

β -Cyclodextrin Polymer Network Sequesters Perfluorooctanoic Acid at Environmentally Relevant Concentrations

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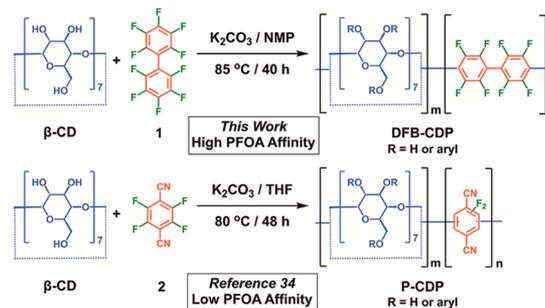
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Supporting Information

ABSTRACT: Per- and poly fluorinated alkyl substances (PFASs), notably perfluorooctanoic acid (PFOA), contaminate many ground and surface waters and are environmentally persistent. The performance limitations of existing remediation methods motivate efforts to develop effective adsorbents. Here we report a β -cyclodextrin (β -CD)-based polymer network with higher affinity for PFOA compared to powdered activated carbon, along with comparable capacity and kinetics. The β -CD polymer reduces PFOA concentrations from 1 $\mu\text{g L}^{-1}$ to <10 ng L^{-1} , at least 7 times lower than the 2016 U.S. EPA advisory level (70 ng L^{-1}), and was regenerated and reused multiple times by washing with MeOH. The performance of the polymer is unaffected by humic acid, a component of natural organic matter that fouls activated carbons. These results are promising for treating PFOA-contaminated water and demonstrate the versatility of β -CD-based adsorbents.

The contamination of ground and surface waters by per- and poly fluorinated alkyl substances (PFASs), including perfluoroalkyl sulfonic acids, fluorotelomer sulfonic acids, and perfluoroalkyl carboxylic acids,^{1–4} has emerged as an environmental and health crisis in many communities. PFASs are used in the manufacture of poly(tetrafluoroethylene) (Teflon) and many other industrial processes, consumer products, and aqueous film-forming foam formulations used to suppress aviation fires.⁵ They are associated with negative ecological and human health effects, including liver damage,⁶ thyroid disease,^{7,8} cancer,⁹ and others.^{10–12} There is particular concern over the occurrence of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in groundwater. The U.S. Environmental Protection Agency assigned a health advisory level of 70 ng L^{-1} for the combined concentration of PFOA and PFOS in drinking water,¹³ and negative effects are noted at lower concentrations.¹⁴ Many communities near industrial sites, military installations, and airports exceed this threshold.^{15,16} For example, states of emergency were declared in Hoosick Falls, New York, and Bennington, Vermont, in 2016 because of PFOA-contaminated drinking water, and many other communities will soon need to address PFOA and PFAS contamination.

Scheme 1



PFOA is environmentally persistent and difficult to degrade because of the high thermodynamic stability of C–F bonds. Oxidative,¹⁷ photochemical,¹⁸ sonochemical,¹⁹ and electrochemical²⁰ methods are expensive and/or produce degradation byproducts of unknown toxicity.^{18,19} Adsorption processes remove PFASs rather than degrading them, and adsorbents based on activated carbon and carbon fiber,^{21–23} carbon nanotubes,^{24,25} organic polymers,^{26,27} and anion exchange resins have been explored. Granular activated carbon (GAC) has emerged as the leading adsorbent because it is inexpensive and has reasonable capacity. However, it performs poorly in the presence of other organic cocontaminants or natural organic matter (NOM).²⁸ ACs also have relatively low affinity for PFOA,^{21,23} which complicates removal at environmentally relevant concentrations, and PFOA-loaded ACs are difficult to regenerate.²⁹ Therefore, adsorbents with high affinity, PFOA specificity, and inexpensive regeneration are needed to address this emerging environmental and health problem.

β -cyclodextrin (β -CD), a macrocycle composed of seven glucose units,²⁷ forms host–guest complexes with thousands of organic compounds. Cross-linked β -CD polymers^{30,31} have been explored for water purification, but their performance has historically lagged ACs. We reported a porous cyclodextrin polymer (P-CDP, Scheme 1) derived from cross-linking β -CD with tetrafluoroterephthalonitrile (TFN, 2).³² P-CDP outperforms ACs for the uptake of many organic micropollutants but has only moderate affinity for PFOA.³³ We hypothesized a β -CD polymer with perfluoroarene cross-linkers would bind PFOA

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more effectively. Here we report a β -CD containing polymer that removes PFOA to $<10 \text{ ng L}^{-1}$ (our limit of quantification) with comparable kinetics and capacity to ACs, and the ability to be easily regenerated. These findings demonstrate the selectivity of β -CD polymers can be tailored to target pollutants of interest, and the newly developed polymer shows promise for treating PFOA-contaminated water.

The nucleophilic substitution of decafluorobiphenyl (DFB, **1**) by β -CD provided the cross-linked polymer network DFB-CDP (Scheme 1). After the monomers and K_2CO_3 were heated in *N*-methyl-2-pyrrolidone (NMP) at 85°C , the suspension gelled after 24 h and was isolated in this form after 40 h. After Soxhlet extraction and solvent removal, the gel collapsed to provide DFB-CDP as an insoluble powder. FTIR spectroscopy of DFB-CDP indicated the presence of **1** and β -CD moieties in the polymer (Figure S4). Bands at 3330 , 2930 , and 1020 cm^{-1} correspond to O–H stretching, aliphatic C–H stretching, and C–O stretching modes, respectively, which are diagnostic of β -CD. The spectrum also showed absorbances at 1460 cm^{-1} , corresponding to aromatic C–C stretches. It is difficult to determine the regiochemistry of the ether linkages formed during the polymerization of DFB-CDP because its solid-state ^{19}F NMR spectrum exhibited broad resonances (Figure S8). Model reactions of **1** with *n*-BuOH and cyclohexanol suggest the DFB-CDP polymer contains the expected fluorinated biphenyls, which are primarily (but not exclusively) 4-substituted or 4,4'-disubstituted by alkoxy groups (Figures S1–S3). These observations, combined with elemental analysis (C, H, N, F; Table S2), confirmed the formation of the DFB-CDP polymer network.

The optimal composition of DFB-CDP for PFOA removal was determined by conducting the polymerization using **1**: 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 (Table S2), corresponding to larger amounts of fluorinated biphenyl groups in the polymer. Given the complex mixture of products observed in model substitution reactions of **1**, it is difficult to determine the **1**: β -CD ratios of a DFB-CDP without further assumptions. For example, **1**: β -CD feed ratios of 3 and 5 provided DFB-CDP with 24.33 and 31.06 wt % fluorine, respectively. These fluorine contents correspond to **1**: β -CD ratios of 3.4 and 5.8, assuming disubstitution of all DFB groups. These estimates are reasonable upper bounds given that they do not account for the partial incorporation of monosubstituted DFB groups, which is increasingly likely at higher **1**: β -CD feed ratios. In contrast to the permanent porosity and high surface area of P-CDP, the DFB-CDP samples were nonporous, with Brunauer–Emmett–Teller surface areas (S_{BET}) $< 10 \text{ m}^2 \text{ g}^{-1}$ (Figure S6). Although in preliminary experiments we obtained a permanently porous sample ($S_{\text{BET}} = 140 \text{ m}^2 \text{ g}^{-1}$) of DFB-CDP, it had lower PFOA affinity compared to the best performing nonporous derivatives described here.

The PFOA removal efficiency of each sample was characterized in a batch experiment using $[\text{PFOA}]_0$ of $1 \mu\text{g L}^{-1}$, similar to that of contaminated water resources, and $[\text{DFB-CDP}]$ of 10 mg L^{-1} (Figure 1A). Each of the DFB-CDP polymers adsorbs PFOA under these conditions and approaches its equilibrium binding concentration after approximately 13 h. Polymers with the highest fluorine content (derived from **1**: β -CD feed ratios ≥ 5) reduced the $[\text{PFOA}]$ concentration by 50–80% within 13.5 h, after which little further change was observed. DFB-CDP polymer derived from **1**: β -CD feed ratio of 3 removed PFOA

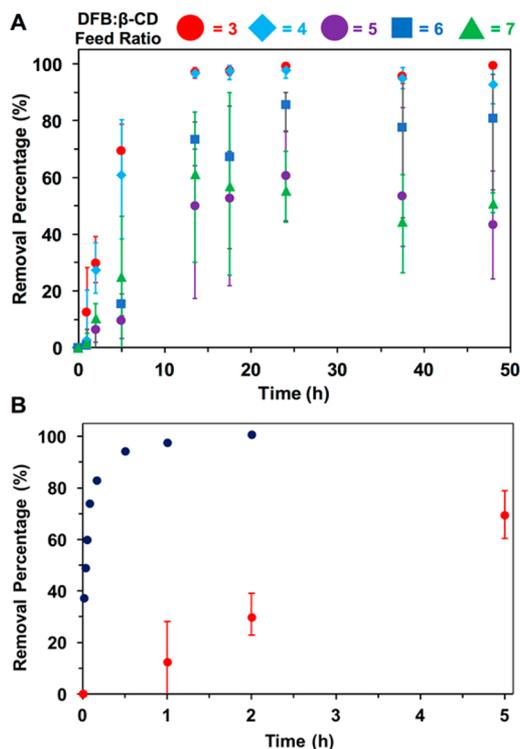


Figure 1. (A) Time-dependent PFOA adsorption ($[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$) of DFB-CDP samples (10 mg L^{-1}) of varying DFB: β -CD feed ratio. Experiments were performed in triplicate; error bars indicate maximum and minimum measured values. (B) Kinetics of PFOA adsorption by DFB-CDP (DFB: β -CD feed ratio = 3) at high concentration (blue, $[\text{PFOA}]_0 = 200 \mu\text{g L}^{-1}$; $[\text{DFB-CDP}] = 400 \text{ mg L}^{-1}$; average of two experiments) and low concentration (red, $[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$; $[\text{DFB-CDP}] = 10 \text{ mg L}^{-1}$; average of three experiments).

to concentrations $<10 \text{ ng L}^{-1}$ within 24 h, and over 95% of the total removal was achieved within 13.5 h. A DFB-CDP sample derived from a **1**: β -CD feed ratio of 4 exhibited similar kinetics and only slightly inferior removal, achieving PFOA concentrations $<20 \text{ ng L}^{-1}$ after 24 h. This PFOA concentration is well below the established health advisory level set by the EPA (70 ng L^{-1}). The inferior performance of the most heavily cross-linked DFB-CDP polymers is consistent with findings of Karoyo and Wilson,^{26,27} who concluded heavily substituted β -CD-containing polyurethanes were too sterically hindered to form inclusion complexes. On the basis of these observations, we speculate that the best performing DFB-CDP polymers provide an optimal combination of accessible β -CDs, cross-linkers, and free hydroxyl groups, which work in combination to bind PFOA. Calorimetry of the PFOA adsorption process and/or isolated PFOA@DFB-CDP samples may provide additional insight into the relevant noncovalent interactions in the future.

DFB-CDP derived from a **1**: β -CD feed ratio of 3 removed PFOA with comparable kinetics relative to GAC. Additional kinetic adsorption experiments conducted at higher $[\text{PFOA}]_0$ ($200 \mu\text{g L}^{-1}$) and $[\text{DFB-CDP}]$ (400 mg L^{-1}) showed nearly complete PFOA removal within 2 h. 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,³⁴ which provides a figure-of-merit for how quickly an adsorbent reaches equilibrium, k_{obs} , which is $2.88 \text{ g mg}^{-1} \text{ h}^{-1}$ at $[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$ and $[\text{DFB-CDP}] = 10 \text{ mg L}^{-1}$ and $64.8 \text{ g mg}^{-1} \text{ h}^{-1}$ at $[\text{PFOA}]_0 = 200 \mu\text{g L}^{-1}$ and $[\text{DFB-CDP}] = 400 \text{ mg L}^{-1}$. These values of k_{obs}

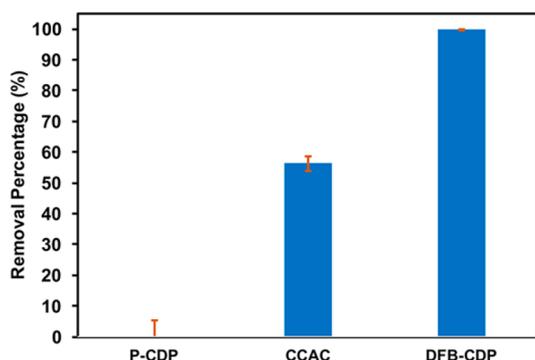


Figure 2. Equilibrium PFOA removal efficiency ($[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$) by equal mass concentrations (10 mg L^{-1}) of P-CDP, CCAC, and DFB-CDP. Error bars: standard deviation of five experiments.

are superior to those of GAC and most PACs reported in the literature (Table S4). In evaluating the kinetics and affinity of a high-end PAC (sieved coconut shell activated carbon, CCAC, $S_{\text{BET}} = 1085 \text{ m}^2 \text{ g}^{-1}$), we measured a k_{obs} of $594 \text{ g mg}^{-1} \text{ h}^{-1}$ under similar low $[\text{PFOA}]_0$ used for DFB-CDP. This value is anomalously high compared to those reported for other PACs in the literature (Table S4), though it is important to note that CCAC achieves inferior PFOA removal under these conditions (see Figure 2). Overall, the kinetics of PFOA adsorption of DFB-CDP appear comparable to leading PAC and are therefore superior to GACs.

DFB-CDP removes PFOA to lower equilibrium concentrations than other adsorbents on an equivalent mass basis (Figure 2). We compared its equilibrium removal efficiency to P-CDP ($S_{\text{BET}} = 218 \text{ m}^2 \text{ g}^{-1}$, Scheme 1), which rapidly removes many organic micropollutants,^{32,33} and CCAC. The equilibrium PFOA removal was evaluated using $[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$ and $[\text{adsorbent}] = 10 \text{ mg L}^{-1}$. 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.

We attribute much of the DFB-CDP's desirable PFOA adsorption performance to its cyclodextrin binding sites with superior PFOA affinity relative to other adsorbents. A PFOA binding isotherm (Figure 3) was constructed using [DFB-CDP] = 100 mg L^{-1} and $[\text{PFOA}]_0$ ranging from 1 to 12 mg L^{-1} . Fitting

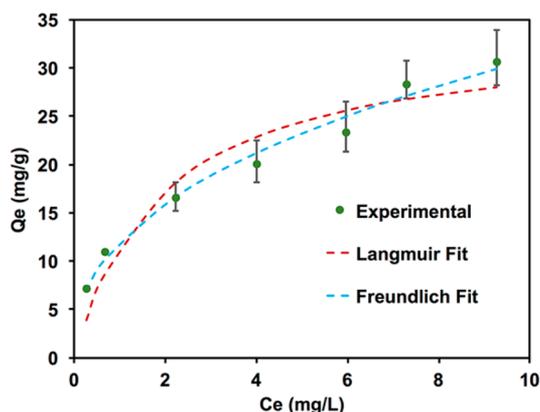


Figure 3. PFOA adsorption isotherm by DFB-CDP ($[\text{PFOA}]_0 = 1\text{--}12 \text{ mg L}^{-1}$; $[\text{DFB-CDP}] = 100 \text{ mg L}^{-1}$). Lines show fits to Langmuir (red) and Freundlich (blue) models. Error bars show the minimum and maximum uptake of three experiments.

Table 1. Langmuir and Freundlich Parameters Derived from Plots of the PFOA Binding Isotherm in Figure 2

Langmuir Fit			Freundlich Fit		
$K_L (\text{M}^{-1})$	$Q_m (\text{mg g}^{-1})$	R^2	$K_F (\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$	n	R^2
$2.2 \cdot 10^5$	34	0.96	12.0	2.4	0.99

the Langmuir model to the isotherm provides an affinity coefficient (K_L) of $2.2 \cdot 10^5 \text{ M}^{-1}$ (Table 1), which is 1 order of magnitude greater than the K_L measured for GAC of $1.8 \cdot 10^4 \text{ M}^{-1}$ and 2.5 times higher than that of PAC.²¹ This value also exceeds those of other adsorbents, such as ion-exchange resins²¹ and a recent triazine-linked polymer,³⁵ 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 34 mg g^{-1} , which is within the range of that reported for GAC (53 mg g^{-1}).³⁶ Furthermore, although the Langmuir and Freundlich models fit the adsorption isotherm well (Table 1), the Freundlich model may be more appropriate to describe equilibrium adsorption because saturation behavior is not observed over this concentration range. In this respect, the estimated capacity of the DFB-CDP polymer should be interpreted as conservative. Finally, the performance of activated carbons is strongly affected by the presence of other organic cocontaminants or NOM, whereas β -CD based polymers are less susceptible to fouling.³³ PFOA adsorption by DFB-CDP ($[\text{PFOA}]_0 = 1 \mu\text{g L}^{-1}$, $[\text{DFB-CDP}] = 10 \text{ mg L}^{-1}$) was unaffected by the presence of humic acid (20 mg L^{-1} , Figure S9), a major component of NOM. These experiments demonstrate the superior affinity and lower propensity for fouling of DFB-CDP.

As was observed for P-CDP loaded with model organic compounds,³² PFOA-contaminated DFB-CDP shows promise for facile regeneration (Figure 4). Four consecutive adsorption/desorption experiments were performed. For the adsorption experiments, $[\text{DFB-CDP}]$ (400 mg L^{-1}) and $[\text{PFOA}]_0$ ($200 \mu\text{g L}^{-1}$) were chosen. Desorption experiments were conducted by suspending the PFOA-contaminated adsorbent in MeOH (400 mg L^{-1}) 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 10 min, which shows promise for rapid and efficient regeneration of the adsorbent, a noted deficiency of PFOA-contaminated ACs.²⁹

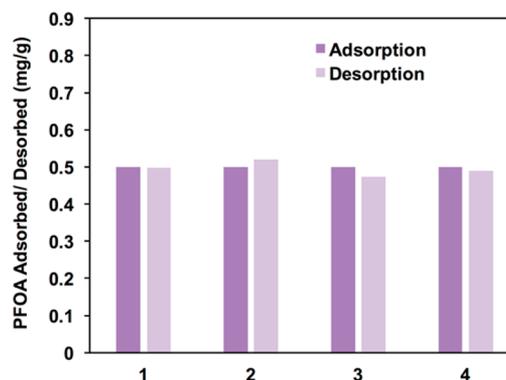


Figure 4. Regeneration and reuse of DFB-CDP by washing with MeOH. Adsorption experiments: $[\text{DFB-CDP}] = 400 \text{ mg L}^{-1}$, $[\text{PFOA}]_0 = 0.2 \text{ mg L}^{-1}$, 12 h. Desorption: DFB-CDP was suspended in MeOH for 24 h.

In conclusion, β -CD was cross-linked with decafluorobiphenyl under nucleophilic aromatic substitution conditions. The resulting DFB-CDP polymer binds PFOA with more than a 10-fold increased affinity along with comparable kinetics and capacity relative to an equivalent mass of activated carbon. Modest amounts of the polymer adsorbent reduce [PFOA] from ppb concentrations, typical of contaminated groundwater, to low ppt concentrations, well below EPA health advisory limits. DFB-CDP was also regenerated and reused multiple times after washing with MeOH at room temperature. These characteristics make DFB-CDP a promising candidate for PFOA remediation, and future work will focus on studying uptake of other PFASs in contaminated groundwater. Finally, this study demonstrates the selectivity of CD-based polymer adsorbents may be tuned through the judicious modification of their composition.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b02381.

Experimental procedures and details (PDF)

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Notes

The authors declare the following competing financial interest(s): Cornell University has filed patent applications related to the cyclodextrin polymer studied in this paper. W.R.D. and D.E.H. serve on the scientific advisory board and have equity and/or stock purchase options in CycloPure, Inc., which is commercializing related cyclodextrin polymers.

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