Rapid and Efficient Removal of Perfluorooctanoic Acid from Water with Fluorine-Rich Calixarene-Based Porous Polymers

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ABSTRACT: On account of its non-biodegradable nature and persistence in the environment, perfluorooctanoic acid (PFOA) accumulates in water resources and poses serious environmental issues in many parts of the world. Here, we present the development of two fluorine-rich calix[4]arene-based porous polymers, **FCX4-P** and **FCX4-BP**, and demonstrate their utility for the efficient removal of PFOA from water. These materials featured BET surface areas of up to 450 m² g⁻¹, which is slightly lower than their non-fluorinated counterparts (up to 596 m² g⁻¹). **FCX4-P** removes PFOA at environmentally relevant concentrations with a high rate constant of 3.80 g mg⁻¹ h⁻¹ and reaches an exceptional maximum PFOA uptake capacity of 188.7 mg g⁻¹. In addition, it can be regenerated by simple methanol wash and reused without a significant decrease in performance.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals that are extensively used in clothing, furniture, cookware, and firefighting industries for their oil, grease, and water repellency.¹ PFAS contain C-F bonds, which are known to be among the strongest chemical bonds resistant to degradation.² On account of the fact that PFAS-producing companies are facing lawsuits to compensate for the environmental problems caused by these persistent perfluorinated compounds, efficient methods for the removal of PFAS from water are now in high demand. Perfluorooctanoic acid (PFOA) is one of the most commonly utilized PFAS. PFOA concentrations three to four orders of magnitude higher than the lifetime health advisory of 70 ng L⁻¹ determined by the Environmental Protection Agency were discovered in ground and surface waters close to civilian airports and fire-fighting training areas.³ Additionally, PFOA was detected in the majority of serum samples collected from populations worldwide, and the most possible exposure pathway was reported to be drinking water.⁴ Therefore, there is a pressing need to find a straightforward, economical, and efficient method to solve the problem of global PFOA and PFAS contamination.

Various oxidative, reductive, photochemical, and electrochemical methods for PFOA sequestration or degradation have been reported.^{5–8} However, PFOA does not lend itself to facile removal techniques; the high stability of C–F bonds with the bond dissociation energy of up to 130 kcal mol⁻¹ results in PFOA's resistance to metabolic degradation and conventional decontamination methods.^{9,10} Certain removal approaches are limited by the sensitivity of the analytical methods used (up to mg L⁻¹) for detection, which is a significant drawback as trace amounts (ng L⁻¹ to low µg L⁻¹) of PFOA in the environment can induce toxic effects in living organisms.¹¹ Many degradation techniques result in the formation of short-chain polyfluorinated alkyl substances of unknown toxicity.¹² For this reason, significant research has been dedicated to using adsorption for the removal of PFOA from water because adsorbents remove PFOA instead of degrading it. In addition, adsorbents have reasonable rates of removal, low costs, high surface-area-to-volume ratios, and an abundance of adsorption sites.¹³ The most commonly used adsorbent for PFOA removal is activated carbon (AC). Despite being affordable and relatively efficient at removing PFOAs, ACs suffer from low affinity for PFOA at environmentally relevant concentrations,¹⁴ and their regeneration is energy-intensive.¹⁵ Thus, developing materials with high

PFOA affinity and ease of regeneration is key to improving the performance of adsorbents used for PFOA removal from water.¹⁶

One class of materials that can address this challenge is macrocycle-containing porous organic polymers, whose utility can be tailored by the rational choice of organic monomers, which allows for optimization of molecular architecture and host-guest interactions.^{17,18} Recently, β -cyclodextrin-containing polymers showed some affinity for PFOA ($Q_{\max} = 34 \text{ mg g}^{-1}$) with uptake kinetics comparable to that of commercial AC ($k_{\text{obs}} = 2.88 \text{ g mg}^{-1} \text{ h}^{-1}$).^{19,20} Highly fluorinated covalent organic polymers (COPs) were found to reduce PFOA concentration from $1 \mu\text{g L}^{-1}$ to $<10 \text{ ng L}^{-1}$.¹⁹ PFOA removal by solid phase extraction²¹ and in packed beds²² has also been explored. However, the cyclodextrin polymers have a relatively low $Q_{\max}$ value and their rate of adsorption is also fairly slow. Therefore, investigation of alternative building blocks for covalent polymers is of high interest.

Herein, we report our efforts to leverage the benefits of porous organic polymers and to introduce porous calixarene-based polymers with fluorinated alkyne-rich linkers that can efficiently remove PFOA from water.^{23–25} Calixarene macrocycles can be exploited for their amphiphilic nature around the rim,²⁶ whereas the fluorinated linkers make the overall network even more hydrophobic and enhance C-F $\cdots$ F-C interactions between the polymers and guest molecules. Furthermore, calixarenes possess a hydrophobic cavity, which can facilitate favorable host-guest interactions.²⁷ The current study aims to investigate the synergy between the inherent host-guest chemistry and hydrophobic properties of polycalixarenes with the enhanced hydrophobicity and C-F interactions of fluorinated linkers.

RESULTS

Given that calixarene-based porous polymers are efficient agents for the removal of various organic micropollutants from water,²⁸ we anticipated that introducing fluorine-rich moieties, in the form of perfluoroarene linkers, would enhance the hydrophobic interactions between the adsorbent and PFOA. Such a system would also simultaneously maintain hydrogen bonding between the hydroxyl groups of the macrocycle and PFOA,²⁹ thus facilitating PFOA removal from water. In line with our hypothesis, one of the designed polymers, **FCX4-P**, displayed excellent adsorption ability, which was quantified by HPLC-MS/MS/MS. The performance analysis of this material indicated that **FCX4-P** was a superior adsorbent as compared to commercial AC and a non-fluorinated analogue of the polymer, **CX4-P**. Moreover, we found that **FCX4-P** has one of the fastest reported PFOA adsorption kinetics at environmentally relevant concentrations and one of the highest maximum adsorption capacities for any class of material.

Non-fluorinated polymers used as benchmark materials in this study were synthesized through Sonogashira-Hagihara coupling between tetrabromo-calix[4]arene-tetrol, **1**, and the non-fluorinated versions of linkers **2** and **3**, either 1,4-diethynylbenzene or 4,4'-diethynyl-1,1'-biphenyl, to form **CX4-P** and **CX4-BP**, respectively.^{30,31} To obtain the fluorinated polymers, the fluorinated versions of linkers **2** and **3** were first synthesized through Sonogashira-Hagihara coupling reactions between either 1,4-diiodo-2,3,5,6-tetrafluorobenzene or 4,4'-dibromooctafluoro biphenyl with (trimethylsilyl)acetylene (compounds **2a** and **3b** in the SI), followed by deprotection of the

silyl groups with tetra-*n*-butylammonium fluoride to afford the linkers in good yields.³² Subsequent Sonogashira-Hagihara coupling of the fluorinated linkers, **2** and **3**, with tetrabromo-calix[4]arene-tetrol, **1**, in a 1:1 mixture of toluene and triethylamine led to the isolation of brown powders, **FCX4-P** and **FCX4-BP**, respectively, after heating at 110°C for 70 h (Scheme 1). The resulting polymers were washed with toluene, ethanol, water, tetrahydrofuran, and dichloromethane, and dried under vacuum for 16 hours. All polymers were insoluble in all tested solvents, indicating the formation of cross-linked polymeric networks. Fourier transform infrared (FT-IR) spectra of **FCX4-P** and **FCX4-BP** exhibited absorption bands at 1267 and 1257 cm^{-1} , respectively (Figure 1a), which corresponded to C–F stretches. For all four polymers, a broad band corresponding to the –O–H stretching vibration of calixarene was observed near 3100 cm^{-1} (Figure S1 and 1a). The presence of the asymmetric C $\equiv$ C– stretching vibrations near 2250 cm^{-1} and the absence of the terminal alkyne C–H stretching vibrations at 3300 cm^{-1} in the polymers confirmed successful crosslinking of the linkers with the brominated calixarene monomers. Further molecular-level characterization of the polymers was achieved by solid state NMR spectroscopy. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra (Figure 1b) exhibited resonances in the range of 105 – 145 ppm , which correspond to the aromatic carbons of the calixarene macrocycle and the fluorinated linkers.

Scheme 1. a) Design strategy for the synthesis of fluorinated and non-fluorinated calix[4]arene polymers, **FCX4-P**, **FCX4-BP**, **CX4-P**, and **CX4-BP**. b) Schematic presentation of representative fluorinated polymer and its utility as PFOA sorbent. Cyan cones correspond to calixarenes, purple hexagons with green endings to the fluorinated linker, pink spirals to PFOA and brown spheres to the OH groups of calixarene.

Figure 1. (a) FT-IR spectra of as-synthesized **FCX4-P** (purple) and **FCX4-BP** (blue), linkers **2** and **3** (red and orange) and 5,11,17,23-tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (**1**) (green); (b) ¹³C CP/MAS NMR spectrum of **FCX4-P** and **FCX4-BP** with corresponding peak assignments; (c) ¹⁹F solid-state NMR spectra of **FCX4-P** and **FCX4-BP**; (d) N₂ adsorption and desorption isotherms for **FCX4-P**, **FCX4-BP** and the corresponding non-fluorinated polymers, **CX4-P** and **CX4-BP**.³¹

The peak near 25 ppm was assigned to the phenylene carbons (-CH₂-) of the macrocycle, while the peak near 90 ppm indicated the presence of the acetylene (-C≡C-) moieties. Solid-state ¹⁹F NMR spectra for both polymers exhibited a signal at -141.4 ppm, reflecting the fact that there is only one fluorine environment in both polymers, a characteristic which is due to strong dipolar coupling between neighboring fluorine atoms (Figure 1c).

The morphology of the resulting polymers was analyzed by electron microscopy techniques. Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses of the polymers revealed the material to be comprised of amorphous clumps (Figure S3). Thermogravimetric analyses (TGA) revealed exceptional thermal stability of the polymers up to 500 °C (Figure S4). At that temperature, ~ 80 % of fluorinated and ~ 90 % of non-fluorinated polymers are degraded.

The porosity of the polymers was studied by N₂ gas adsorption/desorption measurements following degassing of the samples at 85 °C for 24 hours (Figure 1d). Fitting of the N₂ isotherms to the BET model provided calculated surface areas of 596, 468, 417, and 451 m² g⁻¹, for **CX4-P**, **CX4-BP**, **FCX4-P**, and **FCX4-BP**, respectively. The slightly lower surface area of fluorinated polymers could be explained by the larger size of fluorinated linkers whereby the fluorine atoms occupy more space. Average pore diameters for the materials ranged from 48 to 95 Å (Figure S5), with cumulative pore volumes ranging from 0.11 to 0.73 cm³ g⁻¹.

To evaluate the PFOA removal efficiency of each polymer, batch adsorption studies were conducted with 1 µg L⁻¹ of PFOA, which is comparable to the amount of PFOA present in contaminated water resources.³³

Figure 2. PFOA adsorption experiments. (a) Percent removal of PFOA over the course of 80 hours by single batches of **FCX4-P**, **FCX4-BP**, **CX4-P** and **CX4-BP**. The error bars represent the average % removal of three independent experiments. (b) Fitting of the kinetics data in panel (a) to pseudo-second order model of adsorption and the associated rate constants of adsorption (k_{obs}); (c) linear forms of Langmuir isotherms along with calculated Q_{max} values for **FCX4-P** (purple), **FCX4-BP** (blue), **CX4-P** (red) and **CX4-BP** (orange); (d) regeneration experiments with **FCX4-P** and **FCX4-BP** demonstrate uncompromised PFOA removal efficiency in at least four adsorption cycles.

The PFOA adsorption experiments were conducted with vacuum-dried adsorbents at neutral pH, and the concentration of PFOA was measured by HPLC-MS/MS (details in the SI). It was observed that fluorinated polymers (79 – 100 % removal) performed much better than their non-fluorinated analogues (23 – 64 % removal). Polymer **FCX4-P** was particularly efficient at removing PFOA as it reached close to 100 % removal in 80 hours. We quantified the adsorption kinetics by using Ho and McKay's pseudo-second-order adsorption model,³⁴ which enabled us to obtain the apparent rate constant (k_{obs}) of $3.80 \text{ g mg}^{-1} \text{ h}^{-1}$ for **FCX4-P**, $1.40 \text{ g mg}^{-1} \text{ h}^{-1}$ for **FCX4-BP**, $1.30 \text{ g mg}^{-1} \text{ h}^{-1}$ for **CX4-BP**, and $1.13 \text{ g mg}^{-1} \text{ h}^{-1}$ for **CX4-P** (Figure 2b). It is difficult to compare these results to the majority of PFOA adsorbents reported in the literature, because they use initial PFOA concentrations that exceed environmentally relevant levels by several orders of magnitude (Table S1). Nevertheless, there are two reports using comparable concentrations of PFOA in kinetic experiments. A β -cyclodextrin polymer¹⁹ and

poly(ethylenimine)-functionalized cellulose microcrystals³⁵ were reported to have k_{obs} values of $2.88 \text{ g mg}^{-1} \text{ h}^{-1}$ and $0.213 \text{ g mg}^{-1} \text{ min}^{-1}$, respectively. However, these two materials suffer from relatively low maximum PFOA uptake capacities (Q_{max}) of 33 mg g^{-1} and 2.32 mg g^{-1} , respectively. We also investigated the probability of intra particle diffusion mechanism by plotting Q_t as a function of $t^{0.5}$ using the equation: $Q_t = K_p t^{0.5} + C$ where K_p is the intra particle diffusion rate constant and C is the constant that define the boundary layer effect.³⁶ For all the tested polymers we observed that there is a two-step adsorption process, an initial sharper one and a later more gradual one, which is controlled by particle diffusion (Figure S6).

In order to determine the maximum PFOA uptake capacity of our polymers, we conducted isotherm studies in which 5 – 100 mg L^{-1} PFOA solutions were incubated with the adsorbents until equilibrium was reached (details in Supporting Information). After quantifying the residual amounts of PFOA, the data was

fitted to the Langmuir model of adsorption and $Q_{\max}$ values were calculated (Figure 2c). **FCX4-P**, which was already found to have the fastest PFOA uptake in our polymer series, reached the highest $Q_{\max}$ of 188.7 mg PFOA adsorbed per gram of adsorbent. This value is almost six times higher than what is reported

for the β -cyclodextrin-based polymer,¹⁹ nine times higher than the capacity of silica,³⁷ 81 times larger than $Q_{\max}$ of poly(ethyl-enimine)-functionalized cellulose microcrystals³⁵, and over

Figure 3. Radial distribution functions of specific interactions between the polymers and PFOA/water molecules. (a) O-Ho; (b) O-Hw; (c) HL-Ho and F-Ho; and (d) HL-Hw, F-Hw. (O is oxygen of calixarene in all polymers, HL is hydrogen of linkers in **CX4-P** and **CX4-BP**, F is fluorine of linkers in **FCX4-P** and **FCX4-BP**, Ho is carboxyl hydrogen of PFOA, and Hw is hydrogen of water. See Figure S7 for illustration of atom types and Figure S10 for simulation snapshots that illustrates PFOA-polymer interactions).

1,400 times higher than $Q_{\max}$ of granulated activated carbon³⁸ (Table S1). These results combined suggest that **FCX4-P** has one of the fastest PFOA adsorption kinetics at environmentally relevant concentrations and one of the highest maximum adsorption capacities for PFOA of any class of material. The performance of **FCX4-BP** is similar, with a $Q_{\max}$ of 169.5 mg g⁻¹, while non-fluorinated polymers exhibited noticeably lower values of 69.4 mg g⁻¹ and 77.5 mg g⁻¹ for **CX4-BP** and **CX4-P**, respectively. The performance of this material, in comparison with known PFOA adsorbents, demonstrates the great potential of fluorinated calixarene polymers for this type of application.

A major advantage of the herein reported polymers for PFOA adsorption is their ability to be regenerated without compromising their adsorption capacity. Simple methanol washes for an extended period at room temperature were sufficient to regenerate **FCX4-P** and **FCX4-BP** (Figure 2d; details in Supporting information). Both materials retained their percent PFOA removal ability for the four consecutive tested cycles. **FCX4-P** removed 91, 92, 93, and 94 % of the pollutant, while **FCX4-BP** removed 82, 82, 74, and 75 % of PFOA in four respective cycles. These results demonstrate the potential for long-term use

of our porous fluorinated calixarene-based polymers for PFOA removal.

Given the findings of Omorodion et al., who studied the nature of non-covalent interactions in calixarene-PFOA host-guest complexes,²⁹ we speculated that the primary interaction responsible for the successful adsorption of PFOA by the polymers is the hydrogen bond between the carboxylic group of PFOA and a hydroxyl oxygen of the calixarene. We also surmise that additional stabilization may be achieved by C-F $\cdots$ F-C interactions³⁹ between PFOA and the fluorinated linkers in **FCX4-P** and **FCX4-BP**. To test these hypotheses, we resorted to atomistic Monte Carlo (MC) simulations of PFOA and water. Polymer sheets representative of **CX4-P**, **CX4-BP**, **FCX4-P**, and **FCX4-BP** (see SI for details) were sampled for binding sites using a PFOA and a water molecule. Radial distribution functions (RDF) obtained from MC simulations allowed for comparisons to be made between the interactions of the polymers with PFOA/water (Figure 3). For all polymers, we found that hydrogen bonding is the main interaction between the polymer and its environment, and that the effect of C-F $\cdots$ F-C interaction is rather marginal (Figure S9).

The hydroxyl groups of the calixarenes are the preferential binding sites for both PFOA and water. For PFOA, this is evidenced by peaks near 1.8 Å between the oxygen of the calixarenes and the carboxyl hydrogen of PFOA, denoted as O-Ho (Figure 3a). Similarly, water hydrogen bonds with the oxygen atoms of the calixarene ring, denoted as O-Hw (Figure 3b). It is clear that both PFOA and water are expected to compete for the calixarene ring during adsorption for all polymers, whether fluorinated or not.

It was also found that fluorination leads to dramatic changes in the way the linkers interact with PFOA and water. In **CX4-P** and **CX4-BP**, the RDFs for the hydrogen atoms of the linkers and the carboxyl hydrogen atoms of the PFOA, denoted as HL-Ho, exhibited broad peaks around 3.4 Å (Figure 3c), which indicated that there were relatively weak interactions between PFOA and the linkers. For water, the interactions with the linkers are also limited, as such, the RDFs for the hydrogen atoms of the linkers and the hydrogen atoms of water, denoted as HL-Hw, showed only weak structuring around 3.8 Å (Figure 3d). In **FCX4-P** and **FCX4-BP**, however, substitution of the linker hydrogen atoms with fluorine atoms resulted in tighter PFOA binding to the linkers. This is demonstrated by the peaks observed at 2 Å in the RDFs for the fluorine atoms of the linkers and the carboxyl hydrogen atoms of the PFOA, denoted as F-Ho (Figure 3c). To understand the nature of this affinity, we computed the binding energy of PFOA to the polymers (see SI for details). Indeed, energy calculations revealed that fluorination increases the binding strength of PFOA to the linkers (see SI for details). The binding energy was reduced by 3.8 and 2.4 kJ/mol for **FCX4-P** and **FCX4-BP**, respectively, in accordance with the experimental observations and RDF analysis. On the other hand, after fluorination, water-linker interactions became weaker, as the RDFs between the fluorine atoms of the linkers and the hydrogen atoms of water, denoted as F-Hw, did not show any structuring (Figure 3d). This also suggests that fluorine rich PFOA molecules, when adsorbed, can exclude water adsorption in the pores. All in all, our simulations provide strong evidence that fluorination creates new sites on the linkers for the adsorption of PFOA, which no longer needs to compete with water. In addition, fluorination stabilizes PFOA at the new

binding site; resulting in enhanced PFOA binding to **FCX4-P** and **FCX4-BP**, as compared to the non-fluorinated polymers, **CX4-P** and **CX4-BP**.

CONCLUSIONS

In summary, we have developed two fluorine-rich calix[4]arene-based porous polymers and evaluated their efficiency for removing PFOA from water. Polymer **FCX4-P** removed PFOA more efficiently than any other adsorbent tested and exhibited a very high uptake capacity along with fast adsorption kinetics. By comparing its performance with non-fluorinated calixarene polymers, we conclude that the development of favorable C-F $\cdots$ F-C interactions between PFOA and the fluorinated linkers are essential for the excellent performance of our material. Additionally, PFOA adsorption was found to be reversible, as PFOA can be desorbed by simple methanol washing, and the polymers were able to be recycled without significant performance loss. Monte Carlo simulations used to understand the mechanism of PFOA adsorption, highlight the importance of hydrogen bonding between the carboxylic group of PFOA and the hydroxyl groups of calixarenes, and the role of hydrophobic interactions between fluorinated linkers and PFOA. The latter explained the higher affinity of fluorinated polymers for PFOA. Efforts are currently underway to explore the potential large-scale applicability of fluorinated calixarene polymers towards target-specific molecular sequestration and environmental remediation of waters. Our findings illustrate that macrocycle-based porous polymers are a viable alternative technology for water decontamination with horizons trending towards applications for the purification of valuable multi-sourced products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing interests.

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