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Sequestration of poly- and perfluoroalkyl substances (PFAS) by adsorption: surfactant and surface aspects

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ABSTRACT

Per- and polyfluoro alkyl substances (PFAS) are synthetic compounds composed of a fully or partially fluorinated carbon chain. Fluorinated surfactants are a major PFAS subgroup. Their widespread use has resulted in their release into the environment and accumulation in water. The sequestration of PFAS from aqueous solution by adsorption is a pressing and challenging environmental pollution problem which necessitates surface and colloid science to offer solutions for the benefit of a sustainable future. In this review, we first provide an overview of the aqueous solution and self-assembly properties of common PFAS surfactants. Next, we present physical adsorption of PFAS surfactants, which is the first step used to concentrate PFAS prior to their subsequent proper disposal or destruction, with a focus on "natural" materials such as activated carbon and biopolymers, and on surfactant/surface/colloid aspects. In closing, we offer some perspective on gaps in fundamental knowledge and future research directions.

Keywords: PFAS, PFOA, PFOS, formulation, activated carbon, emerging contaminant, remediation

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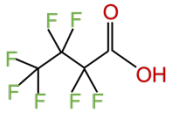
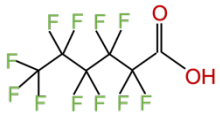
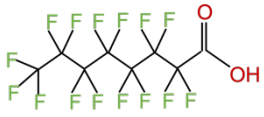
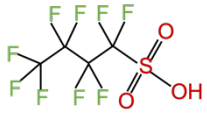
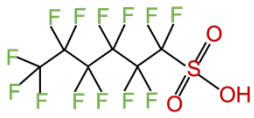
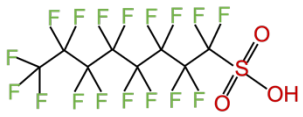
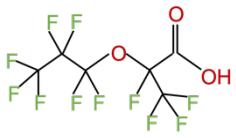
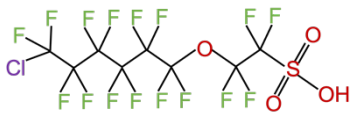
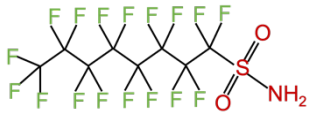
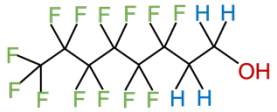
INTRODUCTION

Per- and polyfluoro alkyl substances (PFAS) are synthetic compounds composed of a fully or partially fluorinated carbon chain. PFAS comprise fluorinated polymers, surfactants, ethers, esters, alcohols and thiols.[1, 2] A major PFAS subgroup are fluorinated surfactants that comprise fluorinated hydrophobic chains and hydrophilic headgroups (Table 1). The high electronegativity, low polarizability and small size of fluorine give rise to strong C–F bond, weak $–CF_2–$ intermolecular forces and strong hydrophobic interactions which, in turn, result in outstanding properties of PFAS surfactants, including incompatibility with both water and hydrocarbons, high wetting ability, strong surface activity, and high chemical and thermal stability.[3, 4] These properties render PFAS surfactants useful in many applications, including nonstick cookware, food packaging paper, stain repellant and waterproof clothing, paints, cosmetics, and firefighting foams.[1, 4, 5]

Table 1. Chemical structures of select PFAS surfactants.

Perfluorinated Surfactant	Formula	Chemical Structure
Perfluorobutanoic acid	$C_3F_7CO_2H$	
Perfluorohexanoic acid	$C_5F_{11}CO_2H$	
Perfluorooctanoic acid	$C_7F_{15}CO_2H$	
Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	
Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	
Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	
Hexafluoropropylene oxide dimer acid (GenX)	$C_6F_{11}O_3H$	

6:2 Chlorinated polyfluoroalkyl ether sulfonic acids (F-53B)	$Cl(CF_2)_6O(CF_2)_2SO_3H$	
Perfluorooctane sulfonamide	$C_8F_{17}SO_2NH_2$	
6:2 fluorotelomer alcohol	$C_6F_{13}(CH_2)_2OH$	

The widespread use of PFAS surfactants in industrial processes (mainly fluoropolymer manufacturing), consumer products, and fire-fighting foams has resulted in their release into the environment and accumulation in water including drinking, waste, marine, surface and groundwater.[1, 6-9] Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most extensively produced and frequently detected PFAS in the environment. The presence of PFAS in the aqueous environment poses serious concerns because these compounds are not receptive to conventional water treatment methods, thus their removal is quite difficult. The persistence of PFAS, coupled with their high solubility in water, low vapor pressure, and ability to adsorb to soil and sediments, make many PFAS, particularly perfluoroalkyl acids (PFAA), highly mobile in water. PFAS do not partition in the "usual" hydrophobic places but rather circulate. PFAS surfactants can enter the human body through water and food that got contaminated from contact with PFAS-treated packaging or cookware,[10, 11] and can cause adverse health effects such as thyroid dysfunction, immune response suppression, kidney disease, altered cholesterol levels or metabolic diseases, reproductive toxicity, neurodevelopmental problems, and various cancers.[7, 9, 11, 12]

Consequently, "legacy" PFAS such as PFOA, PFOS, and their related compounds have been banned in many countries, including the US and European Union. Only PFOA, PFOS, perfluorohexane sulphonic acid (PFHxS) and their precursors are currently subject to international regulations, with PFOA and PFOS being included in the International Stockholm Convention's list of globally restricted Persistent Organic Pollutants (POP), and PFHxS proposed for inclusion. The U.S. Environmental Protection Agency (EPA) has established lifetime health advisory levels at 70 ng/L for PFOA and PFOS,[13] and is prohibiting companies from manufacturing, processing, or importing products containing certain long-chain PFAS, without prior EPA review and approval.[14] More recently, EPA unveiled a PFAS Action Plan that will move forward with the Maximum Contaminant Level (MCL) process for PFOA and PFOS. As part of the Action Plan, U.S. EPA will continue their enforcement actions and clarify clean-up strategies, expand monitoring of PFAS in the environment, and enhance research and the scientific foundation for addressing PFAS by developing improved detection and measurement methods, effective treatment and remediation methods.[15]

In response to these restrictions, manufacturers have introduced shorter-chain PFAS and other fluorinated alternatives such as perfluoro-2-propoxypropanoic acid (GenX) and perfluorobutanesulfonic acid (PFBS) for commercial applications.[16, 17] However, in late October 2021 an assessment by EPA concluded that GenX is more toxic than the PFOA surfactant it was intended to replace, and set a safe

daily dose of GenX and PFBA 3 ng/kg and 300 ng/kg of body weight, respectively, while that of PFOA and PFOS is 20 ng/kg of body weight.[18] EPA is currently reevaluating toxicity information for PFOA and PFOS and therefore this value is subject to change. EPA's toxicity assessment for GenX concluded that there is suggestive evidence of carcinogenic potential of oral exposure to GenX in humans, and plans to develop drinking water health advisories for GenX and PFBS in Spring 2022.[18]

These findings necessitate the removal of PFAS present in the aquatic environment. The technologies currently available to this end are based mainly on separation and destruction. Destruction technologies include advanced oxidation (i.e., chemical, electrochemical, and photochemical) and reduction; ultrasonication, biological remediation, and plasma treatment.[19] Some destruction technologies have been demonstrated effective in decomposing PFAS at laboratory scale, however, the destruction of PFAS remains challenging in practice due to the strong C–F bond, risks associated with the final products (it is unclear whether the final products, e.g., shorter-chain PFAS, are less toxic and persistent than the long-chain PFAS), and challenges of scaling up these technologies, e.g., lengthy treatment time, high energy requirements and high capital costs.[19, 20] Separations include conventional techniques of flocculation and coagulation, sedimentation and filtration; sorption techniques with the use of activated carbon, minerals, ion exchange resins, and nanomaterials; foam fractionation, and membrane technologies including nanofiltration and reverse osmosis.[19] Conventional water treatment is not effective for PFAS removal.[19]

Adsorption is effective for sequestering PFAS from water due to cost efficiency, eco-friendliness, high efficacy, simplicity of design, and ease of operation.[21, 22] Commercially available adsorbents for removing PFAS from aqueous media include Calgon Carbon Corporation's FITRASORB granular activated carbon (GAC) filters, Jakobi Carbons group's AquaSorb GAC filters, Cabot's HYDRODARCO® 4000 and NORIT® GAC 400 ACs, Purolite's Purofine PFA694E and Purolite A592E resins, ECT2's SORBIX resins, DuPont Water Solutions Amberlite™PSR2 resins and Cyclopure's DEXSORB+™ porous cyclodextrin polymer adsorbents. The uptake of PFAS on various adsorbents is attributed to multiple interactions such as electrostatic interactions, hydrogen bonding, hydrophobic effects, van der Waals forces and π-π bonding.[23]

Hence, for the design of effective adsorbent materials for PFAS surfactant removal, a fundamental understanding is important of PFAS surfactant interactions and molecular organization in water and with other species present in the aqueous solution, and on surfaces that are in contact with water. It is the objective of this review to highlight recent advances in PFAS surfactant interactions and molecular organization, and to identify needs and opportunities for further studies. The sequestration of PFAS from aqueous solution by adsorption is a pressing and challenging environmental pollution problem which necessitates surface and colloid science to offer solutions for the benefit of a sustainable future. It is notable that some of the more promising solutions involve sustainable materials that are nature-based or derived.

In what follows, we first provide an overview of aqueous solution and self-assembly properties of common PFAS surfactants. Next, we present physical adsorption of PFAS surfactants, which is the first step used to concentrate PFAS prior to their subsequent proper disposal or destruction. Our focus is on "natural" materials such as activated carbon and biopolymers, and on surfactant/surface/colloid aspects. In closing, we offer some perspective on gaps in fundamental knowledge and future research directions.

PFAS SURFACTANTS IN SOLUTION AND AT INTERFACES

A wide range is available of PFAS surfactants that have unique chemical structures and solution properties. Common PFAS surfactants include perfluorinated carboxylic acids (PFCA), perfluoroalkyl sulfonic acids (PFSA), perfluoroalkane sulfonamides (FASA), and functionalized perfluoropolyethers which include perfluoroether carboxylic and sulfonic acids (PFECA and PFESA). The most prevalent and discussed about are PFOS and PFOA. Emerging PFAS are categorized into two groups: (i) shorter-chain homologues of long-chain perfluoroalkyl acids and their precursors, e.g., perfluorobutanesulfonic acid, perfluorohexanoic acid, and (ii) perfluoropolyethers functionalized with acidic functional group attached to a per- or polyfluoroether chain instead of a perfluoroalkyl chain, e.g., GenX from DuPont/Chemours, and ADONA from 3M/Dyneon.[24] Emerging PFAS surfactants are designed with the intent to be less toxic, easier to degrade, and presumably less bioaccumulative compared to legacy PFAS. Introducing a branch is one of effective strategies for synthesizing non-bioaccumulative alternatives to PFOA.[25] It is also plausible that some emerging PFAS surfactants are designed such that they evade the bans put in place for legacy PFAS. DuPont introduced in 2009 with the trade name "GenX" the PFAS compound ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate) (FRD-902) as a safer alternative to replace PFOA in the manufacturing of fluoropolymers such as Teflon (as indicated in the Introduction, we now know that GenX is more toxic than PFOA).[26, 27] GenX is a 6 carbon perfluoroether carboxylic acid compound with a CF_3 side group. Physicochemical properties of select PFAS surfactants are shown in Table 2.

Table 2. Physicochemical properties of select PFAS surfactants. CMC is the critical micelle concentration, K_{OC} the soil organic carbon–water partition coefficient of the fluorinated surfactant, and pK_a the dissociation constant. K_{OC} is commonly used to quantify the potential of a given dissolved compound to associate with, or adsorb to, organic matter present in soil.

Perfluorinated Surfactant	Acronym	Category	Formula	Chain length	MW (g/mol)	CMC (mM)	Log K_{OC}	pK_a
Perfluorobutanoic acid	PFBA	PFCAs	$C_3F_7CO_2H$	4	214.04	759[a]	1.9[c]	0.05[b]
Perfluoropentanoic acid	PFPeA	PFCAs	$C_4F_9CO_2H$	5	264.05	200[a]	1.4[c]	-0.10[b]
Perfluorohexanoic acid	PFHxA	PFCAs	$C_5F_{11}CO_2H$	6	314.05	89.1[a]	1.3[c]	-0.17[b]
Perfluoroheptanoic acid	PFHpA	PFCAs	$C_6F_{13}CO_2H$	7	364.06	28.8[a]	1.6[c]	-0.20[b]
Perfluorooctanoic acid	PFOA	PFCAs	$C_7F_{15}CO_2H$	8	414.07	9.12[a]	1.89-2.63[c]	-0.21[b]
Perfluorononanoic acid	PFNA	PFCAs	$C_8F_{17}CO_2H$	9	464.08	2.63[a]	2.36-3.69[c]	-0.21[b]
Perfluorodecanoic acid	PFDA	PFCAs	$C_9F_{19}CO_2H$	10	514.08	0.85[a]	2.76-2.96[c]	-0.22[b]
Perfluoroundecanoic acid	PFUnDA	PFCAs	$C_{10}F_{21}CO_2H$	11	564.09	0.32[d]	3.3-3.56[c]	-0.22[b]
Perfluorododecanoic acid	PFDoDA	PFCAs	$C_{11}F_{23}CO_2H$	12	614.10	~0.1[d]	n.a.	-0.22[b]
Perfluorobutane sulfonic acid	PFBS	PFSAs	$C_4F_9SO_3H$	4	300.1	22[d]	1.2-1.79[c]	0.14[b]
Perfluorohexane sulfonic acid	PFHxS	PFSAs	$C_6F_{13}SO_3H$	6	400.11	12[d]	2.4-3.1[c]	0.14[b]
Perfluorooctane sulfonic acid	PFOS	PFSAs	$C_8F_{17}SO_3H$	8	500.13	3.1[d]	2.4-3.7[c]	0.14[b]
Perfluorodecane sulfonic acid	PFDS	PFSAs	$C_{10}F_{21}SO_3H$	10	600.13	n.a.	3.53-3.66[c]	0.14[b]
Hexafluoropropylene oxide dimer acid	GenX	PFECAs	$C_6F_{11}O_3H$	6	330.19	150[e]	n.a.	-0.06[c]
6:2 Chlorinated polyfluoroalkyl ether sulfonic acids	9Cl-PF3ONS (F-53B)	Cl-PFAES	$Cl(CF_2)_6O(CF_2)_2SO_3H$	8	532.6	n.a.	n.a.	<1[C]

Perfluorooctane sulfonamide	FOSA	FASAs	$C_8F_{17}SO_2NH_2$	8	499.1	n.a.	4.1[c]	6.56[b]
4:2 fluorotelomer alcohol	4:2 FTOH	n:2 FTOH	$C_4F_9(CH_2)_2OH$	6	264.1	n.a.	0.93[c]	n.a.
6:2 fluorotelomer alcohol	6:2 FTOH	n:2 FTOH	$C_6F_{13}(CH_2)_2OH$	8	364.1	n.a.	2.43c	n.a.
8:2 fluorotelomer alcohol	8:2 FTOH	n:2 FTOH	$C_8F_{17}(CH_2)_2OH$	10	464.1	n.a.	4.13[c]	n.a.

a Ref[28], b Ref[29], c Ref[30], d Ref[8], e Ref[31]

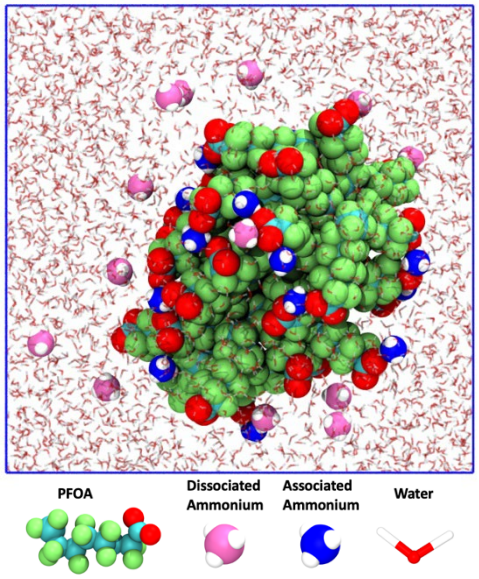
The aqueous solubility of PFCA decreases with increasing number of carbon atoms. Very low pK_a values indicate that ionic PFAS surfactants are completely dissociated in water under typical environmental pH conditions.[32] The dissociated and undissociated species of PFAS surfactants differ greatly in their physicochemical behavior. For example, perfluorooctanoate anion is highly water soluble and has negligible vapor pressure, whereas perfluorooctanoic acid has very low water solubility and sufficient vapor pressure to partition out of water into the air.[30] The low pK_a values of PFAS are relevant to their adsorption based on electrostatic interactions.[33, 34]

PFAS surfactants are extremely surface active in aqueous solutions. The incremental change in free energy of adsorption at the water/air interface per CF_2 group is − 5.1 kJ/mol as compared to − 2.6 kJ/mol for one CH_2 group. This explains the much higher surface activity of fluorinated surfactants compared to hydrocarbon surfactants.[35] The minimum surface tension for PFOA is as low as 15.2 mN/m, whereas the minimum surface tension for commonly used hydrocarbon surfactant sodium dodecylsulfate (SDS) is 38 mN/m.[35] The surface tension of fluorinated surfactants depends on their chemical structure. The minimum surface tension attained in aqueous solutions above the CMC decreases with increasing fluorocarbon chain length. Linear n-perfluoroalkanes exhibit the lowest surface tension, followed by substituted and cyclic and aromatic fluorocompounds.[36] Greater surface activities are observed for perfluoroalkyl carboxylate salts having counterions of smaller hydrated radius, attributed to more surfactant monomers residing within the adsorbed layer.[37]

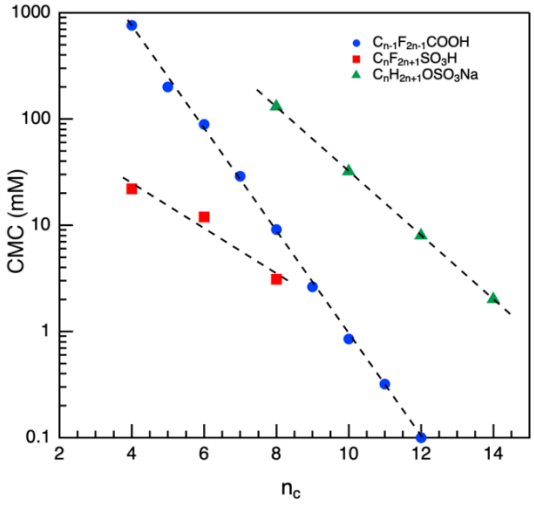
Fluorocarbons are incompatible with hydrocarbons. The wetting properties of fluorinated surfactants on hydrocarbon substrates are poorer than those of hydrocarbon surfactants with similar surface tension.[35] The spreading factor (i.e., ratio of area wetted by surfactant solution to that of water) on parafilm for trisiloxane surfactant having surface tension of 20.5 mN/m is 8.6, whereas the spreading factor is only 1.8 for the fluorinated surfactant FSB (DuPont product) with 18.8 mN/m surface tension.[35] Comparing the interfacial tension of fluorinated and hydrocarbon surfactants at water/hydrocarbon interfaces, hydrocarbon surfactants, in general, have lower interfacial tension, whereas fluorinated surfactants are more effective at the water/air interface.[35] The minimum surface tension attained by NaPFO aqueous solution (24.6 mN/m) is much lower than that of SDS solution (38 mN/m), whereas the minimum interfacial tension against hexane is much lower for SDS (5 mN/m) than for NaPFO (14 mN/m).[35]

PFAS surfactants self-assemble in aqueous solutions and form micelles above the CMC. CMC values vary depending on the PFAS surfactant's hydrophobic chain length, hydrophilic headgroup, counterion, and presence of any additives in the aqueous solution. Short-chain PFAS surfactants are more hydrophilic compared to long-chain ones and they form micelles at much higher CMCs (Figure 1). Information on the CMC of emerging fluorinated surfactants is not available in the literature. A very recent study on GenX interaction and self-assembly reported the CMC of GenX in water to be 150 mM.[31] Comparing the 6-C fluorinated surfactants GenX and PFHxA, the branched fluoroether chain of GenX is found 30% less

hydrophobic than a linear fluorocarbon chain with the same number of carbon atoms.[31] Comparing short chain PFCA and PFSA surfactants with the same fluorocarbon chain but different headgroup, the CMC values of PFBS and PFHxS are much lower than the CMCs of PFPeA and PFHpA, which could be ascribed to the hydrophilic headgroup of PFSA. Counterions play an important role in screening repulsion between ionic surfactant headgroups and, hence, affect the CMC. The tendency of counterions to bind to micelles increases with an increase in counterion's hydrophobicity. The CMC of PFOA ammonium salt (NH_4^+) is 27.2 mM which is 10 times the CMC (2.8 mM) of PFOA tetrabutylammonium salt ($N(C_4H_9)_4^+$).[38] The CMC values of PFOA decrease in the order Li > Na > K, which relates to the hydrated counterion size.[32]



(a)



(b)

Figure 1. (a) Morphology of PFOA micelle obtained from MD simulations.[39] (b) Dependence of CMC on the surfactant chain length (n_c) for (●) perfluorinated carboxylic acids (PFCA), $C_{n-1}F_{2n-1}COOH$,[8, 28] (▪) perfluoroalkyl

sulfonic acids (PFSA), $C_nF_{2n+1}SO_3H$,[8] and (Δ) sodium alkyl sulfates, $C_nH_{2n+1}OSO_3Na$[40]. Reprinted with permission. Copyright, 2021, Royal Society of Chemistry.

In the presence of added electrolyte, the PFAS surfactant CMC decreases.[40-42] The effect of salt on the CMC is stronger for longer-chain fluorinated surfactants compared to shorter-chain ones.[40] The CMC of NaPFO decreased by 80% (from 30 to 5 mM), and the CMC of NaPFHx decreased by 50% (from 200 to 100 mM) upon addition of 0.25 M NaCl.[40] For the same molar concentration of salt, the decrease in CMC of PFOA with NH_4^+ counterion is higher upon addition of NH_4Cl (same counterion) compared to NaCl.[42]

The presence in water of organic compounds can affect the self-assembly of fluorinated surfactants. The CMC of APFO, lithium perfluorononanoate (LiPFN) and lithium perfluorooctane sulfonate (LiPFOS) decreased by 41%, 18% and 27%, respectively, upon 6 M urea addition to the aqueous solution.[43, 44] When 10% ethanol is added to water, the CMC of PFOA decreased to half its value in plain water, indicating a co-surfactant effect, however, at 20% ethanol only a minor additional reduction in the CMC is observed.[39] The information available on the effect of medium-chain alcohols on fluorinated surfactant micellization has been obtained from thermodynamic studies, which suggested solubilization of medium-chain alcohols inside fluorinated surfactant micelles.[45, 46] Effects of short-chain alcohols (methanol, ethanol) on PFAS surfactant micelle formation and structure are scarcely available in the literature.[39]

The size and structure of fluorinated surfactant micelles formed in aqueous solutions depend strongly on the surfactant hydrophobic chain length and can change in the presence of additives. Direct structural information on fluorinated surfactant micelle size and structure is very limited.[31, 39, 40, 47-54] NaPFO at 110 mM forms ellipsoidal micelles with an association number of about 25 and 17.0 Å radius.[40] NaPFHx forms smaller micelles with association number = 15 and radius = 13.0 Å.[40] The size of PFAS surfactant micelles increases with the surfactant carbon chain length. For sodium perfluoroalkyl carboxylates, 2 $–CF_2–$ increase in the surfactant hydrophobic tail increases by 70% the micelle association number and by 30% the radius.[40] Fluorinated carboxylate surfactants have lower CMC and larger association number compared to their hydrocarbon analogues of equal carbon chain length, due to the greater hydrophobicity of the fluorocarbon chain and the smaller effective charge of the fluorinated surfactant headgroups.[40] Structural information on micelles formed by emerging PFAS surfactants is not yet available. The first report on GenX micelle structure and composition was just published, revealing rather small but still well-defined micelles having association number 6 – 8 and 10 Å radius.[31] Added salt in aqueous solution increases the micelle association number and size.[40, 49, 54] The effect of salt on micelle size was observed to be stronger for the rather long-chain NaPFO compared to the shorter chain NaPFHx.[40]

Solvents used to regenerate PFAS adsorbent materials, such as ethanol, can dissolve PFOA micelles at high concentrations.[39] Complementary high-resolution small-angle neutron scattering (SANS) measurements and atomistic molecular dynamics (MD) simulations have shown ethanol at lower concentrations (less than 13 wt%) to localize at the PFOA micelle surface and interior, acting as a co-surfactant.[39] A transition to a co-solvent behavior was observed at higher ethanol concentrations, where ethanol molecules penetrate the PFOA micelles, render them looser, and eventually break them into small clusters.[39] MD simulations, employing parameters properly validated with experimental data, allow for molecular design of surfactant molecules and additives, and predictions on how they will interact with each other.[39]

Aqueous solution properties of PFAS, together with an improved understanding on how to modulate PFAS surfactant self-assembly in water with additives, can inform the fate and transport of PFAS in the environment and PFAS sequestration from aqueous media.[39] These PFAS solution properties reveal and help quantify fundamental interactions which operate also during the adsorption/separation of PFAS surfactants from water. A close connection exists between self-assembly in solution and that on surfaces.[55-57] PFAS surfactant self-assembly may be manifested during adsorption where the local concentration is high and the hydrophobic surface promotes association.[58] Regeneration of the adsorbent involves the use of solvents such as alcohols which modulate the self-assembly of PFAS surfactants.

PFAS ADSORPTION MATERIALS AND MECHANISMS

PFAS adsorption on various adsorbent materials has attracted a lot of attention in the literature. We highlight here recent advances on PFAS adsorption on activated carbon (AC), biopolymers, and fluoropolymers. In what follows, surface properties of sorbent materials and their performance are presented, and intermolecular interactions are invoked to interpret different findings. Sorbent materials are compared in terms of adsorption, and factors affecting adsorption capacity are discussed.

Adsorbents for PFAS removal

Carbonaceous materials: AC is the most widely used adsorbent for PFAS removal from contaminated waters, either as a standalone technology or part of a treatment train, and can be deployed between municipal water treatment and domestic point of entry systems. Adsorption capacity for PFAS surfactants has been shown to relate to the AC surface area, pore size, and surface chemistry.

AC performance as a function of particle size was investigated for 20 anionic PFAS at environmentally relevant concentrations adsorbed by three different AC materials, including commercially available CCAC AquaCarb® (1230C, Westates Carbon), AWAC Filtrasorb® (400-M, Calgon Carbon Co.), and HFAC granular activated carbon.[59] ACs were grouped into four particle size bins (10-75 μm, 125-212 μm, 425-850 μm, 1000-1700 μm particle diameter).[59] The removal of different PFAS after 4 h contact time was in the range 0 – 45% for 425-850 μm and 1000-1700 μm particle diameter ACs, but > 90% for 10-75 μm and 125-212 μm particle diameter ACs.[59] Adsorption of anionic PFAS on larger particle sized AC was relatively slow, which was attributed to intra-particle diffusion limitations that become less important for smaller-sized ACs that have greater specific external surface area.[59] Shorter-chain PFAS were removed from water to greater extents (on average, 2 times more) than longer chain PFAS by larger-sized ACs. There was no big difference in the removal percentage by smaller-sized ACs of longer-chain PFAS and shorter-chain PFAS.[59] This was attributed to the greater importance of intra-particle diffusion for larger-sized ACs and the more rapid diffusion of smaller PFAS.[59] In groundwater experiments, longer-chain PFAS were always removed to greater extents (2-4 times more) than shorter-chain PFAS by all ACs, which was ascribed to the adsorption of PFAS on smaller-sized ACs not controlled by intra-particle diffusion limitations that can favor the adsorption of smaller-sized adsorbates.[59] Rather, the PFAS affinity for binding sites on each of the adsorbents is considered driven in part by hydrophobic interactions which are not diffusion-limited.[59]

Among positively-charged ACs, a microporous AC demonstrated higher adsorption capacities for hydrophilic and marginally hydrophobic PFAS surfactants, whereas a mesoporous AC performed better for more hydrophobic PFAS, possibly due to lower pore blockage by organic matter.[33, 34] Calgon Filtersorb300 and Filtersorb400 (GAC were reported to remove PFOA and PFOS slowly; equilibrium was reached after 5−30 d with initial concentration in the range 5−5000 μg/L.[60] This was attributed to microporosity, i.e., pore size < 2 nm.[60]

Surface charge is another important factor affecting AC performance. The adsorption behavior of 9 different PFAS in groundwaters by four bituminous coal-based ACs, Filtrasorb 400 (F400), Carbsorb 40, HPC Super 8x30 (HPC), and CMR400 by Calgon Carbon Corporation, was studied using rapid small-scale

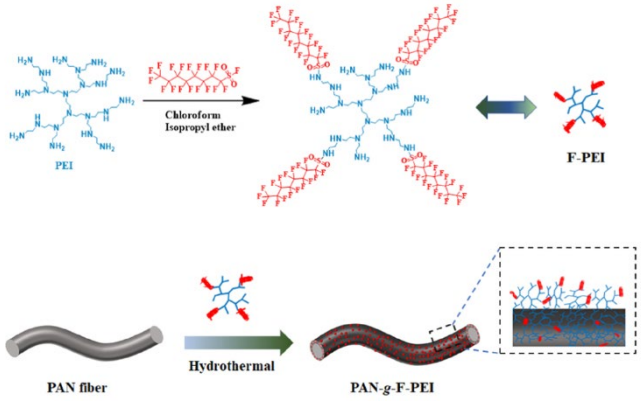
column testing (RSSCT).[34] The pH of the point of zero charges (pH_{PZC}) for F400, Carbsorb40, HPC 8x30 and CMR400 are 9.95, 7.05, 9.05 and 10 respectively.[34] At pH = 7.2 of the groundwater tested, Carbsorb 40 has a net carbon surface charge of zero, and exhibited 0.25 – 0.5 times lower adsorption capacity per unit surface area compared to the other three ACs which carry net positive charges, for PFBA, PFPeA, PFHxA, and PFBS.[34] In another study, positively-charged ACs exhibited 2 – 3 times greater adsorption capacity than neutral surface AC for PFBA, PFPeA, PFBS, PFHxA, PFHpA, PFHxS, PFOA, and PFOS.[33]

Biochar is a sustainable carbonaceous adsorbent produced from biomass pyrolysis. PFAS sorption efficiency depends on biochar characteristics which are affected by biochar preparation factors: feedstock material used, highest pyrolysis temperature, and pyrolysis duration. For example, the surface area of pinewood biochar, 351 m^2/g, was found 4 times higher than that of sugarcane biochar.[61] Higher surface area can provide more binding sites for PFAS. Biochar derived from sewage sludge biosolids exhibited >80% adsorption of long-chain PFAS and 19–27% adsorption of short-chain PFAS from PFAS contaminated water.[62] Reed straw-derived biochar (RESCA-900; pyrolyzed at 900 °C for 5 h) exhibited nearly 100% PFOA removal and 80% PFBA removal efficiency.[63] However, PFBA removal efficiency decreased to <5% when the pyrolysis duration decreased to 3 h or the pyrolysis temperature decreased to 500 or 700 °C.[63]

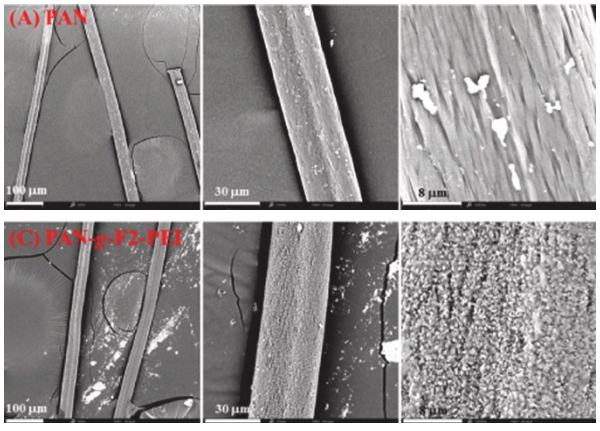
Biopolymers: Natural polymers such as cellulose, starch, cyclodextrins, chitosan, and their derivatives have shown potential for applications in water treatment due to their unique physicochemical properties such as variety of reactive groups, availability, and low cost. Poly(ethylenimine) (PEI)-functionalized cellulose microcrystals (PEI-f-CMC) have been explored for removing 22 PFAS, including legacy and emerging carboxylic and sulfonated PFAS and PFAS-precursors, from aqueous solutions at environmentally relevant concentrations.[60] PEI-f-CMC had 7.8 m^2/g surface area and 0.032 cm^3/g total pore volume (0 vol% micropores (i.e., pore < 2 nm), 81.3 vol% mesopores (i.e., 2 nm < pore < 50 nm), 18.7 vol% macropores (i.e., pore > 50 nm)), and achieved 87% and 67% PFOA removal at initial PFOA concentrations 1 and 100 µg/L, respectively, after 20 min contact time.[60] However, the removal efficienty of short chain PFAS including PFBA, PFPeA, and PFBS was < 10%. Calotropis gigantea fiber (CGF) natural cellulose was functionalized by in-situ growth of polydopamine (PDA), polyaniline (PAN) or poly(m-phenylenediamine) (PmPD) to create adsorbents for PFOA removal from water at mg/L concentrations.[64] Adsorption equilibrium was reached within 3 h, and the maximum adsorption capacity for the three adsorbents was 207–233 mg/g.[64] Reduced graphene oxide-modified zinc ferrite immobilized chitosan beads (rGO-ZF@CB) were used as an adsorbent for the removal of PFOA and PFOS from water.[65] The enhanced adsorption capacity for PFOA and PFOS was explained by cumulative effects from the ferrite-modified rGO and chitosan beads, offering more positive surface.[65] Cross-linked cyclodextrins have been developed for treating PFAS-containing aqueous solutions. β-cyclodextrin monomers are believed to form host-guest complexes with PFAS via hydrophobic interactions, and act as active site for adsorption.[59] Additionally, the presence of protonated crosslinkers can facilitate the transport of anionic PFAS to the β-cyclodextrin monomers or provide alternate adsorption sites through electrostatic interactions.[59]

Fluoropolymers: Fluorinated polymers are capable of selective PFAS sorption.[66] Ionic fluorogels (IFs) were synthesized by perfluoropolyethers (PFPE) as the fluorophilic matrix, and an amine-containing monomer (2-dimethylaminoethyl methacrylate, DMAEMA), whose composition was varied from 10 to 60 wt % with respect to the total weight of the IF, to generate materials with varying ratio of fluorophilic and charged components.[66] IFs containing quaternary ammonium groups (IF-X+, X+ = wt % ammonium comonomer

incorporation) between 20 and 40 wt % (IF-20+ through IF-40+) achieved >80% removal of PFHxA and GenX (1.0 µg/L of each PFAS, 10 mg/L IF, 21 h).[66] The fluorogel made solely of fluorolink (IF-0) exhibited no removal of PFHxA or GenX, and modest PFOA removal (20%). Furthermore, polyethylene glycol dimethacrylate (PEGMA) gels made with a nonfluorous hydrocarbon equivalent of PFPE exhibited 10% removal for all PFAS tested.[66] Polyacrylonitrile (PAN) fiber functionalized by PFOS hyperbranched polyethylenimine (F-PEI) (PAN-g-F-PEI, 0.5 mg/mL) (Figure 2) removed > 99.99% PFOS (10 mg/L initial concentration) in 6 h from firefighting wastewater.[67] Compared to fiber without perfluoroalkyl chains, the introduction of perfluoroalkyl chains improved 1.5 – 1.7 times the PFOS removal efficiency.[67] Two fluorine-rich calix[4]arene-based porous polymers, FCX4-P and FCX4-BP were prepared for PFOA removal from water.[68] Calixarene macrocycles have amphiphilic nature around the rim and possess a hydrophobic cavity, which can facilitate favorable host−guest interactions, whereas the fluorinated linkers make the overall network even more hydrophobic and enhance C−F···F−C interactions between the polymers and guest molecules.[68] FCX4-P and FCX4-BP (79−100% PFOA removal) performed much better than their nonfluorinated analogues CX4-P and CX4-BP (with 23−64% removal).[68]



(a)



(b)

Figure 2. (a) Synthetic route for preparation of PAN-*g*-F-PEIs. Fluorous hyperbranched polyethylenimine (F-PEI) was synthesized by reacting polyethylenimine (PEI) and perfluorooctane sulfonyl fluoride (PFOSF) in a mixed solvent of chloroform and isopropyl ether. Polyacrylonitrile (PAN) fiber was functionalized by adding F-PEI under hydrothermal conditions, generating a series of fluorous PAN-g-F-PEI fibers. (b) SEM images of PAN and PAN-g-F-

PEIs. F content of F-PEIs has a marked influence on the surface morphologies of PAN-g-F-PEIs.[67] Reprinted with permission. Copyright, 2021, Elsevier B.V.

PFAS adsorption behavior and mechanisms

The adsorption of PFAS surfactants on various adsorbents in an aqueous environment is complex and many interactions are possibly involved: hydrophobic interactions, electrostatic interactions, ion exchange, and hydrogen bonding (Figure 3). In addition to the adsorbent chemistry and physical properties, other factors such as PFAS molecular structure and aqueous media composition affect PFAS adsorption efficiency.

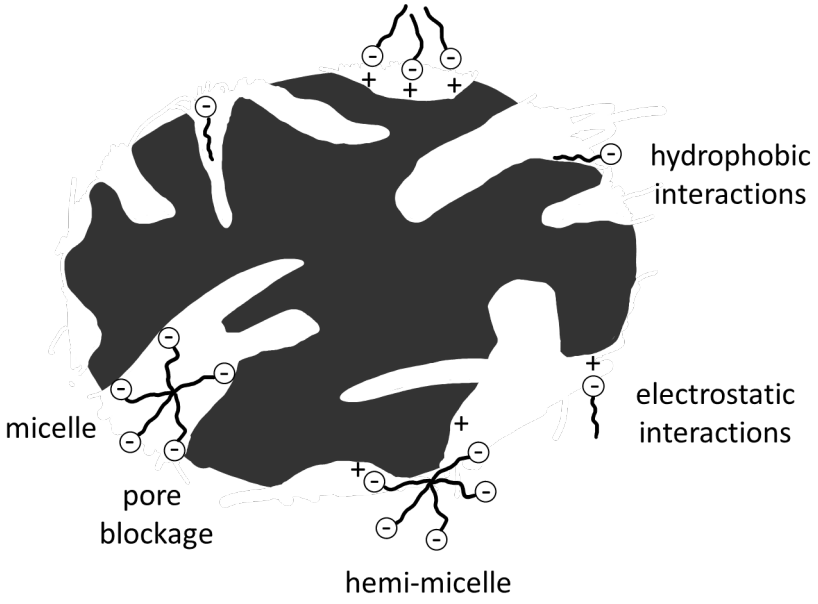


Figure 3. Schematic of anionic PFAS surfactant adsorption on positively charged adsorbent showing various adsorption mechanisms.

The following findings demonstrate the presence of hydrophobic interactions in PFAS sorption. GAC (AWAC Filtrasorb®) has shown an average removal of >95% for long chain PFAS such as PFOA and PFOS after 48 h of contact time in groundwater matrices.[59] However, ACs are less effective for the removal of short-chain PFAS such as PFBA and PFPeA (Figure 4),[34, 59] and adsorption equilibrium takes longer to reach.[60] Shorter chain PFAS surfactants exhibited earlier breakthroughs than longer chain PFAS, which was ascribed to the greater hydrophobicity of longer-chain PFAS, indicating the crucial role of hydrophobic interaction in PFAS breakthrough.[34] In samples containing mixtures of 20 different PFAS, the removal percentage by GAC of short chain PFAS such as GenX (<50%), PFBA (0%), PFPeA (<35%) was much lower compared to that of long chain PFAS such as PFOA and PFOS (>95%) (Figure 4).[59] In both PFAS-spiked milli-Q water and aqueous film-forming foam (AFFF)-impacted groundwater, long chain PFAS exhibited better partitioning on biochar sorbent, with partition coefficients ranging from 0.77 to 4.63 compared to short chain PFAS with partition coefficients < 0.68.[61] The adsorption capacity of rGO-ZF@CB was slightly higher

for PFOS than PFOA, which was ascribed to the stronger interactions between more the hydrophobic PFOS and the hydrophobic portion of rGO-ZF@CB.[65]

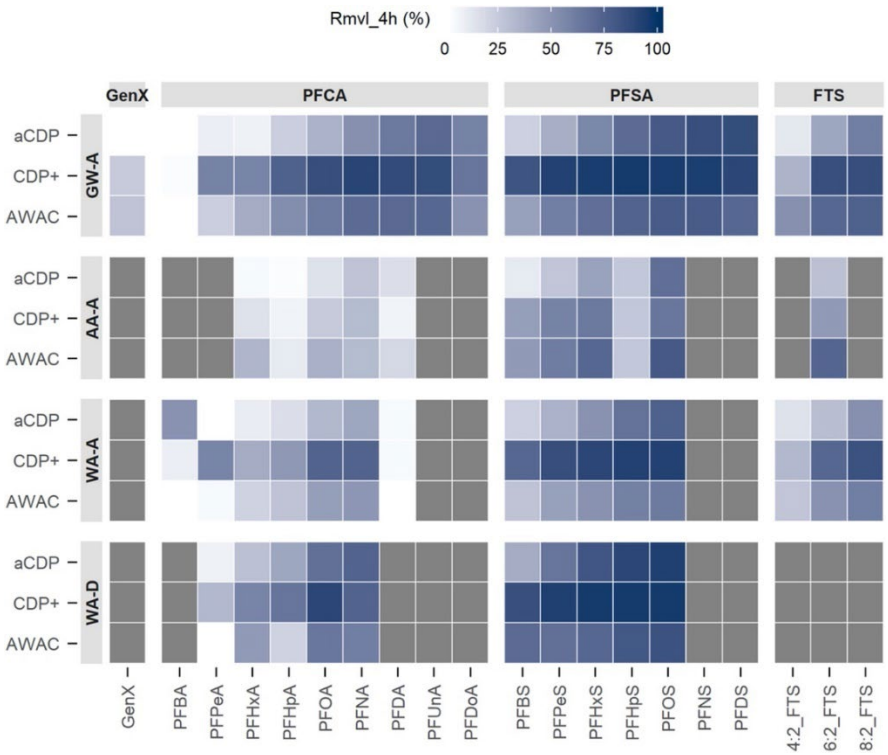


Figure 4. Heatmap of adsorption of 20 PFAS surfactants onto 5 adsorbents in groundwater matrices (GW-A, AA-A, WA-A, WA-D) at 4 h. PFPeS: perfluoropentane sulfonic acid, PFHpS: perfluoroheptane sulfonic acid, PFNS: perfluorononane sulfonic acid; the acronyms for other PFAS shown in the figure are defined elsewhere in the text. Adsorbent materials: aCDP (synthesized amine-CDP), CDP+ (DEXSORB+™, CycloPure, Encinitas, CA), AWAC Filtrasorb® (400-M, Calgon Carbon Co., Pittsburgh, PA). The PFAS compounds are grouped by their corresponding classes and listed with increasing chain length within each group along the x-axis. The adsorbents are grouped by their corresponding types and listed with increasing particle size within each group along the y-axis. The tiles are colored according to the arithmetic average removal for each pair of the coordinates (a gray tile represents that the corresponding PFAS compound had a level below our limit of quantification in the specific groundwater sample).[59] The heatmap demonstrates that longer-chain PFAS were always removed to greater extents than shorter-chain PFAS by all three adsorbents in the groundwater experiments. Among the three adsorbents, for most PFAS and in most groundwater samples, the extent of PFAS removal is the greatest on CDP+.[59] Reprinted with permission. Copyright, 2020, Elsevier Ltd.

Adsorption of some PFAS classes can be associated with increasing length of the perfluorinated tail, while adsorption of other classes is more strongly related to properties of the headgroup. PFSA were retained much more (1.3-fold) than PFCA on biochar sorbent which was ascribed to the smaller size of the PFCA carboxylic headgroup, possibly rendering it less hydrophilic than the sulfonic headgroup.[61] A study has focused on the removal from contaminated groundwater (pH 6.7) of 68 PFAS surfactants, including 43 anionic, 12 nonionic, and 13 zwitterionic, using five adsorbents, including activated carbon Calgon Filtrasorb 400-M, an anion exchange resin Purolite PFA694E, and three different cyclodextrin polymers (CDPs) (DEXSORB, DEXSORB+ and a β-CD polymer (M+) developed by Cyclopure, Inc.) with varying surface

charges (Figure 5).[69] AC and DEXSORB have a negative surface charge, while DEXSORB+ and M+ have positive surface charge. With increasing chain length of PFSA and FASA, the removal percentage increased across all of the CDPs and AC, suggesting that chain length plays a considerable role in the removal of these two families of anionic PFAS.[69] The removal of PFCA and MeFASAA (N-methyl perfluoroalkane sulfonamido acetic acids) by M+ and DEXSORB+ also increased with chain length, again highlighting the role of chain length on the removal of these anionic PFAS by CDPs with a positive surface charge.[69] Across all five adsorbents, removal of PFAS with a sulfonic acid headgroup is always greater than removal of PFAS with a carboxylic acid headgroup, when the rest of the structure is the same.[69] FASAA (perfluoroalkane sulfonamide acetic acids) were consistently removed to greater extents among all adsorbents than the FASA, when the rest of the structure is the same. This was attributed to the increased hydrophobicity of FASAA relative to FASA (resulting from their larger size), which enhanced affinity for all three adsorbents, and the anionic carboxylic acid headgroup of the FASAA, which enhanced affinity for positively charged DEXSORB+ and M+.[69] MeFASAA was consistently removed to greater extents among M+ and DEXSORB+ than MeFASA (N-methyl perfluoroalkane sulfonamide) when the rest of the structure is the same, but the opposite trend emerged for these PFAS classes on AC. The different behavior of MeFASAAs and MeFASAs on AC (relative to FASAA and FASA) was ascribed to increased hydrophobicity of MeFASAAs (resulting from their larger size), insufficient to counteract the effects of the anionic carboxylic acid headgroup of MeFASAA which creates a repulsive electrostatic interaction with the AC negative surface charge.[69]

The presence of branches in the PFAS molecular structure can also affect their adsorption. Among three classes of PFAS, SPr-FASA (perfluoroalkane sulfonamide propanesulfonic acid), SPrAmPr-FASAA (N-sulfopropyl dimethyl ammonio propyl-perfluoroalkane sulfonamide acetic acid) and SPrAmPr-FASAPrS (N-sulfopropyl dimethyl ammonio propyl-perfluoroalkane sulfonamido propylsulfonate) that contain both sulfonamide and sulfonic acid functional groups, SPrAmPr-FASAA and SPrAmPr-FASAPrS are larger in size and have a side branch. M+ and DEXSORB+ exhibit the greater removal of the relatively smaller sized class, SPr-FASA (average 83% removal), and limited removal of the larger sized, branched classes, SPrAmPr-FASAA (average 27% removal) and SPrAmPr-FASAPrS (average 40% removal). This finding was attributed to limited access to the binding sites in the interior cavity of β-CDs for the larger, branched classes of PFAS.[69] However, neither the headgroup nor the branching influenced adsorption on AC.

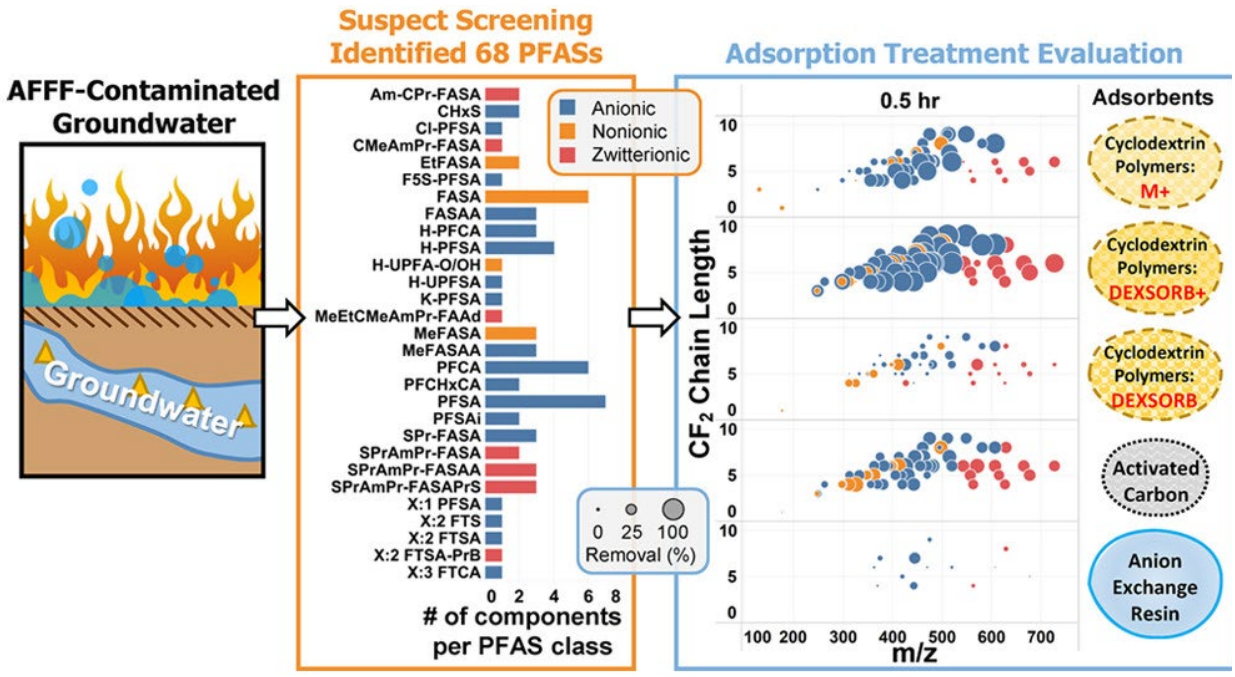


Figure 5. Evaluation of the removal of 68 PFAS from contaminated groundwater with five different adsorbents. Blue data represent anionic PFAS, orange data nonionic PFAS, and red data zwitterionic PFAS. The number of components per PFAS class is shown in the bar plot in the center. The removal percentage of each PFAS on five different adsorbents is shown in the right plot as a function of CF_2 chain length and mass (m/z) tolerance (maximum difference between an experimental mass and a theoretical one, reflecting the mass spectrometry measurement and calibration errors). The larger size of removal data point indicates greater removal percentage.[69] N-dimethylammoniocarboxypropyl-perfluoroalkane sulfonamide (Am-CPr-FASA), cyclohexane sulfonate (CHxS), chloro-perfluoroalkanesulfonate (Cl-PFSA), N-carboxymethyldimethyl ammoniopropyl-perfluoroalkanesulfonamide (CMeAmPr-FASA), N-ethylperfluoro-1-alkanesulfonamide (EtFASA), pentafluorosulfide-perfluoroalkane sulfonate (F5S-PFSA), perfluoroalkane sulfonamide (FASA), hydrido-perfluoroalkanoic acid (H-PFCA), hydrido-perfluoroalkane sulfonate (H-PFSA), unsaturated perfluoroalkane ether/alcohol (-1F, +1H) (H-UPFA-O/OH), hydrido-unsaturated perfluoroalkane sulfonate (H-UPFSA), keto-perfluoroalkanesulfonate (K-PFSA), N-methylethyl-carboxymethyl dimethyl ammonio propyl perfluoroalkane amide (MeEtCMeAmPr-FAAd), perfluoro cyclohexane carboxylic acid (PFCHxCA), perfluoroalkanesulfinate (PFSAi), N-sulfo propyl dimethyl ammonio propyl perfluoroalkanesulfonamide (SPrAmPr-FASA), X:1 perfluoroalkanesulfonate (X:1 PFSA), X:2 fluorotelomer sulfonamide (X:2 FTSA), X:2 fluorotelomer sulfonamido propyl betaine (X:2 FTSA-PrB), X:3 fluorotelomer carboxylic acid (X:3 FTCA), the acronyms for other PFAS listed in the figure are defined inside the text. Reprinted with permission. Copyright, 2020, American Chemical Society.

β-cyclodextrin polymers (CDPs) including commercially available DEXSORB and DEXSORB+ (Cyclopure Inc., Encinitas, CA) containing cross-linkers that impart negative and positive surface charges, respectively and amine-CDP containing cross-linkers that impart a positive surface charge at pH values, are believed to adsorb PFAS through hydrophobic and electrostatic interactions, and were evaluated for the removal of anionic, zwitterionic, and nonionic PFAS from water.[70] The adsorption mechanism was not discussed in detail in the paper. DEXSORB+ and amine-CDP exhibited rapid adsorption of the anionic PFAS PFBA, PFOA, PFBS, PFOS. PFOA, PFBS, and PFOS achieved complete adsorption uptake on amine-CDP at 0.5 h and on DEXSORB+ at 10h. PFBA adsorption on DEXSORB+ and amine-CDP was slightly lower compared to other three anionic PFAS. 10% desorption was observed for PFBA after 48 h contact time; desorption of short-chain anionic PFAS was attributed to competition with long-chain anionic PFAS or with 6:2 FTSA-PrB.[70]

DEXSORB did not remove anionic PFAS to a significant extent; it adsorbed the three zwitterionic PFAS (AmPr-FHxSA, TAmPr-FHxSA, 6:2 FTSA-PrB) with 75% removal, while other adsorbents exhibit <25% removal of zwitterionic PFAS. These data suggest that electrostatic interactions play an important role in determining the affinity of CDPs for PFAS. Nonionic fluorotelomer alcohols (4:2 FTOH, 8:2 FTOH) were not removed to any significant extent by DEXSORB, DEXSORB+, and amine-CDP adsorbents, however nonionic perfluorosulfonamides FBSA (~90% , 60% removal respectively, at 48h), and FOSA (~90% removal at 48h) were rapidly removed by DEXSORB+ and amine-CDP. According to this study, the noted adsorption of PFOA, PFOS, and FOSA among the CDPs suggests that 8:2 FTOH should be of sufficient size to interact with the interior cavity of the cyclodextrin monomer. The authors suspect that the fluorotelomer alcohols may associate or accumulate at air−water interfaces and may not be uniformly dissolved in the aquatic matrix, which limited their transport to the binding sites in the interior cavity of the cyclodextrin monomer.[70]

Adsorption of PFAA, including short-chain PFBA, PFBS, and PFHxA, by RESECA-900 with a negative surface charge and highly hydrophobic surface was found dominated by hydrophobic rather than electrostatic interactions.[63] At an initial concentration of 1 μg/L, RESCA-900 removed 92–96% of the short-chain PFAS PFBA, PFBS, and PFHxA, significantly higher than GAC (71–79%).[63] When the initial concentration increased to 100 μg/L, removal efficiencies of short-chain PFAA by RESCA-900 remained high (80% - 89%), while complete removal of long-chain PFAA was observed. However, adsorption by GAC was negatively affected by increased PFAA concentration, particularly for short-chain PFAA. PFAA adsorption efficiencies by GAC followed the order: PFOS (89%) > PFHxS (76%) ≥ PFOA (75%) > PFBS (43%) ≥ PFHxA (38%) > PFBA (18%).[63] This shows better adsorption on GAC of PFAA with longer chain length and/or sulfonate group.[34] In contrast, RESCA-900 can remove 92% of PFBA within 24 h, suggesting an advantage in short-chain PFAA adsorption kinetics and isotherms. Rapid adsorption of short-chain PFAA was attributed to a combination of highly hydrophobic surface and uniform distribution of mesopores (2–10 nm diameter).[63]

Electrostatic interactions also play an important role in the adsorption process of PFAS. PEI-f-CMC has the pH of the point of zero charges (pH_{PZC}) at 10.9 ± 0.2, which indicates that the surface of the material would be positively charged in solutions with lower pH values. PEI-f-CMC have shown 85% PFOA removal at pH 4.4, which decreased to 79%, 70%, and 20% when the pH increased to 6.5, 7.7, and 9.5, respectively. This reduction was attributed to a reduction in the number of positive sites on PEI-f-CMC at high pH values, and points to the importance of electrostatic interactions in PFAS adsorption on PEI-f-CMC.[60] At PEI-f-CMC PFAS removal efficiency increases with chain length (C = 4−12), and the removal efficiency of PFSA was higher than PFCA with the same chain length (Figure 6).[60] The removal efficiencies of polyfluorinated compounds (e.g., 4:2 fluorotelomer sulfonic acid (FTS) and 6:2 FTS) were higher than perfluorinated compounds with the same chain length. The influencing factors for these trends were not reported. Electrospun PAN nanofibers and amidoxime surface-functionalized electrospun PAN nanofibers (ASFPAN) have been used as adsorbent to remove GenX from water.[71] ASFPAN adsorbent from 10 min surface treatment (ASFPAN10) outperformed PAN for GenX remediation from water at pH = 4. While hydrophobic interaction and dipole-dipole interaction between C≡N and C–F are the main driving forces for adsorption of GenX on PAN nanofibrous adsorbent, the GenX adsorption on ASFPAN10 nanofibrous adsorbent was mainly attributed to electrostatic attractive force between positive-charged amidoxime functional groups $C{=}N^{+}(OH)–H$ from ASFPAN10 and negative-charged carboxylate functional groups COO^{-} from GenX.[71]

Compared to that of PAN, the more hydrophilic surface of ASFPAN10 facilitated water access to the nanofibrous adsorbent surface which may have contributed to the higher GenX removal efficiency.[71]

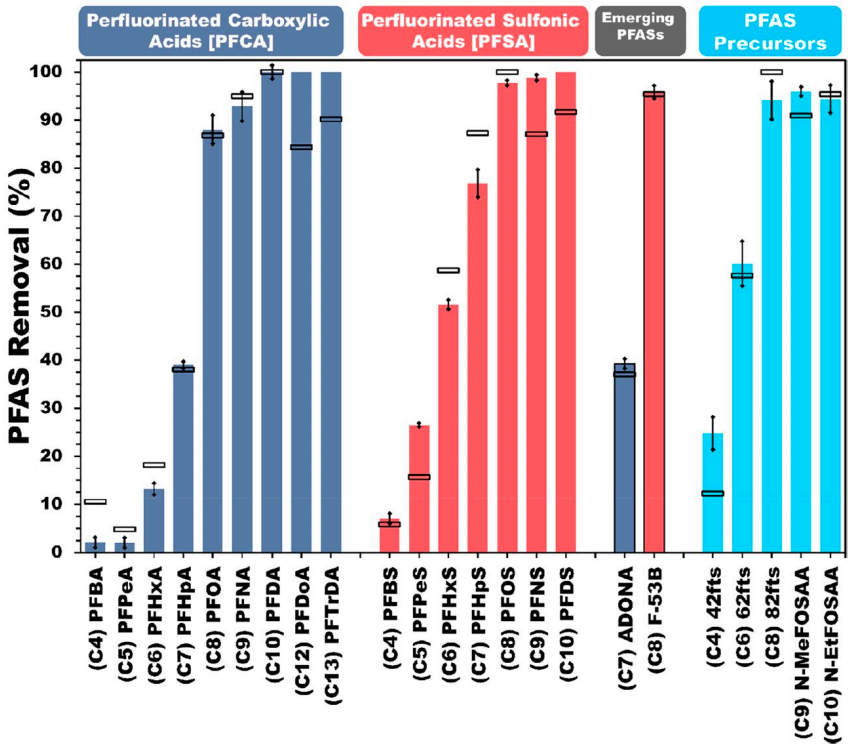


Figure 6. Adsorption of 22 PFAS (1 µg/L) by PEI-F-CMC (25 mg/L) in lake water (vertical bars) and in distilled deionized water (open rectangles) at pH 6.5 following 2 h equilibration. C4–C12 represent the number of carbon atoms in each PFAS compound.[60] Perfluorotridecanoic acid (PFTrDA), perfluoropentane sulfonic acid (PFPeS), perfluoroheptane sulfonic acid (PFHpS), perfluorononane sulfonic acid (PFNS), dodecafluoro-3H-4,8-dioxanonanoate (ADONA), N-methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA), N-Ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA); the acronyms for other PFAS listed in the figure are defined inside the text. Reprinted with permission. Copyright, 2018, American Chemical Society.

Hydrogen bonding could also be responsible for PFAS adsorption. A chitosan ethylene glycol hydrogel produced through physical cross-linking removed PFOA from deionized water under acidic conditions with a maximum adsorption capacity 3.1 mmol/g.[72] The formation of ionic hydrogen bonds between carbonyl groups (COO^-) of PFOA and protonated amine (NH^+) of the adsorbent was considered responsible for PFOA removal.[72] The primary interaction responsible for successful adsorption of PFOA by fluorine-rich calix[4]arene-based porous polymers FCX4-P and FCX4-BP was speculated to be the hydrogen bond between the PFOA carboxylic headgroup and a hydroxyl oxygen of the calixarene. Additional stabilization may be achieved by C–F···F–C interactions between PFOA and fluorinated linkers in FCX4-P and FCX4-BP.[68] Monte Carlo (MC) simulations showed that, for FCX4-P, FCX4-BP, CX4-P and CX4-BP polymers, hydrogen bonding is the main interaction between the polymer and its environment, and that the effect of C–F···F–C interaction is rather marginal. Interactions between PFOA and the linkers were relatively weak in CX4-P and CX4-BP. In FCX4-P and FCX4-BP, however, substitution of the linker hydrogen atoms with fluorine resulted in tighter PFOA binding to the linkers.[68]

Fluorophilic sorption and targeted ion exchange were combined in IFs to remediate PFAS from water.[66] Incorporation of tunable density charged functional groups would enable ion exchange and sequestration of charged PFAS. IFs containing tertiary amines exchibited lower affinity for PFAS than the corresponding materials with quaternary ammonium groups, showing the importance of incorporating permanent charge. The highest performing IFs incorporated 20 - 40 wt % ammonium comonomer (IF-20+ through IF-40+), demonstrating >80% removal of short-chain PFAS (PFHxA and GenX). On the basis of the above, the authors hypothesized that these IFs have enough ammonium content to enable efficient surface wetting while still containing enough fluorous content to provide selective PFAS adsorption.[66]

Factors affecting adsorption capacity

PFAS-contaminated aquatic matrices contain several other constituents such as inorganic ions and dissolved organic matter (DOM) which have been shown to affect the PFAS adsorption capacity.

Solution pH: pH is one of the primary contributors to adsorption inhibition in groundwater. Higher pH values limit anionic PFAS adsorption by deprotonating functional groups on adsorbent surfaces. In a PFOA removal study using functionalized CGF polymers over the 3 – 10 pH range, the surfaces of PDA-CGF and PAN-CGF were positively charged due to PDA and PAN protonation at pH < 3.4 and 3.9, respectively, while the PmPD-CGF surface was negatively charged. The adsorption capacities of PDA-CGF or PAN-CGF decreased monotonically with increasing pH, which was ascribed to a decreased electrostatic attraction between PFOA and CGFs.[64] Interestingly, the adsorption capacity of negatively charged PmPD-CGF was higher than that of PDA-CGF, and PDA-CGF and PAN-CGF still exhibited a certain adsorption capacity for PFOA after zero potential. This was asrcibed to hydrogen bonding and hydrophobic interactions contributing to the adsorption process.[64] m-Phenylenediamine contains two amino groups, thus providing a great possibility for hydrogen bond formation between adsorbent and adsorbate, and the higher modification percentage of PmPD-CGF than PDA-CGF will provide more adsorption sites for PFOA.[64] The removal capacities of PFOA and PFOS onto rGO-ZF@CB gradually decreased as the solution pH increased, suggesting that the protonated functional groups of rGOZF@CB effectively adsorbed anionic PFOA and PFOS by strong electrostatic attractions, and the maximum adsorption capacity was observed for both compounds at pH 3 because of the protonation of rGOZF@CB at acidic conditions.[65]

Inorganic ions: Elevated levels of cations in some groundwater samples attenuate the effects of attractive electrostatic interactions. The effect from cations is reportedly due to interactions with PFAS and not the AC adsorbent.[59] The influence of cation on PFOA adsorption capacity by functionalized CGF polymers was evaluated by using different concentrations (0.1, 1 and 10 mM) of NaCl, $MgCl_2$, or $FeCl_3$ as background electrolyte.[64] At the same concentration, the higher the cation valence, the higher the adsorption capacity. For the same electrolyte, PFOA adsorption capacities gradually increased with increased cation concentration. This was ascribed to: (i) increased density of positive charges on the surface of functionalized CGF, enhancing electrostatic attraction between PFOA and surface, and weakening electrostatic repulsion between PFOA molecules; and (ii) multivalent cation bridging effect, in which Mg^{2+} and Fe^{3+} ions form salt-bridges between functionalized CGF and PFOA.[64]

Dissolved organic matter (DOM): DOM is hydrophobic, resulting in two contradictory influences on PFAS adsorption: competition with PFAS for sorbent sites, and providing additional PFAS binding sites. The

competition or promotion by DOM for PFAS sorption strongly depended on the DOM concentration in groundwater and its composition, i.e., hydrophobicity. Groundwater may contain various organic compounds such as hydrophilic acids, proteins, phenolic groups, amino acids, and Fe/Al oxides. DOM is able to form complexes with PFAS by electrostatic interaction and/or cation bridging with multivalent ions such as Ca^{2+}, Fe^{3+} and Al^{3+}.[73]

CONCLUSIONS

The utilization of PFAS surfactants across a wide range of applications, coupled with the high chemical stability of fluorocarbons, has resulted in PFAS accumulation in the environment and in biota. Emerging PFAS surfactants have been introduced, for which we know very little about, which can be more toxic than the legacy PFOA and PFOS they were intended to replace. Adsorption of PFAS using different materials such as activated carbon, ion exchange resins, biopolymers, and fluoropolymers is an important topic of research, of great interest to colloid and surface science.

This review provides an overview of the aqueous solution self-assembly properties of common PFAS surfactants and highlights resent advances on the physical adsorption of PFAS surfactants using natural materials and synthetic sorbents, with a focus on surfactant/surface/colloid aspects. Surface properties of sorbent materials, their performance, and factors affecting the adsorption capacity are discussed, and intermolecular interactions are invoked to interpret different findings.

PFAS surfactants in aqueous solutions self-assemble into micelles above the CMC. With increasing fluorocarbon chain length, the CMC of PFAS surfactants and the minimum surface tension attained in aqueous solutions above the CMC decrease, and the PFAS micelle size increases. In the presence of electrolyte, the PFAS CMC decreases and micelle size increases while, in the presence of solvents such as ethanol, PFAS micelles can dissolve into smaller clusters. PFAS self-assembly extends onto surfaces, where PFAS can form hemimicelles at concentrations 0.001 – 0.01 times their CMC in water. Such self-assembly can influence the adsorption capacity, sometimes enhancing PFAS adsorption on positively charged surfaces, or other times reducing the adsorption capacity by blocking PFAS diffusion into the inner pores of microporous adsorbents.[23]

PFAS adsorption is impacted by: adsorbent material characteristics, such as surface area, pore size, surface charge; PFAS characteristics such as chain-length, headgroup, molecular structure; and aqueous solution pH, presence of inorganic ions or DOM. In many adsorbents the removal of PFAS relies on hydrophobic and electrostatic interactions, ion exchange and hydrogen bonding, however the relative strength of these interactions, as well as the influence of other interactions should be clarified. For the adsorption of hydrophilic and marginally hydrophobic PFAS, micropore surface area is found important, whereas, for the adsorption of more hydrophobic PFAS, mesopore surface area became increasingly important. The adsorption behavior of PFAS is strongly dependent on the carbon chain length that is associated with the hydrophobicity/hydrophilicity of PFAS, and on the functional groups on the adsorbent. Shorter-chain PFAS are more hydrophilic, and they generally have lower adsorption capacity with hydrophobic adsorbents such as AC. Electrostatic interactions are prevalent during the adsorption of anionic PFAS onto adsorbents that have a net-positive charge while hydrophobic interactions occur during the adsorption of anionic PFAS onto negatively charged hydrophobic adsorbents. Fluorophilic sorption was observed when the adsorbent material is fluorinated. The presence of inorganic cations in aqueous media can increase PFAS adsorption by enhancing electrostatic attraction between PFOA and adsorbent surface, weakening electrostatic repulsion between PFOA molecules, and through multivalent cation bridging effect.

Major knowledge gaps exist regarding the aqueous solution properties and interfacial properties of emerging PFAS surfactants. Remediation technologies have been applied mostly to long-chain PFAS (PFOS

and PFOA) and a few shorter chain PFAS (PFBA and PFBS). More studies on remediation technologies are needed for emerging PFAS surfactants and for aqueous solutions containing a mixture of variety of PFAS, including not only anionic but also neutral, cationic and zwitterionic PFAS. Further research would be beneficial on effects of competition for adsorbent sites between different PFAS molecules (short chain vs long chain, anionic vs nonionic) and between PFAS molecules and co-contaminants. Further research is also required on how to prepare inexpensive, environment friendly adsorbent materials for PFAS, modify them (physically and/or chemically) to increase their adsorption capacity and selectivity, and on adsorbents that are more selective for short chain PFAS surfactants.

Major fundamental and practical challenges for PFAS remediation include: the chemical identities of many PFAS on the global market are yet unknown, and PFAS are encountered in the environment at very low concentrations; hence it is difficult to develop analytical techniques that could detect these PFAS types and concentrations. Another major challenge is the recovery of PFAS from PFAS-loaded adsorbents, and the regeneration or disposal of spent adsorbent materials. Numerous studies have reported the regeneration of spent adsorbent materials using organic solvents, however, as organic solvents are toxic and volatile, it is necessary to develop other safe and effective PFAS eluents. Further, it is challenging to treat or dispose waste eluate containing high concentration of PFAS. Developing large-scale destruction methods for the complete elimination of PFAS is currently associated with relatively high costs.

The information that is reviewed here on PFAS surfactant association properties, adsorption behavior and mechanisms onto various adsorbents can stimulate new research in areas of need, and utilize the available knowledge for the improvement of existing adsorbent materials and processes, and for the development of new materials and processes, all working to the benefit of a sustainable future.

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**** of special interest***

8: This review examines how fluorinated surfactants adsorb onto mineral surfaces, by analyzing the thermodynamics and kinetics of adsorption, and the underlying mechanisms. Adsorption of fluorinated surfactants onto mineral surfaces can be explained by electrostatic interactions, hydrophobic interactions, hydrogen bonding, and ligand and ion exchange. The aqueous pH, varying salt or humic acid concentrations, and the surfactant chemistry can influence the adsorption of fluorinated surfactants onto mineral surfaces.

19: This review discusses processes for chemical degradation/destruction of a wide array of PFAS classes, including short chain PFAS removal. Comparisons are made regarding the efficiencies, effectiveness, energy use, sustainability, cost, and simplicity in laboratory scale to field applications of the various processes.

20: This review presents recent advances in a range of emerging adsorbents, and evaluates their potential as environmentally friendly and more efficient alternatives to conventional activated carbon products for PFAS separation from contaminated water. The adsorption behaviors of various adsorbents for PFAS are compared, and the underlying removal mechanisms are discussed. Their practicality in terms of treatment of real water/wastewater, reusability, and continuous operation is also examined.

21: This review discusses adsorbents (synthesis, capacity, and kinetics), mechanisms (uptake mechanisms and influencing factors), and applications, including large-scale setups and point-of-use/point-of-entry (POU/POE) units, for the removal from water of short-chain perfluoroalkyl acids (PFAAs).

22: This review discusses the technical feasibility of the use of different adsorbents, such as activated carbon, ion exchange resins, minerals, molecularly imprinted polymer (MIP), carbon nanotubes (CNTs), and a wide range of potentially low-cost biosorbents, for PFASs removal from water or wastewater. PFAS sorption behavior in terms of kinetics and isotherms is presented.

23: This review discusses PFAS removal from water via ion exchange process. Various ion exchange resins are compared in terms of kinetics and isotherms. Ion exchange can be effective towards eliminating emerging short-chain PFAS which are not removed by carbon-based adsorption processes.

39: First high resolution information of PFAS surfactant micelle structure and interactions. A joint experimental and simulation approach has been used to investigate the structure of perfluorooctanoate ammonium (PFOA) micelles in aqueous solutions. The capability established in this study to predict from first principles PFAS surfactant micelle structure confirms that the various interactions have been properly accounted for. This knowledge can be deployed to probe computationally PFAS pollutants for which experimental results are lacking.

73: This review discusses recent peer-reviewed studies on the removal of long- and short-chain PFAS by adsorption in the context of the (i) performance of different adsorbents for both long- and short-chain PFAS, (i) effect of organic matter, and (iii) adsorbent regeneration techniques.

***** of outstanding interest***

31: First report on GenX self-assembly and micelle structure in water. Self-assembly into micelles is a key feature of surfactants in aqueous solution and reveals how surfactants such as GenX interact with themselves and with solvent (water) and other molecules present in solution. Micelles are relevant to environment and health in that PFAS surfactants, while typically found in very low bulk solution concentrations, they tend to concentrate a lot (partition) in the vicinity of surfaces in the context of separations (activated carbon, ion exchange resins) and in the context of biointerfaces.

59: This study investigated the key factors that influence the adsorption of anionic PFAS on conventional and emerging adsorbents. Batch adsorption experiments were conducted to evaluate the removal of 20 target PFAS at environmentally relevant concentrations by three different activated carbon (AC) materials and two different beta-cyclodextrin polymers (CDPs). Knowledge of PFAS adsorption mechanisms gained from this study can be used to design more efficient adsorbents and to predict their performance under a range of environmental scenarios.

60: 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.