

A Tunable Porous β -Cyclodextrin Polymer Platform to Understand and Improve Anionic PFAS Removal

Ri Wang,[§] Zhi-Wei Lin,[§] Max J. Klemes,[§] Mohamed Ateia, Brittany Trang, Jieyuan Wang, Casey Ching, Damian E. Helbling,* and William R. Dichtel*



Cite This: <https://doi.org/10.1021/acscentsci.2c00478>



Read Online

ACCESS |



Metrics & More

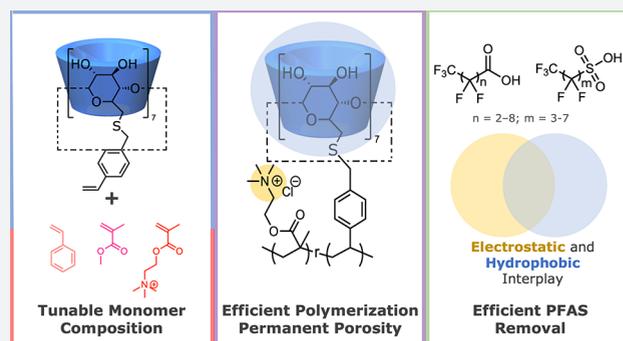


Article Recommendations



Supporting Information

ABSTRACT: Cross-linked polymers containing β -cyclodextrin (β -CD) are promising adsorbents with demonstrated removal performances for per- and polyfluoroalkyl substances (PFASs) from contaminated water sources. Despite the promising performance of some β -CD-based adsorbents for PFAS removal, many of these materials are not amenable for rational performance improvement or addressing fundamental questions about the PFAS adsorption mechanisms. These ambiguities arise from the poorly defined structure of the cross-linked polymers, especially with respect to the random substitution patterns of the cyclodextrins as well as side reactions that modify the structures of some cross-linkers. Here, we report a new β -CD polymer platform in which styrene groups are covalently attached to β -CD to form a discrete monomer that is amenable to radical polymerization. This monomer was polymerized with styrene and methacrylate comonomers to provide three β -CD polymers with high specific surface areas and high isolated yields (all >93%). A β -CD polymer copolymerized with a methacrylate bearing a cationic functional group achieved nearly 100% removal for eight anionic PFASs (initial concentration of 1 μ g/L for each compound) in nanopure water at an exceedingly low adsorbent loading of 1 mg L⁻¹, as compared to previous cyclodextrin polymers that required loadings at least 1 order of magnitude higher to achieve an equivalent degree of PFAS removal. Furthermore, when the adsorbents were studied in a challenging salt matrix, we observed that long-chain PFAS adsorption was controlled by a complementary interplay of hydrophobic and electrostatic interactions, whereas short-chain PFASs primarily relied on electrostatic interactions. This approach demonstrates great promise for anionic PFAS removal, and we anticipate that new compositions will be tailored using the versatility of radical polymerization to simultaneously target PFASs and other classes of micropollutants in the future.



INTRODUCTION

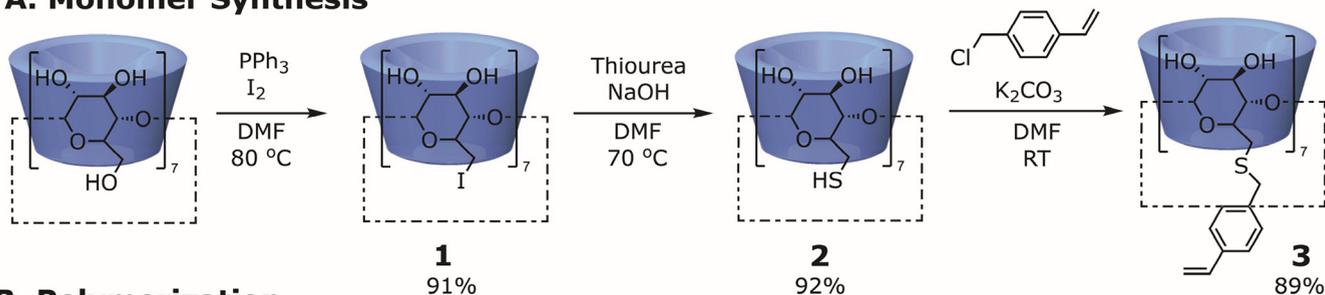
Per- and polyfluoroalkyl substances (PFASs) are fluorinated surfactants¹⁻⁴ applied in industrial processes⁵⁻⁷ (e.g., pesticide formulations, waterproofing textiles, and oil production) and consumer products^{8,9} such as cosmetics, firefighting foams, and food packaging. Their manufacture and use have contaminated water resources around the world, and their bioaccumulative nature, toxicity at low levels of chronic exposure, and environmental persistence motivate efforts to prevent and remediate PFAS contamination.^{4,10-12} Anionic perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFASAs) are the most widely detected classes of anionic PFASs, whose structures include long-chain derivatives, such as the eight-carbon perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), and short-chain derivatives, such as the four-carbon perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS). The short-chain PFASs are now also widespread, more mobile in the environment, and more resistant to degradation or removal efforts than long-chain

PFASs.³ Conventional adsorbents, such as activated carbons (ACs),¹³⁻¹⁵ ion exchange resins,^{15,16} and inorganic minerals,¹⁷⁻¹⁹ have been widely studied and applied for PFAS removal. However, these adsorbents generally suffer from shortcomings, such as a moderate or low affinity for long- and short-chain PFASs and fouling by dissolved natural organic matters and inorganic constituents found in natural and engineered water systems.²⁰⁻²³ These shortcomings have motivated the development of novel adsorbents, such as cyclodextrin polymers,²⁴⁻²⁶ chitosan beads,^{27,28} metal organic frameworks,²⁹ and magnetite nanoparticles.^{30,31}

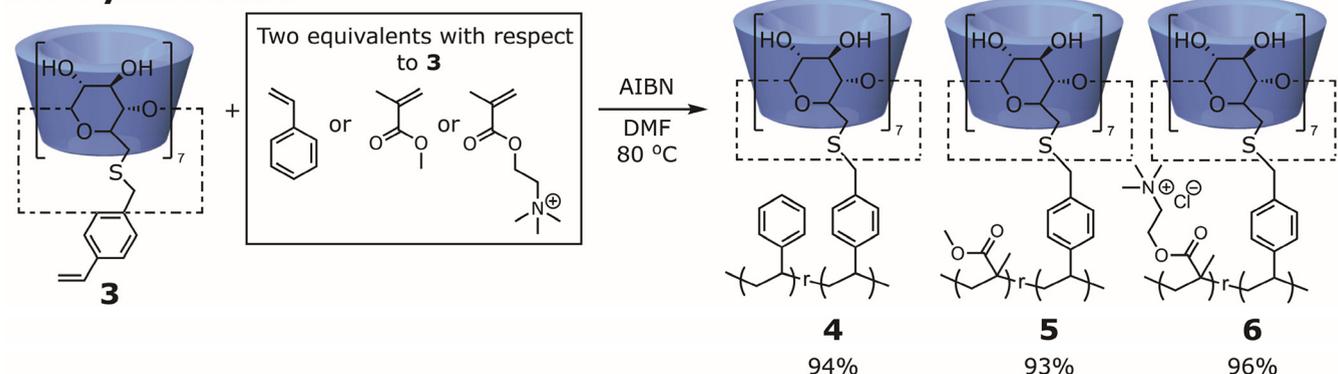
Received: April 21, 2022

Scheme 1. Synthetic Scheme of Styrene-Functionalized Cyclodextrin Monomer and Polymers

A. Monomer Synthesis



B. Polymerization



Cross-linked β -cyclodextrin (β -CD) polymers are promising adsorbents for PFAS removal.^{24,32–37} β -CDs are commercially available, cyclic oligosaccharides consisting of seven glucose subunits. β -CDs have hollow inner hydrophobic cavities capable of forming host–guest complexes with many organic compounds.^{34,38,39} Cross-linked β -CD adsorbents exhibited rapid adsorption kinetics, high adsorption affinity and selectivity for target PFASs, and the potential for facile regeneration and reuse. In particular, β -CD adsorbents that also contain cationic functional groups have demonstrated the most efficient removal of anionic PFASs, including efficacy for removing short-chain PFASs.^{34–36} We developed several β -CD adsorbents derived from nucleophilic aromatic substitution reactions between unmodified β -CD and electron-deficient aromatic cross-linkers, such as tetrafluoroterephthalonitrile-cross-linked β -CD polymers (TFN-CDPs).^{26,32} TFN-CDPs efficiently remove many cationic and uncharged micropollutants from water, and postpolymerization reduction of the nitrile groups to cationic primary amines reversed its selectivity to effectively remove anionic PFASs from water at environmentally relevant concentrations.^{26,40}

Despite their promising performance, β -CD polymers based on TFN or other electron-deficient aromatic cross-linkers are limited in their ability to be rationally improved or further modified. The random nature of cross-linking at the twenty-one hydroxyl groups of each cyclodextrin, as well as further complexity introduced by side reactions, other nucleophiles added to the polymerization, or postsynthetic modifications, gives rise to a nearly limitless number of pollutant binding environments.^{26,37} Furthermore, there are relatively few alternatives to TFN that are compatible with nucleophilic aromatic substitution reactions used for polymerization. Here, we report a structurally well-defined and tunable approach to access many porous β -CD polymers. One of the polymers offers a superior PFAS removal performance as well as insight

into the interactions that drive short- and long-chain PFAS removal that were difficult to elucidate in prior β -CD polymers.

Our approach involves copolymerizing a styrene-functionalized β -CD derivative with various styrenic or methacrylic comonomers to give permanently porous, cross-linked molecules with a more uniform β -CD binding environment and easily tunable compositions of hydrophobic or charged comonomers. The first polymers based on these design principles were evaluated for their ability to bind seven PFCAs and four PFASs of different chain lengths and in different water matrices to elucidate the relative importance of the β -CD interactions, conventionally thought to be hydrophobic, and electrostatic interactions between anionic PFASs and cations embedded in one of the polymer networks. We showed that a β -CD adsorbent containing a cationic functional group exhibits exceptional removal of PFASs with a different chain length from nanopure water at an exceedingly low adsorbent loading of 1 mg L⁻¹ which is at least an order of magnitude lower than required for the previous generation of materials to achieve an equivalent performance. The changes in removal efficiency for both long- and short-chain PFASs as a function of salt concentration provided insight into the combined roles of charge and β -CD binding sites for PFAS adsorption. These studies establish the styrene-functionalized β -CD monomer as a highly promising building block for β -CD adsorbents and for elucidating the contribution of different structural features on PFAS removal.

RESULTS AND DISCUSSION

Styrene groups were installed at each of the seven 6' positions of β -CD, effectively replacing primary alcohol groups (C-6) using an approach adapted from that of Rojas and co-workers.⁴¹ First, the primary alcohols were selectively converted to iodides, yielding **1** (Scheme 1A), which were subsequently converted to thiols using thiourea, yielding **2**.^{41,42} The enhanced nucleophilicity and acidity of the thiols relative

Table 1. Characterization of the Adsorbents

adsorbent	comonomer charge	ζ potential (mV)	average particle diameter (μm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	isolated yield (%)	comonomer incorporation ratio (comonomer:3)
4	neutral	-8.2 ± 0.6	149	402	94	1.8
5	neutral	-9.9 ± 0.9	118	392	93	1.2
6	cationic	$+23.8 \pm 1.6$	162	237	96	2.0

to the remaining hydroxyl groups of β -CD enabled their selective benzylation in the presence of K_2CO_3 and 4-vinylbenzyl chloride, yielding **3**. This sequence was carried out with an isolated yield of 75% over three steps (23 g) with no chromatography required to purify any of 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.⁴¹ The integration 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 (Figure S1). ^{13}C 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 (Figure S2). 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 (see the Supporting Information).

The styrene groups of **3** are potentially compatible with hundreds of commercially available vinyl comonomers and radical polymerization methods. This versatility will be advantageous in targeting a broad scope of micropollutants in the future.^{24,43} For this first study, we polymerized **3** using azobis(isobutyronitrile) (AIBN) as a free radical initiator to prepare three polymers based on **3**: a styrene copolymer **4**, a methyl methacrylate copolymer **5**, and a cationic methacrylate copolymer **6**. Polymers **4–6** 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 cross-linked polymers were subjected to continuous liquid/solid extraction in methanol for approximately 14 h. Following extraction, the polymers were activated by supercritical CO_2 washing and isolated in high yields at multigram scales (Scheme 1B). Notably, the isolated yields of these polymerizations (93–96%) were significantly higher than those of TFN-based β -CD adsorbents, which we attribute to the high efficiency of radical polymerizations of styrene and methacrylic monomers relative to those based on aromatic substitution chemistries.²⁶

Polymers **4–6** formed porous and cross-linked networks with permanent surface charge. Solid-state cross-polarization magic angle spinning ^{13}C NMR spectroscopy confirmed the incorporation of comonomers in **4–6** (Figures S4–S6). In all three spectra, the resonance corresponding to the vinyl carbons of **3** (113 ppm) was not detected, suggesting a high degree of polymerization of the styrene groups. The polymer backbone was formed from the vinyl carbons, as evident from 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 and 2.0 comonomers per β -CD. A feed ratio of 2 equiv of comonomers with respect to **3** was determined to be most promising based on preliminary PFAS binding studies (Figure S14) and was used in subsequent polymerizations. The comonomer incorporation ratios of **4** and **6** were calculated to be 1.8 and 2.0, respectively, which were consistent with the feed ratio. However, the ratio of **5** was 1.2, indicating that methyl methacrylate was not incorporated as readily. The porosity and Brunauer–Emmett–Teller surface area (S_{BET}) of polymers **4–6** were characterized by N_2 porosimetry. Each polymer exhibited permanent porosity and high S_{BET} , ranging from 237 to 402 $\text{m}^2 \text{g}^{-1}$, which is higher than those of previous β -CD adsorbents (Figures S11–S13).^{25,26,33} Lastly, the ζ potentials of suspensions of **4** and **5** were found to be weakly negative whereas that of **6** was strongly positive (Table 1).⁴⁴ IR spectroscopy of the polymers was consistent with their expected structures (Figures S7–S10). These data confirmed the porous and cross-linked nature of the polymers, which were then used to remove PFASs from water.

We first evaluated the removal performances of polymers **4–6** at an adsorbent loading of 10 mg L^{-1} for 4–10-carbon PFASs (initial concentration of 1 $\mu\text{g L}^{-1}$ for each compound) in a nanopure (NP) water matrix and in a 1 mM Na_2SO_4 (SS) matrix (Figure 1). The high salt concentration of the SS matrix was chosen to probe the relative importance of hydrophobic 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 PFASs. The ability of **6** to remove the four-carbon PFBA and five-carbon PFPeA (>99% removal) was notable because these short-chain PFASs are not removed as effectively by ACs and other emerging adsorbents. As an external performance benchmark to a leading ion-exchange resin, Purofine PFA694E anion exchange resin removed 46% of PFBA and 54% of PFOA under identical conditions.³⁵ We attribute the promising performance of **6** to its permanent positively charged ammonium groups that interact favorably with anionic PFASs, as has been shown for other designed adsorbents based on β -CD and other materials.^{45–47} The adsorption kinetics of **6** for 4–10-carbon PFASs (initial concentration of 1 $\mu\text{g L}^{-1}$) at an adsorbent loading of 10 mg L^{-1} in NP matrix was studied (Figure S17A). The time required for reaching adsorption equilibrium was less than 4 h for all PFASs. Notably, the adsorption kinetics of **6** is faster than that of previous β -CD adsorbents (24 h for PFOA) previously reported under the same experimental conditions.^{26,36} For the rest of the removal experiments, a 48 h contact time was used to ensure that equilibrium binding had been reached.

PFCA removal experiments conducted using adsorbents **4–6** in a 1 mM SS matrix indicated that PFASs of different chain lengths interacted with the adsorbents and matrix through different noncovalent interactions. Generally speaking, hydro-

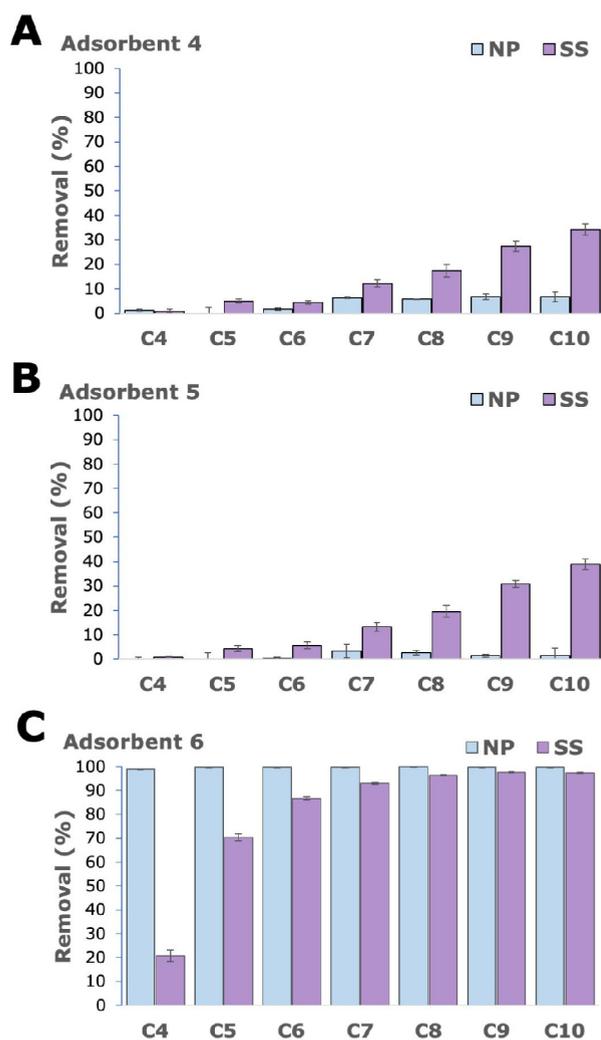


Figure 1. Removal of $1 \mu\text{g L}^{-1}$ PFCAs by 10 mg L^{-1} (A) 4, (B) 5, and (C) 6 in nanopure water (NP, blue bar) and $1 \text{ mM Na}_2\text{SO}_4$ (SS, purple bar) after 48 h of contact time. The *x*-axis denotes PFCAs of different chain lengths. For example, C4 refers to PFBA.

phobic adsorbents 4 and 5 showed enhanced, yet still modest, PFCA removal in SS matrix as compared to NP matrix (Figure 1A,B). In contrast, adsorbent 6 showed inhibited, yet still relatively high, PFCA removal in the SS matrix as compared to the NP matrix (Figure 1C). Inhibition was most pronounced

for PFBA and PFPeA, the shortest-chain PFCAs 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 either direct-site competition, in which inorganic anions compete with anionic PFCAs for adsorption sites, or the increased screening effect that attenuates electrostatic interactions at increased electrolyte concentrations.^{17,19,31} Notably, the removal of 6–10-carbon PFCAs was less inhibited in the SS matrix than that of shorter-chain derivatives. The removal of six-carbon PFHxA decreased from 99% to 87%, and the removal of 8–10-carbon PFCAs was nearly unaffected. The decreased sensitivity of longer-chain PFCAs to ionic strength suggests that hydrophobic interactions between the perfluoroalkyl tails, 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 hydrophobic interactions increase in energy at higher ionic strength as PFCA and electrostatic interactions are attenuated. On the other hand, the performance of adsorbents 4 and 5 was significantly enhanced for most PFCAs, except four-carbon PFBA, with longer-chain PFCAs experiencing a 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 screening effect that reduces the repulsion between negatively charged surfaces of 4 or 5 and the anionic PFCAs.^{17,19,31} Additionally, this enhancement may also result from a salting out effect, in which the presence of inorganic ions decreased the solubility of organic molecules and increased hydrophobic interactions for adsorbents 4 and 5 and long-chain PFCAs.^{1,48,49}

To better investigate the magnitude of inhibitory or enhancement effects for the same concentration of PFCA in NP and SS matrices, adsorbent 6 loading was adjusted from 10 to 1 mg L^{-1} (Figure 2A), and the loadings of adsorbents 4 and 5 were adjusted from 10 to 100 mg L^{-1} (Figure S15). In a separate study, a mixture of 4-, 6-, 7-, and 8-carbon PFSA was also added in both matrices with an initial concentration of $1 \mu\text{g L}^{-1}$ (Figure 2B). 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 PFCAs. The removal percentages of four-carbon PFBA and

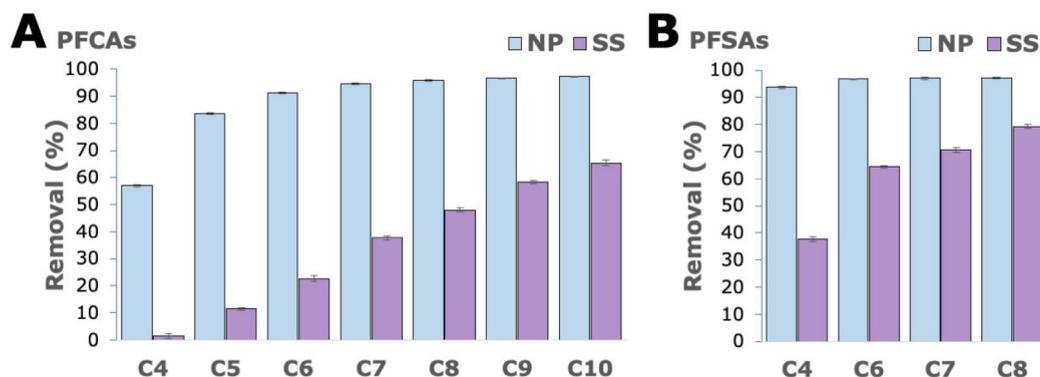


Figure 2. Removal of $1 \mu\text{g L}^{-1}$ PFCAs and PFSA by 1 mg L^{-1} 6 in nanopure water (NP, blue bar) and $1 \text{ mM Na}_2\text{SO}_4$ (SS, purple bar) after 48 h of contact time. The *x*-axis denotes PFAs of different chain lengths. For example, C4 refers to PFBA for (A) and PFBS for (B).

five-carbon PFPeA were 57% and 84%, respectively, which are unsurprisingly lower than their removal percentages at 10 mg L⁻¹ adsorbent loading. However, this performance is still promising because of the difficulty of short-chain PFCA removal.³ Exceptional removal was also observed for PFSA (Figure 2B), which were each removed to a greater extent than their PFCA counterparts with the same number of carbons. 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 those of PFCA on β -CD polymers and other adsorbents.^{15,16,33,36} We attribute this difference to PFSA being more hydrophobic than PFCA, due to PFSA having one more fluorinated carbon atom than PFCA with the same carbon number. The more effective removal of PFASs (relative to 4 and 5) by 6 once again highlights the importance of the cationic feature for anionic PFAS removal. To our knowledge, 1 mg L⁻¹ is the lowest β -CD adsorbent loading 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 PFCA and PFSA is apparent at a lower adsorbent 6 loading in SS matrix, with decreased removal performance as a function of decreasing fluoroalkyl chain length for both PFCA and PFSA. The removal of shorter-chain PFCA and PFSA experienced significantly greater removal interference from inorganic ions than that of longer-chain analogues. The removal of four-carbon PFBA decreased from 57% to 1%, and that of five-carbon PFPeA decreased from 84% to 12%. The virtually complete inhibition of adsorbent 6 implies that the removal of shorter-chain PFCA relies heavily on electrostatic interactions. Four-carbon and five-carbon PFSA removals were less inhibited, with removals decreasing from 94% to 38% and from 97% to 64%, respectively. The removal percentages of longer-chain PFCA 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 -CD cavities. Assuming that electrostatic attraction is rendered ineffective in the SS matrix, such as the case of four-carbon PFBA, hydrophobic interactions become the primary interactions 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 a complementary nature of electrostatic and hydrophobic interactions.

Monovalent and divalent inorganic ions were evaluated to further explore the importance of observed adsorption inhibition. We selected salts and concentrations of 1 mM Na₂SO₄ (SS), 2 mM NaCl (SC), and 1 mM CaCl₂ (CC) in order to generate comparable data with 2 mM monovalent sodium or chloride ions and 1 mM divalent sulfate or calcium ions (Figure 3). The adsorbent 6 loading remained as 1 mg L⁻¹ with 1 μ g L⁻¹ PFCA mixture. No significant differences ($p \geq 0.05$) were found when comparing the removal of PFCA by adsorbent 6 in the 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 percentages of 5–10-carbon PFCA were significantly ($p < 0.05$) more inhibited in the divalent SS matrix than in the monovalent SC matrix. Additionally, the type of anion may

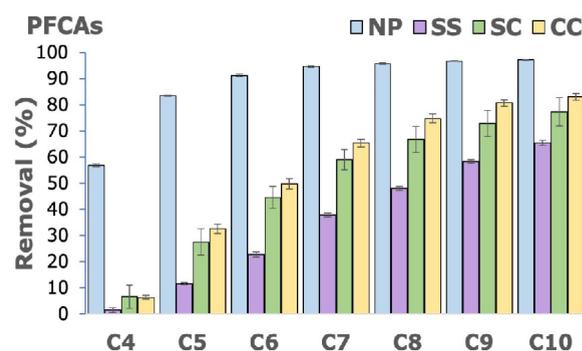


Figure 3. Removal of 1 μ g L⁻¹ PFCA by 1 mg L⁻¹ 6 in nanopure water (NP, blue bar), 1 mM Na₂SO₄ (SS, purple bar), 2 mM NaCl (SC, green bar), and 1 mM CaCl₂ (CC, yellow bar) after 48 h of contact time. The x -axis denotes PFCA of different chain lengths. For example, C4 refers to PFBA.

potentially affect inhibition to a varying extent. We attribute anion valency to either direct-site competition or a screening effect.⁵⁰ 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 valency.

CONCLUSIONS

We used modular, permanently porous, and cross-linked styrene-functionalized β -CD polymers with a controllable binding environment and tunable compositions of comonomers to remove PFASs of different chain lengths from water. 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 PFCA and PFSA at adsorbent loadings as low as 1 mg L⁻¹.

The inhibition effect observed in SS matrix revealed a 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 salts are present in the matrix. The removal of longer-chain PFASs is achieved through both hydrophobic and electrostatic interactions. These results demonstrate that styrene-functionalized β -CD polymers are promising adsorbents for the remediation of anionic PFASs. Furthermore, the materials might be tailored to target other organic micropollutants, including cationic and neutral PFASs by varying the comonomers' structures, including using mixed compositions. The unprecedented control afforded by the platform offers insights into the fundamental binding mechanisms between β -CD polymers and PFASs. Future studies will focus on an in-depth investigation of binding mechanisms and applications in removing micropollutants from real water matrices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscentsci.2c00478>.

Synthesis procedures and characterizations, including ^1H and ^{13}C NMR spectra, IR spectra, HRMS data, N_2 binding isotherms, ζ potentials, elemental analysis, analytical methods, and validation experiments; preparation of PFAS analytical standards; and additional batch removal experiments (PDF)

AUTHOR INFORMATION

Corresponding Authors

Damian E. Helbling – School of Civil and Environmental Engineering, Cornell University, Ithaca, New York 14853, United States; orcid.org/0000-0003-2588-145X;
Email: damian.helbling@cornell.edu

William R. Dichtel – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States;
orcid.org/0000-0002-3635-6119; Email: wdichtel@northwestern.edu

Authors

Ri Wang – School of Civil and Environmental Engineering, Cornell University, Ithaca, New York 14853, United States

Zhi-Wei Lin – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States;
orcid.org/0000-0002-6465-3698

Max J. Klemes – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States;
orcid.org/0000-0002-4481-890X

Mohamed Ateia – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States;
orcid.org/0000-0002-3524-5513

Brittany Trang – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States;
orcid.org/0000-0002-2499-8990

Jieyuan Wang – School of Civil and Environmental Engineering, Cornell University, Ithaca, New York 14853, United States

Casey Ching – School of Civil and Environmental Engineering, Cornell University, Ithaca, New York 14853, United States; orcid.org/0000-0003-3004-3346

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acscentsci.2c00478>

Author Contributions

§ R.W., Z.-W.L., and M.J.K. contributed equally.

Notes

The authors declare the following competing financial interest(s): Northwestern University and Cornell University have filed one or more patent applications related to the findings of this manuscript. W.R.D. owns equity and/or stock options in Cyclopure, Inc. (Cyclopure), which is commercializing β -CD polymers for removing organic pollutants from water. W.R.D. and D.E.H. have previously served as officers and/or advisors for Cyclopure.

ACKNOWLEDGMENTS

We thank Dr. Anna Yang and Mr. Luke Skala for helpful discussion and Mr. Saman Shafaie for conducting the high-resolution mass spectrometry experiments. Z.-W.L. and B.T. are supported by the NSF Graduate Research Fellowship under grant DGE-1842165. This research was funded by the Collaborative Water-Energy Research Center (CoWERC), which is supported by Binational Industrial Research and

Development Foundation under Energy Center grant EC-15. This research was also funded by the Strategic Environmental Research and Development Program under grant ER18-1026.

REFERENCES

- (1) Gagliano, E.; Sgroi, M.; Falciglia, P. P.; Vagliasindi, F. G. 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.
- (2) Sun, M.; Arevalo, E.; Strynar, M.; Lindstrom, A.; Richardson, M.; Kearns, B.; Pickett, A.; Smith, C.; Knappe, D. R. U. Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina. *Environ. Sci. Technol. Lett.* **2016**, *3*, 415–419.
- (3) Ateia, M.; Maroli, A.; Tharayil, N.; Karanfil, T. The Overlooked Short- and Ultrashort-Chain Poly- and Perfluorinated Substances: A Review. *Chemosphere* **2019**, *220*, 866–882.
- (4) Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)CE. *Environ. Sci. Technol.* **2017**, *51*, 2508–2518.
- (5) Adamson, D. T.; Nickerson, A.; Kulkarni, P. R.; Higgins, C. P.; Popovic, J.; Field, J.; Rodowa, A.; Newell, C.; DeBlanc, P.; Kornuc, J. J. Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Areas. *Environ. Sci. Technol.* **2020**, *54*, 15768–15777.
- (6) Houtz, E. F.; Sutton, R.; Park, J. S.; Sedlak, M. Poly- and Perfluoroalkyl Substances in Wastewater: Significance of Unknown Precursors, Manufacturing Shifts, and likely AFFF Impacts. *Water Res.* **2016**, *95*, 142–9.
- (7) Wang, Y.; Yu, N.; Zhu, X.; Guo, H.; Jiang, J.; Wang, X.; Shi, W.; Wu, J.; Yu, H.; Wei, S. Suspect and Nontarget Screening of Per- and Polyfluoroalkyl Substances in Wastewater from a Fluorochemical Manufacturing Park. *Environ. Sci. Technol.* **2018**, *52*, 11007–11016.
- (8) Scher, D. P.; Kelly, J. E.; Huset, C. A.; Barry, K. M.; Hoffbeck, R. W.; Yingling, V. L.; Messing, R. B. Occurrence of Perfluoroalkyl Substances (PFAS) in Garden Produce at Homes with a History of PFAS-Contaminated Drinking Water. *Chemosphere* **2018**, *196*, 548–555.
- (9) Hoffman, K.; Webster, T. F.; Bartell, S. M.; Weisskopf, M. G.; Fletcher, T.; Vieira, V. M. Private Drinking Water Wells as a Source of Exposure to Perfluorooctanoic Acid (PFOA) in Communities Surrounding a Fluoropolymer Production Facility. *Environ. Health Perspect.* **2011**, *119*, 92–7.
- (10) Houck, K. A.; Patlewicz, G.; Richard, A. M.; Williams, A. J.; Shobair, M. A.; Smeltz, M.; Clifton, M. S.; Wetmore, B.; Medvedev, A.; Makarov, S. Bioactivity Profiling of Per- and Polyfluoroalkyl Substances (PFAS) Identifies Potential Toxicity Pathways Related to Molecular Structure. *Toxicology* **2021**, *457*, 152789.
- (11) McKinlay, R.; Plant, J. A.; Bell, J. N.; Voulvoulis, N. Endocrine Disrupting Pesticides: Implications for Risk Assessment. *Environ. Int.* **2008**, *34*, 168–83.
- (12) Crone, B. C.; Speth, T. F.; Wahman, D. G.; Smith, S. J.; Abulikemu, G.; Kleiner, E. J.; Pressman, J. G. Occurrence of Per- and Polyfluoroalkyl Substances (PFAS) in Source Water and Their Treatment in Drinking Water. *Crit. Rev. Environ. Sci. Technol.* **2019**, *49*, 2359–2396.
- (13) Duchesne, A. L.; Brown, J. K.; Patch, D. J.; Major, D.; Weber, K. P.; Gerhard, J. I. Remediation of PFAS-Contaminated Soil and Granular Activated Carbon by Smoldering Combustion. *Environ. Sci. Technol.* **2020**, *54*, 12631–12640.
- (14) Liu, C. J.; Werner, D.; Bellona, C. Removal of Per- and Polyfluoroalkyl Substances (PFASs) from Contaminated Groundwater using Granular Activated Carbon: a Pilot-Scale Study with Breakthrough Modeling. *Environ. Sci. Water Res. Technol.* **2019**, *5*, 1844–1853.
- (15) McCreaf, P.; Englund, S.; Ostlund, A.; Lindgren, K.; Wiberg, K.; Ahrens, L. 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.

(16) 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*, 137–46.

(17) Wang, F.; Shih, K. Adsorption of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) on Alumina: Influence of Solution pH and Cations. *Water Res.* **2011**, *45*, 2925–30.

(18) Parida, S. K.; Dash, S.; Patel, S.; Mishra, B. K. Adsorption of Organic Molecules on Silica Surface. *Adv. Colloid Interface Sci.* **2006**, *121*, 77–110.

(19) Tang, C. Y.; Shiang Fu, Q.; 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*, 2654–62.

(20) Ateia, M.; Helbling, D. E.; Dichtel, W. R. Best Practices for Evaluating New Materials as Adsorbents for Water Treatment. *ACS Mater. Lett.* **2020**, *2*, 1532–1544.

(21) Rizzo, L.; Malato, S.; Antakyal, D.; Beretsou, V. G.; Dolic, M. B.; Gernjak, W.; Heath, E.; Ivancev-Tumbas, I.; Karaolia, P.; Lado Ribeiro, A. R.; Mascolo, G.; McArdell, C. S.; Schaar, H.; Silva, A. M. T.; Fatta-Kassinos, D. Consolidated vs New Advanced Treatment Methods for the Removal of Contaminants of Emerging Concern from Urban Wastewater. *Sci. Total Environ.* **2019**, *655*, 986–1008.

(22) Ling, Y.; Klemes, M. J.; Xiao, L.; Alsaiee, 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*, 7590–7598.

(23) Ling, Y.; Alzate-Sanchez, D. M.; Klemes, M. J.; Dichtel, W. R.; Helbling, D. E. Evaluating the Effects of Water Matrix Constituents on Micropollutant Removal by Activated Carbon and beta-Cyclodextrin Polymer Adsorbents. *Water Res.* **2020**, *173*, 115551.

(24) Liu, Q.; Zhou, Y.; Lu, J.; Zhou, Y. Novel Cyclodextrin-based Adsorbents for Removing Pollutants from Wastewater: A Critical Review. *Chemosphere* **2020**, *241*, 125043.

(25) Alsaiee, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E.; Dichtel, W. R. Rapid Removal of Organic Micropollutants from Water by a Porous beta-Cyclodextrin polymer. *Nature* **2016**, *529*, 190–4.

(26) Klemes, M. J.; Ling, Y.; Chiapasco, M.; Alsaiee, A.; Helbling, D. E.; Dichtel, W. R. Phenolation of Cyclodextrin Polymers Controls their Lead and Organic Micropollutant Adsorption. *Chem. Sci.* **2018**, *9*, 8883–8889.

(27) Zhao, F.; Repo, E.; Yin, D.; Chen, L.; Kalliola, S.; Tang, J.; Iakovleva, E.; Tam, K. C.; Sillanpaa, M. One-pot Synthesis of Trifunctional Chitosan-EDTA-beta-Cyclodextrin Polymer for Simultaneous Removal of Metals and Organic Micropollutants. *Sci. Rep.* **2017**, *7*, 15811.

(28) Zhang, Q.; Deng, S.; Yu, G.; Huang, J. Removal of Perfluorooctane Sulfonate from Aqueous Solution by Crosslinked Chitosan Beads: Sorption Kinetics and Uptake Mechanism. *Bioresour. Technol.* **2011**, *102*, 2265–71.

(29) Li, R.; Alomari, S.; Stanton, R.; Wasson, M. C.; Islamoglu, T.; Farha, O. K.; Holsen, T. M.; Thagard, S. M.; Trivedi, D. J.; Wriedt, M. Efficient Removal of Per- and Polyfluoroalkyl Substances from Water with Zirconium-Based Metal–Organic Frameworks. *Chem. Mater.* **2021**, *33*, 3276–3285.

(30) Wang, W.; Xu, Z.; Zhang, X.; Wimmer, A.; Shi, E.; Qin, Y.; Zhao, X.; Zhou, B.; Li, L. Rapid and Efficient Removal of Organic Micropollutants from Environmental Water using a Magnetic Nanoparticles-Attached Fluorographene-based Sorbent. *Chem. Eng. J.* **2018**, *343*, 61–68.

(31) 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.

(32) Li, C.; Klemes, M. J.; Dichtel, W. R.; Helbling, D. E. Tetrafluoroterephthalonitrile-Crosslinked beta-Cyclodextrin Polymers

for Efficient Extraction and Recovery of Organic Micropollutants from Water. *J. Chromatogr. A* **2018**, *1541*, 52–56.

(33) Yang, A.; Ching, C.; Easler, M.; Helbling, D. E.; Dichtel, W. R. Cyclodextrin Polymers with Nitrogen-Containing Tripodal Cross-linkers for Efficient PFAS Adsorption. *ACS Mater. Lett.* **2020**, *2*, 1240–1245.

(34) Crini, G. Review: A History of Cyclodextrins. *Chem. Rev.* **2014**, *114*, 10940–75.

(35) 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*, 12693–12702.

(36) Xiao, L.; Ling, Y.; Alsaiee, 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*, 7689–7692.

(37) Xiao, L.; Ching, C.; Ling, Y.; Nasiri, M.; Klemes, M. J.; Reineke, T. M.; Helbling, D. E.; Dichtel, W. R. Cross-linker Chemistry Determines the Uptake Potential of Perfluorinated Alkyl Substances by beta-Cyclodextrin Polymers. *Macromolecules* **2019**, *52*, 3747–3752.

(38) Chen, Z.; Bradshaw, J. S.; Yi, G.; Pyo, D.; Black, D. R.; Zimmerman, S. S.; Lee, M. L. Self-Inclusion Complexes Derived from Cyclodextrins. *J. Org. Chem.* **1996**, *61*, 8949–8955.

(39) Rekharsky, M. V.; Inoue, Y. Complexation Thermodynamics of Cyclodextrins. *Chem. Rev.* **1998**, *98*, 1875–1917.

(40) Klemes, M. J.; Skala, L. P.; Ateia, M.; Trang, B.; Helbling, D. E.; Dichtel, W. R. Polymerized Molecular Receptors as Adsorbents to Remove Micropollutants from Water. *Acc. Chem. Res.* **2020**, *53*, 2314–2324.

(41) Rojas, M. T.; Koniger, R.; Stoddart, J. F.; Kaifer, A. E. Supported Monolayers Containing Preformed Binding-Sites - Synthesis and Interfacial Binding-Properties of a Thiolated Beta-Cyclodextrin Derivative. *J. Am. Chem. Soc.* **1995**, *117*, 336–343.

(42) Ashton, P. R.; Koniger, R.; Stoddart, J. F.; Alker, D.; Harding, V. D. Amino Acid Derivatives of beta-Cyclodextrin. *J. Org. Chem.* **1996**, *61*, 903–908.

(43) Liu, Y.; Lin, T.; Cheng, C.; Wang, Q.; Lin, S.; Liu, C.; Han, X. Research Progress on Synthesis and Application of Cyclodextrin Polymers. *Molecules* **2021**, *26*, 1090.

(44) Pullanchery, S.; Kulik, S.; Rehl, B.; Hassanali, A.; Roke, S. Charge Transfer Across C-H...O Hydrogen Bonds Stabilizes Oil Droplets in Water. *Science* **2021**, *374*, 1366–1370.

(45) Ateia, M.; Alsaiee, A.; Karanfil, T.; Dichtel, W. Efficient PFAS Removal by Amine-Functionalized Sorbents: Critical Review of the Current Literature. *Environ. Sci. Technol. Lett.* **2019**, *6*, 688–695.

(46) 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*, 114874.

(47) Munoz, G.; Duy, S. V.; Labadie, P.; Botta, F.; Budzinski, H.; Lestremay, F.; Liu, J.; Sauve, S. 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*, 447–56.

(48) Chen, H.; Zhang, C.; Yu, Y.; Han, J. Sorption of Perfluorooctane Sulfonate (PFOS) on Marine Sediments. *Mar. Pollut. Bull.* **2012**, *64*, 902–6.

(49) Jungwirth, P.; Cremer, P. S. Beyond Hofmeister. *Nat. Chem.* **2014**, *6*, 261–3.

(50) Jordan, J. H.; Ashbaugh, H. S.; Mague, J. T.; Gibb, B. C. Buffer and Salt Effects in Aqueous Host-Guest Systems: Screening, Competitive Binding, or Both? *J. Am. Chem. Soc.* **2021**, *143*, 18605–18616.