

FINAL REPORT

Rational Design and Implementation of Novel Polymer
Adsorbents for Selective Uptake of PFAS from Groundwater

SERDP Project ER18-1026

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14. ABSTRACT Aqueous film-forming foam (AFFF) formulations have been used for decades to suppress hydrocarbon fuel-based fires at United States (US) military facilities. Perand polyfluoroalkyl substances (PFASs) are key constituents of AFFFs and their occurrence in groundwater at many of these facilities has been widely reported. Developing cost-effective remediation strategies to remove PFASs from groundwater remains an important challenge. The goal of this project was to design, characterize, and evaluate the implementation of novel polymer adsorbents for the in situ or ex situ remediation of PFAS-contaminated groundwater. The research objectives of the project were to: (1) discover polymer adsorbents with high affinity, high capacity, and rapid kinetics for priority and environmentally relevant PFASs; (2) characterize the performance of each polymer under scenarios relevant to groundwater remediation; and (3) transition towards the implementation of the new polymer adsorbents into remediation processes by optimizing synthesis pathways and evaluating adsorption process alternatives.						
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LIST OF ACRONYMS

AA	Groundwater sample provided by anonymous community AA
AC	Activated carbon
AE	Anion exchange
AFFF	Aqueous film-forming foam
AIBN	Azobisisobutyronitrile
ANSI	American National Standards Institute
ATR	Attenuated total reflectance
AWAC	Activated carbon sample received from anonymous collaborator AW
AWWA	American Water Works Association
BET	Brunauer-Emmett-Teller surface area
BPA	Bisphenol-A
BV	Bed volumes
CCAC	Coconut shell activated carbon
CD	Constant diffusivity
CDP	Cyclodextrin polymer
CE	Cation exchange
CHNS	Carbon Hydrogen Nitrogen Sulfur
CL	Crosslinker
CoC	Contaminant of Concern
COF	Covalent organic framework
CP-MAS	Cross-polarized magic angle spinning
CSP	Center for Sustainable Polymers
CU	Cornell University
DEXSORB	Specific cyclodextrin polymer (aka P-CDP, TFN-CDP)
DEXSORB+	Specific cyclodextrin polymer (aka CDP+)
DFB	Decafluorobiphenyl
DFB-CDP	decafluorobiphenyl-crosslinked cyclodextrin polymer
DI	Deionized water
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EBCT	Empty-ben contact time
ELVACITE	Commercial acrylic resin
EPA	Environmental Protection Agency
EPI	Epichlorohydrin
ERSON	Environmental restoration statement of need
ESTCP	Environmental Security Technology Certification Program
FASA	Perfluoroalkane sulfonamide

FASAA	Perfluoroalkane sulfonamide acetic acid
FBSA	Perfluorobutane sulfonamide
FDA	Food and drug administration
FOSA	Perfluorooctane sulfonamide
FTAB	Fluorotelomer sulfonamide alkylbetaine
FTB	Fluorotelomer betaine
FTIR	Fourier transform infrared spectroscopy
FTOH	Fluorotelomer alcohol
FTSA	Fluorotelomer sulfonamide
GAC	Granular activated carbon
GW	Groundwater
HFAC	Activated carbon received from anonymous collaborator HF
HPLC	High-performance liquid chromatography
HR	High-resolution
ICP	Inductively coupled plasma optical emission spectroscopy
IEM	Urethane-containing methacrylate
K _D	Solid-water distribution coefficient
K _L	Langmuir affinity coefficient
LFER	Linear free-energy relationship
LOQ	Limit of quantification
MeOH	Methanol
MDI	4,4'-methylene diphenyl diisocyanate
MS	Mass spectrometry
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
NP	Nanopure
NSF	National Science Foundation
NU	Northwestern University
OES	Optical Emission Spectroscopy
P-CDP	TFN-crosslinked porous cyclodextrin polymer
P-CDP@cellulose	P-CDP-functionalized microcrystalline cellulose particles
PAC	Powdered Activated Carbon
PBF	packed-bed filtration
PCA	Principal Component Analysis
PD	Proportional diffusivity
PFAA	Perfluoroalkyl acids
PFAS	Perfluoroalkyl substances

PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonate
PFCA	Perfluorocarboxylic acid
PFDA	Perfluorodecanoic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonate
PFSA	Perfluorosulfonic acid
PI	Principal Investigator
PXRD	Powder X-ray diffraction
QA	Quality assurance
QC	Quality control
Q _M	Maximum adsorption capacity
RPM	Rotations per minute
RSSCT	Rapid small-scale column test
SA	Surface area
SC	Sodium Chloride
SEM	Scanning electron microscopy
SERDP	Strategic Environmental Restoration and Development Program
SON	Statement of Need
SPAC	Superfine Powdered Activated Carbon
SPE	Solid-phase extraction
SS	Sodium sulfate
SUVA	Specific Ultraviolet Absorbance
TFN	Tetrafluorodiphtalonitrile
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TL	Tripodal
TOC	Total organic carbon
TREN	Tris(2-aminoethyl)amine
US	United States
WA	Groundwater sample provided by anonymous community WA
XPS	X-ray photoelectron spectroscopy

KEYWORDS

Per- and polyfluoroalkyl substances (PFAS); novel adsorbents; cyclodextrins; covalent organic framework; aqueous film-forming foam (AFFF); ex situ groundwater remediation; packed-bed filtration process.

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Cyclopure, Inc. was also involved in this project as a small business participant. Cyclopure, Inc. contributed to the discovery of novel cyclodextrin polymer adsorbents, the scale-up of the synthesis procedures, and studies investigating adsorbent granulation, adsorbent durability, and adsorbent regeneration.

ABSTRACT

Introduction and Objectives: Aqueous film-forming foam (AFFF) formulations have been used for decades to suppress hydrocarbon fuel-based fires at United States (US) military facilities. Per- and polyfluoroalkyl substances (PFASs) are key constituents of AFFFs and their occurrence in groundwater at many of these facilities has been widely reported. Developing cost-effective remediation strategies to remove PFASs from groundwater remains an important challenge. The goal of this project was *to design, characterize, and evaluate the implementation of novel polymer adsorbents for the in situ or ex situ remediation of PFAS-contaminated groundwater*. The research objectives of the project were to: (1) discover polymer adsorbents with high affinity, high capacity, and rapid kinetics for priority and environmentally relevant PFASs; (2) characterize the performance of each polymer under scenarios relevant to groundwater remediation; and (3) transition towards the implementation of the new polymer adsorbents into remediation processes by optimizing synthesis pathways and evaluating adsorption process alternatives.

Technical Approach: The PIs have pioneered the development of cyclodextrin polymers (CDPs) as novel adsorbents for water purification. This project was structured around six scientific tasks: (1) develop new polymer adsorbents that maximize the adsorption kinetics, affinity, and capacity for priority PFASs; (2) characterize the uptake of diverse PFASs in laboratory experiments and from AFFF-impacted groundwater; (3) develop structure-activity relationships to understand and strengthen the non-covalent interactions by which promising polymer derivatives sequester PFASs; (4) optimize the synthesis of the most promising polymers to obtain useful morphologies and high yields to facilitate commercialization; (5) evaluate alternatives for ex situ adsorption-based remediation strategies with consideration for adsorbent regeneration and the handling of ancillary waste streams; and (6) develop covalent organic frameworks (COFs) with novel functional groups and translate the most effective functionalities into future generations of CDPs.

Results: Our research resulted in the synthesis of several notable CDP derivatives that exhibit enhanced uptake of PFASs and that were evaluated to explore adsorption kinetics, adsorption affinity, and adsorption inhibition under a variety of groundwater scenarios. Modeling studies have allowed us to identify physicochemical properties of CDPs that enhance their affinity for perfluoroalkyl acids. Importantly, we have learned that the chemistry of the crosslinker plays a large and unexpected role in determining the selectivity and affinity for PFASs. For example, only CDPs synthesized with crosslinkers that provide a positive surface charge exhibit rapid adsorption kinetics and high adsorption affinity for PFAS containing fewer than six carbon atoms. These observations suggest that the hydrophobic interior cavity of the cyclodextrins is accessible and a suitable binding site for more hydrophobic PFAAs, but that complementary electrostatic interactions are essential for enhancing the adsorption kinetics and adsorption affinity for less hydrophobic PFAAs. We have also discovered techniques to control particle size and morphology, demonstrated long-term mechanical and chemical durability of CDPs, and established facile regeneration and reuse procedures.

Benefits: This project provides remediation project managers and the scientific community with alternative adsorbents to implement in adsorption-based remediation processes. These novel polymer adsorbents have tailored affinity for various classes of PFASs, limited interactions with natural organic matter and other matrix constituents, and the potential for facile regeneration and reuse. These features address the most important deficiencies of conventional adsorbents and may lead to the development of more cost-effective adsorption-based remediation processes for AFFF-impacted groundwater.

EXECUTIVE SUMMARY

Introduction: Aqueous film-forming foam (AFFF) formulations have been used for decades to suppress hydrocarbon fuel-based fires at United States (US) military facilities during firefighter training exercises. PFASs are key constituents of AFFFs and include perfluoroalkyl sulfonic acids (PFSAAs), fluorotelomer sulfonic acids (FTSAs), perfluoroalkyl carboxylic acids (PFCAs), and other emerging classes of PFASs derived from electrochemical fluorination and fluorotelomer synthesis processes.^{1–4} Recent studies have reported on the occurrence of a wide variety of PFASs in groundwater samples collected from US military facilities.^{5–7} Whereas many PFASs are persistent in the environment and are known or expected to have negative health effects on exposed ecosystems or human populations,^{8,9} there is particular concern over the occurrence of PFOA and perfluorooctanesulfonate (PFOS) in groundwater. The US Environmental Protection Agency (EPA) assigned a health advisory level of 70 ng L⁻¹ for the combined concentration of PFOA and PFOS in drinking water,¹⁰ which is frequently exceeded in AFFF-impacted groundwater.⁷ Therefore, significant efforts have focused on developing cost-effective remediation strategies to remove PFASs from groundwater at US military facilities.

Many treatment technologies have been explored to remove PFASs from groundwater including adsorption,¹¹ advanced oxidation,¹² advanced reduction,¹³ biological treatment,¹⁴ nanofiltration,¹⁵ reverse osmosis,¹⁶ and thermal¹⁷ or nonthermal¹⁸ destruction. These methods remove PFASs from water with varying effectiveness, but each has well-documented drawbacks. For example, advanced oxidation processes generate toxic by-products from PFASs and other matrix constituents (*e.g.*, co-contaminants), and thermal destruction processes are expensive and energy intensive.^{19,20} As a result, granular activated carbon (GAC) adsorption has emerged as the most widely used approach to remediate PFAS-contaminated groundwater. GAC is an inexpensive and readily available material whose adsorption efficacy derives from its high surface area, nanostructured pores, and hydrophobic surfaces.²¹ Recent studies suggest that PFAS uptake by GAC is an intra-particle diffusion process controlled by the hydrophilic head group of the PFAS, the hydrophobicity of the PFAS, and the surface chemistry of the GAC.^{22–25} These properties make PFAS uptake on GAC rather selective, with longer-chain sulfonates exhibiting greater affinity for GAC than other types of PFASs. Additionally, GAC is readily fouled by natural organic matter (NOM) and co-contaminants (*e.g.*, petroleum hydrocarbons)²⁶ while activation and regeneration of spent GAC is expensive, energy-intensive, and slowly degrades the performance of the material relative to new GAC.²⁷ New adsorbents that address these deficiencies will lead to more efficient and cost-effective removal of PFASs during in situ or ex situ groundwater treatment.

We recently discovered a promising class of alternative adsorbents that remove organic contaminants from water with unprecedented speed and high capacity and can be regenerated without a loss in performance by washing with methanol or other alcohols at ambient temperature.^{28–30} These materials include the first high-surface area polymer of β -cyclodextrin (β -CD, **Figure 1**), which is a macrocycle comprised of seven glucose molecules. β -CD's cup-like shape provides a distinct hydrophobic interior cavity, which forms host-guest complexes with thousands of organic molecules. This property, as well as their inexpensive production from cornstarch,

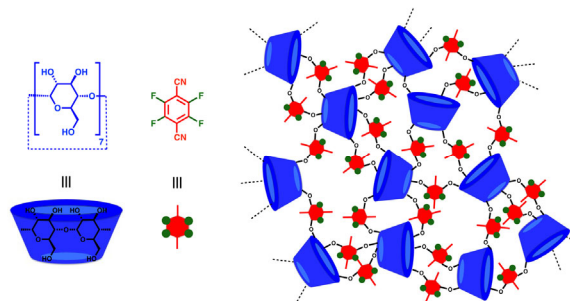


Figure 1: Schematic of the first high-surface area β -CD-containing porous polymer.

has led to insoluble β -CD polymers being explored as adsorbents for water purification. Many crosslinkers have been investigated including epichlorohydrin, polyfunctional carboxylic acids, and chitosan.^{31–35} Although these previous polymers retain well-defined β -CD binding sites, their low-surface areas result in slow adsorption kinetics, such that they perform worse than GAC.³⁶ Our β -CD polymer was derived from an aromatic crosslinker (tetrafluoroterephthalonitrile, TFN) to yield a new adsorbent that combines the desirable molecular recognition properties of cyclodextrins (CDs) with the high-surface area of GAC. Characterization studies have revealed nearly instantaneous uptake of dozens of contaminants of concern at trace concentrations ($1\ \mu\text{g L}^{-1}$) and without interference of NOM.

Preliminary data suggest modest uptake of PFASs (PFOA, PFOS, and perfluorobutanoic acid (PFBA)) by the TFN-crosslinked β -CD polymer (referred to throughout this report as TFN-CDP or P-CDP for porous cyclodextrin polymer) relative to other contaminants. However, varying the chemical nature of the aromatic crosslinker and the type of CDs incorporated into the polymer network provides nearly limitless opportunities to design new polymer adsorbents that target specific contaminants. For example, we designed a new polymer derivative with a decafluorobiphenyl (DFB) crosslinker that completely removes PFOA from water under a variety of scenarios.³⁰ Additionally, PFOA was recovered from the DFB-crosslinked β -CD polymer (DFB-CDP) by rinsing with methanol at room temperature and the polymer was subjected to several adsorption and regeneration cycles with no apparent performance loss. These data provide an excellent example of the rational design of β -CD polymer adsorbents for enhanced specificity for target contaminants.

Objectives: The discovery of P-CDP and DFB-CDP represented an exciting breakthrough for polymer adsorbents used for water treatment. However, there remained opportunities to optimize the affinity of polymer adsorbents for PFASs and to further their development towards practical implementation in engineered processes. The goal of our project was *to design, characterize, and evaluate the implementation of novel polymer adsorbents for the in situ or ex situ remediation of PFAS-contaminated groundwater*. We addressed some of the major deficiencies of contemporary adsorption-based processes including their insufficient affinity for shorter-chain and more hydrophilic PFASs, the propensity for fouling by natural organic matter and other matrix constituents, and costs associated with the regeneration of spent adsorbents. The research objectives of the project were to:

1. Discover polymer adsorbents with high affinity, high capacity, and rapid kinetics for environmentally relevant PFASs using a hypothesis-driven, rational design approach;
2. Characterize the performance of each polymer under scenarios relevant to groundwater remediation to (i) inform polymer development, (ii) elucidate adsorption mechanisms, and (iii) estimate parameters to be used for process design; and
3. Transition towards the implementation of the new polymer adsorbents into in situ or ex situ remediation processes by (i) optimizing synthesis pathways and (ii) evaluating adsorption process alternatives that maximize performance and minimize the life-cycle costs.

Technical Approach: To meet goal of our project, the research plan was divided into six research Tasks that address the technical objectives: (1) develop new polymer adsorbents that maximize the adsorption kinetics, affinity, and capacity for priority PFASs; (2) characterize the uptake of diverse PFASs in laboratory experiments and from AFFF-impacted groundwater; (3) develop structure-activity relationships to understand and strengthen the non-covalent interactions by which promising polymer derivatives sequester PFASs; (4) optimize the synthesis of the most promising

polymers to obtain useful morphologies and high yields to facilitate commercialization; (5) evaluate alternatives for ex situ adsorption-based remediation strategies with consideration for adsorbent regeneration and the handling of ancillary waste streams; and (6) develop covalent organic frameworks (COFs) with novel functional groups and translate the most effective functionalities into future generations of CDPs.

Results and Discussion: *The first set of results* described in Section 4.1 of this report detail the rational design and characterization of new cyclodextrin (CD)-based polymer adsorbents. We first aimed to develop porous derivatives of DFB-CDP as a means to improve its PFAS uptake performance. We performed the DFB-CDP synthesis reaction under a variety of conditions, and managed to synthesize DFB-CDP with varying degrees of porosity. However, our characterization studies performed with these derivatives suggest that porosity is not the primary driver of adsorbent performance. Rather, the surface charge of the adsorbent plays a more important role. We performed model studies between DFB and *n*-butanol to investigate competition between the desired etherification reaction and the putative side reaction that imparts phenolate functional groups into the crosslinker. We identified a way to synthesize polymers with varying degrees of phenolation, and demonstrated that the performance of the DFB-CDP for removing anionic PFASs is determined by the magnitude of the negative surface charge of the adsorbent, not its porosity.

We next aimed to develop CDPs that target short-chain PFASs. We developed a post-synthetic process to reduce the nitrile groups in TFN-CDP to primary amines, which results in a polymer with a positive surface charge (referred to throughout this report as amine-CDP). The amine-CDP exhibits high affinity for anionic PFASs, including short-chain anionic PFASs such as perfluorobutanoic acid (PFBA) and perfluorosulfonate (PFBS). Kinetic studies of the removal of 10 anionic PFASs at environmentally relevant concentrations showed 80–98 % removal of all PFAS after 30 minutes of contact time. This performance was superior to commercial activated carbon. Our findings demonstrate the scope and tunability of CD-based adsorbents derived from a single polymerization and the promise of novel adsorbents constructed from molecular receptors.

We next developed CDPs crosslinked with tripodal crosslinkers containing three amino or amido groups to further study the influence of surface charge (amino groups will be protonated whereas the amido groups will not). CDPs containing amines showed superior removal for ten anionic PFASs compared to CDPs containing amido groups. The amine-functionalized CDP had outstanding affinity and capacity for GenX, underscoring the essential role of electrostatic interactions for removing short-chain and branched PFAS. The amine-containing CDP also exhibited 100-fold higher affinity and twice the capacity for PFOA compared to GenX, which are the highest reported values for CDPs. These results highlight the synergistic effects of electrostatic interactions and host-guest interactions in CDPs as important design criteria for efficient removal of anionic PFAS from water. This study further demonstrates the broad tunability of CDPs and their promise as adsorbents for PFAS remediation.

We finally aimed to develop a CDP platform that yields a modular structure that is more amenable to rigorous investigation and modification. We developed a CDP platform in which styrene groups are covalently attached to β -cyclodextrin to form a discrete monomer amenable to radical polymerization. A β -cyclodextrin polymer copolymerized with a methacrylic monomer bearing a cationic functional group achieved nearly 100% removal for eight PFASs at an unprecedented low adsorbent loading of 1 mg L⁻¹. Furthermore, when the adsorbents were studied in a salt matrix, we observed a complementary interplay of hydrophobic and electrostatic interactions for long-chain PFAS adsorption whereas short-chain PFAS primarily relied on electrostatic interaction as the

mode of adsorption. These materials exhibited great promise for the removal of anionic PFAS from water.

The next set of results described in Section 4.2 of this report detail our synthesis of covalent organic frameworks (COFs) with novel functionalities. COFs are unexplored yet promising adsorbents because of their high surface area and tunable pore sizes. We first demonstrated that imine-linked two-dimensional (2D) COFs bearing primary amines adsorb GenX rapidly under environmentally relevant concentrations. COFs with partial amine incorporation showed the highest capacity and fastest removal, suggesting that the synergistic combination of the polar group and hydrophobic surfaces are responsible for GenX binding. A COF with 28% amine loading also removed more than 90% of 12 out of 13 PFASs. These results demonstrate the promise of COFs for PFAS removal and suggest design criteria for maximizing adsorbent performance.

We then synthesized a COF with neutral chains in the pores that could be post-functionalized into zwitterionic chains. We hypothesized that the resulting zwitterionic COF will exhibit high affinity for a variety of per- and polyfluoroalkyl substances (PFASs) including anionic, zwitterionic, and neutral PFASs. The most promising approach that we developed involves the synthesis of a neutral dialkylamine-appended terephthalaldehyde monomer from which the COF is assembled. We synthesized COFs with this monomer, and the high-surface area neutral COFs were then post-functionalized through reactions between the dialkylamine chains and 1,3-propane sultone to create the zwitterionic COFs. We have performed kinetics and equilibrium studies with these COF materials to evaluate their performance for removing a diverse set of PFASs. Our results suggest that this COF material does not perform as well as expected for PFAS removal. The likely reasons are crowding of pores at higher loadings of the zwitterionic chains and/or limited crystallinity of the resulting COFs.

In Section 4.3 of this report, we describe the selection of four of the most promising CDP derivatives for more rigorous evaluation. The four CDPs that were selected include the original porous cyclodextrin polymer (TFN-CDP or P-CDP), the first cyclodextrin polymer that we synthesized that exhibited a positive surface charge (amine-CDP), a functionalized version of the P-CDP that results in a strongly positive surface charge (CDP⁺ or DEXSORB⁺), and a functionalized polymer of cyclodextrin crosslinked with methylene diphenyl diisocyanate (M⁺). Subsequent sections of this report mostly focus on deeper investigations with these four CDPs.

The next set of results described in Section 4.4 of this report detail our evaluations of CDPs as adsorbents under environmentally relevant scenarios. We first aimed to identify the key environmental factors that influence the adsorption of anionic PFASs on activated carbon and CDPs. Batch adsorption experiments were conducted to evaluate the removal of 20 target PFASs at environmentally relevant concentrations by three different activated carbon materials and amine-CDP and CDP⁺. Experiments were conducted in Milli-Q water and in groundwater. Major physical properties of the adsorbents were measured, along with general water chemistry parameters for each groundwater sample. The distinct performances of ACs and CDPs were attributed to their different surface chemistry and the distinct nature of their adsorption binding sites. pH and the concentration of cations were the primary contributors to adsorption inhibition in groundwater. Higher pH values limit anionic PFAS adsorption by deprotonating the functional groups on adsorbent surfaces. The elevated levels of cations in some groundwater samples limited the effects of attractive electrostatic interactions. Knowledge of PFAS adsorption mechanisms gained here can be used to design more efficient adsorbents and to predict their performance under a range of environmental scenarios.

We then explored the potential for CDPs and ion exchange resins to remove different types of PFASs from water. We evaluated the performance of P-CDP, amine-CDP, and CDP+ alongside an anion exchange resin and a cation exchange resin for the removal of anionic, zwitterionic, and non-ionic PFASs from water. We found that P-CDP rapidly removes all zwitterionic PFASs with log K_D values ranging between 2.4 and 3.1, and the cation exchange resin rapidly removes two zwitterionic PFASs with log K_D values of 1.8 and 1.9. amine-CDP and CDP+ rapidly remove all anionic PFASs with log K_D values between 2.7 and 4.1, and the anion exchange resin slowly removes all anionic PFASs with log K_D values between 2.0 and 2.3. All adsorbents exhibited variable removal of the non-ionic PFASs and some adsorption inhibition at higher pH values and in the presence of groundwater matrix constituents. These findings provide insight on how adsorbents can be combined to remediate groundwater contaminated with complex mixtures of different types of PFASs.

We finally evaluated the performance of CDPs in an AFFF-contaminated groundwater sample collected from a US military facility. We used high-resolution mass spectrometry to identify 68 unique PFASs in a groundwater sample. We then performed batch experiments with activated carbon, an anion exchange resin, and P-CDP, CDP+, and M+ to evaluate their potential to remove the 68 PFASs from the groundwater. We found that each adsorbent exhibits a different removal pattern among the 68 PFASs. The activated carbon is the most non-selective adsorbent, but has relatively slow adsorption kinetics. The CDPs exhibit rapid adsorption kinetics and are more selective than AC, performing better in removing PFAS classes that are complementary to their surface charge. Analysis of the complete dataset revealed that adsorption of some PFAS classes can be associated with increasing length of the perfluorinated tail, while adsorption of other classes is more strongly related to properties of the head group.

The next set of results described in Section 4.5 of this report detail our analysis of the performance of all CDPs that were synthesized as part of this project. Our goal was to use multivariate analyses to identify the physicochemical properties of CDPs that results in enhanced performance. We investigated the adsorption performance of 34 CDPs which consist of 14 different crosslinkers and exhibit a wide range of physicochemical properties. The performance metrics included adsorption kinetics, equilibrium adsorption density, and adsorption affinity for six perfluoroalkylacids (PFAAs). We then used complementary bivariate and multivariate analyses to discover relationships between sixteen measurable physicochemical properties of the CDPs and their performance as adsorbents. We found that: (1) CDPs with a less negative or more positive surface charge will exhibit enhanced adsorption of all types of PFAAs; (2) CDPs with greater porosity and surface area will exhibit enhanced adsorption kinetics for all types of PFAAs; (3) CDPs with greater crosslinker content will exhibit enhanced adsorption of short-chain PFAAs; (4) CDPs containing more hydrophobic crosslinkers will exhibit enhanced equilibrium adsorption density and adsorption affinity for longer-chain PFAAs; and (5) CDPs with smaller particle sizes will exhibit enhanced adsorption kinetics and equilibrium adsorption density for all PFAAs. These insights inform the further development of CDPs to optimize their performance for removing PFAAs during groundwater remediation.

The next set of results described in Section 4.6 of this report detail our efforts to develop techniques to control the morphology and particle size of cyclodextrin-based adsorbents. We optimized polymerization conditions to yield CDP+ in quantities of 2.2 kg in a single batch. However, the as-obtained CDP+ is an insoluble powder with irregular particle sizes on the order of tens of microns (60–80 μm). The ability to control particle size and morphology provides maximum flexibility for incorporating CDP+ into engineered systems for PFAS removal. We therefore

developed spray granulation techniques to control the particle size and morphology of CDP+. For this technique, CDP+ powder is stirred under high shear while a binder solution is sprayed onto the powder to wet the powder surface and enable aggregation of the smaller particles. Two candidate binders were selected: (1) cellulose acetate (trade name: EastmanTM CA-398-3); and (2) acrylic resins (trade name: ELVACITE[®] 2016). Both binders are used in food-packaging applications and are regarded as safe by the FDA, are insoluble in water and alcoholic solvents, and are soluble in acetone which is an easy-to-remove solvent. Our optimized spray granulation procedure yields CDP+ granules with a porous morphology and a narrow particle size distribution ranging up to 1 mm in diameter. The performance of the granulated form of CDP+ is comparable to the performance of the as-synthesized CDP+ powder, demonstrating the efficacy of spray granulation both in terms of PFAS performance and industrial scalability.

The next set of results described in Section 4.7 of this report detail our evaluation of the regeneration potential of CDPs and the selection of optimal regeneration protocols for both powdered P-CDP and CDP+ ELVACITE granules. We support our selections with data comparing the recovery of adsorbates from P-CDP using different regeneration solutions and reuse of CDP+ ELVACITE after regeneration with an optimal regeneration solution. We identified methanol and ethanol as viable solvents for the regeneration of CDPs, identified appropriate amendments for the regeneration of CDPs with negative surface charge (CaCl_2) and positive surface charge (ammonium acetate, NH_4OAc), demonstrated that the ELVACITE binder does not inhibit regeneration, and demonstrated that the performance of P-CDP and CDP+ ELVACITE is not affected by the regeneration protocol. As a result of these studies, we have demonstrated that different CDPs in different forms (*i.e.*, as-synthesized powder and granules) exhibit facile regeneration and reuse potential.

The next set of results described in Section 4.8 of this report detail the durability of CDPs. We have assessed the long-term durability of CDPs using three metrics: (1) long-term PFAS removal performance; (2) long-term mechanical strength; and (3) the leaching of byproducts from the adsorbent. The long-term PFAS removal performance and mechanical strength of CDPs have been demonstrated in a number of pilot-scale column studies. In these pilot-scale column studies (some of which have been run for more than 6 months), we generally observe contaminant breakthrough curves that match those observed in laboratory-scale column studies performed over a much shorter duration; this demonstrates that the long-term performance of CDPs matches the short-term performance observed in the laboratory and provides some evidence that performance is durable over time and under real operating conditions. We also measure the pressure drop through the pilot-scale columns during these studies. We generally observe constant pressure drop through the pilot-scale columns over the period of operation; we interpret this as evidence of mechanical stability, because less mechanically stable CDPs could break down over time and create pressure increases as pores are blocked with fragments of adsorbent particles. Perhaps most importantly, results from this project demonstrated that no byproducts are leaching from CDPs over time. This has been established through completion of the NSF/ANSI 61 certification process. This certification is a mandatory requirement for media for intended use in drinking water treatment processes. The results of certification tests demonstrate that no leaching of hazardous chemicals or synthesis byproducts occurs when CDPs are implemented in simulated drinking water treatment processes. As a result of these studies, we have demonstrated that different CDPs in different forms (*i.e.*, as-synthesized powder and granules) exhibit long-term durability.

The last set of results described in Section 4.9 of this report detail process evaluations with the CDP+ granules. We evaluated the performance of CDP+ granules that range in particle size (d_p =

84-718 μm) in batch studies to evaluate the adsorption kinetics, adsorption capacity, and adsorption affinity for six perfluoroalkyl acids (PFAAs). We also conduct rapid small-scale column tests (RSSCTs) for three of the granules ($d_p = 84, 175, 359 \mu\text{m}$) to evaluate the breakthrough of PFAAs and whether the breakthrough can be predicted based on assumptions of constant or proportional diffusivity as a function of granule size. We found that the smaller CDP granules exhibited more rapid adsorption kinetics for shorter-chain PFAAs, whereas larger CDP granules exhibited more rapid adsorption kinetics for longer-chain PFAAs. Adsorption capacity was more dependent on the PFAA than the granule size, with the granules exhibiting capacity for 2-3 times as many moles of PFBA than other PFAAs. Increases in adsorption affinity correlated with PFAAs of increasing hydrophobicity, with PFHxS and PFOS exhibiting the highest adsorption affinity. For the RSSCTs, we found that CDP granules of different size appear to exhibit different mechanisms of mass transfer and we observed that long- and short-chain PFAS exhibit varying extents of diffusion. Therefore, development of a single RSSCT experiment was not possible and our results provide a range of possible outcomes for PFAS breakthrough from column experiments. Overall, these findings provide insight to understanding the performance of CDP granules in batch and packed-bed filtration systems.

Implications for Future Research and Benefits: This project provides remediation project managers and the scientific community with alternative adsorbents to implement in adsorption-based remediation processes. These novel polymer adsorbents have tailored affinity for various classes of PFASs, exhibit limited interactions with natural organic matter and other matrix constituents, are available in granular forms, and have the potential for facile regeneration and reuse. These features address the most important deficiencies of conventional adsorbents and may lead to the development of more cost-effective adsorption-based remediation processes for AFFF-impacted groundwater.

1.0 OBJECTIVES

The objective of Statement of Need (SON) Number ERSON-18-C2 was to develop cost-effective in situ or ex situ remedial technologies for groundwater contaminated with per- and polyfluoroalkyl substances (PFASs) resulting from the use of aqueous film-forming foam formulations by the Department of Defense (DoD). The PIs have pioneered the development of cyclodextrin polymers (CDPs) as novel adsorbents for water purification. Prior to the start of this project, the PIs had discovered a porous cyclodextrin polymer (P-CDP) that exhibited nearly instantaneous uptake of dozens of contaminants of concern from water at trace concentrations ($1 \mu\text{g L}^{-1}$) and without interference of natural organic matter but with limited uptake of PFASs. A second CDP derivative crosslinked with decafluorobiphenyl (DFB-CDP) exhibited complete uptake of PFOA from water at trace concentrations ($1 \mu\text{g L}^{-1}$) and under a variety of environmentally relevant scenarios. The discovery of P-CDP and DFB-CDP represented an exciting breakthrough for polymer adsorbents used for water treatment. However, there remained opportunities to optimize the affinity of polymer adsorbents for PFASs and to further their development towards practical implementation in engineered processes.

The overarching goal of this project was *to design, characterize, and evaluate the implementation of novel polymer adsorbents for the in situ or ex situ remediation of PFAS-contaminated groundwater*. We addressed some of the major deficiencies of contemporary adsorption-based processes including their insufficient affinity for shorter-chain and more hydrophilic PFASs, the propensity for fouling by natural organic matter and other matrix constituents, and costs associated with the regeneration of spent adsorbents. The research objectives of the project were to:

1. Discover polymer adsorbents with high affinity, high capacity, and rapid kinetics for priority and environmentally relevant PFASs using a hypothesis-driven, rational design approach;
2. Characterize the performance of each polymer under scenarios relevant to groundwater remediation to (i) inform polymer development, (ii) elucidate adsorption mechanisms, and (iii) estimate parameters to be used for process design; and
3. Transition towards the implementation of the new polymer adsorbents into in situ or ex situ remediation processes by (i) optimizing synthesis pathways and (ii) evaluating adsorption process alternatives that maximize performance and minimize the life-cycle costs.

2.0 BACKGROUND

Aqueous film-forming foam (AFFF) formulations have been used for decades to suppress hydrocarbon fuel-based fires at United States (US) military facilities during firefighter training exercises. PFASs are key constituents of AFFFs and include perfluoroalkyl sulfonic acids (PFSAAs), fluorotelomer sulfonic acids (FTSAs), perfluoroalkyl carboxylic acids (PFCAs), and other emerging classes of PFASs derived from electrochemical fluorination and fluorotelomer synthesis processes.¹⁻⁴ Recent studies have reported on the occurrence of a wide variety of PFASs in groundwater samples collected from US military facilities.⁵⁻⁷ Whereas many PFASs are persistent in the environment and are known or expected to have negative health effects on exposed ecosystems or human populations,^{8,9} there is particular concern over the occurrence of PFOA and perfluorooctanesulfonate (PFOS) in groundwater. The US Environmental Protection Agency (EPA) assigned a health advisory level of 70 ng L⁻¹ for the combined concentration of PFOA and PFOS in drinking water,¹⁰ which is frequently exceeded in AFFF-impacted groundwater.⁷ Therefore, significant efforts have focused on developing cost-effective remediation strategies to remove PFASs from groundwater at US military facilities.

2.1 Potential PFAS Treatment Technologies

Many treatment technologies have been explored to remove PFASs from groundwater including adsorption,¹¹ advanced oxidation,¹² advanced reduction,¹³ biological treatment,¹⁴ nanofiltration,¹⁵ reverse osmosis,¹⁶ and thermal¹⁷ or nonthermal¹⁸ destruction. These methods remove PFASs from water with varying effectiveness, but each has well-documented drawbacks. For example, advanced oxidation processes generate toxic by-products from PFASs and other matrix constituents (*e.g.*, co-contaminants), and thermal destruction processes are expensive and energy intensive.^{19,20} As a result, granular activated carbon (GAC) adsorption has emerged as the most widely used approach to remediate PFAS-contaminated groundwater. GAC is an inexpensive and readily available material whose adsorption efficacy derives from its high surface area, nanostructured pores, and hydrophobic surfaces.²¹ Recent studies suggest that PFAS uptake by GAC is an intra-particle diffusion process controlled by the hydrophilic head group of the PFAS, the hydrophobicity of the PFAS, and the surface chemistry of the GAC.²²⁻²⁵ These properties make PFAS uptake on GAC rather selective, with longer chain sulfonates exhibiting greater affinity for GAC than other types of PFASs. Additionally, GAC is readily fouled by natural organic matter (NOM) and co-contaminants (*e.g.*, petroleum hydrocarbons)²⁶ while activation and regeneration of spent GAC is expensive, energy-intensive, and slowly degrades the performance of the material relative to new GAC.²⁷ New adsorbents that address these deficiencies will lead to more efficient and cost-effective removal of PFASs during in situ or ex situ groundwater treatment.

2.2 Cyclodextrin Polymers (CDPs) as Novel Adsorbents

The PIs recently discovered a promising class of alternative adsorbents that remove organic contaminants from water with unprecedented speed and high capacity and can be regenerated without a loss in performance by washing with methanol or other alcohols at ambient temperature.²⁸⁻³⁰ These materials include the first high-surface area polymer of β -cyclodextrin (β -CD, **Figure 1**), which is a macrocycle comprised of seven glucose

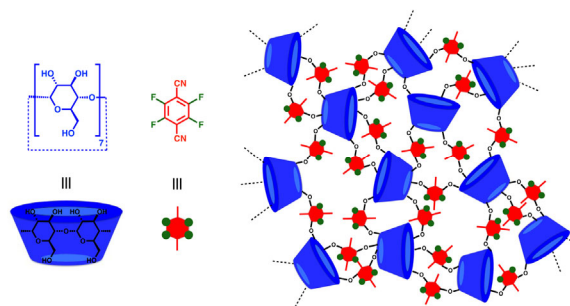


Figure 1: Schematic of the first high-surface area β -CD-containing porous polymer.

molecules. β -CD's cup-like shape provides a distinct hydrophobic interior cavity, which forms host-guest complexes with thousands of organic molecules. This property, as well as their inexpensive production from cornstarch, has led to insoluble β -CD polymers being explored as adsorbents for water purification. Many crosslinkers have been investigated including epichlorohydrin, polyfunctional carboxylic acids, and chitosan.^{31–35} Although these previous polymers retain well-defined β -CD binding sites, their low-surface areas result in slow adsorption kinetics, such that they perform worse than GAC.³⁶

2.2.1 Tetrafluoroterephthalonitrile-crosslinked CDPs (TFN-CDP or P-CDP)

Our first β -CD polymer was derived from an aromatic crosslinker (tetrafluoroterephthalonitrile, TFN) to yield a new adsorbent that combines the desirable molecular recognition properties of cyclodextrins (CDs) with the high-surface area of GAC. Our TFN-crosslinked β -CD polymer (referred to throughout this report as TFN-CDP or P-CDP for porous cyclodextrin polymer) combines the desirable molecular recognition properties of CDs with the high-surface area of GAC, yielding a broad-spectrum adsorbent for organic molecules with superior adsorption kinetics and high adsorption capacity. For example, P-CDP removes bisphenol A (BPA), a known endocrine disruptor, from water more rapidly than equivalent masses of a range of contemporary adsorbents (**Figure 2**) including a high-end activated carbon (Norit RO), the mixed charcoal/zeolite adsorbents used in Brita filters, granular activated carbon, and a low-surface area cross-linked β -CD polymer (Epi-CD polymer).²⁹ This performance difference is substantial: our polymer exhibits a 2nd order rate constant for BPA removal of $1.5 \text{ g mg}^{-1} \text{ min}^{-1}$, which is 100-1000 times higher than the other adsorbents.²⁹ Furthermore, the specific adsorption capacity for BPA uptake on P-CDP at equilibrium is 0.33 mg m^{-2} , which is greater than the highest reported values for BPA uptake on GAC.³⁷ Also, in contrast to the energy intensive and degradative regeneration processes of GAC, the bound BPA is easily removed by rinsing P-CDP with methanol at room temperature. The regenerated adsorbent exhibits similar performance to the as-synthesized polymer for at least five cycles.²⁹ These features of P-CDP may contribute to significant energy savings because less adsorbent is needed to achieve similar pollutant uptake rates and because the adsorbent that is used can be regenerated using a facile, low temperature process.

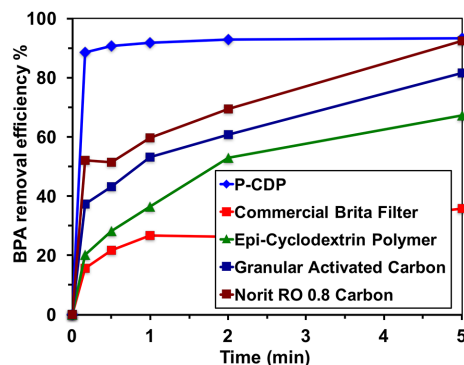


Figure 2: Schematic of Bisphenol A (BPA) uptake as a function of time for P-CDP (blue) and other conventional adsorbents.

The performance difference between P-CDP and GAC is not restricted to kinetics observations made in batch reactors. The instantaneous removal of a diverse set of contaminants of concern (CoCs) from water was evaluated by passing a mixture of 83 CoCs at individual concentrations of $1 \mu\text{g L}^{-1}$ through a thin layer of either P-CDP or GAC immobilized on the surface of a non-adsorbent membrane.²⁸ The P-CDP instantaneously and completely (greater than 90%) removed 32 of the CoCs in these filtration-type experiments whereas the GAC completely removed only one of the CoCs under identical conditions.²⁸ Further, the performance of the P-CDP was unaffected by the presence of NOM (dosed as 20 mg L^{-1} of humic acid), whereas NOM significantly interfered with the adsorption of the CoCs on GAC (**Figure 3**).²⁸ These data further demonstrate the significant performance advantages of β -CD polymers over GAC adsorbents, particularly under environmentally-relevant scenarios. The nearly instantaneous uptake of a variety of CoCs on P-CDP suggests that adsorption is not a diffusion-limited process and that the

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well-defined binding sites of β -CD are instantaneously accessible to adsorbates with varying affinities. Tailoring the chemistry of the binding sites is expected to result in the specific uptake of target adsorbates with high affinity. Additionally, the performance of P-CDP in the presence of NOM demonstrates that the cup-like shape of the β -CD monomer precludes binding with larger organic molecules, presumably due to a size-exclusion mechanism; size-based adsorption selectivity has also been reported for other types of CD-based adsorbent materials.^{38,39} This is an exciting feature of β -CD polymers developed as adsorbents because large NOM molecules in groundwater matrices will not bind to and foul the β -CD polymer, which will significantly extend the lifetime of the adsorbent relative to GAC.

2.2.2 Decafluorobiphenyl-crosslinked CDPs (DFB-CDP)

The above results demonstrate that porous CD polymers show tremendous promise for outperforming GAC for the removal of CoCs from water in the presence of NOM and for exhibiting facile regeneration and reuse potential. Another advantage of these materials is that they have a well-defined chemical composition, such that their performance and selectivity can be varied rationally through the choice of cyclodextrin monomer (*e.g.*, α -CD or β -CD) and crosslinker (hundreds of possibilities). Showcasing the power of this flexible approach, we recently modified the design of P-CDP, which exhibits only moderate removal of PFASs, to obtain a new CD polymer that shows unprecedented affinity for PFOA (**Figure 4**).³⁰ We hypothesized that a β -CD polymer with perfluoroarene cross-linkers would bind PFASs more effectively and tested this hypothesis using heavily fluorinated aromatic crosslinkers, including decafluorobiphenyl (DFB). As shown in **Figure 5**, the DFB-CDP removes PFOA to <10 ng L⁻¹ (our limit of quantification) with excellent kinetics, comparable capacity to GAC, and the ability to be easily regenerated. These findings show promise for treating PFOA-contaminated water and demonstrate that the selectivity of β -CD polymers can be tailored to target pollutants of interest.

The nucleophilic substitution of DFB by β -CD provided the crosslinked polymer network DFB-CDP in a single step. FTIR spectroscopy of DFB-CDP indicated the presence of DFB and β -CD moieties in the polymer.³⁰ Although it is difficult to determine the regiochemistry of the ether linkages formed during the polymerization of DFB-CDP spectroscopically, model reactions of DFB under similar conditions to the polymerization suggest that the DFB-CDP polymer contains the expected fluorinated biphenyls, which are primarily 4-substituted or 4,4'-disubstituted by

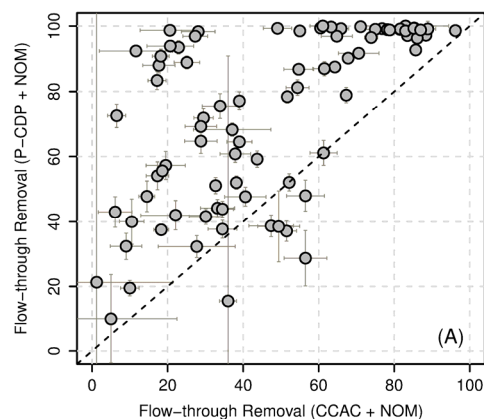


Figure 3: Instantaneous removal of a mixture of 83 CoCs by equivalent masses of P-CDP and GAC (given as CCAC in the x-axis) in the presence of NOM. Error bars represent standard deviation of five replicate experiments.

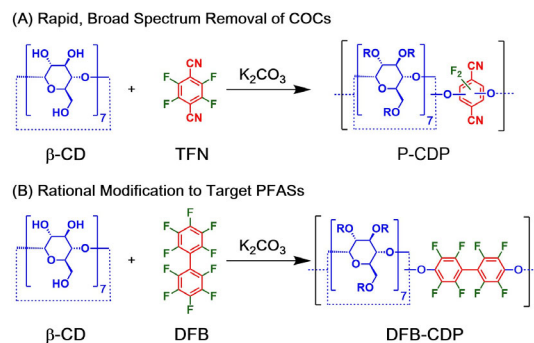


Figure 4: Schematic of the synthesis pathway of (A) the first high-surface area β -CD-containing porous polymer and (B) the first rationally modified β -CD-containing porous polymer that targets PFASs.

alkoxy groups. These observations, combined with elemental analysis (C, H, N, F), confirmed the formation of the DFB-CDP polymer network. It is important to note that the aromatic crosslinkers containing residual organofluorine used in the development of the P-CDP and DFB-CDP are incorporated into the polymer through robust ether bonds, making it unlikely that the resulting polymer will breakdown or that these groups will be released during water treatment. Nevertheless, the complete hydrodehalogenation of polyfluorinated arenes under mild catalytic conditions has been reported,⁴⁰ making the fluorinated aromatic crosslinkers used in the P-CDP and DFB-CDP of much less concern than aliphatic PFASs.

The optimal composition of DFB-CDP for PFOA removal was determined by conducting the polymerization using DFB:β-CD molar feed ratios ranging from 3 to 7. The polymers from polymerizations with increased [DFB] showed increased residual fluorine content, as determined by elemental analysis, corresponding to larger amounts of fluorinated biphenyl groups in the polymer. The optimal composition of DFB-CDP for PFOA removal was determined to arise from a DFB:β-CD molar feed ratio of 3. This composition resulted in a 24.33 wt% fluorine content which corresponds to a DFB:β-CD ratio in the polymer of 3.4, assuming di-substitution of all DFB groups. This estimate is a reasonable upper bound given that it does not account for the partial incorporation of mono-substituted DFB groups. In contrast to the permanent porosity and high surface area of P-CDP, the DFB-CDP derivatives prepared under these conditions were non-porous, with Brunauer-Emmett-Teller surface areas (S_{BET}) $<10 \text{ m}^2 \text{ g}^{-1}$. Nevertheless, the DFB-CDP still exhibited unprecedentedly rapid kinetics that could improve further as we optimize the polymerization to target permanently porous derivatives with high PFAS binding affinities.

DFB-CDP rapidly removes PFOA from water in batch experiments at both low and high PFOA concentrations (**Figure 5**).³⁰ Low concentration experiments were conducted using $[\text{PFOA}]_0$ of $1 \mu\text{g L}^{-1}$ and $[\text{DFB-CDP}]$ of 10 mg L^{-1} , and PFOA was completely removed in approximately 10 hours. Experiments were also conducted using $[\text{PFOA}]_0$ of $200 \mu\text{g L}^{-1}$ and $[\text{DFB-CDP}]$ of 400 mg L^{-1} , which resulted in complete PFOA removal within 2 hours.³⁰ The rates of adsorption at both low and high $[\text{PFOA}]_0$ were best described by Ho and McKay's pseudo second-order adsorption model,⁴¹ which provides a figure-of-merit for how quickly an adsorbent reaches equilibrium with a particular adsorbate. The pseudo second-order rate constant (k_{obs}) for PFOA removal was estimated as $2.1 \text{ g mg}^{-1} \text{ h}^{-1}$ for low concentration experiments and $53 \text{ g mg}^{-1} \text{ h}^{-1}$ for high concentration experiments.³⁰ Many k_{obs} values have been reported for PFOA uptake by conventional adsorbents under a variety of experimental conditions. For example, typical values of k_{obs} for GAC fall between $0.1\text{--}0.001 \text{ g mg}^{-1} \text{ h}^{-1}$ depending on the type of GAC and the experimental conditions (e.g., concentrations, pH).^{42–45} PACs have significantly improved kinetics relative to GAC, with k_{obs} values reported between $0.1\text{--}21 \text{ g mg}^{-1} \text{ h}^{-1}$,^{42,46–48} although the values at the high end of the range are measured at elevated adsorbent ($\geq 1 \text{ g L}^{-1}$) and $[\text{PFOA}]_0$ ($\geq 1 \text{ mg L}^{-1}$) doses. The k_{obs} of DFB-CDP measured under more demanding conditions is much higher than that of GAC and generally exceeds that of

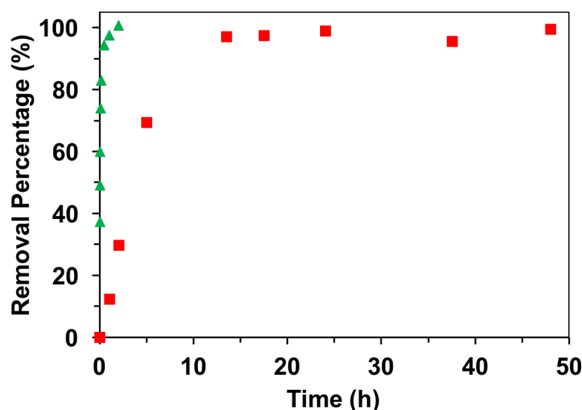


Figure 5: Time-dependent PFOA adsorption by DFB-CDP at low concentration (red squares, $[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$; $[\text{DFB-CDP}] = 10 \text{ mg L}^{-1}$) and high concentration (green triangles, $[\text{PFOA}]_0 = 200 \mu\text{g L}^{-1}$; $[\text{DFB-CDP}] = 400 \text{ mg L}^{-1}$).

PAC. These data confirm that the kinetics of the as-synthesized DFB-CDP already provide significant performance advantages for PFOA removal over GAC. Based on these data, we expect that reasonable amounts of the DFB-CDP can reduce the concentration of PFOA from its typical concentration in contaminated groundwater to concentrations well below the recent EPA health advisory level of 70 ng L^{-1} .

We attribute much of the DFB-CDP's desirable adsorption kinetics to its accessible binding sites with superior PFOA affinity relative to other adsorbents. A PFOA binding isotherm (**Figure 6**) was constructed using [DFB-CDP] of 100 mg L^{-1} and $[\text{PFOA}]_0$ ranging from $1\text{--}12 \text{ mg L}^{-1}$.³⁰ Fitting the Langmuir model to the isotherm provides an affinity constant (K_L) of $2.2 \times 10^5 \text{ M}^{-1}$,³⁰ which is an order of magnitude greater than the K_L of $1.8 \times 10^4 \text{ M}^{-1}$ measured for GAC and 2.5 times higher than that reported for PAC⁴². This value also exceeds those of other adsorbents, such as ion-exchange resins⁴² and a recent triazine-linked polymer,⁴⁹ which explains DFB-CDP's superior removal of PFOA at environmentally relevant concentrations. Based on the Langmuir fit, the estimated capacity of the DFB-CDP polymer is 33 mg g^{-1} ,³⁰ which is within the range of that reported for GAC (53 mg g^{-1}).²⁵ Although both the Langmuir and Freundlich models fit the adsorption isotherm well, the Freundlich model may be more appropriate to describe equilibrium adsorption under these conditions because saturation behavior is not observed over this concentration range and because PFOA is known to form 1:1 and 1:2 complexes with β -CD,^{50,51} and multilayer binding of PFOA has been reported for certain adsorbents.⁴⁶ Based on these considerations, the estimated capacity of the DFB-CDP polymer reported here should be interpreted as conservative. The high affinity of DFB-CDP for PFOA also allows it to remove PFOA to lower equilibrium concentrations than other adsorbents on an equivalent mass basis (**Figure 7**). We compared its equilibrium removal efficiency to P-CDP ($S_{\text{BET}} = 240 \text{ m}^2 \text{ g}^{-1}$), which rapidly removes many CoCs as described in the preceding,^{28,29} and sieved coconut shell granular activated carbon (CCAC, $S_{\text{BET}} = 1085 \text{ m}^2 \text{ g}^{-1}$)³⁰. The equilibrium PFOA removal was evaluated using $[\text{PFOA}]_0$ of $1 \mu\text{g L}^{-1}$ and [adsorbent] of 10 mg L^{-1} . DFB-CDP lowered the concentration of the residual PFOA to below our limit of quantification (10 ng L^{-1}) at equilibrium, whereas CCAC and P-CDP removed only 56.3% and around 0% of the PFOA, respectively.³⁰

As was observed for P-CDP loaded with model organic compounds,²⁹ PFOA-contaminated DFB-CDP shows promise for facile regeneration (**Figure 8**). Four

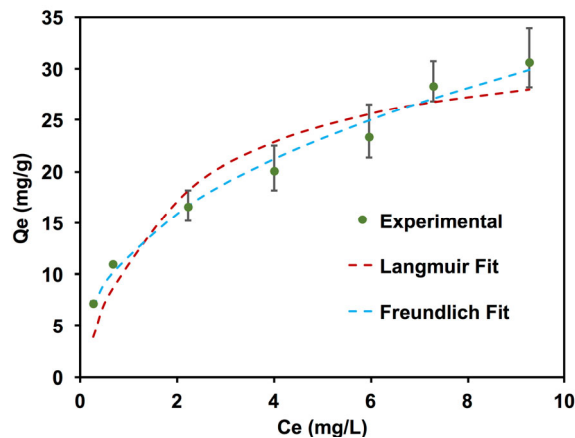


Figure 6: PFOA adsorption isotherm by DFB-CDP ($[\text{PFOA}]_0 = 1\text{--}12 \text{ mg L}^{-1}$; $[\text{DFB-CDP}] = 100 \text{ mg L}^{-1}$). Lines show fits to Langmuir (red) and Freundlich (blue) models. Error bars show the minimum and maximum uptake of three isotherm experiments.

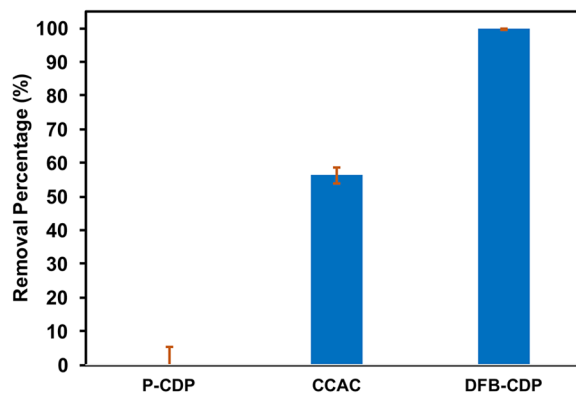


Figure 7: Equilibrium PFOA removal efficiency ($[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$) by equal mass concentrations (10 mg L^{-1}) of P-CDP, CCAC, and DFB-CDP. Error bars represent standard deviation of five replicate experiments.

consecutive adsorption/desorption experiments were performed.³⁰ Adsorption experiments, [DFB-CDP] of 400 mg L⁻¹ and [PFOA]₀ of 200 µg L⁻¹, were designed to provide incomplete PFOA removal, such that any declining performance of the adsorbent over the four cycles would be clearly apparent. Desorption experiments were conducted by suspending the PFOA-loaded adsorbent in MeOH for 24 h. Under these conditions, the amounts of adsorbed and recovered PFOA were very similar over all four cycles, and the DFB-CDP showed no apparent decrease in performance. Further experiments indicated that PFOA may be desorbed fully from DFB-CDP in only 10 minutes,³⁰ which shows promise for rapid and efficient regeneration of the adsorbent, a noted deficiency of PFOA-loaded GACs.⁴⁸

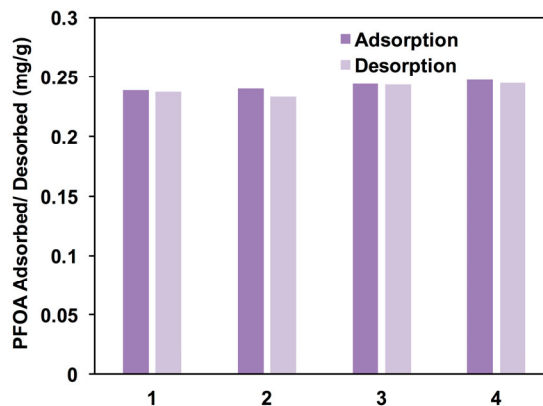


Figure 8: Regeneration and reuse of DFB-CDP by washing with MeOH at ambient temperature. The adsorption experiments were designed to obtain incomplete PFOA adsorption: [DFB-CDP] = 400 mg L⁻¹, [PFOA]₀ = 0.2 mg L⁻¹, 4 h; Desorption: DFB-CDP was suspended in MeOH for 24 h.

These data highlight three important features of CD-based polymer adsorbents that address widely-reported deficiencies of GAC. First, the improved performance for PFAS uptake on the DFB-CDP relative to P-CDP demonstrates the ability to tailor the affinity of CD polymers to target specific molecules. This level of control is not readily available in GAC or other adsorbents and opens the door to rational design of adsorbents that target PFASs (and other contaminants as needed). Second, the well-defined binding sites of CD polymers preclude binding with larger organic molecules including NOM and perhaps larger co-contaminants occurring in groundwater that degrade the capacity of other adsorbents. This feature of CD polymers will significantly extend the lifetime of the adsorbent relative to GAC. Third, the CD polymers we have developed to date can be regenerated by washing with a mild alcohol solution at room temperature with no apparent loss in adsorption performance. This enables complete recovery of adsorbed PFASs in a concentrated solution that can be handled appropriately and will provide significant energy and cost savings relative to GAC over the life-cycle of the remediation process. These features motivate the research described in this report, which aimed to rationally design novel polymer adsorbents for selective uptake of PFASs from groundwater and to implement those adsorbents into in situ or ex situ groundwater remediation processes.

2.3 Progress Towards Particle Size Control

Both DFB-CDP and P-CDP are isolated as insoluble, free-flowing powders with particle sizes on the order of tens of microns, and all characterization studies reported above were performed with these as-synthesized materials. The ability to control the particle size and morphology of these novel adsorbents will be important prior to their implementation in engineered remediation processes. For example, the particle size of a typical PAC is less than 200 µm which makes them more suitable for batch adsorption contactor processes, whereas the particle size of a typical GAC is greater than 300 µm, which makes them amenable to packed-bed filtration processes.⁵² Based on our recent success in functionalizing cotton fibers with P-CDP,⁵³ we developed a versatile approach to access β-CD polymers with a broad range of particle sizes and shapes by polymerizing P-CDP onto microcrystalline cellulose (**Figure 9**). The cellulose substrate is structurally similar to β-CD, such that only minimal modifications to the polymerization are required. SEMs of the

cellulose microparticles before and after functionalization (**Figure 9**) show a rough coating that we attribute to attachment of the P-CDP polymer on the cellulose surface with the overall size and shape of the microparticles still intact. Although the cellulose microparticles shown in **Figure 9** have irregular shapes, uniform spheres or other morphologies are readily available in a variety of sizes and are likely to work interchangeably. Remarkably, these P-CDP-functionalized cellulose particles sequester organic chemicals equally well *or even better* than P-CDP on an equivalent mass basis. For example, we repeated the flow-through experiments described in the discussion of **Figure 3** with equivalent masses of the P-CDP and the P-CDP functionalized cellulose particles (P-CDP@cellulose) and evaluated the instantaneous removal of a diverse mixture of 196 CoCs. The P-CDP@cellulose removed 139 of the CoCs to a greater extent than the P-CDP alone, with the remaining 57 removed to similar extents (most to below the limit of quantification of that CoC). These preliminary data demonstrate that polymerization of P-CDP onto microcrystalline cellulose may be a viable option for controlling the size and morphology of novel polymer adsorbents while retaining or even enhancing their performance. Microcrystalline cellulose is an inexpensive and environmentally benign support material. Our current efforts in this area focus on expanding this work to the DFB-CDP and more fully exploring the synthesis, environmental stability, and scale-up of these promising adsorbents.

2.4 Project Objectives

The discovery of P-CDP and DFB-CDP represented an exciting breakthrough for polymer adsorbents used for water treatment. However, there remained opportunities to optimize the affinity of polymer adsorbents for PFASs and to further their development towards practical implementation in engineered processes. The goal of our project was *to design, characterize, and evaluate the implementation of novel polymer adsorbents for the in situ or ex situ remediation of PFAS-contaminated groundwater*. We addressed some of the major deficiencies of contemporary adsorption-based processes including their insufficient affinity for shorter-chain and more hydrophilic PFASs, the propensity for fouling by natural organic matter and other matrix constituents, and costs associated with the regeneration of spent adsorbents. The research objectives of the project were to:

1. Discover polymer adsorbents with high affinity, high capacity, and rapid kinetics for environmentally relevant PFASs using a hypothesis-driven, rational design approach;
2. Characterize the performance of each polymer under scenarios relevant to groundwater remediation to (i) inform polymer development, (ii) elucidate adsorption mechanisms, and (iii) estimate parameters to be used for process design; and
3. Transition towards the implementation of the new polymer adsorbents into in situ or ex situ remediation processes by (i) optimizing synthesis pathways and (ii) evaluating adsorption process alternatives that maximize performance and minimize the life-cycle costs.

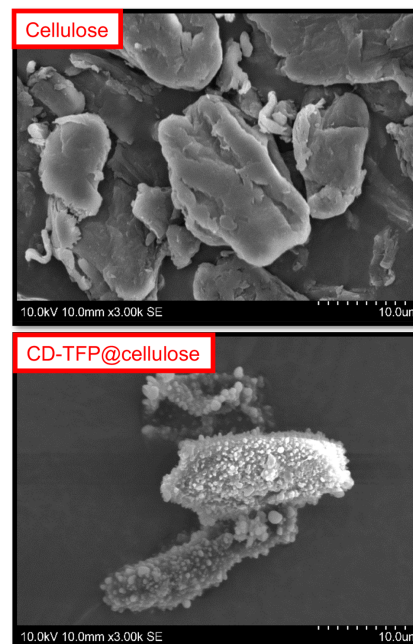


Figure 9: SEM images of unmodified microcrystalline cellulose (top) and P-CDP-functionalized microcrystalline cellulose particles (bottom).

3.0 MATERIALS AND METHODS

For detailed descriptions of materials and methods used throughout this project, we refer the reader to the primary literature provided as a list in **Appendix A**. Here, we provide key details on the acquisition or synthesis of adsorbents, the characterization of novel and commercial adsorbents, PFAS analysis by means of high-resolution mass spectrometry, and batch adsorption experiments to assess adsorption kinetics and adsorption affinity.

3.1 Commercially Available Adsorbents

We benchmarked the performance of novel adsorbents discovered during this project to conventional activated carbon materials and ion exchange resins. The three activated carbon materials include CCAC AquaCarb® (1230C, Westates Carbon, Siemens, Roseville, MN), AWAC Filtrasorb® (400-M, Calgon Carbon Co., Pittsburgh, PA), and HFAC (granular activated carbon used at a local drinking water treatment facility to process PFAS-contaminated groundwater). The two ion exchange resins include the anion exchange (AE) resin marketed as Purofine® PFA694E (Purolite, Philadelphia, PA) and the cation exchange (CE) resin Purofine® PFC100E (Purolite, Philadelphia, PA) marketed for potable water softening.

3.2 Synthesis of cyclodextrin polymers (CDPs)

We synthesized dozens of novel cyclodextrin polymers (CDPs) during the course of this project. All polymers were synthesized using the same general approach with minor variations introduced for different crosslinker chemicals. Briefly, a flame dried 20 mL scintillation vial equipped with a magnetic stir bar was charged with β -cyclodextrin (β -CD), a chemical crosslinker (see **Figure 50** for a partial list of crosslinkers studied during this project), a reaction buffer (*e.g.*, K_2CO_3) and a solvent (*e.g.*, N-methyl-2-pyrrolidone, NMP). The vial was then bubbled with N_2 gas for 10 min. The N_2 inlet was removed and the mixture was placed on a hot stirring plate (85 °C) and stirred at 500 rpm for 40 hours. The gel was cooled and then packed into a teabag with deionized water, and the solid was isolated and activated by water soxhlet extraction for 2 days and methanol soxhlet extraction for 2 days. Finally, the gel was dried under vacuum at room temperature for 1 day and heated under vacuum at 80 °C for 1 day. The resulting CDP was obtained as a powder and subsequently characterized.

3.3 Synthesis of covalent organic frameworks (COFs)

Covalent organic frameworks (COFs) are crystalline, porous polymers whose monomers are organized predictably using directional bonding principles. We targeted hexagonal imine-linked 2D COFs bearing cationic or zwitterionic functionalities to provide high affinity for a diverse set of PFASs and sufficient pore volume to accommodate their binding. We synthesized a number of different COFs during the course of this project. All COFs were synthesized using the same general approach with minor variations introduced for different building blocks and side chains. Briefly, a 20 mL scintillation vial was charged with 1,3,5-tris(4-aminophenyl)benzene and at least two other building blocks (*e.g.*, terephthalaldehyde) at different molar ratios. A 1,4-dioxane / mesitylene solution (4:1 v/v, 12 mL) was added, and the resulting suspension was sonicated at room temperature until the monomers were fully dissolved. Glacial CH_3CO_2H and H_2O were added, and the resulting solution was heated at 90 °C for 72 h. The reaction mixture was transferred to a tea bag and washed with methanol in a Soxhlet extractor for 18 h. The material was then activated by supercritical CO_2 followed by drying under vacuum at room temperature for 5 h that afforded COFs as a solid powder.

3.4 Characterization of adsorbents

Select adsorbents were characterized by a variety of techniques. Infrared spectroscopy was performed on a Thermo Nicolet iS10 with a ZnSe crystal ATR attachment. Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer. Each CDP sample (20-50 mg) was degassed at 90 °C for 24 h and then backfilled with N₂. N₂ isotherms were generated by incremental exposure to ultra high purity nitrogen up to 1 atm in a liquid nitrogen (77 K) bath, and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). Thermogravimetric (TGA) analysis was performed on a TA Instruments Q500 Thermogravimetric Analyzer. Parameters included a heating range of 20-600 °C using a 10 °C/min ramp under N₂. Scanning electron microscopy was performed on a Hitachi S-3400N-II operating at 5.00 kV and a working distance of 10.1 mm. CDP samples were mounted on the stubs with electrically-conductive carbon tape, which was then attached to an aluminum platform sample holder. Liquid state ¹⁹F NMR was performed on an Agilent DD2 500 MHz system. Solid state ¹⁹F NMR was conducted on a Bruker 600 MHz NMR system with 4.0 mm MAS 1H-19F-X probe. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded at 25 °C on Bruker AvanceIII-500 MHz. The spectra were calibrated using residual solvent as internal reference (CDCl₃: 7.26 ppm for ¹H NMR, 77.00 for ¹³C NMR). Elemental analyses were performed on an Elementar Vario Cube EL CHNS elemental analyzer. Powder X-ray diffraction (PXRD) patterns were obtained at room temperature on a STOE-STADIMP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuKα1 radiation, λ = 1.54056 Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi (ThermoFisher Scientific). Zeta potential measurements were performed on a Nano Zetasizer (Malvern Instruments Ltd.) with a He-Ne laser (633nm, Max 5 mW).

3.5 PFAS standards and analysis

Most of our experiments were performed with a mixture of PFCAs (n=4, 5, 6, 7, 8, 9, 10), PFSAAs (n=4, 6, 7, 8), FTSAAs (4:2, 6:2, and 8:2), along with N-methylperfluorooctane sulfonamidoacetic acid (N-MeFOSAA) and N-ethylperfluorooctane sulfonamidoacetic acid (N-EtFOSAA). These 16 PFASs are all relevant for AFFF-impacted groundwater, are anionic at neutral pH (*i.e.*, are PFAAs), and represent different hydrophilic head groups and different hydrophobicities. Select studies also included a set of perfluorosulfonamides, fluorotelomer alcohols, and a variety of zwitterionic PFASs relevant for AFFF-impacted groundwater.⁵⁴ Stock solutions of each PFAS was prepared and used to generate analytical and experimental mixes at appropriate dilution levels and concentrations. Analysis was by means of high-performance liquid chromatography (HPLC) and high-resolution mass spectrometry (HR-MS). PFAS separation was achieved on a reversed-phase C18 analytical column equipped with appropriate guard columns. Compound-specific acquisition parameters including the exact masses of the dominant adducts, voltages, gas flow rates, collision energies, and dominant tandem mass spectral fragments were acquired for all PFASs. Analytical mixtures were used to optimize the mobile phase gradient and determine retention times, limits of detection, limits of quantification, and method precision and accuracy. To the extent possible all analytical methods were adapted from methods currently employed in the PI's laboratory^{28,55-57} or from those described in the literature.^{1,5,58}

3.6 Batch adsorption kinetics experiments

Kinetics experiments were conducted in 15 mL polypropylene centrifuge tubes with nanopure water or groundwater. Batch reactors were prepared with 10 mL water and dosed with 10 mg L⁻¹ of adsorbent and 1 µg L⁻¹ of each PFAS. The adsorbent dose was selected based on previous research investigating pollutant uptake on a variety of adsorbents^{25,28,54,59–62} The PFAS doses were selected to be representative of concentrations measured in AFFF-impacted groundwater.^{5–7} Experiments were conducted on a rotary tumbler and housed in a constant temperature room maintained at 20 °C. Samples were collected from sacrificed reactors at predetermined sampling times and filtered. Control experiments to account for other PFAS losses were performed under the same conditions with no addition of adsorbent. All kinetics experiments were performed in triplicate. Data from the kinetics experiments were used to calculate pseudo second-order adsorption rate constants.⁴¹ In some cases adsorption kinetics were too fast to calculate pseudo second-order adsorption rate constants; in those cases, we report removal at the first sampled time point (*e.g.*, usually 5 or 30 minutes) as a metric of adsorption kinetics.^{54,60}

3.7 Batch adsorption affinity experiments

Affinity experiments for measuring K_D values were conducted in 15 mL polypropylene centrifuge tubes with nanopure water. Batch reactors were prepared with 10 mL water and dosed with varying doses of adsorbent (1, 5, 10, 25, 50 mg L⁻¹ of adsorbent) and at 1 µg L⁻¹ and 2 µg L⁻¹ of each PFAS.⁵⁴ These conditions were selected to provide a range of equilibrium distribution coefficients that can be evaluated together to identify the constant value that represents the linear region of the nonlinear equilibrium adsorption process (*i.e.*, nonlinear isotherm). Experiments were conducted on a rotary tumbler at 20 °C. Samples were collected at a predetermined sampling time based on the results of the kinetics experiments. Control experiments to account for other PFAS losses were performed under the same conditions with no addition of adsorbent. All affinity experiments were performed in triplicate. Data from the affinity experiments were used to estimate K_D values for each PFAS and for each adsorbent as has been previously described.^{54,63–67}

4.0 RESULTS AND DISCUSSION

4.1. Rational Design of New Cyclodextrin (CD)-Based Polymer Adsorbents

One of the most exciting aspects of CD-based polymer adsorbents is the ability to rationally design their structure to target contaminants of interest. We had previously demonstrated this approach by modifying the design of the TFN-CDP (also referred to as P-CDP throughout this report)²⁹ to target PFOA by employing a more extensively fluorinated aromatic crosslinker.³⁰ Having co-developed both a broad-spectrum adsorbent (TFN-CDP or P-CDP) and a highly promising adsorbent for PFOA (DFB-CDP), actionable research efforts in continued adsorbent development were pursued during this project.

The following sections describe work completed during ER18-1026 that resulted in new and promising CD-based polymer adsorbents with improved affinity for PFASs. All evaluations described in Section 4.1 focus on the removal of anionic PFASs (*i.e.*, perfluoroalkyl acids, PFAAs) from nanopure water unless otherwise noted. Subsequent sections describe research with the most promising CD-based polymer adsorbents and their performance under more complex and environmentally relevant scenarios. We started the project by exploring previously unknown side-reactions that occurred during the polymerization of the DFB-CDP to evaluate their influence on its performance as an adsorbent.⁶⁸ We then developed a technique to post-synthetically modify the TFN-CDP to generate a CD-based polymer adsorbent with a positive surface charge (called amine-CDP in this report).⁶⁷ We next explored a variety of other crosslinkers that might directly lead to a CD-based polymer adsorbent with a positive surface charge without the need for post-synthetic modification (called tripodal-CDPs in this report).⁶⁹ Finally, we developed a novel synthesis procedure that is much more flexible and generates a new types of CD-based polymer adsorbent with high yield (called next-generation CDPs in this report).⁷⁰ We note that the discussion in Section 4.1 is not an exhaustive description of all of the CD-based polymer adsorbents developed during this project, but rather a detailed description of the polymers that represented a significant advancement in our understanding of CD-based polymer adsorbents.

4.1.1 Exploring Previously Unknown Side Reactions during the Synthesis of DFB-CDP

We previously reported on the DFB-CDP that reduces PFOA concentrations from 1 $\mu\text{g L}^{-1}$ to <10 ng L^{-1} .³⁰ DFB-CDP was not fouled by humic acids, which are major constituents of natural organic matter (NOM), and was regenerated and reused multiple times by washing with MeOH. These characteristics make DFB-CDP a promising candidate for PFOA remediation. Although DFB-CDP was designed to stabilize β -CD-PFAS inclusion complexes through secondary noncovalent interactions with the crosslinkers, these interactions and the effects of crosslinker chemistry on PFAS uptake were not yet understood.

We also previously reported a side reaction discovered during the polymerization of the TFN-CDP in which a fluorine of TFN could be substituted by a hydroxyl group and the resulting phenolated TFN could be incorporated into the polymer network.⁷¹ More heavily phenolated polymers showed increased capacity to bind Pb^{2+} ions and increased the binding affinity for 83 contaminants of concern (CoCs),⁷¹ yet all of the phenolated TFN-linked polymers had low affinity for anionic PFASs suggesting that

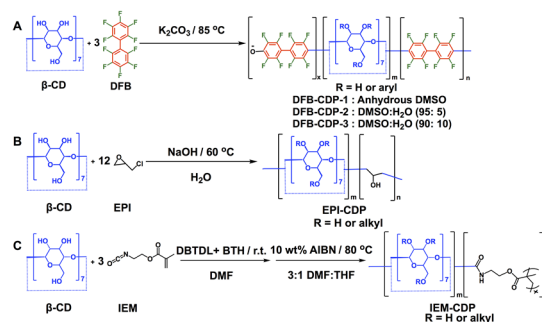


Figure 10. Reaction schematics for CDPs developed in this part of the project.

phenolation may not be desired in β -CD polymers designed for PFAA uptake. In this part of the project, we explored the role of crosslinker chemistry in modulating the removal of PFOA, PFOS, and eight other PFAAs from water. Within the DFB-CDP family, we explored the role of phenolation on the kinetics and thermodynamics of PFAS uptake. Noting the large difference in affinity between the DFB-CDP and β -CD polymers crosslinked by TFN, we also explored β -CD polymers crosslinked by two other chemically distinct strategies: epichlorohydrin, (EPI-CDP), a commonly studied CD-based polymer adsorbent, and a urethane-containing methacrylate β -CD network (IEM-CDP) (**Figure 10**). This broad comparison demonstrates that the nature of the crosslinkers plays an important role in PFAS uptake, and the superior PFAS uptake shown by the DFB-CDP establishes design criteria for further improving PFAS uptake.

4.1.1.1 Model Studies to Characterize Side Reactions

Because DFB-CDP is insoluble, it is difficult to determine the regiochemistry of the ether linkages and side reactions formed during polymerization. Model reactions of DFB with *n*-butanol in anhydrous DMSO imitate the reactions of hydroxyls of β -CD with DFB (**Figure 11**). The dominant product observed by ^{19}F NMR was the 4,4'-dibutyl ether **1a** (83.5%), and minor products include the mono-phenolated **1b** (4.9%) and mono-phenolated, mono-butyl ether **2b** (7.7%) (**Figure 11**). The presence of **2b** suggests the possibility of phenolated DFB being incorporated into the β -CD polymer network.

To control the side reactions and tune the concentrations of phenolated DFB incorporated into the polymer, we added 5% and 10% water to anhydrous DMSO to favor increased phenolation (**Figure 11**). The formation of dibutyl ether **1a** is inhibited in reactions 2 and 3 compared with that in reaction 1, with only 60.8% and 48.3% of **1a** being detected after 48 hours (**Figure 11**). The phenolated product **2b** was formed in increased yield, with 21.4% of **2b** in reaction 2 and 35.8% in reaction 3 (**Figure 11**). These experiments demonstrate that phenolation occurs readily in the presence of water. This model study suggests that polymerizations conducted with increased water content will provide DFB-CDP samples with higher amounts of phenolation.

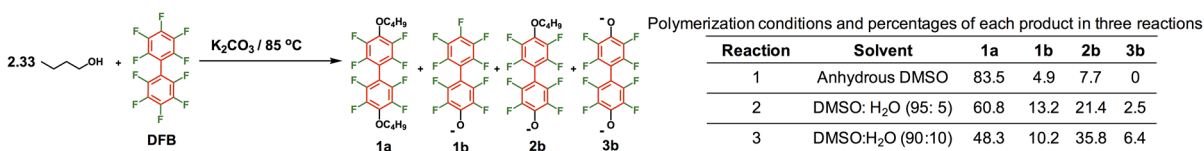


Figure 11. Schematic of reaction pathways during model studies.

4.1.1.2 Characterization of Phenolated DFB-CDPs

To tune the degree of phenolated DFB incorporated into DFB-CDP while keeping the structure and morphology of DFB-CDPs as similar as possible, we polymerized β -CD and DFB with the same molar feed ratio 1:3 in different solvents (DMSO: H₂O = 100: 0, 95:5, 90:10). After the monomers and K₂CO₃ were heated in solvents at 85°C, the suspensions gelled and were isolated in this form after 40-48h. Gels exhibited darker colors from polymer DFB-CDP-1 to DFB-CDP-3, with the colors ranging from light yellow to light brown. Elemental analysis results of C, H, and F suggested that the resulting DFB-CDPs have similar crosslinking densities, with β -CD: DFB incorporation ratios ranging from 1:2.5 to 1:2.9 (**Table 1**). Meanwhile, the DFB-CDPs had different concentrations of phenolated DFB incorporated into the polymers. The phenolate concentration in the polymers was determined by deprotonating the phenols using Li₂CO₃ and determining the amount of bound Li⁺ using inductively coupled plasma optical emission spectroscopy (ICP-OES).⁷¹ DFB-CDP-1 has the lowest phenolate concentration at 0.063±0.008

Table 1. β -CD:Crosslinker Ratio, bound Li^+ concentrations and bound phenolate concentrations in polymer samples.

Sample	β -CD: Crosslinker Incorporation Ratio	$[\text{Li}^+]$ Bound (mmol g^{-1})	$[\text{Phenolate}]$ (mmol g^{-1})
DFB-CDP-1	1:2.5	0.063 ± 0.008	0.063 ± 0.008
DFB-CDP-2	1:2.6	0.22 ± 0.011	0.22 ± 0.011
DFB-CDP-3	1:2.9	0.25 ± 0.018	0.25 ± 0.018
EPI-CDP	1:8	0*	N/A
IEM-CDP	1:3.5	0.031 ± 0.009	N/A

* Li^+ signals of EPI-CDP samples by ICP-OES are below quantification limit.

mmol g^{-1} , which indicates that $4.8 \pm 0.6\%$ of DFB incorporated into the polymer is phenolated. Meanwhile, DFB-CDP-2 and DFB-CDP-3 have similar and much higher phenolate concentrations incorporated into the polymers, with the values being $0.22 \pm 0.011 \text{ mmol g}^{-1}$ ($16.1 \pm 0.8\%$ phenolated DFB) for DFB-CDP-2 and $0.25 \pm 0.018 \text{ mmol g}^{-1}$ ($17.4 \pm 1.3\%$ phenolated DFB) for DFB-CDP-3. These results are consistent with the model studies (**Figure 11**) and demonstrate a way to control the phenolate concentration in the DFB-CDPs.

The presence and relative concentrations of phenolates in the polymers were further confirmed by zeta potential measurements and solid-state ^{19}F NMR. The ^{19}F MAS NMR spectrum of as-synthesized **DFB-CDP-3** exhibited two broad peaks at -142.4 and -159.2 ppm (**Figure 12a**). These chemical shifts are similar to those found in the ^{19}F NMR spectrum of model compound 1a obtained in solution ($\delta = -142.9$ and -159.0 ppm). This observation indicates that the DFB-CDP polymers are linked mostly by 4,4'-disubstituted decafluorobiphenyl groups. The spectrum of as-synthesized DFB-CDP-3 also exhibits a shoulder around -164.0 ppm, which corresponds to the fluorines adjacent to the phenol in the neutral form of 2b (2b', $\delta = -163.3$ ppm). Upon treatment of DFB-CDP-3 with K_2CO_3 to deprotonate the as-synthesized polymer, the chemical shifts of the shoulder shifted to -172.4 ppm, and a similar shift was observed in the solution spectrum of 2b upon deprotonation ($\delta = -171.4$ ppm). These observations suggest that the shoulder corresponds to fluorines on phenolated aryl rings that are incorporated into DFB-CDP-3. Notably, the shoulder at -172.4 ppm is much less prominent in the spectrum of the less-phenolated DFB-CDP-1 (**Figure 12b**), which is consistent with the loadings determined by ICP-OES.

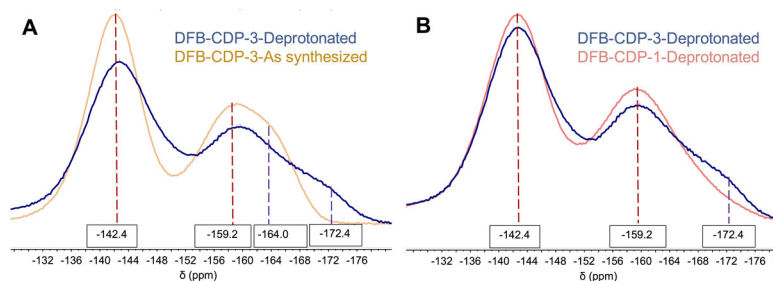


Figure 12. ^{19}F MAS NMR of DFB-CDPs at 600 MHz while spinning at 48 kHz. A. ^{19}F MAS NMR of as-synthesized and deprotonated DFB-CDP-3. Orange trace: As-synthesized DFB-CDP-3; Blue trace: DFB-CDP-3-Deprotonated; B. ^{19}F MAS NMR of deprotonated DFB-CDPs. Red trace: DFB-CDP-1-Deprotonated; Blue trace: DFB-CDP-3-Deprotonated.

4.1.1.3 PFOA Adsorption in Nanopure Water by Phenolated DFB-CDPs

The degree of phenolation incorporated into DFB-CDPs was inversely associated with their PFOA equilibrium removal percentage. The PFOA removal efficiency of each sample was characterized in a batch experiment using $[\text{PFOA}]_0$ of $1 \mu\text{g L}^{-1}$ in nanopure water, and $[\text{DFB-CDP}]$ of 10 mg L^{-1} . Each adsorbent was sieved to between $20 \mu\text{m}$ and $45 \mu\text{m}$ to minimize differences in adsorption behavior that can be attributed to differences in particle sizes. Each of the DFB-CDPs adsorbs PFOA under these conditions and exhibits similar adsorption kinetics when comparing the

rates of adsorption using Ho and McKay's pseudo-second-order adsorption model (Figure 13).⁴¹ The values of k_{obs} from 0 to 25.5 h are 28.2, 27.4 and 19.7 g mg⁻¹ h⁻¹ for DFB-CDP-1, DFB-CDP-2 and DFB-CDP-3 respectively. DFB-CDP-1 removed 86.6±7.1% of PFOA at equilibrium, while DFB-CDP-2 and DFB-CDP-3

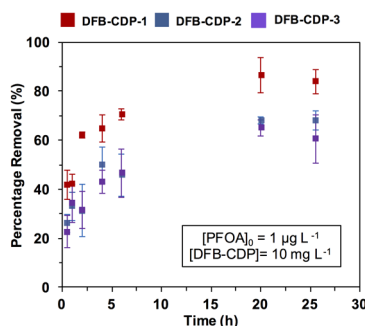


Figure 13. Kinetics of PFOA adsorption by three DFB-CDPs ([PFOA]₀ = 1 µg L⁻¹; [DFB-CDP] = 10 mg L⁻¹) in nanopure water. Error bars: Standard deviation of 3 experiments.

Equilibrium removal at 20 h and pseudo-second order parameters derived from PFOA kinetic adsorption in Figure 2

Adsorbent	Equilibrium Removal at 20 h (%)	Pseudo-second Order Model		
		Q_e (µg g ⁻¹)	K_{obs} (g mg ⁻¹ h ⁻¹)	R^2
DFB-CDP-1	86.6 ± 7.1	85.0	28.2	0.999
DFB-CDP-2	68.2 ± 1.5	68.4	27.4	0.997
DFB-CDP-3	65.0 ± 2.1	63.0	19.7	0.995

exhibited 68.2±1.5% and 65.0±2.1% equilibrium removal of PFOA. The average PFOA removal at equilibrium was inversely associated to the phenolation levels of DFB-CDPs 1-3. Therefore, through comparing three DFB-CDPs with similar crosslinking density and morphology, these experiments demonstrate that the thermodynamics of PFOA uptake by β-CD polymers are negatively influenced by the presence of phenolates.

4.1.1.4 Rationale and Synthesis of EPI-CDP and IEM-CDP

Two other β-CD-based polymers were prepared and evaluated to further understand how crosslinker chemistry influences PFAS adsorption. Epichlorohydrin-cyclodextrin polymer (EPI-CDP, Figure 10B) was selected because it has been studied extensively as an alternative adsorbent and lacks hydrophobic crosslinkers.⁷² Another β-CD polymer was prepared by modifying β-CD with 2-isocyanatoethyl methacrylate (IEM), followed by radical polymerization of the methacrylate groups (IEM-CDP, Figure 10C). IEM-CDP was designed as a more hydrophobic polymer that lacks perfluoroarene linkers. Both materials were formed as insoluble, water swellable solids.

4.1.1.5 Adsorption Studies with a broader set of PFASs

The three DFB-CDPs, EPI-CDP, IEM-CDP were evaluated for their ability to remove a mixture of ten PFASs with different chain lengths and polar head groups. Six PFASs are perfluoroalkyl carboxylic acids (PFCAs) with $n = 4, 6, 7, 8, 9$, and 10 carbons, three are perfluoroalkyl sulfonates (PFSAs) with $n = 5, 7$, and 9 backbone atoms, including sulfur from sulfonic acid groups and the tenth PFAS is an ammonium perfluoroalkyl ether carboxylate associated with the Chemours GenX process. Batch experiments were performed to evaluate the equilibrium removal (contact time = 9 hours) of 1 µg L⁻¹ of each PFAS in the presence of each of the five CD-based adsorbents (10 mg L⁻¹) in a 1 mM phosphate buffer solution at pH 7.5 (Figure 14). DFB-CDP-1 performed the best and exhibited more than 70% removal of

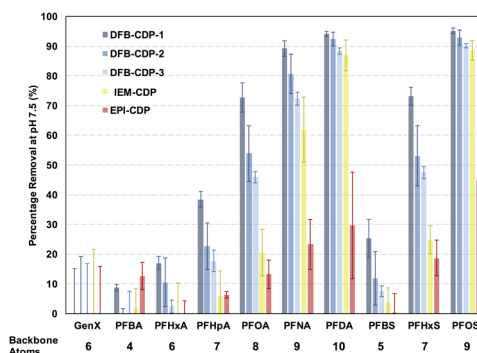


Figure 14. Equilibrium adsorption of ten PFASs by five β-CD-based polymers in 1 mM pH 7.5 phosphate buffer ([PFAS]₀ = 1 µg L⁻¹; [Adsorbent] = 10 mg L⁻¹). Error bars: Standard deviation of 3 experiments. Bottom row: Backbone atom numbers of each PFAS, including polar head groups.

PFOA, PFNA, PFDA, PFHxS and PFOS, along with modest removal of some shorter-chain PFASs, with 5–40% equilibrium removal noted for PFBA, PFHxA, PFHpA, and PFBS. The trend of higher affinity for longer-chain PFASs was observed for all five CDPs, indicating that the hydrophobic interaction between CDPs and PFASs is affecting CDPs' affinity for PFASs. Likewise, all five CDPs exhibited better removal of perfluorosulfonic acids (PFSA) than perfluorocarboxylic acids (PFCA) with the same carbon number (except for PFBA and PFBS removal by EPI-CDP), which is consistent with the adsorption affinity of GAC, anion exchange resins, and other adsorbents for PFASs.^{73,74} Notably, none of the five CDPs exhibited significant removal of GenX. Weiss-Errico and coworkers found that β -CD binds GenX two orders of magnitude more weakly than PFOA because of GenX's branched structure ($K_a = (7.5 \pm 4.3) \cdot 10^2 \text{ M}^{-1}$),⁵⁰ which is consistent with the poor removal of GenX by all five β -CD-based polymers observed here. Furthermore, the observation of poor GenX uptake suggests that β -CD is involved during the adsorption of the other PFASs.

Among the three DFB-CDP polymers, DFB-CDP-2 and DFB-CDP-3 exhibited similar and lower equilibrium removal of several PFAS than DFB-CDP-1, including PFHpA, PFOA, PFNA, PFBS and PFHxS. This observation is consistent with the $1 \mu\text{g L}^{-1}$ PFOA adsorption results in nanopure water (**Figure 13**) and can be explained by more phenolated DFB incorporated into the polymer network of DFB-CDP-2 and DFB-CDP-3 than DFB-CDP-1. The other two CDPs linked with epichlorohydrin (EPI-CDP) and 2-isocyanatoethyl methacrylate (IEM-CDP) exhibited significantly lower removal for 8 out of 10 PFASs than the three DFB-CDPs, in which EPI-CDP had the poorest performance and removed no more than 50% of any PFAS at equilibrium. These results are informative considering that both EPI-CDP and IEM-CDP exhibited less negative zeta potential values at pH 7.5 than DFB-CDPs, with EPI-CDP being close to neutral, $-1.29 \pm 0.55 \text{ mV}$, and IEM-CDP being $-9.16 \pm 0.43 \text{ mV}$. This suggests that surface charge may be one important factor, but not the only factor that determines a β -CD-based polymer's affinity for anionic PFASs.

To further evaluate the role of surface charge on PFAS uptake, we repeated the PFAS experiments in a 1 mM phosphate buffer solution at pH 5.5. The surface charge of four of the five polymers (all except for EPI-CDP) became less negative at pH 5.5. All β -CD-based polymers exhibited improved removal for the majority of the PFASs at pH 5.5 than at pH 7.5.

Figure 15 shows the comparison of equilibrium removal percentage of PFOA and PFHxS at pH 7.5 and pH 5.5 among the five polymers. Each polymer exhibited a broad-spectrum increase of PFAS removal when the pH was lowered from 7.5 to 5.5. The performance gain was largest for polymers that exhibited relatively poor removal of a particular PFAS at pH 7.5. For example, among the three DFB-CDPs, the increase in removal of PFOA at pH 5.5 was greater for DFB-CDP-2 and DFB-CDP-3. Similarly, the increase in

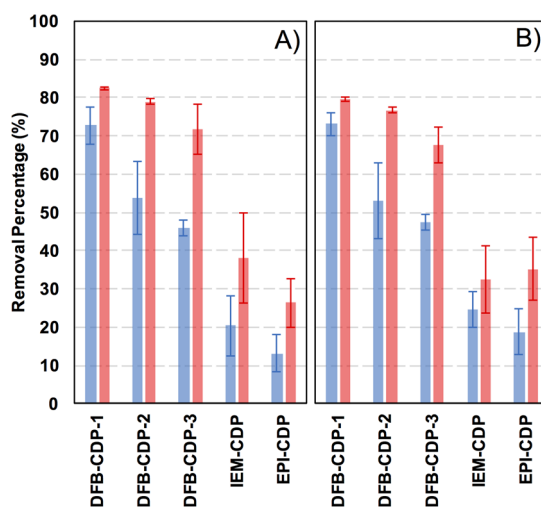


Figure 15. Comparison of equilibrium removal % for (A) PFOA and (B) PFHxS by five β -CD-based polymers at pH 7.5 (blue) and 5.5 (red). ([PFAS]₀ = $1 \mu\text{g L}^{-1}$; [Adsorbent] = 10 mg L^{-1} ; Matrix: 1 mM phosphate buffer). Error bars: Standard deviation of 3 experiments.

removal of PFHxS at pH 5.5 was greater for DFB-CDP-2 and DFB-CDP-3. This further demonstrates the role that polymer surface charge plays in the removal of PFASs among structurally similar CDPs. The performance of the EPI-CDP polymer also increased at pH 5.5 despite more subtle changes in the surface charge. For example, the surface charge of EPI-CDP is -1.29 ± 0.55 mV and -0.87 ± 0.23 mV at pH 7.5 and 5.5, respectively. These results suggest that the enhanced removal of PFASs at lower pH is not only due to the protonation of CDPs' functional groups, but other factors such as the chemical nature of the PFAS. Moreover, despite the fact that EPI-CDP exhibited better removal of PFAS at pH 5.5, the performance of EPI-CDP remains modest, with removal of all PFAS except PFOS remaining less than 50%. This further demonstrates that other properties of CDPs are affecting their affinity to PFAS besides surface charge. Taken together, our data suggests that an optimized microenvironment around β -CD is essential for maximum affinity for PFASs, which is the combination of crosslinker chemistry, crosslinking density,³⁰ and surface charges.

4.1.1.6 Conclusions from Studies of Phenolated DFB-CDP

Three DFB-CDPs with similar crosslinking density and different amounts of phenolated DFB incorporated into the polymer network were synthesized. Both zeta potential measurement and ^{19}F MAS NMR of the three polymers are consistent with the presence and concentrations of phenolated crosslinkers in the polymer network. DFB-CDP-1, the polymer with the lowest phenolate concentration, exhibited the highest affinity for PFOA in nanopure water, and for 10 PFASs in buffered solutions as well. These findings suggest that negative charges around β -CD hinder the capture of negatively charged PFASs. Two other CDPs with different crosslinkers, epichlorohydrin and 2-isocyanatoethyl methacrylate, were synthesized and showed inferior affinity compared to DFB-CDPs for 8 out of 10 PFASs. This finding indicates that other properties of CDPs besides zeta potential will affect their affinity for PFASs, such as the chemical nature of the crosslinker and the crosslinking density. Finally, this study demonstrates that the affinity of CDPs for PFASs can be tuned through the judicious modification of their composition.

4.1.2 Rational Design and Discovery of CDPs with a Positive Surface Charge (amine-CDP)

Cyclodextrin-based polymer adsorbents (CDPs) with aromatic crosslinkers have shown promise to remove CoCs from water.^{28,29} For example, TFN-CDP (also referred to as P-CDP in this report) was formed as a permanently porous network (polymer 1, **Figure 16**) that rapidly removes many CoCs from water,²⁹ resists fouling by natural organic matter,²⁸ and can be regenerated.²⁹ A study of the binding of 83 CoCs under environmentally relevant concentrations revealed that P-CDP rapidly removes many cationic and neutral CoCs, but it showed poor affinity for most anionic CoCs.²⁸ This selectivity for cations was later attributed to anionic phenolate groups introduced to the TFN crosslinkers during the polymerization.⁷¹ The inability of P-CDP to bind anionic CoCs, including PFAAs, is a major limitation to its broad utility and technological promise. Here we reverse the selectivity of 1 for binding cations by reducing its nitriles to primary amines (polymer 2, **Figure 16**), which imparts a strong affinity for anionic CoCs, including twelve PFAAs. We attribute this selectivity for anions to secondary interactions with the amine groups, which are protonated at neutral pH, in combination with the CD receptors. These findings provide clear evidence that the performance of cyclodextrin-based polymer adsorbents depends strongly on secondary

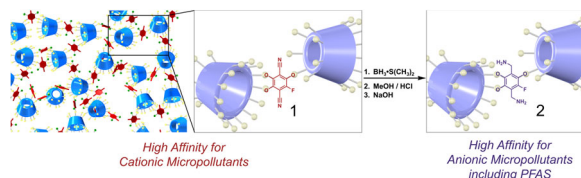


Figure 16. Post-polymerization reduction of **1** yields amine functionalized **2**, which remove anionic MPs and PFASs from water

interactions with their crosslinkers.^{30,68} More importantly, this approach provides two CD adsorbents with complementary binding characteristics from a single polymerization of two commercially available monomers, which will facilitate their scale-up and deployment to remove PFASs from impacted water resources.

4.1.2.1 Synthesis and Characterization of the Novel amine-CDP

The nitriles of P-CDP were reduced to primary amines using excess $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ in THF at reflux for 40 hours, using conditions modified from those used to reduce TFN-based polymers of intrinsic microporosity.⁷⁵ After reduction, insoluble polymer 2 (also referred to as amine-CDP) was subjected to an acidic workup followed by treatment with base. The reduction was characterized by FT-IR, cross-polarized magic angle spinning (CP-MAS) solid-state ^{13}C NMR, a chloranil test for amines, combustion analysis, and zeta potential measurements. FT-IR was consistent with partial reduction of the nitriles, as the spectrum of amine-CDP shows a strongly attenuated nitrile stretch at 2238 cm^{-1} relative to that of P-CDP when each spectrum was normalized at the C-O stretch at 1020 cm^{-1} . The spectrum of amine-CDP also shows an N-H bending signal at 1580 cm^{-1} (**Figure 17a**). In the CP-MAS ^{13}C -NMR, the nitrile carbons of P-CDP resonate at 94.44 ppm. This signal is attenuated in the spectrum of amine-CDP, and a new peak is observed at 36.73 ppm, consistent with that of a benzylic amine carbon. The presence of amines in amine-CDP was also verified by a positive chloranil test (**Figure 17b**), which is commonly used to qualitatively monitor the deprotection, capping, or coupling of amine groups in solid-phase peptide synthesis.^{76,77} In a chloranil test, acetaldehyde reacts with a primary or secondary amine forming an enamine, which then reacts with chloranil to yield a dark blue aminovinyl-quinone chromophore.⁷⁸ In the presence of acetaldehyde and chloranil, the suspension of polymer P-CDP is light yellow-green, indicating the absence of amines, while the amine-CDP suspension is a dark blue-green, indicating the presence of amines (**Figure 17b**). Because the elemental composition of P-CDP and amine-CDP in its free base form are too similar to differentiate by combustion analysis, the conversion of nitriles to amines was estimated by comparing the chloride content of each polymer following treatment with aqueous HCl. Treatment of amine-CDP with HCl protonates its amines to the corresponding hydrochloride salts ($2 \cdot \text{HCl}$), whereas polymer P-CDP does not contain functional groups that are easily protonated to cationic chloride salts. The conversion of nitriles to amines was estimated from the N:Cl molar ratio in $2 \cdot \text{HCl}$ of 0.72, corresponding to approximately 72% conversion of the nitrile reduction. Based on this conversion efficiency and a crosslinker: β -CD ratio of X, nitrile reduction introduces an average of 4.9 primary amines per β -CD. As a control, P-CDP was treated with HCl as above and virtually no chloride was detected by the elemental analysis. Surface charges of the two polymers in neutral water were probed by zeta potential measurements. Aqueous suspensions of P-CDP at neutral pH have a zeta potential of $-28.9 \pm 0.7\text{ mV}$, indicating an anionic surface charge. Aqueous suspensions of amine-CDP at neutral pH show a zeta potential of $+1.7 \pm 0.8\text{ mV}$, indicating a cationic surface charge. amine-CDP also exhibits modest porosity with

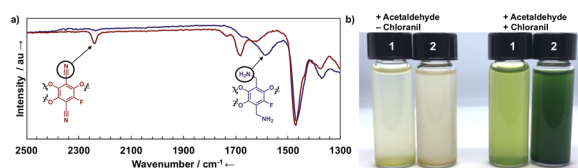


Figure 17. a) FT-IR spectra of polymers P-CDP (red) and amine-CDP (purple). In the spectra of amine-CDP, there is a significant reduction in the nitrile stretch at 2240 cm^{-1} and appearance of an N-H bend at 1580 cm^{-1} b) Chloranil test of P-CDP and amine-CDP. Left two vials contain polymers P-CDP and amine-CDP suspended in DMF and acetaldehyde (5%) and the right two vials contain polymers P-CDP and amine-CDP suspended in DMF, acetaldehyde (5%), and chloranil (5%). The chloranil test turns blue-green in the presence of amine-CDP, indicating the presence of amines.

average surface areas of $135 \text{ m}^2 \text{ g}^{-1}$ (calculated by the Brunauer–Emmet–Teller equation applied to a nitrogen adsorption isotherm) when isolated as a dry solid.

4.1.2.2 Performance of amine-CDP as an Adsorbent

As a consequence of its transformed crosslinkers, amine-CDP has a relatively high affinity for anionic CoCs, including PFAAs, which is opposite selectivity observed for P-CDP. We measured the adsorption coefficients ($\log K_D$ values) of 91 structurally diverse CoCs for P-CDP and amine-CDP ($[\text{CoC}]_0 = 2 \text{ } \mu\text{g L}^{-1}$; $[\text{CDP}] = 25 \text{ mg L}^{-1}$). We found that P-CDP exhibited relatively high $\log K_D$ values for cationic CoCs, along with neutral compounds that bind to CDs well, which is consistent with previous reports^{71,79} and observations (**Figure 18**).^{28,80} All 18 cationic substances exhibited $\log K_D$ values greater than amine-CDP on P-CDP. In contrast, 21 of 25 anionic substances and all 10 anionic PFASs exhibited relatively low $\log K_D$ values between -0.5 and 1.0 on polymer P-CDP. These low affinities make polymer P-CDP an ineffective adsorbent for most anionic CoCs at environmentally relevant concentrations and economically reasonable doses of P-CDP. In contrast, amine-CDP strongly binds anionic substances, with 21 of 25 exhibiting $\log K_D$ values >2.6 and all ten anionic PFASs exhibiting $\log K_D$ values between 2.8-4.0. However, amine-CDP binds cationic CoCs more weakly with $\log K_D$ values for 16 of 18 cationic CoCs between -0.5-1.5. These findings demonstrate that the structure of the crosslinker plays a major role in the selectivity of CD-based adsorbents and that strategies to incorporate charged groups, either during the polymerization (phenolates),^{68,71} or by post-polymerization modification (amines), are powerful techniques to completely change the removal profiles of materials derived from a single crosslinker. Based on the high affinity of amine-CDP for anionic PFASs, removal and uptake kinetics were also measured at environmentally relevant concentrations ($[\text{PFAS}]_0 = 1 \text{ } \mu\text{g L}^{-1}$; $[\text{CDP}] = 10 \text{ mg L}^{-1}$). amine-CDP removes PFOA and PFOS rapidly, as the combined residual PFOA + PFOS concentration was 58 ng L^{-1} after 30 minutes and reached an equilibrium aqueous phase concentration of approximately 25 ng L^{-1} after 9 h (**Figure 19a**). Broad-spectrum PFAS removal was also evaluated across a range of PFAS chain lengths and anionic head groups (carboxylic and sulfonic acids) after 30 min of contact time ($[\text{PFAS}]_0 = 1 \text{ } \mu\text{g L}^{-1}$; $[\text{CDP}] = 10 \text{ mg L}^{-1}$). Under these conditions, 8 of 10 PFASs were removed to at least 95%, with the short, four carbon perfluorobutanoic acid (PFBA) and branched 2,3,3,3-tetrafluoro 2-(heptafluoropropoxy)propanoate (GenX) removed to at least 80%. These two PFASs bind to β -CD with lower affinity,⁵⁰ such that their removal may rely more heavily (or even exclusively) on interactions with amine/ammonium groups in amine-CDP (**Figure 19b**). Benchmarking amine-CDP against GAC (20-40 Mesh, 425-850 μm) for the removal of 10 anionic PFAS shows that amine-CDP exhibits superior performance when compared to GAC in experiments conducted

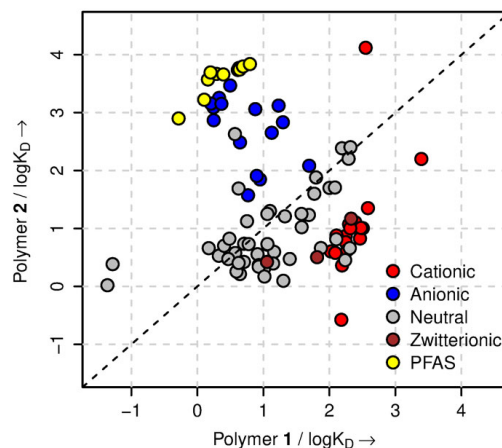


Figure 18. Affinity of 91 organic micropollutants to amine-CDP (Polymer 2) and P-CDP (Polymer 1). amine-CDP has a higher affinity for PFAS and anionic organic micropollutants, and P-CDP has higher affinity for cationic and zwitterionic organic micropollutants. P-CDP and amine-CDP exhibit similar affinity for most neutral organic micropollutants (25 mg L^{-1} polymer, 2 $\mu\text{g L}^{-1}$ MPs).

under environmentally relevant conditions after 30 min and 8 h of contact time. This demonstrates that amine-CDP can outperform the leading adsorbent that is presently available for PFAS remediation. We also benchmarked amine-CDP against powdered activated carbon (PAC, 200-950 Mesh, 10-75 μm) as a means to compare performance against a material with a similar particle size and morphology. PAC is known to exhibit more rapid adsorption kinetics when compared to GAC, but is rarely used for PFAS remediation because its size precludes implementation in continuous-flow processes and enhances its susceptibility to fouling by natural organic matter.⁸¹ In analogous experiments performed with GAC, we found that amine-CDP performs similarly to PAC for the removal of many anionic PFASs, but outperforms PAC for the removal of PFBA. This is particularly exciting because only limited removal of short-chain PFASs such as PFBA has been reported with PAC or other alternative adsorbents.⁷⁴ Together, these findings indicate the promise of amine-CDP for the removal of anionic PFASs regardless of their chain-length.

The performance of amine-CDP is also not significantly affected by the presence of natural organic matter. A 91 CoC removal study for amine-CDP was conducted using water spiked with 20 mg L^{-1} humic acid as a surrogate for natural organic matter. We plotted the log K_D value of amine-CDP for each CoC, with and without the presence of humic acid. These experiments indicate that the presence of humic acids reduce the affinity of anions only slightly. However, the affinities of cationic CoCs were much higher in the humic acid spiked matrix, which may reflect the ability of humic acids to shield cationic CoCs from the electrostatic repulsion of the ammonium groups. Overall, this experiment demonstrated that matrix constituents found in surface waters do not significantly detract from the ability of amine-CDP to sequester anionic CoCs and increase the affinity of amine-CDP towards cationic CoCs. These findings further demonstrate the potential promise of amine-CDP for removing CoCs from surface waters.

4.1.2.3 Conclusions from Studies of amine-CDP

In conclusion, these findings demonstrate the promise of using amine-CDP as an adsorbent to remove anionic PFASs in contaminated ground and surface waters. The selectivity of P-CDP was reversed from strongly binding cationic substances to strongly binding anionic substances through a post-polymerization reduction of its nitrile groups. The conversion of nitriles to primary amines was confirmed by spectroscopy, combustion analysis, and changes in the zeta potential. This effect likely arises from both the presence of amine groups that are partially protonated at pH 7 in water, as well as the increased pK_a of phenolates found on the crosslinkers upon reduction of the strongly electron withdrawing nitrile groups. The reduced polymer binds many anionic CoCs strongly and is particularly effective at the non-selective binding of PFAAs. A relatively low adsorbent loading (10 mg L^{-1}) removed all PFAAs at environmentally relevant concentrations, outperforming leading activated carbon adsorbents. The affinity of amine-CDP for anionic CoCs was not strongly attenuated by the presence of humic acids, yet these matrix constituents improved the binding of cationic CoCs. Characterizing this effect and the nature of PFAS-polymer interactions are important next steps. More broadly, these findings demonstrate the broad tunability of CD-based

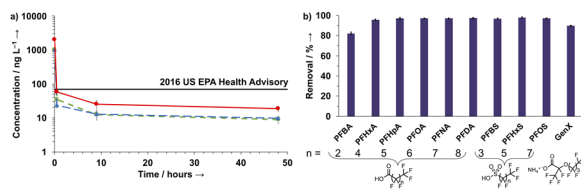


Figure 19. a) Removal of PFOA (green, short dash) PFOS (blue, long dash) and the combination of PFOA and PFOS (red, line) as a function of time, demonstrating that the combined concentration of PFOA + PFOS is reduced from 2000 ng L^{-1} (1000 ng L^{-1} each) to below 70 ng L^{-1} within 30 min by 10 mg L^{-1} of 2. b) PFAS removal by 2 with 30 minutes of contact time; $[\text{PFAS}]_0 = 1 \mu\text{g L}^{-1}$; $[\text{CDP}] = 10 \text{ mg L}^{-1}$.

polymer adsorbents available from a single polymerization as well as the continued promise of novel adsorbents constructed from molecular receptors.

4.1.3 Other CDPs with a Positive Surface Charge (tripodal CDPs)

We have already seen that CDPs are promising for PFAS remediation.^{28,30,67} Variations in the crosslinkers have been used to tune the adsorption kinetics, capacity, and selectivity of CDPs. For example the P-CDP outperformed GAC for the rapid uptake of various CoCs.²⁹ This polymer exhibited rapid removal of many cationic and neutral CoCs, but variable affinity for most anionic CoCs and relatively poor affinity for PFOA. This initially unexpected selectivity was subsequently attributed to anionic phenolate groups introduced to the crosslinker during the polymerization.⁷¹ A post-synthetic reduction of the nitrile groups of TFN to amino groups reversed the selectivity of the polymer to yield high affinity for anionic CoCs, including twelve PFAAs.⁶⁷ The reversed selectivity is associated with amino groups, which are cationic in water at neutral pH. These groups attract PFAAs, including short-chain and branched PFAAs which have relatively weak host-guest binding with β -CD,⁵⁰ through complementary electrostatic interactions.^{82,83} These polymers with more than one means of binding PFASs raise fundamental questions about the relative roles of amines on the crosslinkers and the β -CD binding sites. These questions were challenging to study in polymers subjected to post-polymerization modification and motivated the present study of CD-based polymer adsorbents containing more well-defined crosslinkers.

Here, we describe new CDPs that leverage a synergistic combination of host-guest interactions and electrostatic interactions to show promise as adsorbents for PFAS remediation. We investigate the relative roles of β -CD and crosslinker chemistry on adsorption affinity and capacity for PFAAs. Two CDPs were prepared with comparable physicochemical properties by crosslinking β -CD with Tris(2-aminoethyl)amine (TREN) based tripodal crosslinkers, one containing amino groups for complementary electrostatic interactions and another functionalized with amido groups. The investigation of PFAS removal using the two CDPs showed that both adsorbents have at least an order of magnitude higher affinity for PFOA compared to activated carbons (ACs), suggesting the important role of the host-guest interactions. Notably, the amine-functionalized β -CD polymer exhibits efficient removal of various PFAAs at environmentally relevant concentrations, and the highest reported affinity and capacity from CDPs for both PFOA and GenX. Conversely, the amide-functionalized β -CD polymer shows low removal efficiency towards GenX. These results suggest that removal of short-chain and branched PFAAs may rely heavily on electrostatic interactions and highlight the importance of crosslinker chemistry and the promise of amine-containing CDPs for broad-spectrum PFAS remediation.

4.1.3.1 Synthesis and Characterization of Novel Tripodal-Crosslinked CDPs

A tripodal monomer containing trifunctional amine (**1**) was prepared by condensing TREN with pentafluoro-benzaldehyde under anhydrous conditions, then reducing the imines using sodium borohydride. The trifunctional amide monomer (**2**) was prepared by reacting TREN with pentafluorobenzoyl chloride under anhydrous conditions. Nucleophilic aromatic substitution of crosslinker **1** or **2** with β -CD provided the corresponding amine-containing polymer CDP1 or tris(amide)-functionalized polymer CDP2 as insoluble powders (**Figure 20**). Several variations of β -CD:crosslinker ratio, base amount and identity, and solvent concentration were screened to maximize the

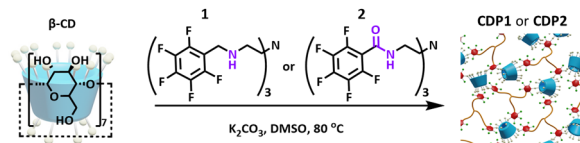


Figure 20. Syntheses of polymers CDP1 and CDP2.

polymer yields. The optimized polymerization conditions used a β -CD:crosslinker ratio of 1:2 in anhydrous dimethyl sulfoxide (DMSO, 0.15M) in the presence of K_2CO_3 (20 equiv) at 80 °C. Under these conditions, both polymers gelled within 3 h to yield CDP1 (tripodal amine) and CDP2 (tripodal amide) in 96% and 93% isolated yield, respectively. Fourier transform infrared (FTIR) spectroscopy of the isolated CDP1 and CDP2 indicated the presence of the crosslinker (1 or 2), and β -CD groups in the polymer network. Aromatic C-C stretches, and C-F stretches from the crosslinkers resonate at 1495 and 1120 cm^{-1} for both polymers. Additional carbonyl stretches at 1650 cm^{-1} are observed for amide-containing polymer CDP2. Strong bands at 3330, 2930, and 1020 cm^{-1} , which correspond to O-H, aliphatic C-H, and C-O stretches confirm the presence of β -CD moiety in the polymer network.

Table 2. Physicochemical properties of polymers.

	Linker: β -CD	Substituted F per linker	Residual F per linker	S_{BET} ($m^2 g^{-1}$)
CDP1	1.7	2.2	12.8	169
CDP2	1.8	2.4	12.6	78

To make the clear comparison between the two polymers, we prepared samples of CDP1 and CDP2 with similar corresponding crosslinking density and number of residual fluorines per linker (**Table 2**). The extent of crosslinking of each polymer was calculated based on elemental C, N, and F content. Under the optimized reaction conditions, CDP1 and CDP2 exhibited similar crosslinker: β -CD ratios of 1.7:1 and 1.8:1, respectively. In addition, CDP1 and CDP2 retained 12.8 and 12.6 fluorines per crosslinker, which corresponds to 2.2 and 2.4 fluorines, respectively, displaced from tripodal crosslinkers 1 and 2 during crosslinking. The tendency of each cross-linker to undergo an average of less than one substitution reaction per pentafluorophenyl ring underscores the importance of using tripodal or higher valency cross-linkers to obtain polymers in high yield. Two polymers displayed similar TGA traces with initial decomposition temperature at around 250 °C and 40-45 % mass remaining at 580 °C, supporting our elemental analysis that two polymers have comparable degree of crosslinking. CDP1 and CDP2 exhibited permanent porosity after activation using supercritical CO_2 . The porosity of CDP1 and CDP2, measured by N_2 porosimetry at 77K gave Brunauer-Emmett-Teller surface area (S_{BET}) of 169 and 78 $m^2 g^{-1}$, respectively. Type IV adsorption isotherms with hysteresis were observed, which is typical for mesoporous materials. Both polymers showed similar pore size distributions. Overall, the two cross-linked CD-based polymer adsorbents were prepared with comparable physicochemical properties to evaluate the role of the amine and amide groups in PFAS adsorption, although it should be noted that differences in performance might also be attributed to their factor of two difference in surface area. We partially deconvolute these effects in the following discussion.

4.1.3.2 Performance of Tripodal-Crosslinked CDPs as Adsorbents

To investigate the role of TREN based amine- and amide- functionalized crosslinkers in new polymer adsorbents on PFAS uptake, the equilibrium GenX removal was first evaluated in a batch experiment using higher concentration ($[GenX]_0 = 200 \mu g L^{-1}$) than those found in most contaminated water resources, along with relatively high polymer concentration (400 $mg L^{-1}$). Each adsorbent was sieved so the final particle size was between 45 μm and 90 μm to minimize effects of particle size differences on adsorption behavior. CDP1 exhibited rapid GenX uptake, reaching an equilibrium removal of 98% within 10 min. In contrast, 61% removal was achieved within 10 min for CDP2, and 98% removal was achieved only after 24 h. The difference in performance between the two materials was even more pronounced at lower GenX and polymer concentrations (10 $\mu g L^{-1}$ GenX and 100 $mg L^{-1}$ polymer). While CDP1 reached 97% removal in

1.5 h, CDP2 removed 69% in 1.5 h and only 85% after 24 h. Despite the similar crosslinking density and amount of β -CD present in 100 mg of polymer loading, CDP1 exhibits a much better and faster removal performance than CDP2 at ppb ($\mu\text{g L}^{-1}$) levels of GenX. Their pore size distributions are comparable ranging 20-71 Å with majority pore volume contributed from pores between 48-71 Å. We attribute major difference in uptake kinetics of GenX from CDP1 and CDP2 to difference in surface area as both polymers consist of comparable pore size distribution and particle size.

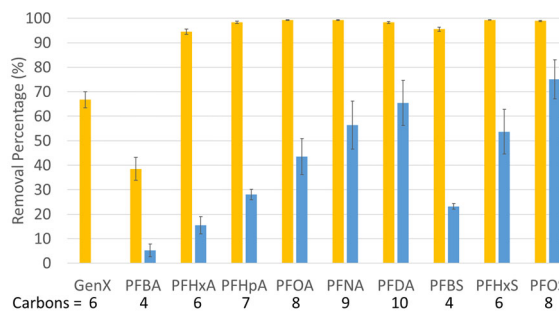


Figure 21. PFAS equilibrium removal percentage on CDP1 (yellow bars) and CDP2 (blue bars) after 48 h ([PFAS]₀ = 1 $\mu\text{g L}^{-1}$; [Adsorbent] = 10 mg L^{-1}). Error bars: standard deviation of 3 experiments.

CDP1 shows superior uptake of ten anionic PFAS at environmentally relevant concentrations compared to CDP2. A set of anionic PFAS, including perfluorinated carboxylates and sulfonates with chain lengths ranging from 4 to 10 carbons, each at 1 $\mu\text{g L}^{-1}$, were removed using 10 mg L^{-1} of polymer over 48 h (**Figure 21**). Under these conditions, CDP1 exhibited excellent equilibrium removal of many anionic PFAS with more than 96% removal of 7 PFAS, achieving a residual concentration that is well below the established health advisory level for PFOA and PFOS set by the EPA (70 ng L^{-1}). In addition, CDP1 exhibited good affinity toward GenX, and the short-chain derivatives, perfluorobutane sulfonate (PFBS) and perfluorobutanoic acid (PFBA), with 65%, 95%, and 40% removal efficiency, respectively. Under the same experimental conditions, CDP2 showed insignificant removal (<5%) of GenX and PFBA. For longer chain derivatives, PFOS and PFDA, CDP2 provided removal efficiencies of 75% and 66%, with a trend of decreasing removal with decreasing perfluorocarbon chain length. This trend is observed when the dominating adsorption mechanism is the hydrophobic interaction between the tail of PFAS and the cavity of β -CD, similar to the trend observed in solution-based titration studies of molecular β -CD and PFAS.⁵⁰ With such a mechanism, binding efficiency for short-chain PFBA and GenX is diminished as a short PFAS tail results in weakened van der Waals interactions in the interior cavity of the β -CD. The substantial difference in PFAS up-take by CDP1 compared to CDP2 suggests that the higher amine loading of the amino groups in CDP1 greatly contribute to superior PFAS binding. Especially, GenX adsorption showed a strong correlation with solution pH. When solution pH decreased from 9 to 3, significantly enhanced sorption of GenX on both CDP1 and CDP2 was observed. Their removal efficiency increased from 6 to 90% and from 1 to 47% for CDP1 and CDP2 from pH9 to pH3, respectively, indicating the important role of electrostatic interaction involved in the adsorption of anionic GenX. While hydrophobic interactions of β -CD with hydrophobic tails of PFAS is an important adsorption mechanism, electrostatic attraction proved to be a critical design criterion for the removal of short-chain and branched PFAS, which are notoriously difficult to remove from water with conventional adsorbents such as ACs.

In addition to their chemical structures, another difference between CDP1 and CDP2 is that CDP1 exhibits nearly double the BET surface area of CDP2. Although, the porosity of an adsorbent allows easier intraparticle diffusion to access adsorption sites, potentially affecting sorption kinetics, the difference in porosity between CDP1 with CDP2 is not the primary factor for the superior adsorption performance of CDP1. We explored whether difference in porosity contributes

to the superior PFAS uptake of CDP1 by preparing a non-porous CDP1 sample and characterizing both the kinetics and equilibrium uptake of ten PFAS at an environmentally relevant concentration. Porous CDP1 showed faster up-take relative to non-porous CDP1. In general, 15-25% higher removal was achieved with porous CDP1 compared to non-porous CDP1 at the 30 min time point. However, at equilibrium, non-porous CDP1 achieved comparable removal capacity as porous CDP1 with over 90% removal efficiency for 8 PFAS and 64% and 32% absorption for GenX and PFBA, respectively. The faster uptake observed in porous CDP1 highlights the advantage of preparing a porous derivative of CDP1. The retained equilibrium removal of non-porous CDP1 suggests that difference in surface area between CDP1 and CDP2 has little effect on the difference in their performance and that the superior uptake observed for CDP1 compared to CDP2 is dominated by the higher amine loading or the closer proximity of the amino groups to the β -CD.

To better understand the role that β -CD and different crosslinker chemistry plays on the removal performance by two polymers, we constructed adsorption isotherms for GenX and PFOA. A fixed concentration of polymer (100 mg L^{-1}) was used to remove $[\text{GenX}]_0$ and $[\text{PFOA}]_0$ ranging from 1 to 200 mg L^{-1} and 10 to 200 mg L^{-1} , respectively (**Figure 22**). Fitting the PFOA and GenX isotherms to the Langmuir model provides an affinity coefficient (K_L) and maximum capacity (Q_M) to describe the adsorption process (**Table 3**). An affinity coefficient of $1.8 \cdot 10^6 \text{ M}^{-1}$ and capacity of 457 mg g^{-1} were calculated from the CDP1 isotherm for PFOA, which is two orders of magnitude greater than the affinity measured for granular activated carbon (GAC) of $1.8 \cdot 10^4 \text{ M}^{-1}$ and powdered activated carbon (PAC) of $5.9 \cdot 10^4 \text{ M}^{-1}$.^{25,42} These values are the highest PFOA binding affinity and capacity values reported for β -CD polymer adsorbents.⁸³ CDP1 also showed excellent affinity and capacity of $8.8 \cdot 10^4 \text{ M}^{-1}$ and 222 mg g^{-1} for GenX removal. Based on the capacity and amount of amine loaded in one gram of polymer, the binding ratio of GenX to amine in CDP1 was calculated to be 1:4.7. We attribute this high amine concentration in CDP1 for its promising GenX removal characteristics. These values are the first affinity and capacity measurements reported for β -CD polymer adsorbents for GenX and are comparable to those reported for highly porous amine-functionalized covalent organic frame-work adsorbents ($K_L = 6.3 \cdot 10^4 \text{ M}^{-1}$ and $Q_M = 200 \text{ mg g}^{-1}$).⁸⁴ CDP1 shows two orders of magnitude higher affinity and twice the capacity towards PFOA compared to that of GenX. These data indicate synergistic effects of the amines and hydrophobic β -CD pockets in CDP1 for binding of PFOA via both electrostatic interactions and host-guest interactions.

Testing CDP2 for the removal of PFOA and GenX at similar concentration ranges as CDP1 resulted in negligible removal (**Figure 22**). Thus, the adsorption isotherms for CDP2 (100 mg L^{-1}) was generated with 1 to 20 mg L^{-1} of $[\text{PFOA}]_0$ and 0.01 to 1 mg L^{-1} of $[\text{GenX}]_0$, which is

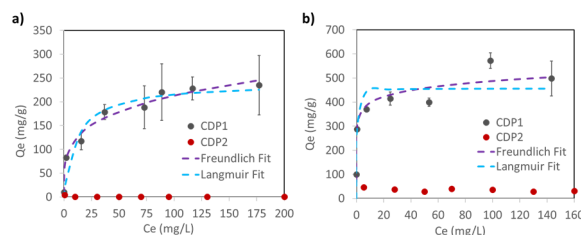


Figure 22. Adsorption isotherm of a) GenX ($1\text{--}200 \text{ mg L}^{-1}$) and b) PFOA ($10\text{--}200 \text{ mg L}^{-1}$) on CDP1 (black circle) and CDP2 (red circle) ($[\text{Adsorbent}]_0 = 100 \text{ mg L}^{-1}$). Experimental data fitted to Langmuir (Purple) and Freundlich (blue) models. Error bars: standard deviation of 3 experiments.

Table 3. Langmuir and Freundlich parameters derived from plots of the GenX and PFOA binding isotherm of CDP1.

	Langmuir Fit			Freundlich		
	$K_L (\text{M}^{-1})$	$Q_M (\text{mg/g})$	R	$K_F (\text{mg/g}) (\text{L/mg})^{1/n}$	n	R
PFOA	1.8×10^6	457	0.97	68	4.0	0.99
GenX	8.8×10^4	222	0.90	321	11	0.96

one and three orders of magnitude lower, respectively. Fitting the PFOA isotherm of CDP2 provided affinity coefficient of $3.3 \cdot 10^5 \text{ M}^{-1}$, which is an order of magnitude lower than the affinity measured for CDP1 but still an order of magnitude greater than that of PAC and GAC.^{25,42} The superior affinity of CDP2 compared to ACs illustrates the effectiveness of the β -CD moiety as a well-defined host to target PFOA. On the other hand, minimal adsorption was observed for GenX using CDP2 under the same concentration range, although CDP2 has a comparable amount of β -CD loading within the polymer network as CDP1 (0.41 and 0.40 mmol β -CD per 100 mg of CDP1 and CDP2, respectively). This observation is likely due to weak host-guest inter-actions between β -CD and GenX and lack of amines in CDP2. An isotherm constructed at much lower $[\text{GenX}]_0$ (0.01 to 1 mg L^{-1}) was suggestive of a very small number of high-affinity sites. The structural components of those binding sites are difficult to characterize, and their favorable interactions do not represent the overall properties of CDP2 for GenX binding. Collectively, these uptake performances demonstrate that host-guest inter-actions set β -CD polymer adsorbents apart from AC based adsorbents. Further, crosslinker chemistry offers a versatile way to tailor the properties of CDPs to introduce additional electrostatic interactions in CDPs, which is an important design principle for effective uptake of short-chain and branched PFAS like GenX.

4.1.3.3 Conclusions from Studies with Tripodal-Crosslinked CDPs

In conclusion, CDPs crosslinked with TREN-based tripodal crosslinkers were prepared and tested as promising materials for PFAS removal from water. When prepared with comparable physicochemical properties, CDP1 with amino groups increased binding of a broad range of PFAAs at environmentally relevant concentrations relative to CDP2, which lacks amino groups. Yet, the isotherm of CDP2 provided high affinity, outperforming that of ACs, and moderate capacity towards PFOA, leveraging well-defined host-guest interactions for enhanced uptake of PFOA. CDP1 with amino groups exhibited outstanding affinity and capacity for GenX, underscoring the importance of electrostatic interactions. Two orders of magnitude higher affinity and double the capacity obtained from CDP1 for PFOA compared to GenX further emphasize synergistic combination of well-defined host-guest interactions and electrostatic interactions as ideal design criteria for promising PFAS remediation. So far, CDP1 presents the highest affinity and capacity obtained from CDPs for both PFOA and GenX. These results suggest CDP1 is a promising candidate for PFAS remediation, and that it may be possible to further improve the performance of CDPs by adjusting the amine loading and crosslinking density. More broadly, this study highlights the broad tunability of CDPs and the importance of crosslinker chemistry.

4.1.4 A Novel Synthesis Pathway to Generate Next-Generation CDPs

We recently discovered a new way to synthesize CDPs by means of radical polymerization, which is the most versatile polymerization method used in industry. These next-generation CDPs feature more uniformly distributed β -CD binding sites that can be co-polymerized with any of hundreds of available styrenic or acrylic comonomers. Next-generation CDPs are also synthesized with excellent yields and reliable permanent porosity, providing additional benefits for technical scale-up and implementation. Importantly, next-generation CDPs also significantly outperform first-generation CDPs for the removal of perfluoroalkyl acids (PFAAs) from water. Our approach to synthesize next-generation CDPs involves copolymerizing a styrene-functionalized β -CD derivative with various styrenic or methacrylic comonomers to give permanently porous polymers with a more uniform β -CD binding environment than first-generation CDPs and a tunable composition of hydrophobic or charged comonomers. The first next-generation CDPs were evaluated for their ability to bind seven PFCA and four PFSA of different chain lengths and in different water matrices to elucidate the relative importance of the β -CD interactions,

conventionally thought to be solvophobic, and electrostatic interactions between PFAA and cations embedded in the polymer network. We showed that a next-generation CDP containing a cationic functional group exhibits exceptional removal of different chain length PFASs in nanopure water at an unprecedented low adsorbent loading of 1 mg L⁻¹. The changes in removal efficiency for both long- and short-chain PFAS as a function of salt concentration also provide insight into the combined roles of charge and β -CD binding sites for PFAS binding. These studies establish next-generation CDPs as a highly promising building block for the continued development of β -CD-based adsorbents for PFAS removal.

4.1.4.1 Synthesis and Characterization of Next-Generation CDPs

Seven styrene groups were installed at the 6' position of each β -CD subunit, effectively replacing primary alcohol groups (C-6) using approaches modified from Rojas and coworkers.⁸⁵ First, the primary alcohols were selectively substituted with iodines following established protocols, yielding **1** (**Figure 23**). The iodines were converted to thiols using thiourea, yielding **2**. The enhanced nucleophilicity and basicity of these thiolate groups enabled their selective benzylation in the presence of stoichiometric K₂CO₃ and 4-vinylbenzylchloride, yielding **3**. This sequence was carried out with an isolated yield of 75% over three-steps (23 g), with no chromatography required to purify the intermediate or final products.

The ¹H NMR spectrum of **3** indicated the successful installation of styrene groups, based on the appearance of resonances in the 5.0 – 7.5 ppm region, as well as the disappearance of thiol S-H resonance at 2.16 ppm.⁸⁵ The integrations of the aromatic resonances (7.0 – 7.5 ppm) relative to the β -CD resonance at 5.0 ppm was consistent with seven styrene groups per β -CD. ¹³C NMR spectroscopy of **3** indicated the correct number of carbon resonances, as well as the successful addition of styrene groups with peaks between 115 and 140 ppm. High-resolution mass spectroscopy of **3** confirmed the addition of seven styrene groups on the primary site based on a single peak in the full-scan chromatogram with an accurate mass corresponding to the theoretical mass of **3**. IR spectroscopy and combustion elemental analysis were also consistent with the expected structure.

The styrene groups of **3** are potentially compatible with hundreds of commercially available vinyl comonomers as well as many radical polymerization methods. This versatility will be advantageous in targeting a broad scope of contaminants of concern in the future. For this study, we polymerized **3** using azobisisobutyronitrile (AIBN) as a free radical initiator. We used these conditions to prepare three polymers based on **3**: a styrene copolymer **4**, a methyl methacrylate copolymer **5**, and a cationic methacrylate copolymer **6**. Polymers **4**, **5**, and **6** were synthesized using similar procedures by heating **3**, the comonomer, and AIBN in DMF for 1 h, with increased viscosity of the solution developing within 15 min. The crosslinked polymer was subjected to continuous liquid/solid extraction in methanol for approximately 14 h. Following extraction, the polymers were activated by supercritical CO₂ washing and isolated in high yields at multi-gram scales (**Figure 23B**). Notably, the isolated yields of these polymerizations (94-96%) were significantly higher than our previous crosslinker based β -CD adsorbents, which we attribute to the high efficiency of radical

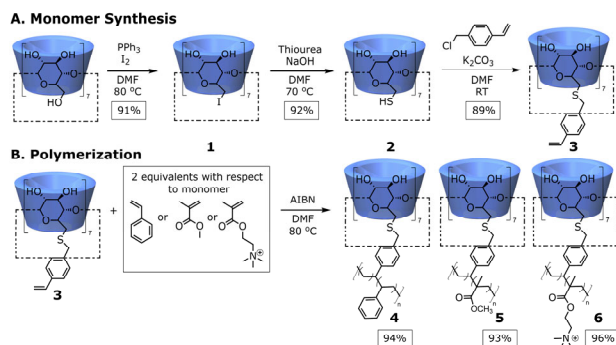


Figure 23. Synthetic scheme of styrene-functionalized cyclodextrin monomer and polymers.

polymerizations of styrene and methyl methacrylate relative to those based on less well-established chemistries.

Polymers 4, 5, and 6 formed porous and crosslinked networks with permanent surface charge. Solid-State cross-polarization mass angle spinning ^{13}C NMR spectroscopy confirmed the incorporation of comonomers in 4, 5, and 6. In all three spectra, the resonance corresponding to vinyl carbons of 3 (113 ppm) were not detected, suggesting a high degree of polymerization of the styrene groups. The polymer backbone was formed from the vinyl carbons, as evident by the broadened alkane regions (20 – 55 ppm). In the spectra of 5 and 6, carbonyl carbons of the comonomers were detected around 180 ppm. Furthermore, the characteristic N-methyl carbons (55 ppm) were detected in the spectrum of 6. The elemental analyses of the three polymers suggested that each polymer incorporated between 1.2 – 2.0 comonomers per β -CD. A feed ratio of two equivalences of comonomers with respect to 3 was determined to be most promising based on preliminary PFAS binding studies, and were used in subsequent polymerizations. The comonomer incorporation ratio of 4 and 6 were calculated to be 1.8 and 2.0, respectively, which were consistent with the feed ratio. The ratio of 5, however, was 1.2, indicating that methyl methacrylate was not incorporated as readily. The porosity and Brunauer-Emmett-Teller surface area (SBET) of polymers 4, 5, and 6 were characterized by N_2 isotherms. Each polymer exhibited permanent porosity and high SBET, ranging from 237 – 402 $\text{m}^2 \text{g}^{-1}$, which is higher than previous β -CD adsorbents.^{29,67,69} Lastly, the zeta potentials of suspensions of 4 and 5 were found to be weakly negative whereas 6 was strongly positive (**Table 4**). IR spectroscopy of the polymers was consistent with their expected structures. These data confirmed the porous and crosslinked nature of the polymers, which can be subsequently used to remove PFAS.

Table 4. Characterization of the adsorbents.

Adsorbent	Co-monomer charge	Zeta Potential (mV)	Diameter (μm)	BET surface area (m^2/g)	Yield %
4	neutral	- 8	149	402	94
5	neutral	- 10	118	392	93
6	cationic	+ 24	162	237	96

4.1.4.2 Performance of Next-Generation CDPs as Adsorbents

We first evaluated the removal performances of polymers 4, 5, and 6 at an adsorbent loading of 10 mg L^{-1} for 4 – 10 carbon PFCAs (initial concentration of 1 $\mu\text{g L}^{-1}$ for each compound) in a nanopure water (NP) matrix and in a 1 mM Na_2SO_4 (SS) matrix (**Figure 24**). The SS matrix was chosen to probe the relative importance of solvophobic and electrostatic interactions in both short- and long-chain PFAS removal. Adsorbents 4 and 5 were inefficient at adsorption in NP matrix with 0 – 5% removal for all tested PFASs. However, adsorbent 6 performed effectively, with nearly 100% removal across the 4 – 10 carbon PFCAs. The ability of 6 to remove the four carbon PFBA and five carbon PFPeA (>99% removal) was notable because these short-chain PFAS are not removed as effectively by ACs and other emerging adsorbents. We attribute this promising performance of 6 to the permanently positive charge that interacts favorably with PFAA, as has been shown for other designed adsorbents based on β -CD and other materials.^{83,86,87} PFCA removal experiments conducted using adsorbents 4, 5, and 6 in a 1 mM SS matrix indicated that PFASs of different chain lengths interacted with the adsorbents and matrix through different non-covalent interactions. Generally speaking, hydrophobic adsorbents 4 and 5 showed enhanced, yet still modest PFCA removal in SS matrix as compared to NP matrix (**Figure 24A** and **24B**). In contrast, adsorbent 6 showed inhibited, yet still relatively high PFCA removal in the SS matrix as compared to the NP matrix (**Figure 24C**). Inhibition was most profound for PFBA and PFPeA, the shortest chain PFCAs that were studied, and was relatively minor for seven carbon and longer PFCAs. The removal of four carbon PFBA by 6 was inhibited substantially from 99% to 21% in SS matrix,

suggesting that electrostatic interactions play a significant role in short-chain PFCA removal. We attribute the interference to direct-site competition in which inorganic anions compete with anionic PFCA for adsorption sites, and/or a screening effect that limits attractive electrostatic interactions due to a compression of electrical double layer.^{88–90} Notably, the removal of longer chain 6–10 carbon PFCA was less inhibited in the SS matrix. The removal of six carbon PFHxA decreased from 99% to 87%, and the removal of 8–10 carbon PFCA were nearly unaffected. The decreased sensitivity of longer chain PFCA to ionic strength suggests that solvophobic interactions between the perfluoroalkyl tails and the hydrophobic portions of the polymer, and the β -CD inner cavity, play a relatively large role in longer chain PFCA removal. Alternatively, it is possible that these solvophobic interactions increase in energy at higher ionic strength as PFCA and electrostatic interactions are attenuated. On the other hand, adsorbents 4 and 5 were significantly enhanced for most PFCA, except four carbon PFBA, with longer chain PFCA experiencing more profound enhancement. For instance, the removal of ten carbon PFDA increased from 7% to 34% by 4 and from 1% to 39% by 5. We attribute this enhancement to a salting out effect, in which the presence of inorganic ions decreased the solubility of organic molecules and increased solvophobic interactions for adsorbents 4 and 5 and long-chain PFCA.^{91,92}

Additionally, this enhancement may also result from a screening effect that reduces the repulsion between negatively charged surfaces of 4 or 5, and the anionic PFCA.

4.1.4.3 Performance of Next-Generation CDPs as Adsorbents at Reduced Loading

To better investigate the magnitude of inhibitory or enhancement effect for the same concentration of PFCA in NP and SS matrices, adsorbent 6 loading was adjusted from 10 mg L⁻¹ to 1 mg L⁻¹ (**Figure 25**), and adsorbents 4 and 5 loadings were adjusted from 10 mg L⁻¹ to 100 mg L⁻¹ (data not shown). A mixture of 4, 6 – 8 carbon PFSA was added in both matrices with an initial concentration of 1 μ g L⁻¹ (**Figure 25B**). Under these conditions, adsorbents 4 and 5 showed modest removal and similar trends of enhancement in the higher ionic strength matrix. However, 6 exhibited promising high PFCA and PFSA removal even at these low adsorbent loadings, such as over 90% removal of 6 – 10 carbon PFCA. The removal of four carbon PFBA and five carbon PFPeA were 57% and 84%, respectively, which is unsurprisingly lower than their removals at 10

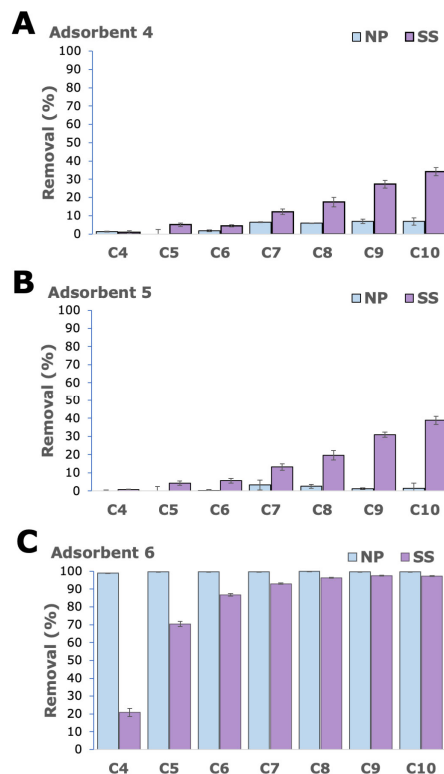


Figure 24. The removal of 1 μ g L⁻¹ PFCA by 10 mg L⁻¹ of (A) 4, (B) 5, and (C) 6 in nanopure water (NP, blue bar) and 1 mM Na₂SO₄ (SS, purple bar) after 48 h of contact time.

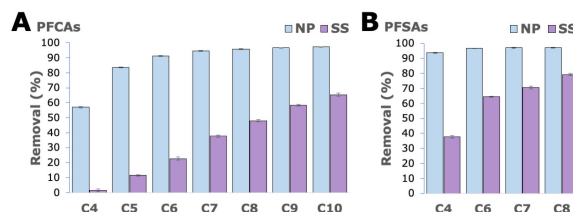


Figure 25. The removal of 1 μ g L⁻¹ PFCA and PFSA by 1 mg L⁻¹ of 6 in nanopure water (NP, blue bar) and 1 mM Na₂SO₄ (SS, purple bar) after 48 h of contact time.

mg L⁻¹ loading. Yet, this performance is still promising because of the difficulty of short-chain PFCA removal. Exceptional removal was also observed for PFSA (Figure 25B), which were each removed to a greater extent than PFCAs counterparts of same carbon numbers. For example, 94% of four carbon PFBS was removed in NP matrix compared to the 57% removal of four carbon PFBA. Similar studies have corroborated the greater adsorptions of PFSA than PFCAs on β -CD polymers and other adsorbents.^{30,69,73,93} We attribute this difference to PFSA being more hydrophobic than PFCAs, due to having one more fluorinated carbon atom than PFCAs with the same carbon number. The more effective removal of PFSA by 6 once again highlights the importance of the cationic feature for PFAA removal. To our knowledge, 1 mg L⁻¹ is the lowest adsorbent loading for this class of adsorbents to achieve exceptional removal for anionic PFCA and PFSA in NP matrix at 1 μ g L⁻¹ pollutant loading.

The inhibitory effect of inorganic ions on short-chain PFCAs and PFSA is apparent at a lower adsorbent 6 loading in SS matrix, with decreased removal performance as a function of decreased carbon numbers for both PFCAs and PFSA. The removal of shorter chain PFCAs and PFSA experienced significantly greater interference by inorganic ions than longer chains. The removal of four carbon PFBA decreased from 57% to 1% and five carbon PFPeA decreased from 84% to 12%. The virtually complete inhibition of adsorbent 6 implies that the removal of shorter chain PFCAs relies primarily on electrostatic interactions. Four carbon and five carbon PFSA removals were less inhibited, with decreased removal from 94% to 38% and 97% to 64%, respectively. The removal of longer chain PFCAs and PFSA were weakly inhibited. The removal of eight carbon PFOS decreased from 97% to 79% and the removal of ten carbon PFDA decreased from 97% to 65%. As noted previously, the uptake of longer chain PFAS was less attenuated because of the more pronounced hydrophobic interaction with the β -CDs. Assuming that electrostatic attraction is rendered ineffective in SS matrix, such as the case of four carbon PFBA, hydrophobic interactions become the primary binding force for removal. In NP matrix, 96% of PFOA was removed by adsorbent 6, whereas the removal decreased to 48% in SS matrix. This difference of approximately 50% in removal performance hints at an additive nature of electrostatic and hydrophobic interactions.

4.1.4.4 Performance of Adsorbents in Presence of Inorganic Ions

Monovalent and divalent inorganic ions were evaluated to further explore the importance of observed adsorption inhibition. We selected the following salts and concentrations: 1 mM Na₂SO₄ (SS), 2 mM NaCl (SC), and 1 mM CaCl₂ (CC) in order to generate comparable data with 2 mM of monovalent sodium or chloride ions and 1 mM of divalent sulfate or calcium ions (Figure 26). The adsorbent 6 loading remained as 1 mg L⁻¹ with 1 μ g L⁻¹ of the PFCA mixture. No significant differences ($p \geq 0.05$) were found when comparing the removal of PFCAs by adsorbent 6 in SC and CC matrix, suggesting that the cation valency does not impact inhibition. However, the anion valency was observed to impact inhibition as the removal of 5–10 carbon PFCAs were

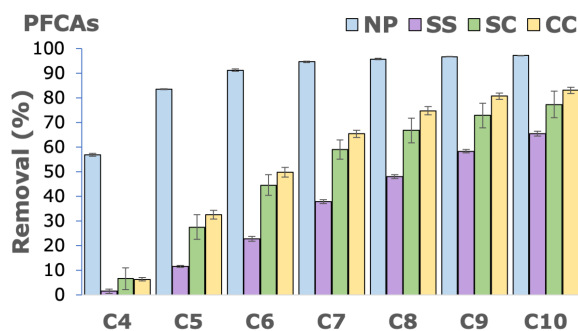


Figure 26. The removal of 1 μ g L⁻¹ PFCAs by 1 mg L⁻¹ 6 in nanopure water (NP, blue bar), 1 mM Na₂SO₄ (SS, purple bar), 2 mM NaCl (SC, green bar), and 1 mM CaCl₂ (CC, yellow bar) after 48 h contact time.

significantly ($p < 0.05$) more inhibited in the divalent SS matrix than the monovalent SC matrix. Additionally, the type of anion may potentially affect inhibition to a varying extent. We attribute anion valency to either direct-site competition and/or a screening effect. For instance, one unit of divalent anion sulfate has a greater screening effect due to compression of the electrical double layer than two units of monovalent anion, where the compression is directly related to ionic strength which is proportional to the square of ion valence.

4.1.4.5 Conclusions from Studies with Next-generation CDPs

In conclusion, we used modular, permanently porous, and crosslinked styrene-functionalized β -CD polymers with controllable binding environment and tunable compositions of comonomer to remove PFAS of different carbon numbers. The modularity of this platform and reliability of radical polymerization enabled a broad range of comonomers to be incorporated. This structural versatility in turn enables performance trends to be studied as a function of the adsorbent structure and water matrix. Adsorbent 6, with its cationic comonomer, achieved exceptional removal efficiencies of PFCAs and PFSAAs at adsorbent loading as low as 1 mg L^{-1} . The inhibition effect observed in SS matrix revealed a fascinating complementary interplay of hydrophobic and electrostatic interactions between the adsorbent and PFASs as a function of fluorocarbon chain lengths. We demonstrated that removal of shorter chain PFASs that are conventionally difficult to remove relies most strongly on electrostatic interactions, which are disrupted when high concentrations of salts are present in the matrix. The removal of longer chain PFASs is achieved through a complementary interplay of hydrophobic and electrostatic interactions. These results demonstrate that styrene-functionalized β -CD polymers are promising adsorbents for the remediation of PFAAs. Furthermore, the materials might be tailored to target cationic and neutral PFAS by varying the comonomer structures. The unprecedented control afforded by the platform offers insights into the fundamental binding mechanisms between β -CD polymers and PFASs.

4.2. Exploring Covalent Organic Frameworks (COFs) with Novel Functionalities

Covalent organic frameworks (COFs) are unexplored yet promising adsorbent materials because of their high surface area and tunable pore sizes.^{94–97} In parallel with our efforts to discover CDPs that can rapidly remove complex mixtures of PFASs from groundwater, we serendipitously discovered that certain COFs remove PFAAs from water rapidly at environmentally relevant concentrations.⁸⁴ Our parallel work with COFs has provided an excellent example of how COFs can be used as novel adsorbents themselves, but also as structurally precise test-beds for exploring functional groups that may provide complementary and synergistic benefits for the adsorption of specific classes of PFASs. The following sections describe work completed during ER18-1026 that resulted in new and promising COFs that were synthesized to simultaneously assess their potential as novel adsorbents and as a means to rigorously explore functional groups that may provide complementary and synergistic benefits for the adsorption of specific classes of PFASs. In this section, we first describe the synthesis of imine-linked two-dimensional (2D) COFs bearing primary amines (reduced from azides) that rapidly remove anionic PFASs from water.⁸⁴ We then describe the synthesis of COFs bearing zwitterionic side-chains that exhibit potential to remove diverse types of PFAS from water.

4.2.1 Imine-Linked Two-Dimensional (2D) COFs Bearing Primary Amines

Covalent organic frameworks (COFs) are crystalline, porous polymers whose monomers are organized using directional bonding principles.^{94–97} Several features of COFs enable them to function as adsorbents with fast uptake and high capacity: their crystallinity positions functional groups into precise arrangements and their few-nanometer 1D channels are readily accessible.^{98–}

¹⁰⁰ COFs have been demonstrated for binding technologically relevant gases, such as CH₄,¹⁰¹ H₂,^{101,102} NH₃,¹⁰³ and CO₂,^{98,104} and heavy metals,^{100,105} but they are unexplored for sequestering PFASs. Here we reduce azide-functionalized COFs to the corresponding amine-functionalized networks and demonstrate their promise as adsorbents for per- and polyfluorinated alkyl substances (PFAS). The COFs studied here present amine groups that interact with the anionic head group of PFAS, along with ample hydrophobic surface area that further support adsorption. The optimized materials, with amine loadings of 20–28%, bind 13 PFAS with high affinity and rapid kinetics.

4.2.1.1 Synthesis and Characterization of Amine-Bearing COFs

We targeted a hexagonal imine-linked 2D COF bearing amine functionalities to provide high affinity for anionic PFAS. The loading of amine functional groups into the final COF was controlled by condensing 1,3,5-tris(4-aminophenyl)benzene (**1**, **Figure 27**) with a mixture of terephthalaldehyde (**3**) and a dialdehyde bearing azide-functionalized ethylene glycol side chains (**2**). **2** and **3** were polymerized in various molar ratios to synthesize COFs (X%[N₃]-COFs) that average 6, 4.5, 3, 1.5, 1, 0.5, and 0.06 azides, respectively, per layer within each hexagonal pore. X%[N₃]-COFs were prepared in a 4:1 mixture of 1,4-dioxane and mesitylene with 6M CH₃CO₂H at 90 °C for 72 hours. The resulting precipitates were collected and purified by Soxhlet extraction with CH₃OH and activated by supercritical CO₂ drying. X%[N₃]-COFs were reduced to the corresponding X%[NH₂]-COFs by PPh₃ in CH₃OH. The amine-functionalized imine COFs (X%[NH₂]-COFs) were washed with 4% (v/v) H₂O in acetone followed by CH₃OH, and subsequently activated by supercritical CO₂ drying.

The complete reduction of azides to amines was characterized by spectroscopy. Fourier-transform infrared spectroscopy (FT-IR) revealed that the azides in X%[N₃]-COFs were reduced, based on the disappearance of the azide stretch at 2098 cm⁻¹ (**Figure 28a**) and the appearance of a broad amine N–H stretch at 3356 cm⁻¹. The incorporation ratios of the COFs with lower azide and amine loadings were slightly higher than the feed ratios, as judged from the quantitative IR analysis, indicating that **2** is slightly more reactive than **3**. X-ray photoelectron spectroscopy (XPS) also indicated the conversion of azides to amines (**Figure 28b**). The spectrum of the 100%[N₃]-COF shows characteristic azide N 1s peaks at 400.0 and 403.7 eV with an area ratio of 2:1.^{106,107} The spectrum of the 100%[NH₂]-COF instead shows a new N 1s peak at 398.6 eV, which was fit to a 1:1 combination of imines and aliphatic amines.^{106,107} Zeta potentials of 100%[N₃]-

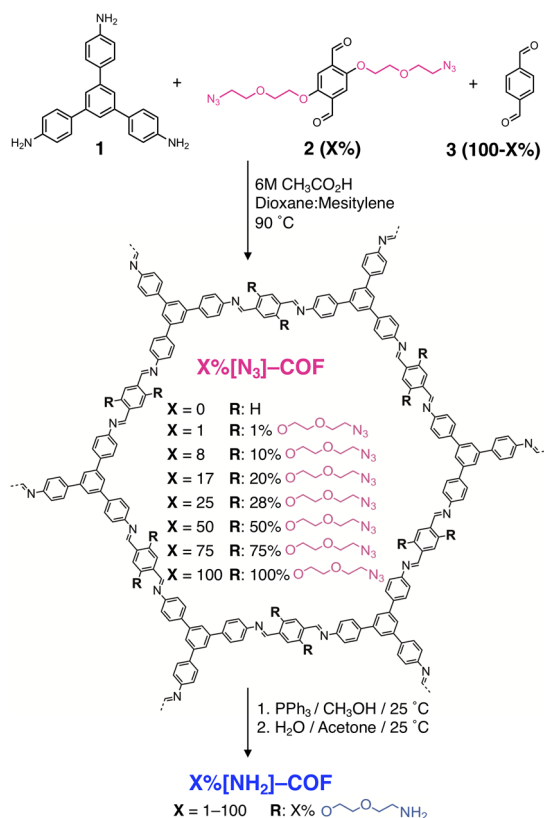


Figure 27. Schematic of COF synthesis.

COF and 100% $[\text{NH}_2]$ -COF at pH 7 were -7 mV and +13 mV, whose change in sign is attributed to protonation of the amines. Collectively, these measurements and elemental analysis indicate the quantitative conversion of azides to amines.

The crystallinity and porosity of X% $[\text{NH}_2]$ -COFs were retained after the reduction, as confirmed by powder X-ray diffraction (PXRD, **Figure 28c**) and N_2 adsorption isotherms (**Figure 28d**). The PXRD pattern of 100% $[\text{N}_3]$ -COF exhibited an intense (100) diffraction peak at 2.8° , along with the (110), (200), and (001) diffraction peaks at 4.8° , 5.6° , and 25.2° , respectively, which is consistent with the reported eclipsed pattern for imine-linked COFs containing dimethoxy side groups. 100% $[\text{NH}_2]$ -COF exhibited an identical PXRD pattern to that of 100% $[\text{N}_3]$ -COF, indicating that the 2D hexagonal structure of 100% $[\text{N}_3]$ -COF was retained upon reduction. Each X% $[\text{NH}_2]$ -COF also exhibited the same PXRD pattern to that of the corresponding X% $[\text{N}_3]$ -COF. The permanent porosity of X% $[\text{N}_3]$ -COFs and X% $[\text{NH}_2]$ -COFs was measured by N_2 adsorption isotherms at 77 K (**Figure 28d**). The Brunauer–Emmett–Teller (BET) surface area of 100% $[\text{N}_3]$ -COF was $1100 \pm 150 \text{ m}^2/\text{g}$, and that of 100% $[\text{NH}_2]$ -COF was $1000 \pm 70 \text{ m}^2/\text{g}$. The BET surface areas of other X% $[\text{NH}_2]$ -COFs were also retained upon reduction. Nonlocal density functional theory analysis of each isotherm provided narrow pore size distributions centered around 2.6 nm. As the concentration of azides and amines (X) decreased, the BET surface areas and average pore sizes of X% $[\text{N}_3]$ -COFs and X% $[\text{NH}_2]$ -COFs increased. These results confirm the formation of a broad range of 2D imine-linked COFs with pendant amine loadings ranging from 1 to 100% of the terephthalaldehyde monomers.

4.2.1.2 Performance of Amine-Bearing COFs as Adsorbents

Each of the X% $[\text{NH}_2]$ -COFs exhibited superior equilibrium removal of GenX compared to both 100% $[\text{N}_3]$ -COF and 0% $[\text{N}_3]$ -COF. The equilibrium Gen-X removal by X% $[\text{NH}_2]$ -COFs, 100% $[\text{N}_3]$ -COF and 0% $[\text{N}_3]$ -COF was first evaluated in a batch experiment using $[\text{GenX}]_0$ of $200 \mu\text{g L}^{-1}$, and $[\text{COF}]$ of 100 mg L^{-1} (**Figure 29a**). GenX removal was inversely correlated to amine loading for 100% $[\text{NH}_2]$ -COF (56%) through 20% $[\text{NH}_2]$ -COF (97%). At lower amine loadings, GenX adsorption decreased slightly for 10% $[\text{NH}_2]$ -COF (94%) and 1% $[\text{NH}_2]$ -COF (73%). The trend of increasing GenX removal from 0% to 20% amine loading and the poor removal by 100% $[\text{N}_3]$ -COF and 0% $[\text{N}_3]$ -COF indicate that the amines are essential for GenX binding. The trend of decreasing GenX removal from 20% to 100% amine loading suggests that dispersing the

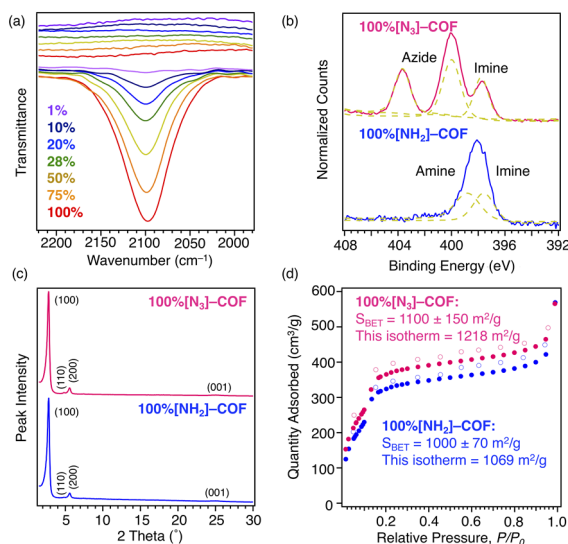


Figure 28. (a) FT-IR spectra ($2300\text{--}1900 \text{ cm}^{-1}$) of X% $[\text{N}_3]$ -COFs (bottom spectra) and X% $[\text{NH}_2]$ -COFs (top spectra), corresponding to the concentration of azides or amines (X) of 100% (red), 75% (orange), 50% (yellow), 28% (green), 20% (blue), 10% (indigo), and 1% (purple). (b) XPS of N 1s core level (392–408 eV) (c) PXRD patterns normalized at the (100) peak at 2.8° and (d) N_2 adsorption isotherm of 100% $[\text{N}_3]$ -COF (pink) and 100% $[\text{NH}_2]$ -COF (blue). For (d), solid and open circles indicate adsorption and desorption, respectively. Surface areas are reported as ± 1 standard deviation of 14 independently prepared samples of 100% $[\text{N}_3]$ -COF, and 3 independently prepared samples of 100% $[\text{NH}_2]$ -COF.

amines in the network is essential for maximum affinity, either to allow for sufficient space within the pores or ad-sorption of the hydrophobic tails to the pore walls.

The GenX binding capacity as a function of amine loading was probed further at higher $[\text{GenX}]_0$ (50 mg L^{-1}), still with a COF loading of 100 mg L^{-1} (**Figure 29b**). 20% $[\text{NH}_2]$ -COF again exhibited the highest capacity for GenX of 240 mg g^{-1} (**Figure 29b**), and 0% $[\text{N}_3]$ -COF adsorbed the least GenX (3 mg g^{-1}). The molar ratio of GenX to amines in $X\%[\text{NH}_2]$ -COFs ($[\text{GenX}]/[\text{NH}_2]$) is approximately 2:1 from 1% to 20% $[\text{NH}_2]$ -COFs and 1:1 for 28% $[\text{NH}_2]$ -COF. The GenX:amine ratio then drops below 1:1 as the amine loading is increased from 28% to 100%, indicating that not every amine can inter-act with GenX at these higher loadings. These results suggest that the amines in the network create a microenvironment that is conducive for GenX binding and that each amine can bind a maximum of two GenX molecules when distributed sparsely in the network.

To better understand the removal of GenX by $X\%[\text{NH}_2]$ -COFs, we constructed a GenX binding isotherm for 28% $[\text{NH}_2]$ -COF and 100% $[\text{NH}_2]$ -COF using $[\text{COF}] = 100 \text{ mg L}^{-1}$ and $[\text{GenX}]_0$ ranging from 0.2 to 100 mg L^{-1} . The isotherm was best fit by the Langmuir model, which provided an affinity coefficient, K_L , of $6.3 \times 10^4 \text{ M}^{-1}$ and the estimated maximum capacity, Q_m , of 200 mg g^{-1} for 28% $[\text{NH}_2]$ -COF and K_L of $7.2 \times 10^4 \text{ M}^{-1}$ and Q_m of 130 mg g^{-1} for 100% $[\text{NH}_2]$ -COF. The high affinity coefficients and capacities of 28% $[\text{NH}_2]$ -COF and 100% $[\text{NH}_2]$ -COF explain their remarkable removal of GenX from water.

Based on the GenX removal experiments, the 28%, 1%, and 100% amine-loaded COFs were evaluated for their ability to remove a mixture of thirteen PFAS with different chain lengths and functional groups at environmentally relevant concentrations (**Figure 30**). Following exposure of nanopure water solutions containing $1 \text{ } \mu\text{g L}^{-1}$ (1 ppb) of each PFAS to 10 mg L^{-1} of each COF, equilibrium binding was observed within 30 minutes, and each COF exhibited broad spectrum removal and high affinity for nearly all of the PFAS. Among the three COFs, 28% $[\text{NH}_2]$ -COF performed the best and removed more than 90% of 12 PFAS and 63% of perfluorobutanoic acid (PFBA). These observations suggest that 28% $[\text{NH}_2]$ -COF has the highest affinity for 13 PFAS compared to 1% $[\text{NH}_2]$ -COF and 100% $[\text{NH}_2]$ -COF, consistent with the GenX studies performed at higher concentration. We also observed that the 1% $[\text{NH}_2]$ -COF and 100% $[\text{NH}_2]$ -COF exhibited partial desorption of the bound PFAS between the 1- and the 24- hour time points. This effect was less pronounced for 28% $[\text{NH}_2]$ -COF. Partial desorption was also observed in experiments conducted only with GenX, ruling out competitive adsorption as an explanation. We are currently investigating the nature of these effects, which indicate a slow, dynamic change to these COFs that is not observed in the 28% $[\text{NH}_2]$ -COF adsorbent. Finally, we benchmarked the GenX adsorption by 28% $[\text{NH}_2]$ -COF against a granular activated carbon (GAC, particle size $>1000 \text{ } \mu\text{m}$) and a powdered activated carbon (PAC, particle size $10\text{--}75 \text{ } \mu\text{m}$) at environmentally relevant

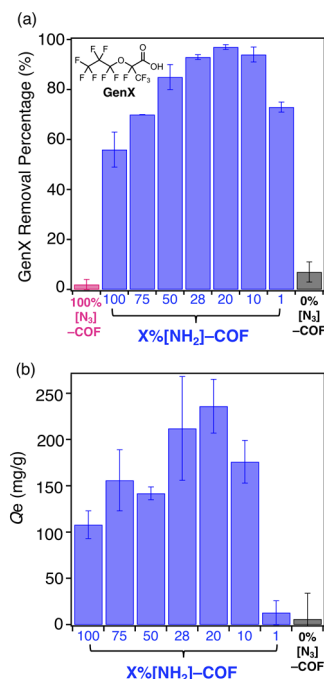


Figure 29. (a) Equilibrium GenX removal percentage at $[\text{GenX}]_0 = 200 \text{ } \mu\text{g L}^{-1}$ and (b) equilibrium adsorption density at $[\text{GenX}]_0 = 50 \text{ mg L}^{-1}$ by equal mass concentrations (100 mg L^{-1}) of 100% $[\text{N}_3]$ -COF (pink), $X\%[\text{NH}_2]$ -COFs (blue), and 0% $[\text{N}_3]$ -COF (black) after the contact time of 22 hours. Q_e (mg g^{-1}) is the equilibrium adsorption density. Error bars: standard deviation of 3 experiments.

concentrations (**Figure 30c**). 28%[NH₂]-COF outperformed both GAC and PAC in these experiments, in which GAC removed 0%, PAC removed 72%, and 28%[NH₂]-COF removed 91% of GenX after 30 min. These combined observations indicate that amine-functionalized 2D COFs are outstanding candidates for GenX and broad-spectrum PFAS removal.

4.2.1.3 Conclusions from Studies with Amine-Bearing COFs

We incorporated a varying density of amine functionalities into the pores of imine-linked COFs while maintaining high surface areas (≥ 1000 m²/g). The amine-functionalized COFs show rapid uptake and high affinity for adsorbing GenX and other PFAS that is strongly influenced by the amine loading. Among the amine-functionalized imine COFs, 20%[NH₂]-COF showed the highest uptake of GenX at high concentrations ([GenX]₀ = 0.2 and 50 mg L⁻¹) and 28%[NH₂]-COF showed the most rapid and the highest uptake of GenX as well as 12 other PFAS at environmentally relevant concentrations, suggesting that the ideal composition of amines for removing PFAS is in this range. The well-defined COF structure and relationships between amine loading and PFAS affinity and capacity also suggest general design criteria to improve the performance of other adsorbent classes.

4.2.2 COFs Bearing Zwitterionic Side-Chains

We next aimed to use structurally defined COFs to further improve our understanding of functional groups that impart high affinity for anionic, cationic, and zwitterionic PFAS. Our goal was to synthesize a series of COFs with zwitterionic chains contained within their pore structure. We hypothesized that the zwitterionic COF will exhibit high affinity for a variety of PFASs including anionic, zwitterionic, cationic, and neutral PFASs. We started by synthesizing a COF with neutral chains in the pores and we then developed a technique to post-functionalize the neutral chains into zwitterionic chains. We evaluated the performance of the resulting zwitterionic COFs with varying loadings of zwitterionic side chains to remove a mixture of PFASs from water. We then developed a procedure to translate the zwitterionic functionality into the structure of a novel CDP. The following sections describe the research performed.

4.2.2.1 Synthesis and Characterization of Zwitterionic COFs

The most promising approach that we developed involves the synthesis of a neutral dialkylamine-appended terephthalaldehyde monomer from which the COF is assembled. COFs

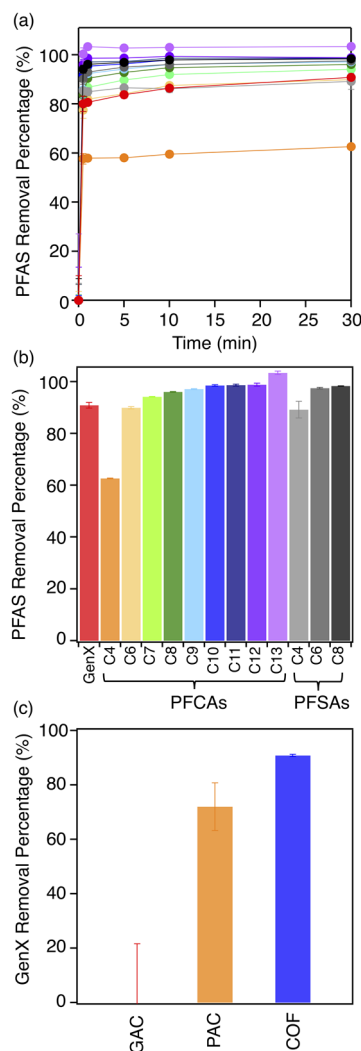


Figure 30. (a) Kinetics of PFAS adsorption by 28%[NH₂]-COF ([PFAS]₀ = 1 µg L⁻¹; [COF] = 10 mg L⁻¹) at 23 °C. (b) PFAS equilibrium removal percentage on 28%[NH₂]-COF after 30 min. PFCAs: perfluoroalkyl carboxylic acids; PFSA: perfluoroalkyl sulfonic acids. (c) GenX adsorption after 30 min by GAC, PAC, and 28%[NH₂]-COF using [GenX]₀ = 1 µg L⁻¹; [Adsorbent] = 10 mg L⁻¹. Error bars: standard deviation of 3 experiments.

were synthesized with this monomer, and synthesis optimization focused on achieving high-surface area materials as evidenced by spectroscopic, porosimetric, and crystallographic analyses. The high-surface area neutral COFs were then post-functionalized through reactions between the dialkylamine chains and 1,3-propane sultone to create the expected zwitterionic COFs (**Figure 31**). We have also examined several experimental conditions for the sultone ring-opening reaction within the COF pores to achieve zwitterionic COFs. The NMR spectroscopic analyses of product COFs have demonstrated the successful conversion of neutral dimethylamine moieties to zwitterionic ammonium sulfate moieties within the COF pores. Although the zwitterionic COF displays less crystallinity and porosity than the starting COF, it contains the functionality required.

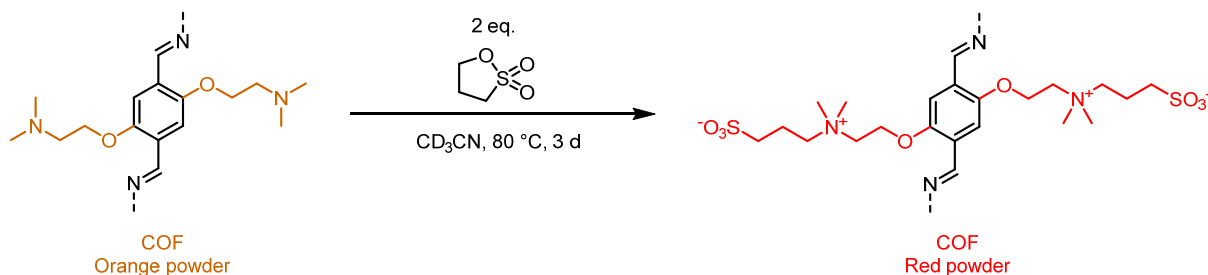


Figure 31. Schematic of the synthesis of the zwitterionic COF from a neutral COF.

We then synthesized two very similar versions of 2D COFs containing zwitterions in the pores (**Figure 32**). One COF (called the C1 COF series) has the non-zwitterionic linkers being inert 1-carbon-long chains into the pores, the other COF (called the C6 COF series) has the non-zwitterionic linkers being inert 6-carbon-long chains into the pores. So the C6 series has pores that are more sterically hindered than the C1 series, but the C6 series can maintain crystallinity when we introduce a higher zwitterionic loading, whereas C1 will lose crystallinity more easily. For both of these COFs, we first made C1 and C6 unfunctionalized COFs and then converted them to zwitterionic (functionalized) COFs using reactions that went ~90%+ to completion.

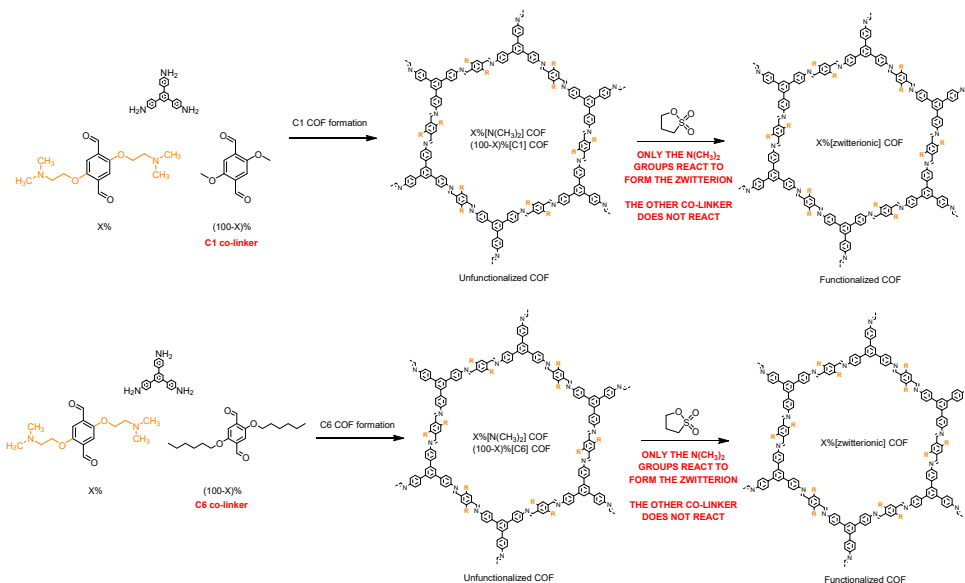


Figure 32. Schematic of the synthesis of P-CDP. The β -cyclodextrin (β -CD) monomer is crosslinked with tetrafluoroterephthalonitrile (TFN) to generate the first porous β -CD polymer (P-CDP).

4.2.2.2 Performance of Zwitterionic COFs as Adsorbents

We next performed kinetics and equilibrium studies with the zwitterionic COF materials to evaluate their performance for removing a diverse set of PFASs including PFBA, PFOA, PFBS, PFOS, FBSA, FOSA, AP-FHxSA, TAmP-FHxSA, 6:2 FTAB, 5:3 FTB, and 5:1:2 FTB. We benchmarked the performance in parallel experiments with a powdered activated carbon material. Our results suggest that the primary COF material (identified as a C1 COF with 95% loading below) does not perform well for PFAS removal (**Figure 33**). This is in contrast to our previous studies with an amine-containing COF that exhibited rapid and complete removal of anionic PFASs from water (**Figure 30**).

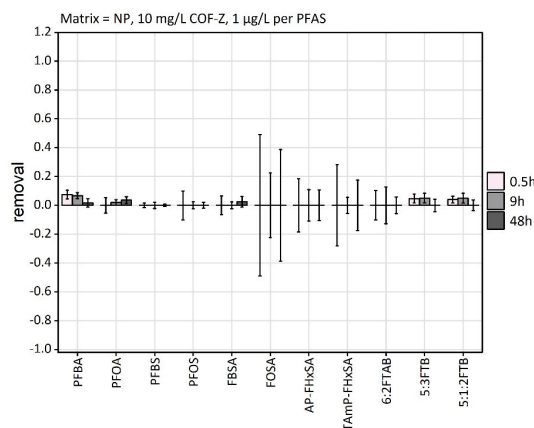


Figure 33. Removal of 11 PFAS by the zwitterionic C1 COF with 95% loading.

This result inspired the synthesis of the C1 COFs with varying loadings of the zwitterionic side-chain along with the C6 COFs. However, this co-linker also determines the extent of crystallinity, and crystallinity is expected to be an important feature for PFAS adsorption. The C1 COF is crystalline at low loadings of zwitterionic side chains whereas the C6 COF remains crystalline at higher loadings of zwitterionic side chains. The first COF that we tested (described in the preceding paragraph) was a C1 COF with 95% loading of the zwitterionic side chain. Our previous amine-containing COF exhibited the best performance for removing anionic PFAS with 20% loading of the amine side chain. We therefore synthesized C1 and C6 COFs with zwitterionic side chain loadings of approximately 10%, 20% and 40%. We found that the C6 COFs with zwitterionic side chain loadings of approximately 10%, 20% and 40% are very hydrophobic and don't mix well in aqueous solution; because of this, we could not perform adsorption experiments with these COFs. The C1 COFs were less hydrophobic but, like the 95% loaded C1 COF (**Figure 33**), did not perform well for PFAS removal from water.

4.2.2.3 Translation of Functional groups from COFs to CDPs

As described in Section 4.1.4, we developed a new class of cyclodextrin polymers that are structurally precise, and compatible with over hundreds of commercially available styrenic and acrylic comonomers by covalently linking a styrene group to each of the of the seven β -cyclodextrin glucose subunits. The styrene-functionalized β -cyclodextrin monomer can be co-polymerized using a radical initiator with styrenic or acrylic comonomers to give rise to permanently porous, crosslinked networks with more uniform β -cyclodextrin binding environments and tunable compositions of comonomers. We have used this cyclodextrin platform to incorporate the same zwitterionic ammonium sulfate moieties as described for the zwitterionic COF into the cyclodextrin polymer structure. We likewise

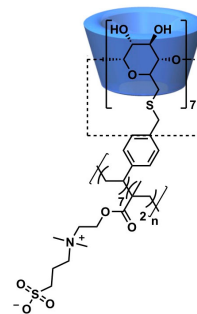


Figure 34. Zwitterionic comonomer designed for incorporation into CDPs.

synthesized cyclodextrin-based adsorbents using other comonomers demonstrating the ease of synthesis with this new approach.

4.2.2.4 Performance of Zwitterionic CDPs

We have performed kinetics and equilibrium studies with the new cyclodextrin-based adsorbents to evaluate their performance for removing a diverse set of PFASs including PFBA, PFOA, PFBS, PFOS, FBSA, FOSA, AP-FHxSA, TAmP-FHxSA, 6:2 FTAB, 5:3 FTB, and 5:1:2 FTB. We have benchmarked their performance in parallel experiments with a powdered activated carbon material. We found that the zwitterionic CDP outperforms the activated carbon material for the removal of zwitterionic PFAS from water including AP-FHxSA, TAmP-FHxSA, 5:3 FTB, and 5:1:2 FTB. The powdered activated carbon material outperformed the zwitterionic CDP for the removal of 6:2 FTAB along with PFOA, PFBS, PFOS, and FOSA. The two materials performed similarly for the removal of PFBA and FBSA from water. These findings demonstrate that novel functional groups can be installed in COFs for future incorporation into CDPs. The performance of the zwitterionic CDPs is not outstanding, but is better than the performance of a conventional adsorbent which suggests it may have some utility as a novel adsorbent for PFAS remediation.

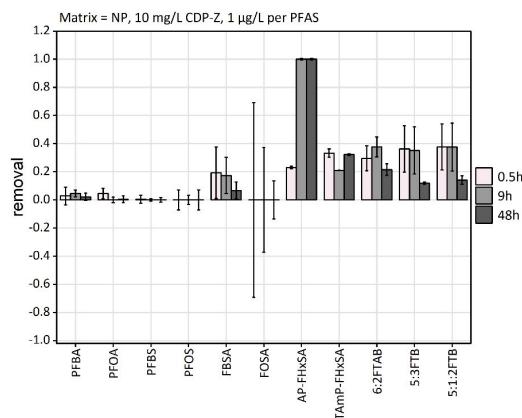


Figure 35. Removal of 11 PFAS by the zwitterionic CDP.

4.3 Selection of Most Promising CDP Derivatives for More Rigorous Evaluation

The goal of Phase 1 of our project was to develop and characterize the performance of new CDPs that target PFAS. We aimed to study (and perhaps improve) the performance of the DFB-CDP and develop new CDPs that target diverse types of PFASs that may be encountered in groundwater. In addition to the specific CDPs described in the preceding sections of this report, we synthesized and evaluated dozens of other CDPs during the first half of this project. During the second project period, we needed to select the most promising CDPs that we had discovered to-date to use in adsorption experiments conducted under more environmentally relevant conditions and to use in Phase 2 studies; the Phase 2 studies included evaluation of procedures for synthesis scale-up of CDPs, exploration of techniques to control polymer morphology and particle size, evaluation of polymer stability/durability, evaluation of regeneration, and evaluation of filtration processes. We selected four CDPs to be included in our later studies.

4.3.1 The Original Porous β -Cyclodextrin Polymer (P-CDP)

Our first CDP was synthesized by using a rigid aromatic crosslinker (tetrafluoroterephthalonitrile, TFN) to generate a permanently porous CD-based polymer adsorbent (P-CDP, **Figure 36**). P-CDP does not have a high affinity for anionic organic chemicals, a phenomenon we now attribute the negative surface charge imparted by the chemistry of the crosslinker. We have confirmed in experiments that P-CDP also has poor affinity for anionic PFAS. However, P-CDP has extraordinarily high affinity for neutral and cationic organic chemicals and our preliminary experiments suggest that P-CDP may rapidly remove neutral, cationic, and zwitterionic PFAS from water. Because we planned to use high-resolution mass spectrometry to screen for the removal of all known PFAS, we expected that P-CDP would

contribute to the removal of neutral, cationic, and zwitterionic PFAS in these experiments, perhaps exhibiting the greatest affinity and capacity for these PFAS constituents.

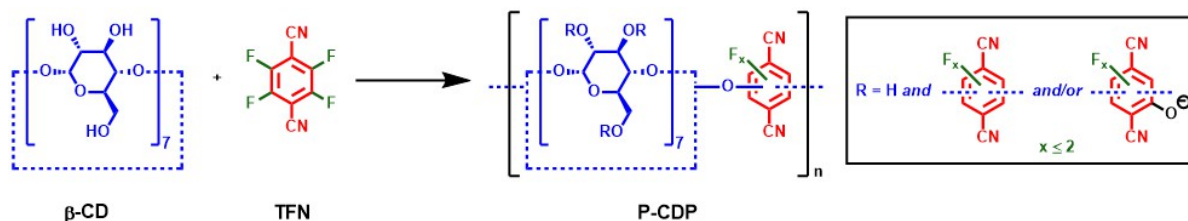


Figure 36. Schematic of the synthesis of P-CDP. The β -cyclodextrin (β -CD) monomer is crosslinked with tetrafluoroterephthalonitrile (TFN) to generate the first porous β -CD polymer (P-CDP).

4.3.2 The Amine-Containing β -Cyclodextrin Polymer (amine-CDP)

As we accumulated evidence that the affinity of P-CDP (and other CDPs exhibiting a negatively charged surface including DFB-CDP) for anionic organic chemicals is relatively weak, we hypothesized that perhaps CDPs exhibiting a positively charged surface would have enhanced affinity for anionic PFAS. One of the most promising derivatives to emerge from these studies is derived from a post-synthetic modification of P-CDP that results in the reduction of the nitriles on the TFN crosslinker to primary amines, as shown schematically in **Figure 37**. We refer to this derivative as amine-CDP, and our measurements indicate that it has a positively charged surface at neutral pH, likely arising from the protonation of the primary amines. In our experiments, we have found that this reduction reaction reverses the affinity of P-CDP and that amine-CDP exhibits an extraordinarily high affinity for anionic organic chemicals including short-chain perfluorocarboxylates, short-chain perfluorosulfonates, and GenX. We expect that amine-CDP will contribute to the removal of anionic PFAS in our experiments with AFFF-contaminated groundwater, perhaps exhibiting the greatest affinity and capacity for these PFAS constituents.

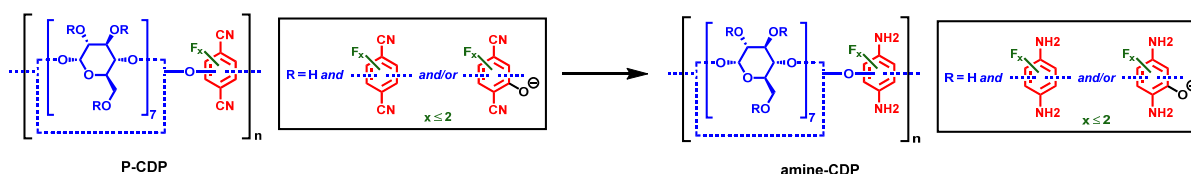


Figure 37. Schematic of the synthesis of amine-CDP. P-CDP is incubated with a strong reductant to generate amine-CDP.

4.3.3 Functionalized TFN-Crosslinked β -Cyclodextrin Polymer (CDP+ or DEXSORB+)

Although the amine-CDP is expected to perform well for the removal of anionic PFAs from AFFF-contaminated groundwater, it is not clear how groundwater chemistry or matrix constituents might influence the removal of PFAS. Therefore, we have selected a third CDP for these studies that likewise exhibits a positively charged surface and extraordinary performance for the removal of anionic PFAS from water. This derivative, which was discovered and characterized in an independent research project funded by the National Institutes of Health, has exhibited outstanding performance for the removal of anionic PFASs from water and to resist fouling by many common groundwater matrix constituents. This CD-based polymer adsorbent (CDP+) was synthesized by including a low-molecular weight quaternary ammonium molecule in the synthesis of P-CDP that competes with the β -CD monomer for nucleophilic substitution on the TFN crosslinker (**Figure**

38). We expect that CDP+ will contribute to the removal of anionic PFAS in our experiments with AFFF-contaminated groundwater, perhaps exhibiting greater resistance to ground water matrix chemistry than amine-CDP.

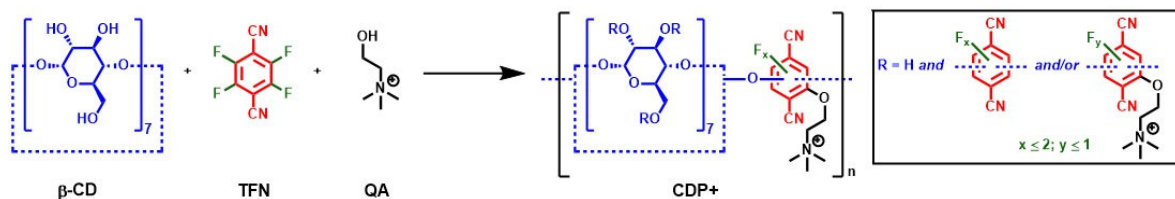


Figure 38. Schematic of the synthesis of CDP+. A low-molecular weight quaternary ammonium (QA) compound is added to the synthesis of P-CDP to generate a functionalized CD-based polymer adsorbent with a permanently positive surface charge (CDP+).

4.3.4 Functionalized MDI-Crosslinked β -Cyclodextrin Polymer (M^+)

Another new CD-based polymer adsorbent is a 4,4'-methylene diphenyl diisocyanate (MDI)-crosslinked β -cyclodextrin polymer that is functionalized with a quaternary ammonium (QA) compound (**Figure 39**). The first MDI-crosslinked β -cyclodextrin polymer emerged in an independent research project funded by the National Institute of Environmental Health Sciences, but the subsequent functionalization of the material occurred more recently. Preliminary data suggest that the M^+ can rapidly remove anionic PFAS from water, and the chemical nature of the crosslinker is much more attractive for commercial application; MDI does not contain any fluorine (or other halogen) and is less expensive than TFN.

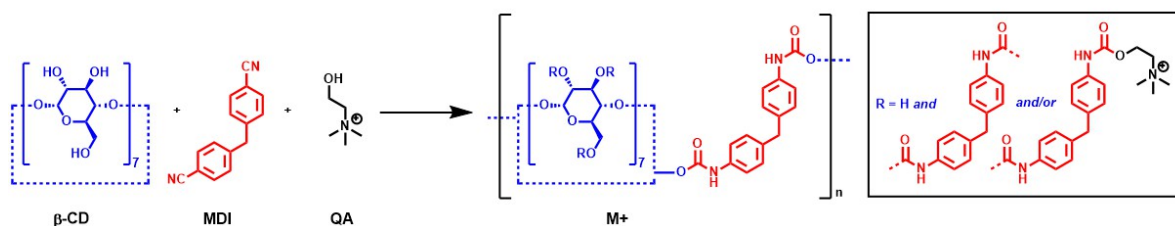


Figure 39. Schematic of the synthesis of M^+ . A low-molecular weight quaternary ammonium (QA) compound is added to the synthesis to generate a functionalized CD-based polymer adsorbent with a permanently positive surface charge (M^+).

4.4 Evaluating Adsorbent Performance under Environmentally Relevant Scenarios

We used the four CDPs described in Section 4.3 to perform adsorption experiments under more environmentally relevant scenarios. In most cases, we benchmark the performance of these four CDPs with conventional adsorbents including activated carbon and ion exchange resins. We first aimed to understand the ways in which groundwater chemistry influences the adsorption of PFAAs on CDPs and activated carbon.⁶¹ We then explored the potential for different CDPs and different ion exchange resins to remove diverse classes of PFASs, including PFAAs and zwitterionic PFASs, from water and groundwater as a function of pH.⁵⁴ We finally evaluated the potential for CDPs, activated carbon, and an ion exchange resin to remove a complex mixture of native PFASs from an AFFF-contaminated groundwater.⁶²

4.4.1 Factors that Influence Adsorption on CDPs

CDPs offer an alternative solution for remediation of PFAS-contaminated water. Previous research with CDPs has primarily focused on the removal of perfluoroalkyl acids (PFAAs) from nanopure water,³⁰ though the efficacy of CDPs for removing broader groups of PFASs from groundwater has not been fully explored. More recently, we demonstrated that a novel CDP crosslinked with a reduced terephthalonitrile (referred to as amine-CDP or aCDP in this section of the report) exhibits high affinity for a set of ten PFAAs, with reported removal efficiencies of 80-98% in nanopure water.⁶⁷ However, no CDP has been evaluated for PFAA removal in a real water matrix, and the effects of water matrix constituents on the performance of CDPs remain unknown.

This study was designed to help bridge these knowledge gaps and to specifically fulfill the following objectives: (1) evaluate the performance of conventional ACs and emerging CDPs to remove a wide range of PFASs from nanopure water and groundwater; (2) explore the physical properties of ACs that contribute to variable performance; and (3) explore the constituents of groundwater that influence the adsorption of anionic PFASs on each adsorbent. To meet the objectives, we first conducted batch adsorption experiments to evaluate the removal of 20 PFAAs at environmentally relevant concentrations by three conventional AC materials and two novel CDPs in nanopure water. The three best-performing adsorbents were subsequently selected to evaluate the removal of the target PFASs in spiked groundwater and in PFAS-contaminated groundwater. Various parameters describing the adsorbent characteristics and groundwater matrices were measured. Principal component analysis (PCA) was then employed to extract the important relationships from the multivariate dataset. The results of this study provide new insights on the factors that influence the adsorption of anionic PFAS on conventional and emerging adsorbents in aquatic matrices.

4.4.1.1 PFAS Removal by Each Adsorbent in Nanopure Water

The data provided in **Figure 40** show PFAS removal in nanopure water after 4 h of contact time on each of the five adsorbents. The three ACs are grouped into four particle size bins (10 – 75 μm , 125 – 212 μm , 425 – 850 μm , 1000 – 1700 μm) and the CDPs were evaluated in their as-synthesized particle sizes (212 – 425 μm for aCDP and <63 μm for CDP+). There is a clear difference in the performance of the ACs as a function of their particle size; ACs from the two larger size bins remove PFAS from Nanopure water to a lower extent after 4 h of contact time than the ACs from the two smaller size bins, though greater extents of removal were observed after longer contact times. This is consistent with previous studies that report slower and lower extents of PFAS adsorption on larger-sized ACs.⁴² It is widely known that the kinetics of adsorption on AC is controlled by relatively slow intra-particle diffusion, which requires adsorbates to diffuse into micropores to access free surfaces. Micropores

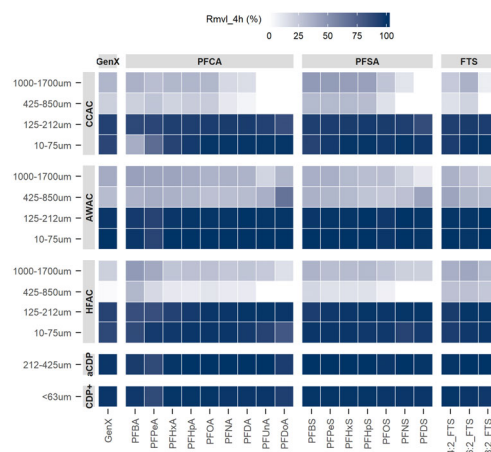


Figure 40. Heatmap of 20 PFASs adsorption onto 5 adsorbents in nanopure water at 4h. The PFAS compounds were grouped by their corresponding classes and listed with increasing chain length within each group along the x-axis. The adsorbents were grouped by their corresponding types and listed with increasing particle size within each group along the y-axis. The tiles were colored according to the arithmetic average removal for each pair of the coordinates.

can also be blocked by larger adsorbates which may limit the capacity of AC adsorbents.^{108–110} We attribute the relatively slow adsorption of anionic PFAS on larger-sized ACs to intra-particle diffusion limitations that become less important for smaller-sized ACs that have greater specific external surface area. It is also interesting to note that shorter-chain PFASs are removed from nanopure water to greater extents than longer-chain PFASs by larger-sized ACs, whereas longer-chain PFASs are removed to greater extents than shorter-chain PFASs by smaller-sized ACs. We also attribute this finding to the greater importance of intra-particle diffusion for larger-sized ACs and the more rapid diffusion of smaller PFAS.

ACs from the two smaller size bins (10 – 75 μm , 125 – 212 μm) remove nearly all of the PFAS from nanopure water after 4 h of contact time with the exception of the shorter-chain PFCAs (*i.e.*, PFBA, PFPeA); similar results on the removal of anionic PFAS on powdered ACs have been previously reported.^{108,109,111} The enhanced performance of powdered ACs has previously been attributed to either the generation of more internal active binding sites during pulverization and the consequent shorter diffusion distances required to access them,⁴² or the increased specific external surface area of smaller-sized AC particles which can provide access to more binding sites even in the presence of larger adsorbates that block access to internal micropores.^{112,113} Therefore, the smaller-sized ACs in this study exhibit more rapid PFAS adsorption kinetics and greater extents of adsorption than the larger-sized ACs.

The two CDPs also remove nearly all of the PFASs from nanopure water after 4 h of contact time. Both of the CDPs evaluated in this study consist of β -cyclodextrin monomers crosslinked with rigid aromatics containing weakly basic (amine-CDP) or permanently cationic (CDP+) functional groups. The interior cavity of the β -cyclodextrin monomer is the most likely active site for adsorption on CDPs, and the β -cyclodextrin monomer is known to encapsulate anionic PFASs to form well-defined host-guest complexes via hydrophobic interactions.^{30,114–116} Additionally, the protonated crosslinkers of both CDPs may facilitate the transport of anionic PFASs to the β -cyclodextrin monomers or provide alternate adsorption sites through complementary electrostatic interactions.^{117,118}

4.4.1.2 Physical Properties that Control PFAS Adsorption on Activated Carbon

To further explore the adsorption behavior of PFAAs on ACs, we constructed a PCA-biplot that describes the relationships between PFAS removal performance and the major physical properties of the ACs in each of the twelve experiments (*i.e.*, three ACs, four size bins) conducted in nanopure water. The four physical properties considered in the PCA analysis were particle size, total pore volume, micropore volume, and zeta-potential. The results of the PCA analysis are provided as **Figure 41**.

It is evident that, when considering PFAS adsorption on ACs in general, particle size is the leading factor to be considered. The particle size was determined as the average particle diameter of each size bin and a strong negative association was discovered between particle size and the weighted average PFAS removal at 4 h. This outcome is consistent with the qualitative findings described in **Figure 41**; removal of anionic PFAS is enhanced with decreasing particle size. The total pore volume is the weight specific total pore volume of an adsorbent and is estimated from the N_2 adsorption isotherm. The micropore volume is the distribution of micropores in the adsorbent and is likewise calculated based on the N_2 adsorption measurements. As demonstrated in **Figure 41**, neither of these properties associate with particle size or with the weighted average PFAS removal at 4 h (Rmvl_4h). This important finding excludes the likelihood that the improved performance of smaller-sized ACs is related to enlarged intra-particle pores, as proposed by a

previous study.¹¹⁹ On the contrary, this finding corroborates several other studies that report that the BET surface area and pore volume distributions of ACs are not altered significantly during pulverization.^{112,113} Therefore, the enhanced performance of smaller-sized ACs must be attributed to other mechanisms, such as an increased specific external surface area^{42,113,120} or the generation of more active binding sites that were originally inaccessible.¹¹³ The zeta potential is used to represent the surface charge of each AC in the pH range of 7 - 8. This property also exhibited little association with the weighted average PFAS removal at 4 h, indicating that hydrophobic interactions dominate the adsorption of anionic PFAS on ACs.

4.4.1.3 PFAS Removal by Each Adsorbent in Groundwater

To examine how PFAS removal changes in natural groundwater matrices, further experiments were conducted with three of the adsorbents in groundwater: CDP+, amine-CDP, and AWAC (the adsorbents were selected based on their performance in nanopure water). We used AWAC from the 125 – 212 μm size bin to increase the validity and reliability of the comparison among different types of adsorbents with minimum impact from their particle size. The data provided in **Figure 42** show PFAS removal in groundwater matrices after 4 h of contact time on each of the three adsorbents. Note that GW-A was a pristine groundwater sample that was spiked with 500 ng L^{-1} of PFAS and that the remaining groundwater samples were not spiked with PFAS and evaluated for removal of the native PFASs that were present in those samples; gray squares in **Figure 42** indicate that a PFAS was not present in a particular groundwater sample above the LOQ.

Overall, the extent of PFAS removal on all three adsorbents in groundwater was less than what was observed in nanopure water (**Figure 42**), which can be attributed to matrix interferences caused by the chemical properties of each groundwater. Unlike the performance of larger-sized ACs in nanopure water, longer-chain PFAS were always removed to greater extents than shorter-chain PFAS by all adsorbents in the groundwater experiments. This is because adsorption of PFAS on CDPs and smaller-sized ACs is not controlled by intra-particle diffusion limitations that can favor the adsorption of smaller-sized adsorbates. Rather, the affinity of PFAS for the binding sites on each of the adsorbents is driven in part by hydrophobic interactions that are not diffusion-

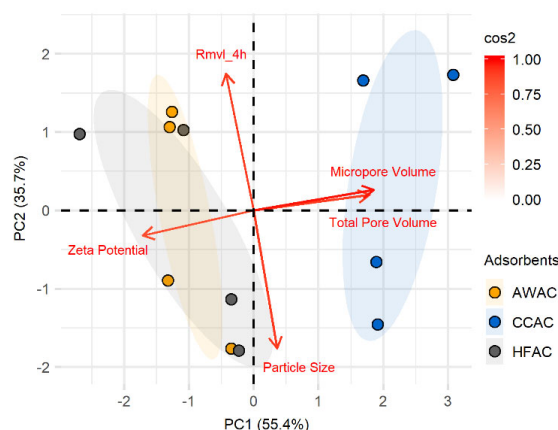


Figure 41. PCA biplot demonstrating the correlations among four adsorbent properties of activated carbons and the weighted average removal of PFASs at 4h in nanopure water. The PCA was established based on a multi-dimensional dataset with 5 variables and 12 observations (four size bins by three types of activated carbon). The biplot was plotted against the first two primary components (i.e. PC1 and PC2), which combined to have explained more than 91% of the total variance in the original dataset. The observations were plotted as scattered points and were colored and grouped by their corresponding adsorbent types, and a 95% confidence ellipse was added for each group of adsorbent. The variables were plotted as straight arrows, and each variable was colored by its quality of representation (labeled as “cos2” in the legend) on the selected primary components (a lighter color indicates that the variable contributed less to the primary components). The correlations between variables were manifested by the angles in between the arrows. The magnitude an observation had for a certain variable was revealed by the point’s position relative to the direction of the arrow (if the point locates in the same direction that an arrow is pointing at, the observation has a higher magnitude of this chosen variable).

limited.^{25,121–123} Therefore, longer-chain PFASs have a higher tendency to partition from the bulk solution to a solid surface.

The data in **Figure 42** also demonstrate that, for most PFASs and in most groundwater samples, the extent of PFAS removal is the greatest on CDP+. This suggests that the matrix interferes with adsorption on AWAC and amine-CDP more than it does for CDP+. To more accurately quantify the differences in performance of each adsorbent in each groundwater, we calculated the Inhibition% for each adsorbent in each groundwater. These data are presented in **Figure 43**. The height of each bar in **Figure 43** represents the total extent to which PFAS removal was inhibited in each groundwater sample relative to nanopure water. These data demonstrate that the extent of PFAS adsorption on CDP+ was always inhibited the least compared to the other adsorbents, except in groundwater AA-A (**Figure 43b**), implying that a particular constituent of groundwater AA-A might selectively inhibit the adsorption of anionic PFAS on CDP+. Further, the extent of PFAS adsorption on amine-CDP was always inhibited the most compared to the other adsorbents, except in groundwater WA-D (**Figure 43d**), implying that a particular constituent of groundwater WA-D might enhance adsorption of anionic PFAS on amine-CDP.

The colors of the bars in **Figure 43** refer to the specific groups of PFAS included in this study (*i.e.*, PFCAs, PFSAs, FTSs, and GenX). Although the FTSs and GenX were not always present at quantifiable levels in the groundwater samples (**Figure 42**), PFCAs and PFSAs were measured in every groundwater sample. Larger bars for a specific group of PFASs in **Figure 43** suggests that the extent of adsorption inhibition was greater for that group of PFASs in a particular groundwater sample. From these data, we can conclude that the extent of adsorption inhibition was significantly less for PFSAs than it was for

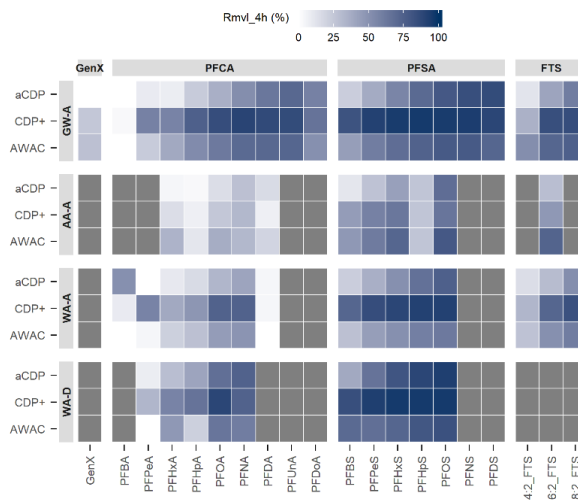


Figure 42. Heatmap of 20 PFASs adsorption onto 5 adsorbents in groundwater matrices at 4 h. The PFAS compounds were grouped by their corresponding classes, and listed with increasing chain length within each group along the x-axis. The adsorbents were grouped by their corresponding types, and listed with increasing particle size within each group along the y-axis. The tiles were colored according to the arithmetic average removal for each pair of the coordinates (a gray tile represents that the corresponding PFAS compound had a level below our limit of quantification).

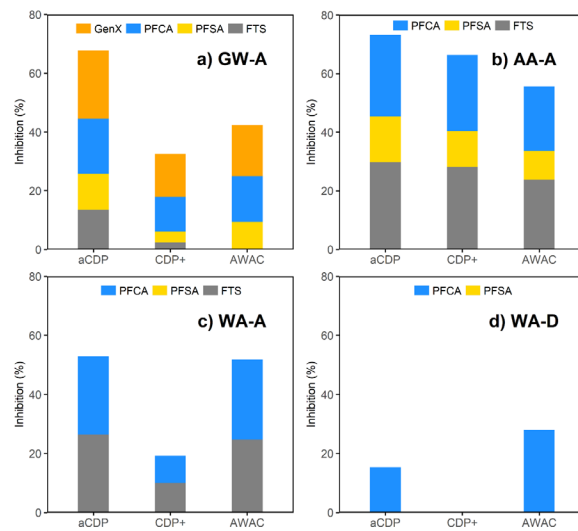


Figure 43. Bar plots exhibiting the adsorption inhibition percentages of 3 adsorbents in 4 groundwater samples at 4h: a) GW-A; b) AA-A; c) WA-A; d) WA-D. The total height of a bar represents the overall percentage of adsorption inhibition a certain adsorbent experienced in a certain groundwater matrix. The fractionated components within each bar represents the relative percentage of decreased adsorption affinity for each class of PFASs comparing to that in nanopure.

PFCAs for all adsorbents; this is especially obvious in **Figure 43c** and **Figure 43d** where the removal of PFASs was not inhibited at all. This observation is consistent with previous studies illustrating the relatively high adsorption affinity of PFASs on a variety of adsorbents.^{25,73,124}

4.4.1.4 Chemical Parameters of Groundwater that Contribute to Adsorption Inhibition

To further explore the role that groundwater chemistry plays in PFAS adsorption inhibition and to develop a mechanistic interpretation of the data, we constructed a PCA-biplot that describes the relationships between Inhibition% (*i.e.*, the height of the bars in **Figure 43**) and the major chemical parameters of each groundwater sample in each of the twelve experiments (*i.e.*, three adsorbents, four groundwater samples). The six chemical parameters considered in the PCA analysis were pH, conductivity, TOC, SUVA, and the molar concentrations of a variety of cations and anions. The results of the PCA analysis are provided as **Figure 44**.

pH exhibited a strong positive correlation with adsorption inhibition (*i.e.*, greater pH values resulted in a greater extent of adsorption inhibition among the anionic PFAS). The anionic PFASs selected for this study have very low pK_a values and are therefore present only as anions within the pH range of the groundwater samples selected for this study. Therefore, the noted pH dependence of Inhibition% is more readily explained by changes to the surface charge of the adsorbents rather than to protonation or deprotonation of the adsorbates. AWAC has a negative surface charge in the pH range of 7 - 8, and the surface charge of AWAC will become increasingly negative at higher pH values. This will lead to greater repulsive electrostatic forces for anionic PFAS at higher pH values, and result in more adsorption inhibition.^{125,126} Both of the CDPs selected for this study have a positive surface charge in the pH range 7 – 8. However, amine-CDP contains weakly basic functional groups that will be deprotonated at higher pH values whereas CDP+ does not undergo acid-base reactions under these conditions and remains cationic over the studied pH range. The deprotonation of amine-CDP at higher pH values can weaken^{89,117} or eliminate⁴² the attractive electrostatic interactions between amine-CDP and anionic PFAS at neutral pH. Our experimental adsorption data suggest that amine-CDP has a positive surface charge in WA-D but a negative surface charge at the higher pH values measured for GW-A, AA-A, and WA-A; the elimination of the attractive

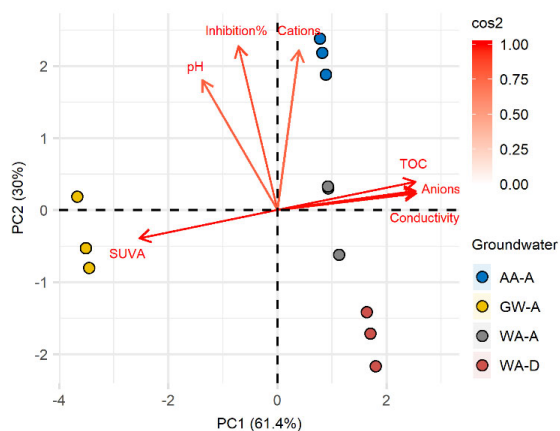


Figure 44. PCA biplot demonstrating the correlations among six groundwater properties and adsorption inhibition at 4h in groundwater matrices. The PCA was established based on a multi-dimensional dataset with 7 variables and 12 observations (three adsorbents by four groundwater matrices). The biplot was plotted against the first two primary components (*i.e.* PC1 and PC2), which combined to have explained more than 91% of the total variance in the original dataset. The observations were plotted as scattered points and were colored by the groundwater matrix with which they belonged. The variables were plotted as straight arrows, and each variable was colored by its quality of representation (labeled as “cos2” in the legend) on the selected primary components (a lighter color indicates that the variable contributed less to the primary components). The correlations between variables were manifested by the angles in between the arrows. The magnitude an observation had for a certain variable was revealed by the point’s position relative to the direction of the arrow (if the point locates in the same direction that an arrow is pointing at, the observation has a higher magnitude of this chosen variable).

electrostatic interactions between amine-CDP and anionic PFAS at higher pH values can explain the higher extent of adsorption inhibition in those groundwater samples, and, particularly, the limited Inhibition% in WA-D (**Figure 43**). The permanently positive charge of CDP⁺ explains the resilience of CDP⁺ to adsorption inhibition in groundwater samples of varying pH, and the relatively low extent of adsorption inhibition observed across all groundwater samples.

The total molar concentration of measured cations (*i.e.*, Ca²⁺, Mg²⁺, K⁺, Na⁺) also exhibited a strong positive correlation with adsorption inhibition (*i.e.*, greater concentrations of cations resulted in a greater extent of adsorption inhibition among the anionic PFAS). A similar effect has been observed in other studies investigating the adsorption of anionic surfactants on a variety of adsorbents.^{90,127} Previous studies have concluded that divalent cations like Mg²⁺ and Ca²⁺ can bind with the anionic head groups of PFAS to form weak, neutral complexes which can decrease the extent of adsorption by weakening potential electrostatic interactions.^{90,128} As is revealed in the PCA-biplot (**Figure 44**), groundwater AA-A had the highest concentrations of cations, including divalent cations, among all groundwater samples, which resulted in the greatest extent of adsorption inhibition among all of the adsorbents. This phenomenon also explains the anomalous behavior of CDP⁺ and AWAC in AA-A noted in the preceding (**Figure 43b**). The permanently positive surface charge of CDP⁺ enhances the removal of anionic PFAS through attractive electrostatic interactions that are diminished in the presence of divalent cations. AWAC has a permanently negative surface charge and relies exclusively on hydrophobic interactions for the adsorption of anionic PFAS and exhibits lower extents of adsorption inhibition in groundwater samples with higher concentrations of divalent cations.

In contrast to the concentration of cations, neither conductivity nor the concentration of anions (*i.e.*, F⁻, Cl⁻, NO³⁻, SO⁴²⁻, PO⁴³⁻) exhibited a significant association with adsorption inhibition, indicating that these parameters do not contribute much to the observed adsorption inhibition in this study. Because we have adsorbents that have positive and negative surface charges and adsorbates that are always anionic, this is further evidence that the effect from cations is likely due to interactions with the PFAS and not the adsorbent; if cations were affecting one type of adsorbent, then we would expect anions to affect the adsorbent of the opposite surface charge in an analogous way. Likewise, neither TOC nor SUVA exhibited a significant association with adsorption inhibition. This finding is notable because dissolved organic matter of a certain size has been previously shown to inhibit adsorption on other types of CDPs,¹²⁹ particularly those that carry a negative surface charge. The lack of an association between TOC and SUVA and CDP adsorption inhibition in this study suggests that anionic dissolved organic matter may only influence adsorption on negatively charged CDPs.

4.4.1.5 Conclusions of the Study and Implications for Practice

Our study sought to explore the potential of conventional and emerging adsorbents to remove anionic PFAS from water, and to identify the factors that lead to adsorption inhibition in groundwater matrices. In WA-D (the un-amended PFAS-contaminated groundwater sample), only CDP⁺ removed PFOA and PFOS to concentrations below the US EPA Health Advisory threshold of 70 ng L⁻¹ in our experiments after 4 hours of contact time (23 and 24 ng L⁻¹, respectively). All three adsorbents (CDP⁺, amine-CDP, and AWAC) exhibited limited removal of the shorter-chain carboxylates and sulfonates in WA-D, but CDP⁺ again exhibited the greatest removal of these PFAS in our experiments after 4 hours of contact time. In comparing the performance of all adsorbents across experiments conducted in nanopure and groundwater, we found that pH and the presence of inorganic cations contribute to adsorption inhibition to varying extents, depending on the adsorbent. These data could be used to help guide the selection of remediation technologies

based on local environmental conditions. Together, the new insights developed in our analyses improve our understanding of PFAS-adsorbent interactions and will lead to the continued development of novel adsorbents targeting a broad family of PFASs and the design of more effective water treatment processes for PFAS-contaminated systems.

4.4.2 CDPs and Ion Exchange Resins to Remove Diverse PFASs from Water

The primary objective of this study was to evaluate the performance of CDPs with different crosslinkers for the removal of different classes of PFASs from water. We selected three CDPs (DEXSORB (also referred to as P-CDP throughout this report), DEXSORB+ (also referred to as CDP+ throughout this report), and amine-CDP) that exhibit different surface charges and evaluated their potential to remove a set of eleven PFASs from water. The PFASs included four anionic PFASs, three zwitterionic PFASs, and four non-ionic PFASs. We simultaneously evaluated the performances of an anion exchange (AE) resin and a cation exchange (CE) resin to evaluate the breadth of their PFAS removal potential. For each adsorbent, we measured: (i) adsorption kinetics for the eleven PFASs; (ii) adsorbent affinity for the eleven PFASs; and (iii) adsorption inhibition across a gradient of pH values in the presence and absence of groundwater matrix constituents. We found that each adsorbent exhibits variable adsorption kinetics and variable adsorption affinity for anionic, zwitterionic, and non-ionic PFASs while also exhibiting some adsorption inhibition at higher pH values and in the presence of groundwater matrix constituents.

4.4.2.1 Evaluating Adsorption Kinetics for Each Adsorbent

We first characterized the adsorption kinetics of the eleven target PFASs on each of the five adsorbents. Data describing adsorption kinetics provide insight on how long it takes for a particular adsorption process to reach equilibrium. Adsorption kinetics experiments also enable evaluation of desorption, which is an important consideration when evaluating PFAS adsorption on any adsorbent; it is often reported that short-chain PFASs will desorb after an initial period of rapid adsorption.^{73,130} The results of our batch kinetics experiments are presented in **Figure 45** as a time series detailing the average and standard deviation (%) of the removal for each of the eleven PFASs by each adsorbent at 0.5, 9, and 48 hours. Whereas the adsorption kinetics of the four anionic PFASs have been previously explored for a variety of adsorbents,^{61,93,125,131} this is the first known study evaluating the adsorption kinetics of the three zwitterionic PFASs and the four non-ionic PFASs using CDPs and ion exchange resins.

DEXSORB exhibits rapid adsorption of the three zwitterionic PFASs (64% average removal for AmPr-FHxSA, 56% for TAmPr-FHxSA, and 47% for 6:2 FTSA-PrB in 0.5 hours) and adsorption equilibrium is attained within 9 hours; the adsorption of the three zwitterionic PFASs is stable at 9 hours and 48 hours ($p < 0.01$) with a removal of approximately 75%. The CE resin likewise exhibits rapid adsorption of AmPr-FHxSA and TAmPr-FHxSA (50% average removal for AmPr-FHxSA and 48% for TAmPr-FHxSA in 0.5 hours) followed by continued slow removal to achieve approximately 71% removal at 48 hours. However, relatively slow removal was

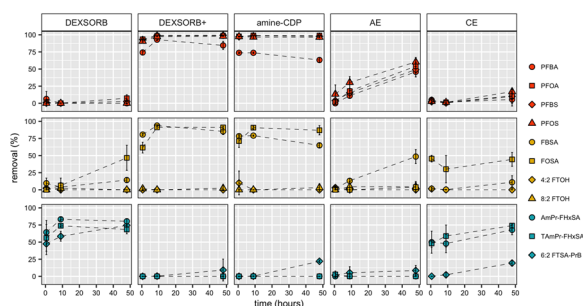


Figure 45. Average and standard deviation (%) of triplicate measurements of removal of each PFAS on each adsorbent after 0.5, 9, and 48 hours of contact time. The kinetics experiments were conducted at $[PFAS]_0 = 1 \mu g L^{-1}$ and $[adsorbent]_0 = 10 mg L^{-1}$.

observed for 6:2 FTSA-PrB, with no removal observed at 0.5 hours and only 19% average removal attained at 48 hours. None of the other adsorbents exhibit rapid removal of any zwitterionic PFASs, with amine-CDP exhibiting only slow removal of 6:2 FTSA-PrB and attaining only 22% average removal after 48 hours. The high and rapid removal of all three zwitterionic PFASs by DEXSORB suggests that DEXSORB is better suited to remove zwitterionic PFASs than the other adsorbents, though the CE resin also shows promise for removing some zwitterionic PFASs from water. DEXSORB also exhibits relatively slow removal of FBSA and FOSA, reaching 14% and 47% average removal by 48 hours, respectively; these observations demonstrate the potential of DEXSORB to remove non-ionic PFAS from water. The CE resin also exhibits some removal of FOSA, but no removal of FBSA. The remaining anionic PFASs and non-ionic PFASs are not removed to a significant extent by DEXSORB or the CE resin.

DEXSORB+ and amine-CDP exhibit rapid adsorption of the four anionic PFASs and the two non-ionic perfluorosulfonamides (>62% average removal in 0.5 hours). The adsorption of all six PFASs increases significantly at 9 hours of contact time with DEXSORB+, reflecting slower adsorption kinetics for these PFASs. Equilibrium adsorption is achieved for all six PFASs on DEXSORB+ at 9 hours with no significant desorption observed. In contrast, all six PFASs achieve complete adsorption uptake on amine-CDP at 0.5 hours. However, some slight but significant desorption was observed for PFBA (~10%) and FBSA (~14%) after 48 hours of contact time; desorption of short-chain anionic PFASs has been previously reported for activated carbon and has been attributed to competition with adsorbates with higher affinity.^{73,124} In this case, competition with long-chain anionic PFASs or with 6:2 FTSA-PrB may have contributed to the noted desorption. Together, these data suggest that DEXSORB+ and amine-CDP are effective at rapidly removing anionic PFASs and two non-ionic perfluorosulfonamides, though DEXSORB+ exhibits slower adsorption kinetics and amine-CDP exhibits some desorption potential.

In contrast to the three CDPs and the CE resin, the AE resin did not exhibit rapid adsorption of any of the PFASs. Instead, slowly increasing adsorption was observed for the four anionic PFASs and FBSA, reaching a maximum of 60% removal of PFOS and a minimum of 46% removal for PFBA at 48 hours. We note that the relatively slow adsorption kinetics observed for the AE resins could be the result of the study design that relied on a fixed concentration of each adsorbent in its as-received morphology. The relatively large particle size of the AE resins likely played a role in the results of the kinetics experiments and improved adsorption kinetics are expected for higher doses of AE resins⁵⁸ or with modified (i.e., ground) AE resin particles.¹³² Nevertheless, it is interesting to note steady adsorption of the four anionic PFASs and FBSA (but not FOSA) without any evidence of desorption; the data from the perfluorosulfonamides suggests that FBSA exhibits some anionic properties at circumneutral pH, whereas FOSA exhibits more non-ionic adsorbate behavior.

None of the adsorbents removed the non-ionic fluorotelomer alcohols to a significant extent. We note that these two PFASs were not reliably measured and had relatively high LOQs. This may be due to the formation of poorly ionized acetate adducts in the mass spectrometer or other analytical challenges.¹³³ Regardless, it is worth noting that these non-ionic PFASs with four- and eight-carbon perfluorinated chains are not well removed by cyclodextrin polymers with either positive or negative surface charges or by ion exchange resins. Other non-ionic molecules have exhibited varying extents of affinity for cyclodextrin polymers, but that variability has been positively associated with molecular size.^{28,79} The noted adsorption of PFOA, PFOS, and FOSA among the CDPs suggests that 8:2 FTOH should be of sufficient size to interact with the interior cavity of the cyclodextrin monomer. We therefore suspect that the fluorotelomer alcohols may

aggregate or accumulate at air-water interfaces (as has been demonstrated for other types of PFASs)¹³⁴ and may not be uniformly dissolved in the aquatic matrix which may limit their transport to the binding sites in the interior cavity of the cyclodextrin monomer.

4.4.4.2 Adsorbent affinity for different PFASs

We next characterized the affinity of each adsorbent for each of the eleven target PFASs. Although the affinity of adsorbents for any adsorbate is typically characterized by adsorption isotherms,^{42,135} PFASs are present at low concentrations in groundwater so complete isotherms do not provide relevant data for this study.¹³⁶ Here, we use distribution coefficients (K_D) calculated from data in the linear region of the adsorption isotherm to provide a better description of adsorption affinity at low concentrations.^{79,137} We used data from our adsorption affinity experiments to calculate K_D values for each PFAS on each adsorbent. We used the experimental conditions of $[PFAS]_0 = 2 \mu g L^{-1}$ and $[adsorbent]_0 = 25 mg L^{-1}$ to first define the K_D value, and then incorporated data from other experimental scenarios for which the calculated K_D value was not statistically different from the defined K_D value. This conservative approach was implemented as a quality control measure to ensure that we were estimating constant K_D values that represent the linear range of the non-linear isotherm.^{65,79} In **Figure 46**, we plot the average $\log K_D$ values and the relative error for each PFAS on each adsorbent.

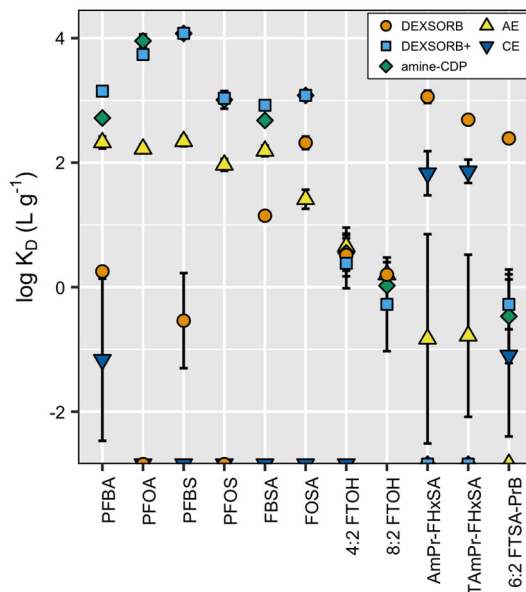


Figure 46. Plots of the average and relative error of the log-transformed distribution coefficients ($\log K_D$) for 11 PFASs and five adsorbents. PFASs that are plotted in the lowest part of the panel have K_D values of $0 g L^{-1}$ (i.e., no affinity for the adsorbent). The PFAS-adsorbent concentrations that were tested were $[PFAS]_0 = 1 \mu g L^{-1}$ and $[adsorbent]_0 = 10 mg L^{-1}$; $[PFAS]_0 = 2 \mu g L^{-1}$ and $[adsorbent]_0 = 10 mg L^{-1}$; $[PFAS]_0 = 2 \mu g L^{-1}$ and $[adsorbent]_0 = 25 mg L^{-1}$; $[PFAS]_0 = 2 \mu g L^{-1}$ and $[adsorbent]_0 = 50 mg L^{-1}$.

DEXSORB exhibits moderate (average $\log K_D > 2$ for TAmPr-FHxSA and 6:2 FTSA-PrB) to high (average $\log K_D > 3$) affinity for the three zwitterionic PFASs. This is notable because none of the other adsorbents exhibit such affinity for the three zwitterionic PFASs; the CE resins have average $\log K_D$ values of 1.8 and 1.9 for AmPr-FHxSA and TAmPr-FHxSA, respectively, but an average $\log K_D$ value of -1.1 for 6:2 FTSA-PrB. This suggests that the cationic functional groups on the zwitterionic PFASs likely play an important role in determining their affinity for CDP adsorbents. Zwitterionic PFASs containing betaine or quaternary ammonium functional groups have been found to bind strongly to negatively charged soil particles^{138–141} providing further evidence for the role that cationic functional groups play in the fate of zwitterionic PFASs. DEXSORB exhibits poor affinity for all four anionic PFASs (average $\log K_D < 0.5$). This is expected, as we previously reported that a similar CDP with a negative surface charge exhibits poor removal of PFBA and PFOA.^{28,80} Interestingly, DEXSORB has average $\log K_D$ values of 1.1 and 2.3 for the non-ionic perfluorosulfonamides FBSA and FOSA, respectively, but poor affinity for the fluorotelomer alcohols (4:2 FTOH and 8:2 FTOH). The variable affinity of DEXSORB for non-ionic PFASs agrees with our previous observations of variable removal of non-ionic CoCs by

CDPs;^{28,79,80,131} further, the moderate affinity for the perfluorosulfonamides suggests either that some significant fraction of these PFASs is indeed non-ionic at circumneutral pH or that the negative charge of the deprotonated sulfonamide group is insufficient to limit their affinity for DEXORB.

DEXSORB+ and amine-CDP exhibit high affinity (average $\log K_D > 3$) for the four anionic PFASs, with the exception being an average $\log K_D$ value of 2.7 for PFBA on amine-CDP. This high affinity is expected, as we previously reported that DEXSORB+ and amine-CDP exhibit generally good removal of anionic PFASs.^{61,131} DEXSORB+ and amine-CDP also exhibit moderate affinity for FBSA and high affinity for FOSA, with a notable improvement of affinity for FBSA relative to DEXSORB. The improved affinity of the sulfonamides for the CDPs with a positive surface charge suggests that electrostatic interactions are important to some degree, and that some fraction of the sulfonamides may be anionic as suggested by their estimated pK_a values. Finally, DEXSORB+ and amine-CDP exhibit poor affinity (average $\log K_D < 0.5$) for the zwitterionic PFASs and the fluorotelomer alcohols.

The AE resin exhibits moderate affinity (average $\log K_D > 2$) for the four anionic PFASs and FBSA. FBSA exhibits identical affinity for the AE resin as PFBA, providing further evidence that FBSA is at least partially anionic at circumneutral pH and relies on electrostatic interactions to be removed by the adsorbents. Interestingly, FOSA has an average $\log K_D$ value of 1.4 on the AE resin providing additional evidence that FOSA is more non-ionic at circumneutral pH and relies more on hydrophobic interactions with the CDP adsorbents. The AE resin exhibits poor affinity for the fluorotelomer alcohols and zwitterionic PFASs. We note that our experimental design limits our ability to compare the absolute values of affinity for the AE resin with the values reported for the CDPs. The CDPs have a greater external surface area and may result in more rapid equilibration than the AE resins; previous studies evaluating AE resins ground the resins into smaller particles,¹³² used greater concentrations of the resins,^{142,143} or relied on contact times up to 10 days to evaluate their performance.¹⁴²

4.4.4.3 Effects of pH on PFAS adsorption

We next explored the effects of pH and water matrix constituents on the adsorption of PFASs on each of the five adsorbents. We performed batch equilibrium experiments across a gradient of environmentally relevant pH values (5.5, 7, and 8.5) to measure the removal of each PFAS at 48 hours in nanopure and groundwater. We exclude 4:2 FTOH and 8:2 FTOH from our data analysis because the analytical data did not meet our quality control criteria. The data presented in **Figure 47** show the removal of each of the remaining nine PFASs at each pH value in a nanopure matrix (blue) and in a groundwater matrix (yellow); data for PFASs that were not removed on certain adsorbents are not shown in **Figure 47**.

pH influences the surface chemistry and surface charge of adsorbents, and also influences the speciation of adsorbates. According to estimated pK_a values for each of the nine PFASs included in this part of our study, the four anionic PFASs should remain anionic over the pH range studied, but the other PFASs may experience some changes in speciation.^{144,145} The predicted pK_a values for the perfluorosulfonamides range between 3.3 and 6.6.¹⁴⁴ Our data from the affinity and kinetics experiments show that the perfluorosulfonamides exhibit behavior that resembles both anionic PFASs (particularly for FBSA) and non-ionic micropollutants (particularly for FOSA). Therefore, the pK_a of FOSA is likely closer to 6.6 and the pK_a for FBSA is likely somewhat lower. Nevertheless, we expect that both FBSA and FOSA will be more non-ionic at lower pH values and more anionic at higher pH values. The three zwitterionic PFASs are all expected to be zwitterionic

at circumneutral pH. However, all three could become cations at lower pH values; AmPr-FHxSA is an anion at higher pH values and 6:2 FTSA-PrB has a second acidic group that can deprotonate at higher pH values. As for the adsorbents, DEXSORB incorporates weakly acidic functional groups in the crosslinker and can therefore become deprotonated (i.e., more negative) with increasing pH;⁷¹ our measurements of zeta potential demonstrate that the surface charge of DEXSORB is significantly more negative at pH 8.5. amine-CDP incorporates weakly basic functional groups in the crosslinker and can likewise become deprotonated (i.e., less positive) with increasing pH.¹³¹ However, no significant change in zeta potential was noted for amine-CDP at the different pH values suggesting that the pK_a value of the weakly basic amine groups is greater than 8.5. The AE resin contains complex amino groups that can likewise deprotonate with increasing pH and adsorption on the AE resin may consequently be influenced by pH changes.¹⁴⁶ DEXSORB+ and the CE resin do not contain weakly acidic or basic functional groups, so the surface charge is not influenced by changes in pH.

The top-left region of **Figure 47** shows the average removal of the zwitterionic PFASs as a function of pH on DEXSORB and the CE resin in nanopure water (blue); the other three adsorbents are not included in the analysis because removal of zwitterionic PFASs on DEXSORB+, amine-CDP, and the AE resin was negligible. We expect lower pH values to change the speciation of the zwitterionic PFAS to be more cationic, whereas higher pH values will change the speciation of AmPr-FHxSA and 6:2 FTSA-PrB making them more anionic while strengthening the negative surface charge of DEXSORB. Our results suggest that these changes in speciation resulting from changes in pH have no significant effect on the adsorption of zwitterionic PFAS on DEXSORB and the CE resin in nanopure water, as no significant changes in removal of the zwitterionic PFASs on DEXSORB and the CE resin were observed across the tested pH range ($p < 0.01$).

The top-right region of **Figure 47** shows the average removal of the anionic PFASs as a function of pH on DEXSORB+, amine-CDP, and the AE resin in nanopure water (blue); DEXSORB and the CE resin are not included in the analysis because removal of anionic PFASs on DEXSORB and the CE resin was negligible. The data here demonstrate that adsorption of anionic PFASs on the AE resin is not significantly dependent on the pH ($p < 0.01$), although a previous study reported adsorption inhibition of anionic PFASs for AE resins (functionalized with tertiary amine groups) due to the decreased adsorption sites at higher pH.¹⁴⁶ Conversely, the adsorption of some anionic PFASs on DEXSORB+ and amine-CDP is pH-dependent; this pH dependency is determined by the chain length and head group of the PFAS. For DEXSORB+, only

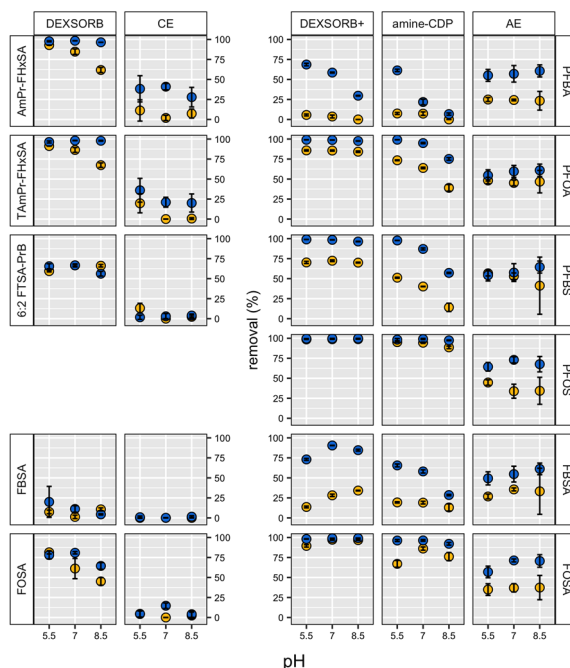


Figure 47. Average removal of PFASs by adsorbents that had non-negligible removal. Effects of pH and matrix constituents were evaluated at pH 5.5, 7, and 8.5. Blue = nanopure water, yellow = groundwater. Samples were collected after a contact time of 48 hours, with $[PFAS]_0 = 1 \mu g L^{-1}$ and $[adsorbent]_0 = 10 mg L^{-1}$.

the adsorption of PFBA is significantly influenced by pH with 70% removal observed at pH of 5.5 and 30% removal observed at pH 8.5. A more dramatic influence of pH is noted for amine-CDP, with the adsorption of PFBA, PFOA, and PFBS all significantly inhibited with increasing pH. Although no statistically significant change in zeta potential was observed for amine-CDP across the gradient of pH values investigated, the adsorption inhibition on amine-CDP may still be linked to some deprotonation of surface functional groups at increasing pH values. The adsorption inhibition on DEXSORB+ is not attributable to deprotonation of surface functional groups and is therefore attributed to competition of cationic surface sites with an increased abundance of hydroxide anions at higher pH values.

The bottom region of **Figure 47** shows the average removal of the non-ionic perfluorosulfonamides as a function of pH on all five adsorbents in nanopure water (blue). We expect that these perfluorosulfonamides will be mostly neutral at a pH of 5.5 and at least partly anionic at pH 8.5. The data here demonstrate again that the adsorption of the perfluorosulfonamides on ion exchange resins is not pH-dependent ($p < 0.01$). However, some interesting trends emerge among the CDPs. DEXSORB does not remove FBSA to a significant extent at any pH, but DEXSORB removes FOSA better at pH 5.5 and 7, when FOSA is expected to be more non-ionic. At pH 8.5, FOSA is expected to be more anionic, and the surface charge of DEXSORB is more negative. Therefore, the adsorption inhibition observed here is likely due to the emergence of repulsive electrostatic interactions. The adsorption of FOSA on DEXSORB+ and amine-CDP is not significantly influenced by pH, suggesting that the increasingly anionic FOSA (at increasing pH) maintains a high affinity for the permanently positively charged DEXSORB+ and amine-CDP. On the other hand, the adsorption of FBSA on amine-CDP is significantly inhibited at increasing pH values, suggesting that some deprotonation of amine-CDP may contribute to the significant adsorption inhibition of FBSA.

Effects of matrix constituents on PFAS adsorption. We also evaluated the performance of each adsorbent in a real groundwater matrix. The groundwater selected for these experiments contained no background levels of any of the PFASs included in the study and had an in situ pH of 8.4. We adjusted the pH of the groundwater in the same way we adjusted the pH of the nanopure, and therefore the results presented in **Figure 47** (groundwater = yellow) describe differences that can be attributed to the presence of inorganic anions, inorganic cations, and natural organic matter (NOM).

The data presented in **Figure 47** show that the presence of matrix constituents significantly inhibited the adsorption of most of the PFASs on each of the adsorbents. The adsorption inhibition noted for the AE resin was most likely resulting from the presence of inorganic anions^{143,147} and NOM^{130,148} that compete with PFASs for adsorption sites on the resin; sulfate (18.7 mg L⁻¹) and chloride (8.9 mg L⁻¹) were the most abundant anions measured in the groundwater and the NOM concentration was 1.1 mg L⁻¹. On the other hand, the adsorption inhibition noted for the CE resin, particularly for AmPr-FHxSA and TAmPr-FHxSA, is attributed to the presence of inorganic cations including calcium (26.8 mg L⁻¹) and sodium (23.2 mg L⁻¹). DEXSORB was the least inhibited adsorbent in the groundwater matrix and the adsorption of 6:2 FTSA-PrB was not inhibited at any pH value. Interestingly, the adsorption of AmPr-FHxSA and TAmPr-FHxSA was inhibited at higher pH values in groundwater but not in nanopure water, suggesting that speciation of matrix constituents was responsible for the adsorption inhibition; it is possible that anionic NOM could interact with the positive charge on the zwitterionic PFAS to contribute to adsorption inhibition. Finally, adsorption of most of the anionic and neutral PFAS on DEXSORB+ and amine-CDP was significantly inhibited in the groundwater; only the adsorption of PFOS and FOSA on

DEXSORB+ was not significantly inhibited in groundwater. We expect that interferences caused by the presence of inorganic ions and low molecular weight NOM may be driving adsorption inhibition in groundwater.^{61,129}

4.4.4.4 Conclusions and Environmental Implications of the Study

This study offers the first systematic exploration on the performance of emerging adsorbent technologies, including CDPs and ion exchange resins, for the removal of different classes of PFASs from water. We found that DEXSORB (a CDP with a negative surface charge) exhibits the best performance for removing zwitterionic PFASs from groundwater. Our findings show that zwitterionic PFASs behave more similarly to cations than anions, which can have important implications in evaluating other remediation technologies, including adsorption with CE resins. We also demonstrated that non-ionic PFASs (perfluorosulfonamides and fluorotelomer alcohols) are removed to varying degrees by CDPs but are generally not removed well by ion exchange resins. Whereas the latter observation was expected, it was not expected that neutral PFASs of the appropriate size would not be removed by CDPs. These data suggest that electrostatic interactions play an important role in determining the affinity of CDPs for PFASs. Although all adsorbents exhibited some level of inhibition in real groundwater, a combination of adsorbents could be used to remove complex mixtures of PFASs from contaminated groundwater. Finally, we note that previous studies with CDPs have also demonstrated facile regeneration and reuse potential in proof-of-concept experiments.^{29,30} These observations, coupled with the findings of the present study, support the continued investigation of CDPs as alternative adsorbents for remediation of PFAS-contaminated groundwater.

4.4.3 Adsorbent Performance in AFFF-contaminated Groundwater

Most studies evaluating PFAS removal and remediation focus on PFAAs.^{149–151} However, over 1,000 unique PFASs have been discovered in AFFF-contaminated groundwater including cationic, nonionic, and zwitterionic PFASs.^{1,3,5,152–154} Further, most experiments aimed at assessing PFAS removal from water are conducted in simulated conditions using a mixture of a few PFAAs at a fixed concentration,^{92,155} whereas relatively few experiments sufficiently replicate the complexities of real systems with respect to matrix chemistry or the concentration and distribution of individual PFAS species.^{120,124} Finally, although some data has emerged describing the role that PFAS properties play in their removal,^{73,93,130} these insights have been mostly derived using homologues of PFAAs and the behavior of other types of PFASs remains unknown.⁹² We aimed to address these knowledge gaps by conducting experiments directly in AFFF-contaminated groundwater. We used a suspect screening approach to identify 68 unique PFASs in an AFFF-contaminated groundwater sample. We conducted batch experiments to evaluate the removal of the 68 PFASs from the groundwater using five different adsorbents. To the best of our knowledge, this is the first study that has evaluated the removal of PFASs from AFFF-contaminated groundwater with a dedicated suspect screening approach.

4.4.3.1 Removal of PFASs in groundwater

Our suspect screening identified 68 PFASs in the AFFF-contaminated groundwater sample. Based on an inspection of functional groups, we expect that 43 PFASs were anionic, 12 PFASs were nonionic, and 13 PFASs were zwitterionic at the pH of the groundwater sample (pH = 6.7). The removal efficiencies calculated for the 68 PFASs by each of the five adsorbents after 0.5 hr, 9 hr, and 48 hr of contact time are provided in the box plots in **Figure 48**. Although the 68 PFAS species were present at widely varying abundances in the groundwater sample, we note that there

is no abundance-dependency in the removal of the 68 PFASs from groundwater by any of the adsorbents. Several additional insights can be derived from these data.

First, each adsorbent exhibits a unique removal profile for the 68 PFASs present in the groundwater. Considering the data from 0.5 hr of contact time, DEXSORB+ exhibits the highest removal across all PFASs, whereas M+ and AC exhibit moderate removal, and DEXSORB and the AE resin exhibit relatively low removal. We have previously shown that DEXSORB+ has high affinity for anionic PFASs and some nonionic PFASs, though the high removal of zwitterionic PFASs by DEXSORB+ is observed here for the first time. We have also previously shown that DEXSORB has relatively weak affinity for anionic PFASs but moderate to high affinity for some zwitterionic PFASs. Interestingly, the only zwitterionic PFAS that exhibits moderate to high removal by DEXSORB in this study (*i.e.*, > 60% removal at 9 hr and 48 hr) is 6:2 FTSA-PrB, which also exhibited moderate to high affinity for DEXSORB in previous experiments. Compared to the other twelve zwitterionic PFASs in the groundwater sample, 6:2 FTSA-PrB has the longest chromatographic retention time, has a relatively long CF₂ chain length, and was measured in positive polarity mode. These features suggest that 6:2 FTSA-PrB is relatively hydrophobic and that the cationic functional group dominates its adsorption behavior compared to its weakly acidic carboxylic acid group, making it a better adsorbate for DEXSORB than the other zwitterionic PFASs.

Second, the adsorption kinetics are relatively rapid for DEXSORB+ and M+, and relatively slow for AC and the AE resin. This observation is consistent with our previous studies reporting nearly instantaneous uptake of organic chemicals on CDPs and the known diffusion-limited kinetics associated with AC.^{124,156} We attribute the relatively slow adsorption kinetics observed for the AE resin to the relatively large particle size of the AE resin and the relatively low concentration of adsorbents used in this study; research conducted with pulverized AE resin particles or at higher resin concentrations has resulted in more rapid adsorption of PFASs.^{132,157}

Finally, considering the data from 48 hr of contact time, AC exhibits the most non-selective removal of the 68 PFASs from groundwater with >80% removal noted for at least one anionic, nonionic, and zwitterionic PFAS. This observation demonstrates that AC has the potential to remove PFASs of all ionized states from AFFF-contaminated groundwater, albeit with relatively slow adsorption kinetics. The removal of 16 PFASs (including PFASs, PFCAs, FASAs, SP-FASAs, and two PFOS-like components) on AC aligns well with previous studies that have evaluated PFAS removal on AC in contaminated groundwater.^{120,124} DEXSORB+ is best suited to rapidly remove anionic PFAS from AFFF-contaminated groundwater, with additional rapid

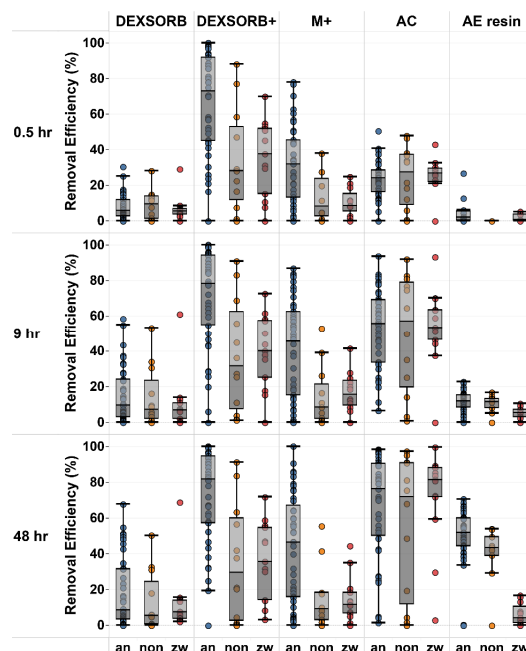


Figure 48. Blue data represent anionic (an) PFASs, orange data represent nonionic (non) PFASs, and red data represent zwitterionic (zw) PFASs. Each data point represents the average removal efficiency of triplicate measurements. Error is generally smaller than the data points and is therefore not plotted.

removal noted for some nonionic and zwitterionic PFASs. DEXSORB, M+, and the AE resin exhibit some potential to remove some specific PFASs from AFFF-contaminated groundwater, but do not exhibit consistent removal among the different classes of PFASs.

4.4.3.2 Effects of PFAS properties on removal from groundwater

To the best of our knowledge, this is the first study that has systematically examined the removal of PFASs from AFFF-contaminated groundwater using five different adsorbents and a dedicated suspect screening approach. As a result, we generated a dataset that offers the best opportunity to examine the effects of chain length and head group on PFAS removal efficiency with both conventional and emerging adsorbents.

Our suspect screening revealed the presence of at least one PFAS constituent among 29 unique classes of PFASs. Eleven of those classes contain at least three unique homologues with varying CF₂ chain length. To evaluate the effect of chain length on PFAS removal efficiency among the five adsorbents, we performed a Pearson correlation analysis between the CF₂ chain length and the removal efficiency observed at 48 hr across the eleven PFAS classes. The slope and

Table 5. Pearson correlation analysis between removal efficiency (%) in groundwater sample and CF₂ chain length for different PFAS classes.

Class Acronym	n	M+		DEXSORB+		DEXSORB		AC		AE resin	
		Slope	R ²	Slope	R ²	Slope	R ²	Slope	R ²	Slope	R ²
PFCa	6	9.3*	0.63	14.2***	0.96	2.8	0.38	16.8***	0.96	2.5	0.40
PFSA	7	12.8***	0.96	9.4***	0.86	8.1***	0.93	15.7***	0.92	-2.4*	0.57
H-PFCA	3	1.0	0.96	17.3	0.93	1.0	0.03	23.9*	0.99	2.0	0.26
H-PFSA	4	-0.2	0.00	0.3	0.04	4.8	0.38	2.8	0.25	-5.0*	0.82
FASA	6	11.7***	0.91	18.2***	0.99	6.2**	0.77	20.0***	0.97	4.7***	0.89
FASAA	3	23.0	0.97	17.0	0.95	1.4	0.31	18.6**	1.00	-4.1**	1.00
MeFASA	3	6.3	0.89	21.0*	0.98	22.1**	0.99	10.9	0.95	2.9	0.87
MeFASAA	3	20.5*	0.98	16.4**	1	3.4	0.63	19.3	0.87	-6.3	0.6
SPr-FASA	3	13.3**	1.00	5.8	0.96	-0.2	0.75	13.0	0.68	-5.6	0.33
SPrAmPr-FASAA	3	13.8	0.91	20.9**	1.00	1.8	0.51	11.0*	0.99	-0.6	0.08
SPrAmPr-FASAPrS	3	16.6	0.94	20.8	0.95	6.7*	0.99	6.7	0.97	5.9**	1.00

***, ** and * represent $p < 0.01$, $p < 0.05$ and $p < 0.10$, respectively; n refers to the number of observations.

coefficient of determination (R²) of the regression for each of the eleven classes and for each of the five adsorbents are provided in **Table 5**. Increasing CF₂ chain length primarily results in increasing hydrophobicity of PFAS species, but may also alter other physicochemical properties of PFAS that influence adsorption including electronic^{132,157} and steric^{158,159} properties. We observed a positive and significant association (p-value < 0.05) for the PFSA (perfluorosulfonic acids) and the FASAs (perfluoroalkane sulfonamide) across all of the CDPs and AC, regardless of the extent of removal observed for any individual member of these classes on any adsorbent. This finding suggests that chain length plays a considerable role in the removal of these two classes of anionic PFASs. Interestingly, a positive and significant association (p-value < 0.01) was also observed for FASA removal on the AE resin, which suggests a role for hydrophobic interactions on the removal of this putatively nonionic class of PFAS on the AE resin or increasing deprotonation of the sulfonamide functional group with increasing chain length.^{157,160} A positive and significant association (p-value < 0.10) was also observed for the PFCAs (perfluorocarboxylic acids) and the MeFASAAs (N-methyl perfluoroalkane sulfonamido acetic acids) on M+ and DEXSORB+, again highlighting the role of chain length on the removal of these anionic PFASs by CDPs with a positive surface charge. No significant association was observed for the PFCAs or the MeFASAAs on DEXSORB or the AE resin, reflecting the limited removal of these two classes of PFASs on DEXSORB and the relative importance of electrostatic interactions on their removal on the AE resin. None of the remaining classes exhibited a consistent set of significant associations among the adsorbents, though the strongest positive associations were consistently found for M+ (SPr-FASA), DEXSORB+ (MeFASA, SPrAmPr-FASAA), and AC (H-PFCA, FASAA, SPrAmPr-FASAA), with weaker positive associations found for DEXSORB (MeFASA, SPrAmPr-FASAPrS) and both positive (SPrAmPr-FASAPrS) and negative (H-PFSA, FASAA) associations found for AE resin.

The same 11 homologous series were examined to evaluate the effect of the head group on PFAS removal efficiency among the five adsorbents. We noted that 10 of these 11 classes contain at least two homologues with either 4, 6, or 8 CF₂ units. Therefore, we compared the removal efficiencies measured at 48 hr for all PFASs in the 10 homologous series with 4, 6, or 8 CF₂ units; we also include H-PFHpS as a representative H-PFSA with 6 CF₂ units. The results are presented in **Figure 49** for M⁺, DEXSORB⁺, and AC. First, we found that the removal of PFASs with a sulfonic acid head group is always greater than the removal of PFASs with a carboxylic acid head group when the rest of the structure is the same across all five adsorbents. This finding corroborates other studies that have noted this trend among PFAAs,^{69,161} but our data can be used to generalize this finding to include the H-PFSAs and H-PFCAs. Interestingly, we also note that H-PFSAs that only differ from PFSAs by one H/F atom are also removed to greater extents by all adsorbents, and the difference is magnified at lower CF₂ chain lengths. Second, we found that the FASAAs (perfluoroalkane sulfonamide acetic acid) were consistently removed to greater extents among all of the adsorbents than the FASAs when the rest of the structure is the same. We attribute this observation to the increased hydrophobicity of FASAAs relative to FASAs (resulting from their larger size) which enhances affinity for all three adsorbents, and the anionic carboxylic acid head group of the FASAAs which enhances affinity for DEXSORB⁺ and M⁺. Third, we found that MeFASAA (N-methyl perfluoroalkane sulfonamide acetic acid) was consistently removed to greater extents among M⁺ and DEXSORB⁺ than MeFASA (N-methyl perfluoroalkane sulfonamide) when the rest of the structure is the same, but the opposite trend emerged for these PFAS classes on AC. The disparate behavior of the MeFASAAs and MeFASAs on AC (relative to the FASAAs and FASAs) may be evidence that the increased hydrophobicity of the MeFASAAs (resulting from their larger size) is insufficient to counteract the effects of the anionic carboxylic acid head group of the MeFASAAs which creates a repulsive electrostatic interaction with the AC with a negative surface charge. Finally, among the three classes of PFASs containing both sulfonamide and sulfonic acid functional groups, we again found similar trends among M⁺ and DEXSORB⁺, and a different trend for AC. M⁺ and DEXSORB⁺ exhibit the greatest removal of the smallest class, SPr-FASA (perfluoroalkane sulfonamide propanesulfonic acid), and limited removal of the larger, branched classes SPrAmPr-FASAA (N-sulfopropyl dimethyl ammonio propyl-perfluoroalkane sulfonamide acetic acid) and

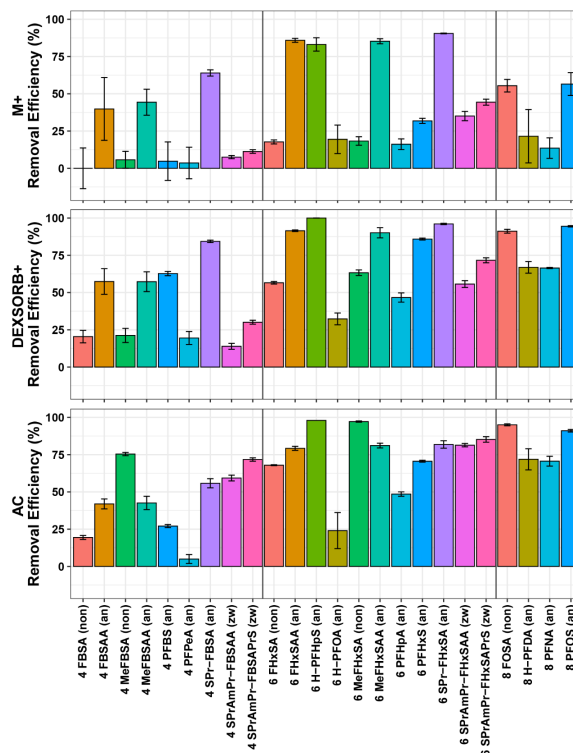


Figure 49. Bar plots showing the removal efficiencies for PFASs in 11 different homologous series grouped by 4, 6 and 8 CF₂ chain length on M⁺, DEXSORB⁺ and AC after 48 hr contact time. On the horizontal axis, the number in front of PFAS acronym represents the CF₂ chain length counted as the total number of perfluorinated carbon atoms. The notations in the parentheses represent anionic (an) PFASs, nonionic (non) PFASs, and zwitterionic (zw) PFASs.

SPrAmPr-FASAPrS (N-sulfopropyl dimethyl ammonio propyl-perfluoroalkane sulfonamido propylsulfonate). We attribute this finding to limited access to the binding sites in the interior cavity of the β -cyclodextrins for the larger, branched classes of PFASs.^{28,79,80} AC exhibits consistent removal among all three classes, demonstrating that neither the head group nor the branching influences adsorption on AC.

4.4.3.3 Conclusions from the Study and Environmental Implications

Remediation of PFAS-contaminated groundwater is challenging and solutions must be evaluated with respect to complex mixtures of PFAS species, variable concentrations among PFAS species, and in the presence of groundwater matrix constituents. Our data reveal that conventional and emerging adsorbents exhibit variable adsorption kinetics and affinity for different types of PFASs in AFFF-contaminated groundwater. These findings suggest that different adsorbents may be better suited for applications that rely on limited contact time or required the removal of specific PFASs. Our analysis of chain length and head groups suggests that removal of some short chain perfluoroalkyl substances (including PFCAs and FASAs) from groundwater will be challenging for all of the adsorbents studied, but removal of PFBS and short chain polyfluoroalkyl substances (including FASAs and substituted sulfonamides or sulfonamide acetic acids) can be achieved with one or more adsorbent.

4.5 Identifying Physicochemical Properties of CDPs that Determine Performance

Although a number of different types of CDPs have been synthesized that show promise as adsorbents for the removal of PFAAs from water,¹⁶² previous studies have not explored the relationship between the physicochemical properties of different types of CDPs and the adsorption of PFAAs. The objectives of this study were to: (1) evaluate the performance (i.e., adsorption kinetics, equilibrium adsorption density, and adsorption affinity) of 34 CDPs synthesized with fourteen different crosslinkers (**Figure 50**) and exhibiting a wide range of physicochemical properties for their potential to remove six PFAAs from water; and (2) use complementary bivariate and multivariate analyses to discover relationships between sixteen physicochemical properties of the CDPs and their performance as adsorbents. We found that the surface charge, the polymer porosity and surface area, the crosslinker content, the hydrophobicity of the crosslinker, and the particle size were selected as important predictors of adsorbent performance across our

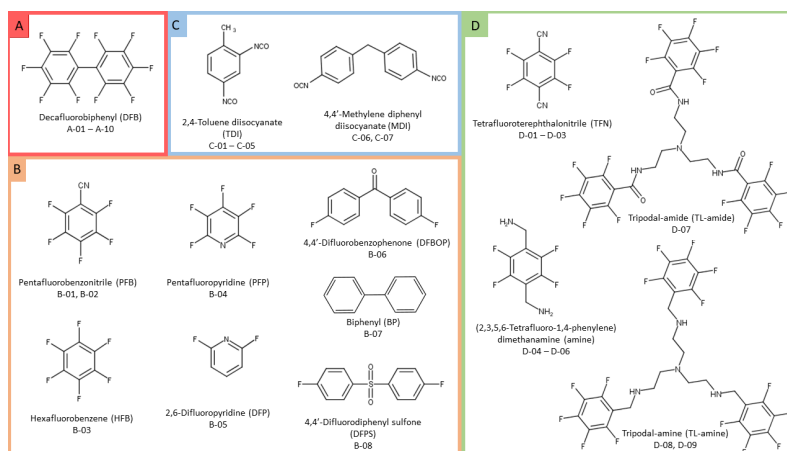


Figure 50. CDPs were synthesized using β -CDs and are organized here in four categories defined by the chemical used as the crosslinker: (A) decafluorobiphenyl; (B) seven different crosslinkers that were selected to test the effects of specific chemical groups on PFAA adsorption; (C) two different diisocyanate crosslinkers (C-01 through C-07); and (D) TFN and amine- or amide-containing crosslinkers (D-01 through D-09).

analyses. Our results identify key physicochemical properties for polymer adsorbents that will lead to the development of next-generation adsorbents that target the removal of PFAAs from water.

4.5.1.1 Performance of Diverse Types of CDPs

We evaluated the performance of 34 CDPs for their potential to remove six PFAAs from water. Specifically, we measured adsorption kinetics (dR_i), equilibrium adsorption density (q_e), and adsorption affinity ($\log K_D$) for PFBA, PFHxA, PFOA, PFBS, PFHxS, and PFOS. Box plots detailing the variability in the average of each of the performance metrics across triplicate experiments for each CDP and each PFAA are provided in **Figure 51**.

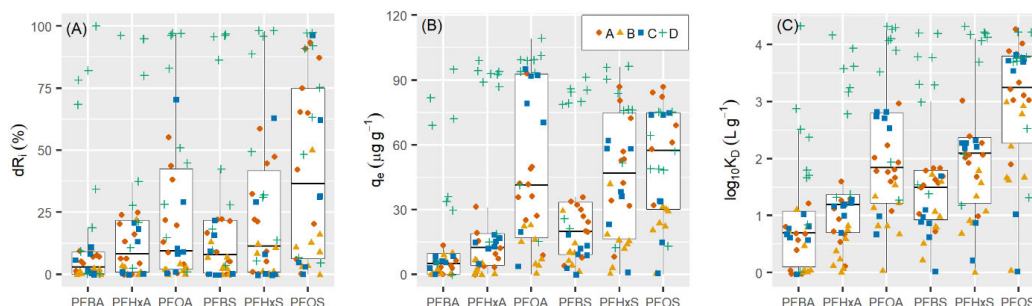


Figure 51. Box plots detailing the variability in average (A) adsorption kinetics, (B) equilibrium adsorption density, and (C) adsorption affinity for each CDP and each PFAA. The data points are assigned colors/shapes based on the four categories of CDPs that were studied. CDPs identified as A-05, A-06, A-07, and B-02 had q_e values that are off the scale. The units provided for $\log_{10} K_D$ are for the untransformed variable. The dark line in the box plots represents the median value and the edges of the box represent the 25th and 75th percent quantile.

Several important observations are worth noting in these data. First, the magnitude of each of the performance metrics is highly variable among the CDPs; dR_i ranges between 0 and 100%, q_e ranges between 0 and 454 mg g⁻¹, and $\log K_D$ ranges between 0 and 4.3. This finding is important because it demonstrates that structural differences (*i.e.*, crosslinker) among the CDPs can have profound effects on its performance. This observation also agrees with previous observations of mixed performance for the removal of PFAAs across different CDPs.^{68,71} We further note that the magnitude of each performance metric is even highly variable among the category A adsorbents, which all incorporate the DFB crosslinker. This nuance further reinforces that subtle differences in the physicochemical properties of a CDP can greatly affect performance.⁶⁸ Second, we note that the median values of each performance metric increase with increasing chain length and are higher for the PFSAFs than the PFCAs. This trend is not necessarily unexpected because longer-chain PFAAs are more hydrophobic than shorter-chain PFAAs and generally exhibit greater removal in adsorption processes.^{92,163} PFSAFs likewise generally exhibit greater removal in adsorption processes than PFCAs with the same number of carbon atoms because PFSAFs have one more fluorinated carbon atom.^{92,163} Nevertheless, it is notable that these trends were clear among data from 34 CDPs and across all performance metrics. Third, despite the observed trends with chain length, there are some CDPs that perform well for shorter-chain PFAAs including several category D adsorbents that exhibit good performance across all performance metrics (e.g., D-02, D-03, D-05, D-06). This ability to remove short-chain PFAAs, such as PFBA and PFBS, is notable because many adsorbents perform poorly for these substances.^{92,163} Fourth, we note that category D adsorbents generally perform the best among the adsorbents, whereas category B adsorbents generally perform the worst. Finally, some CDPs exhibit slow adsorption kinetics and high

adsorption affinity (e.g., D-08 for PFOA) while others exhibit rapid adsorption kinetics and high adsorption affinity (e.g., D-03 for PFOA). This final point suggests that there are different physicochemical properties that determine adsorption kinetics and adsorption affinity.

4.5.1.2 Bivariate Analysis between Physicochemical Properties and Performance

The variable performance of the CDPs across the PFAAs motivated deeper studies into correlations between the physicochemical properties of the CDPs and the magnitude of each of the performance metrics. We performed a Spearman correlation analysis between fifteen of the physicochemical properties (pol.sieve was excluded because it is a binary variable) and the log₁₀-transformed values of each of the performance metrics for each of the PFAAs. The results are presented as a heat map in **Figure 52**. The Spearman correlation analysis revealed several weak positive and negative correlations, with nearly all Spearman correlation coefficients (ρ) in the range of ± 0.50 . Despite the relatively weak correlations revealed in this analysis, a number of significant (p value < 0.01) positive and negative correlations emerged.

Only significant positive correlations were observed for the crosslinker hydrophobicity (CL.K_{ow}), crosslinker content (CL), %F, %Cl, polymer porosity (pol.pore.vol), polymer surface area (pol.SA), and pol.charge. The significant positive correlations with pol.charge and nearly every performance metric reflect enhanced performance for CDPs with a less negative or a more positive surface charge. This agrees with previous studies that have demonstrated improved removal of PFAAs with adsorbents that carry a positive surface charge.^{83,84,136,164} Likewise, chlorine (%Cl) was measured in small quantities (0.2% - 3.4%) in only five of the CDPs (D-01, D-02, D-03, D-04, D-06) as byproducts of the synthesis. These five CDPs also carry a positive surface charge which can explain the significant positive correlations observed between %Cl and nearly all of the performance metrics. Significant positive correlations between CL and dR_i for PFBA, PFHxA, PFBS, and PFHxS demonstrate the importance of crosslinker chemistry for driving the adsorption kinetics of relatively short-chain PFAAs; the significant positive correlation between CL and all of the performance metrics for PFBA are particularly notable because many adsorbents perform poorly for shorter-chain PFAAs such as PFBA and PFBS.^{92,163} Significant positive correlations between pol.pore.vol and pol.SA and dR_i for PFHxA, PFOA, and all of the PFSA demonstrate that polymer morphology is important in driving adsorption kinetics for PFAAs, which agrees with observations from other studies investigating different types of CDPs and different adsorbates.^{29,165} Finally, significant positive correlations between CL.K_{ow} and q_e for PFOS and %F and q_e for PFBS and PFOS demonstrate the importance of hydrophobicity for driving equilibrium adsorption density for more hydrophobic PFAAs.

Only significant negative correlations were observed for %C, %H, and the polymer size (pol.size). Significant negative correlations were discovered between %C and all of the

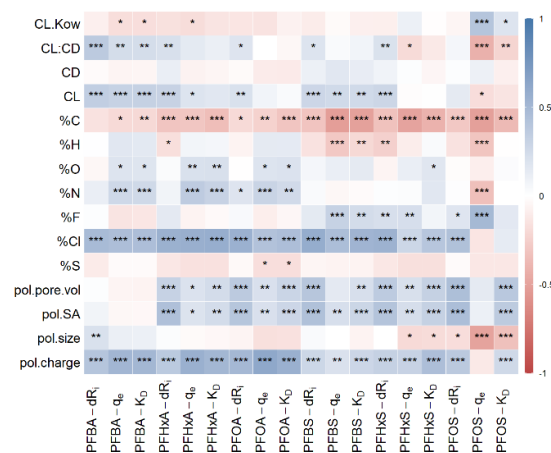


Figure 52. Bivariate association matrix between the log₁₀-transformed responses against the predictors. The associations are only weakly associated (max $\rho \sim \pm 0.50$). Significance is indicated by * ($p < 0.10$, $\rho \pm 0.17-0.20$), ** ($p < 0.05$, $\rho \pm 0.21-0.26$), *** ($p < 0.01$, $\rho \pm 0.27-0.62$).

performance metrics for the PFSA and PFHxA and $\log K_D$ for PFOA. This negative correlation points to the importance of heteroatoms (which would lower %C) in driving adsorption equilibrium and adsorption affinity for relatively long-chain PFCAs and PFSA. Likewise, negative correlations discovered between %H and q_e for PFBS and PFOS reinforce the conclusion that F atoms on the crosslinker (which replace H atoms) can be important for driving equilibrium adsorption density for more hydrophobic PFAAs. The significant negative correlations between pol.size and q_e and $\log K_D$ for PFOS demonstrate that larger particles can inhibit the adsorption of PFOS. Porous adsorbents with relatively large particle sizes rely on diffusion-based transport of adsorbates to binding sites in the interior pore network of the adsorbent; PFOS is the largest PFAA included in this study and its diffusion-based transport may be limited relative to the other PFAAs.

Finally, significant positive and negative correlations were observed for the crosslinker-cyclodextrin ratio (CL:CD) and %N. Interestingly, significant positive correlations were observed between CL:CD and performance metrics for PFBA whereas significant negative correlations were observed for PFOS. This observation reinforces the importance of crosslinker chemistry for driving the adsorption kinetics of relatively short-chain PFAAs, but also demonstrates that the crosslinker-cyclodextrin ratio may inhibit adsorption for long-chain PFAAs. %N exhibits significant positive correlations with nearly all performance metrics for PFCAs, but a significant negative correlation with q_e for PFOS. Nitrogen is a heteroatom that can be protonated under certain conditions (*e.g.*, amine groups in D-04, D-05, D-06, D-08, D-09) which may be driving the positive correlation and would again reflect the importance of electrostatic interactions for the adsorption of PFAAs. Together, the data from the bivariate analysis demonstrate that specific physicochemical properties can either enhance or inhibit the adsorption of short-chain or long-chain PFAAs with different head groups on CDPs. However, the significant correlations that were observed were relatively weak which suggests that no single physicochemical property is sufficient for predicting the adsorption of PFAAs on CDPs.

4.5.1.3 Multivariable Analysis between Physicochemical Properties and Performance

The relatively weak correlations observed between the physicochemical properties of the CDPs and the performance metrics in the bivariate analysis suggest more complex interactions among physicochemical properties that may be better explained with a multivariate analysis. We implemented a multivariate analysis using an all-possible regression approach to identify the combination of physicochemical properties that best predicts the magnitudes of the performance metrics. We first developed a Spearman correlation matrix for all of the physicochemical properties to evaluate correlations among the predictor variables. The strongest correlation was between pol.pore.vol and pol.SA ($\rho = 0.92$), which was expected due to the inherent link between polymer porosity and polymer surface area. Despite this correlation, we elected to keep both variables in our all-possible regression analysis and will evaluate their selection into well-performing models as a pair of correlated predictors. We also observed relatively strong correlations between %H and %F ($\rho = 0.87$) and %N and pol.charge ($\rho = 0.76$). The former correlation is simply because hydrogen and fluorine atoms are often substituted for each other in the crosslinker. However, these remain independent variables and both will remain in the all-possible regression analysis. The latter correlation can be partially explained by the amine groups present in CDPs D-04 through D-06 and D-08 and D-09 which are protonated at neutral pH. Because only these nitrogen-containing CDPs are likely protonated, we elect to keep both of these variables in the all-possible regression analysis.

Despite the fact that we observed some strong correlations ($\rho > 0.70$) among the physicochemical properties, we developed multivariable models between all of the

physicochemical properties of each adsorbent (predictors) and the $\log_{10}$ -transformed values of each of the performance metrics for each of the PFAAs (responses). The number of predictors included in each of the final well-performing models ranged between six and ten. The adjusted R^2 values for each of the final well-performing models ranged between 0.53 and 0.91. All multivariable models exhibited a significant increase in the adjusted R^2 value when compared to the R^2 values obtained in the bivariate analysis.

In general, for predictors selected in the all-possible regression, the signs of the standardized coefficients agree with the signs of the Spearman correlation coefficients observed in the bivariate analysis. For example, positive standardized coefficients were estimated for polymer surface area (pol.SA) and dR_i for all PFAAs and crosslinker content (CL) and all performance metrics for PFBA. Interestingly, crosslinker hydrophobicity (CL: K_{ow}) had positive standardized coefficients for q_e and KD for PFHxA, PFOA, PFHxS, and PFOS which reinforces that CL: K_{ow} is important for adsorption of more hydrophobic PFAAs. Three of the physicochemical properties were implemented in the regression model as categorical variables: whether the polymer was sieved or not (pol.sieve), polymer particle size (pol.size), and pol.charge. pol.sieve was not selected in any of the well-performing regression models. pol.size and pol.charge were recorded in the model as binary dummy variables and their standardized coefficients were normalized by an input predictor in the linear model (pol.size = <45 and pol.charge = -1, respectively) such that the coefficients for the remaining sub-predictors are interpreted in relation to the initial input predictor. The standardized coefficients for neutral polymer charge (pol.charge = 0) take a range of negative to positive values, suggesting that, relative to CDPs with a negative surface charge, a neutral surface charge can either enhance or inhibit adsorption. In contrast, the standardized coefficients for positive polymer charge (pol.charge = 1) were primarily positive across all of the well-performing models, indicating that a positive charge almost always enhances adsorption of PFAAs relative to a CDP with a negative surface charge. The standardized coefficients for the categorical pol.size variable contain primarily negative values suggesting inhibited performance of polymers with larger particle sizes for a broader set of PFAAs when compared to the bivariate analysis. Other adsorbents including activated carbon generally exhibit inhibited adsorption kinetics and affinity at larger particle sizes.^{92,163} Together, the evaluation of the standardized coefficients supports the main conclusions of the bivariate analysis and provides further insights on the relative contributions of each physicochemical property to each of the performance metrics.

4.5.1.3 Identifying Important and Significant Predictors

To further evaluate the contribution of the predictors in the well-performing all-possible regression models, we used metrics of importance and significance. The importance and significance of each of the physicochemical properties selected into the best-performing regression models for PFOA are provided in **Figure 53**. To identify the most valuable predictors for each response variable, we selected those with importance normalized by the adjusted R^2 of the selected model > 5% and significance > 2. The rate (percentage) at which each physicochemical property was identified as an important and significant

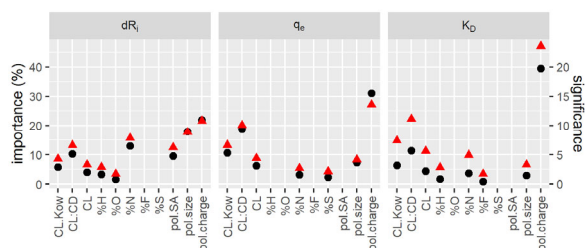


Figure 53. The predictors selected in the all-possible regression are plotted here to indicate importance (black circles) and significance (red triangles) of each of the predictors for the three performance metrics for PFOA. Gaps where no data appears indicates that that predictor was not selected as a predictor in the all-possible regression.

predictor in our analysis is provided in **Table 6**. We present the data based on the performance metric, the PFAA head group, and PFAA chain length.

The physicochemical properties that are most frequently identified as important and significant predictors are polymer surface charge (pol.charge), crosslinker hydrophobicity (CL.K_{ow}), and polymer size (pol.size). pol.charge was selected as an important and significant predictor across 17 of the 18 all-possible regression models. This analysis suggests that pol.charge plays an important role in PFAA adsorption on CDPs independently of the performance metric, the PFAA head group, and the PFAA chain length.

Table 6. Summary of important and significant predictors.

		Performance Metric ^a			Head Group ^a		Chain Length ^a		
	n ^b	dR _i (6)	q _e (6)	K _D (6)	PFA (9)	PFA (9)	C4 (6)	C6 (6)	C8 (6)
pol.charge	17	100%	100%	83%	89%	100%	83%	100%	100%
CL.K _{ow}	12	33%	83%	83%	67%	67%	33%	83%	83%
pol.size	12	83%	83%	33%	56%	78%	50%	67%	83%
%N	8	83%	33%	17%	56%	33%	50%	67%	17%
CL:CD	7	50%	50%	17%	44%	33%	17%	33%	67%
CD	7	50%	33%	33%	22%	56%	17%	67%	33%
CL	7	33%	67%	17%	56%	22%	50%	17%	50%
%O	6	67%	33%	0%	22%	44%	33%	50%	17%
%H	5	33%	50%	0%	22%	33%	33%	17%	33%
pol.SA	5	83%	0%	0%	22%	33%	17%	33%	33%
%Cl	2	33%	0%	0%	0%	22%	17%	17%	0%
%F	1	17%	0%	0%	11%	0%	17%	0%	0%

^aThe frequency of how often an important and significant appears for the associated models by percent of total models. ^bThe frequency of how often each predictor is selected in the 18 models.

Although our previous analyses suggested that pol.charge is particularly important for less hydrophobic PFAAs, it is clear that a positive surface charge of a CDP or other adsorbent will enhance the adsorption kinetics, adsorption density, and adsorption affinity for PFAAs in general. CL.K_{ow} was selected as an important and significant predictor across 12 of the 18 all-possible regression models, and was selected more frequently for q_e and logK_D and for PFAAs with increasing chain length. This agrees with our previous conclusions from the bivariate analysis and the standardized coefficients from the all-possible regression that CDPs that incorporate more hydrophobic crosslinkers will have greater adsorption density and adsorption affinity for longer-chain PFAAs. Finally, pol.size was selected as an important and significant predictor across 12 of the 18 models, and was selected most frequently for dR_i and q_e and for PFAAs with increasing chain length. This also agrees with our previous conclusions and further demonstrates that the adsorption of longer-chain PFAAs with slower diffusion-based transport potential will be more inhibited on CDPs with larger particle sizes.

4.5.1.4 Conclusions from the Study and Implications

β-cyclodextrin-crosslinked polymer adsorbents (CDPs) have the potential to remove perfluoroalkyl acids (PFAAs) from water. We evaluated the performance of 34 different CDPs to quantify adsorption kinetics, adsorption equilibrium density, and adsorption affinity for six PFAAs. The CDPs were synthesized using 14 different crosslinkers and under conditions that resulted in variable physicochemical properties. The CDPs exhibited highly variable performance with some performing poorly and others performing well. These findings demonstrate that crosslinker chemistry and subtle differences in physicochemical properties can determine CDP adsorption performance. A bivariate correlation analysis identified generally weak correlations between fifteen physicochemical properties of the CDPs and the performance metrics for the six PFAAs. The strongest positive correlations were noted between the surface charge of the CDP and the adsorption affinity for PFCAs. Other predictors exhibited weak but significant and exclusively positive (e.g., polymer surface charge, polymer surface area, polymer porosity, crosslinker hydrophobicity, crosslinker content) or negative (e.g., percent carbon, polymer particle size) correlations. These observations help identify physicochemical properties that can be tuned to enhance the adsorption of PFAAs. A multivariable regression analysis was implemented to identify the synergistic effects of multiple physicochemical properties on CDP performance. The well-performing models performed better than the models generated in the bivariate analysis. The

signs and magnitudes of the standardized coefficients in the well-performing models support the main conclusions of the bivariate analysis and provide further insights on the relative contributions of each physicochemical property to each of the performance metrics. We identified the most important and significant predictors and used them to make conclusions about the physicochemical properties that are most important for PFAA uptake on CDPs. We found that: (1) CDPs with a less negative or more positive surface charge will exhibit enhanced adsorption of all types of PFAAs; (2) CDPs with greater porosity and surface area will exhibit enhanced adsorption kinetics for all types of PFAAs; (3) CDPs with greater crosslinker content will exhibit enhanced adsorption of short-chain PFAAs; (4) CDPs containing more hydrophobic crosslinkers will exhibit enhanced equilibrium adsorption density and adsorption affinity for longer-chain PFAAs; and (5) CDPs with smaller particle sizes will exhibit enhanced adsorption kinetics and equilibrium adsorption density for all PFAAs.

4.6 Morphology and Particle Size Control

One of the polymers selected for Phase 2 studies in this project was a positively charged CDP that we refer to as CDP+ (**Figure 38**). CDP+ exhibits outstanding performance for the removal of PFAAs from water and is resistant to fouling by many common groundwater matrix constituents (**Figure 43**). CDP+ was synthesized by including a low-molecular weight quaternary ammonium (QA) molecule in the synthesis of our original tetrafluoroterephthalonitrile (TFN)-crosslinked CD-based polymer (P-CDP) as shown in **Figure 36**.

We optimized polymerization conditions to yield CDP+ in quantities of 2.2 kg in a single batch. However, the as-obtained CDP+ is an insoluble powder with irregular particle sizes on the order of tens of microns (60–80 μm). The ability to control particle size and morphology provides maximum flexibility for incorporating CDP+ into engineered systems for PFAS removal. Therefore, we have evaluated numerous granulation techniques to control the particle size from the obtained CDP+ powders, including: (1) encapsulation of powders through alginate bead formation; (2) melt granulation at high temperatures using polyethylene as a binder; and (3) spray granulation using various FDA approved binders for food contact. Whereas alginate bead formation and melt granulation both provided CDP+ granules that exhibited rapid adsorption kinetics and high adsorption capacity for anionic PFAS, those techniques proved to be inefficient with respect to scale-up and resulted in relatively broad particle size distributions, which is undesirable.

We therefore focused on the use of spray granulation techniques to control the particle size and morphology of CDP+. For this technique, CDP+ powder is stirred under high shear while a binder solution is sprayed onto the powder to wet the powder surface and enable aggregation of the smaller particles. The binder choice is critical because it needs to be: (i) safe for food contact under FDA regulation; (ii) readily available in the industry; (iii) insoluble in water; (iv) soluble in an easy-to-remove solvent; and (v) insoluble in alcohol-based solvents (i.e. methanol and ethanol) that we expect to use to regenerate CDP+ adsorbents. Two candidate binders that meet all of these criteria were selected: (1) cellulose acetate (trade name: EastmanTM CA-398-3); and (2) acrylic resins (trade name: ELVACITE[®] 2016). Both binders are used in food-packaging applications and are regarded as safe by the FDA, are insoluble in water and alcoholic solvents, and are soluble in acetone (an easy-to-remove solvent).

We first optimized the feasibility of spray granulation and the choice of binders for use in the control of particle size and morphology of CDP+. The optimized preparation of granules is straightforward and the protocol is rapid. Briefly, starting with 255 g of CDP+ powder, a solution

of 45 g acrylate resin (ELVACITE® 2016) was added to 300 mL acetone. The mixture was “blended” in a commercial blender for 5 minutes, and then dried under vacuum to remove the acetone. This protocol yielded CDP+ granules with a porous morphology and a narrow particle size distribution.

To establish the kinetic performance and capacity of CDP+ ELVACITE® granules against PFAS, we performed an uptake experiment against a mixture of four target anionic PFAS: (i) PFBS (perfluorobutanoic acid); (ii) GenX (hexafluoropropylene oxide dimer acid); (iii) PFOA (perfluorooctanoic acid); and (iv) PFOS (perfluorooctanesulfonic acid). Experiments were carried out in 50 mL polypropylene centrifuge tubes and were continuously mixed on a tube revolver at 40 RPM. The adsorbents (either the as-synthesized CDP+ powder or CDP+ ELVACITE® granules) were added to triplicate reactor tubes at a concentration of 1000 mg/L and the PFAS were added as a mixture with each PFAS present at an initial concentration of 100 µg/L. Control experiments were conducted in triplicate in the same way in the absence of adsorbent. One mL samples were collected at predetermined time points and centrifuged to separate the adsorbent from the aqueous phase. The supernatant was collected and analyzed for the target PFAS by means of liquid chromatography and mass spectrometry. The average PFAS uptake percentage (%) reported in **Figure 54** was determined based on the average of the control data from each time point and the experimental data from each time point.

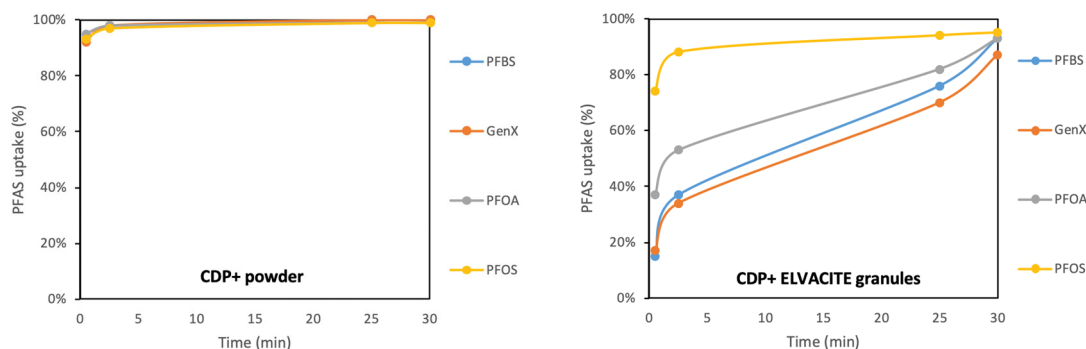


Figure 54. PFAS uptake kinetics and capacity evaluation of CDP+ ELVACITE® granules (~500 µm) benchmarked against CDP+ native powder (<63 µm).

Despite the larger size of CDP+ ELVACITE® granules (~500 µm) compared to the CDP+ native powder (<63 µm), the favorable uptake kinetics and capacity are maintained, highlighting the efficacy of spray granulation both in terms of PFAS performance and industrial scalability. The decreased adsorption kinetics observed for the CDP+ ELVACITE® granules is a result of the reduced surface area of the larger-sized adsorbent particles. We note that the changes in uptake kinetics are relatively small when compared to the change in uptake kinetics when comparing powdered activated carbon (PAC) and granular activated carbon (GAC); whereas PAC with an average particle diameter on the order of 10-75 µm can remove some PFAS from solution in under 30 minutes, GAC with an average particle diameter on the order of 425-850 µm requires more than 48 hours to remove the same PFAS from solution. Therefore, the expected change in adsorption kinetics resulting from changes in particle size (and, consequently changes in surface area) for CDP+ are much less than has been observed for activated carbon. One explanation for this feature is that the CDP+ granules maintain mesoporosity and retain the accessibility of the internal binding sites of the CDP+ adsorbent, whereas GAC is microporous and exhibits diffusion-limited adsorption kinetics.

We anticipate that the favorable kinetics of the CDP+ ELVACITE granules (when compared to GAC of the same particle size) will, at worst, allow us to maintain empty-bed contact times (EBCTs), relative sizes, and configurations of existing GAC-based adsorption reactors. It is also possible, if not likely, that the favorable kinetics of the CDP+ ELVACITE granules will allow for shorter EBCTs, smaller reactors, and alternative configurations that otherwise reduce the footprint and capital costs.

The particle size distribution obtained from the high shear granulator can be controlled by input parameters such as the liquid-to-powder ratio, impeller rate, and granulation time. Any desired particle size range can be obtained, including the standard 12x40 mesh size for adsorbents used in water purification. Our preferred binders are cellulose acetate and acrylic resins, both of which are stable and widely used in the coating industry and for water purification applications.

The data in **Figure 54** are used to demonstrate that the CDP+ ELVACITE granules exhibit somewhat remarkable performance (considering the particle size) for the removal of the target PFAS within 30 minutes. Additionally, we note that we collected samples from these experiments at later time points (up to 24 hours of contact time, data not shown) and our results demonstrate that the ultimate equilibrium adsorption density of the CDP+ ELVACITE granules is the same as the as-synthesized CDP+ powder, indicating that the expected change in adsorption kinetics is the only difference between the performance of the two morphologies.

4.7 Regeneration of CDPs

The goal of Phase 1 of our project was to develop and characterize the performance of new cyclodextrin (CD)-based polymer adsorbents that target PFAS. In section 4.3 of this report, we describe the four most promising CD-based polymer adsorbents to be included in Phase 2 studies (defined as P-CDP, amine-CDP, CDP+ and MDI-CDP+). The proposed Phase 2 studies include evaluation of procedures for synthesis scale-up of CD-based polymers, exploration of techniques to control polymer morphology and particle size, polymer stability/durability studies, evaluation of regeneration, and evaluation of process designs.

In section 4.6 of this report, we describe the most promising scaffolding technique to control the polymer morphology and particle size of our CD-based polymer adsorbents. We present data that demonstrate the efficacy of spray granularization for generating granular CD-based polymer adsorbents of any defined particle size. Further, granularization with acrylic resins (trade name: ELVACITE®) resulted in durable granules (defined as CDP+ ELVACITE) that exhibited limited loss in performance relative to the as-synthesized CDP+ powder. This section of the report describes our evaluation of regeneration of CD-based polymer adsorbents and the selection of optimal regeneration protocols for P-CDP and CDP+ ELVACITE. We will support our selections with data comparing the recovery of adsorbates from P-CDP using different regeneration solutions and reuse of CDP+ ELVACITE after regeneration with an optimal regeneration solution.

4.7.1 Optimizing Regeneration of P-CDP.

We first report on a previous evaluation of the regeneration potential of P-CDP (**Figure 36**), which is a promising CDP that exhibits a negative surface charge and has demonstrated efficacy for removing cationic and zwitterionic PFAS (and other contaminants of concern) from water.⁵⁴ In this study, we used P-CDP grafted on cellulose microcrystals¹⁶⁶ as the adsorbent in small-scale column experiments.⁸⁰ To evaluate the regeneration potential of P-CDP, we performed recovery experiments with a mixture of 178 different contaminants of concern (CoCs), including PFOA. Briefly, small-scale columns were packed with 500 mg of P-CDP sandwiched between porous

frits. The packed columns were loaded with 1 liter of nanopure water that was spiked with a mixture of the 178 CoCs at a concentration of 500 ng L⁻¹ each. To evaluate the capture of CoCs on P-CDP, we collected three 8 mL samples from the eluent of each column and subsequently analyzed them by means of high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS). The loaded small-scale columns were then dried under vacuum and the CoCs were eluted by passing a fixed volume of organic solvent (*i.e.*, a regeneration solution) over each column and collecting the eluate in a 15 mL centrifuge tube. Eluates were then evaporated under a gentle flow of high purity nitrogen gas. The dried eluates were reconstituted in 100 μ L of methanol and 900 μ L of nanopure water, transferred into a plastic syringe, filtered with 4 mm syringe filters into 2 mL amber vials, and analyzed by means of HPLC-MS. To evaluate the potential of different organic solvents to regenerate P-CDP, we calculated the absolute recovery of the 178 CoCs based on the measurements of capture and elution.

We performed a series of experiments evaluating the absolute recovery of CoCs as a function of solvent type, solvent volume, and solvent amendments. A summary of these recovery data is presented in **Figure 55**, where each of the 178 CoCs is grouped into one of six bins representing varying absolute recovery.

We first evaluated absolute recovery as a function of conventional regeneration solvents including methanol, ethanol, acetone, acetonitrile, and ethyl acetate. Acetone, acetonitrile, and ethyl acetate caused P-CDP to swell, making it impossible to elute the CoCs with those solvents. Methanol and ethanol did not cause P-CDP to swell, and both produced similar recovery results. Therefore, methanol was used for further experiments to optimize absolute recovery. There was a significant increase in absolute recovery as the volume of methanol used for regeneration was increased (see two leftmost data groups in **Figure 55**). Increasing the volume of methanol enhances the absolute recovery of neutral and negatively charged CoCs undergoing primarily hydrophobic interactions with P-CDP but has no effect on positively charged CoCs likely undergoing complementary electrostatic interactions with P-CDP. This observation suggests that other modifications to the elution solvent will be required to recover positively charged CoCs from P-CDP, such as the addition of salts.

We first evaluated absolute recovery with 15 mL of methanol amended with 100 mg of NaCl (see third data group in **Figure 55**). Methanol amended with NaCl enabled the recovery of positively charged CoCs, and significantly increased the number of CoCs with an average absolute recovery between 80% and 120% from 68 to 112. We next evaluated absolute recovery with 15

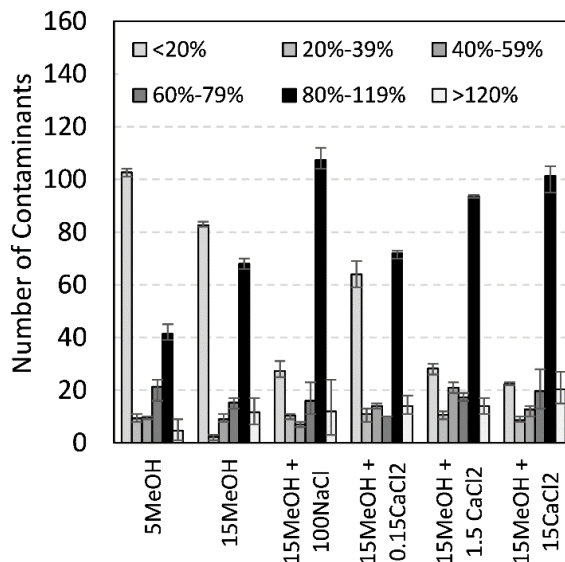


Figure 55. Number of CoCs recovered on 500 mg of P-CDP as a function of volume (5 mL and 15 mL of methanol) and composition (15 mL of methanol amended with 100 mg NaCl, or 0.15, 1.5, and 15 mg of CaCl₂) of regeneration solution. Error bars represent the standard deviation in the binning among independent triplicate experiments.

mL of methanol amended with a gradient of CaCl_2 ranging from 0.15 to 15 mg (see rightmost data groups in **Figure 55**). We selected CaCl_2 because lower molar concentrations of divalent cations are required to regenerate ion exchange resins. As expected, there were significant increases in absolute recovery as the concentration of CaCl_2 in the methanol was increased. We measured 104 CoCs with average absolute recoveries between 80% and 120% with 15 mg of CaCl_2 added to the methanol, of which 36 were positively charged CoCs that were not removed at all with un-amended methanol.

The optimized regeneration protocol for P-CDP requires 15 mL of methanol amended with 15 mg of CaCl_2 (1 g L^{-1}). Under these conditions, 104 of 178 CoCs have average absolute recoveries between 80% and 120%, which is generally considered to be an acceptable recovery range on solid adsorbents. In experiments with a single adsorbate, we also demonstrated that P-CDP can be regenerated at least five times without a loss in performance.²⁹

4.7.2 Optimizing regeneration of CDP+ ELVACITE

We next report on an evaluation of the regeneration potential of CDP+ ELVACITE (**Figure 38**), which is a promising CD-based polymer adsorbent that exhibits a positive surface charge and has demonstrated efficacy for removing anionic PFAS (and other CoCs) from water.⁶¹ Based on our experience in developing a regeneration protocol for P-CDP, we focused on methanol as the regeneration solvent, although ethanol is another option that does not cause CD-based polymer adsorbents to swell. We also note that the ELVACITE binder was selected because it is insoluble in alcohol-based solvents, which makes CDP+ ELVACITE a candidate for regeneration with methanol or ethanol. To evaluate the regeneration potential of CDP+ ELVACITE, we performed a series of recovery experiments with PFOA and PFOS. Briefly, we added 250 mg of CDP+ ELVACITE to 35 mL of nanopure water spiked with the PFOA and PFOS to a concentration of $1 \mu\text{g L}^{-1}$ each in 50 mL polypropylene centrifuge tubes. The centrifuge tubes were then tumbled for 30 minutes to reach adsorption equilibrium. CDP+ ELVACITE was then separated from the water by centrifugation and aliquots of the supernatant were collected and measured by means of HPLC-MS to determine the extent of PFAS adsorption. The collected CDP+ ELVACITE was then washed in a fixed volume of organic solvent (*i.e.*, a regeneration solution), rinsed in nanopure water, and subjected to the same PFAS adsorption experiment to evaluate reuse after regeneration. The organic solvent used to wash CDP+ ELVACITE was also collected and measured by means of HPLC-MS to evaluate the recovery of PFOA and PFOS. All experiments were conducted in triplicate.

We performed these PFOA and PFOS recovery and CDP+ ELVACITE reuse experiments exploring a variety of solvent amendments and solvent volumes. We evaluated methanol amended with calcium chloride (CaCl_2), sodium chloride (NaCl), ammonium acetate (NH_4OAc), and ammonium formate (NH_4HCO_2) at concentrations ranging between 0.5 and 5.0 g L^{-1} . We also evaluated the volume of amended methanol required to fully recover the adsorbed PFOA and PFOS from CDP+ ELVACITE (volumes ranging between 5 and 50 mL) and followed regeneration by a rinse in the same volume of nanopure water.

Our results demonstrate that nearly complete recovery of PFOA and PFOS from 250 mg of CDP+ ELVACITE can be achieved with 20 mL of methanol amended with 2.0 g L^{-1} of NH_4OAc ; smaller volumes of methanol and lower concentrations of NH_4OAc resulted in incomplete recovery of PFOA and PFOS. Our results also demonstrate that CDP+ ELVACITE can be reused following this regeneration protocol and a subsequent rinse in 30 mL of nanopure water without

any loss in performance over at least four cycles of use and regeneration (**Figure 56**). The data provided in **Figure 56** demonstrate that there were no statistically significant changes in the uptake efficiency of PFOA and PFOS over four cycles of use and regeneration. These data corroborate our previous finding that the performance of P-CDP is not affected by the regeneration procedure. Further, we can now confirm that the ELVACITE binder does not inhibit the regeneration of CD-based adsorbents, and is likewise not affected by the regeneration procedure. This is an important finding that will allow us to continue to explore CDP+ ELVACITE and other CD-based polymer adsorbents in granular form.

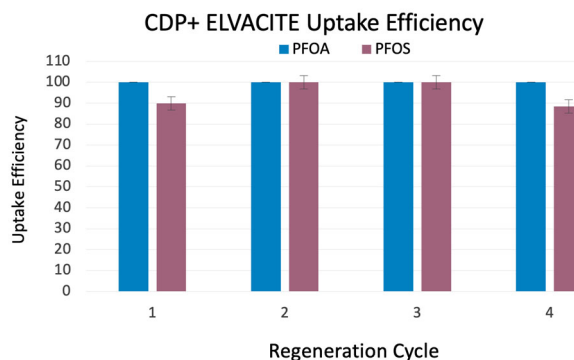


Figure 56. The average PFAS uptake % by CDP+ ELVACITE after consecutive regeneration cycles. Error bars represent the standard deviation among independent triplicate experiments.

In summary, we have identified methanol and ethanol as viable solvents for the regeneration of CD-based polymer adsorbents, identified appropriate amendments for the regeneration of CD-based polymer adsorbents with negative surface charge (CaCl_2) and positive surface charge (NH_4OAc), demonstrated that the ELVACITE binder does not inhibit regeneration, and demonstrated that the performance of P-CDP and CDP+ ELVACITE is not affected by the regeneration protocol.

4.8 Durability of CDPs

The long-term PFAS removal performance and mechanical strength of CD-based polymer adsorbents have been demonstrated in a number of pilot-scale column studies. In these pilot-scale column studies (some of which have been run for more than 6 months), we generally observe contaminant breakthrough curves that match those observed in laboratory-scale column studies performed over a much shorter duration; this demonstrates that the long-term performance of CD-based polymer adsorbents matches the short-term performance observed in the laboratory and provides some evidence that performance is durable over time and under real operating conditions. We also measure the pressure drop through the pilot-scale columns during these studies. We generally observe constant pressure drop through the pilot-scale columns over the period of operation (which again can be longer than 6 months); we interpret this as evidence of mechanical stability, because less mechanically stable CD-based polymer adsorbents could break down over time and create pressure increases as pores are blocked with fragments of adsorbent particles.

Perhaps most importantly, results from this project demonstrated that no byproducts are leaching from CD-based polymer adsorbents over time. This has been established through completion of the NSF/ANSI 61 certification process. This certification is a mandatory requirement for process media for intended use in drinking water treatment processes. The results of certification tests demonstrate that no leaching of hazardous chemicals or synthesis byproducts occurs when CD-based polymer adsorbents are implemented in simulated drinking water treatment processes. In conclusion, we have demonstrated that different CD-based polymer adsorbents in different forms (*i.e.*, as-synthesized powder and granules) exhibit long-term durability.

4.9 Batch and Column Experiments with CDP Granules

We have demonstrated the potential for CDPs to be used as adsorbents to remove diverse types of PFASs from water. However, we must more carefully evaluate the efficacy of CDP granules, which are synthesized from the as-synthesized powdered CDPs and are large enough to be used in packed-bed filtration systems. The objective of this study was to evaluate how the adsorption of PFAAs is affected by CDP granule size, and how the performance differs between batch and packed-bed filtration systems. We conducted batch experiments to estimate the adsorption kinetics of six PFAAs on seven CDP granules. The seven CDP granules had average particle diameters that ranged between 84 and 718 μm . We also conducted batch isotherm experiments to estimate the adsorption capacity and adsorption affinity of six PFAAs on three of the CDP granules ($d_p = 84, 175, 359 \mu\text{m}$). Finally, to gain insight into the performance of full-scale systems, we conducted rapid small-scale column tests (RSSCTs) for three of the granules ($d_p = 84, 175, 359 \mu\text{m}$) to evaluate the breakthrough of PFAAs and whether the breakthrough can be predicted based on assumptions of constant or proportional diffusivity as a function of granule size. We found that the smaller CDP granules exhibited more rapid adsorption kinetics for shorter-chain PFAAs, whereas larger CDP granules exhibited more rapid adsorption kinetics for longer-chain PFAAs. Adsorption capacity was more dependent on the PFAA than the granule size, with the granules exhibiting capacity for 2-3 times as many moles of PFBA than other PFAAs. Increases in adsorption affinity correlated with PFAAs of increasing hydrophobicity, with PFHxS and PFOS exhibiting the highest adsorption affinity. For the RSSCTs, we found that CDP granules of different size appear to exhibit different mechanisms of mass transfer and we observed that long- and short-chain PFAS exhibit varying extents of diffusion. Therefore, development of a single RSSCT experiment was not possible and our results provide a range of possible outcomes for PFAS breakthrough from column experiments. Overall, these findings provide insight to understanding the performance of CDP granules in batch and packed-bed filtration systems.

4.9.1 Characterization of CDP granules

The CDP granules were produced by means of spray granulation and then sieved into seven bins representing different average particle diameters and identified as Bin 1 through Bin 7. Properties of the granules are summarized in **Table 7**. The CDP granules in Bin 1 through Bin 7 have average particle diameters that range from 84 μm to 718 μm . The BET surface area (SA) of the granules ranges from 4.4 to 15.2 $\text{m}^2 \text{g}^{-1}$ with an average of $10.4 \pm 4.0 \text{ m}^2 \text{g}^{-1}$. The range of SA measurements here is less than that previously reported for the as-synthesized CDP powder, which had a SA of 19 $\text{m}^2 \text{g}^{-1}$.⁶⁰ This suggests that some of the surface area of the porous CDP granules may be obscured by the binder material. Furthermore, the binder may partially or completely inhibit access to binding sites. The elemental composition remains constant as a function of particle size, which suggests that the incorporation of binder is proportional to the granule size.

4.9.2 Batch Adsorption Kinetics

We evaluated the adsorption kinetics of the six PFAAs with the seven different sized CDP granules in batch experiments. Kinetics are an important metric for evaluating an adsorbent

Table 7. Summary of important and significant predictors.

Granule name	Average particle diameter (μm)	Particle size range (μm)	BET SA ($\text{m}^2 \text{g}^{-1}$)	C (%)	H (%)	N (%)	F (%)	Cl (%)
Bin 1	84	63-105	13.1	44.95	5.06	5.49	2.85	0.64
Bin 2	127	105-149	4.4	44.71	5.10	5.66	2.92	0.64
Bin 3	175	149-210	9.4	44.71	4.96	5.59	2.81	0.62
Bin 4	254	210-297	15.2	44.41	5.19	5.67	3.03	0.78
Bin 5	359	297-420	9.4	43.65	4.88	5.26	2.74	0.60
Bin 6	508	420-595	7.0	43.05	5.17	5.02	2.65	0.58
Bin 7	718	595-841	14.4	42.41	4.65	4.98	2.68	0.57

because it provides insight to how long it takes for adsorption to reach equilibrium. Although we have previously demonstrated that CDPs exhibit rapid adsorption kinetics, it is not clear if these previous findings will be translated to CDP granules. Here, we estimated pseudo-second order adsorption rate constants (k_{obs}).⁴¹ A quantitative metric like k_{obs} allows us to compare the adsorption kinetics across the various PFAA-CDP granule pairs and has been previously used to evaluate adsorption kinetics for CDPs.^{28,68} The estimated k_{obs} are plotted on a log scale in **Figure 57**.

We found that kinetics is most rapid ($\log k_{obs}$ 0.9-2.7 $\text{g mg}^{-1} \text{min}^{-1}$ for all PFAAs) for the smallest granule (Bin 1), and that kinetics is slowest ($\log k_{obs}$ from 0.4-0.7 $\text{g mg}^{-1} \text{min}^{-1}$ for all PFAAs) for the largest granule (Bin 7), as seen in **Figure 57**. We observe that kinetics and particle size were negatively and significantly associated for PFBA, PFHxA, PFOA, PFBS, and PFHxS ($p < 0.05$). The exception to this observation is PFOS, which exhibits a relatively weak association between kinetics and particle size ($\rho = 0.14$, $p > 0.05$). This negative association was expected, as we expect smaller particles to exhibit more rapid kinetics. However, this association is typically due to smaller particles generally having increased surface area compared to larger particles.^{61,92,163} Interestingly, here we find no significant association between particle size and SA for the CDP granules ($\rho = 0.18$, $p > 0.05$). As a result, we observe a weak association between kinetics and SA of the granules ($p > 0.05$).

We also found that kinetics is dependent on chain-length of PFAAs. For the smallest granule (Bin 1), the most rapid kinetics was exhibited by less hydrophobic PFAAs (*i.e.*, short-chain PFAAs). It has been previously observed that the short-chain PFAAs have more rapid adsorption kinetics on granular activated carbon compared to long-chain PFAAs; this observation is attributed to the smaller molecular size of the short-chain PFAAs which have easier access to pores.¹⁶⁷ As particle size increases, more rapid kinetics are exhibited by PFAAs of increasing hydrophobicity. For larger granules, it is possible that long-chain hydrophobic PFAAs may form hemi-micelles and block the intraparticle diffusion of short-chain PFAAs.¹⁶⁷ The overall slower kinetics exhibited by all PFAAs onto larger granules may be attributed to the slower adsorption kinetics of larger hydrophobic PFAAs that initially occupy binding sites, followed by the hemi-micelle formation of all PFAAs. While the concentration of PFAAs used in this study are not high enough for micelle formation in water, the concentration may be sufficient for micelle formation on the surface of CDP granules.⁷³ For the larger granules, we also found that PFSAAs exhibited more rapid kinetics over the PFCAs. This observation is expected, as PFSAAs with the same chain-length as a PFCAs contain an extra C-F, which results in PFSAAs having a more hydrophobic behavior compared to their PFCAs counterpart.¹⁴²

We find that the adsorption kinetics of the CDP granules is slower compared to that of the as-synthesized CDP. For the CDP granules in this study, equilibrium was not reached until 48-72 hours; this contrasts the rapid adsorption of PFAAs by the powdered CDP, which we previously found to reach equilibrium within 0.5 hours.⁵⁴ This suggests that the binder incorporated into CDP

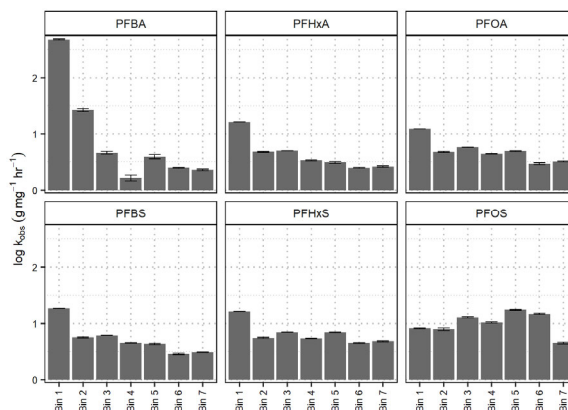


Figure 57. Estimated average and relative error of log-transformed pseudo-second order rate constants ($\log k_{obs}$) for the six PFAAs and the seven sizes of CDP granules. [PFAA]₀ = 1 $\mu\text{g L}^{-1}$ and [adsorbent]₀ = 15 mg L^{-1} . Samples were taken at 0.25, 0.5, 1, 2, 4, 8, 24 and 72.

granules has a significant effect on adsorption kinetics. Generally, the incorporation of the binder decreases access to binding sites for the smallest CDP granules and can further decrease access to binding sites for larger CDP granules. The elemental composition is the same for the CDP granules used in this study, which suggests that the incorporated binder is proportional to the granule size. Thus, slower adsorption kinetics for the largest CDP granule are not due to incorporating of more binder in larger CDP granules. Rather, the slower kinetics of the larger CDP granules may be due to the binder generating micro regions of microporosity, which may require greater extents of diffusion in the larger granules than the more mesoporous smaller granules.

4.9.3 Batch Adsorption Isotherm

We characterized the adsorption capacity and adsorption affinity at equilibrium for each PFAA on CDP granules from three granule sizes using data from batch isotherm experiments. Adsorption capacity (q_{max}) is a metric of the total binding sites that are available for adsorption per mass of an adsorbate. Adsorption affinity, as represented by the Langmuir constant (K_L), is a measure of the interaction between the adsorbate and adsorbent in the linear region of the isotherm at equilibrium; the linear region of the isotherm is relevant for low concentrations of PFAAs. We previously conducted isotherms for two powdered CDPs; for a decafluorobiphenyl-crosslinked CDP (DFB-CDP) we reported a q_{max} of 82 $\mu\text{mol g}^{-1}$ and K_L of 0.5 L mg^{-1} for PFOA, and for the amine-containing tripodal CDPs (TL-CDP) we reported a q_{max} of 1.1 mmol g^{-1} and K_L of 4.3 L mg^{-1} for PFOA.^{30,69} In this study, we are interested in understanding whether capacity and affinity scales as a function of particle size. While we expect that adsorption occurs in the interior cavity of the cyclodextrin, additional factors may impact adsorption capacity of PFAAs on CDP granules. These factors include the extent to which the binder may inhibit access to binding sites, whether the charge on the crosslinker can be a binding site, and the possible role that hemi-micelle and micelle formation may play in the adsorption of PFAAs. We expect to gain insight to understanding how the metrics of adsorption capacity and adsorption affinity vary as a function of particle size. The experiments were conducted for the six PFAAs using a subset of the granules (Bin 1, Bin 3, and Bin 5) that would represent a range of particle sizes. We estimated the adsorption capacity (q_{max}) and affinity for PFAAs (K_L) using the Langmuir adsorption isotherm. The estimates for q_{max} and K_L are summarized in **Figure 58**. The values for q_{max} are presented in molar units of PFAA for easier comparison across the six PFAAs evaluated in this study.

We find that the adsorption capacity for a PFAA does not change significantly with particle size (**Figure 58A**). We note that the capacity for a PFAA increases as chain-length decreases, and the capacity for PFSA is lower than that of PFCAs of the same chain-length. For PFOA, we estimate an average capacity of 224 $\mu\text{mol g}^{-1}$ (215–231 $\mu\text{mol g}^{-1}$ for the three CDP granules evaluated). Compared to the capacity of previously measured CDPs, the granules in this study have one-fifth of the capacity for PFOA compared to TL-CDP and have three times the capacity for PFOA compared to DFB-CDP.^{30,69} Furthermore, we find that adsorption capacity for PFBA is an average of 435 $\mu\text{mol g}^{-1}$ (378–479 $\mu\text{mol g}^{-1}$ for the three granules evaluated) whereas the other

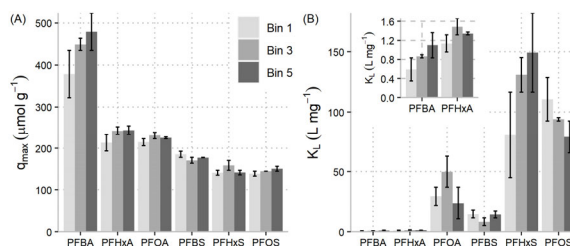


Figure 58. Estimated maximum adsorption capacity (q_{max}) and affinity for PFAAs (K_L). [PFAA] = 10–5000 $\mu\text{g L}^{-1}$, [adsorbent] = 15 mg L^{-1} . Samples were taken at 96 hours. The error bars represent the maximum and minimum values from nonlinear model fits. We report the best-fit estimate as the average of nonlinear regression model.

PFAAs have capacities ranging from 145 to 234 $\mu\text{mol g}^{-1}$. This suggests that a fixed mass of a granule of any size adsorbs 2-3 times more molecules of PFBA compared to the other PFAAs. We hypothesize several mechanisms that may be occurring. First, each cavity may contain more than one PFBA molecule per cavity. However, previous studies with cyclodextrins suggest that each cyclodextrin cavity forms host-guest complexes with only one PFAA molecule.^{82,116} Second, the positive charge on the crosslinker may be an additional binding site for PFBA. Third, there may be hemi-micelle or micelle formation of PFBA; although we may also expect hemi-micelle or micelle formation of other PFAAs, it is possible that the molecular size of other larger PFAAs cannot easily form hemi-micelles or micelles within or on the granule without the presence of short-chain PFAAs, which may more easily access the binding sites of CDP granules. It is also possible that all three of these hypothesized mechanisms are taking place synergistically. Evaluating the influence of these three mechanisms was outside the scope of this study and warrants future studies.

We find that there are mixed results for adsorption affinity (K_L) as a function of particle size (**Figure 58B**). For example, the ranges of affinity of the three granules for PFBA (0.6-1.1 L mg^{-1}) and PFHxA (1.1-1.5 L mg^{-1}) are narrow, which suggests that the relationship of affinity as a function of particle size is not clear for less hydrophobic PFAAs. Furthermore, there are no apparent trends for PFOA and PFBS, despite the values of affinity covering a larger range (24-50 L mg^{-1} and 8-15 L mg^{-1} , respectively). Trends are more apparent for PFHxS and PFOS; for PFHxS, affinity appears to be positively correlated with particle size, whereas for PFOS, affinity appears to be negatively correlated with particle size. However, given the overlap of the error bars, it is difficult to determine whether these trends can be generalized. Overall, affinity for the PFAAs span two orders of magnitude from 0.85 L mg^{-1} (PFBA) to 120 L mg^{-1} (PFHxS). Here, we note the high affinity for PFHxS and PFOS, which are up to two orders of magnitude greater than compared to less hydrophobic PFAAs. We find that larger granules have greater affinity for less hydrophobic PFAAs, while smaller granules have greater affinity for more hydrophobic PFAAs. We find that the granules in this study have estimates of K_L for PFOA that range from 24 to 50 L mg^{-1} , which are 40-100 times higher than the K_L of DFB-CDP and 5-10 times higher than the K_L of TL-CDP.^{30,69} This is important to note because although many studies focus on high adsorption capacity as a metric of comparison across adsorbents, the metric of affinity may be of greater importance as a metric of comparison. For example, the equilibrium adsorption density on an adsorbent in a PBF will be determined by the aqueous phase concentration of the adsorbate and will be significantly less than the capacity for any effective adsorbent. The factor that determines the actual equilibrium adsorption density is the adsorption affinity, and higher values will result in more effective use of the adsorbent.

4.9.4 Evaluating Constant and Proportional Diffusivity in Rapid Small-Scale Column Tests (RSSCTs)

While the conducted batch experiments provide insight to the adsorption of PFAAs on CDP granules, experiments conducted in PBF systems such as RSSCTs provide insight to the breakthrough behavior of PFAAs. When designing RSSCTs, an assumption is made regarding the transport behavior of the solute as a function of particle size; *i.e.*, either constant diffusivity (CD) or proportional diffusivity (PD) is assumed. Numerous studies evaluating adsorbents in RSSCTs use the assumption of CD because it provides a conservative estimate for exhausting an adsorbent compared to an RSSCT that is scaled using an assumption of PD. Studies exploring the relationship of CD and PD have found that both assumptions can be applicable for different GACs.¹⁶⁸⁻¹⁷¹

Furthermore, the scaling equations of CD and PD were initially developed using GAC as the adsorbent, so it is unclear whether the CDP granules used in this study can be appropriately scaled according to assumptions of CD or PD. To improve our understanding of breakthrough of PFAAs in a column packed with CDP granules, we performed RSSCTs packed with CDP granules from Bin 1, Bin 3, and Bin 5; a set of RSSCTs were scaled according to the assumption of CD, and another set of RSSCTs were scaled according to the assumption of PD. DI water spiked with PFAAs at a concentration of $1 \mu\text{g L}^{-1}$ was pumped through the packed columns and was operated over 500,000 bed volumes (BV). RSSCTs packed with CDP granules from Bin 1 and Bin 3 were scaled using an assumption of CD (RSSCT_{Bin 1-CD} and RSSCT_{Bin 3-CD}, respectively) and were designed to simulate a larger-scale PBF system operating with $d_p = 1000 \mu\text{m}$ and $EBCT = 2 \text{ min}$. RSSCTs packed with CDP granules from Bin 1, Bin 3, and Bin 5 were scaled using an assumption of PD (RSSCT_{Bin 1-PD}, RSSCT_{Bin 3-PD}, and RSSCT_{Bin 5-PD}, respectively) and were designed to simulate a larger-scale PBF system operating with $d_p = 1000 \mu\text{m}$ and $EBCT = 0.17 \text{ min}$. The RSSCT data are presented in **Figure 59**.

We found several notable observations in common from the RSSCTs. We note that instantaneous breakthrough was observed for a subset of the RSSCTs; we attribute this behavior to the low $EBCT$ attributed with these RSSCTs. The low $EBCT$ was essential to manage the volume of water required to complete the experiments, but resulted in RSSCTs that are outside the boundaries of the RSSCT paradigm and therefore cannot be used to simulate full-scale breakthrough. Regardless, several observations can still be made regarding the breakthrough curves of the RSSCTs. First, we observed that the order of breakthrough of the PFAAs from fastest to slowest is ordered from least to most hydrophobic (*i.e.*, PFBA > PFHxA > PFBS > PFOA > PFHxS > PFOS), which is agreement with other studies that use activated carbon in PBF systems.^{73,130,172} Second, PFBA exhibits a sharp breakthrough curve and achieves >100% breakthrough in several RSSCTs, such as in RSSCT_{Bin 5-PD} which approaches 150% breakthrough of PFBA after 500,000 BVs. Achieving breakthrough greater than 100% may be explained by the desorption of molecules of PFBA or the desorption of hemi-micelles of PFBA and other PFAAs that may have formed. Third, the sharp slope of the breakthrough curve of PFBA contrasts the gradual slope of the breakthrough curves of the other PFAAs. We hypothesize that adsorption may occur in two stages; first is the rapid uptake of PFBA, which is followed by the slower uptake of other PFAAs which may gradually displace the adsorbed molecules of PFBA or slowly form hemi-micelles and micelles on the surface of the CDP granules.⁷³

To evaluate the assumptions of constant diffusivity (CD) and proportional diffusivity (PD) used to scale the RSSCTs, the breakthrough curves can be compared between the RSSCTs that were performed using the scaling assumption of CD (**Figure 59A**) and the scaling assumption of PD (**Figure 59B**). If the correct scaling assumption has been used, the breakthrough curves of the RSSCTs should plot closely to one another.^{170,171} Based on the similarity between the breakthrough curves for PFBA in RSSCT_{Bin 1-CD} and RSSCT_{Bin 3-CD}, we find that designing RSSCTs scaled

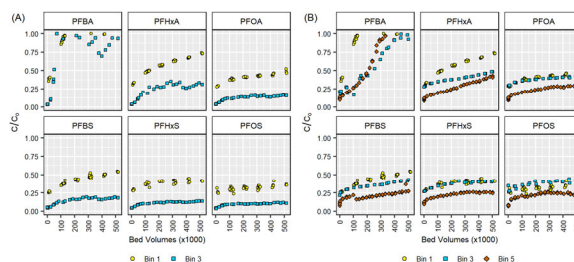


Figure 59. Breakthrough curves of the PFAAs using scaling equations that assume a scaling of (A) constant diffusivity and (B) proportional diffusivity. (A) is scaled from a model system with $d_p = 1000 \mu\text{m}$ and $EBCT = 2 \text{ min}$. (B) is scaled from a model system with $d_p = 1000 \mu\text{m}$ and $EBCT = 0.17 \text{ min}$. $[\text{PFAA}]_0 = 1 \mu\text{g L}^{-1}$ in deionized water.

according to the assumption of CD can be used to model the breakthrough of PFBA on CDP granules. A previous study has generalized that the assumption of CD is appropriate when external mass transfer controls the adsorption rate.¹³⁶ The scaling of CD may be the most appropriate scaling assumption for PFBA because electrostatic interactions via the positive surface charge on the CDPs is essential for the uptake of short-chain PFAAs.

PFOA, PFHxS, and PFOS, which are the most hydrophobic PFAAs in this study and exhibit the slowest breakthrough compared to the other PFAAs, are best scaled in RSSCTs using an assumption of PD. The scaling of PD is appropriate when internal diffusion is the rate limiting step;¹³⁶ PFOA, PFHxS, and PFOS are more likely to be rate-limited by internal diffusion due to the molecular size of these PFAAs. Based on the similarity between the breakthrough curves for PFOA and PFHxS in $\text{RSSCT}_{\text{Bin 1-PD}}$ and $\text{RSSCT}_{\text{Bin 3-PD}}$, we find that designing RSSCTs scaled according to the assumption of PD can be used to model the breakthrough of PFOA and PFHxS on smaller CDP granules. However, the breakthrough curve of PFOA and PFHxS are not well modeled by $\text{RSSCT}_{\text{Bin 5-PD}}$ when compared to the other RSSCTs scaled with PD; this behavior may be due to the differences in the needed minimum *EBCT* for PFOA and PFHxS, or that $\text{RSSCT}_{\text{Bin 5-PD}}$ generally exhibits rate-limited kinetics and may require a scaling a correction factor above a certain granule size. Interestingly, PFOS exhibits mixed behavior for the breakthrough curves for $\text{RSSCT}_{\text{Bin 1-PD}}$, $\text{RSSCT}_{\text{Bin 3-PD}}$, and $\text{RSSCT}_{\text{Bin 5-PD}}$, where the breakthrough curve of $\text{RSSCT}_{\text{Bin 1-PD}}$ is slower compared to the breakthrough curve of $\text{RSSCT}_{\text{Bin 3-PD}}$. This behavior may be attributed to the PFOS having the slowest diffusion onto the smallest CDP granules from Bin 1 compared to the other PFAAs, as demonstrated by our findings from the kinetics study (**Figure C4**); the scaling of PD for PFOS may require a correction factor below a certain granule size.

In contrast to the PFAAs discussed thus far that may be scaled using the assumption of CD or PD, the RSSCTs scaled using CD or PD are not applicable for PFHxA and PFBS. Although the breakthrough curves of PFHxA and PFBS for $\text{RSSCT}_{\text{Bin 1-PD}}$ and $\text{RSSCT}_{\text{Bin 3-PD}}$ initially exhibit the same breakthrough, the breakthrough curve of $\text{RSSCT}_{\text{Bin 3-PD}}$ gradually approaches the breakthrough curve of $\text{RSSCT}_{\text{Bin 5-PD}}$. PFHxA and PFBS are the next least hydrophobic PFAAs after PFBA and may not be rate limited exclusively by internal or external diffusion. Furthermore, it is possible that as more BVs are passed, $\text{RSSCT}_{\text{Bin 3-PD}}$ becomes increasingly rate-limited by internal diffusion. Additional effects of competition and hemi-micelles formation may further affect the adsorption of PFHxA and PFBS on CDP granules. Overall, these findings suggest that additional studies should be conducted to understand the diffusion mechanisms of each PFAA on CDP granules. Effects of competition and hemi-micelle formation of mixtures of PFAAs on CDP granules should also be taken into consideration so that we may better understand how to scale PBF systems for PFAAs and CDP granules.

4.9.5 Conclusions and Environmental Implications of the Study

This study provides a systematic approach to evaluating the effect of particle size on the adsorption of six PFAAs in batch and PFB systems (*i.e.*, RSSCTs). Novel CDP granules were generated using a high-shear spray granulation technique. The CDP granules were sieved to seven average particle sizes ($d_p = 84, 127, 175, 254, 359, 508, 718 \mu\text{m}$). The CDP granules were used in batch studies to evaluate adsorption kinetics, adsorption capacity, and adsorption affinity. The CDP granules were also evaluated in column studies to evaluate breakthrough of PFAAs. Smaller CDP granules exhibit a large range of adsorption kinetics whereas larger granules exhibit a narrower range of adsorption kinetics. Our findings suggest that smaller granules may have binding sites that are more readily available for smaller and less hydrophobic PFAAs, whereas larger granules exhibit some diffusion-limited kinetics for all PFAAs. CDP granules do not exhibit

differences in adsorption capacity as a function of particle size. CDP granules exhibit a capacity for 2-3 times more molecules of PFBA compared to the other PFAAs evaluated in this study, which suggests an additional adsorption mechanism that enhances the adsorption of PFBA. Compared to previously reported CDPs (powders), the CDP granules exhibit higher affinity for PFOA (24-50 L mg⁻¹). This is the first reporting of the affinity of CDP-based materials for PFBA, PFHxA, PFBS, PFHxS, and PFOS using fitted isotherms. The breakthrough of PFOA, PFHxS, and PFOS can be scaled using the assumption of proportional diffusivity for smaller granules, while the breakthrough curve for PFBA can be scaled using the assumption of constant diffusivity for smaller granules. Larger granules may exhibit diffusion limited kinetics that may require an alternate approach to simulate breakthrough.

5.0 CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH/IMPLEMENTATION

Work performed during ER18-1026 resulted in the synthesis of several notable CDP derivatives that exhibit enhanced uptake of PFASs^{30,67–69,71} and that were evaluated to explore adsorption kinetics, adsorption affinity, and adsorption inhibition under a variety of groundwater scenarios.^{54,61,62} Several CDPs discovered during ER18-1026 exhibit high adsorption affinity, high adsorption capacity, and rapid adsorption kinetics for environmentally relevant PFASs, which addresses *Objective 1* of the research project. Four CDPs (those presented in **Figure 36** through **Figure 39**) were further evaluated under scenarios relevant to groundwater remediation to inform further polymer development, elucidate adsorption mechanisms, and estimate parameters to be used for process design. These studies demonstrated that CDPs exhibit relatively rapid adsorption kinetics and high adsorption affinity (compared to activated carbon and ion exchange resins) in groundwater matrices, and that the adsorption performance of specific CDPs can be inhibited under certain conditions (*e.g.*, high pH). These data also allowed us to identify physicochemical properties of CDPs that enhance their affinity for perfluoroalkyl acids (*e.g.*, positive surface charge)⁶⁰ and develop new CDPs that leverage these properties in different ways. Together, these studies address *Objective 2* of the research project. Finally, we have scaled-up the synthesis of CDPs from the milligram to gram scale (as-synthesized in our academic research labs) to the kilogram scale and more through collaborations with Cyclopure, Inc. and other industrial partners. These efforts are intended to make CDPs commercially available for groundwater remediation applications. In parallel to these efforts, we have demonstrated morphological control of the adsorbent materials by developing a spray granulation technique which has led to morphologies that are compatible with packed-bed filtration systems, we have demonstrated mechanical and chemical durability by receiving NSF/ANSI 61 certification for CDP adsorbents, and we have demonstrated the potential for regeneration with a dilute alcohol solution and reuse without any loss in performance. Together, these activities address *Objective 3* of the research project.

5.1 Next-generation CDPs

The CDPs developed during ER18-1026 almost exclusively rely on nucleophilic aromatic substitution reactions between β -CD and an aromatic crosslinker to generate mesoporous polymers with high surface area. The structures of these CDPs were successfully tailored to have high affinity for a wide range of PFASs including short- and long-chain PFAAs and other PFASs with more complex chemical structures. However, several sub-optimal features of these first-generation CDPs have become increasingly apparent. First, relying on nucleophilic aromatic substitution reactions severely limits the number of chemical crosslinkers that can be selected for the synthesis. Considering the outsized importance of crosslinker chemistry to the performance of the resulting CDPs, it is now clear that these limited crosslinker options will ultimately limit the performance of CDPs as adsorbents. Furthermore, many electron-deficient aromatic crosslinkers are not commercially available at a reasonable cost or in sufficient amounts to support subsequent scale-up efforts. Second, nucleophilic aromatic substitution reactions occur randomly at the twenty-one reactive hydroxyl groups on a β -cyclodextrin,⁷¹ which gives rise to a huge range (more than 10^{13} distinct substitution patterns) of potential cyclodextrin binding environments within the CDP. We expect that these variable binding environments exhibit variable affinities for PFASs, but the nature of nucleophilic aromatic substitution polymerizations limits our ability to identify the most effective binding environments, or bias the polymerization to obtain materials enriched in those

effective binding environments. Third, nucleophilic aromatic substitution polymerizations are difficult to control, which means that the resulting CDPs do not have a uniform or easily tunable morphology or particle size. As a result, the uncontrolled particle size and shape of first-generation CDPs require additional processing steps (e.g., spray granulation) to form the uniform morphologies that are needed for packed-bed filtration systems. This additional processing step is a potential impediment for economical scale-up and widespread implementation.

The CDPs described in Section 4.1.4 of this report are synthesized by means of radical polymerization, which is the most versatile polymerization method used in industry. These so-called *next-generation CDPs* feature more uniformly distributed β -CD binding sites that can be co-polymerized with any of hundreds of available styrenic or acrylic comonomers. Next-generation CDPs are also synthesized with excellent yields and reliable permanent porosity, providing additional benefits for technical scale-up and implementation. Importantly, next-generation CDPs also significantly outperform first-generation CDPs for the removal of perfluoroalkyl acids (PFAAs) from water. For example, one of our next-generation CDPs achieved nearly 100% removal of eight PFAAs (including PFBA) at an adsorbent loading of 1 mg L^{-1} , which is ten times lower than adsorbent doses used with first-generation CDPs or other more conventional adsorbents. Radical polymerization methods are also more amenable to emulsion-based conditions, which would provide these high-performance adsorbents as uniform, spherical particles of tunable size and high mechanical strength and durability (as opposed to amorphous powders that require additional processing steps to form the uniform morphologies that are needed for packed-bed filtration systems). The discovery of next-generation CDPs marks another major advance for polymer adsorbents used for water purification, and future research will focus on polymers synthesized by means of radical polymerization.

5.2 Rapid small-scale column tests

The purpose of developing an emulsion polymerization technique is to directly generate next-generation CDPs with the appropriate morphology and durability to be used in packed-bed filtration processes. Rapid small-scale column tests (RSSCTs) are designed to simulate the breakthrough processes that occur in a full-scale system in a fraction of the time. RSSCT theory was developed for activated carbon and a number of studies have demonstrated the ways in which RSSCTs can be used to predict contaminant breakthrough in pilot- and full-scale systems.^{67–72} Designing RSSCTs requires some knowledge on the mechanisms that control adsorption kinetics of and adsorption affinity for a particular adsorbent, and how those mechanisms scale as a function of particle size. We describe efforts to characterize these phenomena using first-generation CDPs of varying sizes prepared by means of spray granulation in Section 4.9 of this report. Our findings so far suggest that RSSCTs can be used to simulate breakthrough in pilot- and full-scale systems, but a different set of scaling equations may be needed than those commonly used for activated carbon adsorbents.^{67,68} This is because the mechanisms by which PFASs are transported to binding sites on CDPs appears to shift as a function of particle size (when using particles generated by means of spray granulation), and because PFASs of varying chain length appear to bind to CDPs through different mechanisms (e.g., electrostatic versus hydrophobic) while exhibiting varying diffusion coefficients. All of these factors complicate our ability to design RSSCTs for CDPs (and other novel adsorbents) and motivate future studies to optimize RSSCT design.

5.3 Handling spent media

Another important consideration for all adsorbent-based remediation technologies is how to handle the spent media following breakthrough of the target contaminants. According to

international conventions, spent adsorbents that contain more than 50 mg kg⁻¹ of PFAS should be treated using a technique that will destroy the PFASs prior to disposal in a landfill,⁷³ although no established technologies are available to meet this criterion. Incineration is an option for activated carbon and ion exchange media, but data suggests that incineration of spent adsorbents may not completely destroy the bound PFAS and may result in transport and deposition of PFAS species downwind from the incinerator.⁷⁴ Another alternative is regeneration of spent media by means of thermal or electrochemical processes^{75,76} or with a solvent brine.⁷⁷ Regeneration with a solvent brine generates a new liquid waste stream with relatively high concentrations of PFASs that must likewise be treated prior to ultimate disposal; treatment technologies for PFAS-enriched solvent brines include plasma-based destruction⁷⁸, sonolysis,⁷⁹ activated persulfate,⁸⁰ electrolysis,¹⁴ and a variety of other physical and chemical destruction techniques.⁸¹⁻⁸³ In this report, we have demonstrated that first-generation CDP powders can be regenerated and reused following a rinse with a dilute alcohol solution.^{30,35} We also report facile regeneration and reuse of the first-generation CDP granules (prepared by means of spray granulation) with ethanol, methanol, and isopropanol. However, as is the case with other adsorbents, regeneration will produce a new liquid waste stream with relatively high concentrations of PFASs that must be treated prior to ultimate disposal. Future studies with CDPs and other novel adsorbents will focus on analyses of techniques to handle spent media (*i.e.*, loaded adsorbents or liquid waste streams) to eliminate PFAS from the environment.

6.0 LITERATURE CITED

- (1) Backe, W. J.; Day, T. C.; Field, J. A. Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from US Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, *47*, 5226–5234. <https://doi.org/10.1021/es3034999>.
- (2) Barzen-Hanson, K. A.; Field, J. A. Discovery and Implications of C-2 and C-3 Perfluoroalkyl Sulfonates in Aqueous Film-Forming Foams and Groundwater. *Environ. Sci. Technol. Lett.* **2015**, *2*, 95–99. <https://doi.org/10.1021/acs.estlett.5b00049>.
- (3) Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; Mccrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A. Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. *Environ. Sci. Technol.* **2017**, *51* (4), 2047–2057. <https://doi.org/10.1021/acs.est.6b05843>.
- (4) Place, B. J.; Field, J. A. Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military. *Environ. Sci. Technol.* **2012**, *46*, 7120–7127. <https://doi.org/10.1021/es301465n>.
- (5) Moody, C. A.; Field, J. A. Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity. *Environ. Sci. Technol.* **1999**, *33*, 2800–2806. <https://doi.org/10.1021/es981355+>.
- (6) Moe, M. K.; Huber, S.; Svenson, J.; Hagenaars, A.; Pabon, M.; Trumper, M.; Berger, U.; Knapen, D.; Herzke, D. The Structure of the Fire Fighting Foam Surfactant Forafac (R) 1157 and Its Biological and Photolytic Transformation Products. *Chemosphere* **2012**, *89*, 869–875. <https://doi.org/10.1016/j.chemosphere.2012.05.012>.
- (7) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environ. Sci. Technol.* **2013**, *47*, 8187–8195. <https://doi.org/10.1021/es4018877>.
- (8) Gorrochategui, E.; Perez-Albaladejo, E.; Casas, J.; Lacorte, S.; Porte, C. Perfluorinated Chemicals: Differential Toxicity, Inhibition of Aromatase Activity and Alteration of Cellular Lipids in Human Placental Cells. *Toxicol. Appl. Pharmacol.* **2014**, *277*, 124–130. <https://doi.org/10.1016/j.taap.2014.03.012>.
- (9) Ding, G.; Peijnenburg, W. J. G. M. Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 598–678. <https://doi.org/10.1080/10643389.2011.627016>.
- (10) U.S. Environmental Protection Agency Office of Water. *Drinking Water Health Advisories for PFOA and PFOS*; Washington DC, 2016.
- (11) Zhang, X.; Lohmann, R.; Dassuncao, C.; Hu, X. C.; Weber, A. K.; Vecitis, C. D.; Sunderland, E. M. Source Attribution of Poly- and Perfluoroalkyl Substances (PFASs) in Surface Waters from Rhode Island and the New York Metropolitan Area. *Environ. Sci. Technol. Lett.* **2016**, *3* (9), 316–321. <https://doi.org/10.1021/acs.estlett.6b00255>.
- (12) Schaefer, C. E.; Andaya, C.; Urtiaga, A.; McKenzie, E. R.; Higgins, C. P. Electrochemical Treatment of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonic Acid (PFOS) in Groundwater Impacted by Aqueous Film Forming Foams (AFFFs). *J. Hazard. Mater.* **2015**, *295*, 170–175. <https://doi.org/10.1016/j.jhazmat.2015.04.024>.
- (13) Qu, Y.; Zhang, C.; Li, F.; Chen, J.; Zhou, Q. Photo-Reductive Defluorination of Perfluorooctanoic Acid in Water. *Water Res.* **2010**, *44*, 2939–2947. <https://doi.org/10.1016/j.watres.2010.02.019>.

- (14) Butt, C. M.; Muir, D. C. G.; Mabury, S. A. Biotransformation Pathways of Fluorotelomer-Based Polyfluoroalkyl Substances: A Review. *Environ. Toxicol. Chem.* **2014**, *33*, 243–267. <https://doi.org/10.1002/etc.2407>.
- (15) Appleman, T. D.; Dickenson, E. R. V.; Bellona, C.; Higgins, C. P. Nanofiltration and Granular Activated Carbon Treatment of Perfluoroalkyl Acids. *J. Hazard. Mater.* **2013**, *260*, 740–746. <https://doi.org/10.1016/j.jhazmat.2013.06.033>.
- (16) Tang, C. Y.; Fu, Q. S.; Criddle, C. S.; Leckie, J. O. Effect of Flux (Transmembrane Pressure) and Membrane Properties on Fouling and Rejection of Reverse Osmosis and Nanofiltration Membranes Treating Perfluorooctane Sulfonate Containing Wastewater. *Environ. Sci. Technol.* **2007**, *41*, 2008–2014. <https://doi.org/10.1021/es062052f>.
- (17) Taylor, P. H.; Yamada, T.; Striebich, R. C.; Graham, J. L.; Giraud, R. J. Investigation of Waste Incineration of Fluorotelomer-Based Polymers as a Potential Source of PFOA in the Environment. *Chemosphere* **2014**, *110*, 17–22. <https://doi.org/10.1016/j.chemosphere.2014.02.037>.
- (18) Vecitis, C. D.; Wang, Y.; Cheng, J.; Park, H.; Mader, B. T.; Hoffmann, M. R. Sonochemical Degradation of Perfluorooctanesulfonate in Aqueous Film-Forming Foams. *Environ. Sci. Technol.* **2010**, *44*, 432–438. <https://doi.org/10.1021/es902444r>.
- (19) Merino, N.; Qu, Y.; Deeb, R. R. A.; Hawley, E. L.; Hoffmann, M. R. M. M. R. M.; Mahendra, S. Degradation and Removal Methods for Perfluoroalkyl and Polyfluoroalkyl Substances in Water. *Environ. Eng. Sci.* **2016**, *33* (9), 615–649. <https://doi.org/10.1089/ees.2016.0233>.
- (20) Trautmann, A. M.; Schell, H.; Schmidt, K. R.; Mangold, K.-M.; Tiehm, A. Electrochemical Degradation of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Groundwater. *Water Sci. Technol.* **2015**, *71*, 1569–1575. <https://doi.org/10.2166/wst.2015.143>.
- (21) Moreno-Castilla, C. Adsorption of Organic Molecules from Aqueous Solutions on Carbon Materials. *Carbon N. Y.* **2004**, *42*, 83–94. <https://doi.org/10.1016/j.carbon.2003.09.022>.
- (22) Yu, J.; Hu, J. Adsorption of Perfluorinated Compounds onto Activated Carbon and Activated Sludge. *J. Environ. Eng.* **2011**, *137*, 945–951. [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0000402](https://doi.org/10.1061/(ASCE)EE.1943-7870.0000402).
- (23) Senevirathna, S.; Tanaka, S.; Fujii, S.; Kunacheva, C.; Harada, H.; Shivakoti, B. R.; Okamoto, R. A Comparative Study of Adsorption of Perfluorooctane Sulfonate (PFOS) onto Granular Activated Carbon, Ion-Exchange Polymers and Non-Ion-Exchange Polymers. *Chemosphere* **2010**, *80*, 647–651.
- (24) Senevirathna, S. T. M. L. D.; Tanaka, S.; Fujii, S.; Kunacheva, C.; Harada, H.; Ariyadasa, B. H. A. K. T.; Shivakoti, B. R. Adsorption of Perfluorooctane Sulfonate (n-PFOS) onto Non Ion-Exchange Polymers and Granular Activated Carbon: Batch and Column Test. *Desalination* **2010**, *260*, 29–33. <https://doi.org/10.1016/j.desal.2010.05.005>.
- (25) Zhang, D.; Luo, Q.; Gao, B.; Chiang, S.-Y. D.; Woodward, D.; Huang, Q. Sorption of Perfluorooctanoic Acid, Perfluorooctane Sulfonate and Perfluoroheptanoic Acid on Granular Activated Carbon. *Chemosphere* **2016**, *144*, 2336–2342. <https://doi.org/10.1016/j.chemosphere.2015.10.124>.
- (26) Quinlivan, P. A.; Li, L.; Knappe, D. R. U. Effects of Activated Carbon Characteristics on the Simultaneous Adsorption of Aqueous Organic Micropollutants and Natural Organic Matter. *Water Res.* **2005**, *39*, 1663–1673. <https://doi.org/10.1016/j.watres.2005.01.029>.
- (27) San Miguel, G.; Lambert, S. D.; Graham, N. J. D. The Regeneration of Field-Spent Granular-Activated Carbons. *Water Res.* **2001**, *35*, 2740–2748.

- [https://doi.org/10.1016/S0043-1354\(00\)00549-2](https://doi.org/10.1016/S0043-1354(00)00549-2).
- (28) Ling, Y.; Klemes, M. J. M. J.; Xiao, L.; Alsbaiee, A.; Dichtel, W. R.; Helbling, D. E. Benchmarking Micropollutant Removal by Activated Carbon and Porous Beta-Cyclodextrin Polymers under Environmentally Relevant Scenarios. *Environ. Sci. Technol.* **2017**, *51* (13), 7590–7598. <https://doi.org/10.1021/acs.est.7b00906>.
 - (29) Alsbaiee, A.; Smith, B. J. B. J.; Xiao, L.; Ling, Y.; Helbling, D. E. D. E.; Dichtel, W. R. Rapid Removal of Organic Micropollutants from Water by a Porous Beta-Cyclodextrin Polymer. *Nature* **2016**, *529* (7585), 190–U146. <https://doi.org/10.1038/nature16185>.
 - (30) Xiao, L.; Ling, Y.; Alsbaiee, A.; Li, C.; Helbling, D. E.; Dichtel, W. R. Beta-Cyclodextrin Polymer Network Sequesters Perfluorooctanoic Acid at Environmentally Relevant Concentrations. *J. Am. Chem. Soc.* **2017**, *139* (23), 7689–7692. <https://doi.org/10.1021/jacs.7b02381>.
 - (31) Crini, G.; Bertini, S.; Torri, G.; Naggi, A.; Sforzini, D.; Vecchi, C.; Janus, L.; Lekchiri, Y.; Morcellet, M. Sorption of Aromatic Compounds in Water Using Insoluble Cyclodextrin Polymers. *J. Appl. Polym. Sci.* **1998**, *68*, 1973–1978. [https://doi.org/10.1002/\(SICI\)1097-4628\(19980620\)68:12<1973::AID-APP11>3.3.CO;2-R](https://doi.org/10.1002/(SICI)1097-4628(19980620)68:12<1973::AID-APP11>3.3.CO;2-R).
 - (32) Crini, G. Recent Developments in Polysaccharide-Based Materials Used as Adsorbents in Wastewater Treatment. *Prog. Polym. Sci.* **2005**, *30*, 38–70. <https://doi.org/10.1016/j.progpolymsci.2004.11.002>.
 - (33) Aoki, N.; Nishikawa, M.; Hattori, K. Synthesis of Chitosan Derivatives Bearing Cyclodextrin and Adsorption of P-Nonylphenol and Bisphenol A. *Carbohydr. Polym.* **2003**, *52*, 219–223. [https://doi.org/10.1016/S0144-8617\(02\)00308-9](https://doi.org/10.1016/S0144-8617(02)00308-9).
 - (34) Martel, B.; Morcellet, M.; Ruffin, D.; Ducoroy, L.; Weltrowski, M. Finishing of Polyester Fabrics with Cyclodextrins and Polycarboxylic Acids as Crosslinking Agents. *J. Incl. Phenom.* **2002**, *44*, 443–446. <https://doi.org/10.1023/A:1023080221850>.
 - (35) Zha, F.; Li, S.; Chang, Y. Preparation and Adsorption Property of Chitosan Beads Bearing Beta-Cyclodextrin Cross-Linked by 1,6-Hexamethylene Diisocyanate. *Carbohydr. Polym.* **2008**, *72*, 456–461. <https://doi.org/10.1016/j.carbpol.2007.09.013>.
 - (36) Morin-Crini, N.; Crini, G. Environmental Applications of Water-Insoluble β -Cyclodextrin–Epichlorohydrin Polymers. *Prog. Polym. Sci.* **2013**, *38* (2), 344–368. <https://doi.org/10.1016/j.progpolymsci.2012.06.005>.
 - (37) Toledo, I. B.; Ferro-Garcia, M. A.; Rivera-Utrilla, J.; Moreno-Castilla, C.; Fernandez, F. J. V. Bisphenol A Removal from Water by Activated Carbon. Effects of Carbon Characteristics and Solution Chemistry. *Environ. Sci. Technol.* **2005**, *39*, 6246–6250. <https://doi.org/10.1021/es0481169>.
 - (38) Cai, X.; Liu, Q.; Xia, C.; Shan, D.; Du, J.; Chen, J. Recyclable Capture and Destruction of Aqueous Micropollutants Using the Molecule-Specific Cavity of Cyclodextrin Polymer Coupled with KMnO₄ Oxidation. *Environ. Sci. Technol.* **2015**, *49* (15), 9264–9272. <https://doi.org/10.1021/acs.est.5b01734>.
 - (39) Mamba, B. B.; Krause, R. W.; Malefetse, T. J.; Sithole, S. P.; Nkambule, T. I. Humic Acid as a Model for Natural Organic Matter (NOM) in the Removal of Odorants from Water by Cyclodextrin Polyurethanes. *Water SA* **2009**, *35*, 117–120.
 - (40) Baumgartner, R.; Stieger, G. K.; McNeill, K. Complete Hydrodehalogenation of Polyfluorinated and Other Polyhalogenated Benzenes under Mild Catalytic Conditions. *Environ. Sci. Technol.* **2013**, *47* (12), 6545–6553. <https://doi.org/10.1021/es401183v>.
 - (41) Ho, Y. S.; McKay, G. Pseudo-Second Order Model for Sorption Processes. *Process*

- Biochem.* **1999**, *34*, 451–465. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5).
- (42) Yu, Q.; Zhang, R.; Deng, S.; Huang, J.; Yu, G. Sorption of Perfluorooctane Sulfonate and Perfluorooctanoate on Activated Carbons and Resin: Kinetic and Isotherm Study. *Water Res.* **2009**, *43*, 1150–1158. <https://doi.org/10.1016/j.watres.2008.12.001>.
 - (43) Yao, Y.; Volchek, K.; Brown, C. E.; Robinson, A.; Obal, T. Comparative Study on Adsorption of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) by Different Adsorbents in Water. *Water Sci. Technol.* **2014**, *70*, 1983–1991. <https://doi.org/10.2166/wst.2014.445>.
 - (44) Senevirathna, S. T. M. L. D.; Tanaka, S.; Fujii, S.; Kunacheva, C.; Harada, H.; Shivakoti, B. R.; Dinh, H.; Ariyadasa, T. Adsorption of Four Perfluorinated Acids on Non Ion Exchange Polymer Sorbents. *Water Sci. Technol.* **2011**, *63*, 2106–2113. <https://doi.org/10.2166/wst.2011.295>.
 - (45) Deng, S.; Nie, Y.; Du, Z.; Huang, Q.; Meng, P.; Wang, B.; Huang, J.; Yu, G. Enhanced Adsorption of Perfluorooctane Sulfonate and Perfluorooctanoate by Bamboo-Derived Granular Activated Carbon. *J. Hazard. Mater.* **2015**, *282*, 150–157. <https://doi.org/10.1016/j.jhazmat.2014.03.045>.
 - (46) Rattanaoudom, R.; Visvanathan, C. Removal of PFOA by Hybrid Membrane Filtration Using PAC and Hydrotalcite. *Desalin. Water Treat.* **2011**, *32*, 262–270. <https://doi.org/10.5004/dwt.2011.2709>.
 - (47) Qu, Y.; Zhang, C.; Li, F.; Bo, X.; Liu, G.; Zhou, Q. Equilibrium and Kinetics Study on the Adsorption of Perfluorooctanoic Acid from Aqueous Solution onto Powdered Activated Carbon. *J. Hazard. Mater.* **2009**, *169*, 146–152. <https://doi.org/10.1016/j.jhazmat.2009.03.063>.
 - (48) Du, Z.; Deng, S.; Bei, Y.; Huang, Q.; Wang, B.; Huang, J.; Yu, G. Adsorption Behavior and Mechanism of Perfluorinated Compounds on Various Adsorbents-A Review. *J. Hazard. Mater.* **2014**, *274*, 443–454. <https://doi.org/10.1016/j.jhazmat.2014.04.038>.
 - (49) Wang, B.; Lee, L. S.; Wei, C.; Fu, H.; Zheng, S.; Xu, Z.; Zhu, D. Covalent Triazine-Based Framework: A Promising Adsorbent for Removal of Perfluoroalkyl Acids from Aqueous Solution. *Environ. Pollut.* **2016**, *216*, 884–892. <https://doi.org/10.1016/j.envpol.2016.06.062>.
 - (50) Weiss-Erriico, M. J.; O'Shea, K. E. Detailed {NMR} Investigation of Cyclodextrin-Perfluorinated Surfactant Interactions in Aqueous Media. *J. Hazard. Mater.* **2017**, *329*, 57–65. <https://doi.org/http://dx.doi.org/10.1016/j.jhazmat.2017.01.017>.
 - (51) Karoyo, A. H.; Sidhu, P. S.; Wilson, L. D.; Hazendonk, P.; Borisov, A. Counterion Anchoring Effect on the Structure of the Solid-State Inclusion Complexes of Beta-Cyclodextrin and Sodium Perfluorooctanoate. *J. Phys. Chem. C* **2015**, *119*, 22225–22243. <https://doi.org/10.1021/acs.jpcc.5b07302>.
 - (52) Margot, J.; Kienle, C.; Magnet, A.; Weil, M.; Rossi, L.; de Alencastro, L. F.; Abegglen, C.; Thonney, D.; Chèvre, N.; Schärer, M.; et al. Treatment of Micropollutants in Municipal Wastewater: Ozone or Powdered Activated Carbon? *Sci. Total Environ.* **2013**, *461–462*, 480–498. <https://doi.org/10.1016/j.scitotenv.2013.05.034>.
 - (53) Alzate-Sanchez, D. M. D. M.; Smith, B. J.; Alsbaiee, A.; Hinstroza, J. P.; Dichtel, W. R. Cotton Fabric Functionalized with a Beta-Cyclodextrin Polymer Captures Organic Pollutants from Contaminated Air and Water. *Chem. Mater.* **2016**, *28* (22), 8340–8346. <https://doi.org/10.1021/acs.chemmater.6b03624>.
 - (54) Ching, C.; Klemes, M. J.; Trang, B.; Dichtel, W. R.; Helbling, D. E. Beta-Cyclodextrin

- Polymers with Different Cross-Linkers and Ion-Exchange Resins Exhibit Variable Adsorption of Anionic, Zwitterionic, and Nonionic PFASs. *Environ. Sci. Technol.* **2020**, *54* (19), 12693–12702. <https://doi.org/10.1021/acs.est.0c04028>.
- (55) Pochodylo, A. L. A. L.; Helbling, D. E. D. E. Emerging Investigators Series: Prioritization of Suspect Hits in a Sensitive Suspect Screening Workflow for Comprehensive Micropollutant Characterization in Environmental Samples. *Environ. Sci. Water Res. Technol.* **2017**, *3* (1), 54–65.
 - (56) Pochodylo, A. L.; Helbling, D. E. *Target Screening for Micropollutants in the Hudson River Estuary during the 2015 Recreational Season*; Prepared for New York State Department of Environmental Conservation's Hudson River Estuary Program, 2016.
 - (57) Wang, M.; Helbling, D. E. D. E. A Non-Target Approach to Identify Disinfection Byproducts of Structurally Similar Sulfonamide Antibiotics. *Water Res.* **2016**, *102*, 241–251. <https://doi.org/10.1016/j.watres.2016.06.042>.
 - (58) Backe, W. J.; Field, J. A. Is SPE Necessary for Environmental Analysis? A Quantitative Comparison of Matrix Effects from Large-Volume Injection and Solid-Phase Extraction Based Methods. *Environ. Sci. Technol.* **2012**, *46*, 6750–6758. <https://doi.org/10.1021/es300235z>.
 - (59) Rossner, A.; Snyder, S. A.; Knappe, D. R. U. Removal of Emerging Contaminants of Concern by Alternative Adsorbents. *Water Res.* **2009**, *43*, 3787–3796. <https://doi.org/10.1016/j.watres.2009.06.009>.
 - (60) Ching, C.; Ling, Y.; Trang, B.; Klemes, M.; Xiao, L.; Yang, A.; Barin, G.; Dichtel, W. R.; Helbling, D. E. Identifying the Physicochemical Properties of β -Cyclodextrin Polymers That Determine the Adsorption of Perfluoroalkyl Acids. *Water Res.* **2022**, *209*, 117938. <https://doi.org/10.1016/j.watres.2021.117938>.
 - (61) Wu, C.; Klemes, M. J.; Trang, B.; Dichtel, W. R.; Helbling, D. E. Exploring the Factors That Influence the Adsorption of Anionic PFAS on Conventional and Emerging Adsorbents in Aquatic Matrices. *Water Res.* **2020**, *182*, 115950. <https://doi.org/10.1016/j.watres.2020.115950>.
 - (62) Wang, R.; Ching, C.; Dichtel, W. R.; Helbling, D. E. Evaluating the Removal of Per- And Polyfluoroalkyl Substances from Contaminated Groundwater with Different Adsorbents Using a Suspect Screening Approach. *Environ. Sci. Technol. Lett.* **2020**, *7* (12), 954–960. <https://doi.org/10.1021/acs.estlett.0c00736>.
 - (63) Platts, J. A.; Butina, D.; Abraham, M. H.; Hersey, A. Estimation of Molecular Linear Free Energy Relation Descriptors Using a Group Contribution Approach. *J. Chemical Inf. Comput. Sci.* **1999**, *39*, 835–845. <https://doi.org/10.1021/ci980339t>.
 - (64) Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Taft, R. W. Linear Solvation Energy Relationships. An Analysis of the Factors That Influence Adsorption of Organic Compounds on Activated Carbon. *Carbon.* **1985**, *23*, 549–554. [https://doi.org/10.1016/0008-6223\(85\)90091-0](https://doi.org/10.1016/0008-6223(85)90091-0).
 - (65) Apul, O. G.; Wang, Q.; Shao, T.; Rieck, J. R.; Karanfil, T. Predictive Model Development for Adsorption of Aromatic Contaminants by Multi-Walled Carbon Nanotubes. *Environ. Sci. Technol.* **2013**, *47*, 2295–2303. <https://doi.org/10.1021/es3001689>.
 - (66) Xia, X.-R.; Monteiro-Riviere, N. A.; Riviere, J. E. An Index for Characterization of Nanomaterials in Biological Systems. *Nat. Nanotechnol.* **2010**, *5*, 671–675. <https://doi.org/10.1038/NNANO.2010.164>.
 - (67) Klemes, M. J. M. J.; Ling, Y.; Ching, C.; Wu, C.; Xiao, L.; Helbling, D. E.; Dichtel, W. R.

- Reduction of a Tetrafluoroterephthalonitrile- β -Cyclodextrin Polymer to Remove Anionic Micropollutants and Perfluorinated Alkyl Substances from Water. *Angew. Chemie - Int. Ed.* **2019**, 58 (35), 12049–12053. <https://doi.org/10.1002/anie.201905142>.
- (68) Xiao, L.; Ching, C.; Ling, Y.; Nasiri, M.; Klemes, M.; Reineke, T.; Helbling, D.; Dichtel, W. R. Crosslinker Chemistry Determines the Uptake Potential of Perfluorinated Alkyl Substances by β -Cyclodextrin Polymers. *Macromolecules* **2019**, 52 (10), 3747–3752. <https://doi.org/10.1021/acs.macromol.9b00417>.
- (69) Yang, A.; Ching, C.; Easler, M.; Helbling, D. E. D. E.; Dichtel, W. R. W. R. Cyclodextrin Polymers with Nitrogen-Containing Tripodal Crosslinkers for Efficient PFAS Adsorption. *ACS Mater. Lett.* **2020**, 2, 1240–1245. <https://doi.org/10.1021/acsmaterialslett.0c00240>.
- (70) Wang, R.; Lin, Z.-W.; Klemes, M.; Ateia, M.; Trang, B.; Helbling, D.; Dichtel, W. A Novel Tunable Porous β -Cyclodextrin Polymer Platform to Understand and Improve Anionic PFAS Removal. *ACS Cent. Sci.* **2022**.
- (71) Klemes, M. J.; Ling, Y.; Chiapasco, M.; Alsbaiee, A.; Helbling, D. E.; Dichtel, W. Phenolation of Cyclodextrin Polymers Controls Their Lead and Organic Micropollutant Adsorption. *Chem. Sci.* **2018**, 9, 8883–8889.
- (72) Morin-Crini, N.; Crini, G. Environmental Applications of Water-Insoluble β -Cyclodextrin–Epichlorohydrin Polymers. *Prog. Polym. Sci.* **2013**, 38 (2), 344–368. <https://doi.org/10.1016/j.progpolymsci.2012.06.005>.
- (73) McCleaf, P.; Englund, S.; Östlund, A.; Lindegren, K.; Wiberg, K.; Ahrens, L.; Ostlund, A.; Lindegren, K.; Wiberg, K.; Ahrens, L.; et al. Removal Efficiency of Multiple Poly- and Perfluoroalkyl Substances (PFASs) in Drinking Water Using Granular Activated Carbon (GAC) and Anion Exchange (AE) Column Tests. *Water Res.* **2017**, 120, 77–87. <https://doi.org/10.1016/j.watres.2017.04.057>.
- (74) Ateia, M.; Attia, M. F.; Maroli, A.; Tharayil, N.; Alexis, F.; Whitehead, D. C.; Karanfil, T. Rapid Removal of Poly- and Perfluorinated Alkyl Substances by Poly(Ethylenimine)-Functionalized Cellulose Microcrystals at Environmentally Relevant Conditions. *Environ. Sci. Technol. Lett.* **2018**, 5 (12), 764–769. <https://doi.org/10.1021/acs.estlett.8b00556>.
- (75) Mason, C. R.; Maynard-Atem, L.; Heard, K. W. J.; Satilmis, B.; Budd, P. M.; Friess, K.; Lanc, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C. Enhancement of CO₂ Affinity in a Polymer of Intrinsic Microporosity by Amine Modification. *Macromolecules* **2014**, 47 (3), 1021–1029. <https://doi.org/10.1021/ma401869p>.
- (76) Marik, J.; Song, A.; Lam, K. S. Detection of Primary Aromatic Amines on Solid Phase. *Tetrahedron Lett.* **2003**, 44 (23), 4319–4320. [https://doi.org/10.1016/S0040-4039\(03\)00984-5](https://doi.org/10.1016/S0040-4039(03)00984-5).
- (77) Vojkovsky, T. Detection of Secondary-Amines on Solid-Phase. *Pept. Res.* **1995**, 8 (4), 236–237.
- (78) Buckley, D.; Henbest, H. B.; Slade, P. Syntheses of Substituted Amino-Aminobutadienyl, Aminovinyl-Aminobutadienyl, and Aminobutadienyl-Para-Quinones. *J. Am. Chemcial Soc.* **1957**, No. DEC, 4891–4900. <https://doi.org/10.1039/jr9570004891>.
- (79) Ling, Y.; Klemes, M. J. M. J. M. J.; Steinschneider, S.; Dichtel, W. R.; Helbling, D. E. QSARs to Predict Adsorption Affinity of Organic Micropollutants for Activated Carbon and Beta-Cyclodextrin Polymer Adsorbents. *Water Res.* **2019**, 154, 217–226. <https://doi.org/10.1016/j.watres.2019.02.012>.
- (80) Li, C.; Klemes, M. J.; Dichtel, W. R.; Helbling, D. E. Tetrafluorotereplithalomtrile-Crosslinked Beta-Cyclodexfrin Polymers for Efficient Extraction and Recovery of Organic

- Micropollutants from Water. *J. Chromatogr. A* **2018**, *1541*, 52–56. <https://doi.org/10.1016/j.chroma.2018.02.012>.
- (81) Bonvin, F.; Jost, L.; Randin, L.; Bonvin, E.; Kohn, T. Super-Fine Powdered Activated Carbon (SPAC) for Efficient Removal of Micropollutants from Wastewater Treatment Plant Effluent. *Water Res.* **2016**, *90*, 90–99. <https://doi.org/10.1016/j.watres.2015.12.001>.
 - (82) Weiss-Errico, M. J.; O'Shea, K. E.; O'Shea, K. E. Enhanced Host–Guest Complexation of Short Chain Perfluoroalkyl Substances with Positively Charged β -Cyclodextrin Derivatives. *J. Incl. Phenom. Macrocycl. Chem.* **2019**, *95* (1–2), 111–117. <https://doi.org/10.1007/s10847-019-00930-w>.
 - (83) Ateia, M.; Alsbaiee, A.; Karanfil, T.; Dichtel, W. Efficient PFAS Removal by Amine-Functionalized Sorbents: Critical Review of the Current Literature. *Environ. Sci. Technol. Lett.* **2019**, *6* (12), 688–695. <https://doi.org/10.1021/acs.estlett.9b00659>.
 - (84) Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.; Dichtel, W. R. Removal of GenX and Perfluorinated Alkyl Substances from Water by Amine-Functionalized Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140* (40), 12677–12681.
 - (85) Rojas, M. T.; Kaifer, A. E.; Königer, R.; Stoddart, J. F. Supported Monolayers Containing Preformed Binding Sites. Synthesis and Interfacial Binding Properties of a Thiolated β -Cyclodextrin Derivative. *J. Am. Chem. Soc.* **1995**, *117* (1), 336–343. <https://doi.org/10.1021/ja00106a036>.
 - (86) Ateia, M.; Arifuzzaman, M.; Pellizzeri, S.; Attia, M. F.; Tharayil, N.; Anker, J. N.; Karanfil, T. Cationic Polymer for Selective Removal of GenX and Short-Chain PFAS from Surface Waters and Wastewaters at Ng/L Levels. *Water Res.* **2019**, *163*. <https://doi.org/10.1016/j.watres.2019.114874>.
 - (87) Munoz, G.; Duy, S. V.; Labadie, P.; Botta, F.; Budzinski, H. H.; Lestremieu, F. F. F. F.; Liu, J.; Sauve, S.; Vo, S.; Labadie, P.; et al. Analysis of Zwitterionic, Cationic, and Anionic Poly- and Perfluoroalkyl Surfactants in Sediments by Liquid Chromatography Polarity-Switching Electrospray Ionization Coupled to High Resolution Mass Spectrometry. *Talanta* **2016**, *152*, 447–456. <https://doi.org/10.1016/j.talanta.2016.02.021>.
 - (88) Gong, Y.; Wang, L.; Liu, J.; Tang, J.; Zhao, D. Removal of Aqueous Perfluorooctanoic Acid (PFOA) Using Starch-Stabilized Magnetite Nanoparticles. *Sci. Total Environ.* **2016**, *562*, 191–200. <https://doi.org/10.1016/j.scitotenv.2016.03.100>.
 - (89) Tang, C. Y.; Shiang Fu, Q.; Gao, D.; Criddle, C. S.; Leckie, J. O.; Fu, Q. S.; Gao, D.; Criddle, C. S.; Leckie, J. O. Effect of Solution Chemistry on the Adsorption of Perfluorooctane Sulfonate onto Mineral Surfaces. *Water Res.* **2010**, *44* (8), 2654–2662. <https://doi.org/10.1016/j.watres.2010.01.038>.
 - (90) Wang, F.; Shih, K. Adsorption of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) on Alumina: Influence of Solution PH and Cations. *Water Res.* **2011**, *45* (9), 2925–2930. <https://doi.org/10.1016/j.watres.2011.03.007>.
 - (91) Chen, H.; Zhang, C.; Yu, Y.; Han, J. Sorption of Perfluorooctane Sulfonate (PFOS) on Marine Sediments. *Mar. Pollut. Bull.* **2012**, *64* (5), 902–906. <https://doi.org/10.1016/j.marpolbul.2012.03.012>.
 - (92) Gagliano, E.; Sgroi, M.; Falciglia, P. P.; Vagliasindi, F. G. A. A.; Roccaro, P. Removal of Poly- and Perfluoroalkyl Substances (PFAS) from Water by Adsorption: Role of PFAS Chain Length, Effect of Organic Matter and Challenges in Adsorbent Regeneration. *Water Res.* **2020**, *171*, 115381. <https://doi.org/10.1016/j.watres.2019.115381>.

- (93) Zaggia, A.; Conte, L.; Falletti, L.; Fant, M.; Chiorboli, A. Use of Strong Anion Exchange Resins for the Removal of Perfluoroalkylated Substances from Contaminated Drinking Water in Batch and Continuous Pilot Plants. *Water Res.* **2016**, *91*, 137–146. <https://doi.org/10.1016/j.watres.2015.12.039>.
- (94) Cote, A. P.; Benin, A.; Ockwig, N. W.; Keeffe, M. O.; Matzger, A. J.; Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. *Science (80-.)*. **2005**, *310*, 1166–1171.
- (95) Deblase, C. R.; Dichtel, W. R. Moving Beyond Boron: The Emergence of New Linkage Chemistries in Covalent Organic Frameworks. *Macromolecules* **2016**, *49*, 5297–5305. <https://doi.org/10.1021/acs.macromol.6b00891>.
- (96) Huang, N.; Wang, P.; Jiang, D. Covalent Organic Frameworks: A Materials Platform for Structural and Functional Designs. *Nat. Rev.* **2016**, *1*, 1–19. <https://doi.org/10.1038/natrevmats.2016.68>.
- (97) Bisbey, R. P.; Dichtel, W. R. Covalent Organic Frameworks as a Platform for Multidimensional Polymerization. *ACS Cent. Sci.* **2017**, *3*, 533–543. <https://doi.org/10.1021/acscentsci.7b00127>.
- (98) Huang, N.; Krishna, R.; Jiang, D. Tailor-Made Pore Surface Engineering in Covalent Organic Frameworks: Systematic Functionalization for Performance Screening. *J. Am. Chem. Soc.* **2015**, *137* (22), 7079–7082. <https://doi.org/10.1021/jacs.5b04300>.
- (99) Sun, Q.; Aguila, B.; Earl, L. D.; Abney, C. W.; Wojtas, L.; Thallapally, P. K.; Ma, S. Covalent Organic Frameworks as a Decorating Platform for Utilization and Affinity Enhancement of Chelating Sites for Radionuclide Sequestration. *Adv. Mater.* **2018**, *30* (20). <https://doi.org/10.1002/adma.201705479>.
- (100) Sun, Q.; Aguila, B.; Perman, J.; Earl, L. D.; Abney, C. W.; Cheng, Y.; Wei, H.; Nguyen, N.; Wojtas, L.; Ma, S. Postsynthetically Modified Covalent Organic Frameworks for Efficient and Effective Mercury Removal. *J. Am. Chem. Soc.* **2017**, *139* (7), 2786–2793. <https://doi.org/10.1021/jacs.6b12885>.
- (101) Furukawa, H.; Yaghi, O. M. Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am. Chem. Soc.* **2009**, *131* (25), 8875–8883. <https://doi.org/10.1021/ja9015765>.
- (102) Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard III, W. A. Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials. *J. Am. Chem. Soc.* **2008**, *130* (35), 11580+. <https://doi.org/10.1021/ja803247y>.
- (103) Doonan, C. J.; Tranchemontagne, D. J.; Glover, T. G.; Hunt, J. R.; Yaghi, O. M. Exceptional Ammonia Uptake by a Covalent Organic Framework. *Nat. Chem.* **2010**, *2* (3), 235–238. <https://doi.org/10.1038/NCHEM.548>.
- (104) Huang, N.; Chen, X.; Krishna, R.; Jiang, D. Two-Dimensional Covalent Organic Frameworks for Carbon Dioxide Capture through Channel-Wall Functionalization. *Angew. Chemie - Int. Ed.* **2015**, *54* (10), 2986–2990. <https://doi.org/10.1002/anie.201411262>.
- (105) Ding, S.-Y.; Dong, M.; Wang, Y.-W.; Chen, Y.-T.; Wang, H.-Z.; Su, C.-Y.; Wang, W. Thioether-Based Fluorescent Covalent Organic Framework for Selective Detection and Facile Removal of Mercury(II). *J. Am. Chem. Soc.* **2016**, *138* (9), 3031–3037. <https://doi.org/10.1021/jacs.5b10754>.
- (106) Lee, M. T.; Ferguson, G. S. Stepwise Synthesis of a Well-Defined Silicon (Oxide)/Polyimide Interface. *Langmuir* **2001**, *17* (3), 762–767. <https://doi.org/10.1021/la000865q>.
- (107) Guerin, D.; Lenfant, S.; Godey, S.; Vuillaume, D. Synthesis and Electrical Properties of

- Fullerene-Based Molecular Junctions on Silicon Substrate. *J. Mater. Chem.* **2010**, *20* (13), 2680–2690. <https://doi.org/10.1039/b924255d>.
- (108) Punyapalakul, P.; Suksomboon, K.; Prarat, P.; Khaodhiar, S. Effects of Surface Functional Groups and Porous Structures on Adsorption and Recovery of Perfluorinated Compounds by Inorganic Porous Silicas. *Sep. Sci. Technol.* **2013**, *48* (5), 775–788. <https://doi.org/10.1080/01496395.2012.710888>.
- (109) Wang, W.; Maimaiti, A.; Shi, H.; Wu, R.; Wang, R.; Li, Z.; Qi, D.; Yu, G.; Deng, S. Adsorption Behavior and Mechanism of Emerging Perfluoro-2-Propoxypropanoic Acid (GenX) on Activated Carbons and Resins. *Chem. Eng. J.* **2019**, *364*, 132–138. <https://doi.org/10.1016/j.cej.2019.01.153>.
- (110) Zhao, D.; Cheng, J.; Vecitis, C. D.; Hoffmann, M. R. Sorption of Perfluorochemicals to Granular Activated Carbon in the Presence of Ultrasound. *J. Phys. Chem. A* **2011**, *115* (11), 2250–2257. <https://doi.org/10.1021/jp111784k>.
- (111) Hansen, M. C.; Borresen, M. H.; Schlabach, M.; Cornelissen, G. Sorption of Perfluorinated Compounds from Contaminated Water to Activated Carbon. *J. Soils Sediments* **2010**, *10* (2), 179–185. <https://doi.org/10.1007/s11368-009-0172-z>.
- (112) Partlan, E.; Davis, K.; Ren, Y.; Apul, O. G.; Mefford, O. T.; Karanfil, T.; Ladner, D. A. Effect of Bead Milling on Chemical and Physical Characteristics of Activated Carbons Pulverized to Superfine Sizes. *Water Res.* **2016**, *89*, 161–170. <https://doi.org/10.1016/j.watres.2015.11.041>.
- (113) Ando, N.; Matsui, Y.; Kurotobi, R.; Nakano, Y.; Matsushita, T.; Ohno, K. Comparison of Natural Organic Matter Adsorption Capacities of Super-Powdered Activated Carbon and Powdered Activated Carbon. *Water Res.* **2010**, *44* (14), 4127–4136. <https://doi.org/10.1016/j.watres.2010.05.029>.
- (114) Karoyo, A. H.; Borisov, A. S.; Wilson, L. D.; Hazendonk, P. Formation of Host-Guest Complexes of Beta-Cyclodextrin and Perfluorooctanoic Acid. *J. Phys. Chem. B* **2011**, *115* (31), 9511–9527. <https://doi.org/10.1021/jp110806k>.
- (115) Tang, P.; Sun, Q.; Zhao, L.; Tang, Y.; Liu, Y.; Pu, H.; Gan, N.; Liu, Y.; Li, H. A Simple and Green Method to Construct Cyclodextrin Polymer for the Effective and Simultaneous Estrogen Pollutant and Metal Removal. *Chem. Eng. J.* **2019**, *366*, 598–607. <https://doi.org/10.1016/j.cej.2019.02.117>.
- (116) Weiss-Errico, M. J.; Ghiviriga, I.; O'Shea, K. E. F-19 NMR Characterization of the Encapsulation of Emerging Perfluoroethoxycarboxylic Acids by Cyclodextrins. *J. Phys. Chem. B* **2017**, *121* (35), 8359–8366. <https://doi.org/10.1021/acs.jpcc.7b05901>.
- (117) Zhang, X.; Niu, H.; Pan, Y.; Shi, Y.; Cai, Y. Modifying the Surface of Fe₃O₄/SiO₂ Magnetic Nanoparticles with C-18/NH₂ Mixed Group to Get an Efficient Sorbent for Anionic Organic Pollutants. *J. Colloid Interface Sci.* **2011**, *362* (1), 107–112. <https://doi.org/10.1016/j.jcis.2011.06.032>.
- (118) Nassi, M.; Sarti, E.; Pasti, L.; Martucci, A.; Marchetti, N.; Cavazzini, A.; Di Renzo, F.; Galarneau, A. Removal of Perfluorooctanoic Acid from Water by Adsorption on High Surface Area Mesoporous Materials. *J. Porous Mater.* **2014**, *21* (4), 423–432. <https://doi.org/10.1007/s10934-014-9788-5>.
- (119) Piai, L.; Dykstra, J. E.; Adishakti, M. G.; Blokland, M.; Langenhoff, A. A. M.; van der Wal, A. Diffusion of Hydrophilic Organic Micropollutants in Granular Activated Carbon with Different Pore Sizes. *Water Res.* **2019**, *162*, 518–527. <https://doi.org/10.1016/j.watres.2019.06.012>.

- (120) Murray, C. C.; Vatankeh, H.; McDonough, C. A.; Nickerson, A.; Hedtke, T. T.; Cath, T. Y.; Higgins, C. P.; Bellona, C. L. Removal of Per- and Polyfluoroalkyl Substances Using Super-Fine Powder Activated Carbon and Ceramic Membrane Filtration. *J. Hazard. Mater.* **2019**, *366*, 160–168. <https://doi.org/10.1016/j.jhazmat.2018.11.050>.
- (121) Ahrens, L.; Taniyasu, S.; Yeung, L. W. Y.; Yamashita, N.; Lam, P. K. S.; Ebinghaus, R. Distribution of Polyfluoroalkyl Compounds in Water, Suspended Particulate Matter and Sediment from Tokyo Bay, Japan. *Chemosphere* **2010**, *79* (3), 266–272. <https://doi.org/10.1016/j.chemosphere.2010.01.045>.
- (122) Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P. Impact of Treatment Processes on the Removal of Perfluoroalkyl Acids from the Drinking Water Production Chain. *Environ. Sci. & Technol.* **2012**, *46* (3), 1708–1715. <https://doi.org/10.1021/es201662b>.
- (123) Inyang, M.; Dickenson, E. R. V. The Use of Carbon Adsorbents for the Removal of Perfluoroalkyl Acids from Potable Reuse Systems. *Chemosphere* **2017**, *184*, 168–175. <https://doi.org/10.1016/j.chemosphere.2017.05.161>.
- (124) Xiao, X.; Ulrich, B. A.; Chen, B.; Higgins, C. P. Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon. *Environ. Sci. Technol.* **2017**, *51* (11), 6342–6351. <https://doi.org/10.1021/acs.est.7b00970>.
- (125) Deng, S.; Zhang, Q.; Nie, Y.; Wei, H.; Wang, B.; Huang, J.; Yu, G.; Xing, B. Sorption Mechanisms of Perfluorinated Compounds on Carbon Nanotubes. *Environ. Pollut.* **2012**, *168*, 138–144. <https://doi.org/10.1016/j.envpol.2012.03.048>.
- (126) Higgins, C. P.; Luthy, R. G. Sorption of Perfluorinated Surfactants on Sediments. *Environ. Sci. Technol.* **2006**, *40* (23), 7251–7256. <https://doi.org/10.1021/es061000n>.
- (127) Kwadijk, C. J. A. F.; Velzeboer, I.; Koelmans, A. A. Sorption of Perfluorooctane Sulfonate to Carbon Nanotubes in Aquatic Sediments. *Chemosphere* **2013**, *90* (5), 1631–1636. <https://doi.org/10.1016/j.chemosphere.2012.08.041>.
- (128) Jeon, J.; Kannan, K.; Lim, B. J.; An, K. G.; Kim, S. D. Effects of Salinity and Organic Matter on the Partitioning of Perfluoroalkyl Acid (PFAs) to Clay Particles. *J. Environ. Monit.* **2011**, *13* (6), 1803–1810. <https://doi.org/10.1039/c0em00791a>.
- (129) Ling, Y.; Alzate-Sánchez, D.; Klemes, M. J.; Dichtel, W. R.; Helbling, D. E. Evaluating the Effects of Water Matrix Constituents on Micropollutant Removal by Activated Carbon and β -Cyclodextrin Polymer Adsorbents. *Water Res.* **2020**, *173*. <https://doi.org/10.1016/j.watres.2020.115551>.
- (130) Appleman, T. D.; Higgins, C. P.; Quinones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-Holady, J. C.; Dickenson, E. R. V. Treatment of Poly- and Perfluoroalkyl Substances in US Full-Scale Water Treatment Systems. *Water Res.* **2014**, *51*, 246–255. <https://doi.org/10.1016/j.watres.2013.10.067>.
- (131) Klemes, M. J. M. J. M. J.; Ling, Y.; Ching, C.; Wu, C.; Xiao, L.; Helbling, D. E.; Dichtel, W. R. Reduction of a Tetrafluoroterephthalonitrile- β -Cyclodextrin Polymer to Remove Anionic Micropollutants and Perfluorinated Alkyl Substances from Water. *Angew. Chemie - Int. Ed.* **2019**, *58* (35), 12049–12053. <https://doi.org/10.1002/anie.201905142>.
- (132) Schaefer, C. E.; Nguyen, D.; Ho, P.; Im, J.; LeBlanc, A. Assessing Rapid Small-Scale Column Tests for Treatment of Perfluoroalkyl Acids by Anion Exchange Resin. *Ind. Eng. Chem. Res.* **2019**, *58* (22), 9701–9706. <https://doi.org/10.1021/acs.iecr.9b00858>.
- (133) Gremmel, C.; Froemel, T.; Knepper, T. P. HPLC-MS/MS Methods for the Determination

- of 52 Perfluoroalkyl and Polyfluoroalkyl Substances in Aqueous Samples. *Anal. Bioanal. Chem.* **2017**, *409* (6), 1643–1655. <https://doi.org/10.1007/s00216-016-0110-z>.
- (134) Schaefer, C. E.; Culina, V.; Nguyen, D.; Field, J. Uptake of Poly- and Perfluoroalkyl Substances at the Air Water Interface. *Environ. Sci. Technol.* **2019**, *53* (21), 12442–12448. <https://doi.org/10.1021/acs.est.9b04008>.
- (135) Zhou, Q.; Deng, S.; Zhang, Q.; Fan, Q.; Huang, J.; Yu, G. Sorption of Perfluorooctane Sulfonate and Perfluorooctanoate on Activated Sludge. *Chemosphere* **2010**, *81* (4), 453–458. <https://doi.org/10.1016/j.chemosphere.2010.08.009>.
- (136) Park, M.; Wu, S.; Lopez, I. J.; Chang, J. Y.; Karanfil, T.; Snyder, S. A. Adsorption of Perfluoroalkyl Substances (PFAS) in Groundwater by Granular Activated Carbons: Roles of Hydrophobicity of PFAS and Carbon Characteristics. *Water Res.* **2020**, *170*, 115364. <https://doi.org/10.1016/j.watres.2019.115364>.
- (137) Luehrs, D. C.; Hickey, J. P.; Nilsen, P. E.; Godbole, K. A.; Rogers, T. N. Linear Solvation Energy Relationship of the Limiting Partition Coefficient of Organic Solutes between Water and Activated Carbon. *Environ. Sci. Technol.* **1996**, *30* (1), 143–152. <https://doi.org/10.1021/es950200o>.
- (138) Munoz, G.; Ray, P.; Mejia-Avendano, S.; Duy, S. V.; Do, D. T.; Liu, J.; Sauve, S. Optimization of Extraction Methods for Comprehensive Profiling of Perfluoroalkyl and Polyfluoroalkyl Substances in Firefighting Foam Impacted Soils. *Anal. Chim. Acta* **2018**, *1034*, 74–84. <https://doi.org/10.1016/j.aca.2018.06.046>.
- (139) Mejia-Avendano, S.; Munoz, G.; Sauve, S.; Liu, J. Assessment of the Influence of Soil Characteristics and Hydrocarbon Fuel Cocontamination on the Solvent Extraction of Perfluoroalkyl and Polyfluoroalkyl Substances. *Anal. Chem.* **2017**, *89* (4), 2539–2546. <https://doi.org/10.1021/acs.analchem.6b04746>.
- (140) Barzen-Hanson, K. A.; Davis, S. E.; Kleber, M.; Field, J. A. Sorption of Fluorotelomer Sulfonates, Fluorotelomer Sulfonamido Betaines, and a Fluorotelomer Sulfonamido Amine in National Foam Aqueous Film-Forming Foam to Soil. *Environ. Sci. Technol.* **2017**. <https://doi.org/10.1021/acs.est.7b03452>.
- (141) Nickerson, A.; Maizel, A. C.; Kulkarni, P. R.; Adamson, D. T.; Kornuc, J. J.; Higgins, C. P. Enhanced Extraction of AFFF-Associated PFASs from Source Zone Soils. *Environ. Sci. Technol.* **2020**, *54* (8), 4952–4962. <https://doi.org/10.1021/acs.est.0c00792>.
- (142) Maimaiti, A.; Deng, S.; Meng, P.; Wang, W.; Wang, B.; Huang, J.; Wang, Y.; Yu, G. Competitive Adsorption of Perfluoroalkyl Substances on Anion Exchange Resins in Simulated AFFF-Impacted Groundwater. *Chem. Eng. J.* **2018**, *348*, 494–502. <https://doi.org/10.1016/j.cej.2018.05.006>.
- (143) Deng, S.; Yu, Q.; Huang, J.; Yu, G. Removal of Perfluorooctane Sulfonate from Wastewater by Anion Exchange Resins: Effects of Resin Properties and Solution Chemistry. *Water Res.* **2010**, *44* (18), 5188–5195. <https://doi.org/10.1016/j.watres.2010.06.038>.
- (144) Ahrens, L.; Harner, T.; Shoeib, M.; Lane, D. A.; Murphy, J. G. Improved Characterization of Gas-Particle Partitioning for Per- and Polyfluoroalkyl Substances in the Atmosphere Using Annular Diffusion Denuder Samplers. *Environ. Sci. Technol.* **2012**, *46* (13), 7199–7206. <https://doi.org/10.1021/es300898s>.
- (145) Zhi, Y.; Liu, J. Sorption and Desorption of Anionic, Cationic and Zwitterionic Polyfluoroalkyl Substances by Soil Organic Matter and Pyrogenic Carbonaceous Materials. *Chem. Eng. J.* **2018**, *346*, 682–691. <https://doi.org/10.1016/j.cej.2018.04.042>.
- (146) Wang, W.; Mi, X.; Zhou, Z.; Zhou, S.; Li, C.; Hu, X.; Qi, D.; Deng, S. Novel Insights into

- the Competitive Adsorption Behavior and Mechanism of Per- and Polyfluoroalkyl Substances on the Anion-Exchange Resin. *J. Colloid Interface Sci.* **2019**, *557*, 655–663. <https://doi.org/10.1016/j.jcis.2019.09.066>.
- (147) Gao, Y.; Deng, S.; Du, Z.; Liu, K.; Yu, G. Adsorptive Removal of Emerging Polyfluoroalkyl Substances F-53B and PFOS by Anion-Exchange Resin: A Comparative Study. *J. Hazard. Mater.* **2017**, *323* (A, SI), 550–557. <https://doi.org/10.1016/j.jhazmat.2016.04.069>.
- (148) Kothawala, D. N.; Kohler, S. J.; Ostlund, A.; Wiberg, K.; Ahrens, L. Influence of Dissolved Organic Matter Concentration and Composition on the Removal Efficiency of Perfluoroalkyl Substances (PFASs) during Drinking Water Treatment. *Water Res.* **2017**, *121*, 320–328. <https://doi.org/10.1016/j.watres.2017.05.047>.
- (149) Du, Z.; Deng, S.; Chen, Y.; Wang, B.; Huang, J.; Wang, Y.; Yu, G. Removal of Perfluorinated Carboxylates from Washing Wastewater of Perfluorooctanesulfonyl Fluoride Using Activated Carbons and Resins. *J. Hazard. Mater.* **2015**, *286*, 136–143. <https://doi.org/10.1016/j.jhazmat.2014.12.037>.
- (150) Du, Z.; Deng, S.; Zhang, S.; Wang, B.; Huang, J.; Wang, Y.; Yu, G.; Xing, B. Selective and High Sorption of Perfluorooctanesulfonate and Perfluorooctanoate by Fluorinated Alkyl Chain Modified Montmorillonite. *J. Phys. Chem. C* **2016**, *120* (30), 16782–16790. <https://doi.org/10.1021/acs.jpcc.6b04757>.
- (151) McGuire, M. E.; Schaefer, C.; Richards, T.; Backe, W. J.; Field, J. A.; Houtz, E.; Sedlak, D. L.; Guelfo, J. L.; Wunsch, A.; Higgins, C. P. Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area. *Environ. Sci. Technol.* **2014**, *48*, 6644–6652.
- (152) Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environ. Sci. Technol.* **2017**, *51* (5), 2508–2518. <https://doi.org/10.1021/acs.est.6b04806>.
- (153) D'Agostino, L. A.; Mabury, S. A. Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates. *Environ. Sci. Technol.* **2014**, *48* (1), 121–129. <https://doi.org/10.1021/es403729e>.
- (154) Liu, Y.; Pereira, A. D. S.; Martin, J. W. Discovery of C-5-C-17 Poly- and Perfluoroalkyl Substances in Water by In-Line SPE-HPLC-Orbitrap with In-Source Fragmentation Flagging. *Anal. Chem.* **2015**, *87* (8), 4260–4268. <https://doi.org/10.1021/acs.analchem.5b00039>.
- (155) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and Fate of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Drinking Water Treatment: A Review. *Water Res.* **2014**, *50*, 318–340. <https://doi.org/10.1016/j.watres.2013.10.045>.
- (156) Patterson, C.; Burkhardt, J.; Schupp, D.; Krishnan, E. R.; Dymont, S.; Merritt, S.; Zintek, L.; Kleinmaier, D. Effectiveness of Point-of-Use/Point-of-Entry Systems to Remove per- and Polyfluoroalkyl Substances from Drinking Water. *AWWA Water Sci.* **2019**, *1* (2), 1–12. <https://doi.org/10.1002/aws2.1131>.
- (157) Park, M.; Daniels, K. D.; Wu, S.; Ziska, A. D.; Snyder, S. A. Magnetic Ion-Exchange (MIEX) Resin for Perfluorinated Alkylsubstance (PFAS) Removal in Groundwater: Roles of Atomic Charges for Adsorption. *Water Res.* **2020**, *181*. <https://doi.org/10.1016/j.watres.2020.115897>.
- (158) Ellis, D. A.; Denkenberger, K. A.; Burrow, T. E.; Mabury, S. A. The Use of F-19 NMR to Interpret the Structural Properties of Perfluorocarboxylate Acids: A Possible Correlation with Their Environmental Disposition. *J. Phys. Chem. A* **2004**, *108* (46), 10099–10106.

- <https://doi.org/10.1021/jp049372a>.
- (159) Knochenhauer, G.; Reiche, J.; Brehmer, L.; Barberka, T.; Woolley, M.; Tredgold, R.; Hodge, P. Do Perfluorinated Chains Always Have to Be Twisted. *J. Chem. Soc. - Chem. Commun.* **1995**, No. 16, 1619–1620. <https://doi.org/10.1039/c39950001619>.
 - (160) Krafft, M. P.; Riess, J. G. Chemistry, Physical Chemistry, and Uses of Molecular Fluorocarbon-Hydrocarbon Diblocks, Triblocks, and Related Compounds-Unique ``Apblar{''} Components for Self-Assembled Colloid and Interface Engineering. *Chem. Rev.* **2009**, *109* (5), 1714–1792. <https://doi.org/10.1021/cr800260k>.
 - (161) Sun, M.; Arevalo, E.; Strynar, M.; Lindstrom, A.; Richardson, M.; Kearns, B.; Pickett, A.; Smith, C.; Knappe, D. Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina. *Enviromental Sci. Technol. Lett.* **2016**, *3*, 415–419. <https://doi.org/10.1021/acs.estlett.6b00398>.
 - (162) Klemes, M. J. M. J.; Skala, L. P. L. P.; Ateia, M.; Trang, B.; Helbling, D. E. D. E.; Dichtel, W. R. W. R. Polymerized Molecular Receptors as Adsorbents to Remove Micropollutants from Water. *Acc. Chem. Res.* **2020**, *53* (10), 2314–2324. <https://doi.org/10.1021/acs.accounts.0c00426>.
 - (163) Zhang, D. Q.; Zhang, W. L.; Liang, Y. N. Adsorption of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) from Aqueous Solution - A Review. *Sci. Total Environ.* **2019**, *694*. <https://doi.org/10.1016/j.scitotenv.2019.133606>.
 - (164) Campos-Pereira, H.; Kleja, D. B.; Sjostedt, C.; Ahrens, L.; Klysubun, W.; Gustafsson, J. P.; Sjöstedt, C.; Ahrens, L.; Klysubun, W.; Gustafsson, J. P.; et al. The Adsorption of Per- and Polyfluoroalkyl Substances (PFASs) onto Ferrihydrite Is Governed by Surface Charge. *Environ. Sci. & Technol.* **2020**, *54* (24), 15722–15730. <https://doi.org/10.1021/acs.est.0c01646>.
 - (165) Wang, Z.; Zhang, P.; Hu, F.; Zhao, Y.; Zhu, L. A Crosslinked Beta-Cyclodextrin Polymer Used for Rapid Removal of a Broad-Spectrum of Organic Micropollutants from Water. *Carbohydr. Polym.* **2017**, *177*, 224–231. <https://doi.org/10.1016/j.carbpol.2017.08.059>.
 - (166) Alzate-Sanchez, D. M.; Ling, Y.; Li, C.; Frank, B. P.; Bleher, R.; Fairbrother, H.; Helbling, D. E.; Dichtel, W. R.; Alzate-Sánchez, D. M.; Ling, Y.; et al. β -Cyclodextrin Polymers on Microcrystalline Cellulose as a Granular Media for Organic Micropollutant Removal from Water. *ACS Appl. Mater. Interfaces* **2019**, *11* (8), 8089–8096. <https://doi.org/10.1021/acsami.8b22100>.
 - (167) Vu, C. T.; Wu, T. Adsorption of Short-Chain Perfluoroalkyl Acids (PFAAs) from Water/Wastewater. *Environ. Sci. Water Res. Technol.* **2020**, No. 11. <https://doi.org/10.1039/d0ew00468e>.
 - (168) Kennedy, A. M.; Reinert, A. M.; Knappe, D. R.; Scott Summers, R.; Carolina, N. Prediction of Full-Scale GAC Adsorption of Organic Micropollutants. *Environ. Eng. Sci.* **2017**, *34*, 496–507. <https://doi.org/10.1089/ees.2016.0525>.
 - (169) Knappe, D. R. U.; Snoeyink, V. L.; Roche, P.; Prados, M. J.; Bourbigot, M. M. The Effect of Preloading on Rapid Small-Scale Column Test Predictions of Atrazine Removal by GAC Adsorbents. *Water Res.* **1997**, *31* (11), 2899–2909. [https://doi.org/10.1016/S0043-1354\(97\)00148-6](https://doi.org/10.1016/S0043-1354(97)00148-6).
 - (170) Crittenden, J. C.; Berrigan, J. K.; Hand, D. W. Design of Rapid Small-Scale Adsorption Tests for a Constant Diffusivity. *Water Pollut. Control Fed.* **1986**, *58* (4), 312–319.
 - (171) Crittenden, J. C.; Berrigan, J. K.; Hand, D. W.; Lykins, B. Design of Rapid Fixed-Bed

- Adsorption Tests for Nonconstant Diffusivities. *J. Environ. Eng.* **1987**, *113* (2), 243–259. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1987\)113:2\(243\)](https://doi.org/10.1061/(ASCE)0733-9372(1987)113:2(243)).
- (172) Rodowa, A. E.; Knappe, D. R. U.; Chiang, S.-Y. D.; Pohlmann, D.; Varley, C.; Bodour, A.; Field, J. A. Pilot Scale Removal of Per- and Polyfluoroalkyl Substances and Precursors from AFFF-Impacted Groundwater by Granular Activated Carbon. *Environ. Sci. Res. Technol.* **2020**, *6* (4), 1083–1094. <https://doi.org/10.1039/c9ew00936a>.

APPENDICES

APPENDIX A – List of Scientific/Technical Publications

Ji, W., L. Xiao, Y. Ling, C. Ching, M. Matsumoto, R.P. Bisbey, D.E. Helbling, and W.R. Dichtel. 2018. Removal of GenX and perfluorinated alkyl substances from water by amine-functionalized covalent organic frameworks. *Journal of the American Chemical Society*, 140(40):12677–12681.

Xiao, L., C. Ching, Y. Ling, M. Nasiri, M.J. Klemes, T.M. Reineke, D.E. Helbling, and W.R. Dichtel. 2019. Crosslinker chemistry determines the uptake potential of perfluorinated alkyl substances by β -cyclodextrin polymers. *Macromolecules*, 52(10): 3747-3752.

Klemes, M.J., Y. Ling, C. Ching, C. Wu, L. Xiao, D.E. Helbling, and W.R. Dichtel. 2019. Reduction of a tetrafluoroterephthalonitrile- β -cyclodextrin polymer to remove anionic micropollutants and perfluorinated alkyl substances from water. *Angewandte Chemie*, 58, 12049-12053.

Wu, C., M.J. Klemes, B. Trang, W.R. Dichtel, and D.E. Helbling. 2020. Exploring the factors that influence the adsorption of anionic PFAS on conventional and emerging adsorbents in aquatic matrices. *Water Research*, 182, 115950.

Yang, A., C. Ching, M. Easler, D.E. Helbling, and W.R. Dichtel. 2020. Cyclodextrin polymers with nitrogen-containing tripodal crosslinkers for efficient PFAS adsorption. *ACS Materials Letters*, 2, 1240–1245.

Klemes, M.J., L. Skala, M. Ateia, B. Trang, D.E. Helbling, and W.R. Dichtel. 2020. Polymerized molecular receptors as adsorbents to remove micropollutants from water. *Accounts of Chemical Research*, 53(10): 2314–2324.

Ching, C., M.J. Klemes, B. Trang, W.R. Dichtel, and D.E. Helbling. 2020. β -cyclodextrin polymers with different crosslinkers and ion exchange resins exhibit variable adsorption of anionic, zwitterionic, and nonionic PFASs. *Environmental Science & Technology*, 54(19): 12693–12702.

Ateia, M., D.E. Helbling, and W.R. Dichtel. 2020. Best practices for evaluating new materials as adsorbents for water treatment. *ACS Materials Letters*, 2(11): 1532–1544.

Wang, R., C. Ching, W.R. Dichtel, and D.E. Helbling. 2020. Evaluating the removal of per- and polyfluoroalkyl substances from contaminated groundwater with different adsorbents using a suspect screening approach. *Environmental Science & Technology Letters*, 7(12): 954–960.

Ching, C., Y. Ling, B. Trang, M. Klemes, L. Xiao, A. Yang, G. Barin, W.R. Dichtel, and D.E. Helbling. 2022. Identifying the physicochemical properties of β -cyclodextrin polymers that determine the adsorption of perfluoroalkyl acids. *Water Research*, 209, 117938.

Wang, R., Lin, Z.W., Klemes, M.J., Ateia, M., Trang, B., Wang, J., Ching, C., Helbling, D.E., Dichtel, W.R. 2022. A tunable porous β -cyclodextrin polymer platform to understand and improve anionic PFAS removal. *ACS Central Science*, Just accepted.

Ching, C., Dichtel, W.R., Helbling, D.E. 2022. Evaluating the performance of novel cyclodextrin polymer granules to remove PFASs from water in batch systems and rapid small-scale column tests. In preparation.

Oanta, A., Wang, J., Helbling, D.E., Dichtel, W.R. 2022. Removal of anionic and zwitterionic PFAS from water by functionalized covalent organic frameworks. In preparation.