafers M, Lindberg J, and Ahrens L. 2019B. Removal of per-and polyfluoroalkyl substances (PFASs) from tap water using heterogeneously catalyzed ozonation. Environmental Science: Water Research and Technology;5:1887-1896. Available from: https://pubs.rsc.org/en/content/articlehtml/2019/ew/c9ew00339h.

Giri R, Ozaki H, and Taniguchi S. 2011. UV photolysis of perfluorooctanoic acid (PFOA) in dilute aqueous solution. Water Science & Technology;63(2):276-282. Available from: https://www.ncbi.nlm.nih.gov/pubmed/21252431.

Greenbank M and Knepper J. 2002. GAC/PAC: Use of Powdered Activated Carbon for Potable Water Treatment in Small Systems. Water Conditioning and Purification Magazine. Available from: http://wcponline.com/2002/11/21/gacpac-use-powdered-activated-carbon-potable-water-treatment-small-systems/.

Huang S and Jaffe P. 2019. Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by Acidimicrobium sp. Strain A6. Environmental Science and

Technology;53(19):11410-11419. Available from: https://pubs.acs.org/doi/10.1021/acs.est.9b04047.

Laramay, F. 2020. In Situ Remediation Technology (InSRT) for Remediation of PFAS Contaminated Groundwater. United States Environmental Protection Agency. Available from: https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/11033/report/0.

Liang S, Pierce R, Lin H, Chiang S, and Huang Q. 2018. Electrochemical oxidation of PFOA and PFOS in concentrated waste streams. Remediation Journal;28(2). Available from: https://onlinelibrary.wiley.com/doi/abs/10.1002/rem.21554.

Lin H, Wang Y, Niu J, Yue Z, and Huang Q. 2015. Efficient Sorption and Removal of Perfluoroalkyl Acids (PFAAs) from Aqueous Solution by Metal Hydroxides Generated in Situ by Electrocoagulation. Environmental Science and Technology;49(17):10562-10569. Available from: https://pubs.acs.org/doi/10.1021/acs.est.5b02092.

Liu Y, Hu X, Zhao Y, Wang J, Lu M, Peng F, and Bao J. 2018. Removal of perfluorooctanoic acid in simulated and natural waters with different electrode materials by electrocoagulation. Chemosphere;201:303-309. Available from: https://www.sciencedirect.com/science/article/pii/S0045653518303412.

Lu D, Sha S, Luo J, Huang Z, and Jackie X. 2020. Treatment train approaches for the remediation of per- and polyfluoroalkyl substances (PFAS): A critical review. Journal of Hazardous Materials;386:121963. Available from: https://www.sciencedirect.com/science/article/pii/S030438941931917X.

Lyu X, Li W, Lam P, and Yu H. 2015. Insights into perfluorooctane sulfonate photodegradation in a catalyst-free aqueous solution. Scientific Reports;5:9353. Available from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4399502/.

Mahendra S. 2016. Bioaugmentation with Vaults: Novel In Situ Remediation Strategy for Transformation of Perfluoroalkyl Compounds. University of California, Los Angeles. Available from: https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2422/ER-2422.

McDonough J. 2019. First Time Use of Ozofractionation to Treat AFFF Release and Validation by TOP Assay. Arcadis. Available from: http://www.newea.org/wp-content/uploads/2019/02/AC19_JMcDonough_26.pdf.

Merino N, Deeb R, Qu Y, and Hawley E. 2016. Degradation and Removal Methods for Perfluoroalkyl and Polyfluoroalkyl Substances in Water. Environmental Engineering Science;33(9). Available from: https://www.researchgate.net/publication/308491366_Degradation_and_Removal_Methods_for_Perfluoroalkyl_and_Polyfluoroalkyl_Substances_in_Water.

Metcalf M, Carney L, and Kitchens B. 2018. Evaluation of PFAS Treatment for Wells 2, 3, 7 & 8 in Merrimack Village District (MVD), Merrimack, NH. Underwood Engineers. Available

from: http://www.mvdwater.org/wp-content/uploads/2018/12/PFAS-Treatment-Feasibility-Report-237-8-Final.pdf.

Mlunguza N, Ncube S, Mahlambi P, and Madikizela L. 2019. Adsorbents and removal strategies of non-steroidal anti-inflammatory drugs from contaminated water bodies. Journal of Environmental Chemical Engineering;7(3):103-142. Available from: https://www.researchgate.net/publication/332966921_Adsorbents_and_removal_strategies_of_non-steroidal_anti-inflammatory_drugs_from_contaminated_water_bodies.

Moriwaki H, Takagi Y, Tanaka M, Tsuruho K, Okitsu K, and Maeda Y. 2005. Sonochemical Decomposition of Perfluorooctane Sulfonate and Perfluorooctanoic Acid. Environmental Science and Technology;39(9):3388-3392. Available from: https://pubs.acs.org/doi/pdf/10.1021/es040342v.

Niven R, Khalili N, Pashley R, Taylor M, Strezov V, Wilson S, Murphy P, and Phillips S. 2019. PFAS source zone remediation by foam fractionation and in situ fluidisation. MacQuarie University. Available from: https://researchers.mq.edu.au/en/projects/pfas-source-zone-remediation-by-foam-fractionation-and-in-situ-fl.

Philips S. 2017. OPEC Systems Delivers PFAS Contamination Breakthrough. OPEC Systems. Available from: https://www.opecsystems.com/article/opec-systems-delivers-pfas-contamination-breakthrough.

Posavic H, Halkijevic I, and Vukovic Z. 2019. Application of electrocoagulation for water conditioning. Environmental Engineering;6(2)59-70. Available from: https://www.researchgate.net/publication/337956616_Application_of_electrocoagulation_for_water_conditioning.

Ross I, Houtz E, McDonough J, and Storch P. n.d. Full-Scale Treatment of PFAS-Impacted Wastewater Using Ozofractionation with Treatment Validation Using TOP Assay. Battelle. Available from: https://www.battelle.org/docs/default-source/conference-proceedings/2019-sediments-conference-proceedings/a7.-characterization-and-remediation-of-pfas-contaminated-sediments-media/532.pdf?sfvrsn=75dc9522_2.

Schaefer C, Andaya C, Higgins C, Strathmann T, Liu H, Burant A, Urtiaga A, Ferguson L, and Choyke S. 2019. Investigating Electrochemical and Catalytic Approaches for In Situ Treatment of PFAS in Groundwater. ESTCP. Available from: https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2424.

Shende T, Andaluri G, and Suri R. 2019. Kinetic model for sonolytic degradation of non-volatile surfactants: Perfluoroalkyl substances. Ultrasonics Chemistry;51:359-368. Available from: https://www.sciencedirect.com/science/article/pii/S1350417718310976.

Sierra-Alvarez R. 2020. Remediation of Per- and Polyfluoroalkyl Impacted Groundwater Using Cationic Hydrophobic Polymers as Ultra-High Affinity Sorbents. University of Arizona. Available from: https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER18-1052.

Simmie J and Curran H. 2009. Formation Enthalpies and Bond Dissociation Energies of Alkylfurans. The Strongest C-X Bonds Known? Journal of Physical Chemistry;113:5128-5137. Available from: https://pubs.acs.org/doi/pdf/10.1021/jp810315n.

Singh R, Fernando S, Baygi S, Multari N, Thagard S, and Holsen T. 2019. Breakdown Products from Perfluorinated Alkyl Substances (PFAS) Degradation in a Plasma-Based Water Treatment Process. Environmental Science and Technology;53:2731-2738. Available from: https://pubs.acs.org/doi/pdfplus/10.1021/acs.est.8b07031?src=recsys.

Soechtig S. 2018. The Devil We Know. Sundance Films.

Stoiber T, Evans S, Temkin A, Andrews D, and Naidenko O. 2020. PFAS in drinking water: an emergent water quality threat. Water Solutions. Available from: https://cdn3.ewg.org/sites/default/files/u352/Stoiber_Evans_WaterSolutions_2020.pdf.

Tetra Tech, Inc. 2013. Emerging Technologies for Wastewater Treatment and In-Plant Wet Weather Management. United States Environmental Protection Agency. Available from: https://www.epa.gov/sites/production/files/2019-02/documents/emerging-tech-wastewater-treatment-management.pdf.

Toure H and Sadmani A. 2019. Nanofiltration of perfluorooctanoic acid and perfluorooctane sulfonic acid as a function of water matrix properties. Water Supply;19(8):2199-2205. Available from: https://iwaponline.com/ws/article/19/8/2199/68839/Nanofiltration-of-perfluorooctanoic-acid-and.

Trojanowicz M, Bojanowska-Czajka A, Bartosiewicz I, and Kulisa K. 2018. Advanced Oxidation/Reduction Processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) – A review of recent advances. Chemical Engineering Journal;335:170-199. Available from: https://www.sciencedirect.com/science/article/pii/S1385894717318776.

Vellanki B, Batchelor B, and Abdel-Wahab A. 2013. Advanced Reduction Processes: A New Class of Treatment Processes. Environmental Engineering Science;30(5):264-271. Available from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3696927/.

Walker B and Rundquist S. 2017. Mapping a Contamination Crisis. Environmental Working Group. Available from: https://www.ewg.org/research/mapping-contamination-crisis.

Wang Y, Pierce R, Shi H, Li C, and Huang Q. Electrochemical degradation of perfluoroalkyl acids by titanium suboxide anodes. Environmental Science: Water Research and Technology;1. Available from: https://pubs.rsc.org/en/content/articlelanding/2020/ew/c9ew00759h#!divAbstract.

Woodard S, Berry J, and Newman B. 2017. Ion exchange resin for PFAS removal and pilot test comparison to GAC. Remediation Journal;27(3). Available from: https://onlinelibrary.wiley.com/doi/abs/10.1002/rem.21515.

Xiao F, Simcik M, and Gulliver J. 2013. Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation. Water Research;47(1):49-56. Available from: https://www.sciencedirect.com/science/article/pii/S0043135412006677?via%3Dihub.

Xu B, Ahmed M, Zhou J, Altaee A, Wu M, and Xu G. 2017. Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanisms, kinetics and controlling factors. Chemosphere;189:717-729. Available from: https://www.sciencedirect.com/science/article/pii/S0045653517315357.

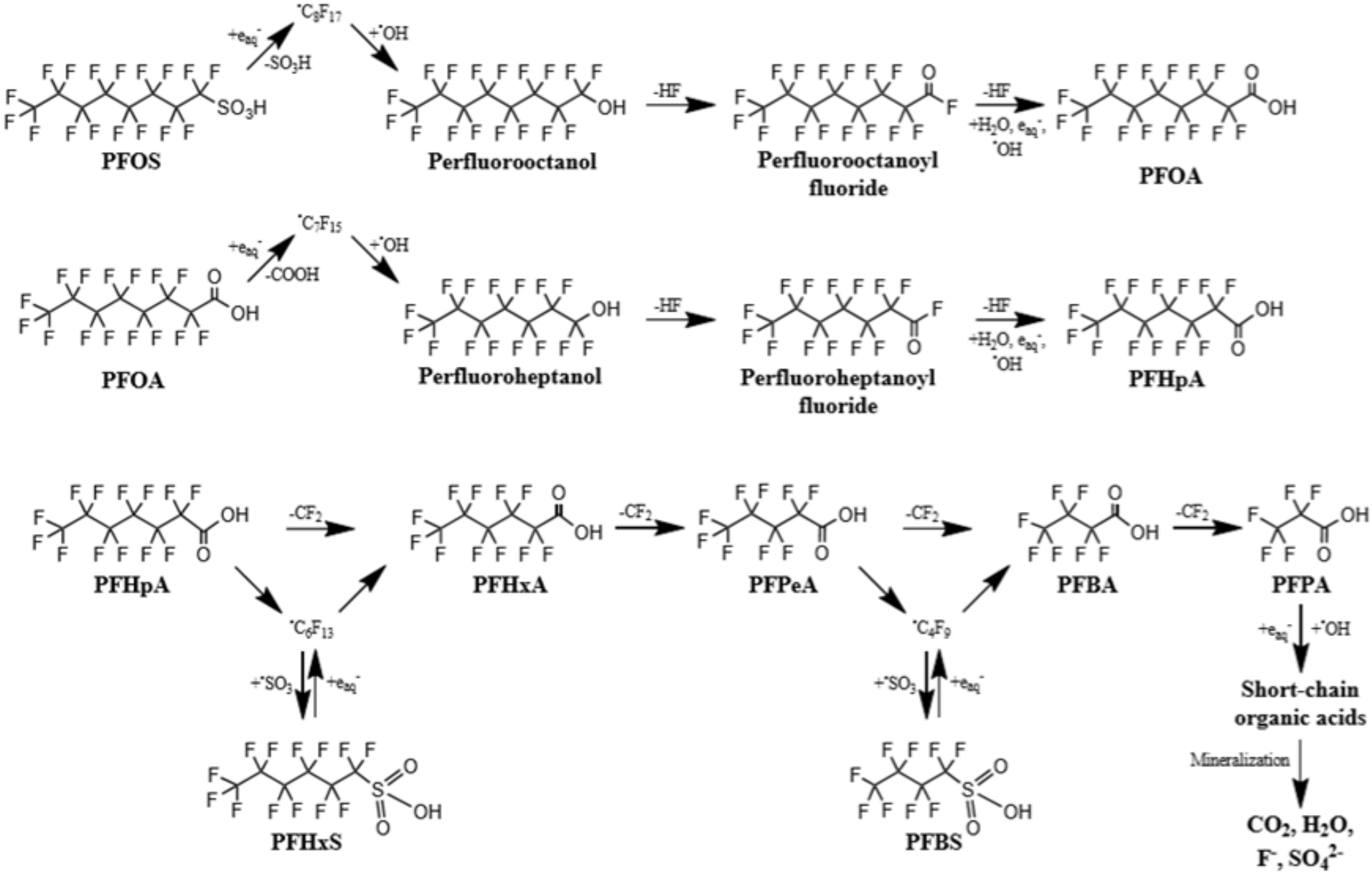
Yamamoto T, Noma Y, Sakai S, and Shibata Y. 2007. Photodegradation of Perfluorooctane Sulfonate by UV Irradiation in Water and Alkaline 2-Propanol. Environmental Science and Technology;41(16):5660-5665. Available from: https://pubs.acs.org/doi/pdf/10.1021/es0706504.

Zaggia A, Conte L, Falleti L, Fant M, and Chiorboli A. 2016. Use of strong anion exchange resins for the removal of perfluoroalkylated substances from contaminated drinking water in batch and continuous pilot plants. Water Research;91:137-146. Available from: https://www.ncbi.nlm.nih.gov/pubmed/26774262.

Zhang D, Zhang W, and Liang Y. 2019. Adsorption of perfluoroalkyl and polyfluoroalkyl substances (PFASs) from aqueous solution – A review. Science of The Total Environment;694(133606). Available from: https://www.sciencedirect.com/science/article/pii/S0048969719335314.

Appendices

Appendix A: Degradation Pathway for PFOS and PFOA (adapted from Singh *et al.*, 2019)



Appendix B: List of Acronyms and Abbreviations

Acronym/Abbreviation	Definition
A6	*Acidimicrobium sp.* Strain A6
AFFF	Aqueous Film Forming Foam
AOP	Advanced Oxidation Process
ARP	Advanced Reduction Process
DO	Dissolved Oxygen
e_{aq}^-	Hydrated electrons
EPA	Environmental Protection Agency
FASA	Perfluoroalkane Sulfonamides
FOSA	N-Alkalated Fluorooctane Sulfonamide
FOSE	N-Alkalated Fluorooctane Sulfonamidoethanol
FTOH	Fluorotelomer Alcohol
GAC	Granular Activated Carbon
g/mol	Grams per mole
K	Kelvin
kg	Kilogram
kHz	Kilohertz
kJ/mol	Kilojoules per mole
MCL	Maximum Contaminant Level
mg/L	Milligrams per liter
mm	Millimeters
MIP	Molecular Imprinted Polymer
NF	Nanofiltration
ng	Nanogram
nm	Nanometers

O&M	Operation and Maintenance
$^{\bullet}OH$	Hydroxyl radicals
PAC	Powdered Activated Carbon
PFAA	Perfluoroalkyl Acid
PFAS	Per- and Polyfluorinated Substances
PFBA	Perfluoro-n-butyric Acid
PFCA	Perfluoroalkyl Carboxylic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PFPeA	Perfluoropentanoic Acid
PFSA	Perfluoroalkylane Sulfonic Acid
POE	Point-of-entry
POU	Point-of-use
ppt	Parts per trillion
RO	Reverse Osmosis
SNUR	Significant New Rule Use
UV	Ultraviolet
V	Volts
WWTP	Wastewater Treatment Plant