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Removal of Per- and polyfluoroalkyl substances (PFAS) from Aqueous Matrices by using Adsorption Processes

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THESIS

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are persistent organic pollutants that have been detected in various aqueous environments. Due to their chemical stability and health risks, effective removal technologies are urgently needed. Among emerging sorbents, β-cyclodextrin (β-CD) polymers have attracted interest due to their tunable selectivity and environmental compatibility.

This thesis conducted a literature review on the adsorption behavior of per- and polyfluoroalkyl substances (PFAS) onto β-cyclodextrin (β-CD)-based polymers, focusing on how surface functionalization and polymer architecture affect removal efficiency. Five case studies and one meta-analysis were analyzed to explore key performance trends across different material chemistries, PFAS types, and water matrices. The results indicate that unmodified β-CD polymers show limited effectiveness, particularly for short-chain PFAS. On the other hand, functionalized variants—especially those incorporating cationic groups—demonstrate high selectivity and fast kinetics even under complex environmental conditions. The study emphasizes the significance of electrostatic interactions, host–guest inclusion, and steric factors in determining adsorption performance. Finally, key challenges related to material scalability, integration into treatment systems, and regulatory pathways are discussed, outlining promising directions for future research and application.

Contents

Chapter 1. Introduction to PFAS and Research Framework

1.1 Definition of PFAS

Human activities, such as rapid urbanization, industrial growth, and intensive agricultural practices, have significantly impacted water resources, by compromising the quality and threatening the availability for both drinking and agricultural purposes.

Water pollution, which poses risks to both environmental and human health, arises from a range of contaminants. Suspended solids increase turbidity and disrupt aquatic ecosystems; excess nutrients (e.g., nitrogen and phosphorus) contribute to algal blooms and oxygen depletion; organic matter accelerates microbial activity; and heavy metals from industry and agriculture cause toxicity in aquatic organisms and humans.

In recent years, attention has shifted toward emerging contaminants—chemicals that are newly detected, insufficiently regulated, or poorly understood, yet pose potential risks to ecosystems and human health. These include pharmaceuticals, personal care products, endocrine-disrupting compounds, and various synthetic industrial substances.

Among the most persistent and environmentally concerning of these are per- and polyfluoroalkyl substances (PFAS), a large group of synthetic organofluorine compounds widely used in industrial processes and consumer products such as non-stick cookware, firefighting foams, water-repellent textiles, and food packaging. PFAS are known for their strong carbon–fluorine bonds, which confer exceptional thermal and chemical stability. As a result, they are extremely persistent in the environment (Wang et al., 2017).

Depending on their specific structure and regulatory status, PFAS can be categorized into multiple overlapping classes of pollutant:

- PFAS (e.g., PFOA, PFOS) are listed as Persistent Organic Pollutants (POPs) under the Stockholm Convention.
- Many newer or replacement PFAS (e.g., GenX, PFBS) are considered emerging contaminants due to limited toxicological data and insufficient regulation.
- Several PFAS fulfill the criteria of Persistent, Bioaccumulative, and Toxic substances (PBTs).

- In environmental monitoring, PFAS are also classified as organic micropollutants, as they are detected at trace concentrations in water bodies but with significant health and ecological effects.

Their widespread use and resistance to natural degradation have resulted in long-term contamination of water, soil, and air. PFAS have been found globally in surface and groundwater, as well as in wildlife and human blood serum. Their presence in aquatic environments raises serious public health concerns and underscores the urgent need for improved monitoring, regulation, and effective remediation strategies.

Studying PFAS in water systems is crucial due to their widespread presence and potential adverse effects on both environmental and human health. Known as "forever chemicals," they have become major contaminants globally, posing challenges for scientists, policymakers, and water treatment professionals. The following sections will examine their classification, environmental impacts, and the challenges they pose in aquatic environments.

1.2. Chemical Structure and Classification of PFAS

1.2.1 General Chemical Structure of PFAS

PFAS are a broad and diverse group of synthetic organofluorine compounds with a distinct chemical structure. They typically consist of a hydrophobic carbon-fluorine chain and a polar functional group such as carboxylates ($-COO^-$), sulfonates ($-SO_3^-$), or phosphonates ($-PO_3^{2-}$). This amphiphilic nature makes PFAS highly stable and resistant to environmental degradation (Usman et al. , 2024).

PFAS are characterized by the formula C_nF_{2n+1}, where fluorine atoms replace either entirely or partially hydrogen atoms along the carbon chain. The distinction lies in the degree of fluorination. Perfluoroalkyl compounds are fully fluorinated, while polyfluoroalkyl compounds retain some hydrogen atoms (Garg et al., 2021) .

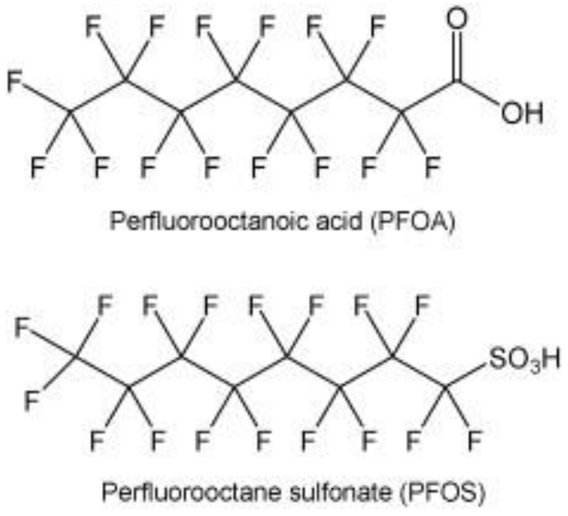
Carbon-Fluorine Bond: The Key to Persistence

The strong carbon-fluorine (C-F) bonds in PFAS provide exceptional thermal and chemical stability. While this makes them highly useful in industrial applications, it also complicates their removal from the environment. The carbon-fluorine bond is one of the strongest in organic chemistry with a high bond dissociation energy of approximately 485 kJ/mol. This strength arises from fluorine’s high electronegativity and short bond length. Indeed, the strong attraction between carbon and highly electronegative fluorine in combination with fluorine’s small atomic radius allows for a short bond length and enhanced orbital overlap, further strengthening the bond.

Additionally, the bond's partial ionic character, poor polarizability, and resistance to nucleophilic attack contribute to its durability. Fluorine’s tightly held electron cloud and lone pairs also reinforce the structure (Garg et al., 2021).

Amphiphilic Nature and Unique Properties

PFAS molecules have a hydrophobic carbon-fluorine chain and a hydrophilic functional group, making them amphiphilic. This allows them to repel both water and oil, making them ideal for applications requiring water resistance and durability, such as coatings and firefighting foams. Many PFAS end with functional groups that give them acidic or polar properties. An example is perfluorooctanoic acid (PFOA), which contains a carboxyl (-COOH) group, making it acidic, or perfluorooctane sulfonate (PFOS), which has a sulfonate ($-SO_3^-$) group, contributing to its polarity. However, the PFAS family extends beyond these functional groups to include compounds with ethers, amides, and polymers, further broadening their applicability and complexity (Usman et al. , 2024) (Shapiro et al., 2025) .



Perfluorooctanoic acid (PFOA)

Perfluorooctane sulfonate (PFOS)

Figure 1.1 Chemical structures of two widely studied perfluoroalkyl substances (PFAS): perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Source: Wikipedia

1.2.2 Types of PFAS

PFAS family exhibits remarkable structural diversity, primarily as a result of variations in fluorination and carbon chain architecture. This diversity has led to the identification of over 12,000 individual PFAS compounds, each with distinct physicochemical properties and varying degrees of toxicity, environmental persistence, and bioaccumulation potential. There can be variations in the length of the carbon chain and the degree of fluorination within PFAS.

PFAS can be classified in categories based on several factors such as their chemical structure, functional groups and carbon chain length.

First of all, as illustrated in *Figure 1.2*, the structural variability of PFAS includes linear, branched, cyclic, and ether-linked configurations, each exhibiting different environmental behaviors and treatment challenges.

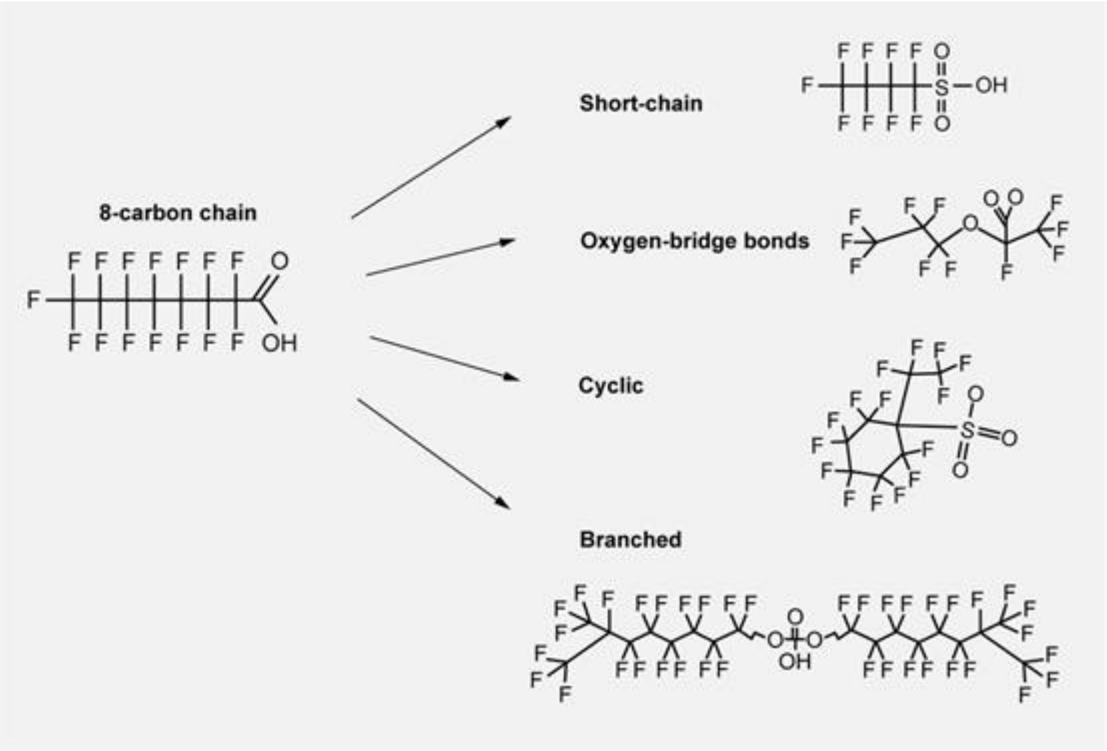


Figure 1.2 Representative examples of PFAS structural diversity. The figure illustrates four major structural variants derived from a base 8-carbon perfluorinated chain: short-chain PFAS, PFAS with oxygen-bridge bonds, cyclic PFAS, and branched PFAS. These variations influence the physicochemical behavior, environmental mobility, and removal efficiency of PFAS (Wang Z et al., 2017).

The major categories based on, functional groups include:

1. **Perfluoroalkyl Substances (PFAS)** – These compounds contain fully fluorinated carbon chains. Prominent examples include perfluorooctanoic acid (PFOA) and

perfluorooctanesulfonic acid (PFOS), which are known for their extreme environmental persistence and tendency to bioaccumulate.

2. **Polyfluoroalkyl Substances** – These are partially fluorinated compounds that may undergo environmental or biological transformation into more persistent perfluorinated analogs.
3. **Chain-Length Classification** – Based on carbon chain length, PFAS are categorized into short-chain and long-chain compounds. Long-chain PFAS typically exhibit greater bioaccumulative behavior and are more challenging to remove from aqueous matrices.

Long-Chain vs. Short-Chain PFAS

PFAS can be classified based on their carbon chain length, which affects their environmental impact, bioaccumulation, and toxicity.

Long-Chain PFAS, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), contain eight or more carbon atoms. Their extended fluorinated chains make them highly hydrophobic and lipophobic. These compounds strongly bind to proteins in the blood and liver, leading to prolonged retention in organisms and high bioaccumulation. Additionally, they exhibit low mobility in water as they tend to adsorb onto sediments and organic matter, creating contamination. Their persistence and toxicity have led to their classification as high-priority contaminants in regulatory frameworks.

Short-Chain PFAS, such as perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS) have fewer than eight carbon atoms. They were introduced as alternatives to long-chain PFAS due to their lower bioaccumulation potential. However, they are more water-soluble and mobile, making them harder to remove from contaminated sites. While generally less toxic, they remain persistent and can still pose environmental and health risks, especially through drinking water contamination.

The contrasting properties of long-chain and short-chain PFAS underline the complexity of managing these substances in the environment. While long-chain PFAS are more localized in their impact due to lower mobility, their higher bioaccumulation and toxicity make them a severe threat to ecosystems and human health. Conversely, short-chain PFAS are more challenging to remediate due to their enhanced solubility and mobility, necessitating innovative approaches for effective management.

In the Figure below, PFAS are categorized by their chain length, ranging from ultra-short to long-chain compounds. The diagram illustrates how shorter-chain PFAS are more mobile in the environment and difficult to remove, whereas longer-chain PFAS tend to bioaccumulate and are subject to stricter regulations.

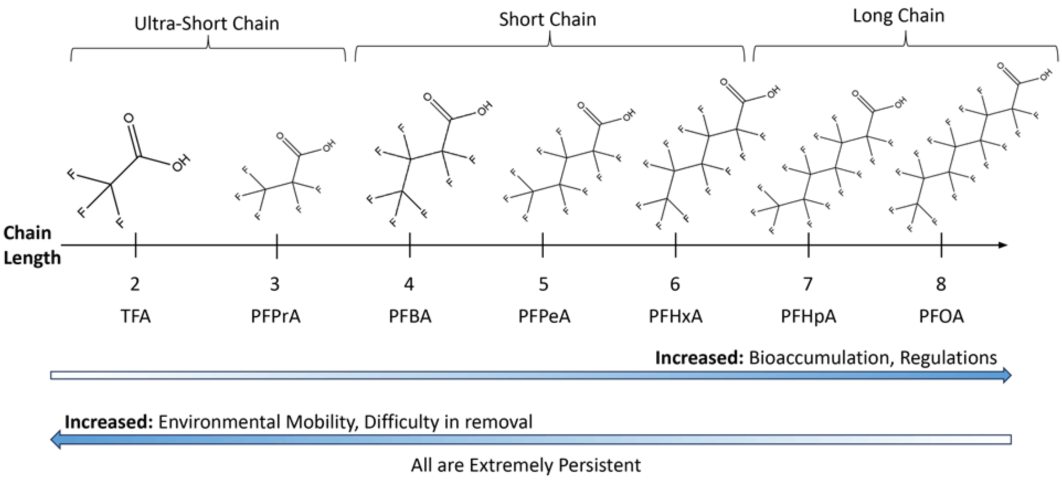


Figure 1.3. Classification of PFAS based on chain length. (SWANA Blog, 2024)

Major Subcategories of PFAS

PFAS compounds can also be categorized based on their functional groups, which affect their chemical behavior in the environment. Structurally, they can be linear, branched, or cyclic, influencing their solubility and bioaccumulation. For instance, branched isomers tend to be more soluble, while linear ones are more likely to accumulate in organisms. Additionally, emerging PFAS, such as perfluoroether carboxylic acids (PFECAs) and fluorotelomer-based compounds, add further complexity to this class of chemicals.

The main subcategories of PFAS compounds commonly reported in the environment and extensively studied in scientific literature include:

1. **Perfluorocarboxylic Acids (PFCAs):** PFCAs are terminate with a carboxylic acid (-COOH) functional group. A well-known example is PFOA, an eight-carbon PFCA widely used in the manufacture of non-stick cookware, textiles, and industrial applications. PFCAs are highly persistent in the environment and exhibit strong resistance to degradation. They are also known for their high bioaccumulation potential, particularly in organisms at the top of the food chain. Short-chain PFCAs, such as PFBA, are less bioaccumulative but more mobile, posing distinct challenges in water

contamination scenarios (Wang et al., 2024). Another example is Perfluorooctanoic Acid (PFOA) which is one of the most extensively studied PFAS due to its widespread use in non-stick coatings and its persistence in the environment, where it bioaccumulates significantly.

2. **Perfluoroalkyl sulfonic acids (PFSAs):** PFSAs are a class of PFAS that contain a sulfonate ($-SO_3^-$) functional group, contributing to their high stability and persistence in the environment. A well-known example is Perfluorooctane Sulfonic Acid (PFOS), a legacy compound widely used in industrial applications, particularly in aqueous film-forming foams (AFFFs) for firefighting, as well as in stain-resistant materials. Due to its extensive use and extreme resistance to degradation, PFOS has been linked to significant ecological and human health concerns, leading to regulatory restrictions in many regions (Abaie et al., 2024).
3. **Perfluoroalkyl Sulfonamides (PFASAs):** PFASAs are commonly found in pesticides and surfactants. Their unique chemical properties contribute to their high environmental mobility and persistence (Garg et al., 2021) .
4. **Perfluoroalkyl Sulfonyl Fluorides (PFASFs):** PFASFs serve as key precursors in the synthesis of various PFAS, including PFOS. Their presence in industrial applications contributes significantly to environmental contamination (Garg et al., 2021).
5. **Polyfluoroalkyl Phosphate Esters (PAPs):** PAPs are frequently used in food packaging materials. Over time, they degrade into more persistent PFAS, such as PFCAs, increasing environmental contamination risks (Garg et al., 2021).
6. **Emerging PFAS**: This category includes newer compounds introduced as alternatives to traditional long-chain PFAS such as PFOA and PFOS. Among the most prominent is GenX, a trade name for ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate ($C_6HF_{11}O_3 \cdot NH_4$), developed as a replacement for PFOA in fluoropolymer manufacturing (Ji et al., 2018). GenX belongs to the perfluoroether carboxylic acids (PFECAs) family and is structurally distinct due to the presence of ether linkages and a shorter fluorinated carbon chain. Despite being marketed as a safer alternative, GenX demonstrates similar physicochemical behavior to its predecessors, including high water solubility, persistence in the environment, and resistance to conventional water treatment technologies. Studies suggest that many of them exhibit similar persistence and toxicity. Data on their long-term environmental and health effects are limited, complicating their regulation and management. A visual overview of their representative structures is provided in *Figure 1.4.*

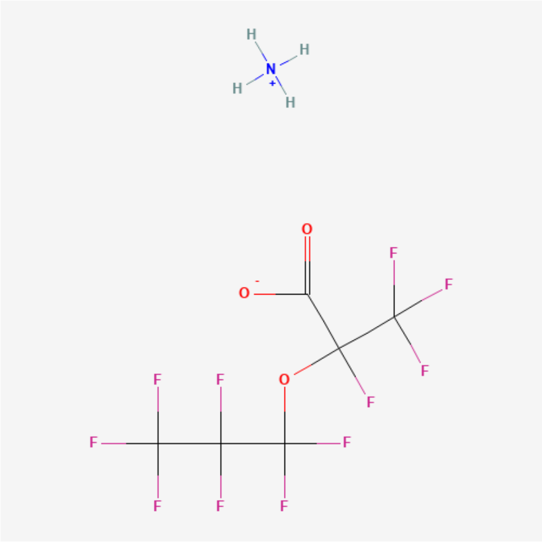


Figure 1.4 Chemical structure of GenX, formally known as the ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA). The molecule features a perfluorinated ether chain, a carboxylate group (in red), and an ammonium counterion (NH_4^+) shown at the top. Source: PubChem (CID: 76991891)

Understanding these subcategories is critical for developing targeted remediation strategies. Their unique chemical properties dictate their interactions with environmental matrices and treatment technologies. This classification also highlights the need for a comprehensive regulatory framework to address both legacy and emerging PFAS contaminants effectively.

1.2.3 Functional Properties Contributing to PFAS Behavior

Chemical Stability

The extraordinary stability of PFAS is primarily attributed to the carbon-fluorine (C-F) bond, one of the strongest in organic chemistry. This bond exhibits exceptionally high bond dissociation energy making these compounds highly resistant to thermal, chemical, and biological degradation. Fluorine's high electronegativity, small atomic radius, and poor polarizability reinforce this inert nature of PFAS, preventing their breakdown through hydrolysis, photolysis, or microbial activity under typical environmental conditions. The poor polarizability of fluorine atoms, prevents interactions with reactive agents, ensuring that PFAS remain intact in various matrices for decades or even centuries.

This durability ensures that PFAS persist in water, soil, and living organisms for decades, accumulating across multiple environmental compartments. Long-chain PFAS, such as PFOA and PFOS, exhibit low solubility and tend to adsorb onto sediments and organic matter, increasing their potential for bioaccumulation. In contrast, short-chain PFAS are more water-soluble, leading to widespread dispersal in groundwater and surface water systems, complicating remediation efforts.

Although PFAS are structurally stable, variations in their molecular structure influence their fate and transport. While fully fluorinated carbon chains remain chemically inert, partially fluorinated variants may undergo transformation under extreme conditions, though such degradation pathways remain limited in natural environments. The interplay between chain length, functional groups, and solubility dictates how these compounds behave in ecosystems, emphasizing the need for targeted remediation strategies.

Environmental Mobility and Bioaccumulation

The amphiphilic nature of PFAS, characterized by a hydrophobic fluorinated tail and a hydrophilic functional head, plays a decisive role in their mobility, persistence, and interaction with biological systems. The hydrophobic tail minimizes interaction with water, allowing PFAS molecules to preferentially adsorb onto organic matter, sediments, and biological membranes. This property of demonstrating a higher tendency for sorption onto organic matter and sediments is particularly pronounced in long-chain PFAS, which are more likely to bind to proteins in organisms, leading to bioaccumulation in tissues such as blood, liver, and kidneys (Shapiro et al., 2025). These compounds are less mobile but more bioaccumulative, binding strongly to proteins in organisms, especially in aquatic ecosystems.

Moreover, studies have shown that long-chain PFAS, such as PFOS and PFOA, are often detected at higher concentrations in organisms at the top of the food chain, indicating their potential for biomagnification. That long-term exposure in humans and wildlife has been linked to toxicological effects, raising concerns about their widespread presence in drinking water sources and agricultural products.

In contrast, short-chain PFAS, while less bioaccumulative, are more persistent in water and harder to remove using traditional treatment method as greater water solubility, allowing them to travel extensively through surface and groundwater systems. This mobility makes short-chain PFAS challenging to contain and remediate once they enter the environment.

The functional groups at the head of PFAS molecules, such as carboxylates ($-COO^-$) and sulfonates ($-SO_3^-$), further contribute to their mobility and solubility. These hydrophobic groups facilitate the solubility of PFAS in aquatic environments, increase their potential to contaminate water supplies and enter the food chain (Garg et al., 2021).

The unique combination of chemical stability, environmental mobility, and bioaccumulation potential makes PFAS among the most challenging contaminants to manage. The resistance of the C-F bond to degradation ensures the persistence of PFAS in ecosystems, while their mobility and bioaccumulation characteristics vary between short- and long-chain variants. These properties underscore the importance of developing targeted remediation strategies tailored to the specific characteristics of PFAS, such as their chain length and functional groups.

1.3 Sources of PFAS

The manufacturing, industrial applications, and consumer use of PFAS are the primary sources of environmental contamination. These substances are introduced into the environment through industrial discharge, emissions from consumer products, and emerging contributors such as wastewater treatment plants (WWTPs) and landfill leachates. Understanding these sources is crucial for developing targeted remediation strategies to mitigate their persistent environmental impact.

1.3.1 Industrial Sources

Manufacturing Processes

The production of PFAS involves two main processes, electrochemical fluorination (ECF) and telomerization, both of which contribute to intentional production (e.g., PFOA and PFOS) and unintentional by-products released into the environment.

- Electrochemical Fluorination (ECF): This process produces fully fluorinated compounds such as perfluorooctanesulfonic acid (PFOS) and its derivatives. During ECF, hydrogen atoms in a hydrocarbon chain are replaced with fluorine, creating a stable perfluorinated molecule. ECF is known to generate a mixture of linear and branched isomers, some of which have varying environmental behaviors and toxicological profiles. Byproducts from ECF are often discharged into wastewater streams, leading to contamination of water sources.
- Telomerization: This process primarily produces partially fluorinated compounds, such as fluorotelomer alcohols (FTOHs) and their derivatives. These compounds can degrade into perfluoroalkyl carboxylic acids (PFCAs), such as perfluorooctanoic acid

(PFOA), in the environment. Telomerization has been promoted as a cleaner alternative to ECF because it produces fewer byproducts, but it still results in the release of residual PFAS into air, water, and soil.

Waste and byproducts from both manufacturing processes, including spent reactants and unreacted materials, enter the environment through direct emissions, improper disposal, and accidental leaks from production facilities. These persistent pollutants accumulate in water, soil, and living organisms, necessitating urgent regulatory interventions (Wang et al., 2024).

Application in Industrial Products

PFAS are widely used in industrial applications due to their stability, non-stick properties, and chemical resistance. However, their use results in severe environmental contamination, particularly in water bodies. The main industrial uses include:

- **Electronics Manufacturing**: PFAS are used in semiconductors and electronics due to their dielectric properties and resistance to extreme conditions. The fabrication of semiconductors, circuit boards, and wiring often involves PFAS-based materials, with potential environmental releases occurring through waste streams and emissions.
- **Metal Plating**: Electroplating industries use PFAS as mist suppressants, leading to contamination through discharge of wastewater and waste by-products.
- **Chemical Synthesis**: PFAS are utilized in producing surfactants and other specialty chemicals, with leaks and improper disposal contributing to environmental releases.

However, usage in those industrial applications has led to severe environmental contamination, particularly in water matrices. Once released, PFAS persist in the environment, accumulating across multiple compartments, posing long-term ecological and human health risks (Garg et al., 2021).

1.3.2 Consumer Product Sources

PFAS are extensively incorporated into consumer products due to their exceptional resistance to heat, chemicals, and moisture. However, this has led to their widespread release into the environment.

Major Consumer Product Sources:

- **Firefighting Foams**: Aqueous film-forming foams (AFFFs), widely used for extinguishing flammable liquid fires are a major source of PFAS. These foams contain high concentrations of PFAS, particularly PFOS and PFOA, which are released into the environment during training exercises, firefighting operations, and foam disposal. (Garg et al., 2021). These foams leach PFAS into soil and groundwater, often creating contamination hotspot.
- **Surface Treatments and Coatings**: PFAS are widely used in industrial coatings to provide resistance to water, oil, and stains. Examples include non-stick coatings for cookware and food packaging materials, anti-fouling paints for ships, cosmetic products and protective coatings for electronic devices and metals. The manufacturing and application of these coatings often result in emissions of PFAS into air and water.
- **Textiles and Fabrics**: PFAS are applied as surface treatments in products to impart water- and stain-resistant properties. These applications include coatings for textiles, carpets, clothing, outdoor gear, and upholstery. Industrial processes for producing treated textiles release PFAS into wastewater over time, contributing to contamination in downstream environments (Garg et al., 2021). This is commonly contributed through abrasion, washing, and degradation. Also, during the lifecycle of these products, PFAS are released into the environment through washing, wear-and-tear, and disposal. These emissions contribute to diffuse contamination, particularly in urban and residential areas (Loi et al., 2022).

1.3.3 Emerging Sources

Wastewater Treatment Plants

WWTPs play a significant role in PFAS contamination, as conventional treatment processes are largely ineffective at removing these substances. PFAS often pass through standard filtration, sedimentation, and chemical treatment stages, accumulating in both treated effluent and biosolids. Moreover, biological processes within the plant can transform precursor compounds into more persistent and mobile perfluoroalkyl acids (PFAAs), increasing their presence in the final effluent. In some cases, concentrations of certain PFAS have been found to be higher in the effluent than in the influent, due to these transformations and low removal efficiency (Lenka et al., 2021).

Treated wastewater discharged into surface waters becomes a major pathway for PFAS entry into aquatic ecosystems, while biosolids used as agricultural fertilizers can lead to soil contamination and potential uptake by crops, contributing to long-term environmental and human exposure (Loi et al., 2022). These findings highlight the urgent need for improved treatment technologies and regulatory frameworks to effectively manage PFAS emissions from wastewater systems.

Landfill Leachates and Recycled Materials

Landfill leachates represent another critical emerging source. PFAS leach from disposed consumer products, industrial waste, and construction materials stored in landfills. These leachates can infiltrate groundwater and surface water systems, creating diffuse and widespread contamination. The challenges posed by landfill leachates are further exacerbated by the lack of uniform regulations and monitoring practices across different regions.

Recycled materials also contribute to PFAS contamination. For instance, compost derived from treated biosolids often contains PFAS, which can transfer these chemicals into agricultural soils and crops. This extends the environmental footprint of PFAS, creating additional pathways for exposure in both humans and ecosystems.

The diverse sources of PFAS contamination underscore their persistent and pervasive nature in the environment. This complexity makes mitigation particularly challenging, as industrial activities, consumer product disposal, and emerging sources contribute to both direct and diffuse contamination over time. Addressing these issues requires the development and implementation of robust regulatory frameworks, improved waste management practices, and advanced treatment technologies that can effectively remove PFAS from various environmental matrices. A comprehensive understanding of these sources is essential for designing targeted remediation strategies and minimizing the risks of human and ecological exposure to these persistent pollutants.

Challenges in PFAS Remediation from Aquatic Environments

The challenges of PFAS remediation in water matrices are multifaceted, driven by:

- **Complex Behavior**: PFAS compounds exhibit diverse physicochemical properties that affect their fate and transport in aquatic systems.
- **Health Implications**: Chronic exposure to PFAS through contaminated water is associated with adverse health outcomes, including developmental, immunological, and carcinogenic effects

- **Regulatory Pressure**: Increasingly stringent guidelines necessitate effective removal technologies, with adsorption emerging as a promising solution.

1.4 Environmental Fate and Transport

Building upon the earlier discussion of PFAS stability and environmental behavior, this section explores in detail the pathways through which PFAS are transported and retained across various environmental compartments, including water, soil, air, and biota. Understanding their transport mechanisms and fate is essential for assessing long-term environmental and health risks.

1.4.1 Persistence in the Environment

PFAS are often referred to as "forever chemicals" due to their exceptional resistance to degradation. The carbon-fluorine bond makes these compounds highly stable against thermal, chemical, and biological breakdown.

- Long-chain PFAS (e.g., PFOA, PFOS) sorb more strongly to sediments and organic matter, making them less mobile but highly bioaccumulative.
- Short-chain PFAS, while less bioaccumulative, remain highly soluble in water, facilitating long-distance transport through groundwater and surface water.

The persistence of PFAS complicates remediation efforts and increases human and ecological exposure through contaminated drinking water, food sources, and atmospheric deposition.

1.4.2 Pathways of Contamination

The transport and distribution of PFAS in the environment occur through multiple pathways, including water, air, and soil. These routes influence their persistence and potential for human exposure.

Water Contamination: Surface and Groundwater

Water is the primary medium for PFAS mobility, as their hydrophilic nature allows them to dissolve and spread across vast distances. Key contamination sources include:

- Industrial Discharges: Effluents from chemical plants, textile industries, and metal plating facilities release PFAS-laden wastewater into rivers and lakes.

- Urban Runoff: Rainwater runoff carries PFAS from consumer products, such as treated textiles, firefighting foams, and waterproof coatings, into storm drains and water bodies.
- Wastewater Treatment Plants (WWTPs): Conventional WWTPs do not effectively remove PFAS, allowing treated effluent to discharge contamination into surface waters.
- Landfill Leachates: As PFAS-containing waste decomposes, the chemicals leach into surrounding soil and groundwater, contaminating drinking water sources.

Once in aquatic environments, short-chain PFAS disperse more extensively, while long-chain PFAS bind to sediments, creating persistent pollution hotspots.

Airborne and Soil Contamination Pathways

PFAS also contaminate the environment through atmospheric and terrestrial pathways. PFAS can enter the atmosphere and settle onto land and water surfaces through:

- Airborne Emissions: PFAS are released as aerosols during industrial manufacturing and firefighting foam applications, later depositing onto soil and water via precipitation.
- Dust and Particulate Matter: PFAS in household dust and industrial areas contribute to indoor and outdoor exposure.
- Soil Adsorption & Leaching: Long-chain PFAS tend to bind to soil particles, whereas short-chain PFAS leach into groundwater, increasing their mobility.

Agricultural contamination can also occur through biosolids applied as fertilizers, allowing PFAS to enter crops and the food chain (Loi et al., 2022).

1.4.3 Bioaccumulation and Food Chain Entry

PFAS accumulate in living organisms due to their affinity for proteins, particularly in blood, liver, and other tissues. Unlike lipophilic pollutants, PFAS bind to albumins and other protein structures, allowing them to persist in aquatic and terrestrial ecosystems.

- Aquatic Life Contamination: Long-chain PFAS, such as PFOA and PFOS, accumulate in fish, shellfish, and aquatic plants, increasing human exposure through seafood consumption.

- Biomagnification in Predators: PFAS concentrations increase at higher trophic levels, as predators consume contaminated organisms, leading to health risks for wildlife and humans.
- Plant Uptake from Contaminated Soil and Water: Crops absorb PFAS from polluted water and soil, introducing them into the human diet through agricultural products.

Humans are exposed through contaminated food and drinking water, heightening the risk of developmental, immune, and endocrine disruptions (Saeidi et al., 2024). These impacts highlight the urgent need for monitoring and regulation to reduce PFAS contamination and exposure risks.

1.4.4 Influence of Physicochemical Properties on Behavior

The mobility and environmental behavior of PFAS are due to their physicochemical properties, particularly chain length and functional groups. Short-chain PFAS, due to their higher solubility, travel extensively in groundwater and surface water, making them harder to remove through conventional treatment methods. In contrast, long-chain PFAS exhibit stronger hydrophobic interactions, leading to their sorption into sediments and organic matter, which limit mobility but significantly increases bioaccumulation risks (Saeidi et al., 2024).

These contrasting behaviors present distinct challenges for contamination control and remediation. Short-chain PFAS persist in water systems, spreading contamination over larger areas, whereas long-chain PFAS remain localized in sediments but accumulate in organisms, magnifying toxicological risks within the food chain.

1.5 Health and Environmental Impacts of PFAS

PFAS are linked to adverse health effects and significant environmental challenges due to their persistence, bioaccumulative nature, and toxicity. PFAS exhibit a strong potential for bioaccumulation and biomagnification due to their amphiphilic nature, which facilitates their binding to proteins in living organisms. Exposure to these chemicals occurs through contaminated drinking water, food, air, and consumer products, posing risks to both human health and ecosystems.

1.5.1 Health Impacts

Unlike many other persistent organic pollutants (POPs), PFAS bind to proteins rather than fats, allowing them to accumulate in blood, liver, and metabolic pathways. Long-chain

PFAS preferentially attach to serum albumins, liver enzymes, and proteins involved in fatty acid metabolism, leading to prolonged retention in biological systems. This protein-binding characteristic, coupled with slow elimination rates, results in higher PFAS concentrations in top predators and human populations through biomagnification.

Mechanistically, long-chain PFAS disrupts multiple biological functions:

- Endocrine Disruption → Interferes with thyroid function and reproductive hormones.
- Metabolic Disruption → Affects peroxisome proliferator-activated receptors (PPARs), which regulate lipid metabolism and inflammatory responses.
- Prolonged Exposure Risks → PFOA has a human half-life of several years, extending the duration of toxic effects and cumulative exposure risks.

Given these health and environmental concerns, remediation strategies and regulatory frameworks must consider the unique persistence and bioaccumulative properties of long-chain PFAS while also addressing the mobility and treatment challenges posed by short-chain PFAS.

Carcinogenic Potential

PFAS have been associated with an increased risk of cancer, particularly kidney and testicular cancers. Studies have shown that prolonged exposure to PFAS, especially long-chain compounds like PFOA and PFOS, leads to bioaccumulation in tissues, where they interfere with cellular functions. Their ability to bind to proteins, such as albumins in the blood, facilitates their persistence in the human body, amplifying their carcinogenic potential. Evidence also suggests that PFAS can disrupt gene expression and induce oxidative stress, both of which are critical pathways in cancer development. These findings are supported by epidemiological studies and toxicological data showing the carcinogenic properties of these compounds (Saeidi et al., 2024), (Ford et al., 2024).

Endocrine Disruption

PFAS act as endocrine disruptors by interfering with thyroid function, reproductive hormones, and metabolic processes. This can lead to significant metabolic and reproductive health issues. These substances disrupt thyroid hormone regulation by binding to transport proteins, thereby altering normal hormonal signaling. Additionally, PFAS exposure has been linked to reproductive health problems, including reduced fertility and developmental abnormalities in offspring. They also interfere with pathways involved in lipid and glucose metabolism, contributing to conditions thyroid dysfunction, dyslipidemia, insulin resistance and other metabolic disorders (Shapiro et al., 2025). These disruptions are particularly concerning for vulnerable populations, such as pregnant women and children (Loi et al., 2022).

Furthermore, recent research highlights that women, due to their unique hormonal cycles and physiological characteristics, may exhibit differential PFAS accumulation patterns and be particularly vulnerable to endocrine disruption. Exposure has been linked to female-specific disorders such as polycystic ovary syndrome (PCOS), endometriosis, and altered onset of menarche and menopause, all of which indicate the complex interaction of PFAS with the hypothalamic–pituitary–gonadal axis (Li et al., 2025).

Developmental and Immunological Effects

PFAS exposure during prenatal and early-life stages is particularly concerning due to its potential to cause developmental delays and immunotoxic effects. These chemicals can cross the placenta and accumulate in fetal tissues, disrupting growth and developmental processes. Also, in children, PFAS exposure has been associated with reduced vaccine efficacy and increased susceptibility to infections. This immunotoxicity stems from PFAS's ability to impair the production of antibodies and disrupt immune cell function, raising concerns about their long-term health impacts.

These concerns are amplified for females, particularly during sensitive life stages such as pregnancy, where PFAS can cross the placenta and affect fetal development. Epidemiological evidence supports associations between maternal PFAS exposure and adverse pregnancy outcomes, reproductive disorders, and autoimmune susceptibility in women (Li et al., 2025).

Systemic Toxicity

PFAS affect multiple organ systems, leading to:

- Liver toxicity and elevated risks of fatty liver disease.
- Kidney damage linked to prolonged PFAS retention.
- Neurological and cardiovascular effects, although further research is needed.

Given their long biological half-life (several years in humans), prolonged exposure amplifies their toxic effects, necessitating urgent regulatory measures to reduce human exposure (Saeidi et al., 2024).

1.5.2 Environmental Impacts

Contamination of Water and Soil

Beyond human health, PFAS pose severe environmental threats, primarily due to their mobility, persistence, and ecological toxicity. PFAS contamination in water and soil represents one of the most widespread environmental challenges. These compounds are highly soluble, particularly short-chain PFAS, enabling them to disperse widely through surface water, groundwater, and drinking water supplies. Industrial discharges, urban runoff, and leachates from landfills and wastewater treatment plants (WWTPs) are major sources of contamination. Also, their strong affinity for soil and sediments exacerbates the problem, leading to localized contamination that is particularly challenging to remediate. In soil, PFAS tend to adsorb onto organic matter, with long-chain PFAS showing greater retention compared to their short-chain counterparts. Their persistence and resistance to degradation result in their accumulation in terrestrial and aquatic ecosystems. This dual behavior—mobility in water and retention in soil—complicates environmental management and underscores the resilience of PFAS in natural settings (Wang et al., 2024).

Ecosystem Toxicity

As previously discussed in Section 1.5.1, PFAS tend to bioaccumulate in organisms due to their affinity for proteins. This bioaccumulative behavior also has significant ecological consequences, particularly through food web magnification and long-term ecosystem disruption. More specifically, long-chain PFAS, such as PFOA and PFOS, are particularly prone to bioaccumulation in aquatic organisms, including fish and shellfish. As these organisms are consumed by predators higher up the food chain, including humans, the concentrations of PFAS increase, leading to heightened exposure risks for humans and wildlife. This bioaccumulative property not only threatens individual species but also poses broader risks to entire ecosystems by disrupting food web dynamics (Saeidi et al., 2024).

Long-Term Ecological Consequences

The long-term ecological consequences of PFAS contamination are profound. These chemicals persist in the environment for decades, leading to cumulative effects on soil and water quality. Their widespread presence in aquatic systems disrupts nutrient cycling, contaminates sediment, and affects the health of aquatic and terrestrial species. The bioaccumulation of PFAS poses risks not only to individual organisms but also to entire ecosystems, potentially altering population dynamics and food web structures. Furthermore, the incomplete degradation of PFAS can lead to the formation of transformation products, which may be as toxic and persistent as their parent compounds, compounding the ecological challenges. As example, emerging PFAS, although less bioaccumulative, still pose risks to ecosystems due to their persistence and widespread distribution (Shapiro et al., 2025).

Thus, the environmental impacts of PFAS are far-reaching, affecting water and soil systems, bioaccumulating in organisms, and causing long-term damage to ecosystems. The combination of these factors—contamination, bioaccumulation, and toxicity—highlights the urgent need for effective strategies to manage and mitigate the environmental impact of PFAS, ensuring the protection of ecosystems and the services they provide. Regulatory and technological efforts must be advanced to address the persistence and toxicity of these compounds and protect environmental health (Wang et al., 2024).

1.6. Regulatory Landscape

Regulatory attention to PFAS has grown significantly worldwide, with increasing efforts to restrict their production, use, and environmental discharge. The persistence and toxicity of PFAS have prompted regulatory actions worldwide, with agencies such as the U.S. Environmental Protection Agency (EPA) and the European Chemicals Agency (ECHA) imposing stringent restrictions on their use and emissions (Abaie et al., 2024). However, the lack of comprehensive data on emerging PFAS compounds continues to hinder effective policymaking and risk assessment.

Addressing PFAS contamination requires multifaceted solutions, including:

- Developing efficient remediation technologies tailored to different PFAS types.
- Enhancing regulatory frameworks to limit PFAS production and emissions.
- Advancing monitoring techniques to detect and track contamination in real time.

Given their global prevalence and potential health risks, ongoing research and policy interventions are essential to mitigate PFAS contamination and safeguard environmental and human health.

1.6.1 Overview of Global Regulations

The Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention is a global treaty aimed at eliminating or restricting the production and use of persistent organic pollutants (POPs). PFOS and its related compounds were added to the Convention's list of controlled substances in 2009, and PFOA was included in 2019. These designations require signatory countries to reduce or phase out the use of these substances and to manage their existing stockpiles safely. While this treaty represents significant progress in addressing PFAS at the international level, the scope is limited to specific compounds like PFOS and PFOA, leaving thousands of structurally diverse and potentially harmful PFAS outside the scope of regulation.

Regional Efforts in the EU, US, and Asia

Similarly, the European Union has adopted stringent measures under the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation, which restricts the use of specific PFAS in industrial and consumer products (Shapiro et al., 2025). Restrictions on the use of PFOS and PFOA have been implemented, and further actions are being taken to regulate entire PFAS classes.

The United States has adopted a more decentralized approach, with individual states setting limits for PFAS in drinking water, while the Environmental Protection Agency (EPA) is developing federal Maximum Contaminant Levels (MCLs) for PFOA, PFOS, and other PFAS. Regionally, countries such as Canada and Australia have similarly implemented drinking water advisory levels for key PFAS, including PFOA and PFOS, and have expanded monitoring efforts to better understand PFAS prevalence in water supplies.

In Asia, countries like Japan and South Korea have started monitoring and regulating PFAS in industrial processes, and China has incorporated PFAS restrictions in its national pollution control strategies. However, enforcement remains a challenge in many regions (Saeidi et al., 2024).

Although the global regulatory landscape for PFAS continues to evolve, it still contains significant gaps that hinder coordinated action and effective enforcement. Addressing these challenges will require coordinated global action, the development of comprehensive regulations for all PFAS, and investments in analytical and remediation technologies to mitigate their environmental and health impacts.

1.6.2 Gaps and Challenges in Existing Policies

Lack of Unified Frameworks

One of the major challenges in regulating PFAS globally is the lack of a unified framework that addresses the entire class of these chemicals. Most regulatory actions focus on a subset of PFAS, such as PFOA and PFOS, ignoring the risks posed by emerging and short-chain PFAS. The absence of standardized testing protocols further complicates efforts to assess PFAS contamination and enforce regulations effectively (Shapiro et al., 2025).

Limitations in Monitoring and Enforcement

Monitoring environmental PFAS contamination remains challenging due to the high cost and technical complexity of detecting these substances at trace levels. Moreover, enforcement of regulations varies significantly across regions, with some countries lacking the resources or political will to implement stringent controls. This variability in enforcement creates loopholes that industries can exploit, exacerbating the problem of PFAS contamination.

1.7. Research Gaps

The environmental fate and transport of PFAS pose critical challenges to water quality and public health, as their persistence, mobility, and chemical resistance mean that even minor releases can lead to extensive contamination. Addressing these issues requires a detailed understanding of PFAS pathways and behaviors and the development of treatment methods capable of removing them from environmental matrices. Also, the combination of structural diversity and functional properties emphasizes the complexity of PFAS behavior in the environment and their removal from aqueous systems. Understanding these characteristics is fundamental for designing effective remediation strategies, particularly adsorption technologies that focus on their amphiphilic and ionic properties to capture PFAS from water matrices. Moreover, stricter exposure limits and integrating advanced monitoring and treatment systems into comprehensive strategies is essential for safeguarding human health and preserving environmental integrity against the risks posed by PFAS.

1.7.1Limitations in Degradation and Removal Technologies

Despite growing regulatory efforts, significant gaps and challenges persist in addressing PFAS contamination comprehensively. One major limitation is the lack of a unified framework for regulating the thousands of PFAS compounds currently in use. Most regulations target a limited subset of well-studied PFAS, such as PFOA and PFOS, leaving many emerging PFAS largely unregulated. Additionally, the absence of standardized testing methods for detecting PFAS at low concentrations hinders effective monitoring and enforcement. Variability in national and regional regulations further complicates global efforts to control PFAS, creating loopholes that industries can exploit (Garg et al., 2021).

Current technologies for PFAS degradation and removal remain limited, particularly given the strong carbon-fluorine (C-F) bonds that confer exceptional stability to these compounds. Conventional treatment methods, such as coagulation, filtration, and biological treatment, are generally ineffective for PFAS removal, particularly short-chain compounds. Advanced technologies like adsorption, ion exchange, and high-pressure oxidation have shown promise for PFAS degradation. However, these methods are often associated with high energy costs, slow reaction kinetics, and the potential formation of toxic by-products. Moreover, many technologies are not yet scalable for widespread implementation, highlighting a critical gap in the development of cost-effective and sustainable PFAS remediation solutions (Shapiro et al., 2025).

1.7.2 Variability in Adsorption Performance Across PFAS Types

Adsorption, a widely used method for PFAS removal exhibits substantial variability in removal efficiency depending on chain length and functional group composition of the PFAS compound. Long-chain PFAS generally exhibit higher adsorption efficiencies due to their stronger hydrophobic interactions with adsorbents like granular activated carbon (GAC). Conversely, short-chain PFAS, which are more soluble and mobile, are more difficult to capture using conventional adsorbents. This variability complicates the design of universal treatment systems and underscores the need for tailored adsorbents, such as cyclodextrin-based materials, that can efficiently capture a wide range of PFAS types. Further research is needed to understand the mechanisms of adsorption for different PFAS and optimize materials for enhanced performance (Loi et al., 2022).

Addressing these regulatory and research gaps requires a coordinated approach that integrates advancements in science, technology, and policy. The main priority should be the development of cost-effective, scalable technologies for PFAS removal and destruction, with a focus on emerging and short-chain PFAS. Policymakers must also strive to harmonize regulations globally, implement comprehensive monitoring systems, and incentivize industries to adopt PFAS-free alternatives. Bridging these gaps is essential to mitigating the environmental and health impacts of PFAS and ensuring sustainable management of these persistent pollutants.

1.8 Thesis Objectives

The objectives of this thesis respond to the urgent need for innovative and sustainable solutions to PFAS contamination. Among available remediation strategies, adsorption has emerged as a particularly promising approach due to its efficiency, adaptability, and ability to target a broad range of PFAS compounds. Adsorption processes exploit the hydrophobic and ionic characteristics of PFAS to capture and remove them from contaminated water, offering a practical and effective pathway for reducing environmental and human exposure.

The persistence, bioaccumulation, and toxicity of PFAS underscore the need for advanced treatment methods that can be applied in real-world conditions. A deep understanding of PFAS interactions with adsorbent materials is essential not only for optimizing removal efficiency but also for informing regulatory actions and risk assessments. In this context, the focus of this research is on adsorption technologies—specifically those based on cyclodextrin materials—which have shown considerable potential in recent studies.

Cyclodextrins, with their hydrophobic inner cavities and hydrophilic outer surfaces, are particularly well-suited for PFAS remediation through host–guest complexation, hydrophobic interactions, and electrostatic forces. Their environmentally friendly nature and chemical tunability make them attractive candidates for scalable water treatment applications. This study will investigate the interactions between PFAS molecules and cyclodextrin-based adsorbents, evaluating their adsorption performance under a range of environmental conditions.

Special attention will be given to environmental variables such as pH, ionic strength, temperature, and the presence of co-contaminants, all of which may influence the efficiency of PFAS capture. By characterizing these effects under both controlled and environmentally relevant conditions, this research aims to provide insights into optimizing cyclodextrin-based systems for practical use.

Finally, the thesis will address the scalability and sustainability of these solutions, including the regeneration and reuse of adsorbents, minimization of secondary pollution, and integration into existing water treatment infrastructure. The ultimate goal is to contribute to the development of viable, cost-effective technologies for mitigating PFAS contamination in real-world water systems.

Chapter 2: Adsorption Processes for PFAS Removal with a Focus on Cyclodextrins

The increasing awareness of the limitations posed by conventional water treatment methods in addressing PFAS has underscored the urgent need for innovative and scalable solutions. Among the most promising approaches, adsorption has emerged as a leading technique for removing PFAS due to its effectiveness, versatility, and compatibility with a range of water chemistries. Traditional processes such as coagulation, sedimentation, biological treatment, and filtration often fall short, especially when targeting PFAS at trace concentrations or in complex aqueous environments. In contrast, adsorption offers high selectivity and operational simplicity, making it particularly suitable for diverse PFAS structures, including those resistant to degradation. This chapter explores the mechanisms, materials, and influencing factors of adsorption processes, with particular attention to the use of cyclodextrin-based adsorbents, which present a sustainable and high-performance alternative for PFAS remediation (Saeidi et al., 2024).

2.1 Introduction to Techniques for PFAS Removal

A wide range of technologies have been investigated for the removal of PFAS from water due to their chemical persistence and resistance to conventional treatment methods (Abbasian Chaleshtari and Foudazi, 2022). The most studied and widely applied alternatives include membrane filtration, advanced oxidation processes (AOPs), electrochemical degradation, thermal treatments, bioremediation and adsorption. Each method presents distinct mechanisms, benefits, and challenges in addressing the complexity of PFAS contamination.

2.1.1 Membrane Filtration

Membrane-based technologies such as reverse osmosis (RO) and nanofiltration (NF) are among the most effective physical separation techniques for PFAS. These systems rely on size exclusion and electrostatic interactions to reject PFAS molecules from water. RO membranes have demonstrated >99% removal efficiency for long-chain PFAS like PFOA and PFOS, making them particularly effective in industrial and municipal applications (Garg et al., 2021). Nanofiltration also shows promising results, especially when membrane surface charge and pore size are optimized to enhance PFAS rejection.

However, membrane filtration technologies are not without limitations. They typically generate concentrated reject streams that require additional treatment and management.

Moreover, membrane fouling, high operating pressures, and energy consumption can affect long-term performance and economic feasibility (Garg et al., 2021).

2.1.2 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) rely on the generation of highly reactive species, such as hydroxyl (•OH) or sulfate ($SO_4^{\bullet-}$) radicals, to degrade organic contaminants. However, traditional AOP configurations, such as ozonation alone or simple H_2O_2/UV systems, have demonstrated limited effectiveness in treating PFAS, primarily due to the extreme chemical stability of the carbon–fluorine (C–F) bond. These systems often lack the oxidative strength or energy input required to cleave such bonds effectively. In contrast, enhanced AOP systems—such as those employing persulfate activation via ultraviolet (UV) radiation, heat, or transition metals, as well as non-thermal plasma technologies—have shown greater potential in PFAS degradation. These advanced techniques generate stronger radicals and more diverse reactive species, which can break down PFAS molecules into smaller, less persistent fragments. While these methods are still under active development and evaluation, their improved performance over conventional AOPs highlights the importance of system design and energy input when selecting oxidation-based treatments for PFAS remediation. Despite their enhanced oxidative potential, advanced AOP systems also face several limitations that challenge their widespread application in real-world PFAS treatment. Many of these processes require high energy input, especially those involving UV light or plasma reactors, which can lead to elevated operational costs. Additionally, the incomplete mineralization of PFAS is a common concern, as partial degradation may result in the formation of toxic intermediate compounds or shorter-chain PFAS, which are often more mobile and difficult to remove. Furthermore, the efficiency of radical generation can be significantly influenced by water matrix components, such as natural organic matter, bicarbonates, and halides, which may act as radical scavengers and reduce treatment efficacy. These challenges highlight the need for continued optimization of reaction conditions, reactor design, and energy efficiency to make advanced AOPs more feasible for large-scale and cost-effective PFAS remediation (Abbasian Chaleshtari and Foudazi, 2022).

2.1.3 Electrochemical Degradation

Electrochemical processes, including electrocatalysis and electro-Fenton reactions, have emerged as effective strategies for PFAS destruction. These methods use electrically driven reactions at the electrode surface to induce oxidative or reductive cleavage of the carbon–

fluorine bonds. For example, boron-doped diamond (BDD) electrodes are capable of achieving high PFAS degradation efficiencies due to their wide electrochemical potential and strong generation of reactive species.

Despite their effectiveness in laboratory-scale studies, electrochemical treatments face challenges related to scalability, cost of materials, and electrode degradation over time. Moreover, side reactions such as hydrogen evolution and energy inefficiencies remain hurdles for practical application (Garg et al., 2021).

2.1.4 Thermal Treatments

High-temperature incineration remains one of the few methods that can completely destroy PFAS compounds, including both short- and long-chain variants. Thermal degradation typically occurs at temperatures exceeding 600–1000 °C, where PFAS are broken down into carbon dioxide, hydrogen fluoride, and other inorganic products. Studies have shown >99.9% degradation of PFOS and PFOA under optimized conditions.

However, thermal methods are energy-intensive and demand extremely high temperatures and involve high operational costs. Also, they may pose risks of toxic by-product generation, such as perfluoroalkylated fragments or greenhouse gases like CF_4 and C_2F_6. Emissions control systems, such as scrubbers, are therefore essential for safe operation (Garg et al., 2021).

2.1.5 Bioremediation

Biological degradation of PFAS is considered a promising but still underdeveloped field. While certain bacteria, enzymes, and plant-based systems have shown the ability to transform PFAS under laboratory conditions, these processes are typically slow, with low degradation rates and limited applicability to complex environmental matrices.

Microbial defluorination is hindered by the chemical stability of PFAS and the toxicity of intermediate products, which often inhibit microbial activity. As such, bioremediation is generally considered supplementary and is most effective when integrated into treatment trains with physical or chemical technologies (Garg et al., 2021).

Biological methods, while environmentally friendly, remain in early stages of development and are hindered by extremely long reaction times, low degradation efficiencies, and challenges in scalability (Saeidi et al., 2024).

2.1.6 Adsorption

Adsorption is a surface-based separation process in which contaminants are removed from water by adhering to the surface of a solid material (adsorbent). This method does not chemically degrade PFAS molecules but instead relies on physical and chemical interactions, such as hydrophobic forces, electrostatic attraction, and host–guest inclusion, to capture PFAS compounds from aqueous solutions. Adsorption is widely used in water treatment due to its operational simplicity, low energy requirements, and broad applicability under different environmental conditions.

Materials commonly used as adsorbents include granular activated carbon (GAC), powdered activated carbon (PAC), ion-exchange resins (IXS), metal–organic frameworks (MOFs), and functionalized polymers, each utilizing distinct mechanisms and structural advantages. Among these, GAC and IXS are the most established, particularly for the removal of long-chain PFAS such as PFOA and PFOS (Wang et al., 2024). However, these materials face notable challenges, including reduced performance in the presence of short-chain PFAS, susceptibility to fouling in complex matrices, and limited regenerability, which can elevate long-term operational costs.

Compared to other PFAS removal techniques, adsorption offers several advantages. Membrane filtration and thermal degradation, while highly effective, are often cost-prohibitive and generate concentrated residual waste. Advanced oxidation and electrochemical techniques show promising degradation potential but continue to face limitations in efficiency, energy demands, and large-scale implementation. Biological methods, though promising, are constrained by slow kinetics and limited real-world scalability. In contrast, adsorption offers a balance of efficiency, operational simplicity, cost-effectiveness, and flexibility, making it suitable for integration into treatment trains and adaptable across a wide range of PFAS types and water matrices (Saeidi et al., 2024). Moreover, when incorporated into treatment train configurations, it can be synergistically combined with filtration, oxidation, or photocatalysis to enhance system performance and broaden the range of removable PFAS (Saeidi et al., 2024).

Because of these advantages, adsorption has established itself as a key method in PFAS treatment and often serves as the standard against which newer adsorbent materials are compared. One group of materials that has attracted growing attention is cyclodextrin-based adsorbents, known for their excellent selectivity, environmentally friendly nature, and ability to be reused. The following sections will explore adsorption in greater depth, with particular emphasis on cyclodextrin-based materials, which have demonstrated exceptional selectivity, reusability, and environmental safety in recent studies.

The various PFAS removal techniques discussed above differ significantly in their mechanisms, effectiveness, and operational requirements. ***Table 2.1*** provides a comparative summary of these methods, highlighting their key strengths and limitations. While each approach has value under specific conditions, adsorption remains one of the most promising due to its adaptability, ease of application, and potential for integration with other technologies. This sets the stage for a closer examination of adsorption processes in the sections that follow.

Table 2.1 Common PFAS Removal Techniques and Their Key Characteristics

Removal Method	**Mechanism**	**Effectiveness**	**Limitations**
Membrane Filtration (RO/NF)	Physical separation via membrane pores and electrostatic repulsion	High for long-chain PFAS (>99%); moderate for short-chain	High cost, energy use, membrane fouling, and brine waste generation
Advanced Oxidation Processes (AOPs)	Chemical degradation using hydroxyl/sulfate radicals, UV, or ozone	Moderate; varies by PFAS type and system design	High energy demand, incomplete mineralization, toxic by-product formation
Electrochemical Degradation	Electrochemical oxidation/reduction using advanced electrodes	High in lab-scale studies; limited in real-world applications	Expensive materials, electrode degradation, low scalability
Thermal Treatment (Incineration)	Thermal destruction of PFAS at high temperatures (>600°C)	Very high (>99.9%) under controlled conditions	Very high energy use; toxic emissions requiring gas treatment systems
Bioremediation	Microbial transformation or enzymatic defluorination	Low to moderate; slow kinetics and incomplete degradation	Slow rates, limited scalability, PFAS toxicity may inhibit biological activity
adsorption	Physical and chemical attraction of PFAS to solid surfaces via	High for long-chain PFAS; moderate for short-chain	Low energy demand; may require regeneration;

hydrophobic, electrostatic, and host-guest interactions	depending on adsorbent type	performance affected by co-contaminants

2.2 Adsorption Mechanisms for PFAS

2.2.1 Fundamental Principles of Adsorption

Adsorption is a physicochemical process in which molecules from a fluid phase (liquid or gas) adhere to the surface of a solid material, known as the adsorbent. The effectiveness of this process is determined by the nature of interactions between the adsorbent surface and the adsorbate—in this case, per- and polyfluoroalkyl substances (PFAS). These interactions are primarily governed by electrostatic forces, hydrophobic interactions, and, in some cases, hydrogen bonding (Garg et al., 2021).

The behavior of PFAS during adsorption is influenced by their amphiphilic structure, characterized by a hydrophobic fluorinated carbon chain and a hydrophilic polar functional group which are typically deprotonated such as carboxylate ($-COO^-$) or sulfonate ($-SO_3^-$). Under typical environmental pH conditions, most PFAS possess negatively charged functional groups which interact preferentially with positively charged sites on the adsorbent through electrostatic attraction. Functionalizing adsorbents to enhance surface charge or introduce ionic exchange groups significantly improves their ability to capture these anionic PFAS (Usman et al. , 2024).

In addition to electrostatic forces, hydrophobic interactions are a dominant mechanism, particularly for PFAS with longer carbon chains. The low polarity of the perfluorinated tail facilitates its attraction to nonpolar regions of the adsorbent surface. This mechanism is especially important in materials such as activated carbon and certain polymers, which possess high surface area and hydrophobic domains (Saeidi et al., 2024).

Hydrogen bonding, although generally weaker, may also contribute when the adsorbent possesses hydroxyl, carbonyl, or amide groups. These can interact with the polar head groups of PFAS, though competition with water molecules often reduces the effectiveness of this mechanism. In some materials, like cyclodextrins, hydrogen bonding can synergize with hydrophobic forces to enhance PFAS retention.

The adsorption process can be further described through equilibrium and kinetic models, which provide valuable insights into how adsorption systems perform. Equilibrium models, known as adsorption isotherms, illustrate the relationship between the concentration of PFAS remaining in solution and the amount adsorbed onto the material once equilibrium is reached. Two of the most widely used isotherm models are the Langmuir and Freundlich models. The Langmuir model assumes a uniform surface with a fixed number of identical binding sites, leading to monolayer adsorption. In contrast, the Freundlich model applies to heterogeneous surfaces and describes multilayer adsorption with sites of varying energies. While these models provide valuable insights, it is important to note that real environmental systems are often more complex, and model fitting may not always capture all interactions accurately.

The Langmuir model is particularly suited to describe PFAS adsorption on materials with uniform and well-defined binding sites, such as functionalized cyclodextrin polymers or engineered resins. In contrast, the Freundlich model better captures adsorption behavior on heterogeneous surfaces, such as granular activated carbon (GAC) or natural materials, where adsorption sites vary in energy and accessibility (Saeidi et al., 2024).

In parallel, kinetic models help describe the rate at which adsorption occurs and provide information about the mechanisms controlling the process. The pseudo-first-order model suggests that the rate of adsorption is proportional to the concentration of PFAS in the solution, while the pseudo-second-order model considers the availability of active adsorption sites and is often associated with chemisorption. By applying these models, researchers can better understand the efficiency of adsorbent materials and optimize conditions for effective PFAS removal.

In addition to the inherent properties of the adsorbent and the PFAS molecules, environmental conditions also play a critical role in determining adsorption efficiency. Parameters such as pH, ionic strength, temperature, and the presence of natural organic matter (NOM) can influence both the availability of binding sites and the strength of adsorbate–adsorbent interactions. For instance, elevated ionic strength can compress the electrical double layer surrounding the adsorbent, which may reduce electrostatic repulsion and enhance PFAS adsorption in certain systems.

In real environmental systems, the presence of co-contaminants such as natural organic matter (NOM), multivalent cations (e.g., Ca^{2+}, Mg^{2+}), and other anions (e.g., nitrate, sulfate) can significantly reduce adsorption efficiency. These substances may compete with PFAS molecules for available adsorption sites or block access to pores, especially in porous materials like activated carbon or ion-exchange resins. Moreover, divalent cations can compress the electrical double layer, reducing the extent of electrostatic interactions that are critical for capturing anionic PFAS. As a result, adsorption performance often varies between synthetic test waters and real-world matrices.

Altogether, the success of PFAS adsorption depends on a complex interplay between adsorbent properties (such as pore structure, surface charge, and functionalization) and PFAS molecular characteristics (including chain length, head group identity, and hydrophobicity). Understanding these fundamental principles is essential for the rational design and optimization of adsorbents capable of achieving efficient and selective PFAS removal from contaminated waters.

2.2.2 Key Adsorption Interactions and the Influence of PFAS Structure

The adsorption of PFAS onto solid materials is primarily governed by a combination of hydrophobic interactions, electrostatic attraction, and hydrogen bonding. The relative contribution of each mechanism depends on the physicochemical properties of both the adsorbent and the specific PFAS compound.

Hydrophobic interactions are among the most dominant forces in PFAS adsorption, especially for long-chain compounds. The perfluorinated carbon backbone of PFAS is extremely nonpolar and repels water, which drives these molecules to preferentially associate with nonpolar or hydrophobic regions on adsorbent surfaces. This process resembles a partitioning mechanism, whereby PFAS diffuse from the aqueous phase into the hydrophobic microenvironments within materials like activated carbon, polymers, or cyclodextrin cavities. As the length of the fluorocarbon chain increases, so does the molecule’s hydrophobicity, leading to stronger interactions and higher adsorption affinity (Abaie et al., 2024).

Electrostatic interactions are particularly relevant for PFAS with anionic head groups—such as carboxylate ($-COO^-$) or sulfonate ($-SO_3^-$)—which are deprotonated and negatively charged under environmental pH conditions. These groups can form attractive interactions with positively charged functional groups on adsorbents, such as protonated amines or quaternary ammonium moieties (Abaie et al., 2024). Materials modified to increase surface charge density, such as functionalized ion-exchange resins or cationic cyclodextrin derivatives, tend to perform better in capturing anionic PFAS, particularly in low ionic strength waters where electrostatic interactions are less shielded.

Hydrogen bonding, while weaker than hydrophobic or electrostatic interactions, may also contribute to PFAS adsorption, especially in systems where the adsorbent features functional groups like hydroxyl, amide, or carbonyl groups. These groups can form hydrogen bonds with the polar head groups of PFAS. However, this interaction is often outcompeted by water molecules forming hydration shells around PFAS in aqueous media, thus making hydrogen bonding a more subtle or secondary mechanism. Nevertheless, in materials with preorganized binding pockets, hydrogen bonding may act synergistically with hydrophobic forces to stabilize PFAS inclusion complexes (Saeidi et al., 2024).

In addition to these primary mechanisms, dipole–dipole interactions can also play a role in PFAS adsorption, particularly for zwitterionic compounds. These molecules, although electrically neutral overall, carry both a localized positive and negative charge. This structural feature enables them to interact with polar sites on adsorbents through permanent dipole alignment. Zwitterionic PFAS analogs or other polar organics may thus require adsorbents with polar or amphiphilic domains for effective capture.

It is also important to distinguish zwitterionic compounds from strictly neutral ones. While neutral compounds possess no net or localized charge, zwitterions contain internal charge separation. This distinction has implications for adsorption behavior, as zwitterionic species may not interact strongly with nonpolar surfaces but can align favorably within structured or charged microenvironments on the adsorbent.

The key adsorption interactions described above are summarized in ***Table 2.2***, along with the typical structural features of PFAS compounds that drive each mechanism.

Table 2.2 Overview of dominant adsorption interactions relevant to PFAS removal, including the driving forces, typical structural traits of target molecules, and representative examples. This classification helps in understanding how specific PFAS structures interact with adsorbent materials via hydrophobic, electrostatic, hydrogen bonding, or dipole–dipole mechanisms.

Interaction Type	**Driving Forces**	**Target Molecule Traits**	**Example**
Hydrophobic	Water exclusion; van der Waals forces	Long-chain, nonpolar PFAS	PFOA, PFOS

Electrostatic	Coulombic attraction between opposite charges	Anionic PFAS with $-COO^-$ or $-SO_3^-$ heads	PFBA, PFHxS
Hydrogen bonding	Polar donor/acceptor interactions	Polar functional groups (–OH, –COOH, $-NH_2$)	GenX, PFPeA
Dipole–dipole	Alignment of permanent molecular dipoles	Zwitterionic or highly polar molecules	Amino acids, beta-blockers

The structure of PFAS compounds strongly influences their adsorption behavior. Long-chain PFAS, typically defined as those with perfluoroalkyl chains of eight or more carbon atoms (e.g., PFOA, PFOS), are more readily adsorbed due to increased hydrophobicity and molecular size, which enhances van der Waals interactions and improves entrapment in porous adsorbents (Wang et al., 2024). In contrast, short-chain PFAS (e.g., PFBA, PFBS) are more water-soluble and have lower affinities for hydrophobic adsorbent surfaces, making them more mobile in the environment and more difficult to remove efficiently (Abaie et al., 2024).

Additionally, the type of functional group on the PFAS molecule affects adsorption. Perfluorosulfonic acids (PFSAs) generally exhibit higher adsorption than perfluorocarboxylic acids (PFCAs) of equal chain length, likely due to the greater electron-withdrawing strength and polarizability of the sulfonate group, which enhances both hydrophobic and electrostatic interactions (Wang et al., 2024). Furthermore, the rigidity and linear geometry of PFAS can influence how easily they align with and penetrate into porous adsorbent structures

In practice, these interactions often act in combination. A single adsorbent may utilize multiple binding mechanisms simultaneously, depending on its surface chemistry and morphology. Understanding the interplay of these forces is essential for the rational design and selection of high-performance adsorbents, particularly for applications where both long- and short-chain PFAS are present in complex water matrices.

A thorough understanding of the physicochemical interactions between PFAS and adsorbent materials—particularly hydrophobic, electrostatic, and hydrogen bonding mechanisms—is essential for evaluating and improving treatment technologies. These interactions, along with the structural diversity of PFAS compounds, directly influence the effectiveness of different adsorbents. As such, selecting an appropriate adsorbent requires not only knowledge of its surface chemistry and functionalization but also how it performs under real environmental conditions. The following section provides an overview of the most commonly used adsorbents for PFAS removal, highlighting their mechanisms, strengths, limitations, and recent advancements in material design—including the promising role of cyclodextrin-based systems (Saeidi et al., 2024) (Wang et al., 2024)**.**

2.3 Common Adsorbents for PFAS Removal

Numerous adsorbent materials have been developed and tested for the removal of PFAS from aqueous environments. These materials vary in surface chemistry, porosity, regeneration potential, and affinity for different PFAS species. This section presents an overview of the most widely studied adsorbents, with an emphasis on their mechanisms, performance characteristics, and applicability in real-world treatment systems.

2.3.1 Activated Carbon (GAC & PAC)

Activated carbon—in both granular (GAC) and powdered (PAC) forms—is one of the most established and commercially available adsorbents for PFAS removal. It is characterized by its high surface area, porous structure, and hydrophobic surface chemistry, which facilitate adsorption primarily through hydrophobic interactions and van der Waals forces (Saeidi et al., 2024).

GAC is commonly used in fixed-bed columns in drinking water treatment systems. It is favored for its mechanical strength, reusability, and ability to process large volumes of water. PAC, on the other hand, is applied in batch systems or added directly into water as a slurry, offering faster adsorption kinetics due to its smaller particle size and higher surface area-to-volume ratio (Wang et al., 2024).

While GAC and PAC are highly effective for the removal of long-chain PFAS such as PFOA and PFOS, their performance is significantly reduced for short-chain compounds like PFBA and PFBS. This is attributed to the lower hydrophobicity and higher water solubility of short-chain PFAS, which limits their affinity for activated carbon surfaces. Additionally, the presence of natural organic matter (NOM), competing anions, and other co-contaminants in real water matrices can lead to adsorbent fouling, reducing available binding sites and overall efficiency (Saeidi et al., 2024).

Another critical limitation of activated carbon is its limited regeneration capacity. Thermal regeneration is possible but energy-intensive and may not fully restore adsorption performance for PFAS-saturated media. Over time, exhausted carbon often requires replacement, which increases operational costs and waste generation (Wang et al., 2024).

Despite these drawbacks, activated carbon remains one of the most widely used technologies for PFAS remediation due to its maturity, availability, and proven field performance. It also serves as a benchmark against which newer adsorbents, such as ion-exchange resins and cyclodextrin-based polymers, are often evaluated. Notably it was demonstrated that conventional activated carbon exhibits relatively slow and non-selective adsorption kinetics for a wide range of micropollutants, and that its performance declines significantly in the presence of natural organic matter and inorganic ions. These limitations are particularly relevant when treating complex water matrices such as those contaminated with PFAS. The study further highlights how alternative materials, like porous β-cyclodextrin polymers, can offer faster kinetics, greater selectivity, and resistance to fouling, underscoring the growing interest in developing next-generation adsorbents (Ling et al., 2017).

2.3.2 Ion-Exchange Resins

Ion-exchange resins (IEX) represent another widely studied class of adsorbents for PFAS removal, particularly effective for anionic PFAS compounds. These materials are typically composed of a polymeric matrix functionalized with charged groups capable of exchanging ions with contaminants in water. In the case of PFAS, the negatively charged functional groups of the compounds (e.g., $–COO^-$ and $–SO_3^-$) are attracted to positively charged quaternary ammonium sites on the resin surface (Wang et al., 2024).

The adsorption mechanism of ion-exchange resins is primarily based on electrostatic interactions, which enable the selective removal of PFAS from complex aqueous matrices. Unlike activated carbon, which relies heavily on hydrophobicity, ion-exchange resins can efficiently capture both long- and some short-chain PFAS, particularly when the resin is designed to enhance surface charge density or includes hydrophobic domains to strengthen secondary interactions (Saeidi et al., 2024).

Resins can be broadly categorized into gel-type and macroporous-type. Gel-type resins have smaller pore sizes and rely primarily on ion exchange, while macroporous resins provide enhanced surface accessibility and improved kinetics, making them more effective in treating contaminated waters with a range of PFAS chain lengths (Saeidi et al., 2024).

Despite their high selectivity and efficiency, ion-exchange resins are not without limitations. Their performance can be compromised by matrix interference from sulfate, nitrate, or natural organic matter, which competes for active sites and may reduce resin capacity over time. In addition, regeneration of spent resin—typically performed with brine solutions—is not always effective in removing strongly bound PFAS, potentially leading to residual contamination and the need for eventual disposal.

Nevertheless, the combination of electrostatic specificity and structural tunability makes ion-exchange resins a promising alternative or complement to activated carbon in PFAS treatment systems, especially when targeting diverse PFAS profiles in industrial or municipal waters.

2.3.3 Metal–Organic Frameworks (MOFs) and Covalent Organic Frameworks (COF)

Metal–Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) are a relatively new class of porous crystalline materials composed of metal ions or clusters coordinated to organic ligands. Their defining features—exceptionally high surface area, tunable pore size, and versatile surface chemistry—have drawn significant attention in recent years for PFAS remediation applications (Wang et al., 2024).

The adsorption mechanisms of MOFs are often a combination of hydrophobic interactions, electrostatic attractions, hydrogen bonding, and size exclusion. Their well-defined and uniform pore structures allow for selective uptake of PFAS molecules based on size and charge. Furthermore, by modifying the functional groups on the organic linkers or incorporating positively charged sites, MOFs can be tailored to enhance selectivity for anionic PFAS.

Several MOFs have demonstrated notable performance in capturing both long- and short-chain PFAS, outperforming traditional adsorbents in controlled lab-scale settings. For instance, materials such as ZIF-8 and MIL-101 have shown strong affinities for PFOA and PFOS through electrostatic and hydrophobic mechanisms, while others have been functionalized with amine groups or fluorophilic domains to further improve PFAS affinity (Saeidi et al., 2024).

However, despite their promising performance, MOFs currently face several challenges limiting their large-scale application. Many MOFs are chemically unstable in water, particularly under acidic or basic conditions, which can lead to framework collapse or metal leaching. Additionally, their high synthesis cost and complex fabrication processes hinder commercial scalability. Some MOFs also suffer from limited regenerability and may degrade after a few adsorption cycles.

Ongoing research is exploring ways to improve the stability and reusability of MOFs, including the incorporation of more robust metal clusters (e.g., Zr, Ti), hybridization with polymers, or post-synthetic modifications. Although not yet widely used in field applications, MOFs represent an innovative and highly tunable platform for future PFAS adsorbent development, especially for systems requiring high selectivity and rapid kinetics.

Covalent Organic Frameworks (COF)

Covalent Organic Frameworks (COFs) are a relatively new class of crystalline, porous polymers constructed from organic building blocks via strong covalent bonds. Similar to MOFs, they possess high surface areas and ordered pore structures, but unlike MOFs, they are entirely metal-free. This characteristic gives COFs exceptional chemical tunability and thermal stability, making them promising candidates for PFAS adsorption in aqueous environments.

Study of Ji et al. (2018), have demonstrated the potential of amine-functionalized imine-linked 2D COFs for efficient GenX and broad-spectrum PFAS removal. The research showed that the incorporation of primary amine groups into the COF structure significantly enhanced their affinity for PFAS, especially GenX, due to the synergistic effects of electrostatic interactions and hydrophobic partitioning within the COF's pores.

Among the tested materials, a COF with 28% amine loading achieved over 90% removal of 12 out of 13 PFAS compounds at environmentally relevant concentrations. These materials exhibited fast adsorption kinetics (within 30 minutes) and high capacity (up to 240 mg/g for GenX), outperforming traditional adsorbents such as granular and powdered activated carbon under similar conditions.

Moreover, COFs maintained their crystallinity and porosity after functionalization, with surface areas exceeding 1000 m^2/g and pore sizes around 2.6 nm. This structural integrity allows for tunable adsorption behavior, as the spatial distribution of functional groups within the pore network significantly influences binding efficiency.

Despite their promise, COFs remain at a relatively early stage of development for environmental applications. Challenges include complex synthesis protocols and limited data on long-term reusability in complex water matrices. However, their modular chemistry and demonstrated selectivity highlight their potential as a next-generation platform for targeted PFAS remediation, particularly for short-chain compounds and emerging alternatives like GenX (Ji et al., 2018).

2.3.4 Cyclodextrin-Based Adsorbents

Among emerging adsorbent materials, cyclodextrin-based systems have gained significant attention for the removal of various organic micro-pollutants, including per- and polyfluoroalkyl substances (PFAS), due to their unique molecular architecture and ability to form host- guest complexes with hydrophobic molecules. Cyclodextrins (CDs) are cyclic oligosaccharides composed of glucose monomers, characterized by a hydrophilic outer surface and a hydrophobic inner cavity. This toroidal structure enables the selective encapsulation of organic micropollutants through hydrophobic interactions and electrostatic attraction. Such properties make CDs particularly effective for adsorbing a wide range of PFAS.

One of the key advantages of CD-based materials is their selectivity. Compared to traditional adsorbents such as activated carbon and ion-exchange resins, functionalized cyclodextrin polymers have demonstrated comparable or superior removal efficiencies. Moreover, certain CD formulations have shown greater resistance to fouling and matrix interference, which is particularly beneficial for treatment applications involving complex environmental waters (Wang et al., 2024).

Table 2.3 summarizes the main characteristics of commonly used PFAS adsorbents. Each material type operates through distinct adsorption mechanisms, including hydrophobic interactions, electrostatic forces, and molecular recognition. While activated carbon remains the most established adsorbent, its limitations—particularly with short-chain PFAS and regeneration—have led to the development of more selective materials such as ion-exchange resins and cyclodextrin-based polymers. MOFs also show excellent potential, though issues related to cost and water stability currently limit their application. This comparison highlights the trade-offs between traditional and emerging materials and sets the foundation for the detailed discussion of cyclodextrins in the next section.

Table 2.3 Comparison of Common PFAS Adsorbents

Adsorbent Type	**Primary Mechanisms**	**Effectiveness**	**Strengths**	**Limitations**
Activated Carbon (GAC & PAC)	Hydrophobic interactions, van der Waals forces	High for long-chain PFAS; lower for short-chain	Widely available, proven performance	Fouling, limited regeneration, less effective for short-chain PFAS
Ion-Exchange Resins	Electrostatic interactions, ion exchange	High for long- and some short-chain PFAS	High selectivity, reusable	Competing ions reduce capacity; regeneration may be incomplete
Metal–Organic Frameworks (MOFs)	Hydrophobic and electrostatic interactions, size exclusion	High for long- and short-chain PFAS (in lab)	High surface area, tunable chemistry	High cost, water stability issues, scalability limitations
Cyclodextrin-Based Polymers	Host–guest inclusion, hydrophobic and electrostatic interactions	High for long-chain PFAS; tunable for broader range	Selective binding, biodegradable, regenerable	Still emerging; requires functionalization for optimal performance

2.4 Cyclodextrins as Adsorbents for PFAS Removal

2.4.1 Introduction to Cyclodextrins

Cyclodextrins (CDs) are cyclic oligosaccharides composed of glucose units linked by α-1,4-glycosidic bonds. Their unique molecular architecture features a hydrophobic internal cavity and a hydrophilic exterior, enabling them to function as molecular hosts for a broad range of organic contaminants (Abaie et al., 2024). This structural configuration facilitates the selective encapsulation of pollutants via host–guest chemistry, primarily driven by hydrophobic interactions and van der Waals forces. CDs have been widely investigated for environmental remediation, particularly in water treatment, due to their ability to efficiently capture organic micropollutants such (Tian and Liu, 2020).

The three native cyclodextrins—α-, β-, and γ-CD—consist of 6, 7, and 8 glucose units respectively, resulting in progressively larger cavity sizes that influence host–guest interactions (Tian and Liu, 2020).

Among the three native CDs (α-, β-, and γ-CD), β-cyclodextrin (β-CD) is the most extensively studied and considered the most suitable for PFAS adsorption. Comprising seven glucose units arranged in a toroidal (doughnut-shaped) structure, β-CD possesses an internal cavity diameter of approximately 6.0–6.5 Å, which is well-matched to the size of many long-chain PFAS molecules, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). Thus, compared to α-CD (smaller cavity) and γ-CD (larger cavity), β-CD offers the most favorable balance of binding affinity, stability, and practical applicability in adsorption processes (Abaie et al., 2024).

The Figure below illustrates the structural formation of a β-cyclodextrin inclusion complex, where the hydrophobic cavity of the β-CD molecule encapsulates a guest molecule, such as a PFAS compound. The hydrophobic tail of the PFAS enters the inner cavity, while the polar head remains near the rim, stabilizing the complex through van der Waals and hydrophobic interactions.

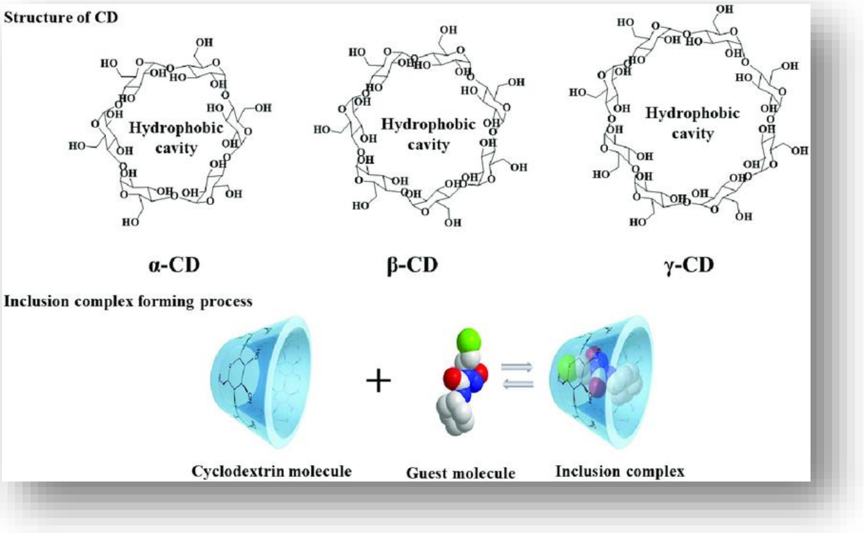


Figure 2.1: Schematic Representation of β-Cyclodextrin Inclusion Complex Formation (Tian & Liu, 2021)

2.4.2 Functionalization of β-Cyclodextrin

While native β-cyclodextrin (β-CD) exhibits promising molecular characteristics for the removal of organic micropollutants, it faces several limitations such as low water solubility, weak structural rigidity, and suboptimal adsorption capacity for certain per- and polyfluoroalkyl substances (PFAS). To overcome these drawbacks and enhance its practical applicability in environmental remediation, a wide range of chemical modifications and functionalization strategies have been explored. These approaches aim to improve the stability, selectivity, surface area, and affinity of β-CD-based materials for PFAS adsorption (Ching et al., 2022).

Functionalization strategies can be broadly classified into three main categories:

1. Polymerization and crosslinking,
2. Surface functional group modification, and
3. Hybridization with inorganic or nanoscale materials.

Polymerization and Crosslinking

One of the most effective ways to enhance β-CD's performance is through polymerization into porous networks. Crosslinkers such as epichlorohydrin (EPI), hexamethylene diisocyanate (HDI), and citric acid are commonly used to create three-dimensional, interconnected structures. These crosslinked β-CD polymers exhibit increased hydrophobicity, surface area, mechanical strength, and improved mass transfer, which are crucial for rapid and efficient PFAS removal (Ching et al., 2022).

A prominent example is the porous β-cyclodextrin polymer (P-CDP) (Alsbaiee et al., 2016), synthesized via nucleophilic aromatic substitution between β-CD and tetrafluoroterephthalonitrile. The resulting polymer featured high surface area (~263 m^2/g) and nanoscale porosity (~1.8–3.5 nm), facilitating the fast uptake of organic micropollutants including PFAS.

Surface Functional Group Modification

Beyond structural crosslinking, β-CD polymers can be chemically functionalized to introduce charged or hydrophobic moieties that increase PFAS selectivity. Functional groups can modulate the surface polarity, electrostatic interactions, and inclusion complex stability.

- **Cationic modifications**, such as quaternary ammonium or amine groups, enhance electrostatic attraction to anionic PFAS like PFOA and PFOS (Wang et al., 2024).
- **Hydrophobic groups**, such as styrene or alkyl chains, strengthen van der Waals and hydrophobic interactions with PFAS fluorocarbon tails.
- **Halogenated modifications**, like **chlorine-functionalized β-CDs (β-CD–Cl)**, have demonstrated high adsorption efficiency under optimized conditions, offering improved affinity for both long- and short-chain PFAS (Abaie et al., 2024).

These modifications not only increase adsorption capacity but also contribute to pH stability and chemical reusability of the polymer materials.

Hybrid and Nanostructured β-CD Materials

Another innovative direction involves the integration of β-CD with inorganic or nanoscale platforms. By incorporating materials such as silica, titanium dioxide (TiO_2), or graphene oxide, hybrid adsorbents combine the host–guest chemistry of β-CD with the catalytic or structural advantages of the inorganic phase.

Furthermore, cyclodextrin-based nanosponges—formed by crosslinking β-CD with agents like carbonyldiimidazole—create hyper-crosslinked networks with high porosity and exceptional adsorption kinetics. These supramolecular assemblies exhibit enhanced removal of a wide range of PFAS, particularly under environmentally relevant conditions, due to their increased surface area, tunable cavity accessibility, and greater structural stability. Recent studies highlight the potential of β-CD nanosponges—hyper-crosslinked porous networks formed through covalent bonding with multifunctional linkers—as highly efficient PFAS sorbents. These materials enable multiple simultaneous adsorption mechanisms, including inclusion complexation, pore diffusion, and surface interactions, offering both structural stability and selective uptake even in complex matrices (Utzeri et al., 2022).

Altogether, these functionalization strategies significantly enhance the chemical stability, reusability, and selectivity of β-CD-based adsorbents, positioning them as leading candidates for next- generation water purification and PFAS remediation technologies.

2.4.3 Adsorption Capacity and Efficiency of β-Cyclodextrins

Although native β-cyclodextrin (β-CD) exhibits limited adsorption efficiency for per- and polyfluoroalkyl substances (PFAS), particularly short-chain variants, the chemical modification and polymerization of β-CD have significantly enhanced its performance. Crosslinked β-CD materials—such as those synthesized using epichlorohydrin (EPI), hexamethylene diisocyanate (HDI), or tetrafluoroterephthalonitrile (TFP)—offer improved structural stability, optimized porosity, and tailored surface properties that promote high PFAS uptake.

The primary mechanisms contributing to PFAS adsorption include:

- **Host–guest complexation** between PFAS fluorocarbon tails and the β-CD hydrophobic cavity.
- **Hydrophobic and electrostatic interactions** enabled by tailored surface chemistry.
- **Optimized porosity and surface area**, allowing rapid diffusion and adsorption kinetics.

Experimental results indicate that polymerized β-CD materials possess high adsorption affinity for PFAS compounds (Alsbaiee et al., 2016).

More specifically in adsorption studies, particularly those involving the removal of PFAS using materials such as cyclodextrins, the distribution coefficient (K_d) is a key parameter used to quantify the affinity between an adsorbent and a contaminant. The K_d value represents the ratio of the concentration of a substance adsorbed onto the solid phase (e.g., cyclodextrin-based polymer) to its concentration remaining in the aqueous phase at equilibrium. It is typically expressed in units of L/kg or mL/g:

$$K_d = \frac{C_{solids}}{C_{aqueous}}$$

A higher K_d value indicates stronger adsorption affinity and greater removal efficiency of the PFAS compound from water.

To facilitate comparison and data interpretation, especially across wide concentration ranges, the logarithmic form of K_d —denoted as log K_d —is commonly used. log K_d allows for clearer visualization of adsorption trends and simplifies statistical treatment. In general, PFAS compounds with higher log K_d values are considered to interact more strongly with the adsorbent material, which is crucial when evaluating the performance of cyclodextrin-based systems for environmental remediation.

The removal efficiency depends significantly on the molecular structure and charge of the PFAS. (Alsbaiee et al., 2016). In general, long-chain PFAS such as PFOA and PFOS exhibit higher affinities due to better fitting into the β-CD cavity and stronger hydrophobic interactions.

However, short-chain PFAS (e.g., PFBA, PFHxA) pose a significant challenge due to their higher solubility and reduced hydrophobic character, which leads to weaker inclusion complexation and less electrostatic affinity. Functionalized β-CD variants incorporating cationic groups or halogenated functionalities have demonstrated better removal of such compounds under optimized pH and ionic strength conditions (Ching et al., 2022) (Utzeri et al., 2022).

Moreover, the degree and type of crosslinking substantially influence adsorption capacity:

- **Higher crosslinking density** (e.g., TFP or DPC-based systems) correlates with increased surface area and enhanced sorption kinetics.
- **Porous β-CD polymers** prepared by nucleophilic aromatic substitution (e.g., β-CD-TFP) achieved **rapid PFAS removal within seconds**, outperforming traditional adsorbents like activated carbon (Alsbaiee et al., 2016).
- **Nanosponges and hybrid β-CD composites** further extend adsorption potential through multifunctional mechanisms such as photocatalysis and redox reactivity (Utzeri et al., 2022).

While β-CD-based materials show high selectivity and reusability, their adsorption performance is sensitive to competing solutes and water matrix complexity. Salt concentration, pH, and the presence of natural organic matter can alter adsorption equilibria, especially for weakly binding PFAS. Despite these challenges, functionalized β-CD polymers remain among the most promising PFAS-targeted sorbents in terms of environmental safety, regeneration potential, and tunable selectivity.

2.5 Factors Affecting PFAS Adsorption by Cyclodextrins

The adsorption efficiency of β-cyclodextrin (β-CD)-based materials for PFAS removal is governed by a combination of material-related, PFAS-specific, and environmental parameters. Understanding these interdependent factors is essential for optimizing β-CD-based adsorbents in real-world applications.

2.5.1 Influence of PFAS Molecular Structure

The chemical structure of PFAS—particularly chain length, functional group, and degree of fluorination—directly affects their interaction with β-CD materials. Long-chain PFAS such as PFOA and PFOS exhibit stronger hydrophobic interactions and better geometric fit with the β-CD cavity, leading to higher adsorption capacities. In contrast, short-chain PFAS, which are more water-soluble and mobile, demonstrate lower affinity due to reduced hydrophobicity and weaker host–guest interactions.

Moreover, sulfonated PFAS (PFSAs) typically show higher adsorption than carboxylated PFAS (PFCAs), due to the greater polarity and electrostatic interaction potential of the sulfonate group.

2.5.2 Role of β-CD Functionalization

The nature of chemical modifications on β-CD strongly influences adsorption behavior:

- Epichlorohydrin (EPI) and hexamethylene diisocyanate (HDI) crosslinking improves surface area, porosity, and mechanical stability.
- Chlorinated or styrenic modifications enhance electrostatic interactions with anionic PFAS.
- Hybrid structures (e.g., β-CD + silica or TiO_2) may introduce additional functionalities such as photocatalytic degradation.

Tailored functionalization allows the adjustment of material selectivity and can mitigate competitive effects in complex matrices.

2.5.3 pH and Ionic Strength

Solution pH plays a crucial role in adsorption by affecting the charge on both the PFAS molecules and the β-CD adsorbent surface. Most PFAS possess negatively charged functional groups (e.g., $–COO^-$, $–SO_3^-$) at environmental pH (4–8), favoring electrostatic attraction with positively charged or neutral β-CD surfaces.

Studies have shown that neutral to slightly acidic pH (4–7) optimizes PFAS removal. Under more alkaline or acidic conditions, charge repulsion or structural changes may reduce efficiency.

Similarly, ionic strength influences the adsorption process via electrostatic screening or double-layer compression. Monovalent (Na^+, Cl^-) and multivalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}) can affect PFAS–β-CD interactions either positively (by facilitating complexation) or negatively (through competition or shielding effects).

2.5.4 Contact Time and Adsorption Kinetics

Adsorption kinetics vary depending on the crosslinking density, pore accessibility, and surface chemistry of the β-CD material. In general:

- Equilibrium is reached within 1 to 4 hours under typical environmental conditions.
- Higher porosity and surface area result in faster uptake.
- Long-chain PFAS are typically adsorbed more rapidly due to stronger hydrophobic interactions.

Kinetics can also be modeled using pseudo-first-order or pseudo-second-order equations, offering insight into the controlling mechanisms (e.g., diffusion-limited vs site-limited).

2.5.5 Temperature Effects

Temperature influences molecular diffusion, interaction energy, and polymer stability:

- Moderate increases (25–35 °C) enhance diffusion rates and facilitate PFAS transport into the β-CD cavity.
- However, elevated temperatures (>45 °C) may cause desorption or polymer degradation, especially in thermally sensitive β-CD frameworks.

Thermodynamic studies have shown that PFAS adsorption on β-CD is generally exothermic, with spontaneity decreasing at higher temperatures.

2.5.6 Presence of Co-contaminants and Natural Organic Matter (NOM)

In real water matrices, PFAS adsorption is affected by coexisting substances, including:

- Natural organic matter (NOM)
- Dissolved organic matter (DOM)
- Heavy metals (e.g., Cu^{2+}, Fe^{3+})

These substances may compete with PFAS for available adsorption sites, block access to pores, or form complexes that alter PFAS behavior. Among them, NOM is particularly problematic due to its tendency to cause steric hindrance and surface fouling, thereby reducing the accessibility of β-CD cavities.

This effect is especially pronounced in β-CD materials with small pore diameters or limited surface functionalization. NOM can mask active binding sites or physically obstruct PFAS molecules from entering the hydrophobic cavity, diminishing the overall adsorption capacity.

To mitigate such interference, several strategies have been proposed:

- **Pre-treatment of water** (e.g., filtration or coagulation) to reduce NOM content,
- **Surface modification** of β-CD materials to enhance hydrophilicity and resistance to fouling,
- **Use of hybrid materials** that combine adsorption with catalytic or size-selective properties.

Addressing the impact of co-contaminants is essential for maintaining high adsorption performance and selectivity in complex environmental systems, particularly when targeting low-concentration PFAS in natural waters (Shapiro et al., 2025) (Fourmentin, Crini and Lichtfouse, 2018).

These interfering factors highlight the importance of designing β-CD adsorbents with robust surface properties and testing them under realistic conditions. To summarize, the following table compiles the key parameters affecting PFAS adsorption performance and their optimal conditions:

Table 2.4. Summary of factors influencing PFAS adsorption by β-cyclodextrin-based materials.

Parameter	Effect on β-CD Adsorption	Optimal Condition
PFAS structure	Longer chains and sulfonate head groups enhance affinity	C6–C10; PFSAs > PFCAs
Functionalization	Improves selectivity and kinetics	EPI, HDI, Cl-, styrene
pH	Affects charge interactions and complexation	Slightly acidic to neutral (pH 4–7)
Ionic strength	Modifies electrostatic interactions	Moderate salinity; avoid excess divalent ions
Contact time	Determines adsorption kinetics	1–4 hours
Temperature	Enhances molecular mobility and sorption kinetics	25–35 °C
NOM / Co-contaminants	Can hinder access to active sites	Pretreatment or hybrid adsorbents recommended

2.6 Regeneration and Reusability of Cyclodextrin-Based Adsorbents

One of the key advantages of β-CD-based adsorbents is their potential for regeneration and repeated use, making them a cost-effective and sustainable solution for large-scale water treatment applications. Various regeneration methods have been investigated, including:

- **Solvent extraction** (e.g., methanol, acetone), which disrupts host–guest complexes without damaging the polymer structure.
- **pH-induced desorption**, using acidic or basic washes to destabilize PFAS binding.
- **Mild thermal treatment**, which helps remove weakly bound molecules without degrading the adsorbent (Fourmentin, Crini and Lichtfouse, 2018).

Studies have shown that crosslinked β-CD polymers can retain up to 80–90% of their initial adsorption capacity after 3–5 regeneration cycles, depending on the PFAS type and desorption method used. This level of reusability is comparable to, and in some cases superior to, conventional materials such as activated carbon, which often suffer from pore blockage and loss of surface area over repeated use (Alsbaiee et al., 2016), (Ching et al., 2022).

However, regeneration is not without limitations. Over time, repeated cycles—particularly under harsh chemical or thermal conditions—may gradually weaken the adsorbent matrix, especially in the case of chemically sensitive or lightly crosslinked β-CD derivatives. Reported challenges include**:**

- **Polymer hydrolysis and pore collapse**, leading to reduced structural integrity and loss of adsorption sites.
- **Partial desorption or irreversible binding** of PFAS molecules, particularly long-chain or strongly hydrophobic compounds.
- **Thermal degradation** during repeated heating, which can compromise the polymer's backbone or surface functionality.
- **Variability in regeneration efficiency** depending on the specific type of PFAS, the desorption method used, and the degree of crosslinking in the adsorbent.

These issues limit the long-term durability and cost-effectiveness of β-CD-based materials, emphasizing the need for more robust frameworks and carefully designed regeneration protocols.

To overcome these issues, current research focuses on the design of more robust β-CD-based frameworks, such as:

- Nanosponges: Highly crosslinked networks with thermal and chemical resilience.
- Inorganic–organic hybrids: Combining β-CD with silica or metal oxides to improve structural integrity.
- Magnetic composites: Facilitating adsorbent recovery and reuse

These developments aim to maintain high PFAS removal efficiency while allowing multiple regeneration cycles without performance loss.

To provide a consolidated overview, the table below summarizes the most common regeneration strategies, their advantages, and limitations:

Table 2.5. Overview of regeneration methods for β-cyclodextrin-based adsorbents.

Method	Advantages	Limitations
Solvent extraction	Effective, simple, preserves structure	Requires solvent disposal; may not fully desorb strong PFAS
pH-induced desorption	Environmentally benign; tunable	Limited efficiency for strongly bound compounds
Mild thermal treatment	Fast and solvent-free	Risk of polymer degradation at high temperatures
Magnetic separation	Easy recovery, good for hybrid systems	Still under development; synthesis complexity

These strategies demonstrate the potential for sustainable operation of β-CD adsorbents in real systems, provided that regeneration is carefully optimized according to the material type and PFAS profile encountered (Abaie et al., 2024), (Wang et al., 2024).

Chapter 3 – Case Studies on PFAS Removal and meta- analysis

Introduction to Case Studies

Following the theoretical foundation of PFAS adsorption mechanisms and the specific role of β-cyclodextrin-based materials, this chapter shifts to applied evaluation through five case studies and one meta-analysis. These studies have been compiled and analyzed to capture the diversity of experimental approaches and environmental conditions under which PFAS remediation has been investigated. They encompass a wide range of experimental conditions - including batch adsorption, column experiments, and real wastewater matrices- and explore a variety of cyclodextrin-based adsorbents, such as TFN–CDP, amine-functionalized polymers, tripodal crosslinked CDPs, and styrenic β-CD frameworks (StyDex).

Through these applications, the performance of CD-based materials has been assessed compared to conventional adsorbents (e.g., activated carbon, ion-exchange resins), as well as, evaluation of their behavior under practical challenges, including short-chain PFAS removal, contact time limitations, and interference from organic matter and ions. Adsorption efficiency, kinetic profiles, and compound-specific selectivity are correlated with functional group chemistry and matrix composition to explain material behavior.

Ultimately, the selected studies illustrate how targeted polymer design—especially functional modification of surface charge and crosslinking structure—can overcome the limitations of traditional materials and contribute to the development of next-generation adsorbents for PFAS remediation.

3.1 Case Study 1

Reduction of a tetrafluoroterephthalonitrile-β-cyclodextrin polymer to remove anionic micropollutants and PFAS (Klemes et al., 2019)

The work by Klemes et al. (2019) demonstrates a strategic advancement in tuning β-cyclodextrin polymer (β-CDP) adsorbents to enhance their affinity for anionic micropollutants such as PFAS. The authors addressed a known limitation of the traditional β-cyclodextrin polymer crosslinked with tetrafluoroterephthalonitrile (TFN–CDP), which tend to exhibit low affinity for anionic micropollutants due to their negatively charged phenolic functionalities formed during polymerization.

Synthesis and Properties of TFN–Crosslinked β-Cyclodextrin Polymer (TFN–CDP)

The β-cyclodextrin polymer crosslinked with tetrafluoroterephthalonitrile (TFN) was first synthesized and reported by Alsbaiee et al. in 2016. The polymer, referred to as porous-CDP (P-CDP), was created through a nucleophilic aromatic substitution reaction between the hydroxyl groups of β-cyclodextrin and the electron-deficient fluorinated aromatic TFN crosslinker. This reaction forms robust C–O bonds and results in a highly crosslinked, permanently porous polymer network.

The synthetic procedure involved reacting β-CD with TFN in tetrahydrofuran (THF) under basic conditions using potassium carbonate (K_2CO_3) at 80 °C under reflux conditions. The resulting polymer exhibited high surface areas (up to 263 m²/g) and mesoporous structure, as confirmed by N_2 sorption isotherms and BET analysis. ***Figure 3.1.1.*** below illustrates the chemical reaction scheme and structural representation of the resulting TFN–CDP. (Alsbaiee et al., 2016).

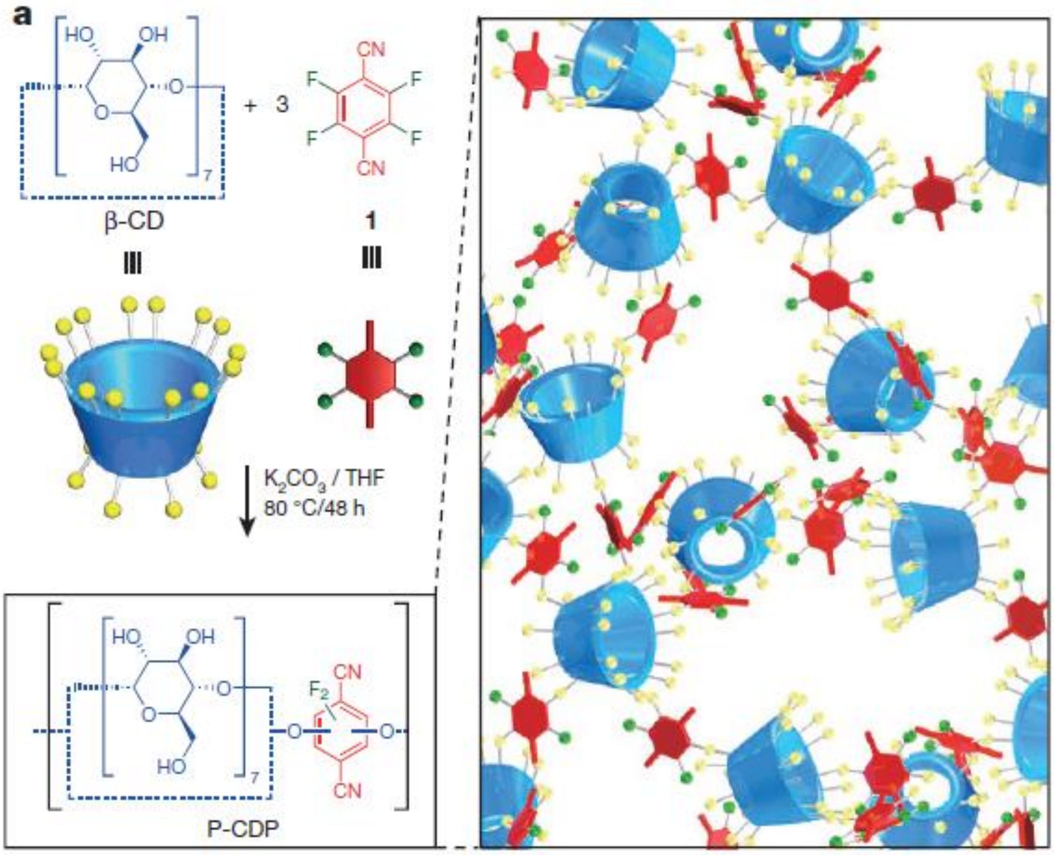


Figure 3.1.1 Schematic representation of the synthesis and structure of the porous β-cyclodextrin polymer (P-CDP). The polymer is formed via nucleophilic aromatic substitution between β-cyclodextrin and tetrafluoroterephthalonitrile (TFN) under basic conditions (K_2CO_3 in THF, 80 °C, 48 h). The resulting network exhibits a high-surface-area, mesoporous architecture that facilitates rapid micropollutant removal. (Alsbaiee et al., 2016)

Due to its unique structure combining β-CD host–guest cavities with a rigid, high-surface-area network, TFN–CDP displayed excellent adsorption kinetics and capacity for a wide range of organic micropollutants. In batch and flow-through experiments, TFN–CDP outperformed commercial activated carbons (e.g., NAC, GAC, Brita AC) in removing pollutants such as bisphenol A (BPA), propranolol, 2,4-dichlorophenol, and ethinyl estradiol, often achieving over 95% removal within seconds.

The high performance was attributed to rapid diffusion through mesopores, efficient accessibility of CD binding sites, and favorable host–guest complexation. Moreover, the polymer was easily regenerated by mild methanol washing, retaining its performance over multiple cycles.

While TFN–CDP showed high affinity for neutral and cationic contaminants, its anionic surface limited its ability to effectively capture negatively charged PFAS compounds. This limitation ultimately motivated the development of a post-synthetic modification strategy—introducing amine groups to reverse the surface charge and enhance PFAS removal—discussed in the following case study (Klemes et al., 2019).

Polymer Modification Strategy

To improve selectivity, the researchers carried out a chemical reduction of the nitrile groups on the TFN crosslinker, converting them into primary amines. This post-polymerization transformation yielded a new material, amine-CDP (Polymer 2) which effectively reversed the net surface charge of the polymer from negative (–28.9 mV) to slightly positive (+1.7 mV) at neutral pH.

This change in surface chemistry was hypothesized to favor adsorption of negatively charged PFAS through electrostatic interactions. The modified polymer was tested against 10 anionic PFAS compounds under environmentally relevant concentrations (~1 µg/L), and its performance was compared to the unmodified TFN–CDP (polymer 1) and to granular activated carbon (GAC).

The transformation is illustrated in ***Figure 3.1.2*** The schematic highlights how the introduction of primary amine groups not only alters the polymer's charge profile but also enhances its ability to interact with anionic contaminants, including PFAS.

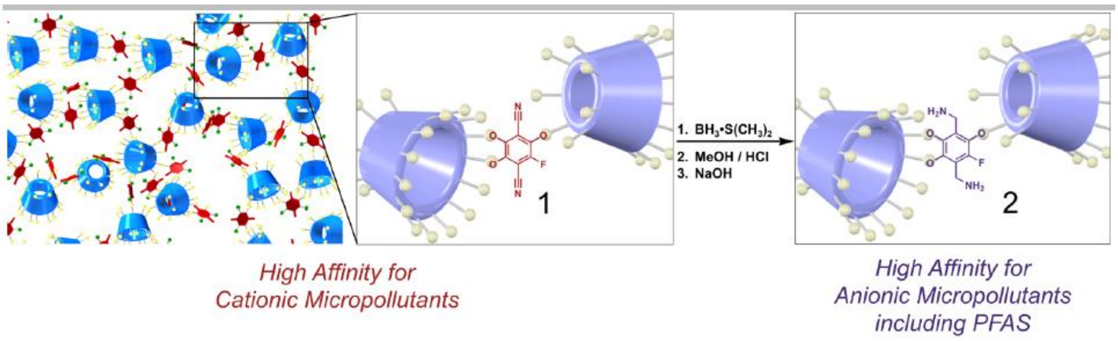


Figure 3.1.2. – Schematic of post-polymerization reduction of TFN–CDP (polymer 1) to amine-CDP (polymer 2), Klemes et al., 2019.

Performance and Quantitative Analysis

The amine-modified CDP showed substantial improvement in affinity for all anionic PFAS tested. Log K_d values ranged between 2.8 and 4.0, indicating strong partitioning of PFAS onto the adsorbent. In contrast, the unmodified polymer exhibited log K_d values typically below 1.5. Importantly, even short-chain and branched PFAS such as PFBA and GenX, which are among the most challenging to remove using conventional adsorbents.

In batch experiments, the combined concentration of PFOA and PFOS was reduced from 2000 ng/L to below 70 ng/L within 30 minutes, reaching a final equilibrium concentration of approximately 25 ng/L after 9 hours, satisfying the U.S. EPA's advisory limit.

Table 3.1. Comparison of Log Kd values for selected PFAS across different adsorbents

PFAS	Polymer 1 (TFN–CDP)	Polymer 2 (Amine-CDP)	GAC
PFOS	1.3	3.8	3.7
PFOA	1.0	3.5	3.2
PFHxS	0.9	3.6	3.4
PFBA	0.5	2.8	1.8
GenX	1.2	3.2	2.3

These findings confirm that functionalization of the crosslinker with amine groups significantly improves PFAS removal performance, particularly for shorter-chain or branched molecules.

Mechanism of Adsorption

The improved adsorption performance is primarily attributed to three synergistic mechanisms:

1. Electrostatic attraction between the protonated amine groups and the anionic head groups of PFAS.

2. Hydrophobic interactions between the fluorinated PFAS tails and the aromatic polymer network.
3. Inclusion complex formation within the β-CD cavity.

The conversion of nitriles to amines not only introduced positive charge but also altered the polymer's hydrogen bonding capacity and electronic structure. The partial reduction (~72% conversion) ensured that key structural features were maintained, while enhancing accessibility of binding sites.

Critical Evaluation

One of the key strengths of this work is its rational polymer engineering approach: a single post-synthetic modification was sufficient to invert selectivity and vastly improve performance. The results demonstrate that cyclodextrin polymers are highly tunable and responsive to structural alterations.

However, the experiments were conducted exclusively in Milli-Q water, meaning no interference from ionic strength, natural organic matter (NOM), or co-contaminants was evaluated. Furthermore, questions remain regarding regenerability and long-term use, which are critical for real-world application.

A comprehensive comparison of the adsorption selectivity between Polymer 1 (TFN–CDP) and Polymer 2 (Amine-CDP) is presented in Figure 3.1.3. This scatter plot depicts the distribution coefficients (log K_d) for 91 structurally diverse organic micropollutants. Each point represents the relative affinity of a compound for the two polymers.

Notably, Polymer 2 exhibits dramatically enhanced binding for anionic compounds, especially PFAS (highlighted in yellow), as evidenced by the clustering of these data points well above the diagonal line. Conversely, cationic pollutants (red) predominantly fall below the diagonal, indicating stronger interaction with the unmodified TFN–CDP (Polymer 1). Neutral and zwitterionic compounds display a more balanced distribution.

This visualization confirms that the amine-functionalization strategy not only reverses the polymer's electrostatic selectivity but also renders it significantly more effective for PFAS adsorption—a key design goal. It further supports the notion that polymer surface charge plays a critical role in target-specific contaminant capture.

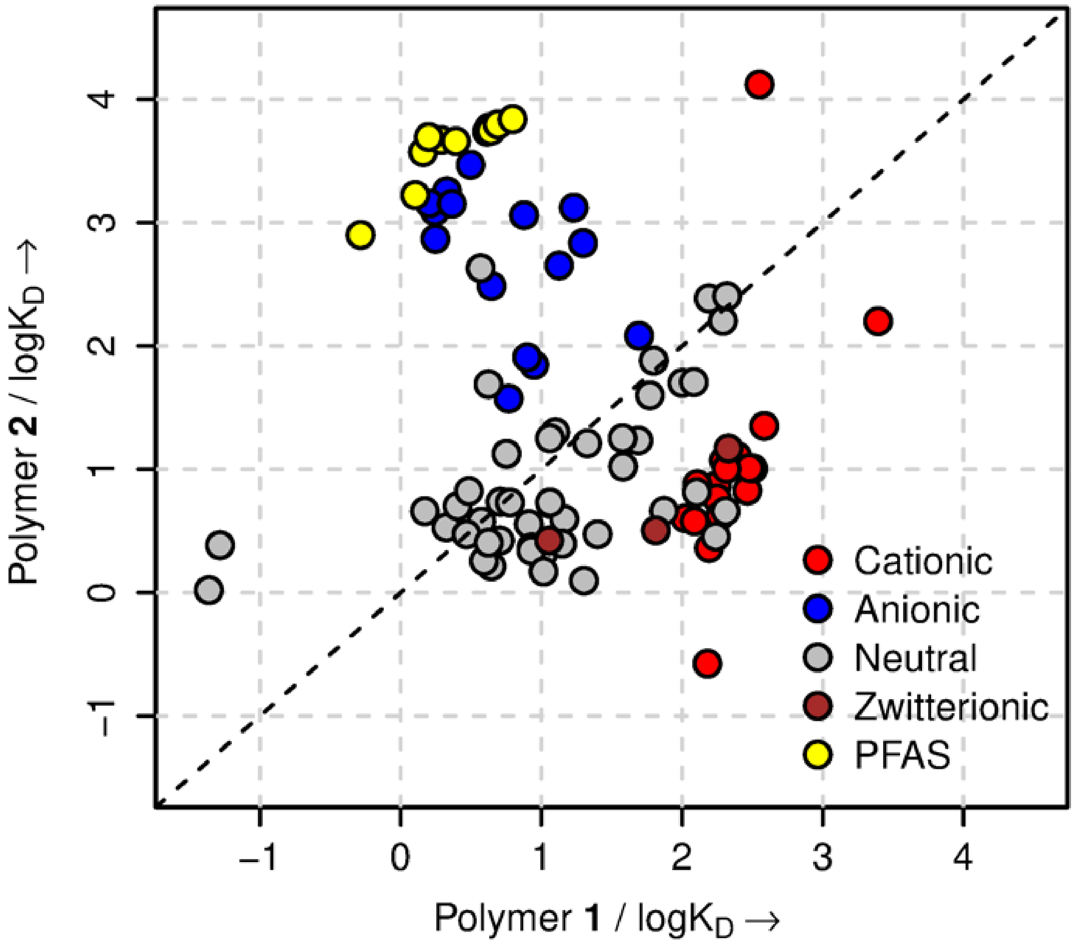


Figure 3.1.3. Comparative adsorption affinities (log K$_d$) of 91 micropollutants for Polymer 1 (TFN–CDP) and Polymer 2 (Amine-CDP). Points above the diagonal represent compounds better adsorbed by Polymer 2. Color coding indicates compound classes (Klemes et al., 2019).

Practical Implications and Future Perspectives

The findings strongly suggest that amine-modified cyclodextrin polymers can serve as next-generation PFAS adsorbents, particularly effective against short-chain and emerging compounds that evade capture by traditional materials. The success of this study sets a precedent for designing charge-targeted adsorbents and combining host–guest chemistry with surface electrostatics.

Future research should explore:

- Testing under real environmental matrices (e.g., surface or wastewater)
- Regenerability and reuse potential
- Implementation in continuous flow systems or fixed-bed configurations

This case study highlights that minor chemical modifications at the polymer design level can yield major improvements in adsorption performance, offering practical tools for targeted water purification technologies. These insights highlight the importance of extending the investigation to real-world matrices and diverse cyclodextrin structures—topics addressed in the following case study.

3.2 Case Study 2

Exploring the factors that influence the adsorption of anionic PFAS on conventional and emerging adsorbents in aquatic matrices (Wu et al., 2020).

This study by Wu et al. (2020) investigates the performance of β-cyclodextrin polymers (β-CDPs) in comparison to conventional adsorbents—such as granular activated carbon (GAC) and ion exchange resins—for the removal of anionic PFAS from aqueous solutions. The key distinction of this work lies in its emphasis on environmentally realistic testing conditions, incorporating real groundwater and wastewater effluent, in contrast to prior studies conducted primarily in idealized laboratory water.

Experimental Design and Tested Adsorbents

The researchers evaluated five adsorbents:

- Three types of activated carbon (AC): AWAC, HFAC, and CCAC, tested in both powdered (PAC) and granular (GAC) forms

- Two β-cyclodextrin-based polymers (β-CDPs): amine-functionalized β-CDP (aCDP) and a permanently cationic β-CDP (CDP^{+})

Batch adsorption experiments were conducted in four distinct water matrices to capture both ideal and environmentally realistic conditions:

- **Milli-Q water** (ultrapure, used as a control)
- **Synthetic groundwater** with controlled ionic composition
- **Natural groundwater** collected from contaminated and uncontaminated sources
- **Treated municipal wastewater effluent**

These matrices were spiked with **20 anionic PFAS compounds**, including short- and long-chain perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), fluorotelomer sulfonates (FTSs), and GenX. PFAS concentrations were adjusted to **environmentally relevant levels (~500 ng/L)**. The performance of each adsorbent was evaluated using **log**

K_d values, while **Principal Component Analysis (PCA)** was employed to interpret the influence of water matrix constituents on adsorption efficacy.

However, focus was on six PFAS compounds, including short- and long-chain representatives (e.g., PFBA, PFHxA, PFOA, PFOS), tested at environmentally relevant concentrations (~1 µg/L). Adsorption affinity was quantified using log K_d values, and Principal Component Analysis (PCA) was applied to evaluate matrix effects.

Key Findings and Observations

Among the tested adsorbents, **CDP^+** demonstrated the highest affinity for anionic PFAS in both Milli-Q water and real water matrices, owing to its permanently cationic surface that enables stable electrostatic attraction. In contrast, **aCDP**, which contains weakly basic amine groups, exhibited reduced performance in natural water matrices, particularly at higher pH where its surface charge becomes less positive or even neutral. This charge shift diminishes the electrostatic interactions required for effective PFAS adsorption.

The conventional activated carbon **AWAC** also showed reasonable adsorption capacity, primarily via hydrophobic interactions. However, **all adsorbents** experienced a measurable decrease in performance when tested in **groundwater** or **wastewater**, compared to Milli-Q water. For example, the log K_d values for PFOS and PFHxA declined by over one order of magnitude in wastewater effluent, indicating significant adsorption inhibition.

These findings highlight that **adsorbent efficacy can be substantially overestimated in idealized laboratory conditions**, and underscore the critical need for evaluation under environmentally relevant scenarios where water chemistry—such as ionic strength, pH, and the presence of multivalent cations—can strongly influence performance.

Interfering Factors in Water Matrices

Several water matrix constituents were found to inhibit the adsorption of anionic PFAS onto both conventional and emerging adsorbents:

- **Multivalent cations** (such as Ca^{2+} and Mg^{2+}) caused **electrostatic screening**, reducing attractive interactions between PFAS and positively charged adsorbent surfaces—particularly affecting aCDP, whose surface charge depends on pH.

- **Natural organic matter (NOM)** contributed to **surface fouling** and **competitive adsorption**, limiting access of PFAS to active sites.
- **High ionic strength** compressed the electrical double layer, further reducing binding site accessibility.

These effects were especially detrimental to **aCDP**, whose amine groups lose their positive charge at higher pH and in cation-rich environments. In contrast, **CDP$^+$**, with its permanently cationic groups, exhibited greater resilience under such conditions.

Mechanisms and Insights

The poor performance of the original TFN–crosslinked β-cyclodextrin polymer (TFN–CDP), as reported by Klemes et al. (2019), was attributed to several factors:

- **Electrostatic repulsion** between the negatively charged polymer backbone and the anionic PFAS head groups.
- **Matrix interference**, such as Ca^{2+} ions and natural organic matter (NOM), which can block access to the cyclodextrin cavities or outcompete PFAS for available binding sites.
- **Limited host–guest interactions**, especially for short-chain or branched PFAS, unless assisted by electropositive functional groups.

To overcome these limitations, the authors proposed incorporating **charge-modifying functionalities**, such as **amine groups**, into the polymer network. This design concept led to the development of the amine-functionalized β-CDP (aCDP), which was further evaluated in real water matrices.

Critical Assessment – Strengths and Limitations

A key strength of this study lies in its **systematic incorporation of environmentally relevant water matrices**, including groundwater and wastewater effluent. This realistic approach is often missing from conventional lab-scale adsorption studies and provides a more accurate assessment of adsorbent performance under field conditions. The study also compares different adsorbent classes—carbon-based and cyclodextrin-based—across varying water chemistries, offering valuable insights for selecting appropriate remediation technologies.

A limitation of the study is that, although it included two advanced β-cyclodextrin polymers (aCDP and CDP^+), it **did not re-evaluate the original unmodified TFN–CDP**, which is known to be ineffective with anionic PFAS due to its negative surface charge. As such, direct performance comparisons between modified and unmodified CDPs under the same test conditions remain unavailable.

Practical Implications

The study highlights that adsorbent performance should be assessed in **environmentally relevant matrices**, as results obtained under idealized laboratory conditions—such as Milli-Q water—can **substantially overestimate efficiency**. This is particularly critical for cyclodextrin-based adsorbents, whose performance may vary depending on pH, ionic strength, and the presence of competing constituents such as natural organic matter.

To better understand the mechanisms behind performance loss in real water matrices, the authors applied **Principal Component Analysis (PCA)**. This multivariate statistical tool revealed patterns and correlations—particularly between groundwater chemistry (e.g., pH, Ca^{2+}/Mg^{2+} concentration) and the **degree of PFAS adsorption inhibition**—that would not be apparent from raw adsorption data alone.

A PCA biplot (***Figure 3.2***.) illustrated the influence of key groundwater parameters on the adsorption inhibition observed across three adsorbents: **AWAC** (a wood-based activated carbon), **aCDP** (amine-functionalized β-cyclodextrin polymer), and **CDP^+** (cationic β-cyclodextrin polymer).

AWAC (Activated Wood-based Activated Carbon) is a conventional carbonaceous adsorbent with a porous surface and predominantly hydrophobic character. It primarily removes PFAS via **hydrophobic interactions** and **van der Waals forces**, particularly favoring longer-chain compounds.

aCDP (amine-functionalized β-cyclodextrin polymer) is a crosslinked polymer composed of **β-cyclodextrin monomers**—cyclic oligosaccharides with hydrophobic inner cavities—linked with partially reduced terephthalonitrile groups. These linkers contain **weakly basic amine moieties**, which contribute positive charges at lower pH but can become neutral at higher pH, reducing electrostatic attraction to anionic PFAS.

CDP^+ is another β-cyclodextrin-based polymer, but crosslinked with **permanently cationic functional groups**. These fixed positive charges allow for stable **electrostatic attraction** to PFAS molecules, regardless of pH fluctuations or ionic composition.

The PCA biplot clearly shows that **higher pH values and increased concentrations of dissolved cations (such as Ca^{2+} and Mg^{2+})** are positively correlated with increased PFAS adsorption inhibition. This trend is especially relevant for **aCDP**, whose amine groups become deprotonated at higher pH, diminishing its ability to bind anionic PFAS. In contrast, **CDP^+ showed the lowest inhibition across all water matrices**, likely due to its stable positive charge that remains effective even in cation-rich, alkaline environments.

Other measured water quality parameters such as **Total Organic Carbon (TOC)** and **Specific Ultraviolet Absorbance (SUVA)** were also included in the analysis.

- **TOC** refers to the total concentration of dissolved organic compounds in water and can be an indicator of natural organic matter (NOM), which may compete with PFAS for adsorption sites.
- **SUVA**, defined as the UV absorbance at 254 nm normalized to TOC (usually in L/mg·m), is used to characterize the aromaticity of NOM; higher values imply more aromatic content, which is more reactive and can interfere with adsorption processes.

However, the PCA results indicate that **TOC and SUVA did not exhibit strong correlations** with PFAS removal inhibition in this study, suggesting that **organic matter competition was not the dominant limiting factor** under the tested conditions. Instead, **inorganic constituents—particularly pH and cation content—emerged as the primary drivers of performance reduction** in CDP- and AC-based PFAS adsorbents.

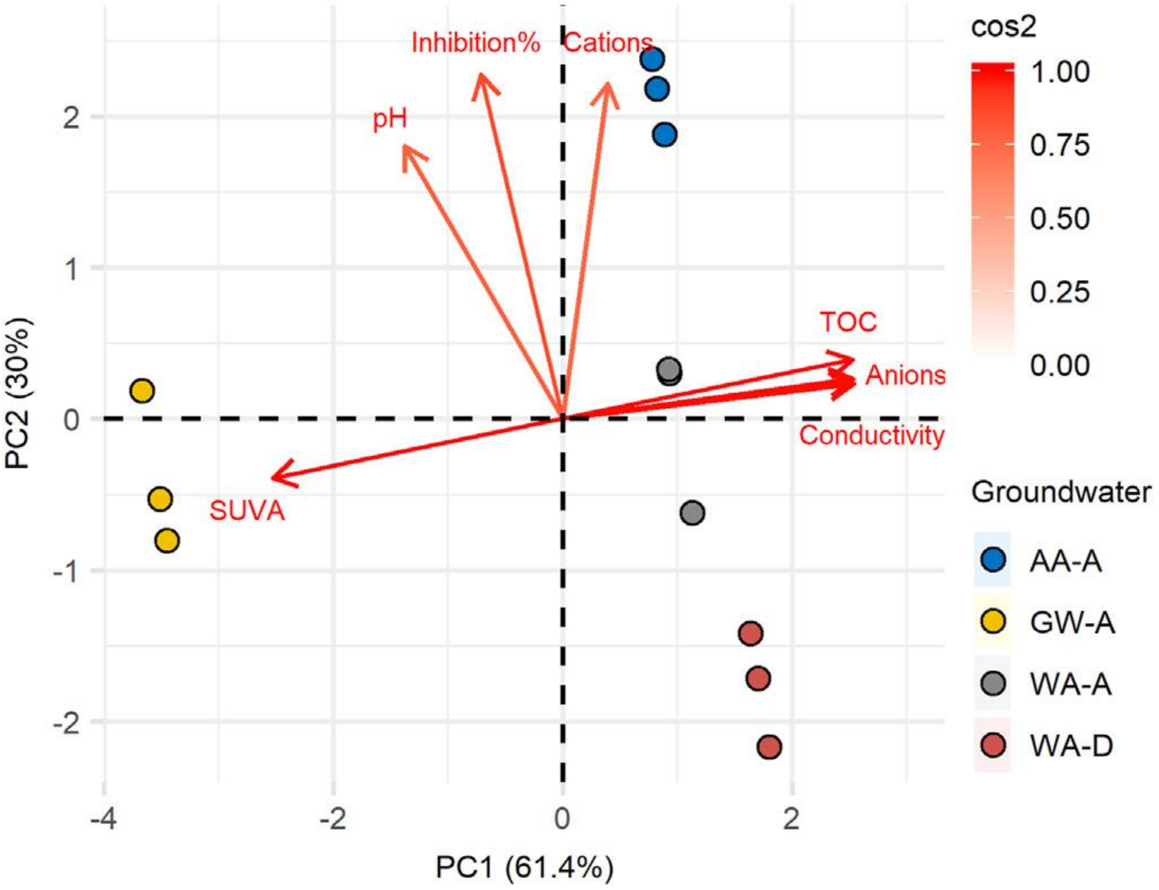


Figure 3.2. PCA biplot showing how groundwater chemistry affects PFAS adsorption by three different adsorbents: AWAC (activated carbon), aCDP (amine cyclodextrin polymer), and CDP⁺ (cationic cyclodextrin polymer). Higher pH and cation levels were linked to lower removal efficiency, especially for aCDP, while CDP⁺ was least affected by changes in water composition. Adapted from Wu et al., 2020.

These findings underscore the importance of not only developing advanced adsorbent chemistries, but also **systematically evaluating their performance under realistic water quality conditions**. The study by Wu et al. (2020) serves as a strong example of how laboratory-scale research can inform the practical application of PFAS remediation technologies in real-world scenarios such as groundwater and wastewater treatment.

Building on these insights, the following case study explores the next generation of β-cyclodextrin-based adsorbents. In particular, we focus on **structurally modified β-CD polymers incorporating nitrogen-rich tripodal crosslinkers**, which aim to overcome the electrostatic limitations observed in earlier anionic versions—such as the TFN–CDP reported in Klemes et al. (2019)—and demonstrate **enhanced PFAS removal** in chemically complex matrices, including treated municipal wastewater.

3.3 Case Study 3

Nitrogen-containing tripodal crosslinkers enhance PFAS adsorption in β-cyclodextrin polymers (Yang et al. , 2020).

Yang et al. (2020) introduced a new class of β-cyclodextrin-based polymers utilizing tripodal crosslinkers to improve PFAS adsorption, particularly for anionic compounds like PFAS. Unlike previous β-CD polymers that employed rigid or hydrophobic crosslinkers, this study focused on the use of tripodal, nitrogen-containing linkers that could provide both electrostatic and hydrophobic interactions, as well as maintain host–guest inclusion capabilities through the β-cyclodextrin cavities.

However, this multifunctionality highlights an important scientific challenge: determining the relative contribution of each binding mode. In particular, it remains essential to assess whether the presence of specific groups on the crosslinkers contributes to PFAS removal in comparison to the intrinsic inclusion capability of β-cyclodextrin.

In earlier systems where functionalization was performed post-polymerization, such distinctions were difficult to isolate due to structural heterogeneity. This challenge motivated the present study by Yang et al. (2020), which introduces β-CD polymers with precisely defined crosslinkers engineered to systematically examine the role of electrostatics in PFAS adsorption.

The goal of this synthetic strategy was to decouple the effects of surface charge from host–guest interactions, enabling a direct comparison of how linker functionality influences PFAS adsorption.

Synthesis and Experimental Design

This study introduces two structurally related but functionally distinct β-cyclodextrin-based polymers: CDP1 and CDP2. Both materials share the same tripodal core, tris(2-aminoethyl)amine (TREN), a branched triamine that serves as a versatile crosslinking scaffold due to its three reactive primary amine groups.

TREN is a small organic molecule that contains one central nitrogen atom and three ethylamine arms. Its tripodal geometry makes it ideal as a crosslinking scaffold, as each of its three $-NH_2$ groups can react with a separate β-cyclodextrin unit. This allows the formation of a robust, three-dimensional polymer network with high porosity and surface accessibility—key features for efficient contaminant capture.

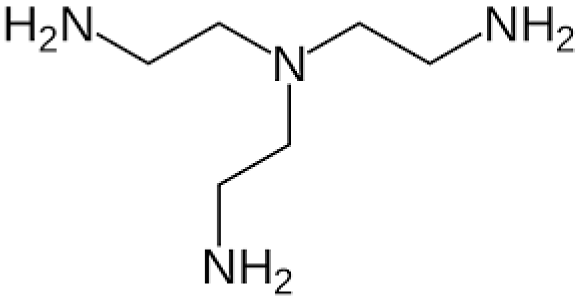


Figure 3.3.1 Molecular structure of tris(2-aminoethyl)amine (TREN) (Wikipedia, n.d.))

The divergence between the two polymers lies in the chemical nature of the functional groups introduced at the crosslinking stage, which determine the polymers' dominant PFAS binding mechanisms.

- CDP1 was synthesized via reaction of TREN with pentafluorobenzaldehyde, under anhydrous conditions, followed by reductive amination using sodium borohydride. This yields a linker bearing three primary amine groups (–NH_2), capable of further condensation with β-CD hydroxyls or participating in ionic interactions. These are positively charged at neutral pH, enabling favorable electrostatic interactions with anionic PFAS.
- CDP2 in contrast, was synthesized through a nucleophilic substitution reaction between TREN and pentafluorobenzoyl chloride, resulting in the formation of three amide linkages per crosslinker. These amide groups are electrically neutral and chemically stable, and therefore do not facilitate electrostatic interactions with anionic PFAS. As a result, CDP2 relies primarily on hydrophobic interactions and host–guest complexation through the β-cyclodextrin cavities to achieve PFAS adsorption.

The structural contrast between CDP1 and CDP2 was intentionally designed to evaluate the effect of electrostatic interactions on PFAS removal, while keeping the polymer backbone and general architecture similar. The use of TREN in both cases ensured a comparable tripodal network, while the differing end groups (amine vs. amide) provided the variable of interest.

Figure 3.3.2 shows the synthesis pathways of these two tripodal linkers. The distinct chemical functionalities—amines versus amides—were introduced at this stage to define the adsorption behavior of the resulting polymers.

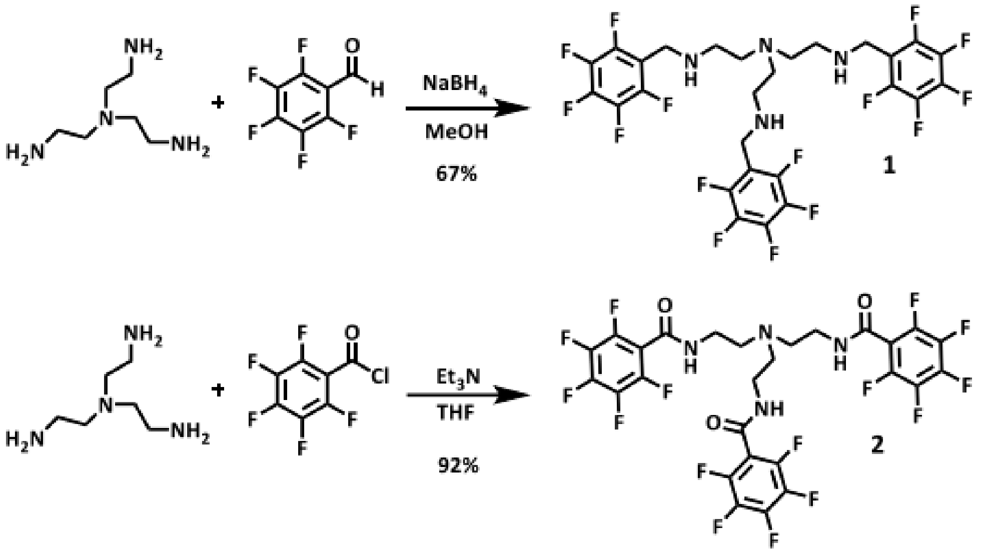


Figure 3.3.2 Synthesis of Tripodal Linkers 1 and 2 (Yang et al. , 2020)

In both cases, the use of tris(2-aminoethyl)amine (TREN) as a tripodal scaffold allows each crosslinker to connect with up to three β-CD units, forming a three-dimensional, permanently crosslinked porous network. This architecture offers high surface accessibility and structural rigidity, promoting rapid mass transfer of PFAS molecules through the matrix.

Both crosslinkers were polymerized with β-CD in anhydrous dimethyl sulfoxide (DMSO) using potassium carbonate (K_2CO_3) as a base, under mild heating at 80 °C. A β-CD to crosslinker molar ratio of 1:2 was employed, and gelation occurred within 3 hours. The final polymers were isolated in high yields—96% for CDP1 and 93% for CDP2.

The polymerization mechanism involves covalent attachment of the tripodal crosslinker to multiple β-cyclodextrin (β-CD) units via nucleophilic substitution or amide coupling, depending on the functional groups.

This approach to polymer design builds upon foundational cyclodextrin polymer strategies developed by Alsbaiee et al. (2016) and expands them by integrating charge-tunable functional groups at the crosslinking nodes, enabling tailored interaction profiles with different classes of PFAS.

Figure 3.3.3 illustrates the synthetic pathway of CDP1 and CDP2. The key difference is the incorporation of a primary amine group in CDP1, which enables favorable electrostatic interactions with anionic PFAS, as compared to the oxygen-substituted linker used in CDP2.

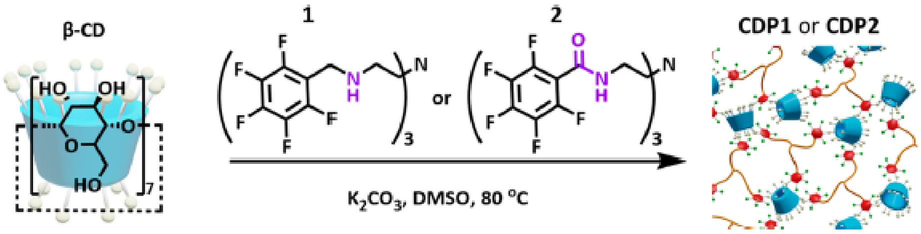


Figure 3.3.3 – Synthetic route and structural representations of β-CD-based polymers CDP1 and CDP2 using two different crosslinkers. The key distinction lies in the presence or absence of a primary amine group. (Yang et al. , 2020)

This structure was expected to:

- Improve water permeability,
- Increase accessibility to β-CD cavities,
- Introduce positive charges to favor attraction with anionic PFAS.

Adsorption was evaluated for 14 PFAS compounds, ranging from short-chain (PFBA) to long-chain (PFOS, PFHxS), and including branched and ether-based structures such as GenX.

Adsorption Performance

CDP1 demonstrated excellent adsorption performance across a broad spectrum of PFAS. At environmentally relevant concentrations (1 µg/L), it achieved removal efficiencies of ≥90% for 12 out of the 14 tested compounds. Its performance was particularly notable against short-chain PFAS, such as PFBA and PFHxA, as well as branched species like GenX, which are typically more difficult to adsorb. In addition, CDP1 exhibited rapid adsorption kinetics, reaching equilibrium within 30 minutes in most cases.

In contrast, CDP2 demonstrated markedly lower removal efficiencies across most tested PFAS, particularly for short-chain compounds such as PFBA and GenX, where performance was comparable to or inferior to commercial GAC. This reduced affinity is attributed to the neutral character of the amide linkages in CDP2, which do not offer favorable electrostatic interactions with anionic PFAS. While CDP2 retained some adsorption capacity for long-chain PFAS through host–guest interactions, its overall performance profile was significantly less favorable than that of CDP1.

Notably, CDP1 not only outperformed CDP2 but also exceeded commercial GAC in removing short- and mid-chain PFAS, which are typically more difficult to adsorb.

Figure 3.3.4 illustrates the observed differences in removal efficiency between CDP1 and CDP2 across a representative range of PFAS. As shown, CDP1 exhibited significantly higher removal percentages than CDP2 across all PFAS tested. This trend is particularly pronounced for short-chain compounds such as PFBA and branched structures like GenX, where CDP2 achieved less than 10% removal in some cases.

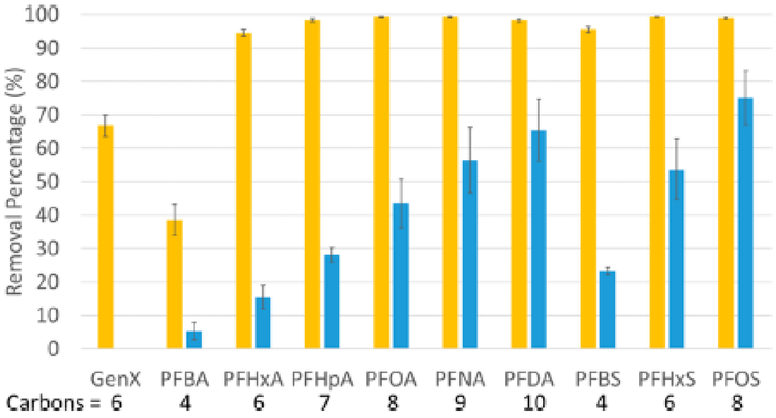


Figure 3.3.4 Removal efficiency (%) of selected PFAS by CDP1 (yellow) and CDP2 (blue). CDP1 consistently outperforms CDP2 across all compounds, especially short-chain and branched PFAS.

These results reinforce the importance of electrostatic interactions in enhancing PFAS affinity, especially for short and branched molecules that exhibit weak inclusion behavior.

Adsorption Mechanisms

The enhanced removal is attributed to a combination of:

- Electrostatic attraction between protonated amines and anionic PFAS,
- Hydrophobic interactions with the crosslinker and the PFAS tail,
- Host–guest inclusion within the β-cyclodextrin cavity.

The open network created by the tripodal crosslinker provided greater site accessibility, while the tertiary amines offered a positive surface charge, enhancing selectivity for anionic species. This dual mechanism is illustrated in ***Figure 3.3.5,*** combining host–guest complexation within the β-CD cavity and electrostatic attraction via the tripodal amine crosslinker. This synergy is what underpins the broad-spectrum efficiency of CDP1.

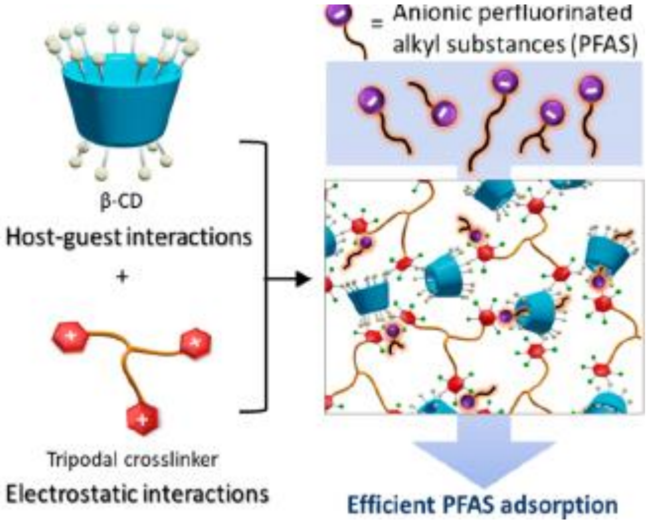


Figure 3.3.5 – Schematic representation of PFAS adsorption mechanism by tripodal β-cyclodextrin polymers, combining host–guest complexation and electrostatic interactions (Yang et al. , 2020).

Critical Assessment

This study highlights the potential of structural control at the crosslinker level to tune adsorption performance. By integrating electrostatic functionality directly into the crosslinker, the authors engineered a material that achieves fast, broad-spectrum PFAS removal under realistic conditions.

The direct comparison between CDP1 and CDP2 isolates the effect of amine functionality, offering a clear structure–function correlation that is often difficult to achieve in adsorbent development.

However, adsorption tests were conducted in Milli-Q water, so further research is needed to evaluate behavior under competitive or fouled conditions (e.g., NOM-rich matrices).

Practical Outlook

The design of TREN-CDP opens avenues for next-generation β-cyclodextrin adsorbents with modular, charge-tunable crosslinkers. Its high performance against short-chain and emerging PFAS suggests that such polymers could fill the gap left by conventional materials like GAC.

Future research should focus on evaluating the performance of these polymers in more realistic conditions. Specifically, further investigations should assess their adsorption capacity in complex matrices such as surface water and wastewater. In addition, long-term stability, potential for regeneration, and scalability in column or continuous-flow treatment systems remain critical aspects for their practical deployment.

3.4 Synthesis of styrene-based β-cyclodextrin polymers (StyDex) and their use for the removal of PFAS and pharmaceuticals from aqueous matrices

Case Study 4

Perfluoroalkyl acid adsorption by styrenic β-cyclodextrin polymers, anion-exchange resins, and activated carbon is inhibited by matrix constituents in different ways (Wang et al., 2024).

The study by Wang et al. (2024) presents an in-depth investigation of the adsorption behavior of styrene-based β-cyclodextrin polymers (StyDex) toward multiple PFAS, under a wide range of environmental conditions. This case study is particularly valuable because it combines practical, experimental data with comparative performance metrics across several adsorbent classes. Unlike literature-based meta-analyses, this study employed direct laboratory experiments using real water matrices, providing insights into the practical feasibility of β-cyclodextrin adsorbents in complex aqueous environments.

Experimental Design and Methodology

The researchers synthesized and evaluated two distinct styrene-functionalized β-cyclodextrin polymers, StyDex-D2 and StyDex-E2, which differ in their cationic functional groups—quaternary ammonium (D2) and quaternary phosphonium (E2), respectively. These materials are derivatives of a modular platform originally developed by the same research group (Wang et al., 2022), designed to enhance adsorption of anionic PFAS via tailored electrostatic and hydrophobic interactions.

The synthesis of styrene-functionalized β-cyclodextrin polymers began with the selective modification of β-cyclodextrin at the primary 6'-hydroxyl positions. The hydroxyl groups were first converted to iodides, then transformed into thiols using thiourea, and finally reacted with 4-vinylbenzyl chloride to yield a cyclodextrin monomer functionalized with seven styrene groups. This monomer (compound 3) was then copolymerized with various vinyl-based comonomers via radical polymerization, using azobisisobutyronitrile (AIBN) as the initiator in *N,N*-dimethylformamide (DMF) at 70 °C. After synthesis, the crude polymeric material was subjected to Soxhlet extraction using methanol — a continuous solvent extraction technique that efficiently removes unreacted monomers, initiators, and low-molecular-weight byproducts. This step ensures the chemical purity and structural integrity of the resulting polymer. Following extraction, the material was dried using supercritical carbon dioxide (CO_2), a technique that avoids capillary stress during solvent removal, preserving the polymer's porous architecture and high surface area, which are critical for its adsorption performance. Three distinct copolymers were synthesized:

- StyDex-4 using neutral styrene,
- StyDex-5 using methyl methacrylate,
- StyDex-6 using a cationic methacrylate bearing quaternary ammonium groups.

These polymers exhibited high surface areas (237–402 m^2/g), permanent porosity, and tunable surface charges. In particular, StyDex-6 demonstrated near-complete removal of both long- and short-chain PFAS at low adsorbent loading (1 mg/L), significantly outperforming earlier β-cyclodextrin-based adsorbents.

The synthetic pathway for the preparation of the styrene-functionalized β-cyclodextrin monomer and the subsequent formation of the porous polymer network is illustrated in the following schematic ***(Figure 3.4.1)***. This figure highlights the sequential chemical transformations required to achieve the vinyl-functionalized monomer (compound 3), as well as the radical copolymerization process used to incorporate functional comonomers and generate the final cross-linked StyDex materials. These steps are essential to ensure uniformity in structure, control over surface functionality, and ultimately, enhanced PFAS removal performance.

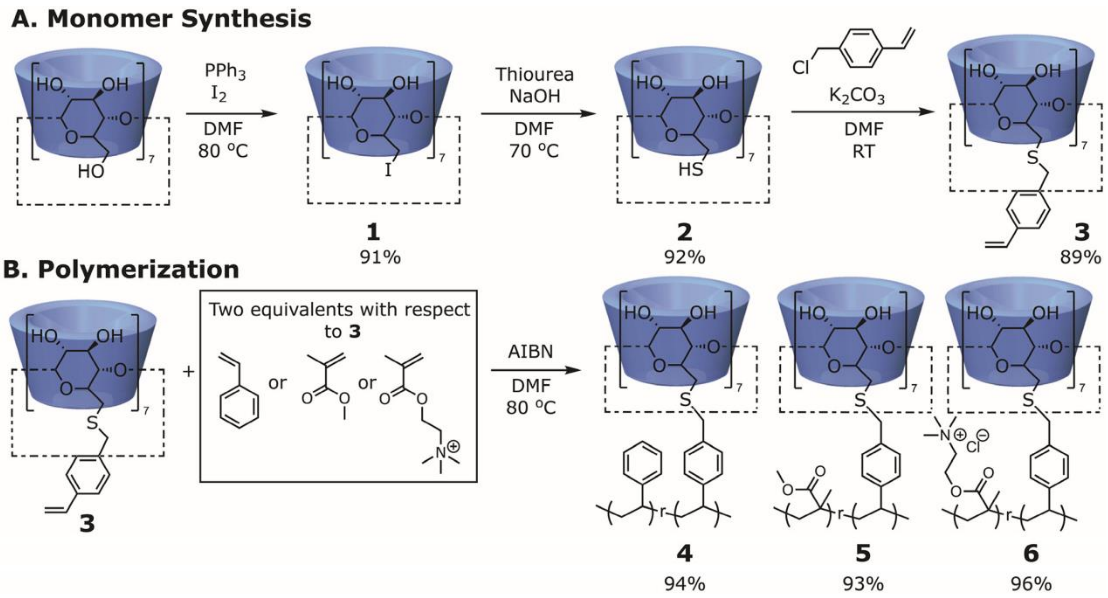


Figure 3.4.1 Synthetic route to styrene-functionalized β-cyclodextrin monomer and its radical copolymerization to form porous StyDex polymers (Wang et al., 2022).

The use of a structurally defined monomer (compound 3) offered significant advantages over previous β-CD polymer platforms that relied on random cross-linking, providing enhanced reproducibility, tunability, and structure–function insight. This modular and chemically tunable design enables targeted optimization for specific contaminants, highlighting the significant potential of StyDex polymers for advanced water treatment applications.

Based on this synthetic framework, further development led to the design of two advanced polymer variants—StyDex-D2 and StyDex-E2—tailored to enhance PFAS removal in environmentally relevant matrices. These were synthesized by radical copolymerization of the styrene-functionalized β-cyclodextrin monomer with styrene derivatives bearing quaternary ammonium (D2) or quaternary phosphonium (E2) groups, incorporating cationic methacrylate-based comonomers. The comonomers were added in a 2:1 molar ratio relative to the β-CD monomer to ensure sufficient cationic functionality while preserving porosity and accessibility to the CD cavities. Polymerization, purification, and drying followed the same protocol as in the parent synthesis. The resulting polymers had comparable particle sizes of 125–212 µm and exhibited strongly positive zeta potentials, consistent with their cationic character.

The performance was tested against 13 PFAS compounds—including short- and long-chain perfluoroalkyl acids, sulfonates, carboxylates, and ether-based species—across 16 water matrices. These matrices included laboratory water, groundwater, wastewater influent/effluent, and surface waters containing common matrix constituents such as Ca^{2+}, NO_3^-, SO_4^{2-}, and humic acid.

Batch adsorption experiments were conducted at environmentally relevant PFAS concentrations (1 μg/L per compound). Adsorption capacity was quantified primarily through adsorption density (ng/mg) and removal percentages after equilibrium, while hierarchical clustering analysis was used to evaluate trends across 16 distinct water matrices with varying ionic and organic composition.

Quantitative Performance and Comparison

Styrene-functionalized β-cyclodextrin polymers (StyDex-D2 and E2) demonstrated consistently high adsorption performance for a broad range of PFAS, including short-chain compounds such as PFBA, PFPeA, and GenX. In contrast to granular activated carbon (GAC) and anion exchange resins (AER), which exhibited reduced affinity for shorter PFAS, the StyDex polymers maintained strong removal capabilities across all chain lengths.

In batch adsorption experiments, both D2 and E2 removed over 90% of several mid- and short-chain PFAS within just 30 minutes of contact time, indicating fast kinetics and strong binding interactions. Across 16 water matrices with varying ionic and organic composition, these materials showed greater resilience to adsorption inhibition compared to GAC and AER.

Notably, the presence of humic acid or multivalent cations such as Ca^{2+} resulted in only minor decreases in removal efficiency for the StyDex polymers, whereas these same conditions significantly reduced the performance of conventional adsorbents. This matrix-independent behavior underscores the robustness of the StyDex platform and supports its potential for practical water treatment applications in complex environmental scenarios.

Figure 3.4.2 illustrates the comparative removal efficiencies of the four tested adsorbents across 13 PFAAs and three contact times. Adsorption was assessed at three distinct contact times (0.5, 9, and 48 hours), providing insights into the time-dependency of PFAS removal for each adsorbent. As shown, the StyDex variants maintained high adsorption for most compounds, especially short- and mid-chain carboxylates, even at short exposure durations. Both StyDex variants removed the majority of PFAAs within just 0.5 h of contact, with removal exceeding 90% for short- and mid-chain compounds such as PFHxA and GenX.

This rapid adsorption supports the hypothesis that host–guest and surface interactions occur concurrently and efficiently.

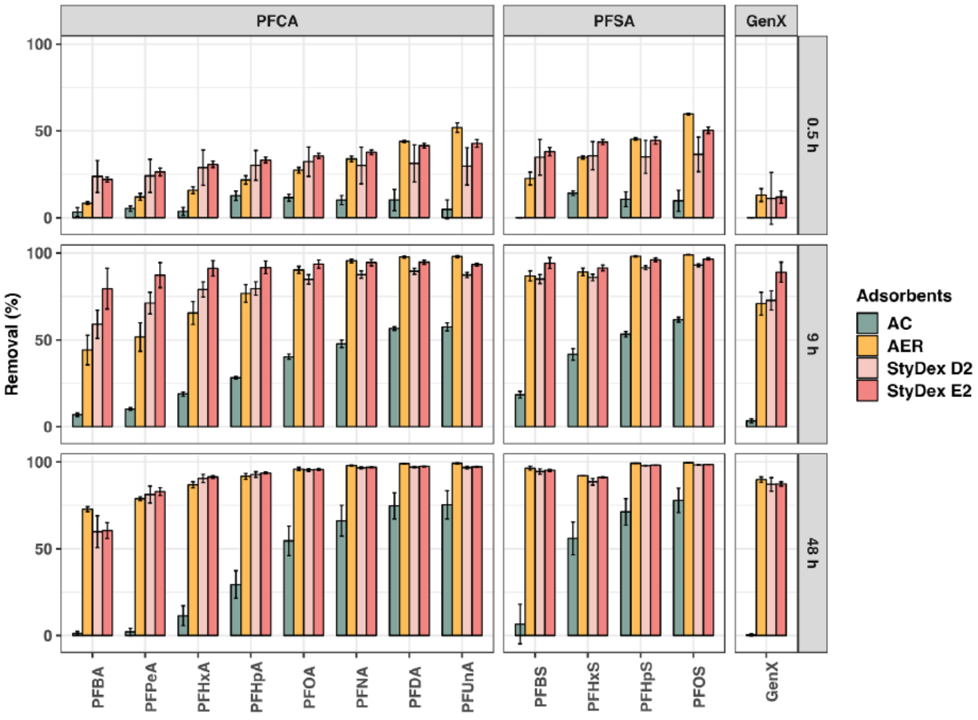


Figure 3.4.2 – Removal of 1 µg L^{-1} PFAAs by 1 mg L^{-1} AC, AER, StyDex-D2, and StyDex-E2 in Milli-Q water at 0.5 h, 9 h, and 48 h. PFAAs are grouped by head group and chain length.

Adsorption Mechanisms and Environmental Interactions

The superior performance of StyDex-D2 and E2 is attributed to a combination of complementary adsorption mechanisms:

1. **Host–guest inclusion** within the hydrophobic cavity of β-cyclodextrin,
2. **Electrostatic attraction** between anionic PFAS head groups and the positively charged surface of the polymer (due to quaternary ammonium or phosphonium),
3. **Hydrophobic and π–π interactions** between the perfluoroalkyl tails of PFAS and the styrenic polymer backbone

This polymer design results in a mesoporous and hydrophilic network that facilitates rapid water transport and enhances accessibility to the β-cyclodextrin cavities. The incorporation of cationic comonomers imparts a positively charged surface, which promotes strong electrostatic interactions with the negatively charged headgroups of anionic PFAS, particularly under neutral to slightly basic pH conditions. Beyond surface charge, these cationic groups also influence the polymer's crosslinking density, thereby modulating porosity, diffusion properties, and the spatial availability of adsorption sites. This structural and functional versatility is critical for maintaining high adsorption efficiency across a wide range of water chemistries.

Both StyDex-D2 and E2 exhibited fast adsorption kinetics and stable performance across various water chemistries, owing to this balanced architecture. Environmental matrix constituents, however, influence adsorbents differently:

- **Sulfate ions (SO_4^{2-})** reduce adsorption via electric double layer compression,
- **Calcium ions (Ca^{2+})** have limited effect, unlike their site-competition behavior in GAC or complexation in AER,
- **Humic acid (HA)** causes mild inhibition via surface accumulation but does not significantly block PFAS access to β-CD cavities.

The nearly identical behavior of D2 and E2 under all conditions suggests that both quaternary functional groups enable similarly strong electrostatic binding while preserving polymer integrity. This robustness under realistic and challenging conditions differentiates StyDex polymers from conventional adsorbents and supports their application in practical water treatment scenarios.

Critical Evaluation – Strengths and Limitations

This study provides a rare direct comparison of cyclodextrin-based materials with both GAC and AER under diverse, real-world water conditions. Its major strengths include the experimental validation across multiple water types and its investigation of 13 PFAS, making it among the more extensive polymer-based studies to date.

However, limitations include the fact that long-chain PFAS, particularly PFOS, were still more effectively adsorbed by GAC. Also, although StyDex polymers performed well overall, the exact influence of matrix complexity (e.g. wastewater influent vs. surface water) could be further elaborated with kinetic data and long-term stability studies.

Future research could further enhance the applicability of StyDex polymers by incorporating surface functional groups to improve binding affinity for charged PFAS, or by embedding magnetic nanoparticles for easier regeneration and recovery in large-scale applications.

Implications and Practical Outlook

The findings demonstrate that β-cyclodextrin-based polymers, such as StyDex, can offer an effective and selective adsorption solution, especially for short-chain and emerging PFAS, where conventional adsorbents fall short. Their relatively high resistance to co-contaminants supports their application in environmentally complex treatment scenarios.

Building upon the promising results obtained in controlled aqueous matrices, the research group proceeded to evaluate the real-world applicability of the StyDex polymers. After demonstrating consistent removal of various PFAS across different water chemistries and minimal sensitivity to ionic strength or natural organic matter, their next step was to assess the material's performance in operationally relevant settings.

The subsequent study, conducted by Shapiro et al. (2025), marks this transition by applying the same class of β-cyclodextrin–styrene polymers to municipal wastewater effluents, incorporating both batch and flow-through experiments (RSSCTs). This shift allowed the researchers to explore kinetic behavior, breakthrough characteristics, and performance stability under dynamic contact times, providing critical insight into the material’s potential for full-scale implementation.

Case Study 5

Shapiro et al. (2025): Removal of PFAS and pharmaceuticals from municipal wastewater using a novel β-cyclodextrin adsorbent over distinct contact times

This study by Shapiro et al. (2025) investigates the effectiveness of a novel styrene-functionalized β-cyclodextrin polymer (StyDex) for the removal of both PFAS compounds and pharmaceuticals from real municipal wastewater. Unlike many previous studies conducted under simplified laboratory conditions, this research included both batch and column experiments using actual effluent from a wastewater treatment plant (WWTP), offering highly relevant insights for real-world applications.

Experimental Design and Methodology

The adsorbent evaluated was StyDex, a β-cyclodextrin-based polymer with styrene modifications designed to enhanced hydrophobic and electrostatic interactions. Sorption experiments were conducted with seven PFAS compounds—including PFOA, PFHxS, PFHxA, PFBS, PFBA, PFOS, and GenX—, which were selected due to their frequent detection in WWTP effluents. Each PFAS compound was spiked in wastewater at an initial concentration of 500 ng/L. The adsorbent dose of StyDex used was 100 mg/L, with particle sizes ranging from 90 to 106 μm.

Tests included both batch experiments and Rapid Small-Scale Column Tests (RSSCTs), designed to simulate real flow-through conditions encountered in full-scale water treatment systems. Batch tests were conducted over 24 hours, with sampling at 2, 5, 10, 30 minutes and 1, 2, 4, 6.5 and 24 hours to evaluate adsorption kinetics. RSSCTs were performed using 4.6 × 30 mm HPLC columns packed with StyDex, simulating large-scale contact times of 2–10 minutes by varying flow rates accordingly.

Contact time emerged as a key variable, with breakthrough curves generated for each scenario to analyze both equilibrium capacity and kinetic performance under competitive loading conditions.

Results and Adsorption Behavior

StyDex showed strong selectivity for long-chain and sulfonated PFAS compounds such as PFOS and PFHxS, while its performance was comparatively lower for short-chain PFAS like PFBA.

PFOA and PFHxS exhibited particularly strong and prolonged adsorption, as indicated by their BV10 values of 11,150 and 9,490, respectively, and the fact that they did not reach BV50 even after 72,000 bed volumes (BV) of treated water. The term "bed volumes" refers to the total volume of water treated relative to the volume of the adsorbent bed. BV10 and BV50 correspond to the points at which the contaminant concentration in the effluent reaches 10% and 50% of the influent concentration, respectively. The inability to reach BV50 highlights the exceptional retention of these compounds by StyDex. In contrast, PFBA reached full breakthrough ($C/C0 = 1$) after approximately 9,370 bed volumes, indicating weaker binding and faster desorption.

Contact time significantly influenced the breakthrough patterns. Longer-chain PFAS remained adsorbed for longer periods, while shorter-chain compounds broke through earlier. These trends were confirmed in binary sorption experiments (e.g., PFBA vs. PFOA), where StyDex consistently favored the more hydrophobic molecule. For example, in a binary system containing PFOA (C8) and PFBA (C4), PFOA showed delayed breakthrough (BV50 at ~27,000), while PFBA reached $C/C0 > 1$ at just 10,000 BV, evidencing desorption due to competitive displacement.

The Figure below (***Figure 3.4.3***) illustrates that the removal efficiency of StyDex is strongly influenced by both the chemical structure of the PFAS compounds and the contact time within the column. The long-chain PFAS (PFOA and PFHxS) demonstrate significantly longer retention, with no BV50 reached even after 72,000 bed volumes at the highest contact time. In contrast, short-chain compounds like PFBA and GenX reach full breakthrough relatively quickly, highlighting the challenges in removing these species. These curves underscore the material's selectivity towards hydrophobic and sulfonated PFAS and provide critical insights for scaling up the treatment system in real wastewater environments.

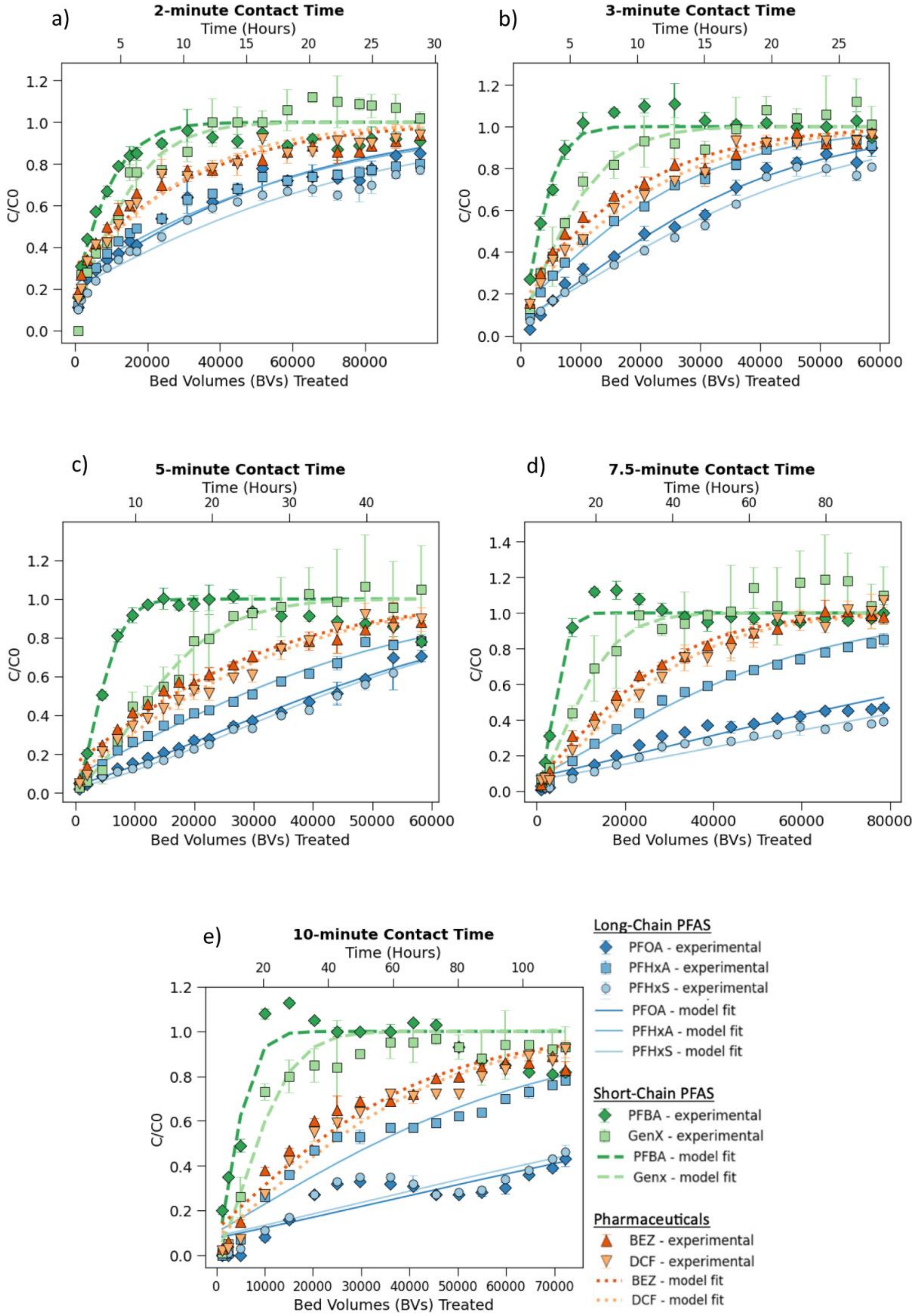


Figure 3.4.3 *Breakthrough curves for seven target contaminants in Rapid Small-Scale Column Tests (RSSCTs) at different contact times (2, 3, 5, 7.5, and 10 minutes). Long-chain and sulfonated PFAS, such as PFOA and PFHxS, exhibit delayed breakthrough, while short-chain PFAS like PFBA and GenX reach full breakthrough rapidly (Shapiro et al., 2025).*

Mechanisms and Interpretation

The study attributes StyDex's selectivity to a combination of three key mechanisms: hydrophobic interactions between the PFAS tails and the polymer matrix, host–guest inclusion within the β-cyclodextrin cavity, and electrostatic attraction to positively charged functional groups on the polymer surface. These mechanisms are especially effective for long-chain and sulfonated PFAS due to their enhanced hydrophobicity and charge-based affinities.

Figure 3.4.4 provides further information for this mechanism by showing a strong positive correlation between the hydrophobicity of PFAS (logKow) and their average BV50 values across different contact times. This means that more hydrophobic compounds are retained longer in the column. The correlation is particularly strong among PFAS compounds (r = 0.91), emphasizing the role of hydrophobicity in dictating adsorption behavior.

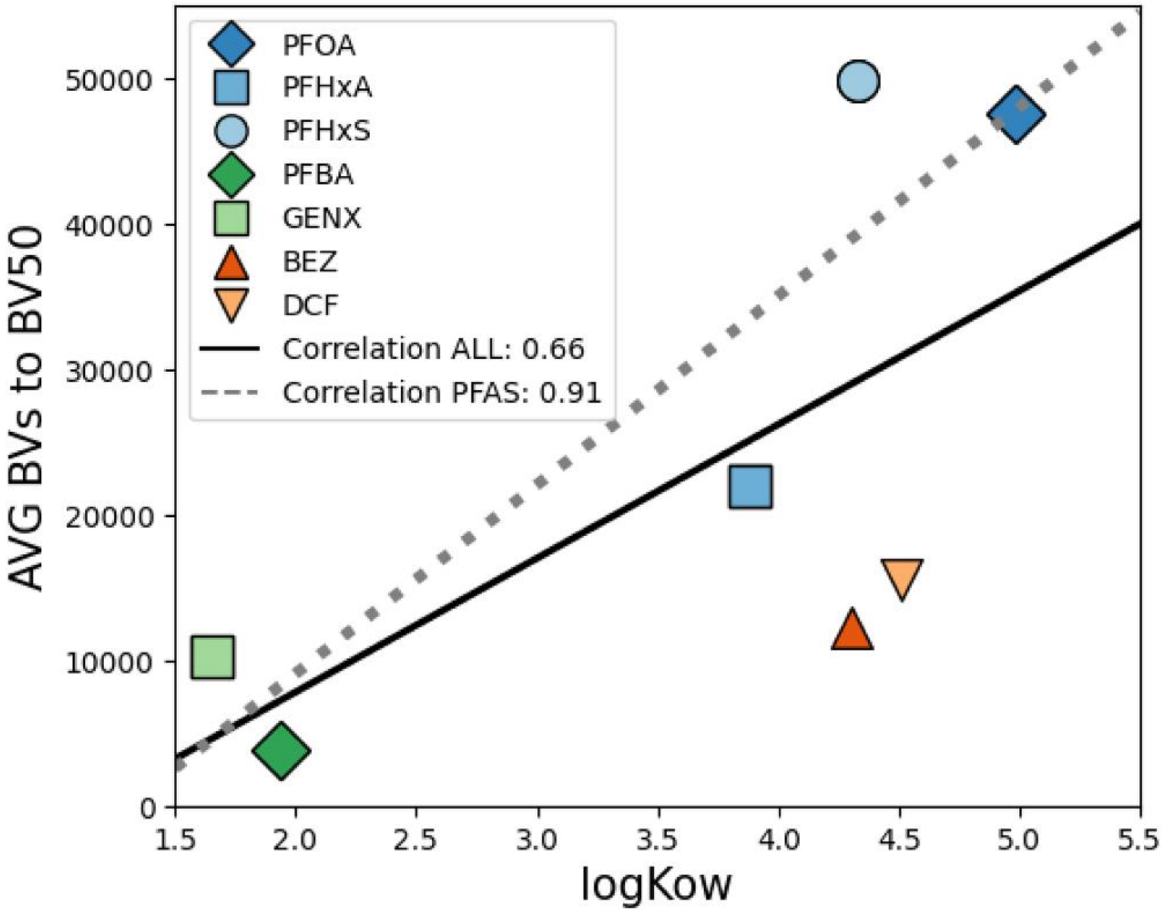


Figure 3.4.4 *Correlation between average BV50 values and the hydrophobicity (logKow) of each contaminant. Compounds with higher logKow values, such as PFOA and PFHxS, exhibit stronger retention and slower breakthrough in column experiments. Short-chain PFAS (PFBA, GenX) show lower BV50 values, indicating weaker adsorption (Shapiro et al., 2025).*

Critical Assessment – Strengths and Limitations

A critical assessment of the study highlights several strengths and limitations. One of its main advantages lies in the use of real wastewater, which significantly enhances the practical relevance of the results. Additionally, by combining batch and column experiments, the researchers gained insight into both adsorption kinetics and long-term column performance. The investigation into contact time was especially valuable, as this parameter is critical for designing effective full-scale treatment systems.

One limitation is that while the column experiments used realistic conditions, scaling up to full-scale operations may still present challenges such as fouling, variability in water composition, and flow dynamics not captured in laboratory-scale tests.

Implications for Full-Scale Applications

This case study highlights the potential of functionalized β-cyclodextrin polymers, especially StyDex, for PFAS removal under realistic conditions. The material's selectivity, fast kinetics, and resilience in complex wastewater matrices make it a promising option for integration into WWTPs, particularly for polishing steps or targeted removal of long-chain and sulfonated PFAS.

Beyond laboratory performance, the incorporation of StyDex materials in wastewater treatment plants could be used effectively at the final stage of water treatment systems, either as part of a final 'polishing' step or in small, separate units designed to specifically remove PFAS that are difficult to eliminate.

Given its effectiveness in retaining long-chain and sulfonated PFAS, StyDex could serve as an alternative to conventional adsorbents like granular activated carbon (GAC), especially in systems where space, contact time, or fouling are limiting factors.

When comparing the findings of Shapiro et al. (2025) and Wang et al. (2024), both studies underline the high performance of styrenic β-cyclodextrin polymers (StyDex) for the selective removal of long-chain and sulfonated PFAS. However, while Shapiro et al. demonstrated StyDex's efficiency in real wastewater matrices and under continuous flow conditions (RSSCTs), Wang et al. provided a complementary perspective by exploring the inhibition of PFAS adsorption by specific matrix constituents (e.g., sulfate, calcium, and humic acid) in controlled batch experiments. Notably, Wang et al. found that sulfate ions can suppress adsorption on StyDex due to electric double layer compression, whereas Shapiro et al. reported persistent PFAS retention even under variable contact times.

Together, these studies highlight not only the robustness of StyDex but also the importance of understanding matrix effects and operational conditions when designing PFAS treatment systems.

3.5 Meta analysis

FAIR comparison of activated carbon, biochar, cyclodextrins, polymers, resins, and metal organic frameworks for the adsorption of per- and polyfluorinated substances (Saeidi et al., 2024):

Saeidi et al. (2024) conducted one of the most comprehensive literature-based comparative evaluations of PFAS adsorbents to date, applying the FAIR principles (Findable, Accessible, Interoperable, and Reusable) to ensure that results could be systematically interpreted and reused across the scientific community. The study addressed a core limitation in PFAS adsorption research: the lack of comparability among published results due to variable testing conditions, such as differing PFAS concentrations, pH levels, co-contaminants, and matrix compositions. To overcome this, the authors harmonized over 500 data points from peer-reviewed studies, focusing on 44 PFAS compounds and six major adsorbent categories, including activated carbon, biochar, cyclodextrin-based materials, ion-exchange resins and metal-organic frameworks (MOFs).

Experimental Design and Methodology

The strength of the study lies in its standardized comparison framework. Only K_d values obtained under environmentally relevant PFAS concentrations (~1 μg/L), near-neutral pH (6–8), and minimal interference from co-contaminants were considered. This provided a level playing field for cross-material evaluation. Cyclodextrin-based adsorbents were analyzed alongside conventional materials such as AC and resins, allowing researchers to observe performance patterns with consistency across all six adsorbent categories.

Performance of Cyclodextrins – Quantitative Overview

Cyclodextrin materials demonstrated a unique adsorption profile. While their performance for long-chain PFAS (e.g., PFOS, PFOA) was generally lower than that of AC, they showed markedly higher affinity for short-chain PFAS, which are typically more challenging to remove. This selective efficiency was attributed to the hydrophobic cavity of β-cyclodextrin, which allows for size- and shape-specific host–guest interactions.

Moreover, emerging PFAS such as HFPO-DA (GenX) showed moderate adsorption onto β-CD materials, in contrast to their typically low interaction with traditional adsorbents such as activated carbon. This suggests that cyclodextrins may offer a route for targeting newer PFAS compounds that are resistant to conventional removal technologies.

Cyclodextrins exhibited less interference from natural organic matter (NOM) compared to activated carbon, likely due to their unique molecular structure and surface chemistry.

Table 3.1 summarizes representative adsorption behaviors for selected PFAS on β-cyclodextrin and activated carbon materials, highlighting the material-dependent variability in performance.

Table 3.1 – Indicative K_d values for selected PFAS on β-cyclodextrin-based adsorbents and activated carbon

PFAS	**Chain Length**	**K_d (β-CD)**	**K_d (Activated Carbon)**	**Comparative Assessment**
PFBA	C4	High	Low	β-CD outperforms AC
PFHxA	C6	High	Medium	Comparable or better than AC
PFOS	C8-Sulfonate	Moderate	High	AC better for long-chain PFAS
GenX	Ether-based	Moderate	Low	β-CD superior for novel PFAS

These findings confirmed the selective nature of β-cyclodextrin-based materials, particularly for short-chain and branched compounds, which are not effectively removed by traditional hydrophobic adsorbents like AC.

The relationship between PFAS structure and adsorption affinity is further illustrated in ***Figure 3.5.1***, which plots K_d values against the number of C–F bonds. Activated carbon and biochar exhibit increasing adsorption capacity with longer PFAS chains, consistent with their hydrophobic and porous nature. In contrast, cyclodextrins show higher adsorption for short-chain PFAS, aligning with the inclusion-complex mechanism described earlier. These patterns reinforce the idea that material selection must be tailored to the specific PFAS profile in contaminated water sources.

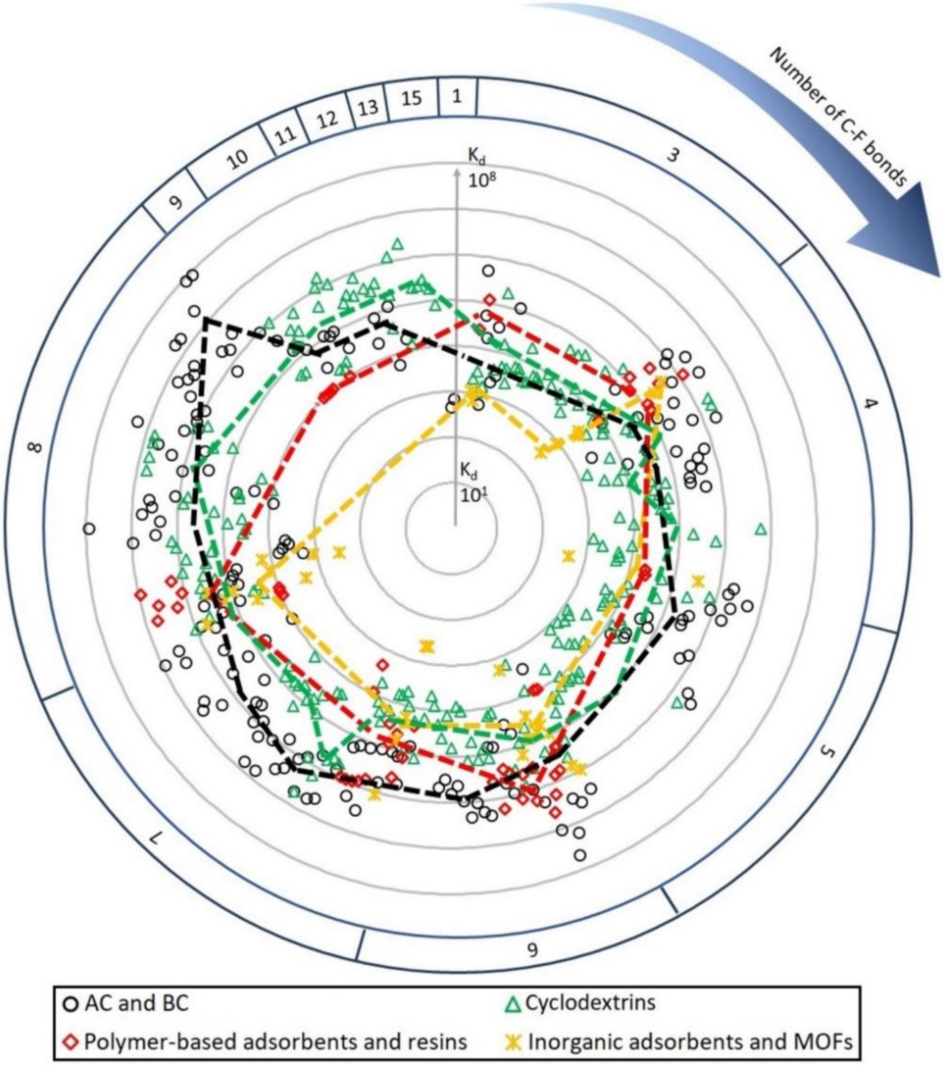


Figure 3.5.1 – Adsorption coefficients (K_d) of 44 PFAS compounds on four adsorbent groups as a function of the number of C–F bonds (Saeidi et al., 2024).

Adsorption affinity increases with fluorinated chain length for activated carbon and biochar (AC/BC), whereas cyclodextrins show higher K_d values for PFAS with shorter chains. The data highlight the selectivity patterns of different adsorbent classes (Saeidi et al., 2024).

Mechanisms of Adsorption in Cyclodextrins

The observed selectivity was attributed to the structural characteristics of β-cyclodextrins. These cyclic oligosaccharides possess a hydrophobic interior cavity capable of forming inclusion complexes with suitably sized PFAS molecules. This host–guest mechanism enables specific interactions that depend on the PFAS's molecular geometry, polarity, and chain length. The mechanism involves the insertion of the PFAS molecule's hydrophobic tail into the inner cavity of the β-cyclodextrin ring, while the polar functional head remains at or near the rim. This host–guest inclusion complex is stabilized by van der Waals and hydrophobic interactions.

Short-chain PFAS are better accommodated within the β-CD cavity, while long-chain PFAS interact more efficiently with the extensive porous surface of activated carbon.

Moreover, β-CD-based adsorbents demonstrated reduced susceptibility to natural organic matter (NOM) fouling, a major issue for AC in environmental applications. This likely results from the size-exclusion nature of β-CD cavities and the more selective adsorption mechanism that reduces competitive interference.

To further explore the mechanisms behind PFAS adsorption, Figure 3.5.2 illustrates the relationship between molecular descriptors and K_d values across different adsorbents. For activated carbon, biochar, and cyclodextrins, a clear positive trend was observed: K_d increases with the number of C–F bonds, hydrophobicity (log D_{ow}), and molar volume. These findings suggest that steric and hydrophobic interactions play a key role in the adsorption process for these materials. In contrast, no consistent correlation was found for polymer-based adsorbents or MOFs, highlighting the need for further study to understand the driving forces in these systems.

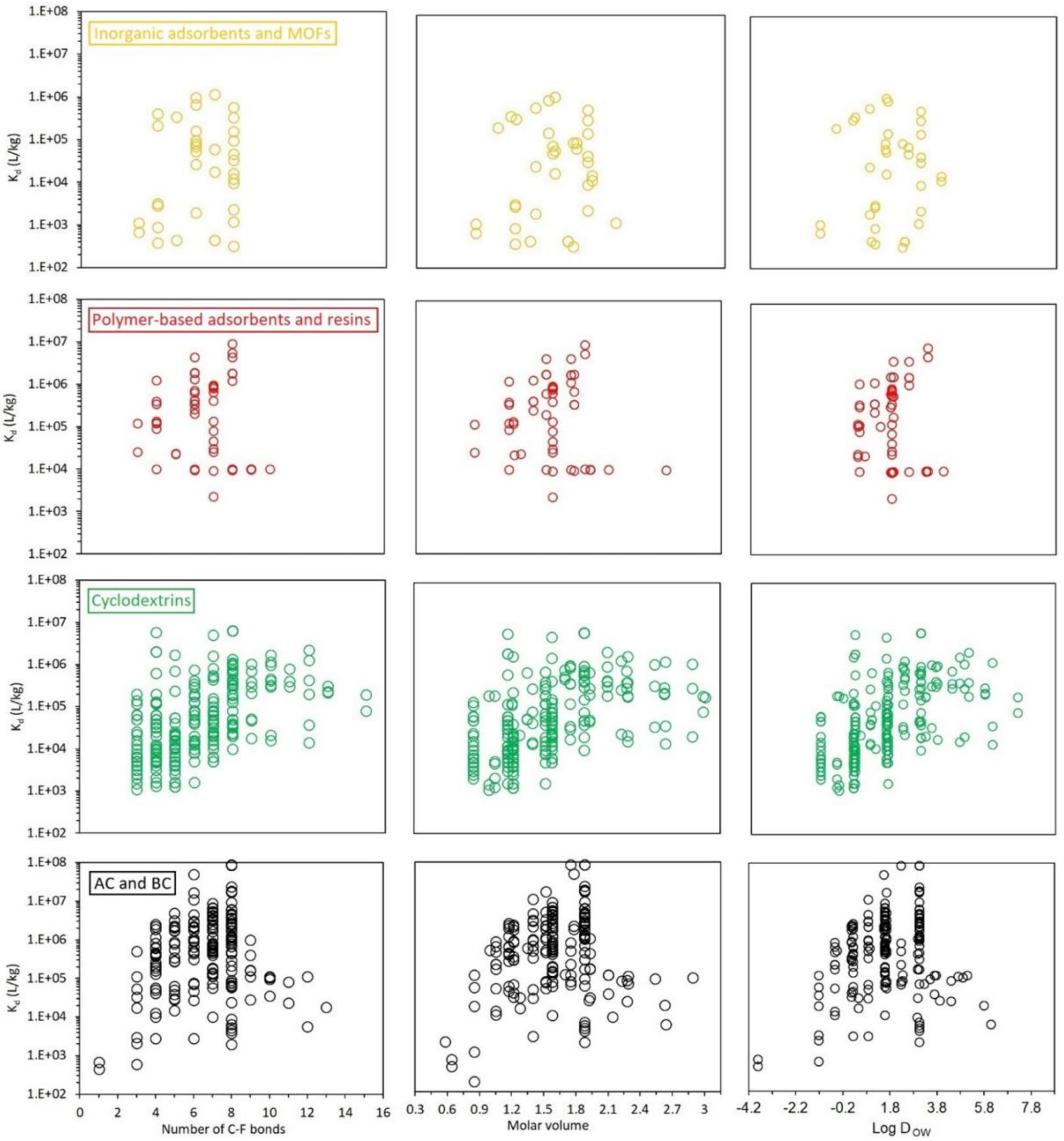


Figure 3.5.2 – Correlation between PFAS adsorption coefficients (K_d) and molecular properties: number of C–F bonds, log D_{ow} (hydrophobicity at pH 7), and molar volume (Saeidi et al., 2024).

Clear positive correlations are observed for AC/BC and cyclodextrins, indicating the influence of hydrophobic and steric factors on adsorption. No strong trends were seen for polymer-based adsorbents or MOFs.

Further analysis by Saeidi et al. (2024) demonstrated that adsorption affinity also varies significantly across structurally distinct PFAS subgroups. Compounds with sulfonic acid head groups and fully fluorinated carbon chains generally exhibited higher K_d values than carboxylic or ether-linked analogues, underscoring the importance of functional group chemistry and backbone composition in adsorption performance.

Critical Evaluation – Strengths and Limitations

One major strength of this case study is the power of the comparative framework. By enforcing uniform experimental parameters and compiling a broad data set, the study enabled a statistically meaningful comparison that few other analyses have achieved in this field. It reinforces prior theoretical insights regarding β-cyclodextrin's selective affinity and offers practical evidence of its strengths in niche PFAS removal.

However, limitations exist. The study was a meta-analysis, relying on literature data rather than new experimental trials. This introduces potential inconsistency in how individual experiments were conducted and limits the ability to control for unreported variables (e.g., minor changes in temperature or ionic strength). Furthermore, while the study grouped all β-CD-based materials into one category, it did not distinguish between chemically modified cyclodextrin polymers and native β-CD, which can have significantly different performance characteristics.

Comparison of Adsorbent Material Structures

To analyze the performance of β-cyclodextrins, ***Table 3.2*** compares the structural and functional characteristics of major PFAS adsorbent classes, including their selectivity profiles and vulnerability to natural organic matter (NOM).

Table 3.2 – Structural comparison of PFAS adsorbents

Adsorbent Type	Key Structural Features	Targeted PFAS Classes	Sensitivity to NOM	Typical Use Cases
Activated Carbon	Amorphous porous structure	Long-chain PFAS (e.g., PFOS, PFOA)	High	Industrial wastewater, GAS filters
β-Cyclodextrins	Cyclic oligosaccharides, inclusion sites	Short-chain, branched PFAS, GenX	Low	Drinking water, hybrid systems
MOFs	Crystalline porous frameworks	Variable (often PFOS-targeted)	Medium - High	Emerging tech, lab-scale
Ion-exchange Resins	Charged polymeric matrix, fixed groups	Charged (e.g. anionic) PFAS	Medium	Resin columns, selective removal

Table 3.2 provides a comparative overview of the major adsorbent classes evaluated for PFAS removal, highlighting their structural characteristics, typical selectivity, sensitivity to natural organic matter (NOM), and common application contexts.

Activated carbon (AC) remains the most widely applied material due to its high surface area and strong affinity for long-chain PFAS such as PFOA and PFOS. However, it suffers from significant fouling when NOM is present. β-Cyclodextrins (β-CDs), on the other hand, demonstrate a more targeted performance toward short-chain and branched PFAS, including emerging compounds like GenX. Their selectivity arises from host–guest inclusion mechanisms and reduced susceptibility to NOM interference, making them promising candidates for hybrid treatment systems.

Metal-organic frameworks (MOFs) offer tunable pore structures and high adsorption capacities for specific PFAS types, but their performance under realistic environmental conditions and stability in aqueous matrices remain research challenges. Ion-exchange resins provide effective removal of charged PFAS through electrostatic interactions but may show variable results depending on pH and water composition.

This comparative analysis sets the foundation for a strategic evaluation of β-cyclodextrin's role in water treatment applications. A key takeaway from this study is that cyclodextrins may not replace conventional adsorbents in all contexts but offer distinct advantages in selectively removing PFAS species that are typically more difficult to capture. Their performance is highly dependent on PFAS structure and environmental context, making them valuable components in combined or hybrid remediation systems.

Thus, cyclodextrins may not universally outperform conventional adsorbents, but they offer clear advantages in specific PFAS subgroups and under chemically complex conditions, making them ideal for integrated or sequential treatment strategies. By employing a harmonized comparison approach, this case study reinforces the theoretical understanding of β-cyclodextrin's selective interaction with PFAS and supports its role as a complementary or alternative adsorbent in tailored water treatment applications.

3.6 Comparative Discussion and Key Insights from the Case Studies

The case studies and meta-analysis analyzed in this chapter collectively highlight the evolving landscape of β-cyclodextrin (β-CD)-based adsorbents for the remediation of per- and polyfluoroalkyl substances (PFAS). These studies cover a wide range of adsorbent chemistries, experimental setups, and water matrices, offering a rich basis for comparative evaluation and insight collection.

3.6.1 Structure–Function Relationships

A central theme across the studies is the critical role of polymer structure—particularly the nature of the crosslinker and the presence of surface functional groups—in determining PFAS adsorption efficiency and selectivity.

Specifically, after establishing the polymer framework through crosslinking, targeted functionalization is often applied to introduce positively charged groups, such as primary amines or quaternary ammonium functionalities. This step is essential to enhance electrostatic attraction toward anionic PFAS, which possess negatively charged head groups (e.g., carboxylates or sulfonates).

For example:

- Post-synthetic amination (Klemes et al., 2019) and the use of tripodal amine-based crosslinkers (Yang et al., 2020) substantially increased affinity for short-chain and branched PFAS via electrostatic interactions.
- In contrast, polymers lacking such cationic functionality—like CDP2 and TFN–CDP—exhibited significantly weaker performance, especially in environmentally relevant matrices containing competing ions and natural organic matter (NOM), which further inhibit adsorption through charge shielding or site blockage.

3.6.2. Short- vs Long-Chain PFAS Behavior

The case studies collectively reveal a clear divergence in adsorption behavior between long- and short-chain PFAS. Traditional adsorbents, such as GAC and AER, consistently performed well for long-chain compounds (e.g., PFOS, PFOA), but struggled with short-chain and branched PFAS like PFBA and GenX—especially in real water matrices.

In contrast, several β-cyclodextrin-based polymers demonstrated notable capacity to capture short-chain PFAS. For instance:

- **StyDex-D2 and E2** maintained high removal rates for short-chain PFAS even under matrix interference, owing to strong electrostatic and hydrophobic interactions via quaternary groups.

- **CDP1**, synthesized with nitrogen-containing tripodal amine crosslinkers, achieved >90% removal across 12 out of 14 PFAS tested, including PFBA and GenX, highlighting the importance of cationic functionalization at the crosslinking level.
- **Amine-modified CDP** (Klemes et al., 2019) also exhibited significantly higher log K_d values for short-chain PFAS compared to its unmodified precursor, indicating that electrostatic attraction is essential for efficient adsorption.

These findings are supported by the FAIR meta-analysis which showed that β-CD-based materials generally outperform activated carbon for short-chain PFAS under environmentally relevant conditions. The results underscore that targeted surface charge engineering is the most effective strategy for overcoming the inherent removal challenge posed by short-chain PFAS.

3.6.3. Matrix Effects and Real-World Performance

Case studies involving real water matrices—such as those by Wu et al., 2020, (TFN–CDP) and Shapiro et al., 2025, (StyDex)—revealed strong differences in PFAS removal performance depending on matrix composition. Unmodified β-CD polymers like TFN–CDP and CDP2 showed significant reductions in adsorption under conditions of high ionic strength, NOM, and cationic competition. By contrast, functionalized materials such as CDP1 (Yang et al., 2020) and StyDex-D2/E2 maintained high removal efficiency, demonstrating resilience to matrix interference. These findings highlight that electrostatic surface tuning and robust polymer architecture are critical for real-world application of β-CD adsorbents.

3.6.4 Kinetics and Contact Time Sensitivity

Contact time was confirmed as a decisive factor in several studies evaluating operational feasibility. StyDex-D2, tested under RSSCT conditions (Wang et al., 2024), exhibited remarkable performance, achieving >80% PFAS removal at contact times under 30 seconds. This rapid kinetic profile was also observed in CDP1 (Yang et al. , 2020), which maintained high removal across a broad PFAS spectrum within 15 minutes of contact, including short-chain species like PFBA and GenX.

Notably, different PFAS compounds behaved differently under flow-through conditions. Long-chain PFAS (e.g., PFOS, PFHxS) showed delayed breakthrough due to stronger retention, while short-chain PFAS broke through faster, even in optimized systems. These results highlight that rapid kinetics alone are insufficient; adsorbents must also balance fast uptake with adequate retention to ensure effective operation in real-time systems.

3.6.5. Meta-Analysis Validation

The meta-analysis by Saeidi et al. (2024) provided strong validation for the case study findings. Cyclodextrin-based adsorbents consistently outperformed activated carbon in the removal of short-chain PFAS, particularly PFBA and GenX, as reflected in higher K_d values. The analysis also confirmed a positive correlation between adsorption affinity and PFAS molecular properties such as log D_{ow} and molar volume, emphasizing the combined influence of hydrophobic and steric interactions. Additionally, β-CD polymers exhibited lower sensitivity to natural organic matter (NOM), supporting their suitability for real-world applications where organic fouling is a concern.

Conclusion - Outlook

This thesis has provided a critical evaluation of β-cyclodextrin (β-CD)-based adsorbents for PFAS remediation, drawing insights from both experimental case studies and broader data-driven analyses published in the literature. Functionalization emerged as a decisive design strategy: introducing cationic groups—such as amines or quaternary ammonium moieties—greatly enhanced adsorption selectivity and efficiency, particularly for challenging short-chain PFAS like PFBA and GenX. Case studies with CDP1 and StyDex variants consistently demonstrated robust performance under variable pH, NOM interference, and multivalent ion presence, outperforming traditional materials such as GAC and ion-exchange resins.

Beyond removal efficiency, the work explored practical parameters affecting field-scale implementation. Rapid adsorption kinetics observed in StyDex and CDP1, coupled with favorable performance under flow conditions, suggest strong potential for integration into real-world systems. These findings were corroborated by meta-analytic results from Saeidi et al. (2024), where cyclodextrins showed higher K_d values and lower sensitivity to NOM fouling compared to activated carbon, especially for short-chain PFAS.

Looking ahead, multiple technological and regulatory challenges must be addressed. Scalable synthesis requires optimization of crosslinking conditions, functional group incorporation, and product consistency. Transitioning from laboratory powders to granular or immobilized formats is essential for compatibility with packed-bed and cartridge systems used in municipal wastewater treatment. Hybrid strategies—such as β-CD coupled with MOFs or magnetic nanoparticles—offer promising directions for enhancing adsorption capacity, antifouling behavior, and regenerability.

From a regulatory and economic standpoint, full life-cycle assessments are needed to compare cost-per-gram removal, regeneration feasibility, and long-term stability relative to existing technologies. Regulatory approval for drinking water applications will also hinge on demonstrating non-toxicity of synthetic by-products and degradation residues.

In terms of research directions, future studies should:

- Develop regeneration protocols that preserve performance over multiple cycles,
- Explore advanced surface chemistries targeting specific PFAS classes,
- Investigate environmental resilience under fluctuating pH and ionic strength,
- Encourage cooperation between scientists in materials, environmental, and health fields.

In conclusion, β-cyclodextrin polymers represent a versatile and scalable platform for PFAS removal. Their chemical tunability, operational flexibility, and favorable environmental profile make them strong candidates for next-generation water treatment technologies—bridging the gap between laboratory promise and real-world implementation.

The development of scalable and sustainable adsorption solutions is vital, with an emphasis on the regeneration and reuse of adsorbents, minimizing secondary pollution and energy consumption, and integrating these materials into existing water treatment systems to enhance PFAS remediation efficiency.

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