Functionalized bio-adsorbents for removal of perfluoroalkyl substances: A perspective

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Abstract
Poly- and perfluoroalkyl substances (PFAS) are known as “forever chemicals” due to their ubiquitous persistence in the environment, and their negative human health effects. Among them, short-chain PFAS are of increasing concern due to their high solubility and mobility in water, while possessing persistency and toxicity nature like their longer-chain analogs. The most common method for PFAS removal from water is by sorption with activated carbons or ion exchange resins, but these adsorbents only exhibit limited removal efficiency against short-chain PFAS, and they require frequent replacement leading to high operational cost. Here we review and discuss the potential of using bio-adsorbents, which can be derived from common biomass feedstocks, as low-cost alternatives to traditional adsorbents, while these materials can also possess good removal efficiency against short-chain PFAS. We further provide the perspective on the designs of low-cost, activated bio-adsorbent systems that can be implemented for effective removal of short-chain PFAS.

KEYWORDS
bio-adsorbents, functionalization, removal, short-chain PFAS

Abbreviations: AC, activated carbon; ADONA, 3H-perfluoro-3-[(3-methoxy-propoxy) propanoic acid]; AFFF, aqueous film-forming foams
ATRP, atom transfer radical polymerization; CD, cyclodextrins; CDF, cyclodextrin polymers; CEC, contaminants of emerging concerns; CMC, cellulose microcrystal; CNF, cellulose nanofiber; DFB, decafluorobiphenyl; FOSA, perfluorooctane sulfonamide; F-53B, 6:2 chlorinated polyfluoroalkyl ether sulfonate [6:2 CI-PFAES] and 8:2 CI-PFAES; 6:2 FTOH, 6:2 fluorotelomer alcohol; FTSA, fluorotelomer sulfonic acids; GAC, granular activated carbon; GenX, hexafluoropropane oxide dimer acid [HFPO-DA]; HDI, hexamethylene diisocyanate; IX, ion-exchange; MIM, macromolecular imprinted material; MIP, molecularly imprinted polymer; NOM, natural organic matter; PAC, powdered activated carbon; PEI, poly(ethyleneimine); PFAS, poly- and perfluoroalkyl substances; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonate; PFCA, perfluorocarboxylic acids/perfluoroalkyl carboxylate; PFHxS, perfluorohexane sulfonate; PFOS, perfluorooctane sulfonate; PFSA, perfluoroalkane sulfonate; SPAC, super-fine powder activated carbon; TFN, tetrafluoroterephthalonitrile.

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1 | INTRODUCTION

The ever-increasing presence and emerging regulations of poly- and perfluoroalkyl substances (PFAS) in drinking water systems have resulted in the development of a multitude of technologies to remove them from contaminated water. Currently, the adsorptive removal method using granular activated carbon (GAC) seems to be the most practical and cost-effective approach for removal of PFAS, especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Ross et al., 2018). However, recent studies indicate that GAC is not an effective sorptive material in removing short-chain PFAS, such as perfluorobutanoic acid (PFBA) and perfluorobutane sulfonate (PFBS), as these compounds are more hydrophilic and water soluble (Ateia, Maroli, et al., 2019; Ross et al., 2018) than long-chain PFAS. Removal of short-chain PFAS will have to rely on the functional groups and surface charge of adsorbents to enhance electrostatic attraction. Although, ion-exchange (IX) resins are effective for this purpose, they are expensive and not sustainable as they are often discarded after one-time use (Kucharzyk et al., 2017; Ross et al., 2018). Adsorbents based on cheap, sustainable, and biodegradable materials, such as woodchips or other biomass feedstocks that can be functionalized for removal of short-chain PFAS are thus attractive alternatives to GAC and IX resins for PFAS removal from the cost perspective (Omo-Okor et al., 2018). In this paper, we summarize the existing works of PFAS treatment technologies using varying bioadsorbents and offer our perspectives as how to design new bio-adsorbent systems for PFAS removal, specifically for short-chain PFAS removal.

2 | THE SHIFT FROM LONG-CHAIN PFAS REMOVAL TO SHORT-CHAIN PFAS REMOVAL

PFAS have been used in many applications, such as aqueous film-forming foams (AFFFs), nonstick cookware, carpets, food packaging, and many more. With different carbon chain lengths and functional groups, a variety of PFAS compounds (more than 4000) can be found in our daily life (Barisci & Suri, 2021; Z. Wang et al., 2017). Concerns were first raised regarding the long-chain perfluorocarboxylic acids (PFCA, $C_nF_{2n+1}COOH, n \geq 7$) and perfluorosulfonic acids (PFSA, $C_nF_{2n+1}SO_3H, n \geq 6$) due to their bioaccumulative nature, long-range transport ability, and especially their persistence in the environment (Buck et al., 2011; Joerss et al., 2019). As a result, PFOS was added to Annex A (restriction of production) of the Stockholm Convention on Persistent Organic Pollutants in 2009 (Joerss et al., 2019). Later, PFOA was added to Annex A in 2019. Perfluorohexane sulfonate (PFHxS) and its related compounds have also been proposed to be added to the Convention and they are currently under review. As of May 2020, 12 US states have developed their own regulatory PFAS limits in drinking water. Out of them, nine states have guidelines for PFOA and PFOS limitations, which were stricter than the 70 ppt level proposed by the EPA health advisory. In addition, six states have included short-chain PFAS compounds, such as PFBA and perfluorohexanoic acid (PFHxA), in their guidelines (Post, 2020).

Due to the concerns over environmental and human health effects of long-chain PFAS, several manufacturing companies in the United States and Europe decided to phase out long-chain PFAS and replace them with short-chain PFAS (e.g., $n \leq 6$ for carboxylic acids and $n \leq 5$ for sulfonic acids). For example, PFOS was replaced by PFBS, and 6:2 chlorinated polyfluoroalkyl ether sulfonate (6:2 Cl-PFAS)/8:2 Cl-PFAES (F-53B); PFOA was replaced by hexafluoropropylene oxide dimer acid [HFPO-DA] (GenX) and 3H-perfluoro-3-[(3-methoxy-propoxy) propanoic acid] (ADONA). However, our knowledge of the replacement compounds remains limited in terms of their environmental impacts. One recent publication tested the bioaccumulation of PFAS in mice, which were exposed to AFFF having both long-chain and short-chain PFAS (McDonough et al., 2020). According to the sample analysis results, C6 and C7 perfluoralkyl sulfonates and C8 PFCA were found to be enriched in the mouse serum. Even though the results also indicated that short-chain PFAS were relatively easy to be excreted due to their higher concentration detected in urine (McDonough et al., 2020), other studies suggested the large dose of short-chain PFAS in the body can induce similar toxic effects as long-chain compounds (Chang et al., 2008). Several reports indicated that the short-chain compounds are also highly persistent and exhibit bioaccumulation potential to damage the liver and kidneys in humans (Bjornsdotter et al., 2019; Buck et al., 2011; Ian Cousins et al., 2016). A recent study focusing on the occurrence and impact of short-chain compounds found that...
short-chain PFAS can be found in land/solid waste, groundwater, and surface water as well as seawater (Li et al., 2020). Short-chain PFAS were also detected in the polar ice and snow, where the study found that the PFBA concentration varied widely from 1.15 to 6280 ng/L, the PFBS concentration from 0.01 to 4520 ng/L, and the concentration of short-chain compounds was in the pg/L level (Li et al., 2020).

Compared to the long-chain PFAS compounds, a large quantity of short-chain PFAS compounds is needed in products, such as fire-fighting foams, to achieve similar performance (Bjornsdotter et al., 2019; Li et al., 2020). The short-chain PFAS are highly mobile in the aquatic environment due to their enhanced hydrophilicity and greater mobility. Furthermore, because of the enhanced hydrophilicity (or reduced hydrophobicity), they exhibit relatively poor adsorption by conventional adsorbents and organic matter (Bjornsdotter et al., 2019; Ian Cousins et al., 2016). These factors, along with those short-chain PFAS formed caused by the decomposition of long-chain PFAS and other precursors (Li et al., 2020), can result in high concentrations of short-chain PFAS in the environment. This notion is clearly illustrated in Figure 1, which compares the ratios of the sum of short-chain PFCA and PFSA (C4 + C6) concentrations to the sum of long-chain PFOS and PFOA (C8) concentrations. The prevalence of short-chain PFAS (C4 + C6) can exceed 30 times the levels of PFOS + PFOA (C8). As these short-chain PFAS compounds become more prevalent, it is essential for us to develop deeper understanding of the health and environmental impacts of these materials and more efficient techniques to remove or remediate these compounds.

3 | SHORT-CHAIN VERSUS LONG-CHAIN PFAS PROPERTIES GOVERNING SORPTION MECHANISMS

In general, depending on the length of carbon-fluorine chain, PFAS could be classified as long-chain and short-chain PFAS. Fluorine atoms having high electronegativity and low polarizability render PFAS major properties. Longer chain length with more fluorine substituted PFAS has more chemical and thermal stability (Rahman et al., 2014). In fact, most PFAS with hydrophilic functional group are surfactants and have been shown to aggregate at the air-water interfaces and form micellar or hemi-micellar structure, therefore, leading to complex behavior in the environmental systems (Rahman et al., 2014).

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**Figure 1** Ratios of the sum of PFCAs and PFSAs (C4 + C6) to PFOS + PFOA (C8) detected in sites across the globe (Boone et al., 2019; Cai et al., 2012; Möller et al., 2010; Zhao et al., 2016; Zhou, Liang, Shi, Xu, & Cai, 2013). Sum C4 represents the sum of concentrations of PFBA and PFBS. Sum C6 represents the sum of concentrations of PFHxA and PFHxS. Sum C8 represents the sum of concentrations of PFOA and PFOS. Data represents mean concentrations, unless specified. *Mean concentration not specified. **Median concentration. PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonate; PFCA, perfluorocarboxylic acids/perfluoroalkyl carboxylate; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexane sulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFSA, perfluoroalkane sulfonate
Both long-chain and short-chain PFAS are typically present in anionic (acid) or neutral (alcohol and sulfonamides) form in water at pH between 3 and 11 because of the low pKₐ values (when PFAS containing acid functional group such as PFCA and PFSA) (Buck et al., 2011; Goss, 2008). The physical and chemical properties of long-chain PFAS have been better studied compared to short-chain PFAS (ITRC, 2020). As a result, a great deal of the physiochemical properties of short-chain PFAS are mainly based on empirical modeling (Lampic & Parnis, 2020). The volatility of PFAS usually decreases with decreasing chain length (Prevedouros et al., 2006) because short-chain PFAS tend to have lower vapor pressure than long-chain PFAS (Gagliano et al., 2020). The decrease in the chain length tends to increase the aqueous solubility of PFAS containing the same functional group, resulting in increased mobility of short-chain PFAS. In terms of PFAS with similar carbon chain length, PFCA exhibit higher water solubility and higher vapor pressure as compared to PFSA (Gagliano et al., 2020). Charged functional groups within PFAS usually improve the water solubility and reduce hydrophobic interactions with particulates (without considering heteroatom or other interactions) (Bhathara & Gramatica, 2011; Gagliano et al., 2020). Water soluble short-chain can travel a longer distance in aqueous environments from the source of contamination compared to long-chain PFAS (Ateia, Maroli, et al., 2019). Due to their high mobility, persistence, and poorer sorption, it has become more challenging to control the spread of short-chain PFAS in water systems (Ateia, Maroli, et al., 2019; Li et al., 2020).

Interactions between absorbents and PFAS can include van der Waals forces, hydrophobic interactions, hydrogen bonding, ion and ligand exchanges, and electrostatic interactions (Du et al., 2014). Among them, van der Waals forces are universal between all molecules that could be negligible in the presence of stronger interactions, whereas hydrogen bonding and ligand exchanges are limited by specific chemical groups. Therefore, the sorption mechanisms of PFAS are mainly due to hydrophobic and electrostatic interactions. For example, many studies demonstrated the presence of hydrophobic interactions between the carbon-fluorine tail of PFAS and the nonpolar carbon surface of adsorbents. However, owing to their low pKₐ values (Gagliano et al., 2020; Kim et al., 2015), PFAS are generally present in an anionic form in solution and can also be removed by positively charged adsorbents through electrostatic interactions. In this case, the adsorption process can be influenced by the pH level, presence of inorganic ions, and other ions that can compete with the adsorption sites (Banks et al., 2020; Gagliano et al., 2020). Theoretically, hydrophobic interactions play a dominant role between long-chain PFAS and sorbents, while electrostatic interactions are the dominant factor affecting the short-chain PFAS removal.

**4 | CHALLENGES WITH SHORT-CHAIN PFAS REMOVAL USING EXISTING TREATMENT METHODS**

Currently, activated carbons (ACs) and IX resins are two common technologies that have been proven effective in removing PFAS from water. Reverse osmosis has also been used to remove PFAS from different sources and it is also highly effective (the removal efficiency >99%) but energy intensive (Appleman et al., 2014; Rahman et al., 2014). For the adsorption approach, a recent study has tested 44 different inorganic and organic sorbents to remove 17 PFAS with different chain lengths and functional groups (Sörengård et al., 2020), where the result indicated that ACs exhibited the best overall removal result (>99.9% on average). Other effective sorbents, including magnesium chloride-fortified biochar, chitosan, bentonite, also indicated 17–25 times higher sorption capacity than sand (Sörengård et al., 2020). As ACs have a nonpolar surface, they are much more effective in removing long-chain PFAS than short-chain PFAS.

There are many reasons for this difference. First, short-chain PFAS have faster adsorption kinetic in the diffusion process due to their smaller size and weaker steric effect (Yu et al., 2009; Q. Zhang et al., 2011). However, they have lower Kₐ values (organic carbon-water partition coefficient) and hence sorption potential becomes lower for short-chain PFAS (e.g., PFBA, PFBS, PFHxA, 6:2 FTOH, Gen) than that for long-chain PFAS (e.g., PFOA and PFOS) (Rahman et al., 2014). Second, the AC surface usually contains negative charges that can cause electrostatic repulsion for anionic PFAS (Zhi & Liu, 2015). Hence, GAC optimized for removal of long-chain compounds would not be effective against the short-chain PFAS for the same length of time (Kucharczyk et al., 2017). In a study that analyzed the breakthrough time for GAC treatment against various PFAS over a 5-year period, PFOS exhibited the highest breakthrough time, whereas PFBA had the lowest (about 2 months) (Appleman et al., 2014). Interestingly, PFHxA and PFOA appeared to have a similar breakthrough time in the lead GAC contactor, but short-chain PFHxA reached full breakthrough in a shorter time (Appleman et al., 2014; Eschauzier et al., 2012). In another GAC treatment setup with coal-based parallel GAC chambers, short-chain PFCA showed only partial removal, but the removal increased with increasing chain length of PFAS.
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require incineration (e.g., at temperatures between 600 and be decomposed by the conventional methods and thus will problems after the sorption process. This is because the implemented to adsorb short-chain PFAS, there would be adsorption between long- and short-chain PFAS (Appleman et al., 2014; Eschauzier et al., 2012; Rahman et al., 2014).

However, even if suitable GAC technology could be implemented to adsorb short-chain PFAS, there would be problems after the sorption process. This is because the short-chain PFAS adsorbed onto the GAC surface cannot be decomposed by the conventional methods and thus will require incineration (e.g., at temperatures between 600 and 1000°C) to breakdown PFAS (Li et al., 2020; Sonmez Baghirzade et al., 2021). In addition, the reactivation of spent carbons can result in the increased cost in full-scale production. The conventional regeneration methods include two different pathways: (i) chemical regeneration using a large amount of sodium salts or organic solvents for desorption of PFAS (Du et al., 2015; Woodard et al., 2017), and (ii) thermal regeneration (Gagliano et al., 2020) at high temperatures using inert gas stream, such as N₂ or CO₂, for GAC to be reactivated (Watanabe et al., 2016; F. Xiao et al., 2020). Both have their own strengths and weaknesses. In one major weakness, besides the increased capital and operational cost for the post-treatment step and waste disposal, the use of organic solvent is not suitable for drinking water treatment because of possible remaining residues, whereas the thermal regeneration process can result in the release of volatile organic fluorine and/or decomposed short-chain compounds (Sonmez Baghirzade et al., 2021; Watanabe et al., 2016).

Similar challenges also exist in the adoption of polymeric adsorbents for PFAS treatment. In a study of using anion-exchange resins for PFAS removal for full-scale water treatments, they are found to be efficient to remove long-chain PFAS such as PFOA, but relatively less efficient for short-chain PFAS removal (Appleman et al., 2014). Functionalized IX resins exhibited enhanced performance for short-chain PFAS removal (Du et al., 2015; Li et al., 2020). For example, under the similar conditions, functionalized IX resins with polyamine showed much higher PFAS removal efficiency than their nonfunctionalized counterparts (Du et al., 2015). This was attributed to the combined hydrophobic and electrostatic interactions between PFAS and the resin (Du et al., 2015; Li et al., 2020). However, polymeric resins also have their limitations. Their systems are generally more costly, and the regeneration of certain resins may not be effective as some common regeneration method cannot desorb all PFAS from the resin surface (Li et al., 2020). In addition, some studies have also showed that short-chain PFAS are harder to remove from the resin surface than long-chain PFAS (Du et al., 2015; Li et al., 2020). That is because organic solvents such as methanol can only diminish the hydrophobic interaction to release adsorbed PFAS, while short-chain PFAS has strong electrostatic interaction with ionic sites on the resin, which is less affected by regenrant. At a higher concentration of PFAS or at higher pH conditions, long-chain PFAS are more favorable to anion-exchange resins and can even replace short-chain PFAS in the coexisting solution (Shi et al., 2019). Besides the regeneration and cost issues, considerations should also be given to the breakthrough and disposal/recycling problems of the used resins (Rahman et al., 2014). The incomplete incineration of the used IX resin will release the majority of PFAS back to the atmosphere (Stoiber et al., 2020).

In addition to the phase separation methods, other destructive techniques have also been demonstrated to degrade PFAS. These techniques include electrochemical oxidation (Chaplin, 2020; Nzeribe et al., 2019), plasma (Hayashi et al., 2015; Nzeribe et al., 2019; Singh et al., 2019), electron beam (Londhe et al., 2021), and activated persulfate (Nzeribe et al., 2019), all exhibiting promising potential to degrade long-chain PFAS, such as PFOA and PFOS. When the degradation of short-chain PFAS has been studied, the degradation efficiencies were poor, compared to their long-chain counterparts (Barisci & Suri, 2020, 2021; Lewis et al., 2020; Londhe et al., 2021; Nzeribe et al., 2019; Wang, Nickelsen, et al., 2020). However, these techniques are generally energy-intensive and not cost-effective except for the remediation of some heavily contaminated solutions. (Nzeribe et al., 2019). Recent trends have suggested the use of such destructive techniques in combination with a pre-concentration step could help offset the overall cost of treatment.

Thus far, the sorption route might be the most easiest and common approach to remove PFAS (Sonmez Baghirzade et al., 2021). As the performance of the adsorbent is varying against PFAS with different chain length, the proper selection of the sorptive materials becomes very critical. Some synthetic materials have already been designed for short-chain PFAS removal, such as covalent triazine-based framework (CTF) (B. Wang et al., 2016) and single wall carbon nanotube (Deng, Zhang, et al., 2012). We argue the most suitable adsorbent systems should have the following three features: (i) they are cheap and abundant in our surrounding, (ii) they can...
be easily functionalized with environmentally friendly chemistries, and (iii) they can remove both short-chain PFAS and long-chain PFAS effectively from water. These features point to the system of bio-adsorbent as alternatives to existing adsorbents and are discussed below.

5 | BIO-ADSORBENTS FOR PFAS REMOVAL

Bio-adsorbents based on underutilized biomass feedstocks, such as biomass waste from nonwoody plants and agricultural residues, have been shown to offer the feature of low-cost, and they can serve as alternatives for commercial ACs or polymer resins (Kucharzyk et al., 2017; Omo-Okoro et al., 2018). We argue that with the advent of new and environmentally friendly methods to extract bio-adsorbents at the microscale or nanoscale from sustainable feedstock materials, these sportive nanomaterials with high surface area can play an important role for PFAS removal, especially for removal of short-chain PFAS compounds. Figure 2 illustrates the potential advantages of bio-adsorbents, and two examples to produce bio-adsorbents at the nanoscale. These examples include nanochitin and nanocellulose (nanocrystals, nanofibers, and nanoparticles) extracted from different raw biomass feedstocks using chemical and/or mechanical treatments such as (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) catalyzed oxidation or mechanical grind methods (Abouzeid et al., 2019; Jin et al., 2021). A multitude of advantages can exist when using nanoscale bio-adsorbents, including cheap raw materials (especially underutilized biomass feedstocks), multiple functionalization possibilities, high efficiency, and even reusability (Abouzeid et al., 2019; Voisin et al., 2017). These advantages make bio-adsorbents very competitive for varying water treatments, especially for PFAS removal, if they are properly modified/functionalized. There are abundant underutilized biomass feedstocks, including agricultural residues, forest waste, and marine waste that can be used to extract polysaccharide-based sorptive materials, such as cellulose, hemicellulose, chitin, and chitosan (Omo-Okoro et al., 2018). These materials can be easily modified by chemical or physical pathways for PFAS adsorption. Chemical modification can enhance or change the content of functional groups on the bio-adsorbents to improve the adsorption efficiency. In polysaccharides, the typical functional groups include carboxyl, aldehyde, and hydroxyl groups, whereas in chitin and chitosan, the typical functional groups include amino, amide, and acetamido groups (Sud et al., 2008). Those surface groups on cellulose or chitin are chemically active, which could be converted to certain cationic or anionic functional groups by esterification, oxidation, quaternization, etc. (Mourya & Inamdar, 2008; Voisin et al., 2017) The physical modification pathways, such as defibrillation or physical cross-linking, can also improve the adsorption properties of the bio-adsorbents by increasing porosity, particle size, and

FIGURE 2 (a) Potential advantages of bio-adsorbents and (b) two examples process to produce nanochitin and nanocellulose bio-adsorbents (Abouzeid et al., 2019; Voisin et al., 2017)
| Bio-adsorbents                                                                 | Features (functional group)                                                                 | Pros                                                                 | Cons                                                                 | References          |
|------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------------------------------|---------------------|
| Poly(ethyleneimine)-functionalized cellulose microcrystal (PEI-f-CMC)        | • PEI functionalization  
• Cellulose microcrystal  
• Use electrostatic interactions       | • Fast adsorption at low concentrations  
• Facial regeneration capability  
• Less interfere by background NOMs   | • Low removal efficiency for short-chain PFAS  
• Less effective at high PH | Ateia et al. (2018) |
| Porous β-cyclodextrin polymers (P-CDP)                                       | • β-cyclodextrin polymer  
• Introduce host-guest interactions  
• Mesoporous structure                      | • Faster and more selective uptake  
• Inorganic ions and NOMs had no effect for adsorption  
• Long life cycle  
• Flow-through experiment was conducted; result was better than batch experiment | • High removal preference for positively charged micropolutants  
• For PFBA and PFOA removal, the result is only marginally acceptable | Ling et al. (2017) |
| Decafluorobiphenyl-β-cyclodextrin (DFB-CDP)                                   | • Use perfluorooarene cross-linker  
• Better affinity for PFAS            | • One-step synthesis  
• Selective for PFOA  
• Regenerable by methanol  
• Perform at environmentally relevant concentration | • Slow removal at low initial concentration  
• Only test for PFOA  
• No pH study  
• Highly fluorinated cross-linker is not environmentally friendly | Xiao et al. (2017) |
| Reduced tetrafluoroterephthalonitrile-β-cyclodextrin (TFN-CDP)                | • Covert nitrile groups to primary amines  
• Reverse the surface charge           | • The reduced amine groups had high affinity for anionic PFAS regardless of chain-length  
• Result is good for PFBA removal over PAC removal  
• Quick adsorption at environmentally relevant concentration | • No recycling test  
• Adsorption only conducted in a neutral PH condition  
• Multistep synthesis | Klemes et al. (2019) |
| Chitosan-bead molecularly imprinted polymer (MIP)                             | • Use PFOS as template  
• Involve electrostatic interactions | • High selectivity for PFOS with little influence of other pollutants and background electrolyte  
• Possible regeneration without loss of adsorption capacity within lifetime | • pH and ionic strength dependent  
• Too specific, not for general PFAS removal | Yu et al. (2008) |
| Cross-linked chitosan                                                         | • Amino groups protonated in acidic condition  
• Multilayer sorption occurs          | • High adsorption capacity with hemimicelles and micelles formation at high concentration  
• Double-exponential model applied to reveal diffusion-controlled process  
• Study the effect of concentration and different chain-length of PFAS | • pH sensitive  
• Conducted concentration of PFAS is too high | Zhang et al. (2011) |
| Bio-adsorbents | Features (functional group) | Pros | Cons | References |
|----------------|----------------------------|------|------|------------|
| Aminated rice husk | • Using atom transfer radical polymerization  
• Rice husk is an abundant agricultural by-product | • XPS study proved the electrostatic interactions via pronated amine groups  
• Hemi-micelles and micelles formation are also possible during hydrophobic interactions | • Multistep synthesis/modification cost  
• PFBA is less effective than PFOA and PFOS  
• No regeneration method | Deng et al. (2013) |
| Quaternized cotton | • Using atom transfer radical polymerization  
• Involve quaternary ammonium cation  
• Fibrous cotton is renewable natural material | • PH tolerance in wide range  
• Good adsorption capacity and kinetics  
• XPS and FTIR analysis revealed anion exchange mechanism between quaternary ammonium cations | • Multistep synthesis/modification cost  
• No test for short-chain PFAS  
• No regeneration method | Deng et al. (2012) |
| Polyurethane based macromolecular imprinted material (MIM) | • Incorporate β-cyclodextrin and HDI (hexamethylene diisocyanate) cross-linker  
• Control different ratios of β-CD and HDI | • High adsorption capacity with multilayer sorption  
• Inclusion sites have better affinity than interstitial sites thus lower cross-link density decreases the PFOA adsorption capacity | • Only test PFOA  
• Amido group may not have good affinity for PFAS | Karoyo & Wilson (2013) |
| Positively charged β-cyclodextrin derivatives | • Positively charged amine  
• Various functional groups and numbers of charge  
• Commerially available modified sorbents | • Higher association constant for positively charged adsorbents and negatively charged PFAS  
• Unique cavity of cyclodextrin is favorable for linear short-chain PFAS without –CF2CF2CF2– segment | • No adsorption experiment | Weiss-Errico & O’Shea (2019) |
| Amine-containing β-cyclodextrin polymer (CDP1) | • Compare different cross-linker containing amino and amido groups | • Polymer containing amine groups had high BET surface area, faster kinetic and higher adsorption capacity  
• Prove the good affinity for amine groups rather than amido | • Complex synthesis and post-treatment  
• Do not have pH study and regeneration test | Yang et al. (2020) |

Abbreviations: NOM, natural organic matter; PAC, powdered activated carbon; PFAS, poly- and perfluoralkyl substances; PFBA, perfluorobutanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; XPS, X-ray photoelectron spectroscopy.
surface area. Therefore, to design suitable bio-adsorbents with high efficiency, both physical and chemical features need to be considered.

In addition to bio-adsorbents, there are carbonaceous materials that can also be derived from biomass feedstocks by sequential pyrolysis and activation steps, such as bamboo-derived activated biochar or AC, exhibiting fast and high adsorption capacities for PFOA (476 mg/g) and PFOS (1160 mg/g) removal (Chen et al., 2011; Deng et al., 2015), while their adsorption capacities for PFHpA and high adsorption capacities for PFOA (476 mg/g) and bamboo-derived activated biochar or AC, exhibiting fast by sequential pyrolysis and activation steps, such as materials that can also be derived from biomass feedstocks need to be considered.

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In addition to bio-adsorbents, there are carbonaceous materials that can also be derived from biomass feedstocks by sequential pyrolysis and activation steps, such as bamboo-derived activated biochar or AC, exhibiting fast and high adsorption capacities for PFOA (476 mg/g) and PFOS (1160 mg/g) removal (Chen et al., 2011; Deng et al., 2015), while their adsorption capacities for PFHpA and PFHxA removal reached only 65.53 and 18.84 mg/g, respectively (Du et al., 2015). This behavior has been illustrated earlier in Section 4. In the case of grape leaf litter-based AC, the large surface area and high carbon content also enabled the effective PFAS removal (removal efficiency 90%–95% for PFOA, and 88%–94% for PFOS) by hydrophobic interactions (Fagbayigbo et al., 2017). However, we note that the activation process can be energy intensive. Without activation, the raw biomass feedstock or as-produced biochar can only have limited efficacy for PFAS removal by physio-sorption. In this paper, we deliberately avoid to further discuss the use of biochar or physically modified bio-adsorbent materials for PFAS removal as there are several excellent reviews (Banks et al., 2020; Du et al., 2014).

Instead, we decide to focus on chemically modified bio-adsorbents through direct functionalization of biomass.

Interestingly, although plenty of PFAS remediation technologies have been demonstrated (Ross et al., 2018), only a small number of publications were reported using bio-adsorbents for PFAS removal (Banks et al., 2020; Du et al., 2014; Kucharzyk et al., 2017; D. Zhang et al., 2019). In contrast, biomass-derived adsorbents have relatively more broadly demonstrated for other types of water purification applications, such as the removal of metal ions and organic dyes, and antibiotics (Bhatnagar & Sillanpaa, 2009; Voisin et al., 2017) mediation. Table 1 provides a summary of most relevant studies that employed bio-adsorbents for PFAS removal with objective assessments, where the relevant parameters used in these studies are summarized in Table 2. One exemplary work demonstrated the use of rice husk, which is an abundant and underutilized agricultural byproduct, the authors synthesized aminated bio-adsorbent by using atom transfer radical polymerization (ATRP) that can remove PFBA, PFOA, and PFOS (Deng et al., 2013). The authors argued that both electrostatic and hydrophobic interactions synergistically increase the adsorption of PFAS on the bio-adsorbent. X-ray photoelectron spectroscopy (XPS) was used to confirm that PFAS were adsorbed by protonated amine groups thru electrostatic interactions (Deng et al., 2013). According to the adsorption isotherm studies, hemi-micelles and micelles were likely to form for long-chain PFAS, which might be the reason of the higher amount of PFOA (2.49 mmol/g or 1031 mg/g) and PFOS (2.65 mmol/g or 1325 mg/g) adsorbed, whereas PFBA only exhibited the adsorption capacity of 1.70 mmol/g (or 363.86 mg/g) at pH = 5. (Deng et al., 2013). We noticed that this PFBA removal result is quite competitive or even better when comparing with AC Calgon (i.e., 0.24 mmol/g or 51.34 mg/g for PFBA removal) (B. Wang et al., 2016) and Calgon F600 GAC (15.3 mg/g for PFBA) (Zhao et al., 2011). A similar study was conducted to design the quaternized cotton by using the ATRP modification method (Deng, Zheng, et al., 2012). As quaternary ammonium cation has better pH toleration in a wide range of pH (2.0–11.0), where the modified compound is a promising bio-adsorbent for PFAS removal under different water conditions. In the study, the spectra before and after the PFAS sorption in Fourier-transform infrared spectroscopy (FTIR) and XPS measurement illustrated the anion exchange due to the presence of quaternary ammonium cations. Meanwhile, a large amount of ammonium groups could contribute to the high sorption capacity against PFOS (3.3 mmol/g or 1650 mg/g) and PFOA (3.1 mmol/g or 1284 mg/g) removal at pH = 5. However, there were two considerations that made it difficult for large scale production and usage of these two bio-adsorbents: (i) the multistep synthesis in these two systems would increase the modification cost, and (ii) the regeneration efficiency has never been tested on these materials. Furthermore, as short-chain PFAS were not the focus of these studies; only PFBA was tested in aminated rice husk and the result was less effective than long-chain PFAS. Here we included the removal data about common ACs and exchange resins for short-chain PFAS as benchmark: for PFBA and PFBS adsorption, ACs have the $Q_{\text{max}}$ between 15.3 and 128.1 mg/g and IX resins has the $Q_{\text{max}}$ between 19.1 and 1050.4 mg/g; for PFHxA and PFHpA adsorption, $Q_{\text{max}}$ for ACs are 18.84–235.54 mg/g and for IX resins are 37.7–1089.8 mg/g (Gagliano et al., 2020; Li et al., 2020). Besides, the previously mentioned CTF ($Q_{\text{max}} = 92–377$ mg/g) (B. Wang et al., 2016) and single wall carbon nanotube ($Q_{\text{max}} = 6.4–67.6$ mg/g) (Deng, Zhang, et al., 2012) could also be references for PFBA, PFBS, and PFHxA removal.

### 6 | VARYING BIOMASS BUILDING BLOCKS SUITABLE TO PRODUCE BIO-ADSORBENTS

#### 6.1 | Cellulose

Cellulose is an inexpensive and abundant natural polymer. Functionalized cellulose fibers at the micro- or nano-scale are proven effective adsorbent materials to remove a wide range of contaminants in water (Mo et al., 2019; Yao et al., 2016). As for PFAS removal, only a
| Bio-adsorbents | Particle size (and surface area) | Application mode | Target PFAS | Initial PFAS concentration | Equilibrium time | Maximum adsorption capacity<sup>b</sup> | pH range | Water matrix | Regeneration method |
|----------------|---------------------------------|------------------|-------------|----------------------------|------------------|----------------------------------------|----------|--------------|-------------------|
| Poly(ethyleneimine)-functionalized cellulose microcrystal (PEI-f-CMC) | 10–50 μm (SA: 7.8 m<sup>2</sup>/g) | Batch | PFCA (C<sub>4</sub>–C<sub>11</sub>), PFSA (C<sub>4</sub>–C<sub>10</sub>), ADONA, F-33B, 42fts, 62fts, 82fts, N-MeFOSA, N-EtFOSA | 2–50 μg/L | 15–20 min (PFOA) | 2.32 mg/g (PFOA) | 4.5, 6.5, 7.5, 9.5 (pH<sub>pzc</sub> = 10.9) | Lake water (containing NOM and competing anions)/DI water | Soaking in 50 ml methanol for 6 h |
| Porous β-cyclodextrin polymers (P-CDP) | 50–60 μm (SA: 218 m<sup>2</sup>/g) | Batch, flow-through experiment | PFOA, PFBA | 1 μg/L | N/A | N/A | 7 | DI water/DI water | N/A |
| Decafluorobiphenyl-β-cyclodextrin (DFB-CDP) | 15 μm (SA: 7.29 m<sup>2</sup>/g) | Batch | PFOA, PFBA | 1 μg/L and 1–12 mg/L | 13 h (1 μg/L PFOA) 2 h (200 μg/L PFOA) | 34 mg/g | N/A | DI water/DI water | Suspend in methanol for 24 h |
| Reduced tetrafluoroterephthalonitrile-β-cyclodextrin (TFN-CDP) | N/A (SA: 142 m<sup>2</sup>/g) | Batch | PFBA, PFHxA, PFHpA, PFOA, FENa, PFFDA, PFBS, PFHxA, PFOS | 1 μg/L and 2 μg/L | 9 h (PFOA + PFOS) | N/A | 7 | DI water/DI water | N/A |
| Chitosan-bead molecularly imprinted polymer (MIP) | N/A | Batch | PFOS | 20–550 mg/L | 32 h | 3202 μmol/g or 1601 mg/g | 3–10 | DI water/DI water | 0.5 M NaOH/acetone (90/10, vol/vol) at 40°C for 24 h |
| Cross-linked chitosan | 2–5 mm (SA: 14.1 m<sup>2</sup>/g) | Batch | PFOS, PFBS, PFHxA | 0.093–0.744 mmol/L | 11 h (PFBS) 35 h (PFHxA) 100 h (PFOS) | 5.5 mmol/g or 2751 mg/g (PFOS) | 3.0, 7.0, 9.5 | DI water/DI water | N/A |
| Aminated rice husk | 500–800 μm (pristine rice husk) | Batch | PFBA, PHOA, PFOS | 0–0.5 mmol/L | 3 h (PFBA) 5 h (PFOA) 9 h (PFOS) | 1.70 mmol/g or 363.9 mg/g (PFBA) 2.49 mmol/g or 1031 mg/g (PFOA) 2.65 mmol/g or 1325 mg/g (PFOS) | 2.0–10.0 (pH<sub>pzc</sub> = 8.5) | DI water | N/A |
| Bio-adsorbents | Particle size (and surface area) | Application mode | Target PFAS | Initial PFAS concentration | Equilibrium time \(^a\) | Maximum adsorption capacity \(^b\) | pH range | Water matrix | Regeneration method |
|----------------|---------------------------------|------------------|-------------|-----------------------------|--------------------------|-------------------------------|----------|--------------|-------------------|
| Quaternized cotton | N/A | Batch | PFOA, PFOS | 0.19-0.92 mmol/L | 4 h (PFOA) 12 h (PFOS) | 3.1 mmol/g or 1284 mg/g (PFOA) 3.3 mmol/g or 1650 mg/g (PFOS) | 3.0-10.0 | DI water | N/A |
| Polyurethane based macromolecular imprinted material (MIM) | N/A (SA: <1 m\(^2\)/g) | Batch | PFOA | 5 μM–5 mM | 3 h | 2.63 mmol/g or 1089 mg/g (Sips model) | 3.85 | DI water | N/A |
| Positively charged β-cyclodextrin derivatives | N/A | | PFBA, PFPA, PFMOPrA, PFMOB, PFPiOPyA, PFDMMMOB | 2.42 × 10\(^{-3}\) M | N/A | N/A | 7 | 50% DI water + 50% D\(_2\)O | N/A |
| Amine-containing β-cyclodextrin polymer (CDP1) | 45–90 μm (SA: 169 m\(^2\)/g) | Batch | GenX, PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS | 1 μg/L and 1–200 mg/L | 2 h (GenX) | 222 mg/g (GenX) 457 mg/g (PFOA) | 4 and 9 | DI water | N/A |

Note: N/A means data is not available in the reference.

Abbreviations: ADONA, 3H-perfluoro-3-[3-methoxy-propoxy] propanoic acid; NOM, natural organic matter; PFAS, poly- and perfluoroalkyl substances; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonate; PFCA, perfluorocarboxylic acids/perfluoroalkyl carboxylate; PFHxA, perfluorohexanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFSA, perfluoroalkane sulfonate; PFHxS, perfluorohexane sulfonate.

\(^a\)The equilibrium time was retrieved from data interpretation or estimated based on kinetic graphs.

\(^b\)The maximum adsorption capacity represents the highest value for certain PFAS at different conditions. The data was retrieved from interpretation of \(Q_{\text{max}}\) value or estimated based on isotherm graphs. The data may not be suitable for direct comparison because of large difference from the PFAS adsorption condition.
few studies based on cellulose-derived adsorbents have been demonstrated. For example, poly(ethylenimine)-functionalized cellulose microcrystal (PEI-f-CMC) was demonstrated by Ateia et al. (2018). They test the removal of 22 PFAS compounds, including carboxylic and sulfonated PFAS and PFAS precursors. As PEI-f-CMC contained many positively charged amine groups, the electrostatic interaction was thought to be the primary factor responsible for the PFAS adsorption. Under real polluted water conditions with PFAS concentration <1000 ng/L, the PEI-f-CMC material exhibited rapid and efficient adsorption of PFOA with an equilibrium time of ~20 min. The removal efficiency was positively correlated with the chain length from C4 to C12. For C8 and longer chain PFAS as well as PFAS precursors, the removal percentage was larger than 90% by PEI-f-CMC, but for short-chain PFAS, it exhibited lower removal efficiency (5%–60% from C4 to C6) (Ateia et al., 2018). Although this study only provided the isotherm study and calculated the adsorption capacity for PFOA, while the result in the batch study for short-chain PFAS is not ideal, this bio-adsorbent system still has illustrated one successful feature, that is, PEI-f-CMC was found to be insusceptible to natural organic matter (NOM) in water and exhibited good regeneration ability by washing with methanol. At the time of this manuscript preparation, there has been no further publication found using cellulose-based adsorbents for PFAS removal, but this PEI-f-CMC material and the work about aminated rice husk ($Q_{\text{max}} = 364 \text{ mg/g}$ for PFBA removal) (Deng et al., 2013) have demonstrated an effective pathway to create new cellulose scaffolds with suitable functionalization for short-chain PFAS removal.

6.2 Chitin

Chitin is the second most abundant natural polymer in the world, which also has a polysaccharide structure as cellulose, but differs in the substitution groups at the C2 position. The main source of chitin comes from marine crustaceans, such as shrimp and crab shells. Its derivative, chitosan contains amino groups, which can be used as an inexpensive bio-adsorbent without complex modification that can remove heavy metals and dyes from contaminated water (Bhatnagar & Sillanpää, 2009; Liang et al., 2018). For example, Yu et al. designed and demonstrated chitosan-based molecularly imprinted polymer (MIP), which could remove PFOS by electrostatic interaction (Yu et al., 2008). In the sorption experiment, the adsorbed amount of PFOS (560 μmol/g or 280 mg/g) by MIP was significantly higher than that of nonimprinted polymer (258 μmol/g or 129 mg/g). Furthermore, the study indicated MIP has good selectivity to remove PFOS even in the presence of other anionic pollutants. Such chitosan-based adsorbents could also be recycled by rinsing with NaOH/acetone solution without significant loss of the adsorption capacity, where five regeneration cycles were demonstrated (Yu et al., 2008). In another study, crosslinked chitosan bead was developed, containing porous structures with a large amount of amino groups (Q. Zhang et al., 2011). The authors proposed that the diffusion-controlled process was dominated by the multilayer sorption mechanism based on the isotherm fitting using the Freundlich model and the double-exponential kinetic model. In the kinetic study, the removal of PFBS and PFHxS with different chain lengths was also compared with that of PFOS. The results indicated that long-chain PFAS required a longer equilibrium time as they were rearranged to form micelle first, whereas short-chain PFAS exhibited fast adsorption kinetics because of the small size (Q. Zhang et al., 2011). The adsorption capacity was found to reach 5.5 mmol/g (2751 mg/g) for PFOS at an equilibrium concentration of 0.33 mmol/L, where the possible formation of bilayer sorption and micelles at high PFOS concentrations was due to both hydrophobic and electrostatic interactions (Q. Zhang et al., 2011). Unfortunately, the authors did not carry out the isotherm study for short-chain PFAS removal. In addition, such chitosan-based adsorbents possessed the shortcomings of pH sensitivity and ionic strength dependence during adsorption. In the optimal adsorption conditions, the initial PFAS concentration was usually too high to be practical under the environmentally relevant conditions. As discussed above, although there is no specific data about short-chain PFAS removal efficiency by chitin-based adsorbent, the chitin/chitosan has the great potential of short-chain PFAS remediation since many amine-functionalized materials, including high-efficiency IX resin (IRA910), was demonstrated to have good affinity for PFAS (Ateia, Alsbaeei, et al., 2019), where the abundant amino groups on chitin/chitosan backbone could serve as adsorption sites for short-chain PFAS through electrostatic interaction.

6.3 Cyclodextrins

Cyclodextrins (CDs) are a family of cyclic oligosaccharides, consisting of a macrocyclic ring of glucose subunits joined by α-1,4 glycosidic bonds. They are natural industrial products made from starch with typically three types of CDs (α-CD, β-CD, γ-CD) produced, containing 6, 7, 8 glucopyranose units, respectively (Schneiderman & Stalcup, 2000). Their unique cone-shaped structures with the inner hollow cavity can result in good host-guest
interactions, due to hydrophobic interactions, for suitable molecules. Meanwhile, the limited size of the interior cavity could exclude the trapping of larger natural organic molecules. Due to the many hydroxide groups on the outer surface of CD, it can also bond with target molecules and provide active sites for cross-linking.

Currently, many modified CD-based sorbents have been designed to adsorb pollutants such as heavy metals or dyes for water treatment through host-guest inclusion and electrostatic interactions (Q. Liu et al., 2020; Wu et al., 2018). With more attention to PFAS in water, CD-based MIPs for PFAS adsorption have been recently reviewed (Karoyo & Wilson, 2015). Ling et al. (2017) first synthesized a kind of porous β-cycloextrin polymers (P-CDP) and benchmarked their removal efficiency for 83 organic pollutants in water, including PFBA and PFOA and compared with the performance of coconut-shell based ACs. The results indicated that ACs exhibited slower but more uniform uptake than P-CDP, but P-CDP exhibited faster but more selective adsorption for positively charged and relatively larger molecules (Ling et al., 2017). However, P-CDP only exhibited moderate affinity for PFOA and PFBA. To improve its selectivity for PFAS, the authors replaced the linker of tetrafluoroterephthalonitrile (TFN) with deca-fluorobiphenyl (DFB), which has a higher affinity for fluorine atoms (L. Xiao et al., 2017). The modified DFB-CDP resulted in more than 10-fold increased affinity (\( K_L = 2.2 \times 10^5 \text{ M}^{-1} \text{ in Langmuir model} \)) for PFOA binding compared to the equal mass concentration of AC and 2.5 times higher than that in PAC, easily drop concentration of PFOA from 1 \( \mu \text{g/L} \) to \(<10 \text{ng/L} \) (L. Xiao et al., 2017). However, the use of highly fluorinated compound to attract PFAS is not an ideal solution as for environmental treatment and the introduction of another organofluorine into the treatment system is less than desirable.

Cross-linker tuning and molecular design for β-CD based polymers were also demonstrated to enhance the PFAS removal efficiency (L. Xiao et al., 2019). Besides using perfluorinated aromatic cross-linker, reduction of nitrile groups on TFN into primary amine groups to convert negative surface charge into positive charge was also found to enhance the interactions between β-CD based polymers and anionic micropollutants (Klemes et al., 2019). With this reduced polymer, anionic PFAS with C4-C10 were indiscriminately removed at high efficiency (80%–95% after 30 min), which outperformed GAC and PAC, especially for short-chain PFAS (PFBA removal >80%, while GAC and PAC have the removal of 40%–50%) (Klemes et al., 2019). To better understand the effect of the amino groups on the interactions between β-CD polymer and anionic PFAS, Yang et al. (2020) selected two different tripodal crosslinkers containing amino or amido groups, respectively. They found that the CDP1 with amino groups outperformed the amide-functionalized polymer CDP2 with amido groups for the removal testing of 10 anionic PFAS (C4-C10). It was confirmed that the high loading of amino groups in CDP1 was mainly responsible for the superior removal PFAS performance, while amido groups in CDP2 cannot be protonated, underscoring the importance of electrostatic interactions to sequester PFAS (Yang et al., 2020). As the result, CDP1 exhibited the highest affinity and adsorption capacity among CD-based sorbents for GenX (222 mg/g) and PFOA (457 mg/g). All these studies confirmed the feasibility of using modified CD-based adsorbents for PFAS remediation, however, there are still concerns regarding the use of highly fluorinated cross-linkers and the modification cost of these CD-based polymer.

For CD compounds, the selection of appropriate cross-linking agents plays an important role in creating adsorbents with adequate functionality and structural integrity. Clearly, the different compositions in the linkers to connect β-CD can affect the PFAS adsorption performance of β-CD polymers. For example, Karoyo and Wilson (2013) synthesized polyurethane-based macromolecular imprinted materials (MIM) incorporating β-CD and hexamethylene diisocyanate (HDI) cross-linker at different ratios. The MIM system outperformed GAC regarding the PFOA adsorption capacity, which exhibited monolayer sorption versus multilayer sorption at high equilibrium concentrations of adsorbates, respectively. Two driving forces were thought to be responsible for the PFOA adsorption to the MIMs framework: hydrophobic interactions occurred within the β-CD inclusion sites and dipolar interactions occurred at the interstitial domains with -NH and -OH groups (Karoyo & Wilson, 2013). The copolymer sorbent system having the molar ratios between HDI and β-CD of 1:1 seemed to be preferable for the PFOA sorption over the system with higher cross-link density. This may be because the larger cross-linking density attenuates the interactions from the inclusion site in β-CD, where the inclusion sites have a better affinity to PFOA in the absence of steric effect (Karoyo & Wilson, 2013; Karoyo & Wilson, 2016). Similar results were found in the study of Xiao et al. (2017), indicating that densely cross-linked polymers exhibited inferior adsorption performance.

Further studies have been carried out to elucidate the mechanisms and selectivity of CD-based adsorbents regarding PFAS removal. For example, a great deal of research has been conducted on the CD-based polymer to remove anionic, zwitterionic, and nonionic PFAS (Ching et al., 2020; Wang, Ching, et al., 2020). Compared to ACs and IX resins, CDP exhibited relatively high selectivity for certain charged PFAS. For example, DEXSORB
(a commercial CD adsorbent from Cyclopure, Inc., Encinitas, CA) with negative charges was effective to remove zwitterionic PFAS (Am-CPr-FASA), while DEXSORB+ and amine-CDP (Klemes et al., 2019) containing positive charges was effective to remove anionic PFAS (PFCA and PFSA) (Wang, Ching, et al., 2020). This review emphasized the advantages of functionalized-CDP, including rapid adsorption kinetic and high selectivity for PFAS, and this kind of CDP can be combined with other adsorbents such as AC and exchange resin to achieve broad adsorption. In addition, four different commercially available positively-charged β-CD derivative products were found to be effective to remove six short-chain PFAS with varying molecular structures (i.e., branched and linear) due to the enhanced host-guest complexion (Weiss-Errico & O'Shea, 2019). These authors performed the Fluorine-19 nuclear magnetic resonance spectroscopy (19F NMR) titration experiment and estimated the association constants for various charged β-CD derivatives with different short-chain PFAS. They concluded that the primary driving force of the host-guest complexation is the van der Waals force between the interior cavity of CD and C-F chains, where the secondary driving force pertains to the hydrogen bonding between the hydroxyl groups at the perimeter of β-CD and the carboxylate groups of PFAS (Weiss-Errico & O'Shea, 2019). When the hydroxyl groups are replaced by positively charged amine groups, enhanced complexation of β-CD/PFAS can be formed due to electrostatic attraction, while negatively charged adsorbents can result in poor adsorption efficiency due to electrostatic repulsion (Weiss-Errico & O'Shea, 2019). In this study, it was also found that the cavity of CD possesses a favorable size for the –CF₂CF₂CF₃– segment, such that the introduction of positively charged groups on CD is effective for the removal of short-chain PFAS without the –CF₂CF₂CF₂– subunit (Hept-am-β-CD has 20 times increase about the association constant for PFMOPrA when compared with native β-CD) due to weaker influence of van der Waals forces (Weiss-Errico & O'Shea, 2019). This result indicated the potential of using positively charged CD derivatives for short-chain or ultrashort-chain PFAS removal.

To summarize this section, varying functionalization schemes to modify bio-adsorbents with desired chemical structures, leading to the creation of optimal hydrophobic and electrostatic interactions can be the optimal path to tailor the adsorption performance. Since most bio-adsorbents contain hydrophilic polysaccharide backbones, excepts CD and its hydrophobic cross-linker, and likely charged groups, the use of electrostatic interactions should be considered a major path to address short-chain PFAS removal. In terms of the ideal adsorption conditions, since most used amino groups (as in chitosan) is protonated at low pH (pKₐ = 6.5), where PFAS with the low pKₐ value is also present as an anion, the lower pH value (3–4) usually results in higher removal efficiency than higher pH value. In addition, higher PFAS concentration usually can result in higher adsorption capacity with a longer equilibrium time (especially for long-chain PFAS when they can form micelles) (Q. Zhang et al., 2011). However, the environmentally relevant concentration (μg/L–ng/L) for the remediation process should be concerned and also be carefully addressed in the future research. As a result, the adsorption capacity from various papers may not be compared directly due to huge difference of PFAS adsorption condition (e.g., initial concentration range). Based on the existing data of above summarized bio-adsorbents, the short-chain PFAS adsorption capacity is 363.9 mg/g for PFBA (Deng et al., 2013) and 222 mg/g for GenX (Yang et al., 2020), and the average removal range for long-chain PFAS is from 457 to 2751 mg/g. Unfortunately, we cannot provide more data about bio-adsorbents for short-chain PFAS due to limited number of relevant publications. Generally, the existing deficiencies in existing bio-adsorbents’ demonstrations include the missing data about kinetic and isotherm studies for short-chain PFAS and the lack of column experiments. In addition, the antifouling and regeneration studies of demonstrated bio-adsorbents for PFAS removal are still very limited.

7 | PERSPECTIVES ON THE DESIGN OF NEW BIO-ADSORBENTS FOR SHORT-CHAIN PFAS REMOVAL

As discussed above, there are several unique features in the chosen bio-adsorbent examples, making them ideal platforms for further development of cost-effective and sustainable sorptive materials for removal of both long-chain and short-chain PFAS. These features include: (1) low-cost feedstocks from a broad range of underutilized sources (e.g., wood trims, agriculture residues, grass, and shrubs from lignocellulose plants), (2) natural polysaccharide scaffolds (building blocks) are biodegradable and can be easily modified to offer functional sites to enhance the adsorption of short-chain PFAS via electrostatic interactions, (3) the polysaccharide modification schemes can include both positive and negative charged surface enhancement to tailor the interactions with different short-chain PFAS, and (4) the nanoscale polysaccharide scaffold can offer the specific surface area significantly higher than those of GACs and approaching the level of hydrogels. It has been shown that some ionic polymer hydrogels with a large density of positively charged groups can remove both long-chain and short-chain PFAS effectively within several minutes, including PFBS and GenX (Q_max = 278 mg/g) (Ateia,
These ionic polymer hydrogels can be used as benchmarks for us to design the modification of nanoscale polysaccharide scaffolds (building blocks) for short-chain PFAS removal. Cost-effectiveness is the major concern for industry when developing a novel method to scale up. As for the utilization of bio-adsorbents, compared to the conventional adsorption system, it is estimated that the biosorption process could lower 20% of capital costs, 36% of operational costs, and 28% of total treatment costs (Ata et al., 2012). There is a rough estimation for carboxycellulose nanofibers costing $1.4 per g and the energy consumption is about 1.49 kWh/g (Sharma et al., 2017). When looking into the price of typical bio-adsorbents, the coconut shell charcoal, rice husk, lignin, chitosan, spheroidal cellulose, and cork waste cost 0.34, 0.025, 0.06, 2.2–15.43, 1.07, and 0.48 (USD/kg), respectively (Tran et al., 2015), which were much cheaper than commercialized AC (20 USD/kg) (Rafatullah et al., 2010). Meanwhile, the thermal regeneration of spent GAC could even increase the cost (Sonmez Baghirzade et al., 2021). All these evidences support the low-cost bio-adsorbents being alternatives for conventional AC adsorbents for PFAS removal.

7.1 Functionalization of bio-adsorbents

In Figure 3, a general strategy to functionalize the varying nanoscale polysaccharide scaffolds is illustrated to design new bio-adsorbents for removal of short-chain PFAS. In this figure, we argue that both chitin (or chitosan—with positively charged amino groups) and cellulose (generally with negatively charged groups such as carboxylate or sulfonate groups) based nanoscale scaffolds can both be modified to attach a high loading of positively charged functional groups, such as quaternary ammonium group or cationic metal nanoparticles through electrostatic interactions and metal complexation, to enhance their removal capability against short-chain PFAS. We do not include the class of CD materials here as they are generally more costly to produce and do not really offer the low-cost potential. Cellulose or chitin nanofibrils could be easily obtained through chemical treatments or defibrillation processes after adding surface charges. We note that the low-cost and sustainable extraction methods to fabricate nanoscale polysaccharide scaffolds have been rapidly developed such as nitro-oxidation (Sharma et al., 2017) and more will follow (Phanthong et al., 2018). They are also not included here because the development is out of scope to this work. Some likely functionalization schemes that can be adopted to modify nanoscale polysaccharide scaffolds are as follows. We have to admit that functionalization could eventually increase the total cost. To lower the cost of existing bio-adsorbents, it is ideal to use cheaper feedstocks, simpler synthesis steps, and greener chemicals during the modification.

Since many amine-functionalized adsorbents, including carbohydrate-based sorbents, synthetic-based sorbents, and...
IX sorbents were received attention and they showed good affinity for PFAS adsorption (Ateia, Alsbaiee, et al., 2019), chitosan-based nanomaterials should be considered one of the top bio-adsorbents for anionic short-chain PFAS removal because of their abundant amino groups on backbone without complex functionalization. Several studies using chitin or chitosan nanofibers to remove metal ions or dyes in water treatments have been demonstrated (Bhatnagar & Sillanpaa, 2009; D. Liu et al., 2013), where these systems can be further modified for the goal of short-chain PFAS removal. The easiest way to obtain amino groups in chitin nanofibers is through deacetylation (Fan et al., 2010), where the amount of amino groups can directly impact the adsorption efficiency for anionic PFAS. However, highly deacetylated chitin or chitosan materials may not be suitable as adsorbent materials because of their good solubility in water. So how to balance the degree of deacetylation will be a key in modification. Another issue for amine-functionalized sorbents is their poor pH tolerance during adsorption. To overcome this concern, we can adopt the approach in a study to prepare chitosan with quaternized ammonium groups (Rosa et al., 2008), which were found to have good pH stability for treating PFAS (Deng, Zheng, et al., 2012). Furthermore, a large number of cationization reagents and grafting methods that can provide positively charged groups have been reported (Mourya & Inamdar, 2008), and they have not been fully explored for the modification for chitin/chitosan-based nanomaterials for the purpose of short-chain PFAS removal. Some of those grafting approaches may also be useful for the modification of cellulose-based nanomaterials (or nanocellulose) (Abouzeid et al., 2019).

Another approach to modify the polysaccharide nanoscale scaffold, especially nanocellulose with negatively charged surface (e.g., carboxylate groups on cellulose nanofibers (CNF) (Sharma et al., 2017), or sulfonate groups on cellulose nanocrystals (CNC) (Song et al., 2019) is by the surface coupling with positively charged (i) metal ions and (ii) metal oxide nanoparticles thru metal complexation and/or electrostatic interactions. This approach may also work for chitin and chitosan for difference reasons. For (i), it is known that some multivalent metal ions can bind to oxygen atoms of the hydroxyl groups, which are readily available on the surface of both chitin/chitosan and cellulose scaffolds. These metal complexes can serve as active sites for adsorption of charged short-chain PFAS. In the case of chitosan, it has also been shown that the N atom on the NH₂ group can also act as an electron donor for metal ion chelation. Many examples of multivalent metals incorporated to chitosan exist, such as Fe(III) loaded carboxylated chitosan beads and chitosan-Zr nanocomposite (Natrayasamy & Meenakshi, 2008; Prasad et al., 2014). These materials offer electrostatic and metal complex sites, suitable for short-chain PFAS adsorption, and these adsorption sites should also have good pH stability. For (ii), the metal nanoparticles incorporation in polysaccharide scaffold has also been demonstrated (Gong et al., 2016). In this study, magnetite nanoparticles were incorporated in a

![FIGURE 4](image_url)

FIGURE 4  (I) Chemical structures of exemplary bio-adsorbents: cyclodextrin polymer (Ling et al., 2017), cross-linked chitosan (Q. Zhang et al., 2011), and quaternized cellulose (Deng, Zheng, et al., 2012); (II) some possible formats for the use of bio-adsorbents to remove short-chain PFAS: (a) membranes in adsorption-filtration, (b) powders/granules in packed column, (c) gels or beads as coagulants.
starch scaffold, where the anchored magnetite nanoparticles offered inner-sphere surface complexation (based on the FTIR results) to remove PFOA. The presence of carboxylate or sulfonate groups on nanocellulose to anchor metal oxide nanoparticle may offer unique advantages over chitin/chitosan nanomaterials, as the strong ionic interactions between nanocellulose-metal oxide may reduce the release of nanoparticles as secondary contaminants.

7.2 Varying formats of bio-adsorbent for removal of short-chain PFAS

In Figure 4, we outline three major formats for the use of bio-adsorbents short-chain PFAS removal: (a) membranes in filtration; (b) powders/graules in packed column; and (c) gels and beads as coagulants. Perhaps the most straightforward method to implement bio-adsorbents in real-life water treatments is by column filtration. The laboratory experiments, such as rapid small scale column tests (RSSCT) can be carried out to evaluate the performance of bio-adsorbent, where RSSCT are representative of full-scale water treatments (Ateia, Alsbaie, et al., 2019). For example, a column adsorption study was demonstrated by packed column containing CD incorporated in the microcrystalline cellulose substrate. Such a system exhibited good PFAS removal efficiency, good stability, and promising regeneration ability (Alzate-Sánchez et al., 2019). In principle, bio-adsorbents can also be combined with microfiltration or ultrafiltration membranes and provide dual adsorption/filtration functions. The dense coating of bio-adsorbents as barrier layers will no doubt decrease the pore size of the membrane and reduce the permeation flux, but the inclusion of loosely structured layer with sufficient adsorption functionality without the sacrifice of membrane flux can offer the opportunities to simultaneously remove multi-scale contaminants (e.g., larger scale contaminants by filtration, and short-chain PFAS by adsorption) (Ma et al., 2011). In fact, bio-adsorbents can be used in many other formats, such as gel, powder, bead, sponge, fiber, and so on, which has been illustrated before (Miretzky & Cirelli, 2011). Meanwhile, since highly charged nanocellulose has been demonstrated to be applied in coagulation–floculation treatment (Morantes et al., 2019), cationic, or metal nanoparticles deposited bio-adsorbents can also be used as coagulants and flocculants for anionic PFAS and even be combined with existing treatment materials, such as GAC and ion exchange resins, to achieve more effective and comprehensive PFAS removal. We sense there can be good synergy in the combined usage of bio-adsorbents and GAC materials, and these advantages are worthy of being explored further.

8 CONCLUDING REMARKS

In this paper, we point out the emerging concerns of short-chain PFAS and the difficulty to remove them by conventional methods. To solve this problem, we argue nanoscale bio-adsorbents derived from raw biomass can be an ideal scaffold to remove short-chain PFAS compounds, where the scaffold needs to be properly modified/functionalyzed to enhance the removal capability and efficiency through electrostatic interactions. The clear advantages of nanoscale materials are their larger surface to volume ratio and higher concentration of functional groups. The most important feature of these bio-adsorbents is their cost-effectiveness as they can be derived from diverse biomass feedstocks through chemical means without the use of high energy-consuming processes, such as acid hydrolysis or oxidation. To think about the future path of bio-adsorbents, the idea is to take green chemistry by simplifying the synthetic steps and reducing the chemical use. The usage of under-utilized biomass feedstocks, such as wood trims and agriculture residues can offer additional incentives. We further argue the nanoscale bio-adsorbents based on polysaccharide scaffold can offer a diverse range of functional groups, enabling further modification schemes to enhance the surface charge and offer more electrostatic interactions to adsorb negatively charged short-chain PFAS. These modification schemes include the conversion of existing functional groups, metal complexation and electrostatic coupling with metal nanoparticles. As for the thermal regeneration process, high temperature can close the pores of AC and thus trap PFAS from being released (Sonmez Baghirzade et al., 2021), but this can be avoided in biomaterials. As the polysaccharide scaffolds are biodegradable and not stable at high temperatures (such as AC), the disposal cost of PFAS-adsorbed materials will be significantly lowered compared to traditional sorbents (e.g., by avoiding the incomplete incineration of used bio-adsorbents).

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CONFLICT OF INTEREST

The authors declare no conflict of interest.
DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

AUTHOR CONTRIBUTIONS

Duning Li: Resources; data curation; investigation; methodology; writing – original draft. Kaushik Londhe: Resources; data curation; investigation; writing – original draft. Kai Chi: Resources; methodology. Cheng-Shiuan Lee: Resources; methodology. Arjun K. Venkatesan: Supervision; funding acquisition; writing – review and editing. Benjamin S. Hsiao: Supervision; funding acquisition; investigation; writing – review and editing.

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