

Challenges in PFAS Separation and Concentration Technologies

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In the first of a two-part article, the author considers the challenges of the current technologies available for removing and concentrating PFAS from landfills. Part 2 will appear in the June issue and will focus on the cost of PFAS removal.

Wastewater and landfill leachate PFAS removal will become a critical and costly requirement as state and federal regulations are on the horizon.^{1,2} For example, removing and destroying PFAS from water and biosolids leaving Minnesota's wastewater treatment facilities could cost between \$14 billion and \$28 billion over 20 years.¹

PFAS consist of a wide range of chain lengths (C2 and longer) and a variety of different head groups. The diverse range of PFAS chemistries, high stability of the carbon-fluoride (C-F) bond, and high-water solubility make PFAS-impacted wastewater difficult to treat as conventional wastewater treatment technologies are limited in effectiveness.

Many of these technologies are in use for treating groundwater and drinking water. There are no identified PFAS removal installations in municipal wastewater treatment systems; therefore, speculative approaches are presented here. A number of landfills are evaluating PFAS removal from landfill leachate, because as much as 11% of PFAS that enters a landfill may exit in leachate.³ The technologies presented here are candidate technologies for removing and concentrating PFAS. Limited work relating to PFAS destruction with wastewater or landfill leachate has been documented above the laboratory investigation phase, and only one full-scale PFAS removal and destruction facility for U.S. landfill leachate is operating in Michigan.⁴

An important distinction is made between the separation of PFAS from a liquid flow (e.g., wastewater, landfill leachate, stormwater, or other drainage) and the management or destruction of the concentrated PFAS from a separation approach. PFAS destruction of the entire liquid flow can result in significant costs that would be neither economical nor practical. Therefore, it is more practical to manage a small, concentrated residual from a PFAS separation process. This article presents a list of technologies that are suggested for PFAS separation.

Separation and Concentration Technologies

Granular Activated Carbon

Granular activated carbon (GAC) is a common treatment for drinking water, but is rarely seen for treating landfill leachate or other highly contaminated liquids without pretreatment. This technology utilizes liquid-solid transfer of PFAS to sorb the PFAS molecules to the solid surface via hydrophobic adsorption. Sorption is a well-proven method for removal of regulated PFAS. GAC has shown to remove PFAS in both bench-scale and field pilot studies. GAC is often less effective in removing short-chain PFAS than long-chain PFAS (C7 and larger) and results in residual waste of spent media. Spent media after adsorption breakthrough must be removed and either regenerated or disposed. Regeneration provides a sustainable approach to remove PFAS from the solid phase and return the adsorbent to treatment service. GAC would be a useful technology for leachate treatment with appropriate pretreatment, but using GAC solely for landfill leachate has a lower probability because of competing compounds including high concentrations of organics that would lower the GAC useful life. GAC treatment may be used for polishing for the removal of residual PFAS after a prior pretreatment step(s), but there are some limitations:

- Effectiveness: It is not effective for all types of PFAS. Some PFAS compounds may be more difficult for a carbon adsorber to remove than others. Some may be small enough to slip through the carbon structure pores, or not be adsorbed as well as other PFAS. Generally, GAC is better at removing larger PFAS molecules, like GenX, and longer-chain PFAS, like PFOA and PFOS.⁵ Short-chain PFASs, are defined as having carbon atoms n<6 for perfluorosulfonic acids (PFSAs) and n<7 for perfluorocarboxylic acids (PFCAs).⁶
- Competing lons: GAC can adsorb various ions, and when present in high concentrations, competing ions such as natural organic matter, chloride, and sulfate can reduce the efficiency of PFAS removal.⁷ It is possible that longer chain PFAS displace sorbed shorter chain PFAS.⁸
- Regeneration Challenges: Regenerating spent activated carbon is challenging, especially for PFAS removal. Thermal regeneration may release PFAS back into the environment, and alternative regeneration methods are still under development.⁹ The spent activated carbon or the regeneration byproducts may contain high concentrations of PFAS that need to be disposed of or destroyed safely.
- Saturation: GAC has a finite adsorption capacity for PFAS. Once the carbon reaches its saturation point, it must be replaced or regenerated, leading to increased operational costs.¹⁰ Activated carbon loses adsorption capacity over time as PFAS and other contaminants compete for the same adsorbing site.¹¹ Therefore, they need to be replaced or regenerated regularly to maintain their effectiveness. However, the regeneration process can be costly and complex, and may not completely restore the original adsorption capacity.
- Particle Fouling: GAC particles can be prone to fouling, reducing their efficiency over time due to the accumulation of particulate matter and biofilm formation.¹²
- Particle Handling: The use of GAC or powdered a ctivated carbon (PAC) can require specialized equipment and careful handling to prevent dust generation and ensure uniform distribution in water treatment systems.¹³
- Long-Term Maintenance: Maintaining an activated carbon treatment system over the long term can be resource-intensive and may require periodic replacement of the carbon media, as well as monitoring for consistent PFAS removal.¹⁴

Addressing these operational challenges often requires careful system design, monitoring, and in some cases, the use of additional treatment processes in conjunction with activated carbon to optimize PFAS removal. The effectiveness of activated carbon for PFAS removal can vary depending on the specific type of PFAS compounds present in the water, the concentration levels, and the water chemistry. Site-specific pilot testing and monitoring are essential for successful PFAS removal using activated carbon. These problems indicate that activated carbon treatment alone may not be sufficient or sustainable for PFAS removal in landfill leachate. This is an adequate process for polishing residual PFAS after reverse osmosis, biological treatment processes such as the membrane bioreactor process (MBR), or similar treatment technologies.

Ion Exchange

Ion Exchange (IX) processes are increasingly being used for full-scale implementation of groundwater treatment, but no significant use was identified for landfill leachate. Resins are used in either single use and disposal or regenerative-reuse mode. IX may be appropriate for PFAS control; although most installations currently use IX resins are single-use and thus require spent resin to be managed through incineration or disposal. Regenerable resins may be applicable for lower flows and higher concentrations (industrial wastewater, source zones, etc.), but are not currently employed for largescale, dilute applications. The regenerant (a blend of steam, solvent, and brine) significantly reduces the volume of liquid requiring disposal. Numerous co-contaminants impact the ability of IX media to remove PFAS, and these may require preliminary treatment for IX to be effective. Pretreatment for removal of dissolved oxygen, iron, organics, or other flocculants should be considered before the IX process. Evaluation and testing of this technology would be required to include IX as a potential treatment technology in this evaluation. On balance, IX may be used for stormwater with appropriate pretreatment, but similar to activated carbon, IX is not anticipated to be appropriate for landfill leachate as a sole separation technology.

IX is a process that uses resin beads to exchange ions between a solution and the resin. It can be used as a final polishing step for PFAS from landfill leachate, but it also has some problems and challenges. Some of the limitations with IX are:

 PFAS Selectiveness: IX resins are more effective for removing long-chain PFAS than short-chain PFAS. IX resins can have different affinities for different PFAS compounds, depending on their charge, size, and structure. Generally, anionic resins are more effective for removing long-chain PFAS, such as PFOA and PFOS, but may be less effective for removing shortchain PFAS, such as PFBA and PFHxA.^{8,13} Other ions, such as chloride, may interfere with ion exchange resins and impose difficulty for some PFAS to be captured by various resins, as well as competing with other ions in the leachate for binding sites.¹⁵

- Regeneration: IX resins can lose their capacity over time as they become saturated with PFAS and other contaminants; therefore, they need to be regenerated or disposed of regularly to maintain their performance. The regeneration process can be costly and complex and may generate concentrated PFAS waste streams that need further treatment or disposal.¹⁶ The disposal of spent resins may also pose environmental or health risks if the PFAS are not stabilized or destroyed.¹⁷
- Selective PFAS Removal: IX may not be able to remove all the PFAS present in the landfill leachate, especially if there are high concentrations or complex mixtures of PFAS. Some PFAS may pass through the resin without being exchanged or may be released from the resin due to changes in pH, temperature, or pressure.¹⁵ Therefore, IX may need to be combined with other treatment technologies, such as activated carbon, membrane filtration, or advanced oxidation, to achieve the desired removal of target PFAS from the leachate. This is an adequate process for polishing residual PFAS after reverse osmosis, MBR, or similar treatment technologies.

Modified Bentonite Clay FluoroSorb Adsorbent®

FluoroSorb Adsorbent[®] is a modified bentonite clay with a proprietary surface technology to preferentially adsorb and lock PFAS on a clay structure. When adsorption capacity is reached, the media is replaced, and contact vessels are replaced with new FluoroSorb[®]. The media is configured to various grain sizes to allow permeability in treatment vessels. With empty bed contact time (EBCT) between 2 to 10 minutes, FluoroSorb[®] effectively removes PFAS from drinking water and groundwater, but has not been previously used in full scale for removing PFAS from landfill leachate.

Civil & Environmental Consultants, Inc. bench tested and pilot tested FluoroSorb® at a Massachusetts landfill for leachate PFAS removal.¹⁸ In a bench test, FluoroSorb® removed the six Massachusetts regulated PFAS constituents (PFAS6) from a pretreatment concentration of over 1,000 parts per ton (ppt) to a post-treatment concentration of 3 ppt. The pilot test program continued through 2021, comparing downflow treatment vessels with upflow continuous backwash filters to compare long-term removal capabilities and approaches to minimize media fouling. Fouling of the media from iron and biological growth impacted longer term operation, such that pretreatment for landfill leachate was recommended. The used media in landfill leachate applications is designed to be blended with a small amount of cementitious material and deposited in a landfill. Regeneration of the used media is not possible. Testing has shown

significant retention and minimal to no leaching of PFAS from the solidified material.^{18,19}

Although FluoroSorb[®] is a type of adsorbent material that can be used to remove PFAS from landfill leachate, it also has some treatability limitations. Some of the limitations with FluoroSorb[®] include:

- Saturation Capacity: FluoroSorb[®] will eventually reach its saturation point and need to be replaced. The adsorption capacity of FluoroSorb[®] depends on the type and concentration of PFAS, the pH and temperature of the leachate, and the presence of other organic or inorganic compounds that may interfere with the adsorption process.²⁰ For example, PFHxS does not adsorb well to FluoroSorb[®].
- Secondary Waste Streams: The spent FluoroSorb[®] may contain high concentrations of PFAS that need to be disposed of or destroyed safely. However, there are limited options for PFAS waste management and destruction, and some of them may pose environmental or health risks.⁸ Moreover, the PFAS may leach out from the FluoroSorb[®] if it is not stabilized or solidified.¹⁵
- Selective PFAS Removal: It may not remove all PFAS from the leachate. FluoroSorb[®] may not be able to remove all the PFAS present in the landfill leachate, especially if there are high concentrations or complex mixtures of PFAS. Some PFAS may have low affinity for FluoroSorb[®] or may compete with other compounds for binding sites.²⁰

Therefore, FluoroSorb[®] may need to be combined with other treatment technologies, such as ion exchange, membrane filtration, or advanced oxidation, to achieve complete removal of PFAS from the leachate. Iron and biology may foul FluoroSorb[®] and reduce bed life.¹⁸

Reverse Osmosis

Reverse osmosis (RO) technology using semi-permeable membranes has been reported to remove PFAS compounds to below about 5 ng/L and in some cases to below detection levels of 2 ng/L.²¹ RO is used for leachate treatment and is effective for the removal of both short- and long-chain PFAS compounds. PFAS management has been achieved with RO and recorded removal over 99.9% for a wide range of compounds, including PFOS, PFOA and others, both linear and branched compounds.²¹ In landfills with high total dissolved solids (TDS) concentrations, metals, oils and grease, or silica RO membranes may exhibit operational difficulty.

RO generates a residual or reject flow that may be in the 10–30% range of the incoming flow. That volume of reject flow must be managed; therefore, a reject volume reduction step should be considered. A possible step would include a thermal evaporator system that may reduce the reject flow

to as little as 3%. If a design leachate flow of 10,000 is treated by RO, then the reject flow may be 1,000–3,000 gallons per day (gpd). A thermal evaporator residual may then yield a volume as low as 30 and 90 gpd (i.e., 3% of the 1,000–3,000 gpd RO reject flow). Residuals can be further reduced in subsequent technologies and the reduced volume of wastes solidified and redeposited in a landfill.

RO is a process that uses a semi-permeable membrane to separate contaminants from water. It can be used to remove PFAS from landfill leachate, but it also has some limitations, including:

- Membrane Fouling: Membrane fouling is the accumulation of organic and inorganic substances on the surface or within the pores of the membrane, which reduces its permeability and performance. Landfill leachate contains high concentrations of dissolved solids, organic matter, metals, and other compounds that can cause membrane fouling. Therefore, RO requires frequent cleaning and maintenance to prevent fouling and extend the membrane life.¹⁵
- Residuals Generation: Concentrate is the liquid stream that contains the rejected contaminants from the RO process. Depending on the quality of the leachate and the RO system, the concentrate can account for 10–30% of the feed volume.²² The concentrate can be further reduced by evaporation or other technologies. The concentrate contains high concentrations of PFAS and other pollutants that need to be further treated or disposed of safely. However, there are limited options for PFAS waste management and destruction, and some of them may pose environmental or health risks.²³
- Selective PFAS Rejection: RO can remove most of the PFAS present in the landfill leachate, especially the long-chain PFAS, such as PFOA and PFOS. However, some PFAS may have low molecular weight or size, or may have weak interactions with the membrane, which makes them difficult to remove by RO. For example, some short-chain PFAS, such as PFBA and PFHxA, may have lower rejection rates by RO than long-chain PFAS.¹⁵

RO may need to be combined with other treatment technologies, such as activated carbon, ion exchange, or advanced oxidation, to achieve a high degree removal of PFAS from the leachate.²⁴

Foam Fractionation

Foam fractionation is a physical-chemical process that relies on air bubbles to separate contaminants from water based on their surface activity. The process generates fine air bubbles rising through a water column. PFAS that accumulate at the top of the column as foamate are vacuumed for concentration and disposal. Using columns in series, PFAS are progressively separated from the leachate. Data show that PFAS compounds greater than 6 carbons are most effectively removed by this treatment.¹⁸ The process reduces the volume of PFAS-contaminated water to a small liquid concentrate (foamate). This volume can be solidified and disposed in a landfill or destroyed by technologies, such as low temperature plasma, electrochemical oxidation, or others. Air emissions are controlled by activated carbon air filters. Foam fractionation systems have been successfully used for groundwater PFAS removal in Australia and the United States, and PFAS removal from leachate is gaining popularity.

Foam fractionation removes PFAS from landfill leachate, but it also has some limitations, including:

- Incomplete Removal: Foam fractionation is well suited for most of the larger long-chain PFAS, such as PFOA and PFOS. Foam fractionation may not be effective for all types of PFAS, especially those with very short or very long chains, as these PFAS may have low surface activity or low affinity for foam adsorption or are impacted by high concentrations and complex mixtures of organic and inorganic compounds.²⁵ Research is progressing to improve short-chain effectiveness by the addition of surfactants, varying bubble formation intensity, and timing of various bubble formation stages.
- Selective PFAS Removal: Some short-chain PFAS, such as PFBA and PFHxA, may have lower removal rates by foam fractionation than long-chain PFAS.²⁵ Therefore, foam fractionation may need to be combined with other treatment methods or repeated multiple times to achieve a high removal efficiency.
- Foamate Disposal: Foam fractionation generates a foamate that contains the concentrated contaminants from the leachate. The foam needs to be skimmed off and collected regularly to maintain the performance of the process and prevent overflow.²⁶ This may incur additional costs and challenges, such as waste transportation, storage, handling, and treatment.
- Reactor Plugging: The breakdown of PFAS in the foamate or in the subsequent destruction process may produce fluoride salts, which are not toxic but can create reactor plugging issues and reduce system performance. Therefore, careful attention to system maintenance is required to prevent or remove the salt deposits.²⁵
- Operational Parameters: Foam fractionation is influenced by various operational parameters, such as aeration rate, pH, temperature, salinity, and presence of other surfactants or contaminants. These parameters may affect the formation, stability, and quality of the foam, as well as the adherence of PFAS to the bubble surface. Therefore, optimal conditions need to be determined and maintained for each specific leachate matrix.²⁷

Evaporation Technology

Evaporation of landfill leachate involves either passive evaporation in ponds (with or without spraying devices) or heating the leachate to produce a water vapor leaving behind the dissolved solids and contaminants. Metals in the leachate concentrate and precipitate, primarily as salts, while lighter organics volatilize and are stripped away by the water vapor. The heavier organics concentrate to a residual slurry that may be 2–5% of the feed concentration.

The organics are transferred from the liquid leachate phase to the exhaust vapor phase by a process analogous to air stripping. Because the operating temperature of a thermal evaporator is low, most of the heavy metals do not vaporize. There exists a risk of PFAS emissions in the evaporated flow. Further treatment with thermal oxidation at temperatures over 1,000 °C or adsorption with activated carbon may reduce the PFAS emissions. Numerous studies are in progress to identify PFAS emissions from evaporative sources. Evaporation technologies will result in a significant vapor plume that may result in public objection and negative public reaction. Evaporative systems typically require an air permit for implementation, so approval may prove difficult.

Although the evaporation process can be used to remove PFAS from landfill leachate, it also has some limitations. Some of the limitations with evaporation include:

- Energy-intensive: Thermal evaporation requires a large amount of heat to vaporize water from leachate, which consumes a lot of energy and increases the operational costs. The energy consumption and cost depend on the quality and quantity of the leachate, the type and efficiency of the evaporator, and the availability and price of the energy source.^{8,15}
- Concentrate Volumes: Concentrate is the liquid stream that contains the concentrated contaminants from the evaporation process. The concentrate contains high concentrations of PFAS and other pollutants that need to be further treated or disposed of safely. However, there are limited options for PFAS waste management and destruction, and some of them may pose environmental or health risks.²²
- Selective PFAS Removal: Evaporation can remove most of the PFAS present in the landfill leachate, especially the larger long-chain PFAS, such as PFOA and PFOS. However, some PFAS may have low boiling points or volatility, which makes them difficult to remove by evaporation. For example, some short-chain PFAS, such as PFBA and PFHxA, may have vapor pressures that may enable PFAS to escape into the vapor stream.¹⁵ Therefore, evaporation may need to be combined with other treatment technologies, such as activated carbon, ion exchange, or advanced oxidation, to achieve removal of PFAS from the leachate.

Table 1. Innovative Technologies in Development.	
Emerging Technology	First Impressions
Biochar adsorption	Less effective than GAC or resins, non-regenerable.
Direct treatment with IX resins	Resin fouling and premature breakthrough.
Electrocoagulation	PFAS removal not demonstrated with leachate; however, a pilot test at the Brainerd, MN landfill reported nondetect PFAS concentrations at pilot scale
Other adsorptive technologies that have been used for PFAS control in groundwater include CycloPure, Rembind, MatCare, Plumestop, PerfluorAd, Polydadmac, and zeolites.	None of these have documented performance on leachate.
Ferric and alum	Ferric and alum or other coagulation technologies have not been evaluated for landfill leachate.
Ozofractionation	Has not been evaluated for landfill leachate, but this technology is similar to foam fractionation.
UV scenarios	UV photolysis; UV with nanoscale materials; UV oxidation, including Fenton's reagent, persulfate, periodate, and UV reduction.
CycloPure ("Dexsorb")	A modified corn-based adsorbent that can desorb PFAS for further destruction and the corn-based adsorbent can be reused for further adsorption.
Nanoscale technologies (zero-valent iron coated Mg aminoclay; Nano scale zero-valent nickel and iron coated on activated carbon)	These technologies have not been evaluated for landfill leachate.

Summary

Various developing technologies—or combinations of technologies—may prove to be appropriate at a landfill. Table 1 provides a list of possible future technologies currently in development, including PFAS separation from a liquid flow followed by PFAS destruction of concentrates. Time will tell which technologies prove to be sufficient and sustainable. **em**

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