Reversible Functionalized Hydrogel Sorbents for Removing Long- and Short-Chain Perfluoroalkyl Acids (PFAAs) and GenX from Aqueous Solution

Po-Jung Huang,*,† Myung Hwangbo,§ Zheyuan Chen,‖ Yina Liu,‡ Jun Kameoka,*†∥ and Kung-Hui Chu∗§†

1Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77840, United States
2Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
3Zachry Department of Civil Engineering and 4Department of Electrical and Computer Engineering, Texas A&M University, College Station, Texas 77843, United States
5Geochemical and Environmental Research Group, Texas A&M University, College Station, Texas 77845, United States

ABSTRACT: Per- and poly-fluoroalkyl substances (PFAs) are man-made chemicals that are toxic and widely detected in the environment, including drinking water sources. A cost-effective treatment process for PFAs is currently not available. We developed reversible hydrogel sorbents to remove long- and short-chain perfluoroalkyl acids and 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX), which is an emerging PFAS. Through fluoridation and amination of poly(ethylene glycol) diacrylate (PEGDA), the newly synthesized sorbents can sorb the five targeted PFAs (perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorobutanesulfonic acid (PFBS), and perfluorobutanoic acid (PFBA)) and GenX to different degrees from aqueous solution. Aminated PEGDA showed the highest sorption capacity for all five PFAs, particularly for PFOA and PFBS. The bifunctionalized PEGDA showed higher capacities for PFOA and PFBS, suggesting that both hydrophobic interactions and charges contribute to the sorption. Both aminated and bifunctionalized sorbents can remove GenX from water, with the highest sorption capacity of 98.7 μmol g−1 aminated PEGDA−1 within 6 h. The absorbed PFASs on the sorbents were observed and characterized by Fourier-transform infrared spectroscopy. The spent sorbents were reusable after readily regenerated with 70% methanol containing 1% NaCl.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAs) are groups of synthetic compounds with low surface tension and unique hydrophobic and hydrophilic characteristics. PFASs are broadly used in various industries, including paintings, clothing, electrical conductors, and polytetrafluoroethylene coatings for many decades.1 Exposure to PFASs has been demonstrated to cause developmental effects, liver and kidney toxicity, immune effects, and cancer in animal studies. Long-chain perfluoroalkyl acids, like perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are of particular concern.2,5 The United States Environmental Protection Agency has set health advisory levels for PFOA and PFOS in drinking water at 70 ng L−1 of individual or combined concentrations.2,4,5 Due to the phase out of the long-chain PFASs (≥C₈) in 2015, short-chain PFASs such as C₄ polyfluoroalkyl substances and a new PFAS such as 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX) have been widely manufactured and used by industries in recent years. The shift of using different PFASs has resulted in increasing occurrences of a wide range of PFASs, particularly short-chain PFASs like perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS), and GenX in the environment.2–8 The State of Minnesota has issued health-based guidelines for drinking water for PFBA (C₄) and PFBS (C₄) of 7 and 2 μg L−1, respectively.9 GenX can induce necrosis of liver cells in male mice after 28 days of oral exposure to GenX, suggesting that GenX is more toxic to liver than PFOA10,11. As such, a drinking water provisional goal for GenX at a concentration lower than 140 ng L−1 has been issued by the North Carolina Department of Health and Human Services in the state of North Carolina.12 Thus, an effective treatment process to remove both legacy and emerging PFASs is warranted.

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Sorption processes have shown better PFAS removals from water than other treatment processes such as coagulation/flocculation/sedimentation, filtration, and advanced oxidation. Activated carbons and ion-exchange resins are two commonly used sorbents for removing long-chain PFAS from water. Granular activated carbon (GAC) can achieve a sorption capacity of 1.1 mg g GAC$^{-1}$ for PFOA. However, GAC or ion-exchange resin is not as effective for short-chain PFASs and GenX removal. High costs are common associated with the applications of these sorbents. For example, ion-exchange resins are expensive to operate despite that they allow pollutants in water to diffuse easily into the hydrogels. Among many materials used for manufacturing hydrogel-based sorbents, poly(ethylene glycol) diacrylate (PEGDA) is an ideal substrate because of its hydrophilicity of PEG backbone and its diacrylate groups that allow adjustable functionalization. Accordingly, we hypothesize that PEGDA-based hydrogel sorbents can be functionalized using 1H,1H,2H,2H-perfluorooctyl methacrylate (13FOMA) and 2-(methacyrloyloxy)ethyltrimethylammonium chloride solution (MTAC) to create hydrophobic regions and/or electrostatic attractive interaction. In this study, the functionalization of PEGDA is achieved by amination, fluoridation, and bifunctionalization (Figure 1). The amination of PEGDA contributes electrostatic force, whereas the fluoridation of PEGDA presents the hydrophobic interaction. The bifunctionalization of PEGDA integrates amination and fluoridation, which contributes electrostatic force and hydrophobic interaction simultaneously. This work is aimed at evaluating their performance for removing long-chain (PFOA and PFOS), short-chain fluorinated substances (PFBA and PFBS), and perfluoroalkyl ether carboxylic acid group (GenX) from the water. Moreover, the regeneration of the functionalized PEGDA was investigated in this study.

**RESULTS AND DISCUSSION**

**Characteristics of Sorbents A–C.** Three newly synthesized sorbents A–C were characterized using Fourier-transform infrared (FTIR) analysis (Figure 2). Details of characterized peaks in the FTIR spectra of PEGDA and sorbents A–C are available in Table S1 (Supporting Information). Figure 2a shows the FTIR spectra 2a of PEGDA. The peaks between 2981 and 2881 cm$^{-1}$ were corresponded with the stretching of C–H from PEGDA, whereas the peaks between 1450 and 1407 cm$^{-1}$ were corresponding with the bending of C–H from PEGDA. In addition, the peaks between 1348 and 1093 cm$^{-1}$ present the $\nu$(C–O) and $\nu$(C–O–C) from PEGDA, respectively. Compared to the FTIR spectra of sorbent A (Figure 2b), the peaks between 1243,
1189, and 1141 cm\(^{-1}\) correspond to \(\nu(CF_{2})\), whereas the rocking and wagging vibrations of \(C-F\) were shown at the range from 746 to 650 cm\(^{-1}\).\(^{25,36}\) These peaks indicated that sorbent A has been successfully functionalized via fluorination.

FTIR spectra of sorbent B (aminated PEGDA) are shown in Figure 2c. Compared to those of PEGDA (Figure 2a), the new peaks located at 1247 cm\(^{-1}\) was assumed as \(\nu(C-N)\).\(^{31}\) Moreover, the peaks shown in peak deconvolution, 1141 and 1485 cm\(^{-1}\) (Figure S2a), could be assigned as \(\nu(C-N)\) and \(\nu(N\rightarrow(CH_{3})_{3})\), respectively.\(^{27,32}\) The FTIR spectra of sorbent C, which is bifunctionalized, are shown in Figure 2d. The characterized peaks for \(C-F\) and \(C-N\) were recognized in the FTIR spectra, and the locations of these peaks were similar to those presence in the FTIR spectra of sorbent A and sorbent B. These results indicated that PEGDA has been successfully functionalized with 13FOMA, MTAC, and both via photocrosslinking.

\(\zeta\)-Potentials of PEGDA and sorbents play a crucial role in determining the sorption capability toward PFASs. Table 1 shows the \(\zeta\)-potential of PEGDA and sorbents, ranging from negative to positive. Sorbent A has a negative \(\zeta\)-potential of \(-27.1 \pm 0.4\) mV, which is contributed not only from the backbone of PEGDA (\(-25.4 \pm 1.6\) mV) but also from the fluorine of 13FOMA.\(^{37}\) The \(\zeta\)-potential of sorbent B is positive (\(39.0 \pm 1.6\) mV) due to the combination of the negative charge of 13FOMA and the positive charge of MTAC. Accordingly, the \(\zeta\)-potential of sorbent C is less positive than that of the sorbent B.

### Sorption of PFASs by Sorbents A–C

The three sorbents showed different sorption abilities, with respect to PFAS removal (%) and sorption capacity (mass of PFAS/mass of sorbent), toward these model PFASs (Figure 3a,b and Table S1 in Supporting Information). PFAS removal ratio, calculated based on the changes of PFAS concentration in liquid before and after incubation with sorbents divided by initial PFAS concentration in the solution, is shown in Figure 3a. PFAS sorption capacity, defined as the amount of PFAS sorbed per the amount of sorbent, is calculated and summarized in Table S1 and shown in Figure 3b. PEGDA showed no sorption capacity toward PFOA and PFOS (Table S1).

Although sorbent A can sorb low levels of PFOA, PFOS, and PFBA in 6 h (less than 10%), sorbent A was unable to sorb PFBS and GenX (Table S1). Sorbents B and C showed improved sorption abilities toward all five PFASs tested in this study (Figure 3), compared to sorbent A. Within 6 h, sorbent B was able to completely (100%) sorb PFOA and PFBS, and 91 and 78% for PFOS and PFBA, respectively (Figure 3a). Sorbent C also showed excellent removal toward PFOA and PFBS. However, sorbent C showed a less removal for PFBA (62%) than those observed for sorbent B. Both sorbents B and C showed greater than 95% of removal toward GenX.

The sorption capacities of sorbent B and sorbent C for PFOA were estimated to be greater than 109.8 and 110.0 \(\mu\)mol g sorbents\(^{-1}\), respectively. The PFOA sorption capacities by sorbents B and C are approximately 5 times higher than that by sorbent A (20.0 \(\mu\)mol g sorbents\(^{-1}\)). Compared to sorbent C, sorbent B showed a slightly higher sorption capability short-chain PFAAs, PFBA, and PFBS. However, higher GenX sorption capacities of sorbent C than those of sorbent B suggested that hydrophobic force play an important role in the sorption of long-chain PFASs. The sorption capacities for GenX by sorbent B and sorbent C are 86.7 ± 5.1 and 98.7 ± 3.9 \(\mu\)mol g sorbent\(^{-1}\), respectively.

The differences in sorption ability of these three sorbents toward the five PFASs can be explained by the chemical properties of these PFASs and the \(\zeta\)-potentials of these sorbents. PFAAs, consisting of fluoroalkane and carboxylic acid or sulfonic acid, are commonly present with negative charge, and the hydrophobicity of PFAAs decrease as the chain length decreases.\(^{34}\) For GenX, consisting of short chain of fluoroalkyl ether and carboxylic acid, also usually provide negative charge and hydrophobicity.\(^{35}\) Thus, hydrophobic interaction and electrostatic force are considered as two most effective strategies to sorb and retain these PFASs from aqueous solution.

Different \(\zeta\)-potentials of sorbents might explain their different sorption capabilities toward PFASs observed in this study. The poor sorption capability toward these PFASs by sorbent A might be due to its negative \(\zeta\)-potential (Table 1), despite that the fluorine in sorbent A contributes hydrophobic force to interact with PFASs. The negative charge on the surface of the sorbent A might create an electrostatically repulsive force between PFASs and sorbent A, resulting in poor

| Table 1. \(\zeta\)-Potentials of PEGDA, sorbent A–C |
|-----------------|----------------|----------------|----------------|
|                 | PEGDA          | sorbent A       | sorbent B       | sorbent C       |
| \(\zeta\)-potential (mV) | \(-25.4 \pm 1.6\) | \(-27.1 \pm 0.4\) | \(39.0 \pm 1.6\) | \(31.4 \pm 0.6\) |

Figure 2. Fourier-transform infrared (FTIR) spectra of PEGDA and functionalized PEGDA: (a) PEGDA (b) sorbent A, (c) sorbent B, and (d) sorbent C. The characterized peaks of PEGDA, 13FOMA, and MTAC are marked in FTIR spectra. The dash line indicated the peak, \(\nu(C-F)_{13FOMA}\), \(\nu(C-N)_{MTAC}\), and \(\nu(C-O-C)_{PEGDA}\).
sorption of these PFASs. The charge repulsive force can also be explained why the unmodified PEGDA (which has a negative ζ-potential) failed to sorb tested PFASs.

Unlike sorbent A and unmodified PEGDA, the ζ-potentials of sorbent B and sorbent C are positive, which can spontaneously generate electrostatically attractive force between the negatively charged PFASs and the positively charged sorbents. As a result, the sorbents can remove all PFASs from water under the tested conditions (over 6 h of incubation) and were particularly effective for PFOA and PFBS removal. These results strongly suggested that electrostatically attractive force is the dominant interaction for capturing PFASs by sorbents B and C.

Sorbent B has higher surface charge (39.0 ± 1.6 mV) than sorbent C (31.4 ± 0.6 mV), resulting in absorbing higher concentrations of PFBA and PFBS. Sorbent C provided additionally hydrophobic interaction to compensate the lower surface charge, leading to the similar sorption capacity for PFOS. Overall, sorbent C showed preference for long chain PFASs, whereas sorbent B preferred to capture negatively charged and/or short chain PFASs. As the structure of GenX (shown in Figure S1) is similar to PFOA, it was not surprising to observe comparable PFAS removal and sorption capacity of GenX by the sorbent B and sorbent C.

**Characterization of Spent Sorbents.** The FTIR spectra of the spent sorbents were compared to those of the freshly synthesized sorbents (Figures 4–6 for spent sorbents A–C, respectively). The peak deconvolutions for sorbents before and after absorbing PFASs are shown in Figures S2–S5 and Tables S3–S16 (Supporting Information).

As sorbent A showed poor sorption ability toward PFASs, only subtle changes in the FTIR spectra of the spent sorbent A are observed (Figure 4). For example, a broad peak in the range from 3600 to 3000 cm⁻¹ is noted in spectra 4b (Figure 4).
Figure 5. Fourier-transform infrared (FTIR) spectra of sorbent B before and after sorption of PFASs: (a) before sorption, (b) PFOA sorption, (c) PFOS sorption, (d) PFBA sorption, (e) PFBS sorption, (f) GenX sorption.

Figure 6. Fourier-transform infrared (FTIR) spectra of sorbent C before and after sorption of PFASs: (a) before sorption, (b) PFOA sorption, (c) PFOS sorption, (d) PFBA sorption, (e) PFBS sorption, (f) GenX sorption.

4b), indicating the $\nu$(O–H) of PFOA. The peak at the range of 1300–1000 cm$^{-1}$ could be deconvoluted as 1241, 1189, and 1143 cm$^{-1}$ contributed from 13FOMA, whereas the peak of $\nu$(CF$_2$) at 1189 cm$^{-1}$ became a broader peak in the range from 1205 to 1170 cm$^{-1}$ resulting in the sorption of PFOA. However, as the amount of PFOA sorbed on the sorbent A was too low, the peak representing the carbonyl group, which is shown at the range from 1700 to 1630 cm$^{-1}$, was not substantial in the FTIR spectra 4b. Similar FTIR spectra are observed for PFOS spent sorbent A (Figure 4c). In the Figure S2b, the shoulder peak at 1265 cm$^{-1}$ could be assigned as $\nu$(CF$_3$) contributed from PFOS after capturing on sorbent A. Due to the poor sorption of PFBA and PFBS by sorbent A, the peak for carbonyl group is not clear and not distinguishable in the FTIR spectra 4d and 4e (Figure 4d,e). However, additional peaks were deconvoluted in the range from 1300 to 1000 cm$^{-1}$ shown in Figure S2c,d, Tables S5 and S6. The peaks at 1201, 1176, and 1132 cm$^{-1}$ are responding to $\nu$(CF$_2$) of PFBA, whereas the peaks at 1280, 1205, 1172, 1130, and 1103 cm$^{-1}$ are related with $\nu$(CF$_2$) of PFBS.

Sorbent B was able to capture PFOA effectively (Figure 3) and was evident by the stronger intensity of the peaks at 1681 and 1240 cm$^{-1}$ in FTIR spectra 5a and 5b (Figure 5). These peaks corresponded to $\nu$(COO$^-$) and $\nu$(CF$_2$)$^{26,30}$ indicating the occurrence of PFOA sorption on the sorbent. The intensity of C–F peaks in the range from 750 to 530 cm$^{-1}$ also increases due to the absorbed PFOA. In the peak deconvolution (Figure S3a and Table S7), a new peak appeared at 1203 cm$^{-1}$ and the intensity of the peak at 1240 cm$^{-1}$ increased, providing additional evidence of occurrence of PFOA sorption by sorbent B. Moreover, the peak at 1141 cm$^{-1}$ was partially shifted to 1174 cm$^{-1}$ due to the sorption of PFOA by the quaternary ammonium groups on sorbent B. Compared to the sorption of PFOS by sorbent B, the new peak located at 1189 cm$^{-1}$ was assumed as $\nu$(CF$_3$) contributed from PFOS (Figure S3b and Table S8). The broader peak shown at 1251 cm$^{-1}$ was also due to sorption of PFOS. The FTIR spectra 5d and 5e were observed from the sorbent B after sorption of PFBA and PFBS (Figure 5d,e). Sorption of PFBA on the sorbent B was evident by the presence of peaks at 1689 and 1222 cm$^{-1}$ in FTIR spectra, corresponding to $\nu$(COO$^-$) and $\nu$(CF$_3$) of PFBA. In the deconvoluted spectra, the peaks at 1106, 1203, and 1222 cm$^{-1}$ are corresponding to $\nu$(CF$_2$) of PFBA (Figure S3c and Table S9). Sorbed PFBS on the sorbent B could be observed in the deconvoluted spectra (Figure S3d and Table S10). The new peaks at 1286 and 1211 cm$^{-1}$ are corresponding to $\nu$(SO) and $\nu$(CF$_2$) of PFBS and the peak at 1141 cm$^{-1}$ was partially shifted to 1173 cm$^{-1}$, which is similar as the sorption of PFOA of sorbent B. In addition, the peak for quaternary ammonium captures PFBS shifted from 1240 to 1255 cm$^{-1}$. It demonstrated that quaternary ammonium of sorbent B captures PFBSs through electrostatic attractive force.

Sorbent C, fluoridation, and amination of PEGDA can provide hydrophobic and electrostatic force simultaneously. Figures 6a–6c and S4a–c present the FTIR of sorbent C before and after sorption. The new peak of PFOA at 1234 cm$^{-1}$ in the presence of sorbent C indicated $\nu$(CF$_3$). The peak at of $\nu$(CF$_3$) was slightly shifted to higher wavenumber, from 1190 to 1199 cm$^{-1}$, which demonstrated the interaction of C–F between sorbent and PFOA. In addition, the peaks at 1259 and 1239 cm$^{-1}$ were integrated as 1240 cm$^{-1}$ and the intensity of peak at 1240 cm$^{-1}$ was stronger, which is corresponding with the sorption of PFOA. The detail information of deconvoluted peak at the range 1300–1000 cm$^{-1}$ is listed in Table S11. Other peaks showing stronger intensity were detected at the range from 750 to 520 cm$^{-1}$ because of wagging and rocking vibration of absorbed PFOA. The peaks of $\nu$(CN) at 1144 cm$^{-1}$ were shifted to 1166 cm$^{-1}$ and the peaks of $\nu$(COO$^-$) at 1459 cm$^{-1}$ were shifted to 1477 cm$^{-1}$,
The regenerated sorbents were further characterized based on FTIR analysis (Figures S6 and S7). The FTIR spectra of the regenerated sorbent A to that of the newly synthesized sorbent A were similar (Figure S6). On the other hand, the desorption of PFASs from sorbent B and sorbent C could be recognized in FTIR spectra (Figure S7a,b). Specifically, the intensity of carbonyl group (1681 cm$^{-1}$) decreases and even disappears, suggesting that part of absorbed PFOA and PFBA was extracted and released by methanol and NaCl. Similarly, the release of absorbed PFOS and PFBS was observed in the peak deconvolution. The intensity of $\nu(\text{CF}_2)$ of PFOS and PFBS also decreases and even reaches to zero after desorption. As only 70–84% of sorbed GenX was desorbed from the spent sorbent B and sorbent C, the characteristic peak of GenX was obviously observed in the FTIR spectra of the regenerated sorbents B and C. Overall, the results of FTIR analysis of the regenerated sorbents were consistent to the results of desorption of PFASs from the spent sorbents, suggesting that spent sorbents B and C can be regenerated for reuse.

**Implications.** This study reported reusable new sorbents with high sorption capacity for long- and short-chain PFAs and GenX. The new hydrogel-based sorbents were synthesized by functionalizing PEGDA to create both electrostatic attractive force (MTAC) and hydrophobic interaction (13FOMA) for PFAS sorption. Moreover, hydrogel provides higher water content and porous three-dimensional structure network so that the diffusion resistance could be reduced. As a result, the sorption and diffusion model would be different from those used for activated carbons.

Introducing fluorographene into sorbents to create strong hydrophobic regions in the sorbent has enabled high PFOA and PFOS removal (92–97%) at a short equilibrium time of 2 min. In our study, 13FOMA was introduced into sorbents A and C to create hydrophobic regions in the sorbents. Thus, a rapid removal of PFASs at a short equilibrium time is expected. Future studies using these newly developed sorbents to evaluate the sorption kinetics for PFASs under environmental relevant conditions such as PFAS-contaminated groundwater or surface water are thus needed. To the best of our knowledge, it is the first report describing hydrogel-based sorbents to effectively remove short chain of PFASs. Most commercial resins, like Purolite A600E and Purolite AS20E, have better sorption capacities for PFOA and PFOS, compared to those by the sorbents developed in this study. However, these two resins have much lower sorption capacities for PFBA and PFBS than those of our sorbents. For resin A600E, the sorption capacities for PFBA and PFBS were 10 and 3 µmol g sorbent$^{-1}$, respectively. For resin AS20E, the sorption capacities for PFBA and PFBS were 20 and 8 µmol g sorbent$^{-1}$, respectively. Our sorbents showed 8 to 63 folds higher sorption capacities than these commercial resin for shorter-chain PFASs. Accordingly, these hydrogel-based sorbents have a potential to remove these concerned shorter-chain PFASs from water. Increasing environmental occurrences of GenX and short-chain PFAS have been reported in America, Europe, and China. Similar to long-chain PFASs, GenX and short-chain PFASs have been detected in food and fish and suggested that they are bioaccumulative. The sorbents developed in this study showed potential to sorb the five model PFASs. Future studies are needed to examine the effectiveness of these sorbents for treating water contaminated with various types and concentrations of PFASs.

demonstrating the interaction between COO groups and CN groups. Compared to the sorption of PFOS in sorbent C, the peak intensity of C–F also increases in the same range as absorbed PFOA. The new peaks at 1068 and 1241 cm$^{-1}$ were corresponding to the $\nu(\text{SO}_3^{-})$ from PFOS. Peak deconvolution (Figure 6d) indicated that the intensity of peaks at 1267 and 1240 cm$^{-1}$ increased after absorbing PFOS. In addition, the new peak at 1122 cm$^{-1}$ was also assigned as the $\nu(\text{CF}_2)$ from PFOS. The peak of $\nu(\text{SO}_3^{-})$ in the presence of sorbent C was slightly shifted to lower wavenumber, from 1201 to 1193 cm$^{-1}$, whereas the $\nu(\text{SO}_3^{-})$ was also shifted to lower wavenumber, from 1074 to 1058 cm$^{-1}$ (Figure S4b and Table S12). From these shifts, it can be assumed that the C–N$^+$ in the presence of sorbent C can also capture PFOS using electrostatic force. Considering the sorptions of PFBA and PFBS using sorbent C, we also can see the similar spectra, Figure 6d,6e, as PFOA and PFOS. The carbonyl groups and C–F are obviously shown at 1683 and 1226 cm$^{-1}$, respectively. In the peak deconvolution, the additional peak is shown at 1226 and 1110 cm$^{-1}$ for absorbed PFBA (Figure S4c and Table S13). The peaks of quaternary ammonium of MTAC and the fluoride of 13FOMA shifted from 1144 to 1182 and 1190 to 1203 cm$^{-1}$, respectively. In addition, absorbed PFBS on sorbent also can be observed on FTIR spectra. The additional peak is shown at 1051 and 1128 cm$^{-1}$, which is corresponding to $\nu(\text{CF}_2)$ and C–F of PFBS. The peak of quaternary ammonium of MTAC and the fluoride of 13FOMA shifted from 1141 to 1189, 1190 to 1211, and 1259 to 1280 cm$^{-1}$ (Figure S4d and Table S14).

Sorbent GenX on sorbent B and sorbent C was observed on the FTIR spectra. As shown in Figure 6f, the additional peak was observed at 1635 cm$^{-1}$ and at the range from 1570 to 1683 cm$^{-1}$. In the peak deconvolution (Figure S5a,b, Tables S15 and S16), the additional peak of absorbed GenX on sorbent B is shown at 1101 and 1228 cm$^{-1}$ for $\nu(\text{CF}_2)$. The peak at 1259 cm$^{-1}$ indicates the interaction between quaternary ammonium and carboxylic acid. Additionally, new peak of absorbed GenX on sorbent C illustrates $\nu(\text{CF}_2)$ at 1128 cm$^{-1}$, and the peak at 1166 cm$^{-1}$ demonstrates the interaction between quaternary ammonium and carboxylic acid.

**Desorption of PFASs from Spent Sorbents.** The ability to desorb PFASs from the spent sorbents is a favorable feature, since the spent sorbent can be regenerated for reuse and thus reduce the overall treatment costs for PFASs. In this study, different desorption solutions were tested for regeneration of the spent sorbents. All desorption percentages, calculated as the amount of PFASs released into the extraction solution over the amount of PFASs in the spent sorbent, are shown in Table S17 in Supporting Information.

PFOA absorbed on sorbent A cannot be extracted well and released only 5% using 100% methanol or 100% acetonitrile as extraction solution. In contrast, PFOS absorbed on sorbent A can be extracted and released over 100% by treating with 100% methanol. Also, 70% methanol with 1% NaCl was effective for extracting PFOA and PFBA from the spent sorbent A over 121 and 72%, respectively. More than 90% of PFASs on the spent sorbent B and sorbent C can be extracted with 70% methanol containing 1% NaCl. The good extraction efficiency using this extraction solution might be due to the alteration of the ionic strength that led to breakage of the electrostatic interaction between PFASs and the sorbents. Using the same extraction solution, approximately 84 and 70% GenX were released from sorbent B and sorbent C, respectively.

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Electrostatically attractive force appeared to be the dominant interaction for sorbing PFAs on to the functionalized PEGDA sorbents. This finding implicates that one can improve the sorption capacity for PFAS, particularly soluble anionic PFASs, by increasing the $\zeta$-potential of functionalized PEGDA sorbents. The $\zeta$-potential of unmodified PEGDA is negative, whereas MTAC-modified PEGDA shifts the $\zeta$-potential from negative to positive. Therefore, manufacturing higher $\zeta$-potential of functionalized PEGDA can be achieved by changing the concentration of precursors, MTAC, during synthesis. At low pH, higher sorption capabilities of PFOA and PFOS were observed. 20 On the other hand, presence of ions such as Na$^+$ and Ca$^{2+}$ have shown to interfere the absorption of PFASs. 42 Thus, future study is needed to investigate the effects of pH and these ions on the sorption capacity of PFAS by these newly developed sorbents. The MTAC-modified PEGDA can be also extended to remove metallic anion, like chromium ion from water. Furthermore, PEGDA can be functionalized to be more negatively charge by using sulfonic or carboxyl groups to capture or chelate cationic PFASs. Hydrophobic interaction is another mechanism for sorbing PFASs. In this study, however, less sorption capacities of PFASs were observed for polymer A than those for polymers B and C. It is possible that more 13FOMA is needed to bond with PEGDA to generate a stronger hydrophobic interaction in the sorbent for PFAS removal. This aspect should be further investigated in the future by using a higher amount of 13FOMA to functionalize the PEGDA sorbent, followed by confirming the degree of fluorination using the NMR spectroscopy analysis.

Thermal regeneration is commonly used for regeneration of spent activated carbons and ceramic oxides. However, this method is costly and unable to regenerate the sorbents to its original sorption capacity. The extraction solution (methanol with NaCl) to regenerate the functionalized PEGDA will be less expensive than thermal regeneration. Nevertheless, future studies are needed to determine the reuse cycles of the regenerated sorbents. It is also expected that the functionalized PEGDA sorbents can be further developed for continuous treatment of PFAS-contaminated water using packed and/or fluidized bed reactors.

**MATERIALS AND METHODS**

**Materials.** Poly(ethylene glycol) diacrylate (PEGDA, average molecular weight of the polymer = 575), 2,2-dimethoxy-2-phenylacetophenone (C$_6$H$_5$COC(OCH$_3$)$_2$C$_6$H$_5$, >99%), 1-vinyl-2-pyrrolidinone (C$_6$H$_9$NO, >99%), 1-(methacyrloyloxy)ethyltrimethylammonium chloride (MTAC) into 200 $\mu$L of deionized (DI) water, resulting in final moles of 0.52 mmol PEGDA and 0.26 mmol of MTAC. The precursor solution for bifunctionalization of PEGDA was prepared by adding 352 $\mu$L of PEGDA, 346 $\mu$L of 13FOMA, and 260 $\mu$L of MTAC into 400 $\mu$L of isopropanol, resulting in final moles of 1.04 mmol PEGDA, 1.04 mmol of 13FOMA, and 1.04 mmol of MTAC. Each of the precursor solution was then mixed with 3% 2,2-dimethoxy-2-phenylacetophenone. The mixture was filled into a PDMS mold for sorbent synthesis through soft lithography as described previously with some modifications. Briefly, the precursor solutions were poured into the wells of PDMS mold and allowed for solidification under 365 nm UV light (80 W) for 5 min. After solidification, these functionalized PEGDA were released from PDMS mold and were washed by DI water three times. These sorbents were stored in oven at 60°C for experimental use. All sorbents were synthesized in duplicate, and the size of the sorbents was 1 mm × 1 mm × 0.3 mm.

**PFASs Sorption and Desorption Tests.** The sorbents were used for PFASs sorption/desorption experiments. Five model of PFASs: PFOA, PFBA, PFOS, PFBs, and GenX were used. PFOA and PFOS were chosen to represent long-chain PFASs, whereas PFBA and PFBs were chosen to represent short-chain PFASs. GenX was chosen to represent perfluoroether carboxylic acids (PFECAs). The experiments were carried out in 20 mL glass vials containing 5 mL of each of target PFASs in DI water with 10 mg of each of sorbents (sorbent A or sorbent B or sorbent C). The vials were capped with polypropylene caps. To determine the sorption capacity of each PFASs by the sorbents, high initial concentrations of PFASs (~100 mg L$^{-1}$, except PFOS) were used. The vials were incubated at room temperature with shaking at 150 rpm for 12 h. During the sorption experiments, liquid samples were collected at 6 and 12 h. Collected liquid samples were analyzed for PFASs.

Following the sorption experiment (i.e., after 12 h of incubation), desorption experiments were conducted in 20 mL glass vials using a range of different extraction solution, including 100% methanol, 100% acetonitrile, or 70% methanol with 1% NaCl. Briefly, the spent sorbents in the vials were washed with DI water twice before adding 5 mL of extraction solution. The mixture was incubated at room temperature with shaking at 150 rpm for 12 h. The spent sorbents after desorption were washed with DI water two times. Duplicate samples were used in each set of sorption/desorption experiments.

**PFAS Analysis.** The concentrations of PFOA, PFOS, PFBA, and PFBs in liquid samples were determined using high-performance liquid chromatography (HPLC, UltiMate 3000, Thermo Scientific)/triple quadrupole mass spectrometer (LC/MS/MS) (QqQ-MS, Quantiva, Thermo Scientific), as described previously. Briefly, 10 $\mu$L of samples was injected and then separated by a Hypersil Gold 5 $\mu$m 50 × 3 mm column (Thermo Scientific, Waltham, MA) maintained at 30°C using the solvent gradient method. The flow rate was 0.5
μL min⁻¹. Chromatographic separation was achieved on a solvent A, water (0.1% formic acid) and solvent B, acetonitrile (0.1% formic acid). The separation gradient method used was of 0–4 min (20% B to 80% B), 4–4.1 min (80% B to 95% B), 4.1–6 min (95% B, 6–6.5 min (95% B to 20% B), and 6.5–8 min (20% B). MS parameters were optimized for each of these PFAAs under direct infusion at 5 μL min⁻¹ to identify the selected reaction monitoring (SRM) transitions (precursor/product fragment ion pair). Sample acquisition and analysis were performed with TraceFinder 3.3 (Thermo Scientific).

The concentrations of GenX in liquid samples were analyzed by high-performance liquid chromatography (HPLC, Agilent 1290 Infinity II)/triple quadrupole mass spectrometer (QqQ-MS, Agilent 6470) equipped with a Jet Stream electrospray ionization source. Samples (10 μL) were injected and then separated by an Agilent ZORBAX Eclipse Plus C-18 narrow bore (2.1 mm × 100 mm, 1.8 μm) HPLC column maintained at 40 °C. The flow rate was 0.5 mL min⁻¹. Chromatographic separation was achieved on solvent A (5 mM ammonium acetate in water) and solvent B (95% MeOH and 5% water with 5 mM ammonium acetate). The separation gradient method used was of 0–0.5 min (holding at 5% B), 0.6–3 min (5% B to 95% B), 3.1–4 min (holding at 95% B), 4.1–5 min (95% B to 5% B) and stabilize column at 5% B for 5 min. MS parameters were optimized for GenX under direct infusion at 0.4 mL min⁻¹ to identify the MRM (multiple SRM) transitions (precursor/product fragment ion pair). 13C isotopically labeled GenX was used as an internal standard. Sample acquisition and analysis were performed with MassHunter B.08.02 (Agilent).

**Characterization of Sorbents.** Fourier-transform infrared (FTIR) analysis was used to characterize the sorbents before and after PFAS sorption. All of the sorbents were dried in a vacuum dryer at 25 °C for 4 hours before the FTIR analysis using a Thermo Nicolet 380 FTIR spectrometer in the Materials Characterization Facility at Texas A&M University. The wavenumber ranges from 400 to 4000 cm⁻¹ was used, and the absorbance was recorded with 0.9 cm⁻¹ resolution. The peak deconvolution was analyzed using software Origin in the range from 1000 to 1300 cm⁻¹. The ζ-potentials of the newly synthesized sorbents and the pure PEGDA were measured using a Zetasizer Nano ZS90 (Malvern, U.K.) in the Biomedical Engineering Facility at Texas A&M University.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02279.

Chemical structures of GenX and PFOA; FTIR spectrum in peak deconvolution for sorption/desorption of PFASs for sorbent A–C; sorption capacity of sorbent A–C; the characterized peaks list for PEGDA and sorbent A–C for sorption of PFASs (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: kameoka@tamu.edu. Phone: +1 (979)-845-7564 (J.K.).
*E-mail: kchu@civil.tamu.edu. Phone: +1 (979) 845-1403. Fax: +1 (979) 862-1542 (K.H.C.).

ORCID

Po-Jung Huang: 0000-0003-1273-3060

Notes

The authors declare no competing financial interest.

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