

# Rapid Removal of Poly- and Perfluorinated Alkyl Substances by Poly(ethylenimine)-Functionalized Cellulose Microcrystals at Environmentally Relevant Conditions

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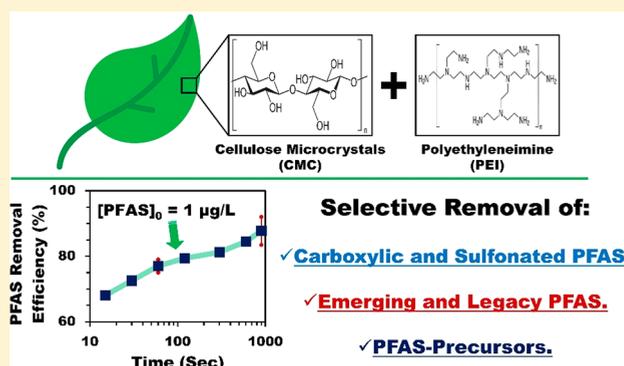
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## S Supporting Information

**ABSTRACT:** Per- and polyfluoroalkyl substances (PFAS) are ubiquitous in many consumer products and present serious environmental challenges due to their persistent nature. Currently, conventional water treatment methods fail to remove PFAS, and other newly proposed materials/techniques face challenges when employed under realistic conditions. This study reports on poly(ethylenimine)-functionalized cellulose microcrystals (PEI-*f*-CMC) that showed a near-instant and high removal of PFAS under concentrations relevant to their actual occurrence in the natural environment (i.e., <1000 ng/L). The selective removal efficiency of 22 PFAS from different classes (i.e., legacy carboxylic and sulfonated PFAS, emerging carboxylic and sulfonated PFAS, and PFAS-precursors) using PEI-*f*-CMC was confirmed in lake water as well as solutions codosed with two additional types of natural organic matter. The performance of PEI-*f*-CMC was maintained in eight consecutive adsorption/regeneration cycles to remove PFAS. The PEI-*f*-CMC with its unique fast kinetics and high adsorption activity toward PFAS exhibits a great potential for being a promising alternative adsorbent for PFAS control.



## INTRODUCTION

Poly- and perfluorinated alkyl substances (PFAS) represent a large family of organic compounds that are widely used as processing additives during fluoropolymer production and as surfactants in consumer applications (e.g., surface coatings for textiles, furniture, and paper products) over the past seven decades.<sup>1–3</sup> The molecular structures of these compounds have an aliphatic chain (or multiple chains) with either all (i.e., per-) or part (i.e., poly-) of the hydrogens replaced by fluorine atoms in such a way that they contain at least one perfluoroalkyl moiety (C<sub>n</sub>F<sub>2n+1</sub>). In recent years, the occurrence, fate, and removal of PFAS in the aquatic environment have been documented as a key emerging environmental issue.<sup>4–7</sup> Thus, the U.S. Environmental Protection Agency issued a health advisory level of 70 ng/L for the combined concentrations of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in drinking water.<sup>8</sup> However, emerging PFAS like chlorinated poly-(fluorinated ether sulfonate) (F53B) and ADONA, used as fluorinated alternatives of PFOS and PFOA in fluoropolymer industry, are now being increasingly detected in the environment.<sup>9</sup>

The most studied technique to remove of PFAS is adsorption on different carbonaceous materials (e.g., granular activated carbon (GAC), powdered activated carbon (PAC), and carbon nanotubes (CNT)) and anion-exchange resin (AIX) (e.g., Merino et al.,<sup>10</sup> Du et al.<sup>11</sup> and references therein), because these techniques are operationally simple and require minimal energy expenditure. The two main PFAS adsorption mechanisms are hydrophobic and electrostatic interactions.<sup>11</sup> Hence, coexisting natural organic matter (NOM) in fresh waters have shown an adverse effect on the efficiency of PFAS adsorption.<sup>12–14</sup> As a result, the development of selective adsorbents with high affinity and rapid removal of PFAS is critical to overcoming this emerging environmental and health problem.

Cellulose is inexpensive, renewable, eco-friendly, and is the most abundant polymer in nature.<sup>15</sup> Functionalized cellulose microcrystals (CMC) have been tested for the removal of

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Table 1. Characteristics of CMC before and after Functionalization with PEI

material	SA (m <sup>2</sup> /g) <sup>a</sup>	PV <sub>total</sub> (cm <sup>3</sup> /g) <sup>a</sup>	PV <sub>macro</sub> (%) <sup>a</sup>	PV <sub>meso</sub> (%) <sup>a</sup>	PV <sub>micro</sub> (%) <sup>a</sup>	C (%) <sup>b</sup>	O (%) <sup>b</sup>	N (%) <sup>b</sup>	pH <sub>pzc</sub> <sup>c</sup>
CMC	3.3	0.018	27.8	72.2	0.0	57	48		6.1 <sup>d</sup>
PEI-F-CMC	7.8	0.032	18.7	81.3	0.0	76	11	9	10.9

<sup>a</sup>SA is surface area (m<sup>2</sup>/g), VP<sub>total</sub> is the total pore volume (cm<sup>3</sup>/g), VP<sub>micro</sub> is the volume of micropores (i.e., pore < 2 nm), VP<sub>meso</sub> is the volume of mesopores (i.e., 2 nm < pore < 50 nm), VP<sub>macro</sub> is the volume of macropores (i.e., pore > 50 nm). <sup>b</sup>Elemental analysis was performed by Atlantic Microlab, Inc. <sup>c</sup>pH<sub>pzc</sub> is pH of the point of zero charges. <sup>d</sup>The pH<sub>pzc</sub> for CMC was obtained from reference 22.

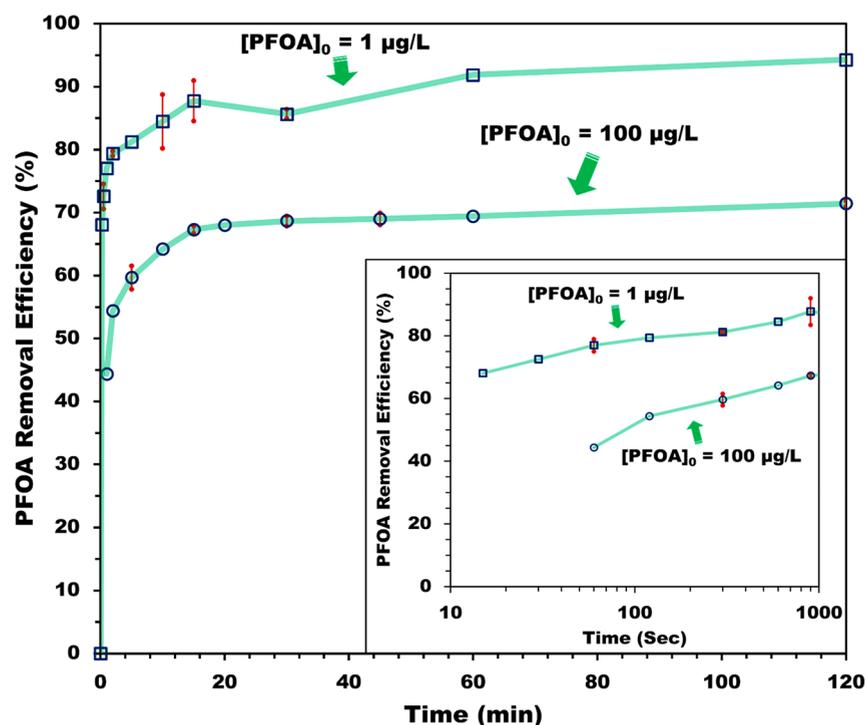


Figure 1. Effect of contact time on the adsorption for PFOA onto PEI-*f*-CMC at initial PFOA concentrations of 1 and 100 µg/L and an adsorbent dose of 20 and 50 mg/L, respectively. (inset) Magnification for the removal at the first 100–500 s. Vertical error bars represent standard deviation from 3–5 replicated experiments.

various types of water contaminants (e.g., metals, dyes, organics, inorganic anions, and radionuclides).<sup>16</sup> Among those functionalities, poly(ethylenimine) (PEI) showed an excellent performance for the adsorption of heavy metals,<sup>17</sup> anionic dyes,<sup>18</sup> and volatile organic compounds<sup>19,20</sup> due to the presence of a large number of primary and secondary amine sites that can be easily protonated in a broad pH range.<sup>21</sup> Herein, we explored poly(ethylenimine)-functionalized cellulose microcrystals (PEI-*f*-CMC, Scheme S1) for the rapid and selective sequestration of PFAS at concentrations relevant to their actual occurrence in the natural waters.

## MATERIALS AND METHODS

The PEI-*f*-CMC was prepared by (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO)-mediated oxidation and ion exchange followed by amine-functionalization as described in Section S1. The detailed material characterization for PEI-*f*-CMC using Brunauer–Emmett–Teller (BET) analyzer, scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA) are provided in Table 1 and in the Supporting Information Section S2 (Figures S1–S3). The tested 22 PFAS in this study were obtained from Wellington Laboratories Inc. (Table S1). The determination method is described in Section S3. The experimental procedures for the kinetic, effect of pH,

isotherm, effect of NOM, and regeneration tests are in Sections S4–S8.

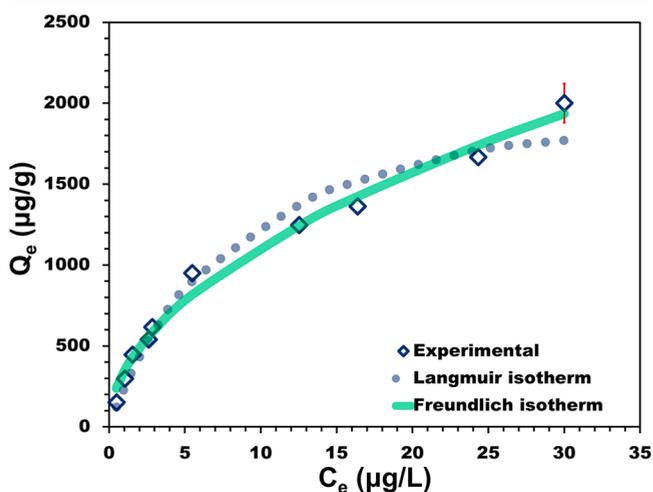
## RESULTS AND DISCUSSION

At initial PFOA concentration of 1 µg/L, PEI-*f*-CMC showed near instant removal of PFOA, and the adsorption equilibrium was observed in ~15 min with 70–80% removal within just the first 100 s (Figure 1). A similar trend was observed when the initial PFOA concentration was elevated to 100 µg/L (equilibrium time = 20–25 min). In comparison, adsorption of PFOA and PFOS on GAC Calgon Filtersorb300 (F300) and Calgon Filtersorb400 (F400) was reported to reach an equilibrium after 5–30 d at an initial concentration in the range of 5–5000 µg/L.<sup>23,24</sup> The slow removal of PFAS by GAC is attributed to its microporosity character (i.e., pore size < 2 nm). Recently, Xiao et al.<sup>25</sup> reported on the selective removal of PFOA using β-cyclodextrin polymer at low PFOA concentration conditions ([PFOA]<sub>i</sub> = 1 µg/L). However, one drawback was the slow removal at low initial concentrations with PFOA removal efficiency of only 11 ± 10% after 1 h and an equilibrium time of 15–24 h. Although other studies reported an adsorption equilibrium time of less than 48 h, they were excluded from the comparison, because they were run at initial PFAS concentrations of several hundred milligrams per

liter, which is  $1 \times 10^5$  to  $1 \times 10^7$  times higher than environmentally relevant concentrations.

As shown in Figure S4, the results showed best fitting with the pseudo-second-order kinetic model with  $R^2$  value in the range of 0.77–0.98 (Table S2). Further, the effect of pH (4.5, 6.5, 7.5, and 9.5) on the PFOA removal efficiency by PEI-*f*-CMC was tested by adding certain amounts of 0.1 M NaOH or HCl solutions. As shown in Figure S5, the pH of the point of zero charges ( $\text{pH}_{\text{PZC}}$ ) for PEI-*f*-CMC was  $10.9 \pm 0.2$ , which indicates that the surface of the material would be positively charged in solutions with lower pH values. At pH 2 to  $\sim 4$ , apparently, a small retention of protons occurs in the surface materials.<sup>26</sup> However, at pH above 11, the surface of PEI-*f*-CMC started releasing protons to the solution and decreased the final pH of the solution compared to its initial value.<sup>22</sup> The  $\text{pK}_a$  of PFOA has been reported to be between 2.8 and 3. However, there is a study that has determined the  $\text{pK}_a$  to be substantially lower ca.  $-0.5$ .<sup>27,28</sup> Whichever value is most representative, PFOA is likely deprotonated within the pH range (4.4–9.5) adopted in this study. Figure S6 shows that the removal efficiency of PFOA was as high as 85% at pH 4.4 and that the removal efficiency decreased to 78.8%, 70.4%, and 19.9% when the pH was elevated to 6.5, 7.7, and 9.5, respectively. This reduction was attributed mainly to the reduction in the number of positive sites on PEI-*f*-CMC at elevated pH values. These observations, regarding the role of PEI in the removal, were further confirmed by comparing the removal of PFOA [ $1 \mu\text{g/L}$ ] by PEI-*f*-CMC with both of pristine CMC and TEMPO-oxidized CMC. The results showed that both pristine CMC and oxidized CMC did not show any PFOA removal, while PFOA concentration dropped to less than our detectable limits (limit of detection (LOD) for PFOA =  $5 \text{ ng/L}$ ; Table S1) after adsorption on PEI-*f*-CMC.

The adsorption isotherm was obtained by fixing the PEI-*f*-CMC concentration at  $10 \text{ mg/L}$  and elevating PFOA concentration in the range from  $2$  to  $50 \mu\text{g/L}$  (Figure 2). The experimental data were fitted with Langmuir and Freundlich isotherm models, and the results showed a better fit with the Freundlich model ( $R^2 = 0.99$ ; Table 2). Although PEI-*f*-CMC has low surface area ( $\text{SA}_{\text{BET}} = 7.8 \text{ m}^2/\text{g}$ ), compared to conventional carbonaceous adsorbents ( $\text{SA}_{\text{BET}} =$



**Figure 2.** Adsorption isotherm of PFOA on PEI-*f*-CMC. Initial PFOA =  $2$ – $50 \mu\text{g/L}$  with adsorbent dose of  $10 \text{ mg/L}$  at pH 6.5. Vertical error bars are standard deviation from triplicated experiments.

**Table 2.** Parameters for Isotherm Models' Fitting for PFOA Adsorption on PEI-*f*-CMC

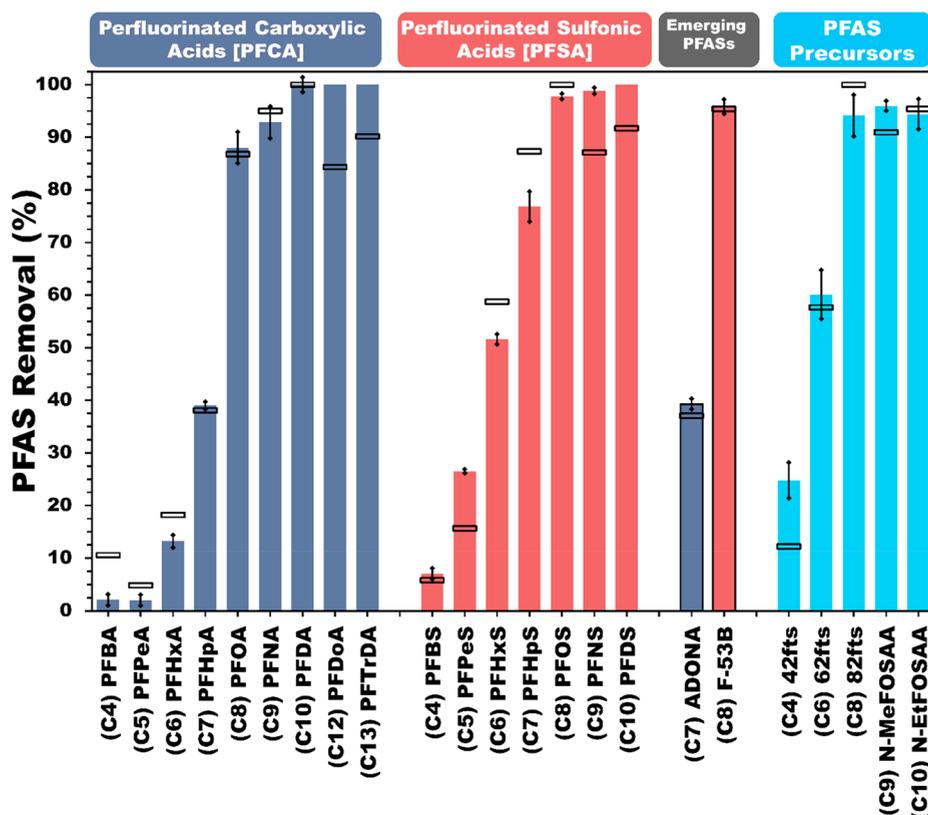
Langmuir model			Freundlich model		
$Q_{\text{max}}$ (mg/g)	$b$	$R^2$	$K_F$ ((mg/g)(L/mg) <sup>1/n</sup> )	$1/n$	$R^2$
2.32	115.2	0.96	11.46	1.97	0.99

$900$ – $2000 \text{ m}^2/\text{g}$ ) and minerals ( $\text{SA}_{\text{BET}} = 80$ – $300 \text{ m}^2/\text{g}$ ), the adsorption affinity was high as compared to GAC (i.e., coconut shell-, coal-, biochar-, wood-based GAC), activated carbon fibers, boehmite, alumina, and  $\beta$ -cyclodextrin polymer (detailed comparison in Table S3). It must be highlighted that most of these previously tested adsorbents were evaluated at high PFOA concentrations and that the equilibrium time ranged from 24 h to 14 d.

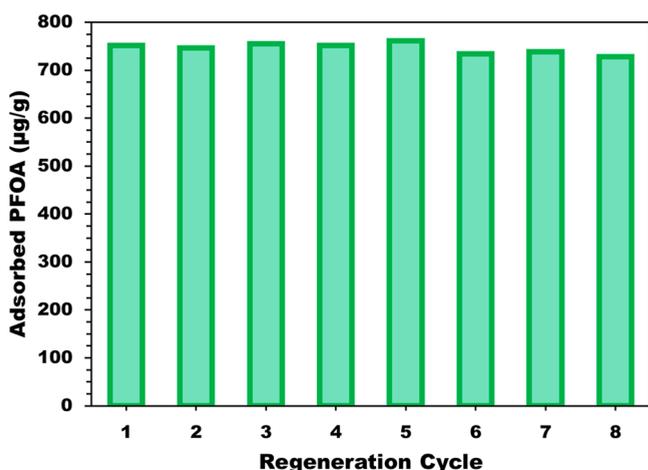
Conventional adsorbents (e.g., GAC or AIX) exhibited a dramatic drop in the PFAS removal efficiency in the presence of NOM, which is omnipresent in natural waters.<sup>29–31</sup> More specifically, the competitive adsorption of organic molecules with low specific ultraviolet absorbance ( $\text{SUVA}_{254}$ ) and small molecular weight ( $\text{MW} < 1 \text{ kDa}$ ) was much higher than that of macromolecules ( $\text{MW} > 30 \text{ kDa}$ ) with high  $\text{SUVA}_{254}$ .<sup>32,33</sup> In this study, the removal of 22 PFAS from different classes (i.e., legacy carboxylic and sulfonated PFAS, emerging carboxylic and sulfonated PFAS, and PFAS precursors) using PEI-*f*-CMC was tested in different NOM solutions (Table S4). Figure 3 illustrates that the removal of all PFAS from lake water ( $2.2 \pm 0.3 \text{ mg-C/L}$ ) was in the same range as compared to the experiments in distilled deionized water. Further, the PEI-*f*-CMC maintained its high removal efficiency when mixed with  $5 \text{ mg/L}$  of two NOM solutions of low  $\text{SUVA}_{254}$  ( $1.7 \text{ L/mg}\cdot\text{m}$ ) and high  $\text{SUVA}_{254}$  ( $4.9 \text{ L/mg}\cdot\text{m}$ ) (Figure S7). These results demonstrate the superior adsorption affinity of PEI-*f*-CMC for legacy and emerging PFAS as well as PFAS precursors.

Two consistent trends, regardless of the background water composition, were observed for the adsorption of PFAS on PEI-*f*-CMC. First, the removal efficiency of PFAS positively correlates with their chain length ( $C = 4$ – $12$ ). Second, the removal efficiency of sulfonated PFAS (PFSA) was higher than carboxylic PFAS (PFCA) with the same chain length. Similar trends were observed for adsorption of PFAS on GAC,<sup>29</sup> fluorinated graphene sheets,<sup>34</sup> and metal–organic frameworks.<sup>35</sup> It was also observed that the removal efficiencies of polyfluorinated compounds (e.g., 4:2 FTS and 6:2 FTS) were higher than the perfluorinated compounds with the same chain length (Figure 3). A recent study on the removal of different classes of PFAS by GAC has also reported on a higher removal of polyfluorinated compounds than the perfluorinated compounds with the same number of carbon atoms.<sup>36</sup> Thus, future studies should elucidate the influencing factors for such a phenomenon.

The regeneration performance of adsorbents is one of the important considerations for practical applications.<sup>37,38</sup> In this study, PEI-*f*-CMC ( $50 \text{ mg}$ ) was mixed with  $50 \text{ mL}$  of PFOA solution ( $1 \text{ g/L}$ ) for 2 h. Then, the spent adsorbents were collected by centrifugation ( $10\,000 \text{ rpm}$ ), and the desorption of PFOA was performed in  $50 \text{ mL}$  of methanol. The performance of PEI-*f*-CMC was maintained in eight consecutive adsorption/desorption cycles to remove PFOA (Figure 4). These results illustrate the facile and high regeneration capability of the PEI-*f*-CMC as a promising adsorbent for PFAS.



**Figure 3.** Adsorption of 22 PFAS (1  $\mu\text{g/L}$ ) by PEI-*f*-CMC (25 mg/L) in lake water (vertical colored bars) and in distilled deionized water (black rectangular) at pH 6.5 and equilibrium time of 2 h. Vertical error bars show the standard deviation from triplicated experiments. C4–C12 represents the number of carbon atoms in each compound.



**Figure 4.** Cyclic adsorption/regeneration of PFOA on PEI-*f*-CMC. Initial PFOA = 1 mg/L, adsorbent = 50 mg, solution volume = 50 mL, reaction time = 2 h, and pH = 6.5.

Overall, PEI-*f*-CMC has unique characteristics of being cheap with high adsorption activity toward PFAS. This is the first material to demonstrate fast PFAS adsorption under environmentally relevant concentrations. PEI-*f*-CMC has also exhibited promising potential for being an effective adsorbent for PFAS in waters with different background NOMs compared to conventional adsorbents with facile regeneration capability. These findings also suggest that future studies should test the potential of applying PEI functionalization for

enhancing the performance of other conventional adsorbents.<sup>39</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.8b00556](https://doi.org/10.1021/acs.estlett.8b00556).

Preparation method and characterization of PEI-*f*-CMC. List of tested PFAS. PFAS measurement method. Adsorption and regeneration experimental details (PDF)

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### Notes

The authors declare no competing financial interest.

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