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

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A. Materials and Instrumentation

I. Materials

β-Cyclodextrin (97%) was provided by Wacker Chemical and dried at 80 °C under high vacuum prior to monomer synthesis. Iodine (>99.8%), triphenylphosphine (99%), thiourea (>99.0%), 4-vinylbenzyl chloride (90%), methyl methacrylate (99%), styrene (>99%), [2-(Methacryloyloxy)ethyl] trimethylammonium chloride solution (MATMA, 80% in H2O), 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%), sodium sulfate, and calcium chloride were purchased from Sigma Aldrich and used as received. Sodium chloride was purchased from Fisher Scientific and used as received. The chemicals were stored at room temperature and used as received. Two PFAS mixtures of anionic PFASs (PFC-MXA and PFS-MXA) and one mixture of PFAS isotope-labelled internal standards (ILISs) (MPFAC-MXA) were purchased from Wellington Laboratories, Inc. See PFAS and Internal Standards (Section F, Table S4) for a detailed list of the two PFAS mixtures and internal standards. For PFAS mixture preparation, see descriptions in that section.

Safety Statement

No unexpected or usually high safety hazards were encountered.

II. Instrumentations

Critical Point Dryer: Activation of polymers by supercritical CO2 washing was performed on a Leica EM CPD 300. The polymer samples were stored in teabags for both Soxhlet extraction and supercritical CO2 washing. After 14 h of Soxhlet extraction in methanol, the polymer samples were immediately transferred to the drying chamber of the critical point dryer (samples contain residual methanol). The drying chamber was cooled to 15 °C and filled with CO2 at the “slow” setting with 120 s delay. After the delay, CO2 exchange occurred at the
speed setting of "5" for 20 cycles. The samples were then cooled to 40 °C on the "slow" setting and the pressure in the chamber was also relieved on the "slow 50%" setting.

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** Solution $^1$H and $^{13}$C NMR spectra were acquired on a Bruker AvanceIII-500 MHz spectrometer with a TXO 5mm Prodigy probe w/ Z-Gradient, or a Bruker AdvanceIII-500 MHz spectrometer with a CryoProbe 5mm DCH w/ Z-Gradient. All solution spectra were recorded at 25 °C, and calibrated using DMSO-$d_6$ as an internal reference, 2.50 ppm for $^1$H NMR and 39.52 ppm for $^{13}$C NMR. $^1$H NMR data are reported as follows: chemical shift, multiplicity (d = doublet, dd = doublet of doublets, m = multiplet), and integration.

Solid-State Cross-Polarization Mass Angle Spinning $^{13}$C NMR spectra were acquired on a Bruker AvanceIII HD 400 MHz spectrometer with a 4mm HX probe w/ Z-Gradient. All solid-state NMR spectra were recorded at 25 °C, and calibrated using adamantane as an external reference at 38.3 ppm for $^{13}$C NMR. The reference was converted to tetramethylsilane at 0.00 ppm. The sample spinning rate was controlled by a Bruker pneumatic MAS unit at 10 kHz, and 2048 scans were collected for each sample.

**Fourier-Transform Infrared (FTIR) Spectroscopy:** FTIR data were collected at room temperature on a Bruker Tensor 37 FTIR Spectrometer equipped with a Mid IR detector and KBr beam splitter. The spectrum was collected in attenuated total reflectance mode in the range of 3600 to 600 cm$^{-1}$. The data were averaged over 32 scans. The OPUS software was used for the data acquisition.

**High-Resolution Mass Spectroscopy (HRMS):** High-resolution mass spectrum was acquired on an Agilent 6545 Q-TOF Mass Spectrometer, with Electro spray Ionization (ESI) as an ion source. The instrument is equipped with an Agilent 1200 Series HPLC binary pump and autosampler. Analysis was performed with direct injection with methanol as solvent. Data
acquisition and analysis were done using Agilent MassHunter Data Workstation and Qualitative Analysis software.

Batch adsorption experiments were quantified using a ThermoFisher Scientific QExactive high-resolution quadrupole-orbitrap mass spectrometer coupled to a high performance liquid chromatography system. The trap column, a Hypersil Gold dC18 12 µm 2.1 x 20 mm, was purchased from Fischer Scientific. The analytical column, an Atlantis® dC18 5 µm 2.1 x 150 mm, was purchased from Waters. See Analytical Methods (Section E) for a detailed description of sample preparation and data collection and analysis.

**Surface Area Analysis:** The polymer porosity and Brunauer-Emmett-Teller surface areas (\(S_{\text{BET}}\)) were collected on a Micromeritics ASAP 2420 Accelerated Surface Area and Porosity Analyzer. Approximately 40 mg of polymer was used for each analysis. The polymers were degassed at 100 °C for 24 h until the off-gas rate was constantly reading less than 0.2 µmHg/min. \(N_2\) isotherms were generated by incremental exposure to ultrahigh purity nitrogen up to 1 atm in a liquid nitrogen bath at 77K. The \(S_{\text{BET}}\) were calculated using the linear region \((P/P_0 \text{ of } 0.05-0.1)\) of the isotherm using adsorption models included in the instrument software (Micromeritics ASAP-2420 V4.00).

**Elemental Analysis of C, H, N, and S:** Elemental analysis was performed by Robertson Microlit Laboratories. Combustion analysis was used for carbon, hydrogen, and nitrogen on a Perkin-Elmer Model 2400 CHN Analyzer, and titration was used for sulfur. For monomer, the elemental analysis result was compared to calculated values. For polymers, see the Polymer Characterization (Section D, V. Elemental Analysis) for a detailed analysis for determining the ratio of comonomers with respect to monomers.
B. Synthesis Procedures

A. Monomer Synthesis

*Synthesis of 1* (Heptakis-(6-deoxy-6-iodo)-β-Cyclodextrin): Literature procedures\(^1,2\) were followed to replace the primary alcohol at 6’ position with iodine with the following modifications: Soxhlet in methanol was not carried out, because the large scale of products rendered Soxhlet ineffective. Instead the product was suspended in methanol for several days and filtered until filtrate ran clean. Note: Solvents do not need to be dried or degassed. (Yield 91%)

*Synthesis of 2* (Heptakis-(6-deoxy-6-mercapto)-β-Cyclodextrin): Literature procedures\(^1,2\) were followed to convert the iodines to thiols with the following modifications: After NaHSO\(_4\) precipitation and filtration, the product was suspended in methanol and filtered twice. The solid was then subjected to a rotary evaporation at 30 °C for 3 h before being placed on a high vacuum line for 48 h at room temperature. Note: Solvents during synthesis must be degassed and the product must be stored away from light in a freezer. (Yield 92%)

*Synthesis of 3* (Heptakis-(6-deoxy-6-vinylbenzyl)-β-Cyclodextrin): 2 (17.591 g, 14.102 mmol) was dissolved in DMSO (170 mL) and degassed with nitrogen sparging for 30 min. Potassium carbonate (6.8213 g, 49.357 mmol) was added and the solution was stirred for an additional 30 min. 4-vinylbenzyl chloride (14.11 mL, 100.123 mmol) was then added dropwise to the solution under N\(_2\) pressure. The solution was stirred at room temperature. After 24 – 32 h the solution was precipitated into water (1500 mL) and stirred for an additional 10 min before filtering. The filtrate was wash with copious amounts of methanol, superficially dried,
then resuspended in methanol (600 mL). After 30 min, the solution was filtered again, and the filter cake was resuspended in methanol (600 mL). After 30 min, the solution was filtered again, superficially dried and transferred to a drying flask and subjected to rotary evaporation for an additional 3 h at 35 °C. The powder was then transferred onto a high vacuum line and dried at room temperature for 24 – 48 h. Note: Powder is not bench stable for long periods of time (>30 days); store in freezer away from light. (Yield 89%)

\( ^1 \)H NMR (500 MHz, DMSO-d\(_6\) \( \delta \) 7.24 (d, 14H), 7.14 (d, 14H), 6.62 (dd, 7H), 5.95 (d, 7H), 5.90 (d, 7H), 5.71 (dd, 7H), 5.20 (dd, 7H), 4.92 (d, 7H), 3.75 (m, 7H), 3.58 (m, 14H), 3.35 (m, 14H), 3.11 (d, 7H), 3.81 (dd, 7H) ppm.

\( ^{13} \)C NMR (126 MHz, DMSO-d\(_6\)\): \( \delta \) 138.64, 136.60, 135.89, 129.62, 126.26, 114.26, 102.36, 85.54, 72.90, 72.65, 72.44, 36.92, 33.48 ppm.

ESI HRMS \( m/z \) calculated for \( \text{C}_{106}\text{H}_{126}\text{O}_{28}\text{S}_7 \): \([M-H]^− \) 2059.65; found 2058.6437.

Elemental Analysis (%) calculated for \( \text{C}_{106}\text{H}_{126}\text{O}_{28}\text{S}_7 \): C, 61.20; H, 6.18; O, 21.74; S, 10.89. Found C, 58.84; H, 5.99; O, 10.73; S, 24.28.

**B. Polymerization**

General Polymerization for 4, 5, and 6: Monomer 3 (0.600 g, 0.291 mmol) and AIBN (0.019 g, 0.116 mmol) were dissolved in DMF (2 mL). Two equivalences of comonomer (0.582 mmol) were added as a liquid; comonomers consisted of styrene, methyl methacrylate, or MATMA (aqueous 80%). Note: Two equivalents were determined to be optimal equivalency, see **Optimal Comonomer Equivalency Test** (Section H). The monomer solution was transferred into a dry Schlenk flask, subjected to 3 freeze-pump-thaw cycles, and heated to
80 °C for 1 h. Polymer gelled after 15 min and was heated for an additional 45 mins. After 1 h total reaction time, the solid gel was broken apart with a metal spatula, suspended in methanol, transferred to a teabag, and sealed with staples. This teabag was subjected to a Soxhlet extractor with methanol for 14 h before activating the polymer with supercritical CO₂ (80 cycles, 4 h). The polymer was then crushed into a fine powder and isolated. (yields: 89–97%)

See $^{13}$C ssNMR spectra of (4), (5), and (6) below.

$S_{\text{BET}}$: (4) 402 m$^2$g$^{-1}$, (5) 392 m$^2$g$^{-1}$ and (6) 237 m$^2$g$^{-1}$.

Elemental Analysis was used to calculate comonomer:β-CD ratio: (4) 1.76, (5) 1.21, and (6) 1.99. See Section D, V for a sample calculation.

C. Monomer Characterization

I. $^1$H NMR and $^{13}$C NMR Spectra

![Figure S1. $^1$H NMR spectrum (500 MHz, 298K, DMSO-d$_6$) of 3.](image-url)
**Figure S2.** $^{13}$C NMR spectrum (126 MHz, 298K, DMSO-$d_6$) of 3.

**II. HRMS Spectrum**

**Figure S3.** HRMS of 3 in chloroform. Most abundant adduct is 2058.6437, corresponding to [M-H]$^-$ (calculated 2059.65). Other peaks correspond to the isotopic masses of 3. The spectrum was obtained in negative mode.
D. Polymers Characterization

I. Solid-State $^{13}$C NMR Spectra

**Figure S4.** Solid State $^{13}$C NMR spectrum (400 MHz, 298K, Adamantane/KBr) of 4 (bottom) with respect to solution $^{13}$C NMR spectra of 3 (top) and comonomer styrene (middle). The lack of vinyl carbons of 3 and comonomer (113 ppm) and broadened alkane region of polymer backbone (55-20 ppm) in the spectrum of 4 indicates successful polymerization. Black dotted line was added for clarity.
Figure S5. Solid State $^{13}$C NMR spectrum (400 MHz, 298K, Adamantane/KBr) of 5 (bottom) with respect to solution $^{13}$C NMR spectra of 3 (top) and comonomer methyl methacrylate (middle). The presence of carbonyl carbon of comonomer (180 ppm), the lack of vinyl carbon of 3 (113 ppm), broadened alkane region of polymer backbone (55-20 ppm), and the lack of vinyl carbon of comonomer (20 ppm) in the spectrum of 5 indicate successful polymerization. Black dotted lines were added for clarity.
Figure S6. Solid State $^{13}$C NMR spectrum (400 MHz, 298K, Adamantane/KBr) of 6 (bottom) with respect to solution $^{13}$C NMR spectra of 3 (top) and comonomer (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (middle). The presence of carbonyl carbon of comonomer (180 ppm), the lack of vinyl carbon of 3 (113 ppm), the presence of N-(CH$_3$)$_3$ of comonomer (55 ppm), broadened alkane region of polymer backbone (55-20 ppm), and the lack of vinyl carbon of comonomer (20 ppm) in the spectrum of 6 indicate successful polymerization. Black dotted lines were added for clarity.
II. FTIR Spectra

Figure S7. FT-IR spectrum of 3.

Figure S8. FT-IR spectrum of 4.
Figure S9. FT-IR spectrum of 5.

Figure S10. FT-IR spectrum of 6.
III. N\textsubscript{2} Isotherms

**Figure S11.** N\textsubscript{2} adsorption and desorption isotherms of 4 at 77 K.

**Figure S12.** N\textsubscript{2} adsorption and desorption isotherms of 5 at 77 K.
Figure S13. N₂ adsorption and desorption isotherms of 6 at 77 K.

IV. Zeta Potentials

Table S1. Zeta potentials of polymers (100 mg L⁻¹) measured in 0.9 mM CaCl₂ solution.

| Adsorbent | Zeta Potential (mV) |
|-----------|---------------------|
| 4         | -8.2 ± 0.6          |
| 5         | -9.9 ± 0.9          |
| 6         | +23.8 ± 1.6         |

V. Elemental Analysis

Table S2. Comonomer:β-CD Ratio for 4, 5, and 6.

| Adsorbents | C (%) | H (%) | N (%) | S (%) | Comonomer:β-CD |
|------------|-------|-------|-------|-------|----------------|
| 4          | 56.84 | 6.20  | 8.92  | 0.14  | 1.76           |
| 5          | 54.50 | 6.31  | 9.17  | 0.21  | 1.21           |
| 6          | 52.56 | 6.50  | 8.11  | 1.18  | 1.99           |

aN content for 4 and 5 is below the instrument threshold.
The Comonomer:β-CD ratio was calculated from a system of equations. The following sample calculation was for 4, but 5 and 6 were calculated with the same analysis.

Sample Calculation for 4.

The system of equations was set up such that,

\[ a = \text{mol modified of β-CD} \]

\[ b = \text{mol of comonomer} \]

Polymer 4 consists of two components: modified β-CD and the comonomer styrene. The molecular formula of modified β-CD is C\(_{105}\)H\(_{126}\)O\(_{28}\)S\(_{7}\), and the molecular of the comonomer styrene is C\(_8\)H\(_8\). The total mol of C, H, or S follows,

\[ \text{Total mol C} = 105a + 8b \]

\[ \text{Total mol H} = 126a + 8b \]

\[ \text{Total mol O} = 28a \quad \text{and} \quad \text{Total mol S} = 7a \]

where the total mol of C is a sum from modified β-CD and comonomer. Because styrene does not contain O or S, it is primarily from modified β-CD portion of 4. S was used to calculate the mol of modified β-CD.

\[ a = \frac{S}{7} \]

We converted the raw % elemental analysis data (Table S2.) to mol for each element by arbitrarily assuming a 1 g of the sample and dividing it by the element’s molar mass. The converted mol amount of each element was used in the system of equations equation:

\[ b = \frac{\text{Total mol C} - 105a}{8} \]

where resulting b is the mol of the comonomer in 4. The comonomer:β-CD ratio was determined by diving a into b.
E. Analytical Methods

Quantification of target PFCAs or PFSAs after Batch Equilibrium Adsorption Experiments (Section G) was conducted using a HPLC coupled with HRMS (QExactive, qudrupole-orbitrap, ThermoFischer Scientific) using an established parallel reaction monitoring (PRM) method optimized for PFAS quantification.³ Previously established methods were also used for HPLC parameters.⁴⁻⁶ HPLC-MS was operated with electrospray ionization in negative polarity mode for all PFAS measurements. A detailed list of analytical information is provided in Table S3, and a summary of PFAS mixtures and their isotope-labeled internal standards (ILISs) is provided in Table S4. Matrix-matched calibration standards (n = 9) were prepared with concentrations ranging between 0 ng L⁻¹ to 1000 ng L⁻¹. Analytes were quantified from the calibration standards (spiked with same concentration of ILISs) based on the PFAS target-to-ILIS peak area ratio responses of the designated quantitation product ion by linear least-squares regression. Calibration curves were run at the beginning of the analytical sequence. Instrument blanks and quality control (QC) samples were run before and after the calibration curve to ensure minimal carryover and adequate MS performance (QC tolerance set at ± 30%). PFAS spike controls were used to determine the PFAS recovery rate during analysis; recovery rate threshold was set at ± 50% for each PFAS to be considered as reliable data.

The mobile phase consisted of (A) LC-MS grade water amended with 20 mM ammonium acetate and (B) LC-MS grade methanol. Samples were injected at 5 mL volumes onto a Hypersil Gold dC18 12 μm 2.1 x 20 mm trap column (Fisher Scientific) at room temperature using an isocratic mobile phase of 99% (A), pumped at 1 mL·min⁻¹ via a low-pressure loading pump. Elution from the trap column and subsequent separation of analytes on an Atlantis® dC18 5 μm 2.1 x 150 mm analytical column (Waters) at 25°C was achieved.
using an initial mobile phase of 60% (A), pumped at 0.3 mL·min⁻¹ via a high-pressure elution pump. The isocratic mobile phase delivered from the loading pump changed to 2% (A) at 37.3 minutes to rinse the trap column and returned to 99% (A) at 41.3 minutes to prepare for the next sample injection. The mobile phase gradient delivered from the loading pump remained at 60% (A) until 6.1 minutes and then increased linearly to 10% (A) at 30.1 minutes. The mobile phase was held at 10% (A) until 37.1 minutes before it returned to 60% (A) to prepare for the next sample. The chromatography program had a total duration of 42.1 minutes.

Table S3. Analytical information of PFAS target compounds and their ILISs for PRM.

| Acronym | Molecular Formula | Adduct | Precursor Ion Mass (Da) | Product Ion Mass (Da) | Retention Time (min) | Normalize d Collision Energy | ILISs          |
|---------|-------------------|--------|-------------------------|-----------------------|----------------------|-----------------------------|-----------------|
| PFBS    | C₄H₅F₂O₂S        | [M-H]-  | 298.9430                | 79.9557               | 13.71                | 60                          | 18O2 - PFHxS   |
| PFHxS   | C₆H₁₂O₃S         | [M-H]-  | 398.9366                | 79.9557               | 19.80                | 60                          | 18O2 - PFHxS   |
| PFHpS   | C₇H₁₅O₃S         | [M-H]-  | 448.9334                | 79.9557               | 22.11                | 60                          | 13C4 - PFOS    |
| PFOS    | C₆H₁₇O₃S         | [M-H]-  | 498.9302                | 79.9558               | 24.04                | 60                          | 13C4 - PFOS    |
| PFBA    | C₄H₇F₂O₂          | [M-H]-  | 212.9792                | 168.9897              | 9.70                 | 20                          | 13C4 - PFBA    |
| PFPeA   | C₅H₉F₃O₂          | [M-H]-  | 262.9760                | 218.9863              | 13.19                | 20                          | 13C2 - PFHxA   |
| PFHxA   | C₆H₁₁O₂           | [M-H]-  | 312.9728                | 268.9829              | 16.79                | 20                          | 13C2 - PFHxA   |
| PFHpA   | C₇H₁₃O₂           | [M-H]-  | 362.9696                | 318.9794              | 19.75                | 20                          | 13C4 - PFOA    |
| PFOA    | C₈H₁₅O₂           | [M-H]-  | 412.9664                | 368.9767              | 22.16                | 20                          | 13C4 - PFOA    |
| PFNA    | C₉H₁₇O₂           | [M-H]-  | 462.9632                | 418.9737              | 24.17                | 20                          | 13C5 - PFNA    |
| PFDA    | C₁₀H₁₉F₁₀₂        | [M-H]-  | 512.9600                | 468.9703              | 25.87                | 20                          | 13C2 - PFDA    |

F. PFAS and Internal Standard List

Table S4. PFAS target compounds and their isotopically labeled internal standards (ILISs)

| Mixture Name | Name                | Acronym | Molecular Formula | Concentration | Solvent                     |
|--------------|---------------------|---------|-------------------|---------------|-----------------------------|
| PFC-MXA      | Perfluorobutanoic acid | PFBA   | C₄H₇F₂O₂          | 2 mg/L        | MeOH:H₂O (H₂O<1%)           |
| PFC-MXA | Perfluoropentanoic acid | PFPeA | C$_3$HF$_5$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
|---------|-------------------------|-------|-----------------|--------|-------------------------|
| PFC-MXA | Perfluorohexanoic acid  | PFHxA | C$_6$HF$_7$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluoroheptanoic acid | PFHpA | C$_7$HF$_9$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluorooctanoic acid  | PFOA  | C$_8$HF$_{13}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluorononanoic acid  | PFNA  | C$_9$HF$_{15}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluoreodecanoic acid | PFDA  | C$_{10}$HF$_{19}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluoroundecanoic acid| PFUnA | C$_{11}$HF$_{21}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluorododecanoic acid| PFDoA | C$_{12}$HF$_{23}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluorotridecanoic acid PFTrDA | C$_{13}$HF$_{25}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFC-MXA | Perfluorotetradecanoic acid PFTeDA | C$_{14}$HF$_{27}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| PFS-MXA | Perfluorobutanesulfonic acid PFBS | C$_4$HF$_5$O$_3$S | 2 mg/L | 100% Methanol |
| PFS-MXA | Perfluorohexanesulfonic acid PFHxS | C$_8$HF$_{13}$O$_3$S | 2 mg/L | 100% Methanol |
| PFS-MXA | Perfluoroheptanesulfonic acid PFHpS | C$_{10}$HF$_{15}$O$_3$S | 2 mg/L | 100% Methanol |
| PFS-MXA | Perfluoroctanesulfonic acid PFOS | C$_{11}$HF$_{17}$O$_3$S | 2 mg/L | 100% Methanol |
| PFS-MXA | Perfluorodesanesulfonic acid PFDS | C$_{10}$HF$_{21}$O$_3$S | 2 mg/L | 100% Methanol |
| MPFAC-MXA | Perfluro-o-[1,2,3,4-13C4]butanoic acid 13C4 - PFBA | [13]C$_4$HF$_7$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Perfluro-o-[1,2-13C2]hexanoic acid 13C2 - PFHxA | [13]C$_2$C$_4$HF$_{11}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Perfluro-o-[1,2,3,4-13C4]octanoic acid 13C4 - PFOA | [13]C$_4$C$_4$HF$_{15}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Perfluro-o-[1,2,3,4-13C5]nonanoic acid 13C5 - PFNA | [13]C$_5$C$_4$HF$_{17}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Perfluro-o-[1,2,3,4-13C5]decanoic acid 13C2 - PFDA | [13]C$_2$C$_6$HF$_{19}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Perfluro-o-[1,2,3,4-13C5]undecanoic acid 13C2 - PFUnA | [13]C$_2$C$_6$HF$_{21}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Perfluro-o-[1,2,3,4-13C5]dodecanoic acid 13C2 - PFDoA | [13]C$_2$C$_{10}$HF$_{23}$O$_2$ | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Sodium perfluoro-1-hexane[18O2]sulfonate 18O2 - PFHxS | C$_8$HF$_{13}$[18]O$_2$OS | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |
| MPFAC-MXA | Sodium perfluoro-1-[1,2,3,4-13C4]octanesulfonate 13C4 - PFOS | [13]C$_4$C$_4$HF$_{17}$O$_3$S | 2 mg/L | MeOH:H$_2$O (H$_2$O<1%) |

Note: All of the above chemicals were purchased from Wellington Laboratories. Certain PFCAs and PFSAs did not make the spike-recovery threshold and were subsequently removed from the rest of the studies.
The PFC-MXA mixture contains eleven PFCAs (C4 through C14) dissolved in methanol each at a concentration of 2 mg L⁻¹. The PFS-MXA mixture contains five PFSAs (C4, C6-C8, and C10) dissolved in methanol each at a concentration of 2 mg L⁻¹. The MPFAC-MXA mixture contains seven isotope-labelled PFCAs (C4, C6, C8-C12) and two isotope-labelled PFSAs (C6 and C8) dissolved in methanol each at a concentration of 2 mg L⁻¹. The PFAS standard spike mixtures were diluted from the stock mixtures (PFC-MXA and PFS-MXA) using nanopure water to yield a concentration of 1 mg L⁻¹. The ILIS spike mixture was diluted from MPFAC-MXA using nanopure water to yield a concentration of 250 µg L⁻¹. The stock mixtures and the spike mixtures were stored at -20 °C and 4 °C, respectively.

**G. Batch Equilibrium Adsorption Experiments**

Adsorption experiments (also referred to as removal experiments) were conducted in 15 mL polypropylene centrifuge tubes (Corning) with either 10 mL of nanopure water or salt-amended nanopure water, with the following concentrations: 1 mM Na₂SO₄, 2 mM NaCl, or 1 mM CaCl₂ as previously described.⁴⁻⁶ All adsorption experiments were conducted with either the PFCA or the PFSA mixture (Table S3) at an initial concentration of 1 µg L⁻¹ at pH of 5.5 to 6, and adsorbent loadings at 1 mg L⁻¹, 10 mg L⁻¹, or 100 mg L⁻¹ in triplicate. Prepared centrifuge tubes were placed on a tube revolver and rotated at 40 rpm at 23 °C for 48 h to reach equilibrium in adsorption. After rotating, samples were filtered through 0.45 µm cellulose acetate filters (Restek) and transferred into 10 mL glass LC-MS vials (Fischer Scientific). All triplicate samples were spiked with ILISs and stored at 4 °C until analysis. Control experiments were conducted in triplicate using the same procedure, but without adsorbents. The average and the standard deviation of PFAS removal efficiency were calculated based on the triplicate concentrations of each PFAS in the experimental group and
the control group. The PFAS removal efficiency (%) by adsorbents were determined using Eq. S2:

\[
\text{Equation S2: Removal (\%) } = \frac{C_o - C_f}{C_o} \times 100;
\]

where \(C_o\) (\(\mu\)g L\(^{-1}\)) and \(C_f\) (\(\mu\)g L\(^{-1}\)) are the initial and residual concentration at 48 h of PFAS, respectively. The initial concentration \(C_o\) was obtained from the average concentration of control samples to account for the loss of PFAS from experimental conditions.

H. Optimal Comonomer Equivalency Test

The optimal equivalency of the comonomer for polymerization was determined. Polymer formulations of 0.5, 1, 4, or 10 equivalencies of comonomer MMA, with respect to 3, were synthesized in the same condition as 5, which all resulted in high yields (90-93\%) and high \(S_{BET}\) (150-300 \(m^2 g^{-1}\)) [denoted as 5_0.5, 5_1, 5_4, and 5_10]. Note, 5 contains two equivalents of comonomer MMA. Each polymer was subjected to the same equilibrium adsorption experiment as previously described (see Section G). Specifically, the polymers were loaded at 40 mg L\(^{-1}\) to remove PFOA with an initial concentration of 40 mg L\(^{-1}\) in nanopure water (NP) or 1 mM NaSO\(_4\) (SS) matrix (Figure S14). No statistical significances were found in removal efficiencies among the adsorbents in SS matrix. In NP matrix, two equivalents of MMA (5) yielded best removal performance. Based on this data, two commoner equivalencies were selected for the remaining polymerizations and PFAS removal studies. We acknowledge this study is not meant to be accurate or representative for the other comonomers in 4 and 6. However, selecting a particular equivalence allowed us to minimize the number of conditions to test and obtain comparable data.
Figure S14. The removal of 40 mg L\(^{-1}\) PFOA by 40 mg L\(^{-1}\) of 5 with various equivalencies of comonomer in nanopure (NP) water and in 1 mM Na\(_2\)SO\(_4\) (SS) after 48 h of contact time. For example, 5\_0.5 denotes half equivalent of MMA, respect to one equivalent of 3, used in the polymerization.
I. Additional Removal Experiments of Adsorbents 4 and 5

Figure S15. The removal of a mixture of PFCAs at 1 µg L⁻¹ each by 100 mg L⁻¹ of (A) 4 and (B) 5 in nanopure water (NP) matrix and 1 mM Na₂SO₄ (SS) matrix after 48 h of contact time.
Figure S16. The removal of a mixture of PFSAs at 1 µg L\(^{-1}\) each by 100 mg L\(^{-1}\) of (A) 4 and (B) 5 in nanopure water (NP) matrix and 1 mM Na\(_2\)SO\(_4\) (SS) matrix after 48 h of contact time.

Adsorbent loadings of 4 and 5 were adjusted from 10 mg L\(^{-1}\) to 100 mg L\(^{-1}\) to better probe the magnitude of the enhanced adsorptions of PFCAs and PFSAs observed in SS matrix (Figure S15 & S16). In NP matrix, 4 and 5 exhibited very low adsorption of PFCAs and PFSAs. In SS matrix, the adsorption was significantly enhanced, such as the removal of eight carbon PFOA from 8.5% to 83.9% by 4 and the removal of eight carbon PFOS from 0% to 90.3% by 5. The enhancement effect was more profound for longer-chain PFCAs and PFSAs, highlighting the importance of hydrophobic interactions.

J. Ruling Out Competitive Adsorption

The experiments with the mixture of PFSAs (Figure 2B, see main article) ruled out competitive adsorption among the PFASs in the same mixture as a confounding variable. Competitive adsorption of PFASs is usually explained by longer-chain PFASs replacing shorter-
chain PFASs on the adsorbent surface over time due to the greater hydrophobic interactions. If competitive adsorption were a factor for the PFCAs where eleven species were examined at 1 µg L⁻¹, then the four PFSAs which were also at 1 µg L⁻¹ should exhibit less of a chain-length effect because there would be fewer long-chain PFSAs to compete with the short-chain PFSAs. Because we observed no weaker extent of adsorption inhibition or enhancement as a function of chain-length for the PFSAs as we observed with the PFCAs (i.e., the absolute values of slopes between removal difference and CF₂ chain length of PFSAs are all 10%-20% larger than those of PFCAs for all three adsorbents), competitive adsorption was ruled out as a possible confounding factor in the study. Finally, considering 6 in both matrices, and 4 and 5 in 1 mM SS matrix, the PFSAs are better removed than the PFCAs with the same CF₂ chain length, which corroborates other studies that have noted the greater adsorption of PFSAs on CDPs and other adsorbents.
K. Adsorption Kinetics of Adsorbent 6

Figure S17. The adsorption kinetics of 1 μg L\(^{-1}\) (A) PFCAs and (B) PFSAs by 10 mg L\(^{-1}\) of 6 in nanopure water at room temperature and neutral pH. Equilibrium removal is reached for all PFCAs and PFSAs within 4 h.
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