This is a benefit of your awwa membership Drinking Water Treatment for PFAS Selection Guide

Technical Support on Per- and Polyfluoroalkyl Substances Policy



American Water Works Association

Dedicated to the World's Most Important Resource®



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Glossary of Abbreviations and Acronyms

6:2 FTS	6:2 Fluorotelomer sulfonate	PFCA	Perfluoroalkyl carboxylic acid
8:2 FTS	8:2 Fluorotelomer sulfonate	PFDA	Perfluorodecanoic acid
AOP	Advanced oxidation process	PFDoA	Perfluorododecanoic acid
AWWA	American Water Works Association	PFPeA	Perfluoropentanoic acid
CEC	Compound of emerging concern	PFHpA	Perfluoroheptanoic acid
DAF	Dissolved air flotation	PFHxA	Perfluorohexanoic acid
DBP	Disinfection byproduct	PFHxS	Perfluorohexanesulfonic acid
DOC	Dissolved organic carbon	PFNA	Perfluorononanoic acid
EBCT	Empty bed contact time	PFOA	Perfluorooctanoic acid
GAC	Granular activated carbon	PFOS	Perfluorooctanesulfonic acid
GFD	Gallons per square foot per day	PFOSA	Perfluorooctanesulfonamide
IX	lon exchange	PFSA	Perfluoroalkyl sulfonic acid
MCL	Maximum Contaminant Level	PFTriA	Perfluorotridecanoic acid
MF	Microfiltration	PFUnA	Perfluorundecanoic acid
MGD	Million gallons per day	RO	Reverse osmosis
MWCO	Molecular weight cut off	RSSCT	Rapid small-scale column testing
NF	Nanofiltration	SBA	Strong base anion
ng/L	Nanogram per liter	тос	Total organic carbon
NMeFOSAA	N-methyl perfluorooctane	UF	Ultrafiltration
DAG	sultonamidoacetic acid	USEPA	Environmental Protection Agency
PAC	Powdered activated carbon	UV	Ultraviolet
PFAA	Perfluoroalkyl acid	VOC	Volatile organic compound
PFAS	Per- and Polyfluoroalkyl Substances	WBA	Weak base anion
PFBA	Perfluorobutanoic acid	WTP	Water treatment plant
PFBS	Perfluorobutanesulfonic acid		

Introduction

Background

he presence of per-and polyfluoroalkyl substances (PFAS) in drinking water is a potential health concern and consequently an area of state regulatory activity. The U.S. Environmental Protection Agency (USEPA) announced its intent to set drinking water standards for at least two members of this a group of industrial chemicals, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA).

PFAS are used largely for their oil and water repellent properties. Applications include consumer products (e.g., raincoats, food packaging, nonstick cookware) and aqueous film-forming foam (AFFF) to fight petroleum-based fires. The chemical properties of PFAS that lead to their use also make their removal from drinking water difficult with conventional water treatment processes. The two most studied groups of PFAS are two long-chain, subclasses of PFAS: perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA). Long-chain PFAS (PFCAs with \geq 8 carbons and PFSA with \geq 6 carbons) are easier to remove through some advanced treatment processes compared to short-chain PFAS (PFCAs with < 8 carbons and PFSAs with < 6 carbons). Examples of individual compounds that are categorized as a PFSA and PFCA are PFOS and PFOA, respectively.

Purpose

The purpose of the American Water Works Association's (AWWA's) Drinking Water Treatment for PFAS Selection Guide is to assist water systems with drinking water treatment decisions for PFAS. PFAS are expensive to analyze and challenging to remove from water. Selecting drinking water treatment requires the consideration of many factors including the potential unintended consequences. This guide reviews the treatment technologies with demonstrated ability to remove PFAS, technical questions important to the technology selection process, and how data may be developed and organized to support decision-making.

What are PFAS?

PFAS are stable because of their carbon-fluorine bonds and are unlikely to react or degrade in the environment. PFAS can attach to soil or sediment and leach to groundwater and surface water, which can impact drinking water sources. Long-chain PFAS are thought to be more likely to attach to soil and sediment than shorter chain PFAS (ATSDR, 2018; ITRC, 2020).

PFAS may bioaccumulate in plants, animals, and people at levels reported as nanogram/liter (ng/L). Table 1 provides an example of how PFAS are named to provide insight on the complexity of these chemicals. The root of the chemical name is *perfluoro*, followed by a name indicating the number of carbons in the structure and then the name for the attached functional group.

ROOT NAME	CARBON CHAIN LENGTH	FUNCTIONAL GROUP	ACRONYM	PFAS NAME
Perfluoro	0 = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate
				Perfluorooctanoic acid
		S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate
				Perfluorooctane sulfonic acid

Table 1 – PFAS Naming Example

The following subsections describe the naming conventions and physical/chemical properties recognized by the Interstate Technology Regulatory Council (ITRC) to provide context for further discussions presented in later sections (ITRC, 2017).

Families

PFAS can be grouped into polymer and nonpolymer families, with polymer PFAS including perfluoroalkyl acids (PFAAs) the most commonly studied PFAS in drinking water. Precursors are PFAS that may degrade into PFAAs. More recently, manufacturers have developed compounds to replace commonly used PFAAs that have been phased out of production. Replacement compounds may use fluorinated ether carboxylates to produce shorter-chain PFAS with similar properties as the long-chain compounds (ITRC, 2017). One example of a replacement PFAS is GenX—a perfluoropolyether carboxylate surfactant previously detected in high concentrations in the Cape Fear River in North Carolina as a result of an industrial discharge.

CLASSES

Nonpolymer PFAS can be separated into two main classes of PFAS: perfluoroalkyl substances and polyfluoroalkyl substances (ITRC, 2018b).

PERFLUOROALKYL SUBSTANCES

Perfluoroalkyl substances consist of a carbon atom chain of two or more carbon atoms with a functional group attached at one end and fluorine atoms attached to all possible sites along the chain, with no additional carbon to hydrogen bonds in the chain. One example is the chemical structure of PFOS, as shown in Figure 1.



Figure 1 – PFOS Structure (USEPA, n.d.)

POLYFLUOROALKYL SUBSTANCES

Polyfluoroalkyl substances are similar to perfluoroalkyl substances; however, they are not fully fluorinated and may have another atom (e.g., hydrogen, oxygen) attached to the carbon chain. Polyfluoroalkyl substances are, therefore, the more varied group of PFAS. Polyfluoroalkyl substances include thousands of compounds that have carbon to fluorine bonds (e.g., fluorotelomers as shown in Figure 2) with others having complex functional groups.



Figure 2 – 6:2 fluorotelomer sulfonate (6:2 FTSA) structure (USEPA, n.d.)

Figure 3 provides a visual representation of PFAS physical/ chemical characteristics and relationships, as presented in Wang et al. (2017).

REPLACEMENT PFAS

As long-chain PFAS were phased out of production, replacement compounds with similar chemistries were developed. Replacement compounds may use fluorinated ether carboxylates to produce shorter-chain PFAS with similar properties (ITRC, 2017). One example of a replacement PFAS is GenX.



	Sub-classes of PFASs	Examples of Individual compounds*	Number of peer-reviewed articles since 2002**
		O PEBA (n=4)	028
		O PEPeA (n=t)	720
		O PEHXA (n=6)	1081
		P PEHpA (n=7)	1001
		O PEOA (n=8)	4066
	PFCAso	O PENA (n=q)	4000
		0 PFDA (n=10)	1470
	(C _n F _{2n+1} -COOH)	P PFUnA (n=11)	1407
		O PFDoA (n=12)	1016
		O PFTrA (n=13)	426
	/	0 PFTeA (n=14)	587
		O PERS ($n=4$)	454
		0 PEHvS (n=6)	1091
	PFSAso	PEOS(n=8)	3507
	(C.FSO.H)	P PFDS (n=10)	340
perfluoro	palkyl acids o	DEBDA (D-4)	540
/DE	(AAc)	O PEHypA (n=4)	3
(PT	PFPAso	O PEOPA (n=0)	33
	(CE -POH)	0 PEDPA (n=8)	31
	(Cn ¹ 2n+1 1 3 2)	0 FFDFA (II=10)	35
		 C4/C4 PFPiA (n,m=4) 	4
	PFPiAso	 C6/C6 PFPiA (n,m=6) 	12
		0 C8/C8 PFPIA (n,m=8)	12
	(Cn ² n+1) - C ² n - Cm ² m+1)	0 C6/C8 PFPIA (n=6,m=8)	8
		ADONA (CF ₃ -O-C ₃ F ₆ -	O-CHFCF ₂ -COOH) 4
	PFECAs & PFESAso	GenX (C ₃ F ₇ -CF(CF ₃)-CC	ООН) 26
		• EEA (C2F5-0-C2F4-0-	-CF ₂ -COOH) 6
	$(C_n F_{2n+1} - O - C_m F_{2m+1} - K)$	F-53B (CI-C ₆ F ₁₂ -O-C ₂ F	F ₄ -SO ₃ H) 14
		MeFBSA (n=4,R=N(CH ₃)	H) 25
/		 MeFOSA (n=8,R=N(CH₃) 	H) 134
		O EtFBSA (n=4,R=N(C ₂ H ₅))	H) 7
DEAC	PASF-based	 EtFOSA (n=8,R=N(C₂H₅)) 	H) 259
PFASS	substanceso	 MeFBSE (n=4,R=N(CH₃) 	C ₂ H ₄ OH) 24
$(C_n F_{2n+1} - R)$		 MeFOSE (n=8,R=N(CH,) 	C ₂ H ₄ OH) 116
	$(C_n F_{20+1} - SO_2 - K)$	 EtFBSE (n=4,R=N(C₂H₅)C 	C ₂ H ₄ OH) 4
N 0000 2000		o EtFOSE (n=8,R=N(C ₂ H ₅))	C ₂ H ₄ OH) 146
7 UVEI 3000		 SAmPAP {[C₈F₁₇SO₂N(C₂] 	H ₅)C ₂ H ₄ O] ₂ -PO ₂ H} 8
PFASs may	PFAA o	o 100s of others	
have been	precursors	4:2 FTOH (n=4,R=OH)	106
on the global		0 6:2 FTOH (n=6,R=OH)	375
market	fluorotelomer-based	0 8:2 FTOH (n=8,R=OH)	412
market	substanceso	0 10:2 FTOH (n=10,R=OH)	165
		0 12:2 FTOH (n=12,R=OH)	42
	$(C_n F_{2n+1} - C_2 H_4 - R)$	6:2 diPAP [(C ₆ F ₁₃ C ₂ H ₄ O) ₂	-PO ₂ H] 23
		0 8:2 diPAP [(C8F17C2H4O)2	-PO ₂ H] 25
		o 100s of others	
		 polytetrafluoroethylene 	e (PTFE)
	fluoropolymers	 polyvinylidene fluoride 	(PVDF)
	nuoropolymerso	 fluorinated ethylene pro 	opylene (FEP)
	otherso	 perfluoroalkoxyl polyme 	er (PFA)
	operfluoro	polyethers (PEPEs)	
	perhuoro	polyculcis (in res)	

PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).
 The numbers of articles (related to all accesses) users retrianed from Spirinder® on New 2016.

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 3 – Grouping of PFAS from Wang et al. (2017). Reprinted with permission from "A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?" Wang et al. Environmental Science & Technology. Copyright © 2017. American Chemical Society.

The following subsections describe the naming conventions and physical/chemical properties recognized by the ITRC

to provide context for further discussions presented in later sections (ITRC, 2017).

Treatment Technologies

reatment technologies currently available for full-scale use in water treatment plants (WTPs) are effective for removal but not PFAS destruction. PFAS are highly soluble, have both hydrophobic and hydrophilic properties, low volatility, and contain strong carbon-fluorine bonds. PFAS are generally resistant to chemical, physical, and biological degradation, which limits many potential removal mechanisms (Rahman et al., 2014).

This section provides a review of the available treatment technologies and their ability to remove PFAS and a discussion on how process performance can be impacted by PFAS properties and background water quality. Treatment technologies that provide little PFAS removal include conventional treatment (coagulation, flocculation, and sedimentation), granular media filtration (without activated carbon), oxidation, advanced oxidation processes (AOPs), biofiltration, and low-pressure membranes.

Advanced treatment processes that can effectively remove PFAS from drinking water include granular activated carbon (GAC), ion exchange (IX), nanofiltration (NF), and reverse osmosis (RO). These treatment processes can be used in conjunction and with different configurations to provide more robust PFAS removal. Additionally, novel technologies in development such as ozofractionation, chemical oxidation, and other destructive technologies are in development. These novel

Note: Our current understanding of PFAS removal is constrained by the relatively small number of PFAS that can be reliably measured and the smaller number of PFAS for which treatment has been studied with enough rigor to support peer-reviewed papers. Where studies are occurring at full-scale, concentrations of PFAS are often so low as to make discerning the effect of treatment, if any, difficult.

that will affect the sustainability of reliable removal levels, including

- Type of PFAS targeted for removal
- Influent PFAS concentration
- Target finished water concentration
- Other water quality parameters that may interfere with treatability (e.g., total organic carbon (TOC), nitrate, sulfate)

Activated Carbon Adsorption

Adsorption is a mass transfer process where substances present in a liquid phase are adsorbed on a solid phase and consequently removed from the liquid (Crittenden et al., 2012). Figure 4 illustrates the four steps that occur prior to PAC or GAC adsorption: bulk, film, pore, and surface diffusion.

• Movement of the adsorbate (the constituent to be adsorbed) from

the bulk solution (water) to the liquid film or boundary layer surrounding the adsorbent solid (carbon media), known as *bulk diffusion*

- Diffusion of the adsorbate through the liquid film, known as *film diffusion*
- Diffusion of the adsorbate inward through the capillaries or pores within the adsorbent solid, known as *pore diffusion*
- Diffusion along the surface of the pores, known as *surface diffusion*

Adsorption occurs once surface diffusion of the adsorbate is complete, and the rate of adsorption is limited by one of these mass transport mechanisms. Generally, a longer contact time between water and media will allow for greater diffusion through the pores.

technologies show promise for removing PFAS but have not been adequately demonstrated to remove PFAS from drinking water. Additional approaches and technologies will continue to be developed and evaluated in the future.

The following section will focus on effective treatment processes for PFAS removal from drinking water that have been demonstrated and used at full-scale. Appendix A provides an overview of conventional and novel technologies for PFAS removal.

Technologies including powdered activated carbon (PAC), GAC, IX, NF, and RO have shown the greatest promise for PFAS removal, although they each come with challenges and important considerations. PFAS removal efficiency using these advanced treatment processes is site-specific. A decision to provide treatment entails considering factors





PAC and GAC are common adsorption media that can be derived from different carbonaceous materials including bituminous coal, wood, lignite, and coconut shells (Dickenson and Higgins, 2016; USEPA, 2018). These materials are activated using high pressure/heat and/ or carbon dioxide to increase pore size and create a continuous pore structure, which increases micropore volume and internal surface area. The pore size distribution defines the available pore volume of a type of carbon over three regions: micropore region (< 100 Angstroms), mesopore region (between 100 and 1,000 Angstroms), and macropore region (>1,000 Angstroms). GAC adsorption is largely related to the mesopore and macropore region (Chowdhury, 2013).

POWDERED ACTIVATED CARBON (PAC)

BACKGROUND AND APPLICATIONS

PAC is generally added to WTP source waters to aid the adsorption of taste and odor compounds, organics, and/or color (USEPA, 2014). PAC can be used when needed to save on operating and maintenance (O&M) costs. For example, PAC is often used in warmer months for seasonal taste and odor control in surface water WTPs (Crittenden et al., 2012). PAC systems require very little space and can be installed at WTPs or source water intakes. Figure 5 shows a PAC system used at the City of Greensboro WTP (Greensboro, North Carolina).



Figure 5 – PAC System at the City of Greensboro, NC

PAC performance is impacted by the type of PAC, dose, dosing location, contact time, and the presence of other water quality constituents that may compete for adsorption sites. Jar testing typically is conducted to simulate conventional treatment to determine the appropriate design parameters and/or to evaluate the performance of various PAC types. PAC types can be characterized by carbon source, activation method, iodine number, pore volume, and particle size (Crittenden et al., 2012). PAC can be added as a dry powder or as a slurry, which is often dictated by usage frequency and dose. Dry PAC is often implemented when PAC is used intermittently or for small dosage rates, whereas a slurry system is generally used if PAC is frequently added or the doses are high. Table 2 presents typical PAC design criteria for PFAS removal, including a range of PAC doses and PAC contact times.

Table 2 – Typical PAC Design Criteria for PFAS Removal

DESIGN CRITERIA	VALUE OR RANGE
PAC Material*	Coal-based
PAC Dose ⁺	> 15 mg/L
Contact Time [‡]	> 15 min
PAC Diameter	< 0.1 mm
PAC Density	23 to 46 lb/ft ³

*Material selection should be validated through bench- and pilot-scale testing; †Higher PAC doses can be used for greater PFAS removal; ‡Longer contact times can be used for greater PFAS removal.

PFAS REMOVAL CAPABILITIES

PAC has been shown to be at least moderately effective at removing long-chain PFAS, however, it is not as effective for short-chain PFAS removal. Performance is significantly impacted by dose and other water quality parameters (Hopkins et al., 2018; Sun et al., 2016). Sun et al. (2016) found that PFAS removal increased with increasing chain length, with removal values < 40% for a majority of shortchain PFAS and removals of > 80% for long-chain PFAS. This research was conducted at PAC doses ranging from 30 to 100 mg/L with a contact time of one hour. At a PAC dosage of 30 mg/L, removal of long chain PFAS was often > 50%. However, other research has indicated that PAC dosages > 45 mg/L were required to achieve PFAS removal greater than 90% (Dudley, 2012), further highlighting the variability of PAC performance due to differences in water quality.

Table 3 provides a summary of the potential PFAS removal using PAC treatment, according to the USEPA's Drinking Water Treatability Database (USEPA, 2014).

Table 3 – PFAS Compound Removal Performance with PAC Treatment (USEPA, 2014)

PFAS COMPOUND	MAXIMUM REMOVAL
Perfluorobutanoic acid (PFBA)	10%
Perfluorobutanesulfonic Acid (PFBS)	90%
Perfluoropentanoic acid (PFPeA)	40%
Perfluorohexanesulfonic acid (PFHxS)	99%
Perfluorohexanoic acid (PFHxA)	90%
Perfluoroheptanoic acid (PFHpA)	90%
PFOA	95%
PFOS	99%
Perfluorononanoic (PFNA)	98%
Perfluorodecanoic acid (PFDA)	90%

POTENTIAL DOWNSTREAM WATER QUALITY CHANGES

The PAC doses considered for PFAS removal (e.g., 45–100 mg/L) are at least double those considered for taste and odor control (e.g., 1–20 mg/L) (USEPA, 2014). Potential downstream water quality changes that may result from adding PAC can include removal of TOC, taste and odor compounds, and color adsorption in addition to PFAS removal. Enhanced TOC removal using PAC can provide reduced disinfection byproduct (DBP) formation.

PAC can provide constituent removal from the point-ofaddition until it reaches adsorption capacity or is removed. To the degree that PAC is absorbing other constituents in the influent water (e.g., TOC), that absorptive capacity is not available to remove PFAS. If PAC is not adequately removed prior to filtration, a WTP may experience shorter filter run times and higher head loss accumulation due to increased solids loading to the filters. PAC dosage should be optimized to promote acceptable constituent removal without overloading solids removal at the WTP.

PROCESS INTEGRATION

Figure 6 illustrates where PAC is typically included in a drinking water treatment train. PAC is added upstream of other treatment processes, adsorbs compounds, such as PFAS and TOC, and is subsequently removed through settling or filtration. As mentioned previously, PAC addition will likely increase solids filter loading, which may result in shorter filter run times. PAC efficacy improves with contact time; therefore, adding PAC upstream from the sedimentation and filtration processes will generally result in greater PFAS and organics removal. PAC dosed ahead of rapid mix basins also ensures an adequate distribution of PAC within the water. Using a sludge blanket clarifier process provides more PAC contact time that may also improve PFAS removal; however, this concept has not been validated specifically for PFAS (Kassam et al., 1991).



Figure 6 – Water Treatment Process Train Utilizing PAC

ADVANTAGES AND DISADVANTAGES

Table 4 presents advantages and disadvantages of using PAC adsorption for PFAS removal. One of the major advantages of using PAC is that it can be implemented relatively quickly at the full-scale and a significantly less capital cost than other removal technologies. Design components are relatively minor compared to the design and construction of GAC, IX, or membrane systems, and units are prefabricated and can be rented or purchased from vendors. Additionally, if PFAS are only an infrequent issue, PAC may be the best treatment alternative because it can be used intermittently. One important disadvantage with PAC is that it will increase residuals loading that must be handled. PAC will adsorb PFAS, then the PAC particles will be removed during settling or in filter backwash. This residuals stream is typically sent to a wastewater treatment facility, landfill, or dewatering facility for disposal. Residuals dewatering efficiency can be negatively impacted with high PAC doses. PFAS are not currently regulated in the environment, but reintroducing PFAS into the environment via residuals disposal through land application of dewatered biosolids is an issue of rising public concern and may pose potential permitting and future liability challenges.

|--|

PAC ADVANTAGES	PAC DISADVANTAGES		
 Relatively quick implementation at full-scale Suitable for intermittent application Generally reliable process Small footprint requirements Easily incorporated into existing WTP process trains Relatively low capital costs Beneficial secondary water quality impacts: reduction of DBPs, taste and odor compounds, and TOC 	 Potential competitive adsorption reduces efficiency for PFAS removal Increased residuals loading can impact filter run times Residual dewatering can be adversely impacted PAC systems can be messy, require frequent maintenance to ensure accurate dose rate is achieved May require an additional contact vessel to enhance PFAS removal PFAS-containing residuals may present future disposal challenges. Process optimization is required Not as effective at removal of PFAS compared to other PFAS removal processes O&M cost may range greatly, depending on dose requirements for adequate PFAS removal Potential dust explosion hazard 		

GRANULAR ACTIVATED CARBON

BACKGROUND AND APPLICATIONS

GAC has a larger media size compared to PAC, with diameters ranging from 1.2 to 1.6 millimeters (USEPA, 2014). Because of the larger media size, GAC processes use a pressure vessel or filter box to allow water to pass through the media. GAC vessels are an independent treatment unit that must be integrated into the overall treatment plant design. GAC can be used to treat surface water or groundwater. Like PAC, GAC performance is impacted by water quality constituents, and organic compounds will compete with one another for adsorption sites. GAC benefits can be realized by adding GAC media to conventional granular media filters, either as a replacement for anthracite or as another media layer creating a filter adsorber. Filter adsorbers are gravity systems, while post-filter contactors can be either pressure or gravity systems. GAC filtration systems are also available for rental as temporary systems, which can be used for immediate response to PFAS contamination and/or full-scale demonstrations of GAC media types. Table 5 presents key considerations when implementing gravity filter adsorbers or pressure vessels. Figure 7 illustrates GAC pressure vessels and gravity filter boxes.

Table 5 – Gravity and Pressure System Key Considerations

CATEGORY	GRAVITY FILTER ADSORBERS	PRESSURE VESSELS
Cost	Generally, more cost-effective than pressure vessels in facilities greater than 10 MGD. Can be converted from conventional WTP filters, saving on capital costs, although this is site-specific and dependent on filter depth.	More cost-effective in WTPs < 10 MGD. As capacity increases, more vessels are needed, and equipment costs become less economical. Can be temporarily installed, if desired.
Space Requirements	Space requirements depend on flow rate and empty bed contact time (EBCT). For systems less than 10 MGD, gravity filters require similar site space to vessels. For systems greater than 10 MGD, gravity filters are more compact, due to filter dimensions and reduced piping and valve requirements.	Space requirements depend on flow rate and EBCT. For systems less than 10 MGD, vessels require similar site space to gravity filters. For systems greater than 10 MGD, larger space requirements are required for additional vessels and appurtenances.
Sizing	Optimized basin sizing	Restricted by manufacturer vessel sizing
Operation and Maintenance Requirements	Lower operation and maintenance requirements	Higher operation and maintenance requirements for a pressurized system
Pumping Requirements	Hydraulic gradient established by filter level. May require pumping to provide sufficient EBCT and maintain plant production capacity.	Pressure vessels typically require pumping of influent to feed at the top of the vessel. This additional pressure head may be used in the plant hydraulics to reduce pumping downstream.
Architecture	Can provide architectural consistency	Tank farm aesthetics
Media Change-Out Requirements	Requires less frequent media change-outs but change-outs often require multiple days due to the larger size of filter boxes compared to pressure vessels.	Requires more frequent media change-outs, but change out is often simpler, due to multiple loading options, such as manhole access and direct pumping of media into vessels from trucks.
Lead/Lag Conversion Capabilities	Conversion to lead/lag or staggered operations is more difficult	Facilitates lead/lag or staggered configuration that is readily achievable and increase EBCT
IX Conversion Capabilities	Does not readily allow conversion to IX if this is to be considered in the future	Allow conversion to IX if different treatment process is necessary in the future



Figure 7 – GAC Filter Vessels at the City of Issaquah, Washington (left) and Gravity Filter Boxes for the Northern Kentucky Water District (right)

Table 6 presents typical design criteria for filter adsorber and post-filter GAC systems for PFAS removal. Media selection is not influenced by whether the contactor is a filter adsorber or a post-filter system. To date, research has shown that coal-based media provides greater PFAS removal and is more cost-effective compared to media derived from alternative sources (Brewer, 2017; ITRC, 2018; Nowack, 2017). However, GAC media selected for full-scale use should be determined during bench- or pilot-

testing. Additional information on pilot testing is discussed later. Other design criteria, including EBCT, loading rate, and contactor sizing are significantly impacted by whether the contactor is a filter adsorber versus a post-filter contactor. These criteria vary in different applications.

Table 6 – Typical GAC Design Criteria for PFAS Removal

DESIGN CRITERIA	FILTER ADSORBER VALUE OR RANGE	POST-FILTER SYSTEMS VALUE OR RANGE	
Media Material	Coal-based ⁺		
Media Diameter	1.2 to 1.6 millimeters		
Media Apparent Density	25 to 31 lb/ft ³		
EBCT**	10 to 20 minutes		
Ratio of media depth to media effective size	> 1,200		
Loading Rate	2 to 6 gpm/sf 4 to 8 gpm/sf		
Filter Sizing	Rectangular with aspect ratios between 2:1 and 4:1, 4 to 6 feet deep 10 to 14 feet in diameter		

*Longer EBCTs generally result in greater constituent removal.; †(Brewer, 2017; ITRC, 2018; Nowack, 2017).

PFAS REMOVAL CAPABILITIES

At present, GAC is the most studied treatment method for PFAS removal (USEPA, 2018). The highly porous characteristics and large surface area of the media allows for GAC to remove PFAS as well as other organic compounds in water sources through adsorption processes. GAC can also be regenerated and reactivated.

In addition to factors noted previously, PFAS removal with GAC media is highly dependent on operating conditions of the system, including flow rate, GAC media volume and type, and other filter operational parameters such as EBCT, and hydraulic loading rate (Rahman et al., 2014). Influent water quality is particularly important and must be fully characterized when evaluating GAC selection. Evaluations of GAC technologies in bench-scale studies have found that the presence of dissolved organic carbon (DOC) reduces the capacity of GAC for PFAS removal. DOC may influence competition with PFAS in GAC applications and promote desorption, or decreased removal of PFAS through the release of PFAS previously adsorbed onto the GAC (Appleman et al., 2013; McCleaf et al., 2017; Rahman et al., 2014).

In addition to analyzing the source water quality for organic matter and nontarget contaminants, evaluating the speciation of PFAS in the source water before determining the treatment method is necessary. GAC has been evaluated to have total PFAS removal ranging from 66% to 100%, depending on the species of PFAS present (Appleman et al., 2014; McCleaf et al., 2017; Rahman et al., 2014). Studies have shown GAC to have greater removal of longerchain PFAS including PFOA and PFOS than short-chain PFAS such as PFBA, PFBS, and perfluorophosphonic acid (Rahman et al., 2014). The more effective removal of longchain PFAS is attributed to the hydrophobic effects of GAC. Removal of short-chain PFAS has been shown to be more ineffective when DOC concentrations are higher. This has been attributed to competition and displacement of shorterchain PFAS by DOC, long-chain PFAS, or other contaminants (Franke et al., 2019).

Table 7 provides an overview of maximum demonstrated removal rates of PFAS compounds by GAC, according to the USEPA's Drinking Water Treatability Database (USEPA, 2014).

Table 7 – PFAS Compound Removal Performance with GA	С
Treatment (USEPA, 2014)	

PFAS COMPOUND	MAXIMUM REMOVAL
PFBA	99%
PFBS	98%
PFPeA	90%
PFHxS	98%
PFHxA	95%
PFHpA	90%
PFHpS	82%
PFOA	98%
PFOS	99%
PFNA	93%
PFDA	97%
6:2 FTS	77%
8:2 FTS*	88%
PFOSA	90%
PFDoA	90%
PFTriA ⁺	90%
PFUnA [‡]	90%

*8:2 Fluorotelomer Sulfonate. †Perfluorotridecanoic acid. ‡Perfluoroundecanoic acid.

POTENTIAL DOWNSTREAM WATER QUALITY CHANGES

Potential downstream water quality changes associated with GAC include additional adsorption of organic constituents TOC, color, taste and odor compounds, and volatile organic compounds (VOCs) if present. While the removal of TOC can result in decreased DBP formation, high ammonia levels (>1.5 mg/L) can lead to nitrification within the GAC and distribution systems. Additionally, GAC will catalyze chlorine residual on the media surface, reducing residual concentrations. Consequently, introduction of GAC will require consideration revision of current disinfection practice to achieve the equivalent primary disinfection contact time required by the Surface Water Treatment Rule or Groundwater Rule (USEPA, 2015a, 2006).

Because GAC can adsorb a diverse array of contaminants, a phenomenon known as chromatographic peaking may occur. This phenomenon occurs when compounds desorb from the GAC media surface as preferential compounds are adsorbed (AWWA, 2002). Preventing such release requires understanding co-occurring contaminants and adequate monitoring of indicators of performance to prevent undesirable levels of contaminant release. In some cases, release of arsenic or iron has been reported during idling or start up periods as oxidation reduction properties change (Zou et al., 2010).

PROCESS INTEGRATION

Figure 8 illustrates the optimal location for GAC systems in drinking water process trains. GAC contactors can be incorporated easily within treatment plants for PFAS removal. As mentioned previously, GAC adsorbers can take the place of traditional media filters as shown in Figure 8 or be post-filter GAC systems. The GAC treatment process benefits significantly from pretreatment to ensure that the media does not suffer from contaminant competition, such as TOC.



Figure 8 – Water Treatment Process Train Utilizing GAC Filter Adsorbers

GAC can be operated in parallel or series, as shown in Figure 9. In parallel operation, contactors operate side-byside with the primary flow path split and treated by each reactor. This operational strategy allows for effluent flows to be combined. This strategy has several operational benefits. First, contactors can be taken out of service or placed on-line, as needed. Second, the exhaustion of the media is slowed and the media life is extended (AWWA, 1998). However, in series operation, contactors are staggered one in front of the other to allow for redundant treatment of the source water. In this mode of operation, the efficacy of GAC adsorption is maximized. Operating in series provides the highest removal capabilities. This mode of operation is typically used for specific contaminant removal where breakthrough may cause undesirable finished water quality (AWWA, 1998). This has been favored for PFAS removal as it permits water systems to monitor intermediate effluent for target PFAS breakthrough from the first contactor.



Figure 9 – Series vs. Parallel GAC Contactor Operation

ADVANTAGES AND DISADVANTAGES

GAC systems can provide high PFAS removal efficiency compared to conventional treatment technologies and are a relatively low capital cost compared to membrane systems. However, GAC effectiveness is site-specific, and dependent on design and treatment goals. GAC can provide additional water quality benefits, such as the removal of other contaminants of emerging concerns (CECs), making it a useful technology for a variety of applications. A summary of the advantages and disadvantages of GAC for PFAS removal is provided in Table 8. The operation of GAC systems is generally less energy intensive and does not produce the same waste products that are produced with membrane processes (discussed in detail in the Nanofiltration and Reverse Osmosis Membranes Section). However, GAC media will require replacement over time as adsorption sites are exhausted. This can be accomplished either through replacement or reactivation.

Media *replacement* is simply removal and disposal spent media from contactors and bringing in new media. Reactivation refers to removing contaminants and destroying them at high temperatures (Chowdhury, 2013). The reactivation process is especially favored in PFAS treatment applications because PFAS may be destroyed at the high temperatures (> 1,500 \Vertice{F}). Reactivation and the ability of this process to destroy PFAS is an ongoing research topic at USEPA. Open questions include

GAC USED FOR DRINKING WATER TREATMENT IS NOT "REGENERATED"

Regeneration refers to the removal of contaminants from GAC without destroying them by exposing GAC to steam or hot gas. **Regeneration is not frequently used in water treatment** due to its inability to restore media adsorption capacity because much of the adsorbed material is non-displaceable.

- Do current reactivation facilities and practices assure complete removal of PFAS adsorbed to GAC from the GAC?
- Is additional treatment needed for reactivation facility stack emissions to assure that volatilized PFAS are indeed fully destroyed?
- What parameters should be monitored to assure complete removal and destruction of PFAS during GAC reactivation?

GAC should be replaced or reactivated prior to breakthrough of PFAS at concentrations that exceed removal goals established by the water system, regulatory guidance levels, or maximum contaminant levels (MCLs). This may equate to replacement or reactivation two to three times per year, although the PFAS breakthrough will vary depending on other organic compounds present, PFAS speciation and the total concentration of PFAS (Rahman et al., 2014).

GAC ADVANTAGES	GAC DISADVANTAGES	
High removal of long-chain PFAS and moderate removal or short-chain compounds	f • Potential competitive adsorption reduces PFAS removal efficacy	
Reliable PFAS removal	O&M costs can be a burden if GAC is replaced/reactivated frequently	
Vessels/filter systems do not require large footprint	Desorption of PFAS or other contaminants is possible	
Opportunities to retrofit conventional sand filters for GAC	 Backwash water must be disposed of (or recycled), although backwash is relatively infrequent compared to traditional media filters: PEAS concentrations 	
• Provides additional constituent removal, such as taste and	in backwash streams are not well characterized	
odor compounds, TOC (and associated DBP reduction), and CECs	Potential for nitrification within the GAC system or within the distribution system	
Can be temporarily installed for short-term PFAS removal applications	GAC media will need to be reactivated or disposed and future regulatory requirements for air emissions from reactivation and disposal are uncertain	

Table 8 – Advantages and Disadvantages of GAC Treatment for PFAS Removal

Ion Exchange Technologies BACKGROUND AND APPLICATIONS

IX is a treatment process that uses a resin material to remove either negatively charged molecules (anions) or positively charged molecules (cations). The IX process is illustrated in Figure 10, specifically anion exchange. Anion exchange, which is used in PFAS applications, is used to remove negatively charged species (anions) from solution with mobile counter ions. The negatively charged contaminant ion, PFAS, becomes bound to the IX resin. The IX process works by exchanging constituents in water with a mobile counter ion (e.g., the ions exchanged with the contaminant) present in resin. This mobile counter ion resin material is usually chloride or sodium but can also be hydroxide or the hydrogen ion.

IX resins are held in vessels with EBCTs ranging from 1.5-7.5 minutes for column treatment (Clifford, 1999). Typical IX EBCTs are a fraction of GAC EBCTs (60% to 80% shorter), which makes this process advantageous if equivalent PFAS removal is achievable. The smaller EBCT equates to smaller footprint and less energy for pumping. There are factors specific to IX resins that must be evaluated when determining the best resin material to use for PFAS removal: resin matrix, pore structure, and functional group. To-date in PFAS applications, the quaternary ammonium or dimethyl ethanol ammonium polyacrylic gel resins have been the most effective (Rahman et al., 2014), although other types of resins are being explored.



Figure 10 – *IX* Treatment Description

Table 9 presents typical IX design criteria for PFAS removal, and Figure 11 depicts a sample of IX resin. There are several resin types that can be used in IX processes. While weak base anion (WBA) resins have shown the most promise in PFAS reduction applications, strong base anion (SBA) resins can be used as well. The design of IX systems is similar to the design of GAC systems. The primary differences between these systems are the differences in GAC media and IX resin characteristics and required EBCTs for effective contaminant removal.

Table 9 – Typical IX Design Criteria for PFAS Removal

DESIGN CRITERIA	VALUE OR RANGE
Resin Type	WBA or PFAS-selective resin
EBCT*	2.5 to 7.5 min
Flow Rate per Vessel	8 to 40 bed volumes per hour
Bed Depth: Vessel Diameter	0.2:1 to 2:1
Bed Depth [†]	30 in. to 12 ft
Loading Rate	6 to 12 gpm/ft ²

Longer EBCTs generally result in greater removal; † Bed depth is dependent on EBCT required for contaminant removal (Clifford, 1999).



Figure 11 – IX Resin

RESIN REGENERATION

Because of the toxicity and persistence of PFAS, regeneration of the resins has not been preferable. If regeneration is done, the spent brine may need disposal or treatment. Conventional methods of regeneration are inefficient for IX removal when PFAS removal is desired. Using only a brine solution may target desorption of the anionic head of PFAS; while the use of solely organic solvents (usually ethanol and methanol) targets desorption of the hydrophobic tail and would be less effective at removing the electrostatic interact portion of PFAS. Resins are instead regenerated more efficiently using a salt or base mixed with methanol or ethanol (Gao et al., 2017). Therefore, the combination of organic solvent and brine solution is recommended for PFAS regeneration. While regeneration of resin poses challenges, so does disposal of exhausted resin. Disposal will be necessary. At present, water systems can dispose of spent resins at waste disposal sites or incinerate the material for PFAS destruction. As with GAC and PAC related-residual streams, the regulatory framework for disposal technologies is not clear at this time. It is possible that these waste streams will be subject to hazardous waste disposal requirements.

PFAS REMOVAL CAPABILITIES

Functional groups (e.g., tertiary and quaternary amines) and resin type (e.g., WBA) can affect the IX treatment of PFAS. Short-chain PFAS are more likely to be removed in IX exchange, as the negatively charged functional groups provide effective ion pairing with resin functional groups (Li et al., 2020). WBA resins operate only when the functional group is in a protonated state, which means that treatment is pH dependent. Altering the pH must be considered in the overall treatment goals.

The characteristics of the polymer matrix are critical for estimating PFAS removal due to the diversity in diffusion rates (Deng et al., 2010). The polyacrylic matrix is known to be more hydrophilic than polystyrene, allowing the more hydrophilic PFAS to be easily transported into the pores of polyacrylic resins (Deng et al., 2010).

Though not likely with PFAS treatment, if regeneration is an option for exhausted resin, WBA resins are more efficiently regenerated than SBA resin (Li et al., 2020). Polyacrylic SBA resin is generally associated with faster PFOS and PFBS

uptake kinetics compared to corresponding polystyrene resin (Li et al., 2020). Also, polyacrylic resins are more resistance to organic fouling, which means that more capacity is available for PFAS removal.

Macroporous resin is another type of resin that has been evaluated for PFAS removal. Macroporous resins consist of small microgels with interconnection of pores ranging from 10 –100 nm in size, while gel resins consist of micropores with uniform solid phase and closely spaced functional groups with pore size less than 2 nm (Deng et al., 2010; Li and SenGupta, 2000). Macroporous resins have preferential uptake of PFAS.

For example, WBA macroporous resins (IRA900 and IRA96) exhibited about 6-8 times higher uptake of PFOS compared to gel type resins (IRA 400 and IRA410) due to easier accessibility to the exchange sites (Li et al., 2020). Macroporous SBA resins exhibited higher exchange capacity for PFOS, but lower exchange capacity for shortchain PFBS than gel type SBA resins, which indicates that gel type resins are more suitable for shorter chain PFAS (Li et al., 2020). Looking at pore and resin structure, both gel and microporous polystyrene resins have achieved > 90% removal of PFBA, PFPeA, PFHxA, and PFHpA at a dose of 5 mL/L (Li et al., 2020). Table 10 presents a summary of resin capacities for short-chain PFAS removal that were identified in Li et al. (2020). Resin types are from a variety of manufacturers, including Purolite and DuPont. Resin capacity ranges from 19.1 to 1089.8 mg/g, depending on the resin type.



SPECIES	RESINS	RESIN TYPE	EXCHANGE CAPACITY (MG/G)
2524	A600E	SBA, gel, PS, T1 QA	19.1
	A520E	SBA, MP, PS, T1 QA	29.5
Prda	A532	SBA, gel, PS, QA	52.3
	IRA910	SBA, MP, PS, T2 DMEA	635.7
	IRA67	WBA, PA, gel, TA	37.7
PFRXA	IRA910	SBA, MP, PS, T2 DMEA	1089.8
PFHpA	IRA67	WBA, PA, gel, TA	193
	A600E	SBA, gel, PS, T1 QA	34.6
	A520E	SBA, MP, PS, T1 QA	53.8
DEDC	A532E	SBA, gel, PS, QA	109.2
PFDS	IRA410	SBA, gel, PS, DMEA	1020.3
	IRA910	SBA, MP, PS, T2 DMEA	1023.3
	IRA400	SBA, gel, PS, T1 QA	1050.4

Table 10 – Resins Exchange Capacities for Short-Chain PFAS Removal (Source: F. Li et al., 2020)

PS = polystyrene; PA = polyacrylic; MP = macroporous; T1 QA = Type 1 quaternary ammonium; DMEA = dimethyl ethanol ammonium; T2 = Type 2; TA = tertiary amine.

Table 11 provides a summary of the maximum demonstrated PFAS removal using IX treatment, according to the USEPA's drinking water treatability database.

Table 11 – PFAS Compound Removal Performance with IX Treatment (USEPA, 2014)

PFAS COMPOUND	MAXIMUM REMOVAL
PFBA	97%
PFBS	98%
PFPeA	90%
PFHxS	99%
PFHxA	97%
PFHpA	94%
PFHpS	99%
PFOA	97%
PFOS	99%
PFNA	98%
PFDA	98%
6:2 FTS	89%
8:2 FTS	99%
PFOSA	90%
PFDoA	90%
PFTriA	90%
PFUnA	90%

PH EFFECT ON SORPTION

PFAS removal using IX resin is significantly influenced by the pH, where a higher pH (> 10) results in less exchange

(Gao et al., 2017). While pH does not affect PFAS state, pH may impact IX resin properties (Li et al., 2020). For SBA resins, pH ranging from 6-9 for influent groundwater did not affect the sorption of PFAS, however high pHs (>10) can result in degradation of SBA resin (Maimaiti et al., 2018). For WBA resins, optimal performance is observed in low pH ranges (5.5 to 6.0) (Bell et al., 2019).

POTENTIAL DOWNSTREAM WATER QUALITY CHANGES

The presence of inorganic and organic groups coexisting in the same treated water can affect the removal of PFAS. Divalent cations can form a bridge between negatively charged PFAS resulting in co-removal or reduced PFAS uptake. For example, magnesium forms bridges between carboxyl groups while calcium forms bridges between carboxyl and sulfonate groups. This can result in coremoval by forming a compound that is positively charged, hence attracting the negative mobile counter ion on the resins (Du et al., 2014). While anion exchange resins are not intended to remove divalent cations, co-removal may impact alkalinity of effluent water. Therefore, corrosion control efforts through alkalinity and pH adjustment should be revisited to ensure that corrosion control treatment goals are still met (USEPA, 2015b).

Additionally, presence of organics can interact with PFAS and may result in co-removal (Kothawala et al., 2017a) while concurrently considering how background levels of dissolved organic matter (DOM. Anions, such as sulfate, sulfide, nitrate, chloride, and chromate, decrease PFAS exchange in IX applications due to being preferentially favored by the resin (Du et al., 2014; Kim and Benjamin, 2004; Swistock, 2016). Additionally, TOC and bromide removal using IX can result in reduced disinfection byproduct (DBP) formation (Singer and Bilyk, 2002) each representing a different element of the USEPA's 3×3 enhanced coagulation matrix. The effect of MIEXpretreatment on the requisite alum dose needed for subsequent coagulation of turbidity was also evaluated. Enhanced coagulation with MIEX was found to be very effective for removing trihalomethane (THM.

As described with GAC, chromatographic peaking may occur in IX systems when anions are released at problematic levels if the treatment process is not effectively monitored and controlled. Pretreatment of influent water to IX resins must be free of oxidants (e.g., chlorine, ozone, etc.). This necessitates consideration of how placement of the IX treatment in the WTP affects calculation of primary disinfection credit (USEPA, 2015c).

PROCESS INTEGRATION

Figure 12 illustrates that the IX treatment process, similar to the GAC process, is best suited for treating water postfiltration. Both GAC and IX treatment processes rely on adequate pretreatment to reduce any constituents that may compete with target contaminants for exchange sites and accelerate contaminant breakthrough. Generally, IX resin pretreatment should include adjustment of influent water pH to avoid scaling and optimize performance, reduction of TOC levels to prevent fouling, and control of influent total suspended solids. IX treatment process configuration is a critical element to ensure both removal performance and reliable compliance with applicable regulations. As with GAC vessels, there are two possible configurations for IX: parallel and inseries (refer to Figure 9 for an illustration). While parallel configurations allow for flow to be split between vessels and are commonly used to provide equipment redundancy, vessels in series can enhance treatment by increasing the EBCT while also providing equipment and removal redundancy. Each site is unique and may require its own type of configuration depending on site-specific constraints (available footprint, regulatory limits, and raw concentrations, etc.).



Figure 12 – Water Treatment Process Train Utilizing IX

ADVANTAGES AND DISADVANTAGES

Table 12 presents advantages and disadvantages of using IX for PFAS removal. One major advantage is that IX manufacturers have developed and are continuing to fine-tune PFAS-selective resin. This allows preferential removal of PFAS with less competition of other constituents. However, like GAC media, IX resin becomes exhausted over time until breakthrough is reached, at which time resin must be regenerated or replaced.

IX ADVANTAGES	IX DISADVANTAGES
 PFAS-selective resins are available and research continues. Reliable treatment process with high removal of long-chain PFAS and moderate to high removal of short-chain PFAS, although this selectivity is resin dependent. Smaller footprint compared to GAC. Moderate capital costs. Potential removal of other contaminants. Relatively short EBCTs compared to GAC. Resin is not replaced as often as GAC media. 	 Potential competitive exchange and fewer secondary water quality benefits compared to other processes. O&M costs may be significant if frequent resin replacement is required. Backwash water must be disposed of (or recycled), although backwash is relatively infrequent. Piloting will be required prior to full-scale implementation. IX resin is more costly on a pound-for-pound basis than GAC media, however generally less resin is required than GAC. Future regulatory requirements for waste disposal is uncertain. Spent media may need to be disposed of as a hazardous waste or low-level radioactive waste due to removal of co-occurring contaminants.

Table 12 -	- Advantages	and Disadvantages	of IX for	PFAS Removal
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Nanofiltration and Reverse Osmosis Membranes

BACKGROUND AND APPLICATIONS

Small pore size membranes (RO and NF) can be used in groundwater or surface water applications. The primary purpose of using RO is for the removal of dissolved salts such as sodium chloride, making RO the process of choice for seawater and brackish water treatment. Nanofiltration (NF) is often used for softening (hardness removal) and organics removal, although RO can also soften water and remove organics (Jacangelo et al., 1997).

NF and RO work by pushing water through a semipermeable membrane. The pressure that must be applied to force water through the semipermeable membrane is known as the osmotic pressure. The feed pressure forces water through the membrane, increasing the dissolved contaminant concentrations on one side of the membrane (termed the concentrate stream), and increasing the volume water with reduced dissolved constituent concentrations on the other (termed the permeate stream). Permeate continues for post-treatment to eventually become finished water, while concentrate must be disposed of as a waste stream. Figure 13 illustrates a simplified schematic of a semipermeable membrane, showing the three membrane process streams.



Figure 13 – Simplified Schematic of Membrane Separation

Figure 14 provides three photos of a NF system, showing pressure vessels (not to be confused with GAC pressure vessels) and associated piping, and a photo of a membrane element. The NF train and element look identical to a RO train and RO element; the core difference is that NF membranes have a larger pore size than RO membranes.

In RO/NF applications, there are typically 6 to 8 elements per pressure vessel, although fewer and greater elements can be used.





Figure 14 – (a) Front View of NF Train. (b) Side View of NF Train. (c) A Single Membrane Element.

RO and NF membranes can remove constituents through several mechanisms: size exclusion, adsorption, and electrostatic interactions (Banks et al., 2020; Rahman et al., 2014). The mechanism used for removal depends on the constituent being removed, other water quality parameters, and membrane properties. Additionally, multiple removal mechanisms can be used cohesively to provide removal. While RO membrane molecular weight cut offs (MWCOs) are small enough so that size exclusion is the dominant removal mechanism, constituent removal in NF membranes is more significantly impacted by constituent properties, water quality, and membrane characteristics, as shown in Table 13 (Bellona et al., 2004; Steinle-Darling and Reinhard, 2008; Tang et al., 2006). Table 13 – Factors that Impact Membrane Removal Capabilities

FACTORS THAT IMPACT MEMBRANE REMOVAL CAPABILITIES	PROPERTIES
	Molecular weight
	• Geometry
Constituent properties	Functional group
Constituent properties	Hydrophobicity/hydrophilicity
	Acid dissociation constant
	Feed concentration
	• pH
Water quality parameters	Temperature
	Inorganics concentration
	Organics concentration
	Membrane charge
Membrane properties	Hydrophobicity
	Feed pressure
	Time since last cleaning

Membranes can provide consistent removal throughout the life of the membranes (usually 10 years), unlike GAC and IX technologies, which experience decreased removal over time as sites become exhausted.

Membranes are often characterized by their MWCO. The MWCO refers to the lowest molecular weight of a solute that will be 90% retained. For example, a membrane with a MWCO of 500 Daltons will reject 90% of constituents with a molecular weight of 500 Daltons, such as PFOS. Removal of constituents with a lower molecular weight, such as PFBS (338 Daltons) and PFOA (414 Daltons) would be removed at a lower rate.

RO and NF membrane processes operate at certain recovery set points. The recovery of a system indicates how much of the feedwater will become permeate and continue for further treatment. Concentrate will contain a significantly higher mass of constituents compared to the feed and permeate streams and will require disposal. Target RO recoveries generally range from 70% to 85% for brackish water systems and 40% to 60% for seawater systems. NF recoveries typically range from 80% to 95% recovery. The flux rate of a membrane system describes the throughput of water and is expressed in units of gallons per square foot per day (gfd). The higher the flux rate, the more water produced, but the more fouling or scaling potential of the membrane system. Feed pressures are dependent on the size (e.g., MWCO) of the membranes, where "tighter" membranes require greater pressures compared to "looser" membranes. NF feed pressures generally range from 70 to 150 psi, while RO feed pressures can be significantly higher. Feed pressures will be higher in seawater applications due to the number of dissolved constituents present in the feed water.

Both NF and RO systems will require some form of pretreatment to protect membranes from fouling or scaling; there may be less requirements for a system polishing conventional WTP effluent in comparison to a system treating raw source water. Post-treatment will be required for RO and sometimes NF systems to provide permeate stabilization and prevent corrosion instability in the distribution system. RO and NF membrane use in water treatment is becoming more and more viable with advances in energy efficiency, operating efficiency, and lowered capital costs (Rahman et al., 2014). RO operation is generally more costly compared to NF, all other considerations (e.g., pretreatment, post-treatment, etc.) remaining equal. If treatment objectives can be accomplished using NF, this lower-pressure technology is the more cost-effective choice compared to RO. Energy recovery devices do exist for higher pressure RO systems to harness residual energy in the concentrate. Table 14 presents a summary important NF and RO considerations, differences between the two technologies, and what these differences might mean in terms of PFAS removal.



DESIGN CRITERIA	NF	RO
Source water treated	Groundwater	Brackish groundwater and surface water or seawater
Primary function	Softening (Ca ²⁺ and Mg ²⁺ removal) or organics removal	Removal of dissolved salts (NaCl, CaCl ₂ , etc.)
MWCO (Daltons)*	200-1,000	150-300
Target recovery	85%-95%	70%–85% (brackish water) 40%–60% (seawater)
Flux rate	14 to 20 GFD	7 to 15 GFD
Feed pressure	70 to 150 psi	150 to 600 psi (brackish water treatment) 600 to 1,200 psi (seawater treatment)
Pretreatment	Sometimes granular media filters or low-pressure membranes. Always use cartridge filters.	Sometimes granular media filters or low-pressure membranes, especially if treating surface water. Always use cartridge filters.
Post-treatment ⁺	Stabilization may be required, depending on membrane type.	Stabilization will be required for pH and alkalinity.
Challenges	Concentrate disposal, fouling, scaling	Concentrate disposal, fouling, scaling
Capital cost	High when considering elements, trains, pre- and post- treatment requirements.	High when considering elements, trains, pre- and post- treatment requirements
Energy use	High, but lower than RO	Higher than NF, but energy recovery devices can be used to harness energy in RO concentrate

Table 14 – NF and RO Summary and Design Criteria

*Molecular weight cut off in Daltons. The molecular weight of the molecule that is 90% retained by the membrane; †Post-treatment beyond stabilization, including corrosion inhibitor addition and disinfection, will likely be necessary. Other post-treatment can include hydrogen sulfide stripping, if present.

PFAS REMOVAL CAPABILITIES

NF and RO have been proven to remove both short-chain and long-chain PFAS, (Appleman et al., 2014; Banks et al., 2020; Steinle-Darling et al., 2010; Steinle-Darling and Reinhard, 2008; Tang et al., 2007, 2006; Thompson et al., 2011; Yoon and Lueptow, 2005)these chemicals have become a global issue as emerging organic contaminants. Aliphatic PFASs with saturated carbon-fluorine bonds appear to be incompletely removed during conventional chemical/physical (coagulation, flocculation, sedimentation, and filtration. Appleman et al. (2014) showed that RO membranes removed several short- and long-chain PFAS to below detection limits at multiple WTPs. Loose NF membranes (typically considered to be those with a MWCO of \geq 300 Da) can provide substantial PFAS removal (>99%) (Banks et al., 2020; Franke et al., 2019).

Size exclusion is believed to be the primary mechanism of PFAS removal, especially for RO membranes. The size

of pores in RO membranes are small enough such that size exclusion can be the sole PFAS removal mechanism (Trojanowicz et al., 2018; Yoon and Lueptow, 2005).

Other removal mechanisms (e.g., adsorption, electrostatic interactions) are likely to have a role in membrane performance, particularly with NF membranes (Steinle-Darling et al., 2010; Yoon and Lueptow, 2005). Multiple researchers have shown removal of target PFAS to be chain length dependent and for removal to extend to PFAS smaller than nominal molecular weight cutoffs based on size exclusion alone (Banks et al., 2020; Franke et al., 2019).

PFAS with molecular weights lower than the MWCO can be rejected, although to a lesser extent than PFAS with molecular weights greater than the MWCO. For example, one study evaluating NF membranes found that only 70% of PFPeA was removed, which is much less than removals reported for longer-chain PFAS (Steinle-Darling and Reinhard, 2008). Source water variability (both quantity and quality of other constituents) also impacts removal efficiency of NF membranes (Franke et al., 2019). Yu et al. (2016) found that 20 mg/L of humic acids in the source water decreased PFAS removal efficiency and increased transmembrane pressure. Other constituents that may impact NF efficiency include source water metal complexes (such as iron, aluminum), and organics, and microorganisms (biofouling) (Schäfer et al., 2004).

Membranes can provide consistent removal throughout the life of the membrane module, unlike GAC and IX media, which experience decreasing removal of PFAS as adsorption sites become exhausted. RO and NF membranes are most particularly viable treatment options when PFAS concentrations are high enough to make GAC or IX adsorbent replacement too frequent and cost-prohibitive and when total PFAS water quality goals or future MCLs are too low to be met by adsorption technologies (Mobley and Tadanier, 2019).

Table 15 provides a summary of the potential PFAS removal using IX treatment, according to the USEPA's drinking water treatability database.

Table 15 – PFAS Compound Removal Performance with NF and RO Membrane Treatment (USEPA, 2014)

PFAS COMPOUND	MAXIMUM REMOVAL
PFBA	99.9%
PFBS	99.8%
PFPeA	99%
PFHxS	99%
PFHxA	99.2%
PFHpA	99%
PFOA	99%
PFOS	99%
PFNA	99%
PFDA	99%
PFDS	99%
6:2 FTS	99.5%
PFOSA	98.5%
PFDoA	87%
PFUnA	99%
NMeFOSAA*	84%

*N-methyl perfluorooctane sulfonamidoacetic acid.

POTENTIAL DOWNSTREAM WATER QUALITY CHANGES

Potential downstream water quality changes with RO and NF include PFAS removal as well as enhanced TOC, color, and dissolved constituent removal. RO and NF can generally remove TOC to below detection levels, resulting in minimal DBP formation.

Disinfection credits can be achieved when using NF and RO because of their ability to remove pathogens and viruses. The introduction of these membranes may require altering current primary disinfection practice as membrane materials are degraded by exposure to chlorine. Determination of total disinfection via the combination of membrane removal and remaining oxidant contact time must be considered and approved by the primacy agency under the Surface Water Treatment and Ground Water Rules (USEPA, 2015a, 2006). Continued preoxidation to manage mollusks, algae, or water quality concerns may necessitate dechlorination prior to membrane units.

Consumers who are currently experiencing hard water will benefit from the softening effect of this treatment, but an unintended consequence of implementing RO and NF membranes is the removal of hardness, manganese, iron, TOC, and alkalinity required for water stabilization that can lead to corrosive water. Post-treatment is often required to mitigate this issue. The Lead and Copper Rule requires review of treatment changes that have the potential to significantly impact corrosion control (USEPA, 2015b).

PROCESS INTEGRATION

Figure 15 illustrates an example process train showing the use of RO or NF membranes. RO and NF membranes require pretreatment. Pretreatment options to remove solids include full conventional treatment or sand filtration. Cartridge filters are used to remove smaller constituents, reducing fouling potential of membranes. A scale inhibitor and acid are often added upstream to reduce ions from binding together, which would form salts that can cause membrane scaling. Depending on the treatment train, process considerations should be made to dechlorinate prior to membrane filtration and monitor finished water stability from a corrosion and biological standpoint. Additional plant modifications may be needed to pump at the adequate membrane pressure.

Because membrane treatment leads to a significant loss (10%–30%) of influent water to the concentrate waste stream, integration into an existing facility or development of a greenfield installation must consider how to optimize

use of the available supply. This can involve consideration of split-stream treatment where only a portion of the total plant flow is subject to membrane treatment. Reliably achieving target finished water PFAS concentrations, piping and pumping constraints, as well as concentrate stream disposal options must be considered.



Figure 15 – Water Treatment Process Train Using NF or RO Membranes

ADVANTAGES AND DISADVANTAGES

Table 16 presents advantages and disadvantages of using NF and RO for PFAS removal. One of the major advantages is the effective removal of a wide variety of PFAS, even at high concentrations. One of the major challenges with RO and NF membrane operation is the disposal of the concentrate stream created by the process. NF and RO concentrate disposal methods are costly and potentially limited, based on region. Concentrate disposal options include: discharge to sanitary sewer, a dedicated regional concentrate treatment facility, or discharged to an outfall; deep well injection, land application (rapid infiltration systems), thermal incineration, and evaporation ponds (AWWA, 2007). Available disposal options are site-specific.

- Evaporation ponds are limited to those regions with appropriate climates.
- Deep well injection requires an appropriate underlying geology and permitting regime.
- Dedicated regional concentrate treatment facilities are only economically feasible if there is a critical mass of user facilities and an appropriate discharge outfall or injection site.
- Concentrated constituents can include not only salt but also heavy metals, radionuclides, and industrial contaminants, in some instances necessitating disposal as hazardous waste or technologically enhanced naturally occurring radioactive materials.

Given the available treatment options, design considerations should include whether and how to further concentrate the initial concentrate stream prior to disposal.

The previously stated challenges are not unique to PFAS but are complicated further by the uncertain regulatory environment surrounding PFAS. NF or RO membrane concentrate streams can be four to five times higher than the PFAS concentrations found in the permeate (Franke et al., 2019). For example, one bench-scale study showed that 64 mg/L of PFHxA in the feed stream resulted in 6 mg/L in the NF permeate stream and 344 mg/L in the concentrate stream, which is more than five times the concentration of the feed stream PFHxA concentration. While this feed concentration is significantly higher than what would be normally be detected in source waters, the concentration factor of PFHxA is representative (Soriano et al., 2017).

Given the current regulatory environment, there is considerable uncertainty regarding disposal to sewer and permitting expectations for other disposal options. PFAS may be considered pollutants as part of the Clean Water Act, and states have the right to use National Pollutant Discharge Elimination System (NPDES) permits to enforce discharge limits on PFAS into receiving waters (USEPA, 2019). A current compendium of those standards is available in AWWA's Summary of State Policies to Protect Drinking Water (AWWA, 2020).

Franke et al. (2019) evaluated GAC and IX for the treatment of PFAS (i.e., PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS) in NF concentrate. In this study, PFAS adsorption in IX and GAC applications was more efficient when treating NF concentrate compared to treating raw water, with up to four times more PFAS removal per volume of adsorbent material. The authors attributed this occurrence to the higher PFAS loading rate experienced when concentrate was used as influent to the adsorption technologies. Additionally, this research found that GAC was more effective at removing PFAS from concentrate by up to 50% when compared to IX (Franke et al., 2019). Another study evaluated the potential for NF concentrate treatment with electrochemical oxidation and found that this technology could remove PFHxA up to 95% in concentrate (Soriano et al., 2017).

rable to Advantages and Disadvantages of Membrane Separation for FFAS Removal				
RO/NF ADVANTAGES	RO/NF DISADVANTAGES			

Table 16 – Advantages and Disadvantages of	Membrane Separation for PFAS Removal
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	Demonstrated removal of all PFAS tested and anticipated removal of PFAS broadly	 Concentrate disposal challenges complicated by regulatory uncertainty Post-membrane treatment necessary to ensure stable finished water
•	Reliable and stable process	Pretreatment is important to avoiding membrane fouling or scaling and reduced finished water recovery
•	Compact systems provide smaller footprint	
Additional contaminant removal including CECs, TOC.	Additional contaminant removal including CECs, TOC, and	• Energy intensive
	pathogens	 Relatively high capital and O&M costs due to influent head pressure required and membrane module maintenance

Summary of Treatment

PFAS removal from water is variable across a range of water treatment processes and influent water quality conditions. Conventional treatment, oxidation (e.g., chlorine, ozone), UV light, existing AOP technologies, biofiltration, dissolved air flotation (DAF), and low-pressure membranes provide minimal removal of PFAS. It is unlikely that individually or in combination any of these technologies would prove to be an adequate treatment barrier when considering treatment options for targeted PFAS removal.

Table 17 provides a summary of treatment technologies discussed herein and expected outcomes with respect to PFAS removal and operations, as well as the relative cost associated with each technology. The success of each technology is site-specific and careful consideration should be given to process performance versus relative cost. Processes should be evaluated holistically, not just based on PFAS removal abilities, to determine any unintended consequences of implementation.

Existing technologies can be further evaluated and optimized for PFAS removal once several installations have operated consistently and collected PFAS removal data. Specifically, cost-effectiveness of using existing technologies for PFAS removal should be delineated, and PFAS removal could be standardized in terms of nanograms of PFAS removed per day. Future bench- and pilot-scale research needs to be conducted to evaluate the efficacy of emerging PFAS reduction technologies prior to full-scale implementation, although these methods do show promise for lowering PFAS in water supplies.

Treatment technologies can be coupled for enhanced performance. In particular, research related to RO and NF membrane concentrate treatment using adsorptive/ exchange methods is being explored. This option could provide the benefit of enhanced PFAS removal and the solution to the concentrate disposal problem. In this scenario, exhausted media or spent resin should be disposed of using high temperature incineration to prevent subsequent PFAS discharge into the aqueous environment. GAC and IX processes can be combined to provide both short-chain and long-chain PFAS removal.

Table 17 – Treatment Technology Summary

TREATMENT TECHNOLOGY	RELATIVE Cost	SHORT- CHAIN PFAS REMOVAL	LONG- CHAIN PFAS REMOVAL	WASTE STREAMS AND PFAS ENDPOINTS	ADDITIONAL OBSERVATIONS
					Useful for intermittent use.
	Moderate	< 40%	> 80%	PAC residuals removed via settling or filtration	 Increases residuals loading and decreases dewaterability.
PAC Adsorption ^b					• PFAS removal is dependent on PAC type and dose.
					• Performance impacted by competition for adsorption sites on carbon.
					Media disposal will be required.
	Moderate to High	< 96%	40% to 96%	Backwash stream or GAC media	• PFAS removal decreases as adsorption sites become exhausted, and there will be no removal once breakthrough is reached.
GAC Adsorption ^{a, b, c, e}					• PFAS will compete for sites with other organic compounds.
					 Less economically feasible at higher concentrations (mg/L) due to relatively quick PFAS breakthrough.
			5 55% to 97%		 Resin can be specialized specifically for PFAS, allowing for a higher capacity than activated carbon (site-specific).
	Moderate to High	< 95%			• Resin disposal will be required.
Ion Exchange ^{a,b,e}				Backwash stream or IX resin	 Removal decreases as IX and adsorption sites become exhausted, and there will be no removal once breakthrough is reached.
					• PFAS will compete for sites with other organics.
					 Less economically feasible at high concentrations (mg/L) due to relatively quick PFAS breakthrough.
					 NF concentrate will contain high PFAS concentrations and will require disposal, which can be costly.
Nanofiltration ^{a, b, e, f}	High	> 95%	> 95%	Concentration stream	 Post-treatment may be required for corrosion mitigation, depending on the type of NF membrane used.
					High energy requirements.
	High	> 99%	> 99%	Concentrate stream	 RO concentrate will contain high PFAS concentrations and will require disposal, which can be costly.
Reverse Osmosis ^{a, b, d}					• Post-treatment will be required for corrosion mitigation to restabilize RO permeate.
					Highest energy requirements.
					• Likely not necessary for the sole purpose of treating PFAS.

^aAppleman et al., 2014; ^bRahman et al., 2014; ^cTakagi et al., 2011; ^dThompson et al., 2011; ^eFranke et al., 2019; ^fSoriano et al., 2017.

Selecting PFAS Treatment

well-designed and executed planning process is important for selecting the right PFAS treatment solution for a given water system. As will be described, the appropriateness of treatment technologies is dependent both on the technology's ability to remove PFAS and how well that treatment fits into a water system's existing facilities, operations, and water quality constraints. Elements of a planning process to make changes in drinking water treatment are not unique to PFAS, and include

- Characterizing water supply(ies)
- Using consistent analytical support to ensure accuracy of data
- Setting well-grounded treatment objectives
- Understanding existing water demand and the condition of available assets
- Having an effective communication plan and engage your community throughout the selection process
- Supporting technology selection with bench and pilot-scale data (additional information on pilot testing can be found in Appendix A – Preliminary Treatment Evaluation)
- Maintaining a rapport with your primacy agency throughout the planning process

Planning Considerations

The following sections will discuss the planning elements listed in greater detail to provide additional context for initiating PFAS treatment of drinking water.

PFAS PLANNING QUESTIONNAIRE

As described in the following sections, planning for PFAS treatment has several steps. To assist with initial planning efforts, the following questionnaire for PFAS treatment methods was developed to help guide the reader through important considerations:

- 1. Will this treatment method remove PFAS present in the water from this water source/water treatment facility?
- 2. Will this treatment provide ancillary water quality benefits important to my community?
 - a. Reduced taste and odor issues
 - b. Reduced levels disinfection byproducts
 - c. Reduced hardness
 - d. Reduced microbial risk
 - e. Reduced levels of CECs

- 3. What additional measures will be needed to avoid water quality issues if this treatment process is installed at this water source/water treatment facility?
 - a. Finished water stability/pH or alkalinity adjustment/ revisit corrosion control treatment
 - b. Modify primary disinfection strategy/CT
- 4. What additional treatment will be needed to prepare water from this water source/water treatment facility for this treatment process?
 - a. Modify preoxidation practices
 - b.Additional pretreatment
 - c. Additional filtration
 - d.pH or alkalinity adjustment
- 5. Where in the pipe network treatment train would this treatment be installed? What are the resulting implications for facility and operations?
 - a. Will additional pumping be required?
 - b. Will process controls need to be updated or replaced?
- 6. Are there viable recycling/disposal options for treatment process (and associated pretreatment process) waste streams at this water treatment facility and do those options destruct PFAS?
 - a. What are likely impacts on existing residual processing and disposal?
 - b. What is a viable strategy for recycling/disposing of liquid waste streams?
 - c. What is a viable practice for recycling/disposal of solid waste stream(s)?

Note: these considerations are in addition to expected civil engineering due diligence for developing a planning level design (e.g., structural, electrical, site, piping, access, and safety considerations).

ESTABLISHING TREATMENT OBJECTIVES

PFAS CONCENTRATION RANGE OF INTEREST There are state and federal advisory levels to inform PFAS

Water systems evaluating drinking water treatment for PFAS will need to consider

 Applicable federal and state standards and administrative policies for drinking water quality, discharges to surface water and aquifers, and disposal of solid wastes

 Customer expectations, including the perspectives of community leaders

 Implication of new treatment on achieving and sustaining other water quality objectives and capital program priorities

- Financial implications of treatment changes for the water system and its rate payers
- · Potential changes in regulatory requirements
- · Timeline for operationalizing treatment objectives

UNDERSTAND WATER DEMAND AND AVAILABLE ASSETS

Selecting PFAS treatment requires a reliable understanding of current conditions and projection of future conditions, including

- · Current and anticipated water demand
- Current and anticipated water supplies (e.g., permitted wells, surface water withdrawals, purchased capacity, current blending strategies, capacity to divert future demands to alternative supplies, etc.)
- State of current capital facilities (e.g., remaining useful life of existing wells, treatment facilities, pumps, etc.)
- Technical capability of system staff and information systems

The balance of this selection process focuses on choosing between one of four treatment strategies: PAC, GAC, IX, or NF/RO membranes. As a practical matter, water systems will also need to weigh considerations like source abandonment, purchasing water on a wholesale basis, and blending alternatives. Evaluating the complete list of options will entail cost and policy decisions as to which option is most sustainable for the community(ies) served.

EFFECTIVE COMMUNICATION PLANNING

- Connect effort to system
 strategic communication plan
- Actively and transparently engage the community(ies) served
- Employ effective communication strategies

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of long-chain PFAS. In these states, consideration will need to be given not just to individual PFAS removal but also to cumulative removal.

Some stakeholders are interested in setting PFAS removal goals based on total PFAS or a surrogate analytical value. No current U.S. benchmarks exist for such a value. In Europe, the following benchmarks have been developed:

- Sweden, has a cumulative standard of 90 ng/L based on 11 PFAS (PFBS, PFHxS, PFOS, 6:2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA)
- European Union has a standard for PFAS similar to its pesticide standard of 100 ng/L for individual PFAS and 500 ng/L for PFAS in total. Currently, the cumulative standard is method-defined (ISO 25101:2009). An updated method is under development.

To put this PFAS concentration range in perspective, see Table 18. The values in the table are in nanograms per liter. One nanogram per liter is one billionth of a gram in one liter of water. Six of the nine effluent water concentrations (gray cells) are indistinguishable given detection limits of current analytical methods, if the PFAS of interest was PFOA/ PFOS monitored using USEPA method 537.1. Moreover, realized effluent concentrations will vary over time as a function of variability in process control, treatment media, membrane integrity, influent water characteristics, and operational factors. Table 18 - Scale PFAS Concentrations based on StartingConcentration

REMOVAL	RESULTING EFFLUENT CONCENTRATION (NG/L)		
Example Influent	1,000	100	10
After 95% Reduction	50	5.0	0.5
After 99% Reduction	10	1.0	0.1
After 99.9% Reduction	1.0	0.1	0.01

WATER QUALITY CONSIDERATIONS

Understanding which PFAS or groups of PFAS are present is important for selecting a PFAS treatment process. For example, removal efficiencies are affected by

- Carbon chain length: Longer chain length promotes greater adsorption in GAC treatment, whereas IX has shown to have more reliable removal of short-chain PFAS.
- PFAS functional groups: Functional groups, such as sulfonic acid and carboxylic acid, can influence removal. For example, sulfonic acids are more readily adsorbed compared to carboxylic acids.

Treatment design and ultimately the efficiency of its operation will also involve understanding patterns in current and forecasted PFAS occurrence and the potential to terminate reliance on a contaminated source or manage influent concentrations at the new treatment process through placement or managing blending. Characterizing source water is described in "Source Water Evaluation Guide for PFAS", a companion document to this guide. Sampling and analysis for PFAS is time consuming and expensive but making a major capital and operations investment should be supported by a robust dataset.

Key questions to organize data collection to answer are

- What is the anticipated long-term and short-term PFAS loading?
- Are targeted PFAS present on a continuous or sporadic/ seasonal basis?
- Are the occurrence and abundance of PFAS consistent over time?

- In addition to characterizing influent PFAS concentrations, understanding water quality to design a drinking water treatment system for PFAS requires understanding water quality at the anticipated treatment installation site. Factors that affect may impact
- Scaling potential—pH, alkalinity, hardness. To the degree possible, developing data from existing source waters or plant records and analyzing patterns as function of anticipated future flows and blends of source waters will inform how robust pretreatment will need to be to support potential treatment options. Understanding alkalinity will also inform the feasibility and approach for chemical modification of such parameters before and after treatment process option addition.
- Fouling potential—TOC, iron, and sulfate concentrations depending on the source water and existing treatment train warrant attention. As with pH and alkalinity, representative data over an extended period will be beneficial in process option selection and design.
- Temperature–GAC, IX, and membrane process performance are impacted temperature.

Collecting source water and finished water data is also an opportunity to assess the stability of current process control and to determine hydraulic or operational constraints that need to be resolved prior to installation of PFAS treatment system.

IMPLEMENTATION CONSIDERATIONS

All three of the treatment processes available for PFAS removal will trigger state review of corrosion control treatment practice. Consequently, in addition to understanding water quality with respect to PFAS removal, analysis will also have to prepare the system for evaluating corrosion control. Review of existing LCR and customer requested lead and copper in-home tap sample data would be a preliminary step. Evaluating WTP effluent data as well as available distribution system data (disinfectant residual, corrosion inhibitor concentration, pH, alkalinity, etc.) would likewise inform understanding of how well current corrosion control is working and ascertain how detailed additional analysis will be given PFAS treatment options.

Similarly, each of these treatment processes may require adjustments to the current disinfection practice in the WTP. A review of disinfection strategies will discern if there are any major challenges caused by reduced disinfectant contact time, revisions to oxidant practice for manganese oxidation, algae control, or other purposes. Alternatively, some NF or RO treatment processes may provide additional disinfection credit.

Each PFAS treatment option generates a waste stream with concentrated PFAS and potentially other problem constituents. Depending on applicable regulations, the disposal of these waste streams may play a critical role in the selection process. Membrane filtration concentrate, for instance, may need to be managed with an underground injection well; GAC reactivation will need to be assessed; and IX resins will need to be properly disposed.

Preliminary Treatment Evaluation

Prior to full-scale implementation, bench- and/or pilot-scale testing can be used to validate a treatment technology for effective PFAS removal. Bench- and pilot-scale testing are encouraged to help determine treatability of the PFAS in the water because the degree of PFAS removal greatly depends on the chemical structure and number of PFAS present. At a minimum, pilot-scale testing should be conducted to assess the PFAS treatability and provide an estimate of treatment costs that meet water quality objectives.

- Planning processes must set aside adequate time and budget for testing, as described by the following:
- Rapid small-scale column testing (RSSCT) for GAC and IX requires 1–3 months, low to moderate cost.
- Pilot-scale testing for GAC or IX typically take 6–12 months, moderate to high cost.

Bench- or pilot-scale testing for NF/RO must continue until the rate of water passing through the membrane has stabilized (permeate flux rate—which is dependent on the water quality and reject flow stabilization), moderate to high cost.

Bench-scale and pilot-scale testing can be an iterative process requiring multiple test cycles to determine the adjustments needed to obtain desired performance. There is a role for both bench and pilot-scale testing; pilot-scale test results are important to translating the findings from preliminary screening tests to full-scale implementation.

For the purposes of this guide, bench- and pilot-scale testing are discussed for drinking water treatment applications with example data outputs plotted as figures. This may include testing of the following waters:

- Source waters with no PFAS detected that are spiked with PFAS to known concentrations
- Finished waters that will be tested for PFAS polishing treatment

It should be noted that all example data in the following section is fabricated and not associated with actual PFAS bench- or pilot-scale testing; consequently, data should not be used to determine the best treatment type but rather to inform data outputs.

BENCH-SCALE TESTING

Bench-scale testing provides information on treatment capabilities through jar testing, isotherm batch testing, and rapid small-scale column testing. Bench-scale testing is used to predict treatment performance with a specific water supply without installing a pilot or full-scale system. When evaluating PAC, the bench-scale testing consists of conducting jar tests that simulate PAC addition through relevant treatment processes.

For water systems considering GAC or IX, isotherm testing may be beneficial when evaluating multiple media (e.g., carbon or resin) types. Because the isotherm testing can be conducted quickly, it is useful for screening a larger array of media quickly. Isotherm testing indicates the adsorptive capacity and kinetics for each media (Lampert et al., 2007). RSSCT is used to compare GAC and IX media efficacy. RSSCT data provides a tool to estimate PFAS breakthrough (i.e., the number of bed volumes prior to media passage of contaminant) over a shorter period than a pilot-plant test. This initial estimate of breakthrough can guide subsequent pilot-testing and inform design and costing steps.

JAR TESTING

Jar testing is frequently used by researchers and water systems to simulate PAC addition, coagulation and flocculation treatment at the bench-scale level. Figure 16 shows a photo of a jar tester and Figure 17 is an example of typical jar testing data. Jar testers are programmed to simulate a specific WTP's operation, and relevant pretreatment chemicals (e.g., PAC, coagulant, caustic, etc.) are added during testing. In a jar test experiment, raw water is added to the jars, PAC is added, and the jar tester is turned on. Prior to starting a jar test experiment, a protocol should be developed to ensure treatment is accurately simulated. In PFAS applications, specific PFAS stock solutions can be added to water prior to testing, or raw water that already contains PFAS can be used.

Source waters with known PFAS concentrations



Figure 16 – Jar Tester Evaluating PAC Addition and Conventional Treatment



Figure 17 – Example Jar Testing Data for Testing Three PAC types (Constant PAC Dose)

ISOTHERM TESTING

Isotherm batch testing is conducted in laboratories with small flasks or batch reactors to evaluate the adsorptive behaviors of GAC media or IX resin material under equilibrium (constant temperature and pressure). Adsorption isotherm testing includes adding known amounts of treatment media (adsorbents) to a flask or bench-scale reactor with raw water containing a known water quality (PFAS concentrations) and allowing the sample to achieve equilibrium. Isotherm equilibrium is met when the adsorption process reaches a steady state and is no longer changing (Real et al., 2017). Once the sample is at adsorptive equilibrium, or, steady state and no longer changing, it is tested for PFAS removal and the adsorptive capacity of the media is assessed. The adsorption isotherm data is fitted with Langmuir and Freundlich models and evaluated for adsorption capacity (Real et al., 2017).

Typical monitoring protocols for isotherm testing include set sampling times and water quality tests for analyzing data. Figure 18 provides an example bench-scale GAC isotherm setup and Figure 19 shows typical experimental data for isotherm testing. Isotherm testing includes varying contact times, concentrations based on application. The amount of PFAS in the sample can be calculated using the following equation (Desta, 2013):

Equation 1 – Adsorbed PFAS Concentration

$$Q_e = \frac{(C_i - C_e)V}{m}$$

Where C_i and C_e are the initial and equilibrium concentrations (mg/L), m is the mass of the adsorbent (g), and V is the volume of the solution (mL). The percent removal of PFAS can be calculated using the following equation (Desta, 2013):

Equation 2 – Adsorbed PFAS Concentration

$$\% R_{PFAS} = \frac{(C_i - C_e)}{C_i} \times 100$$

Advantages of bench-scale isotherm testing include fast preliminary adsorption capacity data results for different types of GAC and IX media. GAC media can be derived from different materials including bituminous coal and coconut shells (Dickenson and Higgins, 2016). Bench-scale isotherm tests allow the utility to evaluate multiple media at once and prioritize media that are more effective at removing the PFAS in the source water. Drawbacks to isotherm testing include the static conditions of the test, limited scalability to full-scale, and the inability of the test to provide design parameters such as hydraulic performance, loading rates, or EBCT. Isotherm data alone is inadequate to support fullscale design.



Figure 18 – Isotherms for Rapid GAC Treatment Assessment



Figure 19 – Example Isotherm Testing Data for One PAC Type

RSSCT TESTING

RSSCT studies are conducted with either GAC media or IX resin material to simulate full-scale GAC or IX performance by producing kinetic performance predictions at a fraction of the time and cost compared to pilot-scale testing. The RSSCT involves filling small columns (typically 0.25 to 2 in. in diameter) with either GAC media or IX resin that has been ground to a fraction of the original size and feeding

water at a known flow rate through the columns. The sizing of RSSCT media can be determined based on a scaling ratio of the RSSCT EBCT and larger pilot-or full-scale column desired EBCT.

The correct size ratio between RSSCT and full/pilot-scale is dependent on several parameters: hydraulic loading, particle diffusivity, material densities and pore volume (Crittenden et al., 1991; Poddar, 2013). Consequently, it can be difficult to determine the most appropriate ratio to use when sizing media to use in RSSCT. RSSCT is well recognized as a useful tool, but considerable care and experience are necessary to reliably apply the results directly to full-scale conditions.

Testing plans for RSSCT bench-scale studies are unique to each treatment scenario and will include set GAC or IX media amounts, influent flow rates, effluent sampling frequency and water quality analysis. RSSCT testing plans typically are aimed to

- Evaluate which media can achieve target EBCT values that are based on full-scale EBCT design goals, and
- Determine when breakthrough is predicted to occur based on finished water quality goals.

Figure 20 provides an example bench-scale RSSCT setup with GAC media and Figure 21 shows typical experimental data. The flow rate evaluated during RSSCT is generally low (in milliliters per minute [mL/min]), and automation and in-line monitoring are not typically practiced. The raw water flows through the column media and the effluent water is collected and analyzed to determine the removal capabilities and breakthrough of PFAS. Results from the testing provide information on GAC adsorption capacity, allowing the performance of multiple types of GAC to be evaluated, and the kinetics provide breakthrough curves that provide information on effectiveness and EBCT indication for pilot-and full-scale implementation.

Some of the drawbacks to RSSCT studies include not addressing seasonal variability of the source water, impacts of media pulverization on PFAS removal performance vs. full-scale, and low scalability to full-scale implementation. For example, a one-time RSSCT study could miss the effect of seasonal differences in organics on media performance (Dickenson and Higgins, 2016).



Figure 20 – RSSCT GAC Bench-Scale Testing



Figure 21 – Example RSSCT Testing Data for One GAC Type

Pilot-Scale Testing

Pilot-scale testing involves evaluating treatment technologies at a larger scale and is generally performed at a field location using larger columns (typically 6 to 12 in. in diameter) or vessels, and higher flow rates. Pilot-scale testing is used by water systems to confirm the results of bench-scale testing or validate a treatment technology and associated design criteria. Additionally, pilot-scale testing allows for a more complete evaluation of treatment technologies, because multiple design parameters can be compared and optimized during the study. Due to the larger scale, pilot-scale testing involves additional design considerations and typically includes the installation of automatic chemical feed lines, in-line flow meters, pressure gauges, turbidimeters, and other monitoring devices.

Pilot-scale testing is used to evaluate GAC, IX, and RO/NF membrane technology and typically requires 6 to 18 months to complete, depending on the test objectives. Membrane technology pilot-scale systems (NO or RF) use small scale membrane units with set design parameters to match fullscale implementation (Appleman et al., 2013; Steinle-Darling and Reinhard, 2008). The design of pilot-scale studies using GAC or IX (or both) often contain columns or vessels in series, parallel, or with lead/lag systems. Examples of pilotscale contact columns and membrane pilots are shown in Figure 22 and Figure 23, respectively. Figure 24 shows typical monitoring results for pilot-scale testing over the course of several months.

Pilot-testing is advantageous to water systems aiming for a comprehensive evaluation and prediction of full-scale treatment results and waste stream impacts. Additionally, pilot-scale testing is the most scalable testing to fullscale implementation and can elucidate potential design issues such as targeted EBCT, splash plate design, and pressurizing requirements. Pilot-testing is often completed over a longer timeframe (months to a year) to account for varying seasonal water quality impacts, and varying design parameters including membrane permeate flux and flushing, GAC/IX hydraulic loading rate, EBCT, and backwashing frequency to achieve optimum design criteria. Although pilot-testing provides the best scalability to full-scale implementation, the primary disadvantages include the long timeframe of testing and higher associated costs.

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100



Figure 22 – Pilot-Scale GAC or IX Columns



Figure 23 – Pilot-Scale Membrane Skids



Figure 24 – Example Pilot-Scale Data for Comparing Treatment of PFOA with GAC and IX

When water systems are evaluating pilot-scale testing, there are several aspects that must be considered prior to implementation, including budget, timing/duration, treatment objectives, testing conditions, equipment, monitoring, staffing, and quality control measures. Table 19 describes considerations for each pilot-scale decision component.

PROTOCOL Component	DESCRIPTION
Budget	Dependent on the degree of operator attention, length of pilot test, water quality parameters evaluated, number of pilots (for multi-process testing) and system procurement drive budget
	The pilot test duration can be dependent on several items
	Seasonal variations—it is important to capture water that represents the worst-case influent water quality for at least a portion of testing. Generally, only applies to surface water because groundwater is relatively consistent.
nining and Duration	Breakthrough-operating until breakthrough is complete will provide an idea of operational costs (for GAC and IX).
	Membrane acclimation—If new membranes are evaluated, the pilot will need to operate until a steady flux is reached prior to evaluating constituent removal.
Water Quality Objectives	Appropriate water quality objectives should be identified prior to implementing a pilot test. Objectives to consider for applications in addition to PFAS removal include turbidity, organics, and trace organic compound removal goals. Another objective could be to determine the number of bed volumes that can be treated prior to media change-out (for GAC and IX).
Testing Conditions	Pilot operating conditions, such as media type (for GAC), resin type (for IX), flow rate, EBCT, loading rate, membrane recovery (for NF or RO), etc., that will be evaluated during pilot testing should be established. Multi-process test conditions will need to be considered holistically.
Equipment	Procurement of pilot equipment will be required prior to starting the pilot testing. Equipment can typically be constructed by a water system, borrowed or rented from a major supplier or purchased from a reputable pilot equipment manufacturer. Multi-process testing will require the procurement of additional pilot equipment, if desired.
Monitoring	A robust monitoring protocol should be established to include the analysis of water quality and hydraulic parameters. Performance trends should be evaluated daily, weekly, or biweekly, depending on the parameter, to timely identify and correct any operating issues. Frequency of monitoring at each location should be established.
Staffing	Roles of individuals involved with the pilot test should be established, including those who will be collecting and analyzing samples, evaluating and trending data, and making operational adjustments and equipment repairs. Staffing can be provided by the water system, a carbon/resin/membrane supplier, a third party, or by a combination of these staffing methods.
Quality Control	A control column (for GAC and IX) should be used if optimization testing is occurring, and a baseline should be established prior to changing variables. Pilots should be operated until hydraulic and water quality results reach steady state prior to evaluating PFAS removal.

Table 19 - Pilot-Scale Testing Implementation Considerations

Key Parameters to Monitor

Water quality and hydraulic performance parameters are critical to

- Initial data collection to support the treatment evaluation process
- Pilot-scale testing
- Ongoing operations once a selected treatment is installed

In addition to PFAS levels that need to be monitored during PFAS treatment, influent water quality parameters can give insight into the need for and success of pretreatment to eliminate interferences. TOC, UV absorbance at wavelength at 254 nm (UV₂₅₄), and pH are a few parameters that are imperative to be analyzed during pilot testing. Several studies have demonstrated that organic matter plays a

Table 20 - Example Sampling Plan during Treatment

significant role in the removal of PFAS (Bao et al., 2014; Kothawala et al., 2017b) Other parameters that can affect treatment are iron, manganese, and sulfate. Iron and manganese can cause fouling to treatment media and equipment-reducing capacity for contaminant removal, while sulfate is a competing ion during IX treatment.

Hydraulic parameters should also be monitored in both pilot and full-scale operation. These parameters are essential for effective process control. Flow rate, loading rate (calculated using flow rate), and pressures/head loss should be routinely tracked in GAC, IX, and membrane processes. Additionally, any chemical addition used during bench or pilot testing should also be recorded and tracked. Table 20 provides a list of parameters appropriate for monitored during treatment of PFAS.

PARAMETER	FREQUENCY*
Flow Rate	Continuous/Daily ⁺
Water Level/Pressure	Continuous/Daily ⁺
Cumulative Volume	Continuous/Daily ⁺
Pressure across membrane and permeate flow (membrane applications)	Continuous/Daily ⁺
рН	Daily [‡]
Temperature	Daily [‡]
Dissolved Oxygen	Daily [‡]
Conductivity	Daily [‡]
Total Organic Carbon	Daily [§]
UV (specifically 254 nanometer wavelengths)	Daily [§]
Redox Potential	1 x Week [§]
Turbidity	1 x Week [§]
PFAS	1 x Week [§]
Anions such as nitrate, chloride, and sulfate (especially for IX applications)	1 x Week [§]
Metals such as arsenic, iron, manganese	1 x Week [§]
Silt Density Index (membrane applications)	1 x Week [§]
CECs and nonroutine compounds	Site specific [§]
Alkalinity	1 x Week [§]
Hardness	1 x Week [§]
Total Dissolved Solids	1 x Week [§]

*Parameters evaluated daily should be monitored around the same time each day. Parameters evaluated weekly should be evaluated on the same day each week. The date and time of initial pilot startup and all sample collection shall be recorded along with any interference with treatment process due to shutdowns, significant increase, or drop in flow rate, etc. †Continuously monitored parameters will be manually checked daily using the appropriate gauges/meters to ensure the instrumentation is operating correctly. ‡Parameter should be monitored and tracked at source/treatment influent. §Parameter should be monitored and tracked at source/treatment influent and finished water.

PFAS Treatment Testing Summary

Table 21 summarizes the benefits and implications of testing options described in this chapter.

Table 21 – PFAS Treatment Validation Summary

	ISOTHERMS	RSSCT	PILOT TESTING
Primary Objective	Feasibility and equilibrium testing for kinetic model/screening of media/resin	Development of predictive modeling of kinetic performance of media/resin	Treatment assessment for process validation that is implementable at full-scale
Treatment Processes Tested	GAC IX	GAC IX	GAC IX Membranes
Typical Length of Study	1 to 4 weeks	4 to 16 weeks	6 to 18 months
Key Data Derived	Relative removal rates Indication of adsorptive/reactive capacity of media or resin	Indication of adsorptive/reactive capacity of media or resin Complete breakthrough curves	Long-term removal rates Water quality data that can inform competition or potential treatability issues Design criteria based on scalability of pilot systems Water corrosivity after treatment
Limitations	Mostly qualitative data that can inform media/resin selection for a pilot-scale validation. Seasonal variation in water quality is not accounted for.	Scalability issues especially with GAC due to loss of pore characteristics during media grinding Seasonal variation in water quality is not accounted for.	Informs full-scale but may fully represent treatability at full-scale
Relative Cost*	<\$100,000	\$50,000 to \$200,000	\$200,000 to \$800,000

*Includes engineering, equipment costs, laboratory labor, analytical costs, and data analysis. Estimates are provided for relative cost assessment. The costs will be largely dependent on scope of treatment validation study.



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Appendix A

Review of Conventional and Novel Technologies

This section provides a review of conventional and novel treatment technologies for the removal of PFAS. PFAS are highly soluble, have both hydrophobic and hydrophilic properties, low volatility, and contain strong carbonfluorine bonds. PFAS are generally resistant to chemical, physical, and biological degradation, which limits many potential removal mechanisms (Rahman et al., 2014). These challenges are encouraging innovative research to discover novel treatments for PFAS as well. Treatment technologies that provide little demonstrated PFAS removal include conventional treatment (coagulation, flocculation, and sedimentation), granular media filtration (without activated carbon), oxidation, advanced oxidation processes (AOPs), biofiltration, and large-pore membranes (microfiltration, MF, and ultrafiltration, UF). Additionally, novel technologies in development, such as ozofractionation, chemical oxidation, and other destructive technologies, are in development. These novel technologies show promise for removing PFAS but have not been adequately demonstrated to remove PFAS from drinking water. Additional approaches and technologies will continue to be developed and evaluated in the future.

CONVENTIONAL TREATMENT PROCESSES AND PFAS REMOVAL

Multiple studies have shown that typical treatment processes used for drinking water treatment do not significantly impact influent PFAS concentrations (Boiteux et al., 2017; Boone et al., 2019; Rahman et al., 2014). These treatment technologies are discussed in detail in the following sections.

CONVENTIONAL COAGULATION AND FLOCCULATION

Both full-scale and bench-scale data on removal of specific PFAS illustrates that coagulation, softening, and flocculation, as commonly used in surface water applications, provide little reduction in PFAS levels (Appleman et al., 2014; Bao et al., 2014; Belkouteb et al., 2020; Dauchy, 2019; Rahman et al., 2014; Takagi et al., 2011; Xiao et al., 2013)alum (Al2(SO4. Multiple researchers report removals of less than 20% and often less than 10% (Appleman et al., 2014; Kim et al., 2020; Xiao et al., 2013). This limited removal is true of both ferricand alum-based coagulants (Appleman et al., 2014). For facilities using magnetic ion-exchange resin, minimal data is available; however, one study found PFAS removal of 33% (Lundgren, 2014).

There is some bench-scale analysis illustrating somewhat improved but still poor removal under enhanced coagulation conditions expected by the Stage 1 Disinfection Byproduct Rule (Xiao et al., 2013). Removal using enhanced coagulation is influenced by the concentration of background organic compound concentrations, as these compounds will complete with PFAS for coagulant adsorption sites (Bao et al., 2014). Research to date suggests less effective removal of short-chain PFAS and PFAS containing a charged functional group than long-chain PFAS (Appleman et al., 2014).

OXIDATION AND ADVANCED OXIDATION PROCESSES

The properties of PFAS reduce the breakdown capabilities of oxidative processes. For example, the presence of the strong carbon-fluorine bonds with electron withdrawing functional groups (e.g., carboxylic acid and sulfonic acid) provides minimal opportunity for oxidation using chlorine, ozone, or peroxide to de-fluorinate these compounds (Appleman et al., 2014; Rahman et al., 2014; Thompson et al., 2011; Trojanowicz et al., 2018)whilst the second uses membrane processes and advanced oxidation to produce purified recycled water. At both facilities perfluorooctane sulfonate (PFOS. In fact, research has shown that ozone can lead to an increase of certain PFAS as a result of the breakdown of PFAS-related precursors to PFOS and PFNA (Pan et al., 2016; Rhoads et al., 2008).

The combination of an oxidant with either another oxidant or irradiation (e.g., ultraviolet, UV) is known as an AOP. In drinking water treatment applications, AOPs are typically the combination of ozone/peroxide (referred to as peroxone), UV/peroxide, or UV/ozone, although other types of AOPs exist. AOPs produce hydroxyl radicals, resulting in significantly stronger oxidizing power than chlorine, ozone, or peroxide by themselves (Trojanowicz et al., 2018).

Appleman et al. (2014) studied PFAS removal from 20 treatment trains throughout the U.S. with a range of treatment processes. They found that oxidation processes, including chlorination, ozonation, potassium permanganate, and UV-based AOPs were ineffective at removing PFOS and PFOA at multiple treatment facilities. Additionally, research has shown that PFAS removal using ozone is insignificant, even at high ozone doses and long contact times (Takagi et al., 2011). Trojanowicz et al. (2018) evaluated ozone-based AOPs for the removal of PFOA at the bench-scale level and found that PFOA removal was negligible when using ozone. Removal when using UV and UV/ozone was insignificant (10% to 25%, depending on contact time). Supplementing titanium oxide with UV/ozone resulted in up to 45% removal, depending on contact time.

BIOFILTRATION

PFAS are generally resistant to biodegradation, making biofiltration an unlikely candidate for PFAS removal (Pan et al., 2016; Rahman et al., 2014; Sun et al., 2016). However, one study showed that biofiltration, when coupled with GAC, could remove long-chain PFAS, but the extent to which biological removal played a role over adsorptive removal is unknown (Thompson et al., 2011).

MICROFILTRATION AND ULTRAFILTRATION MEMBRANES

Given the large pore size $(0.001-10 \ \mu m)$ of MF and UF membranes, there is limited potential for the removal of PFAS by size exclusion. Based on the expectation that negligible PFAS removal can be achieved using low-pressure membranes, minimal research has been attempted to evaluate these technologies for PFAS removal.

One study showed that UF membranes were unable to provide any PFAS removal (Thompson et al., 2011)whilst the second uses membrane processes and advanced oxidation to produce purified recycled water. At both facilities perfluorooctane sulfonate (PFOS, and a second study showed no removal through MF (Appleman et al., 2014). This second study did observe partial removal of some PFAS, including PFOS, PFDA, and PFOSA, in full-scale data where MF and UF were operated in in parallel (Appleman et al., 2014).

DISSOLVED AIR FLOTATION

In drinking water treatment, DAF is most often used after coagulation and flocculation for the removal of suspended solids using fine bubble diffusion. Observed removal of long-chain PFAS is believed to be caused by these molecules having a higher affinity for the air/water interface resulting from DAF air bubbles, and subsequent removal with the surface scum (Appleman et al., 2014).

Studies to-date show that DAF is able to provide partial removal of long-chain PFAS (Dickenson and Higgins, 2016). Partial removal of PFOS (49%) and PFNA (29%) was observed but shorter chain PFCAs and PFSAs tested were not removed well (Dickenson and Higgins, 2016; Thompson et al., 2011).

NOVEL METHODS IN DEVELOPMENT

Significant research investment has been made for technologies to remediate contaminated sites. Emerging drinking water treatment processes include electrocoagulation, plasma, ozofractionation, chemical oxidation, and sonolysis. Many emerging processes are energy intensive and full-scale demonstration has not yet occurred. Once these technologies meet treatment goals at a demonstration scale, implementation for drinking water treatment will require

- Development of practical insight to guide scalability, design, and construction.
- An understanding of capital and operation considerations including associated costs.
- Evaluation of consequences for water quality beyond the removal of PFAS.
- Introduction to and acceptance by regulators.

As discussed previously, existing PFAS treatment processes remove PFAS from water but do not destroy PFAS. Identifying alternative technologies are affordable, practical to implement, and do not have a PFAS contaminated waste stream or waste product is a current research priority. The following section describes technologies currently being explored by the research community. Further research is required before any of these processes can be used for PFAS treatment by drinking water systems.

THERMAL TREATMENT

Thermal treatment can be used for complete PFAS destruction. In this application, heat is applied directly to PFAS-contaminated soil, media, or resin, then PFAS become vaporized or destroyed. Vaporized PFAS can be captured and destroyed in off-gas treatment (ITRC, 2018). The use of this technology is still in development and several data gaps exist. There is discrepancy as to the appropriate temperature needed for PFAS destruction, and it appears as though various PFAS species require differing temperature. A drawback of using thermal destruction is that this process is energy intensive and subsequent off-gas treatment may be required (ITRC, 2018).

Another type of thermal treatment is plasma, which uses ionized air or gas to create a very hot electrical discharge (similar to lightning in the environment). Temperatures can reach the thousand degree level and have been shown to reduce PFAS up to 90% to PFAS chemical elements (e.g., fluorine, carbon) (Lewis et al., 2020)

OZOFRACTIONATION

Ozofractionation is a multiphase process that uses a catalyzed reagent to aid in organics removal by chemically oxidizing organic contaminants and forming concentrated foam fractionates (Ross et al., 2018)commonly in the parts per trillion range. PFASs comprise >3,000 individual compounds, but the focus of analyses and regulations has generally been PFASs termed perfluoroalkyl acids (PFAAs. Ozofractionation occupies a relatively small footprint compared to alternative treatment technologies and can treat a wide range of PFAS. The process consists of a series of columns where water is contacted with ozone bubbles that remove PFAS. This technique has been shown to chemically oxidize short- and long-chain PFAS, resulting in foams that are removed at the top of ozofractionation columns to lower concentrations in treated water (Ross et al., 2018) commonly in the parts per trillion range. PFASs comprise >3,000 individual compounds, but the focus of analyses and regulations has generally been PFASs termed perfluoroalkyl acids (PFAAs. However, the foam produced by this process is highly concentrated with PFAS and would need to be further treated or disposed of appropriately. More research at the pilot-scale level is required prior to fullscale implementation.

ALTERNATIVE ADVANCED OXIDATION PROCESSES (AOPS)

As discussed previously, advanced oxidation using chlorine or ozone as well as AOPs are forms of chemical oxidation. Persulfate is an alternative chemical oxidant that has been evaluated for PFAS removal from soil and drinking water (Dombrowski et al., 2018; Hori et al., 2005) which are some of the strongest bonds in chemistry. High energy is required to break C-F bonds, which results in this class of compounds being recalcitrant to many degradation processes. Many technologies studied that have shown treatment effectiveness for PFAS cannot be implemented in situ. Chemical oxidation is a demonstrated remediation technology for in situ treatment of a wide range of organic environmental contaminants. An overview of relevant literature is presented, summarizing the use of single or combined reagent chemical oxidation processes that offer insight into oxidation-reduction chemistries potentially capable of PFAS degradation. Based on the observations and results of these studies, bench-scale treatability tests were designed and performed to establish optimal conditions for the formation of specific free radical species, including superoxide and sulfate radicals, via various combinations of oxidants, catalysts, pH buffers, and heat to assess PFAS treatment by chemical oxidants. The study also suggests the possible abiotic transformations of some PFAS when chemical oxidation is or was used for treatment of primary organic contaminants (e.g., petroleum or chlorinated organic compounds. Persulfate must be activated to generate free radicals. Persulfate can be activated in multiple ways, including photochemically (UV light), with microwave energy, using elevated temperatures (at least 35 to 40 °C), with a base (pH > 11), with iron, or with hydrogen peroxide (Huling and Pivetz, 2007).

The most common activation method evaluated for PFAS removal is the use of heat activation. Research has shown that PFOA and other PFCAs were degraded with 99% removal after a six hour contact time (Hori et al., 2005). Others have shown that heat-activated persulfate achieved the greatest PFCA degradation compared to alternative activation methods (Dombrowski et al., 2018) which are some of the strongest bonds in chemistry. High energy is required to break C-F bonds, which results in this class of compounds being recalcitrant to many degradation processes. Many technologies studied that have shown treatment effectiveness for PFAS cannot be implemented in situ. Chemical oxidation is a demonstrated remediation technology for in situ treatment of a wide range of organic environmental contaminants. An overview of relevant literature is presented, summarizing the use of single or combined reagent chemical oxidation processes that offer insight into oxidation-reduction chemistries potentially capable of PFAS degradation. Based on the observations and results of these studies, bench-scale treatability tests were designed and performed to establish optimal conditions for the formation of specific free radical species, including superoxide and sulfate radicals, via various combinations of oxidants, catalysts, pH buffers, and heat to assess PFAS treatment by chemical oxidants. The study also suggests the possible abiotic transformations of some PFAS when chemical oxidation is or was used for treatment of primary organic contaminants (e.g., petroleum or chlorinated organic compounds. However, PFSAs appear to be more recalcitrant to chemical oxidation compared to PFCAs, suggesting that if developed further persulfate and other alternative chemical oxidants will be best suited to site-specific applications (Ross et al., 2018).

Electrochemical oxidation (also referred to as *electrocoagulation*) is emerging as an additional oxidative strategy to reduce PFAS through use of hydroxyl radicals and reaction with free-flowing electrons between an anode

and cathode surface. Liang et al. (2018) found removals of 96% and 99% of PFOA and PFOS, respectively, through a titanium/sulfate electrochemical oxidation process. This method has been proposed for concentrate waste stream management, because some studies have shown that PFAS defluorination may be achieved (Bentel et al., 2019).

SONOLYSIS

Sonolysis refers to the use of sound waves to generate chemical reactions in a solution. Sound waves in the liquid produce high vapor temperatures that support pyrolysis and promote the combustion of target chemicals (Arias Espana et al., 2015). This technique has been used with some degree of success to remove PFAS. A sound wave frequency ranging from 20 kilohertz (kHz) to 1,100 kHz can be used to achieve cavitation in water, where PFAS can be degraded using frequency between 500-1,100 kHz (Campbell and Hoffmann, 2015; Ross et al., 2018).

The exploration of higher frequencies has also been favorable for PFAS destruction, but high energy costs associated with this application should be evaluated. It has been reported that the energy requirement of sonolysis ranges from 0.1 to 0.3 kilowatt-hour per liter of water treated, which is comparable to NF (Ross et al., 2018) commonly in the parts per trillion range. PFASs comprise >3,000 individual compounds, but the focus of analyses and regulations has generally been PFASs termed perfluoroalkyl acids (PFAAs. PFOS and PFOA has been reported to decompose due to pyrolysis, which is the decomposition at high temperatures, at the bubble/water interface (Campbell, 2010). This process can be limited by capital cost requirements because large-scale systems cannot currently be designed cost-effectively (Li et al., 2020; Ross et al., 2018).

NOVEL SORBENTS

Noncarbon-based sorbents have shown promise for PFAS removal but have not yet been fully explored (ITRC, 2018). These sorbents include minerals (clays, silica, iron oxides, zeolites) and modified organoclays. The effectiveness of these sorbents is dependent on-site conditions (e.g., organics) and type of PFAS. Novel sorbents have been evaluated in soil remediation applications, although their use in full-scale drinking water applications only just emerging (Kambala and Maidu, 2013; Zhu and Chen, 2016). Organoclays have high sorption capacity and can be easily modified to enhance sorption capacity with mesopores. Organoclays are hydrophilic, therefore they are ineffective for the sorption of hydrophobic organic compounds such as long-chain PFAS, although modification using cations can change the surface to lipophilic (ITRC, 2018). One challenge with novel sorbents is the subsequent disposal of spent media, similar to GAC media and IX resin disposal challenges.

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