

Perspective

Advancing PFAS Sorbent Design: Mechanisms, Challenges, and Perspectives

Published as part of ACS Materials Au virtual special issue "2023 Rising Stars".

Yutong He, Xinrong Cheng, Samruddhi Jayendra Gunjal, and Cheng Zhang*

Cite This: ACS Mater. Au 2024, 4, 108–114		Read Online	
			_
AULESS	Metrics & More	□ IIII Article Recommendations	

ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals characterized with persistence and multisurface resistance. Their accumulation in the environment and toxicity to human beings have contributed to the rapid development of regulations worldwide since 2002. The sorption strategy, taking advantage of intermolecular interactions for PFAS capture, provides a promising and efficient solution to the treatment of PFAS contaminated sources. Hydrophobic and electrostatic interactions are the two commonly found in commercially available PFAS sorbents, with the fluorous interaction being the novel mechanism applied for sorbent selectivity. The main object of this Perspective is to provide a critical review on the current design criteria of PFAS sorbents, with particular focus on their sorption and interaction mechanisms as well as limitations. An outlook on future innovative design for efficient PFAS sorbents is also provided.



KEYWORDS: PFAS capture, sorbents, environmental remediation, fluorous interaction, hydrophobic, electrostatic

INTRODUCTION

Per- and polyfluoroalkyl substances, short for PFAS, are a group of over 10,000 synthetic chemicals with a history of over 50 years.¹ PFAS substances are grouped via their carbon chain length: perfluoroalkyl sulfonic acids with ≥6 carbons and perfluoroalkyl carboxylic acids containing ≥7 carbons are considered long-chain PFAS, whereas those with shorter chain lengths are considered short-chain PFAS.² Their specialties in durability, dielectricity, and water and heat resistance made them favorable in various industrial and household applications;³ however, concerns regarding the safety and persistence of PFAS have emerged over the years. Being termed as forever chemicals, their nature of great persistence and chemical stability have resulted in widespread distribution in the environment and accumulation in the human body.⁴

More than two decades ago, in 2002, the United Nations Organization of Economic and Development (OECD) published the first PFAS hazard assessment, raising public awareness of its potential risk to health.^{5,6} Pathways of human exposure include ingestion of contaminated water and food sources, inhalation of indoor air, and contact with affected media.⁷ The impact of PFAS on health has also been evaluated, considering that measurable levels of PFAS in blood, tissues, and organs have been detected in populations living in contaminated areas.⁸ Current studies have indicated their direct association with various diseases, including developmental and reproductive toxicity, immune system dysfunction, cardiovascular diseases, and cancer.^{9–11} Thus, PFAS contamination has become not only a growing environmental concern but also an issue of significant global public health importance.

In 2002, the U.S. Environmental Protection Agency (EPA) issued regulations toward PFAS manufacture and import, marking the beginning of PFAS regulation.⁶ To date, many countries and organizations have started to regulate the use of PFAS in certain products and limit their release into the environment. Regulation of long-chain PFAS resulted in the rapid phase out of these chemicals in the early 2000s and their substitution by shorter carbon chain alternatives.^{12,13} More recently, in February 2023, the European Chemicals Agency (ECHA) unveiled a proposal to prohibit approximately 10,000 "forever" fluorinated PFAS chemicals. According to ECHA, PFAS chemicals are defined as any substances containing at least one fully fluorinated methyl or methylene carbon atom without attachment of either hydrogen, chloride, bromide, or iodine atoms.¹⁴ Although production of PFAS can be rapidly phased out by alternation of chemical synthesis strategies, their accumulation in soils, ocean, terrestrial food chains, and

Received:August 20, 2023Revised:September 30, 2023Accepted:October 24, 2023Published:November 9, 2023





pubs.acs.org/materialsau

a result, the development of strategies to accelerate PFAS elimination is of great importance in the treatment of previously accumulated environmental PFAS and relief of public concerns.

To satisfy the urgent needs of efficient PFAS remediation, a wide range of concentration strategies has been proposed and developed. At the present time, granular activated carbon (GAC) and ion exchange (IEX) resins remain the two dominant and mostly established treatment methods,^{13,15} with applications of reverse osmosis, advanced oxidation processes (ACP), membrane filtration, and foam fractionation entering the mainstream.^{7,16} By capitalizing on a range of interactions between PFAS and the sorbent, PFAS compounds can be efficiently accumulated on the surface of a sorbent to achieve successful capture. Various interaction types, encompassing hydrophobic, electrostatic, and fluorophilic, along with their possible combinations, play a role in sorbing PFAS.^{13,17} In this Perspective, we will introduce a range of types of PFAS sorbents, with a specific emphasis on their sorption and interaction mechanisms. We outline and assess their distinctive features, strengths, and limitations while also providing an outlook on forthcoming directions in PFAS remediation.

■ INTERACTION MECHANISMS WITH PFAS

Hydrophobic Interaction with PFAS Tails

Explained as a noncovalent interaction between water-repellent molecules, the hydrophobic interaction plays a dominant role in facilitating PFAS sorption onto certain sorbent materials, including the well-established GAC and nanoporous carbon materials.^{18,19} First being recognized in 1937,²⁰ the hydrophobic interaction poses greater influence in the comparison with van der Waals interaction.²¹ The nonpolar carbonfluorine bonds in PFAS tails are naturally hydrophobic and unfavorable in the means of interaction with water, resulting in the highly ordered formation of water molecules surrounding them.^{22,23} Positively associated with elevated free energy, this compactly ordered water arrangement is energetically unfavorable.²²⁻²⁴ To reduce unfavorability, as well as decrease the likelihood of contact with water molecules, hydrophobic compounds have a higher tendency to associate with each other.²⁵ The same mechanism applies in the situation when PFAS interacts with hydrophobic sorbent materials. In the contact with PFAS-contaminated water, the hydrophobic surface of the sorbent material preferentially interacts with the hydrophobic PFAS tails, as both of them are averse to water.

Being one of the most established PFAS sorbents, granular activated carbon has been found to have commendable performance on long-chain PFAS removal such as perfluor-octanoic acid (PFOA) and perfluoroctanesulfonic acid (PFOS).^{13,26} Its high efficiency as well as low cost made it a favored strategy in industrial applications.^{27,28} The micropore surface area on GAC was found to be essential in the hydrophobic interaction with PFAS, and preference of pore sizes has also been found to be associated with PFAS chain lengths.^{29,30} Mesopores (0.002–0.05 μ m) are found to be favored over micropores (<0.002 μ m) in the adsorption of long-chain PFAS such as PFOS and PFOA, whereas contradictory findings are associated with the adsorption of short-chain PFASs.^{26,31}

Currenlty, featuring larger overall hydrophobic surface areas, novel strategies including powdered activated carbon (PAC), nanoporous carbon, enhanced biochars, and cellulose are developed pursuing higher efficiency and capacity than GAC.^{19,28,30,32–35} However, the efficiency of activated carbon base strategies is commonly compromised in the presence of other soluble co-contaminants.³⁶ Sorption of those non-fluorinated impurities can result in the sorbent reaching capacity prior to the capture of PFAS. In addition, there is no regeneration strategy available for these carbon-based sorbents, which negates their previous advantages in cost-efficiency.³⁷ Besides, limited removal efficiency may be found in the encounter with less hydrophobic and short-chain PFAS, resulting in remaining residues in treated water.

Fluorous Interaction with PFAS Tails

Unlike the above-mentioned hydrophobic interaction, the fluorine-fluorine interaction appears to be a promising force to provide sorption selectivity especially in the presence of large quantity of co-contaminants. Being recognized as the most electronegative element in the periodic table, fluorine is enabled to polarize nearby atoms, enhancing their ability to interact with other electron-rich substances. It has been reported that the fluorine atom has low atomic polarizability and exhibits a reduced propensity to interact with other molecules.³⁸ Consequently, they tend to segregate, minimizing intermolecular contacts with nonfluorous matter while maximizing contacts with fluorinated compounds. Recall that PFAS substances are also synthetic aliphatic chemicals in which hydrogen atoms bonded to carbon skeletons are completely or partially replaced by fluorine atoms.²⁶ Such fluorous interaction distinguishes fluorinated sorbents from others and has promoted interests in employing fluorinecontaining sorbents for selective and specific capture of PFAS.

In the circumstance of PFAS sorption, fluorinated segments in sorbents can provide specific fluorous interactions with the fluorinated tail of PFAS molecules, enhancing the capture of PFAS substances in water while reducing the sorption of other co-contaminants. In a trial carried out by Tan et al., the fluorinated block copolymer synthesized was found to have commendable performance on rapid PFOA sorption, as well as minimized impact from soluble co-contaminants.³⁹ To be more specific, the presence of dissolved proteins and other biomolecules, e.g., 10% (v/v) fetal bovine serum, has no adverse impact on the removal of PFOA from the solution.

Although the fluorous interaction is inherently stronger than the hydrophobic interaction, relying solely on it in sorbents proves inadequate for capturing PFAS at low parts per billion (ppb) concentrations in aqueous environments. Thus, cooperation with hydrophobic and/or electrostatic interactions is commonly seen in the design of fluorinated sorbents. A number of studies carried out in recent years have investigated the practicality of fluorinated compounds in sorbent design for selective sorption, making it a promising solution to one of the primary challenges in selective PFAS capture which will be introduced in the later section.^{39–41}

Electrostatic Interaction with PFAS Heads

The electrostatic interaction is a noncovalent interaction between charged particles and can be either attractive or repulsive depending on types of charges. PFAS compounds, containing a hydrophilic head and a hydrophobic/fluorophilic tail in structure, are normally ionic under aqueous conditions. This makes the use of electrostatic interaction for PFAS



Figure 1. Summarization of chemical structures of interplay PFAS sorbents. (a) Porous β -cyclodextrin polymers [adapted from refs 58, 60, 61. Copyright 2022, 2017, and 2020, respectively, American Chemical Society], (b) magnetic fluorinated polymer, (c) ionic fluorogels [adapted from ref 50. Copyright 2020, American Chemical Society], and (d) fluorophilic amine-functionalized redox-active copolymers.

sorption a promising strategy.²² Mechanisms behind the scenes include well-established electrostatic attraction and ion exchange, whereas the existence of Coulombic repulsion is found to hinder sorption.^{35,42,43}

Taking IEX resin as an example, it is able to attract molecules with opposite charge onto its large surface area and release an equal number of same charged ions to the solution until formation of equilibrium.⁴⁴ The ion exchange sites can be either cationic or anionic depending on the charge of fixed functional groups attached to its matrix. The anion exchange resins are favored and better developed as the majority of currently established PFAS compounds are found to be anionic.45 The ionic characteristics of IEX are commonly gained in the production process by methylation or quaternization. $^{13,46-50}$ Both iodomethane and chloromethane are considered forms of methylation, depending on the designed resin structure and can result in the transfer of a cation methyl group to the resin matrix; while quaternization, on the other hand, adds a quaternary ammonium group composed of charged nitrogen atoms. Being one of the most established PFAS sorbents, the viability of IEX has been investigated in multiple trials in recent decades, with merits reported in versatility, regenerability, efficiency, and capacity.

However, restricted performance of IEX resins have been found in trials with involvement of other soluble ionic impurities, resulting in sorption competition.⁵¹ Current PFAS removal technologies featuring electrostatic interaction typically remove waterborne contaminants nonspecifically, resulting in saturation by nonfluorinated species.⁵² The competition sorption of other co-contaminants can clog ion-exchange sorbents, thus significantly impacting their PFAS sorption capacity and reducing their lifespan.⁵³ This makes the applications of these sorbents cost prohibitive.

Interplay among Different Types of Interactions

The cooperation between hydrophobic, fluorous, and electrostatic segments in the sorbent design maximizes the sorption capacity, selectivity, and kinetics in the removal of PFAS, including the challenging short-chain PFAS. For instance, the porous polymers with quaternary ammonium segments are a good representation of combining hydrophobic and electrostatic interactions. Liu et al. reported in their trial that

electrostatically modified porous aromatic framework (PAF) scored 14.8 times better performance in PFOA adsorption than nonquaternized parent material, and 24.1 times higher than activated carbons accordingly.⁵⁴ Optimal performance on PFOS adsorption was also witnessed in a modified cationic porous chitosan bead biosorbent.⁵⁵ The metal-organic frameworks, a novel field of coordination polymers, can be another example of where hydrophobic and electrostatic interactions collaborate with each other.⁵⁶ A positive correlation was found between value of specific surface area (SSA) and sorption capacity, whereas cationic characteristics was found to augment capacity even in conditions with decreased SSA.⁵⁷ In another study regarding the sorption of both short-chain and long-chain PFAS, extraordinary removal efficiency was found using cationic porous β -cyclodextrin polymer (cyclic oligosaccharides containing seven D-glucose units) even at low resin concentrations at 1 mg L^{-1} (Figure 1a).⁵⁸ The PFOA concentration was reduced from 1 μ g L⁻¹ to less than 10 ng L⁻¹ using β -cyclodextrin, which is approximately 7 times lower than the regulatory requirements of the U.S. EPA.^{58,59} As found in those studies, combination of electrostatic interaction with hydrophobicity can elevate resin adsorption performance, while lack of selectivity remains unsolved in this combination strategy.

Recent achievements seek combinations of fluorous, electrostatic, and/or hydrophobic interactions to overcome the above challenges and enable efficient capture of PFAS under a real contaminated environment, including short-chain PFAS. A recent study in our group reported the innovation of a new magnetic fluorinated polymer sorbent (Figure 1b), featuring incorporation of fluorous (perfluoropolyether) and electrostatic (quaternary ammonium) interactions. Such a sorbent was found to have improved performance on the removal of both short-chain and long-chain PFAS, reaching >99% removal efficiency within 30 s, even in the presence of cocontaminants.⁴⁶ Notably, the removal of an emerging ammonium salt of hexafluoropropylene oxide dimer acid (GenX) reaches a high sorption capacity of 219 mg g^{-1} based on the Langmuir model. The superior performance is also evidenced by the ease of multiple regenerations by washing with a methanol salt solution. In addition to the previously mentioned porous β -cyclodextrins based on hydrophobic and



Figure 2. Chemical structures of widely explored PFAS compounds.

electrostatic interactions, fluorinated β -cyclodextrins have also been employed in PFAS adsorption, incorporating fluorous interactions (Figure 1a). Examples include decafluorobiphenyl β -cyclodextrins (DFB-CDP) and pentafluorobenzaldehyde amine β -cyclodextrins. Both modifications have demonstrated exceptional performance in PFAS removal. DFB-CDP, for instance, was reported to be ten times more effective than GAC, while amine β -cyclodextrins exhibited the highest affinity for PFAS and GenX among the designed CD-based adsorbents.^{60,61} In addition, an ionic fluorogel (IF) (Figure 1c) is another form of design that creditably illustrates the combination of electrostatic and fluorophilic interactions. In trials carried out by Kumarsamy et al., a commercially available perfluoropolyether was copolymerized with an amine monomer, ionized, and sieved for assessments of PFAS removal.⁵⁰ Their study indicates significantly higher affinity and capacity for both long- and short-chain PFAS removals in batch studies. In real water trials, water sourced from PFAS contaminated sites with 1.3 mg/L total organic content (TOC) were tested, with liquid chromatography-mass spectrometry (LC-MS) results indicating nondetectable long-chain PFAS concentration and over 95% removal efficiency of shorter chain PFAS including perfluorobutanesulfonic acid (PFBS), GenX, and perfluorohexanoic acid (PFHxA). The flexibility and diversity in monomer selection have also made the improvement in IF structure and design easier to be achieved. In another trial carried out in 2022, hydrolytically stable IF sorbents were reported to be effective sorbents for removing 21 legacy and emerging PFAS from natural water, and they demonstrated regenerability across multiple reuse cycles.⁶² The fluorophilic amine-functionalized redox-active polymer reported by Román Santiago et al. (Figurer 1d) has also demonstrated the role of fluorous interaction in facilitating binding of shorter chain PFAS, particularly those with lower hydrophobicity.⁶³ A 2% fluorination was also found to be the percentage demonstrating optimal cooperation between electrostatic and fluorous interactions.

The role of each type of interaction plays was assessed in our previous reports, of which the relative contributions of fluorous



and electrostatic interactions were assessed using 1D and 2D ¹⁹F nuclear magnetic resonance (NMR) and isothermal titration calorimetry (ITC).¹⁷ A fast exchange between bonded and free PFOA was observed in the sorbent material featuring the fluorine-fluorine interaction, whereas electrostatic interaction was associated with tight binding without such exchange. Evidence also shows that fluorous interaction exhibits greater strength and efficiency at higher PFAS concentrations, whereas electrostatic interaction plays dominantly in low PFAS concentrations.¹⁷ In a research trial conducted by Román Santiago et al., various copolymers incorporating redox-active, electrostatic, and fluorophilic interactions were evaluated against perfluoroalkyl acids ranging from chain lengths four to seven.⁶³ The copolymers, especially those with introduced fluorinated segments, exhibited notably improved capture efficiency for shorter-chain PFAS. This suggests a pivotal role of the fluorine-fluorine interaction in capturing more hydrophilic PFAS compounds, particularly those with shorter chain lengths. Additionally, their adsorption and desorption studies highlighted differing mechanisms of PFAS adsorption in the presence of long-chain PFHxS and short-chain PFBA, underscoring the effectiveness of employing various interactions in designing advanced PFAS sorbents.

PERSPECTIVES AND OUTLOOK

First being recognized as a potential health risk factor in 2002, PFAS chemicals are globally distributed pollutants that rapidly gained concern worldwide. Regulatory bodies are increasingly emphasizing the need to reduce the release and distribution of PFAS into the environment due to their persistent and potentially hazardous nature. To date, the granular activated carbon (GAC) and ion exchange (IEX) resins remain the two dominant and mostly established treatment methods through hydrophobic and electrostatic interactions. Yet limited performance of these sorbents has been found in trials associated with the removal of short-chain PFAS (C < 6) and the presence of soluble co-contaminants. Challenges posed in current sorbent development include (1) limited removal capacity and selectivity due to competitive sorption of other

co-contaminants; (2) low effectiveness in the removal of shortchain PFAS; and (3) difficulty in regeneration of the sorbent.

Perspective from PFAS Structure

When designing an efficient PFAS sorbent, it is crucial to consider the influence of the functional group and chain length of PFAS compounds. These factors determine the electrostatics, hydrophobicity, and fluorophilicity, all of which play significant roles in how sorbent materials perform in capturing PFAS compounds effectively. Figure 2 provides an overview of widely explored PFAS compounds categorized based on functional groups and chain length. Chain length, strongly linked to hydrophobicity and fluorophilicity, is a critical factor. For instance, in various trials, resins designed to target longchain PFAS such as PFOA and PFOS often demonstrate constrained performance for short chain PFAS such as PFBA due to increased hydrophilicity. Additionally, the type of charged head of targeted PFAS compounds, influencing the strength of the electrostatic interaction, should be considered. Although the majority of PFAS compounds are anionic, cationic, and neutral, PFAS compounds can also be present under specific conditions. Therefore, designing efficient sorbent, e.g., cationic exchange resin and porous sorbent, targeting the removal of cationic and neutral PFAS compounds is also required.

Perspective from Sorbent Design

Currently, the majority of newly reported PFAS sorbents have been tested for sorption of PFAS with carbon numbers ranging from 4 to 12. However, it is imperative to design efficient sorbents that can effectively remove ultrashort chain PFAS which present a significant challenge due to their high water solubility. Besides, the importance of parameters chosen for assessing resin performance, such as sorption kinetics, sorption capacity, and removal efficiency, should be considered. The adsorption capacity emphases on the maximum amount of PFAS sorbed per unit, whereas sorption kinetics assesses the time length required for reaching sorption equilibrium, and removal efficiency mimics how much PFAS can be captured by a certain amount of sorbent. In addition, a primary challenge for developing PFAS removal technology is the presence of nonfluorinated organic and inorganic species at 3-8 orders of magnitude higher concentration than PFAS. Current PFAS removal technologies typically remove waterborne contaminants nonspecifically, resulting in saturation by nonfluorinated species. The competition sorption of other co-contaminants can clog ion-exchange sorbents and saturate activated carbons, thus significantly impacting their PFAS sorption capacity and reducing their lifespan. Therefore, developing novel sorbents that have good selectivity to the removal of PFAS is a key research direction in the future.

In summary, we summarized three predominant interactions behind current sorbent development, i.e., hydrophobic, fluorous, and electrostatic interactions, as well as the key role of PFAS structure. The mechanism behind the scenes is explained, with applications of each interaction type and their combinations illustrated. The combined strategies have higher sorption capacity and removal efficiency compared with monointeraction type, whereas the fluorine–fluorine interaction gained a particular trend of interest due to its extraordinary performance on sorption selectivity. The fluorous interaction, referred to as the attractive force between molecules or functional groups with fluorine atoms, distinguishes this strategy from others. Thus, the development of fluorine-cooperated charged sorbents could be a promising solution to circumvent deficiencies in the current design of efficient PFAS sorbents. However, it is noteworthy that existing regulations could introduce additional complexities into the production of fluorinated sorbents. Consequently, the development and use of fluorinated sorbents might encounter more stringent requirements and approval processes to ensure that their production, application, and eventual disposal are in alignment with environmental and human health protection.

AUTHOR INFORMATION

Corresponding Author

Cheng Zhang – Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane 4072, Australia; The Centre for Advanced Imaging, The University of Queensland, Brisbane 4072, Australia; orcid.org/0000-0002-2722-7497; Email: c.zhang3@ uq.edu.au

Authors

- Yutong He Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane 4072, Australia; The Centre for Advanced Imaging, The University of Queensland, Brisbane 4072, Australia
- Xinrong Cheng Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane 4072, Australia; The Centre for Advanced Imaging, The University of Queensland, Brisbane 4072, Australia
- Samruddhi Jayendra Gunjal Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane 4072, Australia; The Centre for Advanced Imaging, The University of Queensland, Brisbane 4072, Australia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmaterialsau.3c00066

Author Contributions

CRediT: Yutong He conceptualization (supporting), writingoriginal draft (lead), writing-review and editing (supporting); Xinrong Cheng conceptualization (supporting), writing-original draft (supporting), writing-review and editing (supporting); Samruddhi Jayendra Gunjal writing-original draft (supporting); Cheng Zhang conceptualization (lead), writing-original draft (supporting), writing-review and editing (lead). CRediT: **Yutong He** conceptualization, writing-original draft, writing-review & editing; **Xinrong Cheng** conceptualization, writing-original draft, writing-review & editing; **Samruddhi Jayendra Gunjal** writing-original draft; **Cheng Zhang** conceptualization, writing-original draft, writing-review & editing.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the Australian Research Council (LP220100036), the United States Army International Technology Center-Pacific (ITC-PAC) and The University of Queensland Knowledge Exchange & Translation Grants for funding of this research. C.Z. acknowledges the Australian Research Council for his Discovery Early Career Researcher Award fellowship (DE230101105).

REFERENCES

(1) Scher, D. P.; Kelly, J. E.; Huset, C. A.; Barry, K. M.; Hoffbeck, R. W.; Yingling, V. L.; Messing, R. B. Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water. *Chemosphere* **2018**, *196*, 548–555.

(2) *PFAS*; American Water Works Association. www.awwa.org. https://www.awwa.org/Resources-Tools/Resource-Topics/PFAS (accessed 2023-09-28).

(3) Gluge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environ. Sci.: Process. Impacts.* **2020**, *22* (12), 2345–2373.

(4) Kempisty, D. M.; Racz, L. Forever Chemicals; CRC Press: Milton, 2021. DOI: 10.1201/9781003024521.

(5) Brennan, N. M.; Evans, A. T.; Fritz, M. K.; Peak, S. A.; von Holst, H. E. Trends in the Regulation of Per- and Polyfluoroalkyl Substances (PFAS): A Scoping Review. *IJERPH* **2021**, *18* (20), 10900.

(6) US EPA. Risk Management for Per- and Polyfluoroalkyl Substances (PFAS) under TSCA; US EPA. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas (accessed 2023-09-28).

(7) McCleaf, P.; Englund, S.; Östlund, A.; Lindegren, K.; Wiberg, K.; Ahrens, L. Removal efficiency of multiple poly- and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests. *Water Res.* **2017**, *120*, 77–87.

(8) Graber, J. M.; Alexander, C.; Laumbach, R. J.; Black, K.; Strickland, P. O.; Georgopoulos, P. G.; Marshall, E. G.; Shendell, D. G.; Alderson, D.; Mi, Z.; et al. Per- and polyfluoroalkyl substances (PFAS) blood levels after contamination of a community water supply and comparison with 2013–14 NHANES. *JJESEE* 2019, 29 (2), 172–182.

(9) Sunderland, E. M.; Hu, X. C.; Dassuncao, C.; Tokranov, A. K.; Wagner, C. C.; Allen, J. G. A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *J. Expo. Sci. Environ. Epidemiol.* 2019, 29 (2), 131–147.

(10) Li, K.; Gao, P.; Xiang, P.; Zhang, X.; Cui, X.; Ma, L. Q. Molecular mechanisms of PFOA-induced toxicity in animals and humans: Implications for health risks. *Environ. Int.* **2017**, *99*, 43–54. (11) Banwell, C.; Housen, T.; Smurthwaite, K.; Trevenar, S.; Walker, L.; Todd, K.; Rosas, M.; Kirk, M. Health and social concerns about living in three communities affected by per- and polyfluoroalkyl substances (PFAS): A qualitative study in Australia. *PLoS One* **2021**, *16* (1), e0245141–e0245141.

(12) Zhao, P.; Xia, X.; Dong, J.; Xia, N.; Jiang, X.; Li, Y.; Zhu, Y. Short- and long-chain perfluoroalkyl substances in the water, suspended particulate matter, and surface sediment of a turbid river. *Sci. Total Environ.* **2016**, *568*, 57–65.

(13) Ateia, M.; Alsbaiee, A.; Karanfil, T.; Dichtel, W. Efficient PFAS Removal by Amine-Functionalized Sorbents: Critical Review of the

Current Literature. Environ. Sci. Technol. Lett. 2019, 6 (12), 688–695. (14) Registry of restriction intentions until outcome; ECHA. echa. europa.eu. https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b (accessed 2023-09-28).

(15) Murray, C. C.; Safulko, A.; Vatankhah, H.; Liu, C. J.; Tajdini, B.; Marshall, R. E.; Bellona, C. PFAS adsorbent selection: The role of adsorbent use rate, water quality, and cost. *J. Hazard. Mater.* **2023**, 454, 131481–131481.

(16) Meegoda, J. N.; Bezerra de Souza, B.; Casarini, M. M.; Kewalramani, J. A. A Review of PFAS Destruction Technologies. *IJERPH* **2022**, *19* (24), 16397.

(17) Tan, X.; Sawczyk, M.; Chang, Y.; Wang, Y.; Usman, A.; Fu, C.; Král, P.; Peng, H.; Zhang, C.; Whittaker, A. K. Revealing the Molecular-Level Interactions between Cationic Fluorinated Polymer Sorbents and the Major PFAS Pollutant PFOA. *Macromolecules* **2022**, 55 (3), 1077–1087.

(18) Tan, H.-M.; Pan, C.-G.; Yin, C.; Yu, K. Toward systematic understanding of adsorptive removal of legacy and emerging per-and polyfluoroalkyl substances (PFASs) by various activated carbons (ACs). *Environ. Res.* **2023**, 233, 116495–116495.

(19) Singh, G.; Lee, J. M.; Kothandam, G.; Palanisami, T.; Al-Muhtaseb, A. a. H.; Karakoti, A.; Yi, J.; Bolan, N.; Vinu, A. A Review on the Synthesis and Applications of Nanoporous Carbons for the Removal of Complex Chemical Contaminants. *BCSJ.* **2021**, *94* (4), 1232–1257.

(20) Butler, J. A. V. The energy and entropy of hydration of organic compounds. *Trans. Faraday Soc.* **1937**, *33*, 229.

(21) Bier, M. A symposium on the mechanism of enzyme action. *Arch. Biochem. Biophys.* **1955**, 54 (1), 254–256.

(22) Meyer, E. E.; Rosenberg, K. J.; Israelachvili, J. Recent Progress in Understanding Hydrophobic Interactions. *PNAS USA* **2006**, *103* (43), 15739–15746.

(23) Hermann, R. B. Theory of hydrophobic bonding. II. Correlation of hydrocarbon solubility in water with solvent cavity surface area. *J. Phys. Chem.* **1972**, *76* (19), 2754–2759.

(24) Blokzijl, W.; Engberts, J. B. F. N. Hydrophobic Effects. Opinions and Facts. *Angew. Chem., Int. Ed.* **1993**, 32 (11), 1545–1579.

(25) Kong, I. Design and Applications of Nanostructured Polymer Blends and Nanocomposite Systems; Elsevier, 2016; pp 125–154.

(26) Du, Z.; Deng, S.; Bei, Y.; Huang, Q.; Wang, B.; Huang, J.; Yu, G. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents——A review. *J. Hazard. Mater.* **2014**, 274, 443–454.

(27) Leung, S. C. E.; Shukla, P.; Chen, D.; Eftekhari, E.; An, H.; Zare, F.; Ghasemi, N.; Zhang, D.; Nguyen, N.-T.; Li, Q. Emerging technologies for PFOS/PFOA degradation and removal: A review. *Sci. Total Environ.* **2022**, 827, 153669–153669.

(28) Deng, S.; Nie, Y.; Du, Z.; Huang, Q.; Meng, P.; Wang, B.; Huang, J.; Yu, G. Enhanced adsorption of perfluorooctane sulfonate and perfluorooctanoate by bamboo-derived granular activated carbon. *J. Hazard. Mater.* **2015**, *282*, 150–157.

(29) Carey, G. R.; Hakimabadi, S. G.; Singh, M.; McGregor, R.; Woodfield, C.; Van Geel, P. J.; Pham, A. L. T. Longevity of colloidal activated carbon for in situ PFAS remediation at AFFF-contaminated airport sites. *Remediation* (N Y) **2022**, 33 (1), 3–23.

(30) Saha, D.; Khan, S.; Van Bramer, S. E. Can porous carbons be a remedy for PFAS pollution in water? A perspective. *J. Environ. Chem. Eng.* **2021**, *9* (6), No. 106665.

(31) Siriwardena, D. P.; Crimi, M.; Holsen, T. M.; Bellona, C.; Divine, C.; Dickenson, E. Influence of groundwater conditions and co-contaminants on sorption of perfluoroalkyl compounds on granular activated carbon. *Remediation* (N Y) **2019**, *29* (3), 5–15.

(32) Chen, W.-f.; Zhang, Z.-Y.; Li, Q.; Wang, H.-Y. Adsorption of bromate and competition from oxyanions on cationic surfactant-modified granular activated carbon (GAC). *J. Chem. Eng.* **2012**, *203*, 319–325.

(33) Chen, X.; Xia, X.; Wang, X.; Qiao, J.; Chen, H. A comparative study on sorption of perfluorooctane sulfonate (PFOS) by chars, ash and carbon nanotubes. *Chemosphere* **2011**, *83* (10), 1313–1319.

(34) Hokkanen, S.; Bhatnagar, A.; Sillanpää, M. A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Res.* **2016**, *91*, 156–173.

(35) Lei, X.; Lian, Q.; Zhang, X.; Karsili, T. K.; Holmes, W.; Chen, Y.; Zappi, M. E.; Gang, D. D. A review of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities. *Environ. Pollut.* **2023**, *321*, No. 121138.

(36) Inyang, M.; Dickenson, E. R. V. The use of carbon adsorbents for the removal of perfluoroalkyl acids from potable reuse systems. *Chemosphere* **2017**, *184*, 168–175.

(37) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014**, *50*, 318–340.

(38) Pollice, R.; Chen, P. Origin of the Immiscibility of Alkanes and Perfluoroalkanes. J. Am. Chem. Soc. 2019, 141 (8), 3489–3506.

(39) Tan, X.; Zhong, J.; Fu, C.; Dang, H.; Han, Y.; Král, P.; Guo, J.; Yuan, Z.; Peng, H.; Zhang, C.; et al. Amphiphilic Perfluoropolyether Copolymers for the Effective Removal of Polyfluoroalkyl Substances from Aqueous Environments. *Macromolecules* **2021**, *54* (7), 3447– 3457.

(40) Quan, Q.; Wen, H.; Han, S.; Wang, Z.; Shao, Z.; Chen, M. Fluorous-Core Nanoparticle-Embedded Hydrogel Synthesized via Tandem Photo-Controlled Radical Polymerization: Facilitating the Separation of Perfluorinated Alkyl Substances from Water. *ACS Appl. Mater. Interfaces.* **2020**, *12* (21), 24319–24327.

(41) Koda, Y.; Terashima, T.; Nomura, A.; Ouchi, M.; Sawamoto, M. Fluorinated Microgel-Core Star Polymers as Fluorous Compartments for Molecular Recognition. *Macromolecules* **2011**, *44* (12), 4574–4578.

(42) Hussain, F. A.; Janisse, S. E.; Heffern, M. C.; Kinyua, M.; Velázquez, J. M. Adsorption of perfluorooctanoic acid from water by pH-modulated Brönsted acid and base sites in mesoporous hafnium oxide ceramics. *iScience* **2022**, *25* (4), 104138–104138.

(43) Dixit, F.; Dutta, R.; Barbeau, B.; Berube, P.; Mohseni, M. PFAS removal by ion exchange resins: A review. *Chemosphere* **2021**, *272*, No. 129777.

(44) Parker, B. A.; Knappe, D. R. U.; Titaley, I. A.; Wanzek, T. A.; Field, J. A. Tools for Understanding and Predicting the Affinity of Perand Polyfluoroalkyl Substances for Anion-Exchange Sorbents. *Environ. Sci. Technol.* **2022**, *56* (22), 15470–15477.

(45) Crone, B. C.; Speth, T. F.; Wahman, D. G.; Smith, S. J.; Abulikemu, G.; Kleiner, E. J.; Pressman, J. G. Occurrence of per- and polyfluoroalkyl substances (PFAS) in source water and their treatment in drinking water. *Crit. Rev. Environ. Sci. Technol.* **2019**, 49 (24), 2359–2396.

(46) Tan, X.; Dewapriya, P.; Prasad, P.; Chang, Y.; Huang, X.; Wang, Y.; Gong, X.; Hopkins, T. E.; Fu, C.; Thomas, K. V.; et al. Efficient Removal of Perfluorinated Chemicals from Contaminated Water Sources Using Magnetic Fluorinated Polymer Sorbents. *Angew. Chem., Int. Ed.* **2022**, *134* (49), e202213071.

(47) Clemens, A. L.; Jayathilake, B. S.; Karnes, J. J.; Schwartz, J. J.; Baker, S. E.; Duoss, E. B.; Oakdale, J. S. Tuning Alkaline Anion Exchange Membranes through Crosslinking: A Review of Synthetic Strategies and Property Relationships. *Polym. J.* **2023**, *15* (6), 1534.

(48) Wang, L.; Hickner, M. A. Low-temperature crosslinking of anion exchange membranes. *Polym. Chem.* **2014**, *5* (8), 2928–2935.

(49) Sung, S.; Chae, J. E.; Min, K.; Kim, H.-J.; Nam, S. Y.; Kim, T.-H. Preparation of crosslinker-free anion exchange membranes with excellent physicochemical and electrochemical properties based on crosslinked PPO-SEBS. *J. Mater. Chem.* **2021**, *9* (2), 1062–1079.

(50) Kumarasamy, E.; Manning, I. M.; Collins, L. B.; Coronell, O.; Leibfarth, F. A. Ionic Fluorogels for Remediation of Per- and Polyfluorinated Alkyl Substances from Water. *ACS Cent. Sci.* **2020**, *6* (4), 487–492.

(51) Ross, I.; McDonough, J.; Miles, J.; Storch, P.; Kochunarayanan, P. T.; Kalve, E.; Hurst, J.; Dasgupta, S. S.; Burdick, J. A review of emerging technologies for remediation of PFASs. *Remediation* (N Y) **2018**, 28 (2), 101–126.

(52) Zhang, C.; Yan, K.; Fu, C.; Peng, H.; Hawker, C. J.; Whittaker, A. K. Biological Utility of Fluorinated Compounds: from Materials Design to Molecular Imaging, Therapeutics and Environmental Remediation. *Chem. Rev.* **2022**, *122* (1), 167–208.

(53) Oyetade, O. A.; Varadwaj, G. B. B.; Nyamori, V. O.; Jonnalagadda, S. B.; Martincigh, B. S. A critical review of the occurrence of perfluoroalkyl acids in aqueous environments and their removal by adsorption onto carbon nanotubes. *Rev. Environ. Sci. Biotechnol.* **2018**, *17* (4), 603–635.

(54) Liu, X.; Zhu, C.; Yin, J.; Li, J.; Zhang, Z.; Li, J.; Shui, F.; You, Z.; Shi, Z.; Li, B.; et al. Installation of synergistic binding sites onto porous organic polymers for efficient removal of perfluorooctanoic acid. *Nat. Commun.* **2022**, *13* (1), 2132–2132.

(55) Zhang, Q.; Deng, S.; Yu, G.; Huang, J. Removal of perfluorooctane sulfonate from aqueous solution by crosslinked chitosan beads: Sorption kinetics and uptake mechanism. *Bioresour. Technol.* **2011**, *102* (3), 2265–2271.

(56) Baptista, J. M.; Sagu, J. S.; kg, U. W.; Lobato, K. State-of-the-art materials for high power and high energy supercapacitors: Performance metrics and obstacles for the transition from lab to industrial scale – A critical approach. J. Chem. Eng. 2019, 374, 1153–1179.

(57) Liu, K.; Zhang, S.; Hu, X.; Zhang, K.; Roy, A.; Yu, G. Understanding the Adsorption of PFOA on MIL-101(Cr)-Based Anionic-Exchange Metal–Organic Frameworks: Comparing DFT Calculations with Aqueous Sorption Experiments. *Environ. Sci. Technol.* **2015**, *49* (14), 8657–8665.

(58) Wang, R.; Lin, Z.-W.; Klemes, M. J.; Ateia, M.; Trang, B.; Wang, J.; Ching, C.; Helbling, D. E.; Dichtel, W. R. A Tunable Porous β -Cyclodextrin Polymer Platform to Understand and Improve Anionic PFAS Removal. *ACS Cent. Sci.* **2022**, *8* (5), 663–669.

(59) Chen, C.; Ng, D. Y. W.; Weil, T. Polymer bioconjugates: Modern design concepts toward precision hybrid materials. *Prog. Polym. Sci.* **2020**, *105*, No. 101241.

(60) Xiao, L.; Ling, Y.; Alsbaiee, A.; Li, C.; Helbling, D. E.; Dichtel, W. R. β -Cyclodextrin Polymer Network Sequesters Perfluorooctanoic Acid at Environmentally Relevant Concentrations. *J. Am. Chem. Soc.* **2017**, 139 (23), 7689–7692.

(61) Yang, A.; Ching, C.; Easler, M.; Helbling, D. E.; Dichtel, W. R. Cyclodextrin Polymers with Nitrogen-Containing Tripodal Crosslinkers for Efficient PFAS Adsorption. *ACS Mater. Lett.* **2020**, *2* (9), 1240–1245.

(62) Manning, I. M.; Guan Pin Chew, N.; Macdonald, H. P.; Miller, K. E.; Strynar, M. J.; Coronell, O.; Leibfarth, F. A. Hydrolytically Stable Ionic Fluorogels for High-Performance Remediation of Perand Polyfluoroalkyl Substances (PFAS) from Natural Water. *Angew. Chem., Int. Ed.* **2022**, *134* (41), e202208150.

(63) Román Santiago, A.; Yin, S.; Elbert, J.; Lee, J.; Shukla, D.; Su, X. Imparting Selective Fluorophilic Interactions in Redox Copolymers for the Electrochemically Mediated Capture of Short-Chain Perfluoroalkyl Substances. J. Am. Chem. Soc. **2023**, 145 (17), 9508– 9519.