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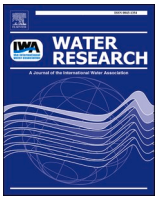

Surface modifications of biopolymers for removal of per- and polyfluoroalkyl substances from water: Current research and perspectives

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are highly recalcitrant organic contaminants that have attracted ever-increasing attention from the general public, government agencies and scientific communities. To remove PFAS from water, especially the enormous volume of drinking water, stormwater, and groundwater, sorption is the most practical approach. Success of this approach demands green, renewable, and sustainable materials for capturing PFAS at ng/L or μg/L levels. To meet this demand, this manuscript critically reviewed sorbents developed from biopolymers, such as chitosan (CTN), alginate (ALG), and cellulose (CEL) covering the period from 2008 to 2023. The use of different cross-linkers for the surface modifications of biopolymers were described. The underlying removal mechanism of biosorbents for PFAS adsorption from molecular perspectives was discussed. Besides reviewing and comparing the performance of different bio-based sorbents with respect to environmental factors like pH, and sorption kinetics and capacity, strategies for modifying biosorbents for better performance were proposed. Additionally, approaches for regeneration and reuse of the biosorbents were discussed. This was followed by further discussion of challenges facing the development of biosorbents for PFAS removal.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been recognized as the contaminants of emerging concern and listed in the top group of unregulated contaminants by the U.S. EPA due to their toxicity and bioaccumulation (Fenton et al., 2021; Hu et al., 2016). The physico-chemical properties of representative PFAS are shown in Table S1. Although most public and regulatory attentions have so far focused on anionic PFAS with polar (carboxylate (COO^-) or sulfonate (SO_3^-)) head groups, zwitterionic and cationic PFAS have been detected in numerous environmental matrices (Cordner et al., 2019). Due to the widespread use and environmental persistence, PFAS have entered surface water, groundwater, soil and sediment (Bai and Son 2021; Mussabek et al., 2019; Podder et al., 2021; Zhang and Liang 2022b) that may very possibly impact human health and the ecosystems (Xiao, 2017).

The U.S. EPA and Centers for Disease Control and Prevention (CDC) have reported that exposure to high levels of PFAS may lead to adverse health effects, such as developmental effects in children, decreased immunity and fertility in women and cancers (Lei et al., 2023). The U.S. Environmental Protection Agency (EPA) in June 2022 published the interim lifetime health advisory levels of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in drinking water as 0.004 ng/L and 0.02 ng/L, respectively (Rabinow 2022). These extremely low levels and stable C-F bonds in their structures pose a serious challenge to remediation and demand innovative and sustainable technologies to remove PFAS in water to such low concentrations (Stratton et al., 2017).

During the past several decades, a wide range of techniques, for instance advanced oxidation (Wang et al., 2021d), and photocatalytic reduction (Chen et al., 2021) have been investigated for removing PFAS from water. However, these technologies have limitations like high energy consumption and harsh reaction conditions that restrain their potential for large-scale applications (Espana et al., 2015). Phytoremediation, a green and sustainable approach, however, is challenged by its slow uptake of PFAS by plants (Zhang and Liang 2020, 2021, Zhang and Liang, 2022a; Zhang et al., 2022; Zhang et al., 2019b; Zhang et al., 2021; Zhang et al., 2019c). On the other hand, PFAS removal by adsorption is an established technology (Hassan et al., 2020; Kancharla et al., 2022). Adsorption can be used as a single process for point-of-use applications and as an unit operation in the process of treating water at municipal scale (Carter and Farrell 2010; Liu et al., 2016).

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Numerous adsorbents have been reported in the literature for PFAS removal. Among them, a few are commercially available, such as granular activated carbon (GAC) (McCleaf et al., 2017), powdered activated carbon (PAC) (Chen et al., 2017; Ilango et al., 2023b), natural clays (Luft et al., 2022), resins (Zaggia et al., 2016), etc. At pilot scales, GAC showed a higher capacity to remove long chain PFAS compared to biochar and anthracite (Inyang and Dickenson 2017). However, both bench and pilot scale experiments revealed the ineffectiveness and slow kinetics of both biochar and GAC to remove short chain PFAS (Gibert et al., 2013). The frequent reactivation or change-out process for both GAC and biochar is a concern in their large-scale applications for treatment of real water containing natural organic matter (NOM). The NOM can lead to growth of biofilm on the sorbent's surface over limited periods of operation (Crone et al., 2019). The resins, on the other hand, can bind with non-PFAS molecules in real water, which reduces their sorption towards PFAS and creates a need for more frequent regeneration to meet the desired criteria for PFAS removal (Ateia et al., 2019c; Contea et al., 2015).

Modified clay or organoclay, has been reported to possess much higher sorption capacity and faster kinetics than those of GAC given their fine powder form with large specific surface area for sorption (Jiang et al., 2022; Mukhopadhyay et al., 2021; Zhi and Liu 2015). These powders, once in water, may form stable colloids which are difficult to remove from water (Zhi and Liu 2015). The powder particles themselves also necessitate centrifugation or filtration for separation. These drawbacks thus may hinder their application in real-world drinking water treatment (Oladipo and Gazi 2014).

Considering the different drawbacks associated with conventional and new sorbents, green, renewable, and sustainable biomaterials are needed for removing PFAS in water (Li et al., 2022). Among various biopolymers, chitosan (CTN) is a natural amino-polysaccharide consisting D-glucosamine and N-acetyl-D-glucosamine residues attained from deacetylation of chitin (Kumar and Viswanathan 2017; Sowmya and Meenakshi 2014). Alginate (ALG), extensively abundant in brown algae, is a linear copolymer with mannuronic acid (M) and guluronic acid (G) residues (Kumar and Viswanathan 2020; Pandi and Viswanathan 2015). Cellulose (CEL) formed from the condensation of D-glucose units through β(1→4) glycosidic bonds is widely present in almost all plant materials (Ateia et al., 2018). Their chemical structures, strengths and disadvantages are given in Table 1.

These biopolymers can be fabricated to desirable shapes, such as aerogels (Li et al., 2018; Wang et al., 2022a), fibers (Dangi et al., 2022), membranes (Vedula and Yadav 2021) and beads (Aswin Kumar et al. 2020; Kumar et al., 2019; Sujana et al., 2013) . These shapes and forms enable the biosorbents to be easily separated from PFAS treated water without using centrifugation or filtration that is required for commercial sorbents (i.e., PAC, clay) and other fine powder materials (De Gisi et al. 2016; Luo et al., 2021; Wang et al., 2021a).

A few studies have reported the use of biosorbents for removing PFAS in water (Ateia et al., 2018; Deng et al., 2013; Verma et al., 2022). As discussed in later sections, most of these biosorbents are amine-modified natural materials used to remove only PFOA or PFOS at mg/L. These mg/L concentrations are rarely observed in the natural environment even contaminated by PFAS (Li et al., 2022; Yan et al., 2017). Although high sorption capacities have been reported, it is questionable whether these sorbents can achieve complete removal of PFAS mixtures containing these compounds with different chain lengths, functional groups, structures and at μg/L or ng/L concentrations. It is noteworthy that PFAS oftentimes exist as mixtures in different environments.

To further facilitate PFAS removal using bio-based sorbents, a systematic assessment of their sorption performances under different environmental conditions, and better understanding of PFAS sorption mechanisms are vital. By now, to the best of our knowledge, there is no review on PFAS remediation by biopolymers (CTN, ALG and CEL) based sorbents published in the open literature. Therefore, the purpose of this paper is to review the progress in surface modified CTN, ALG and CEL with a focus on the removal mechanisms from the molecular interaction's perspective covering the period from 2008 to 2023. We also identified the shortcomings of the bio-based sorbents and proposed a few ideas that may enable effective PFAS removal through using such sorbents.

2. Necessity for surface modification of biopolymers

CTN, ALG, and CEL have enriched functional groups (-NH_2, -OH, -COOH) (Billah et al., 2023; Syeda and Yap 2022; Zhao et al., 2021). The direct use of these biopolymers as adsorbents, however, is not promising due to: (1) the water solubilities of ALG and raw CTN, specifically in acidic medium (Kuczajowska-Zadrożna et al., 2020; Quesada et al., 2020); (2) although CEL is insoluble in water, the raw CEL does not possess much adsorption of anions due to its abundant -OH groups (Deng et al., 2013); and (3) the kinetics of sorption by virgin biopolymers are slow due to their tight non-porous structure (Mousa et al., 2016), which limits the diffusion of ions. Hence, to improve the adsorption performance of biopolymers and to enhance their structural stability and mechanical performance in aqueous solutions, surface modifications are essential using different cross-linkers (Ateia et al., 2018; del Mar Orta et al. 2020; Gonçalves et al., 2005; Pandi and Viswanathan 2014) (Table 2). A study by Li et al. (Li et al., 2019) reported that using $CaCl_2$ as a cross-linker in ALG/κ-carrageenan gel beads resulted in an enhanced mechanical property. The beads displayed a stress tolerance of 1.07 MPa, an elastic modulus of 1.3 MPa at 90 %

Table 1
Chemical structures, advantages, and disadvantages of CTN, ALG and CEL.

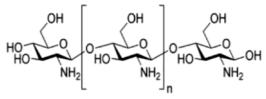
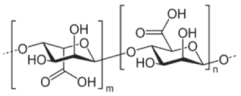
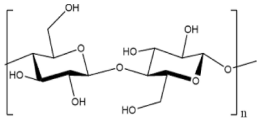
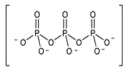
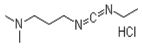
S. no	Natural scaffold	Chemical structure	Strength	Disadvantage
1.	CTN Billah et al. (2023)		Excellent biodegradability, rich functional groups, biocompatibility, low toxicity, antibacterial activity	Low porosity and poor mechanical resistance
2.	ALG Zhao et al. (2021)		Amenable to functionalization, low-cost, biocompatibility, antibacterial activity	Soluble in water, low porosity, poor mechanical performance
3.	CEL Syeda and Yap (2022)		Non-toxic, low cost, low density, renewable, biocompatible, antibacterial activity	Water insoluble, poor interfacial adhesion

Table 2
Structure and role of cross-linkers for surface modification of biopolymers.

S. No	Name of the cross-linker	Chemical structure	Cross-linked with	Role in surface modification
1	Glutaraldehyde (GTH) Gonçalves et al. (2005), Wang et al. (2022a)		CTN and ALG	During polymerization reaction with CTN, it reacts with NH_2 group and form N=C bond. With ALG, it reacts with OH group and forms O—C.
2	Epichlorohydrin (ECH) Gonçalves et al. (2005), Wang et al. (2021b)		CTN	Cross-links with CH_2OH group of CTN to form CH_2O—C.
3	Glycidyl methacrylate (GMA) Yin et al. (2021)		CTN and ALG	Cross-links with the CH_2OH group of CTN and ALG.
4	Sodium tripolyphosphate He et al. (2022)		CTN	Cross-links with the protonated amine (NH_3^+) groups of CTN.
5	Sodium hydroxide (NaOH) Elanchezhiyan et al. (2021)	Na^+OH^-	CTN	Acidic CTN is precipitated under NaOH forming beads.
6	Calcium chloride ($CaCl_2$) Lai et al. (2010)	$Ca^{2+}(Cl^-)_2$	ALG	Cross-links with the -COO^- of ALG forming beads.
7	N-(3-Dimethyl aminopropyl)-N'-ethyl carbodiimide hydrochloride (EDC) Ateia et al. (2018)		CEL	Cross-links with the -COO^- of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) modified CEL to form intermediate.
8	Tetrahydrofuran (THF) Deng et al. (2013)		CEL	It is used to connect the ethylenediamine with CEL chain.

strain and reduced swelling compared to a single κ-carrageenan/Ca^{2+} network. Furthermore, these beads exhibited excellent adsorption capacity of 291.6 mg/g for ciprofloxacin hydrochloride removal in water.

Similarly, the CEL nanofiber/CTN/montmorillonite-based composite aerogel (Rong et al., 2021) demonstrated a three-dimensional directional pore structure with excellent mechanical properties as it could withstand heavy objects 1124 times its own weight. It also showed superior adsorption performance and reusability when removing heavy metals (Cu^{2+}, $Pb^{2+}$and Cd^{2+}) in water. The modification of biopolymers via different methods, such as grafting, crosslinking, blending, and coating is a promising way to improve the physicochemical properties of the bio-based adsorbents (Vahidhabanu et al., 2019; Yaashikaa et al., 2022).

3. Reports available on the CTN, ALG and CEL based sorbents for PFAS removal

A small number of studies have considered the CTN, ALG and CEL based sorbents for PFAS removal in batch systems in the literature (Table 3). Among them, most of the sorbents are in powder form with a few of them as beads. As shown in the following sections, CTN and CEL modified are effective for PFAS removal, while the ALG based need more investigations. For all these sorbents, enhancing and maximizing the electrostatic and hydrophobic interactions between a given sorbent and PFAS have been the main goal (Harris et al., 2022; He et al., 2022; Verma et al., 2022).

3.1. CTN based sorbents

The -NH_2 functional groups of CTN protonated in an acidic solution can attract the anionic head groups (COO^- and SO_3^-) of PFAS via electrostatic interactions (He et al., 2022). CTN and epichlorohydrin (ECH) cross-linked beads reported by Zhang et al. (Zhang et al., 2011) showed 5.5 mmol/g capacity for removal of PFOS spiked at 0.33 mmol/L. The performance of the beads was highly dependent on the solution pH. At pH 3, electrostatic interactions were the dominant force for sorption of PFOS while the hydrophobic interactions were insignificant. Compared to some conventional sorbents, such as PAC (1.04 mmol/g), GAC (0.37 mmol/g), resin AI400 (0.42 mmol/g) and NaY80 zeolite (0.213 mmol/g) (Ochoa-Herrera and Sierra-Alvarez 2008; Yu et al., 2009), these beads have higher sorption capacity of 1.83 mmol/g (pH 7). At higher pH, however, the crosslinked CTN beads did not show much PFOS sorption due to low porosity and a low surface area of 14.1 m^2/g. Besides, the ECH is considered as carcinogenic and may thus not be suitable for use in removing PFAS in drinking water (Verma et al., 2022).

Long et al. (Long et al., 2019) prepared CTN-ethylene glycol (EG), namely CTN-EG hydrogels, which showed the highest PFOA sorption of 1024 mg/g at pH 2. This is due to high cationic surface (NH^+) of the hydrogels and strong electrostatic interactions. However, there are several drawbacks related to these hydrogels. First, since no cross-linkers were used for hydrogel preparation, the hydrogel is expected to be weakly stable considering the fact that both CTN and EG are water soluble. Second, the sorption process is highly pH dependent. At pH 10, the capacity was close to 0 mg/g. Third, the hydrogel was not porous even after a freeze and thaw step used during the preparation (Tang et al., 2020). Aside from these inherent disadvantages, the hydrogel was used to remove PFOA at 100–2000 mg/L which is environmentally irrelevant. In addition, it is unclear whether these hydrogels can be regenerated and reused.

In a later study, reusable and reduced graphene oxide-zinc ferrite loaded CTN (rGO-ZF@CB) beads synthesized by Elanchezhiyan et al. (Elanchezhiyan et al., 2021) had better removal capacity for PFOA and PFOS at 13–20 mg/g than CTN beads at 3–5 mg/g. This higher sorption capacity is due to the higher surface area of rGO-ZF@CB beads at 26.36 m^2/g. CTN in this sorbent allowed the formation of beads which could be easily separated from water after sorption. Similar to the CTN-EG hydrogels, the performance of the beads was highly dependent on pH. At pH 10, the PFAS sorption capacity was <4 mg/g. The beads could be reused up to five cycles, but significant loss of sorption capacity was observed after each cycle.

Recently, some noticeable modifications of CTN were reported for PFAS removal. For instance, the mixing of two biopolymers, CTN and β-CD cross-linked with GTH (Verma et al., 2022) led to a sorbent that removed 85 % of PFBS at low pH mainly due to the protonation of the NH_2 groups of CTN. At pH 10, however, the removal efficiency was only 11.30 %. β-CD is known to possess electron-deficient cavities (Wang et al., 2022b). These relatively hydrophilic cavities could allow faster diffusion of short chain PFBS molecules and form a host-guest inclusion complex even at extreme pH (Wang et al., 2022b).

Wang et al. (Wang et al., 2021c) also reported the adsorption of four sulfonates (PFSAs) molecules onto β-CD covalent organic frameworks (COFs) (β-CD-COFs) through pores and hydrophobic interaction with the electron-deficient β-CD cavities. COFs are a class of newly developed crystalline porous materials that have demonstrated great potential toward environmental applications (Bagheri et al., 2021; Liu et al., 2021c). Most COFs exhibit high hydrophobicity, which restricts their applications in aqueous environment (Pan et al., 2019). To overcome this issue, CTN supported fluoro functionalized-COF (CTN/F-COF) (He

Table 3
Recent reports on CTN, ALG and CEL based sorbents available for PFAS sorption in literature.

CTN, ALG and CEL based sorbents		Cross-linkers/ reagents	Target PFAS	Removal mechanism
CTN based	Crosslinked CTN Zhang et al. (2011)	ECH	PFOS	Electrostatic interactions between NH_3^+ of CTN and SO_3^- of PFOS and hydrophobic surface of beads attracts PFOS via hydrophobic interactions.
	CTN-ethylene glycol hydrogel Long et al. (2019)	No cross-linker	PFOA	The ionic hydrogen bond formed between carboxyl groups (COO^-) in PFOA and NH^+ of hydrogel.
	CTN/β-cyclodextrin sorbent Verma et al. (2022)	GTH	PFBS	Electrostatic attraction between -NH^+ and the negatively charged PFBS molecule; host-guest inclusion formations with β-CD cavity.
	Reduced GO-zinc ferrite loaded CTN beads (rGO-ZF@CB) Elanchezhiyan et al. (2021)	NaOH	PFOA, PFOS	Electrostatic interactions at pH 3 due to high zeta potential (+7.56 mV) of beads; and hydrophobic interactions due to beads surface.
	CTN-based molecularly imprinted polymer (MIP) beads Yu et al. (2008)	ECH	PFOS	Electrostatic attraction played an important role, and other factors including molecule size and different functional groups also affected the sorption selectivity for PFOS.
	CTN/F-COF He et al. (2022)	Sodium tripolyphosphate	PFOA, PFOS, GenX	Electrostatic interaction between NH_3^+ of CTN and anionic heads PFAS; hydrophobic interactions between CTN/F-COF and C-F chain of PFAS; F-F interactions also occur by the formation of halogen bond between PFAS and fluorinated groups of CTN/F-COF; and CTN/F-COF has channel diameter of approximately 32 Å and size of PFAS (8.6–12.9 Å) which are well adapted to the cavities of chitosan/F-COF via size selection.
	CTN loaded GAC Liu et al. (2022)	NaOH	PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA	PFAA adsorption is facilitated through the air-water interface and electrostatic interactions.
	PEI functionalized CTN based aerogel Ilango et al. (2023a)	GTH	9 PFAAs, GenX, and 2 PFAS precursors	Hydrophobic interaction on aerogels' surface was the dominant mechanism controlling PFAS sorption while electrostatic interactions played a minor role.
ALG based	*Moringa oleifera* seed powder (MSP) encapsulated ALG beads Militao et al. (2022)	$CaCl_2$	PFBS, PFOS	Hydrophobic interaction of beads' surface plays a dominant role for PFOS sorption while amine/amide-II groups of MSP offer active binding sites for PFBS removal.
	Rice draw derived biochar-ALG composite beads Militao et al. (2023)	$CaCl_2$	PFBS, PFOS	Dominant hydrophobic interaction on beads surface for PFOS sorption while pore filling/electrostatic interactions played a minor role for PFBS removal.
	ALG immobilized β-CD/ multi-walled carbon nanotubes as hybrid hydrogel beads Zakaria et al. (2023)	$CaCl_2$	PFOS	Hydrophobic interactions between surface functional moieties of ALG, β-CD, CNTs and hydrophobic PFOS while minor hydrogen bonding interactions between OH groups of beads and F and OH groups of PFOS.
	PEI functionalized ALG based aerogel Ilango et al. (2023a)	GTH	9 PFAAs, GenX, and 2 PFAS precursors	Dominant hydrophobic interaction for long-chain PFAS adsorption, while weak electrostatic interaction for short-chain PFAS adsorption.
CEL based	(Quaternized wood pulp (QWP)) i.e., CEL fibers functionalized with glycidyl trimethyl Ammonium chloride Harris et al. (2022)	NaOH, isopropanol	PFBA, PFBS, GenX, 6:2 FTS, PFOA, PFOS	Cationic amine (1.5 mmol -NR_3^+/g charge density) loaded CEL rapidly adsorbs anionic PFAS via., electrostatic attraction; CEL hydrophobic backbone enhances QWP1.5's ability to easily adsorb more hydrophobic PFAS.
	PEI functionalized CEL microcrystals (PEI-f-CMC) Ateia et al. (2018)	N-(3-Dimethyl aminopropyl)-N'-ethyl carbodiimide hydrochloride (EDC)	22 PFAS (9 PFCA; 7 PFSA; 2 PFAS, 5 PFAS precursors)	—NH_2 rich PEI plays vital role for PFAS uptake.
	Quaternized cotton Deng et al. (2012)	THF	PFOA, PFOS	Anion exchange dominates the sorption of PFOA and PFOS on quaternized cotton.
	Aminated rice husk Deng et al. (2013)	THF	PFOA, PFBA, PFOS	Electrostatic and hydrophobic interactions are involved in the sorption process, and the micelles/hemi-micelles of PFOA and PFOS may form on the adsorbent surface.
	Quaternized cationic nanocellulose (QCN) Li et al. (2023)	NaOH	PFOS, PFOA, PFBS and PFBA	Short-chain PFAS were strongly adsorbed to quaternary amines via electrostatic interactions, while long-chain PFAS were removed through hydrophobic interactions, forming a dimer or small aggregation structure with another PFAS molecule tethered to the quaternary nitrogen center (QNC) backbone.

et al., 2022) was fabricated. This material has desirable hydrophilicity, surface wettability, and high specific surface area of 211.11 m^2/g. Sorption of PFAS (i.e., PFOA, PFOS, GenX) was through electrostatic interactions, hydrogen bonding, F-F interactions, and channel size selection (Table 3). This CTN/F-COF was successfully applied to simultaneously remove PFAS from lake water and sewage samples, with removal efficiencies over 88.4 %. This sorbent composite, however, cannot be regenerated successfully, which could limit its potential large-scale application.

Wang et al. (2021c) also reported the adsorption of four sulfonates (PFSAs) molecules onto β-CD covalent organic frameworks (COFs) (β-CD-COFs) through pores and hydrophobic interaction with the electron-deficient β-CD cavities. COFs are a class of newly developed crystalline porous materials that have demonstrated great potential toward environmental applications (Bagheri et al., 2021; Liu et al., 2021c). Most COFs exhibit high hydrophobicity, which restricts their applications in aqueous environment (Pan et al., 2019). To overcome this issue, CTN supported fluoro functionalized-COF (CTN/F-COF) (He et al., 2022) was fabricated. This material has desirable hydrophilicity, surface wettability, and high specific surface area of 211.11 m^2/g. Sorption of PFAS (i.e., PFOA, PFOS, GenX) was through electrostatic interactions, hydrogen bonding, F-F interactions, and channel size selection (Table 3). This CTN/F-COF was successfully applied to simultaneously remove PFAS from lake water and sewage samples, with removal efficiencies over 88.4 %. This sorbent composite, however, cannot be regenerated successfully, which could limit its potential large-scale application.

CTN was also used to support GAC for removal of PFAAs (PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA) in floatation with aeration (Liu et al., 2022). PFAAs' adsorption onto the sorbent was facilitated through the air-water interface and electrostatic interactions. Compared with PFOA removal by GAC (0.36 mmol/g), the CTN/GAC resulted in higher capacity of 0.72 mmol/g.

The above reviewed CTN based sorbents generally showed better removal for PFOS than PFOA. This is due to the fact that PFOS is more hydrophobic than PFOA and can attach itself to the hydrophobic surface of CTN based sorbents via hydrophobic interactions (Liu et al., 2020; Takagi et al., 2011). To use these sorbents for PFAS removal, short chain PFAS and reusability of the spent biosorbents need to be investigated. In addition, other kinds of surface modification of CTN warrant further research in order to achieve enhanced PFAS sorption under a wide range of pH and in complex environments.

3.2. ALG based sorbents

In the literature, only a few research papers are available on the ALG

Table 4
PFAS adsorption capacity of the bio-based sorbents reported in the literature.

S. No	Biosorbent	Dose (mg/L)	Target PFAS	C_0 (mg/L)	Sorption time (h)	Isotherm	Adsorption capacity (mg/g)
1	CDP1 Yang et al. (2020)	100	PFOA, GenX	PFOA: 10–200 GenX: 1–200	22	Langmuir	PFOA: 457 GenX: 222
2	Modified lignin Li et al. (2022)	20	PFOA, PFOS	0.000001–400	5–10	Langmuir	PFOA: 4104 PFOS: 4262
3	β-CD copolymer Karoyo and Wilson (2013)	N/A	PFOA	400–8000	2–5	Sips	300–400
5	CTN-ethylene glycol hydrogel Long et al. (2019)	N/A	PFOA	50–900	24	Freundlich-Langmuir	1275.9
6	rGO-ZF@CB Elanchezhiyan et al. (2021)	1000	PFOA, PFOS	20	2	Langmuir	PFOA: 16.1 PFOS: 21.6
7	CTN/β-CD Verma et al. (2022)	N/A	PFBS	1–160	N/A	Sips	135.70
8	MIP beads Yu et al.)2008)	N/A	PFOS	10	30–50	Langmuir	1460
9	Crosslinked CTN Zhang et al. (2011)	15.2–15.3	PFOS	50–500	30–60	Freundlich	2500
10	CTN/F-COF He et al. (2022)	5	PFOA, PFOS, GenX	1–1000	4	Empirical and Langmuir	PFOA: 6177.1 PFOS: 8307.1 GenX: 4603.3
11	CTN/GAC Liu et al., 2022)	10	PFOA	10–200	72	Langmuir	298.13
12	MSP-ALG beads Militao et al., 2022)	0.1–1.0	PFOS	0.1–1	<1	Langmuir	941.71
13	Rice draw derived biochar-ALG beads Militao et al. (2023)	500–1500	PFOS	0.1–2	16	Freundlich and Langmuir	3.168
14	QWP Harris et al. (2022)	10	PFOA, PFOS	~ 0.0025	24	Langmuir	PFOA: 763 PFOS: 605
15	PEI-f-CMC Ateia et al. (2018)	10	PFOA	0.002–0.05	0.25–0.33	Freundlich	2.32
16	Quaternized cotton Deng et al. (2012)	N/A	PFOA, PFOS	50–500	3–9	Langmuir	PFOA:1240 PFOS: 1750
17	Aminated rice husk Deng et al. (2013)	10	PFOA, PFBA, PFOS	50	PFOA: 5 PFBA: 3 PFOS: 9	Langmuir	PFOA: 1085 PFBA: 365 PFOS: 1425
18	Magnetic biochar (Hassan et al. (2022)	1000	PFOS	200	24	Freundlich and Langmuir	120.44
19	Maize straw-derived biochar Zhang et al. (2019a)	200–1200	PFOS	100	2	Freundlich	91.6
20	ALG-β-CD/multi-walled CNTs hydrogel beads Zakaria et al. (2023)	1000	PFOS	1000	0.45	Langmuir	0.32
21	PEI-glycidyl trimethyl ammonium modified pine bark Ren et al. (2023)	400	PFOA	10–1000	24	Langmuir	1165.28
22	GTH—CTNPEI aerogel Ilango et al. (2023a)	100	9 PFAAs, GenX, and 2 PFAS precursors	0.01–0.5	24	Sips	12,133.14 (Total PFAS)
23	GTH-ALGPEI aerogel Ilango et al. (2023a)	100	9 PFAAs, GenX, and 2 PFAS precursors	0.01–0.5	24	Sips	3045.28 (Total PFAS)
24	Quaternized cationic nanocellulose (QCN) Li et al. (2023)	32–320	PFOS, PFOA, PFBS and PFBA	PFOS: 1–50 PFOA: 1–50 PFBS: 1–250 PFBA: 1–100	2	Langmuir	PFOS: 559 PFOA: 405 PFBS: 319 PFBA: 121

*N/A - not available; C_0 is the initial PFAS concentration (mg/L).

based beads for PFAS sorption (Table 3). Native ALG is an anionic biopolymer (Deze et al., 2012), thus, without surface modifications, the -COOH groups on ALG are not beneficial for interacting with anionic PFAS. The COO^- groups, however, can react with divalent metal cations (Ca^{2+}, Fe^{2+}) to form metal-ALG beads (Fig. S1). A recent report by Zakaria et al. (Zakaria et al., 2023) on the ALG immobilized β-CD/multi-walled carbon nanotubes (CNTs) as hybrid hydrogel beads showed low sorption capacity (0.4980 mg/g) towards PFOS removal from water. The incorporation of CNTs to ALG-β-CD improves the surface area of the bead from 24.77 m^2/g (ALG-β-CD) to 193.73 m^2/g, which helped to attain the complete PFOS sorption within 45 min. At least two drawbacks are associated with this type of bead. First, its high dependency on pH. The sorption capacity was 0.482 mg/g at pH3 and 0.078 mg/g at pH 11. Second, CNTs are expensive. Fortunately, increasing the dose of CNTs from 1.0 g to 2.0 g resulted in decreased sorption capacity from 0.1512 mg/g to 0.1086 mg/g, respectively. The beads could be reused up to four cycles, but significant loss of sorption capacity was observed after each cycle.

A recent report by Militao et al. (Militao et al., 2022) on the *Moringa oleifera* seed powder (MSP) encapsulated Ca-ALG beads showed 70 % removal of PFOS at 100 μg/L compared to 20 % by pristine Ca-ALG beads. The amine/amide-II groups on MSP of ALG beads supported PFOS adsorption via electrostatic attraction. For shorter chain PFBA at the same concentration, however, the removal was less than 10 % for both pristine and modified ALG beads. To enhance the sorption performance of Ca-ALG beads towards PFBS, Militao et al. (2023) prepared biochar pre-treated by ammonium sulphate and diammonium phosphate. The biochar loaded Ca-ALG beads achieved PFBS and PFOS removal of 30–40 % and >90 %, respectively after <16 h. The less sorption of PFAS was due to the non-porous nature of the ALG beads.

It is worth noting that a comparable trend was also reported for commercial GAC. Calgon Filtrasorb 820 removed 89 % of PFOS and only 43 % of PFBS spiked at 100 μg/L (Liu et al., 2021a). GAC sold by Fisher Scientific showed removal of 90 % of PFOS and again 40 % of PFBS at an initial concentration of 1000 μg/L (Zhang et al., 2021).

Although both MSP encapsulated Ca-ALG beads and biochar-ALG beads did not have strong affinity to PFAS, especially the shorter chains, these beads appeared to be pH independent. The presence of natural organic matter (NOM) did not greatly reduce the removal of either PFOS or PFBS. Therefore, for PFAS removal by these beads, hydrophobic interactions were the dominant force rather than electrostatic interaction. Furthermore, compared to powdered sorbents, such as biochar and PAC which are difficult to be used in packed columns or fluidized adsorbers, the ALG beads are suitable for flow-through systems and can potentially be an inexpensive and environmentally friendly alternative to GAC (Aswin Kumar and Viswanathan 2018; Karthikeyan et al., 2019).

Further improvements of ALG beads could focus on introducing more cationic surface and/or the improvement of the morphological characteristics, such as surface area and pore volume. It is noteworthy that ALG based beads have low porosity and low surface area. Therefore, using these materials in a porous form, such as cryogel, may increase their sorption performance towards PFAS, especially shorter chains as discussed in Section 4. In addition, methods for regeneration and reuse of the spent adsorbent need to be further evaluated.

3.3. CEL based sorbents

In the case of CEL, some satisfactory modifications were made for PFAS removal in the literature. PEI, a water-soluble polymer, has been used for modifying CEL. PEI has repeating units composed of abundant $-NH_2$ and two carbon aliphatic $-CH_2-CH_2-$ spacers (Yan et al., 2019). Sufficient protonation of the $-NH_2$ groups forms, i.e., $-NH_3^+$ under acidic conditions, leading to immobilization of anionic ions through electrostatic and coordination attractions (Lu et al., 2020).

Ateia et al. (Ateia et al., 2018) prepared PEI-functionalized CEL microcrystals for removal of a suite of 22 PFAS (Table 3), each at <1000 ng/L. Fast kinetics and high removal efficiency for long chain PFAS were observed. For example, 95 % of PFOA was removed in 15 min. For PFBA and PFBS, however, the efficiency was <10 %. The spent sorbent could be regenerated by methanol and reused for eight cycles without losing much of its sorption capability. However, synthesizing this PEI-functionalized CEL microcrystals is tied to high cost of material and energy considering: (1) CEL microcrystals are expensive; (2) the conversion of $-CH_2OH$ group of CEL to $-COO^-Na^+$via energy intensive TEMPO oxidation (Fig. S2); and (3) role of EDC cross-linker is not clear.

Wood pulp (WP) would be an inexpensive alternative to CEL for PFAS remediation. Quaternary ammonium (N^+) functionalization of WP is more beneficial than PEI on CEL due to easier synthesis as reported by Harris et al. (2022) It was reported that the -OH activation of WP by

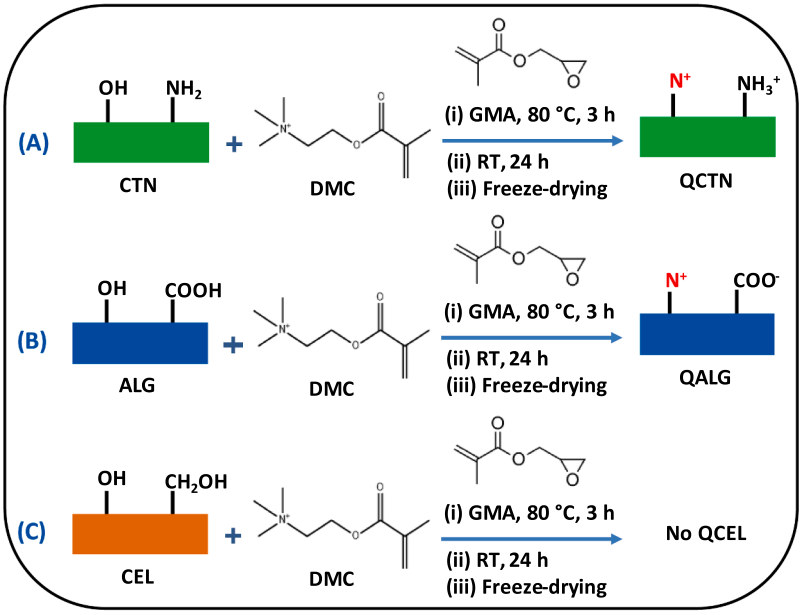


Fig. 1. (A) QCTN, (B) QALG cryogel synthesis and (C) no QCEL formation.
Note: the QCTN systhesis pathway was inspired from Yin et al. (2021) and simplified for readers.

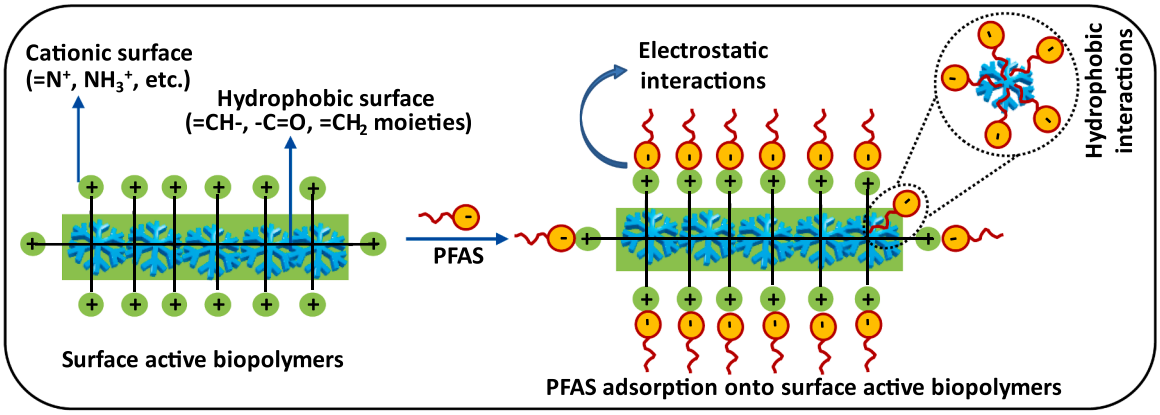


Fig. 2. Surface active biopolymers for PFAS adsorption.

Table 5
Recent reports of the amine modified β-cyclodextrin for PFAS adsorption in the literature.

S. No	Surface modified biopolymers	Cross-linkers/ reagents used	Target PFAS	Removal mechanism
1	Trifunctional amine containing β-cyclodextrin polymer (β-CD) (CDP1) Yang et al. (2020)	Tris(2-aminoethyl) amine	PFOA; GenX	Higher loading of -NH_2 groups in CDP1 contribute to the superior PFAS binding.
2	Functionalized β-CD Wang et al. (2022b)	Tetrafluoroterephthalonitrile	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA	Removal of shorter-chain PFCAs that are conventionally difficult to remove relies strongly on electrostatic interactions between anionic PFAS and cations embedded (N^+) polymer. Long-chain PFAS adsorption is controlled by a complementary interplay of hydrophobic and electrostatic interactions.
3	Functionalized β-CD Ching et al. (2020)	Tetrafluoroterephthalonitrile	Zwitterions: AmPr-FHxSA, TAmPr-FHxSA, 6:2 FTAB; Non-ions: FBSA, FOSA ; Alcohols : 4:2 FTOH, 8:2 FTOH; Anions: PFBA, PFBS, PFOS	CDPs with a positive surface (amine) charge remove all anionic PFAS via electrostatic attractions.

glycidyl trimethyl ammonium chloride (GMAC) using NaOH and 2-proponal exhibited >80 % removal for most prevalent PFAS and <30 % for short chain PFAS at environmentally relevant concentrations (~2.5 μg/L). The quaternary amines rapidly (<30 s) and efficiently adsorbed anionic PFAS by electrostatic interactions. It is unclear, however, whether the modified WP could be reused.

Quaternized cationic nanocellulose (QCN) by Li et al. (2023) showed higher sorption capacities of PFOS, PFOA, PFBS and PFBA at 559, 405, 319 and 121 mg/g respectively, within 2 h. This QCN adsorbent was also tested to treat PFAS-contaminated groundwater, which showed >95 % removal for long-chain PFAS (C7-C9) even at a low QCN dose of 32 mg/L. Short-chain PFAS, PFBA and PFPeA, however, were removed at 0 % and 10 % respectively, due to competing constituents in the groundwater matrix.

Aminated rice husk by Deng et al. (2013) showed good sorption capacities of PFBA, PFOA and PFOS were 1.70, 2.49 and 2.65 mmol/g at 3, 5, and 9 h respectively. The PFOA sorption of 2.49 mmol/g was higher than commercial PAC (0.67 mmol/g) and alumina (0.03 mmol/g) (Wang and Shih 2011; Yu et al., 2009). The modified rice husk, however, had lower sorption compared to resin AI400 at 2.92 mmol/g and quaternized cotton at 3.1 mmol/g. in addition, the sorption performance is highly dependent on pH. When the pH is above 8.5, the adsorbed

Table 6
Regeneration of spent biosorbents for PFAS adsorption in literature.

S. No	Biosorbent	Sorbent dose (mg/L)	PFAS targeted	C_o (mg/L)	Extraction detail		Cycle
					Solvent	Time (h)	
1	CTN/β-CD Verma et al. (2022)	12	PFBS	50	methanol	N/A	4
2	rGO-ZF@CB Elanchezhiyan et al. (2021)	1000	PFOA, PFOS	20	0.1 M ethanol	2	5
3	MIP beads (0.01 g) Yu et al. (2008)	10	PFOS	50	0.5 M NaOH/10 % acetone	24	5
4	ALG-β-CD/CNTs beads Zakaria et al. (2023)	1000	PFOS	10	0.1 M HCl	0.45	4
5	Magnetic carbonized *Calotropis gigantea* fiber (MC-CGF) Niu et al. (2020)	10	PFOA, PFOS	50	100 % methanol	N/A	6
6	PEI-f-CMC Ateia et al. (2018)	50	PFOA	1	100 % methanol	2	8
7	Decafluorobiphenyl (DFB) cross-linked β-CD (Xiao et al., 2017)	400	PFOA	0.2	100 % methanol	24	4
8	Poly (N-[3 (dimethylamino) propyl] acrylamide, methyl chloride quaternary hydrogel Ateia et al. (2019b)	25	GenX, PFBA, and PFOA	10	1% NaCl/methanol (30/70, v/v)	12	6
9	PG-PB Ren et al. (2023)	400	PFOA	100	0.05 % NaOH + 20 % methanol	4	3

N/A - not available; C_o is initial PFAS concentration.

amounts of the three PFAS were less than 1 mmol/g.

The aforementioned CEL based sorbents are functionalized with amine, which are promising for PFAS removal. It is noteworthy that WP and rice husk are alternatives to CEL microcrystals. Further improvements of functionalization could focus on simple and inexpensive ways for functionalization and use of other low-cost CEL sources, such as cotton stalk (Song et al., 2015) to improve their sorption capability toward short chain PFAS.

The maximum adsorption capacity of biosorbents in the literature towards PFAS adsorption is shown in Table 4. It is observed that: 1) most of the reported biosorbents achieved good sorption capacity for long and hydrophobic PFAS (PFOA and PFOS) compared to short chain PFBA and PFBS in synthetic water; 2) the fact that Langmuir and Freundlich isotherm model fitted well with sorption data demonstrates a multilayer PFAS sorption on the biosorbent's surface; 3) Due to the non-porous nature, cross-linked CTN and ALG beads necessitated longer time of 30–60 h (Yu et al., 2008; Zhang et al., 2011) to attain equilibrium sorption. To shorten the time to equilibrium, porous bio-beads could be prepared; 4) the biosorbents have been narrowly tested on a few PFAS, especially PFOA and PFOS at mg/L levels. Since PFAS often show up in contaminated environments as mixtures (Gagliano et al., 2020), it is questionable whether for the reported sorbents are effective to remediate environments containing mixed PFAS at low concentrations, such as ng/L or low end of μg/L levels (Ateia et al., 2019a).

4. Surface modifications of CTN, ALG and CEL for efficient PFAS removal

In addition to -NH_2 and -COOH functional groups, CTN and ALG contain -OH groups that are stable in the aqueous solution. Activation of these -OH groups via chemical grafting provides potentially enormous binding sites for PFAS sorption.

4.1. Chemical grafting with quaternary ammonium salt

[2-(methacryloyloxy) ethyl] trimethyl ammonium chloride (DMC) is a polymer consisting of rich quaternary cations (R_3-N^+). Grafting CTN or ALG with DMC produces cryogel with a large cationic surface (Yin et al., 2021) (Fig. 1A and B). Glycidyl methacrylate (GMA), as a cross-linker, can be used to improve the structural and chemical stability of the quaternized CTN (QCTN) and QALG based cryogels. It is noteworthy that the fabricated material shown in Fig. 1A was used for removing cationic and anionic dyes and for antibacterial applications (Yin et al., 2021). Use of these materials for PFAS removal has not been reported yet.

In the case of CEL, the formation of QCEL is not possible (Fig. 1C) under the same reaction conditions. This is because of the water insoluble nature of CEL. In such case, a different cross-linkers, for instance NaOH and 2-proponal can be used to produce cationic CEL as discussed in Section 3.3 (Harris et al., 2022). The selection of cross-linkers is dependent on the properties of biopolymers in the aqueous solution. CTN and ALG can use similar cross-linkers (e.g., glutaraldehyde (GTH), and epichlorohydrin (ECH)) for functionalization since both are readily soluble in water (Gonçalves et al., 2005; Verma et al., 2022).

4.2. Chemical grafting with a source of amine

PEI is a rich source of amine. It can be easily mixed with both CTN and ALG using GTH as a cross-linker to form aerogels (Wang et al., 2022a; Wang et al., 2021b). The content of PEI could play a vital role for PFAS sorption. A high dose of PEI may completely cover the biopolymer's surface (Liu et al., 2021b), leading to a decrease of porosity of the aerogels (Zhao et al., 2020). But at the same time, more electrostatic attractions will benefit sorption of anionic PFAS (Fig. 2). On the other side, the hydrophobic surface of the aerogels may have high sorption of relatively hydrophobic PFAS under a wide range of pH conditions.

A recent report by Ren et al. (Ren et al., 2023) on PEI and glycidyl trimethylammonium chloride (GTMAC) modified pine bark (lignin) (PG-PB) showed good removal efficiency (94.8 %) of PFOA at 10 μg/L. Treatment of groundwater using 0.8 g/L of PG-PB at pH 7 after 24 h reduced the concentrations of six PFAS, i.e., PFOA from 1200 to 680 ng/L, PFOS from 120 to 15 ng/L, PFHxA from 1900 to 1800 ng/L, PFHxS from 9700 to 3900 ng/L, PFPeS from 1300 to 880 ng/L, PFBS from 1400 to 1100 ng/L. The amine from PEI and quaternary ammonium cation from GTMAC played a significant role for PFAS sorption via electrostatic interactions.

Our recent study (Ilango et al., 2023a) reported the synthesis of glutaraldehyde (GTH) cross-linked CTN and ALG-based, PEI-functionalized (GTH-ALGPEI and GTH-CTNPEI) aerogels for removing PFAS in water. These aerogels were able to remove a mixture of 12 PFAS in water at 10 μg/L each, with 100 % removal of eight long and relatively hydrophobic PFAS. Both aerogels had fast and superior sorption of relatively hydrophobic PFAS from pH 2 to 10. Even at extreme pH conditions, the aerogels retained their shape perfectly. Moreover, these aerogels had the highest adsorption capacity than most of the PFAS sorbents reported in the literature (Table 4). However, the effectiveness of these aerogels is limited to 70–90 % for short-chain PFAS and GenX due to their limited porosity and large particle size (Ching et al., 2023; Li et al., 2021).

Recently, different amine sources, such as tris(2-aminoethyl)amine (Yang et al., 2020), tetrafluoroterephthalonitrile (Ching et al., 2020; Wang et al., 2022b), were used to functionalize β-CD polymers (Table 5). Study by Wang et al. (Wang et al., 2022b) on tetrafluoroterephthalonitrile functionalized β-CD showed 100% removal for C4-C10 PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA) in nano pure water. Similarly, a report by Ching et al. (2020) on tetrafluoroterephthalonitrile functionalized β-CD showed 100 % removal for PFBS, PFOA and PFOS while the removal of non-ionic perfluorosulfonamides and zwitterionic PFAS was less than satisfactory.

A report by Yang et al. (2020) on tris(2-aminoethyl)amine functionalized β-CD (CDP-1) showed 100 % removal for hydrophobic and long chain PFAS (PFOA, PFNA, PFDA, PFHxS and PFOS) and >90 % removal for short chain PFBS and PFHpA. For GenX and PFBA, however, the removal was ~65 % and ~35 %, respectively.

In addition to electrostatic interactions by amine, the unique cavity of β-CD has shown a stable inclusion of linear perfluoroalkyl chains (C4-C10 PFCAs) through a good size-fit within the cavity (Wang et al., 2022b). All amine functionalized β-CD removed PFAS at 1 μg/L which is environmentally relevant. To improve the sorption performance of CTN, ALG and CEL towards short chain PFAS under environmentally realistic conditions, these amines could be evaluated.

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5. Regeneration of bio-based sorbents

The fate of the eventually spent biosorbents needs to be considered. Thermal regeneration (350–900 °C) under inert atmospheric (N_2) condition is commonly used for spent activated carbons and ceramic oxides (Márquez et al., 2022; Peng et al., 2006). Thermal regeneration is not applicable for biosorbents since the biopolymers lose their structural stability at temperatures over 200 °C (Zhao et al., 2018). Instead, solvent

extraction is more appropriate for regeneration of biosorbents. To date, only limited studies are available on the effective regeneration of PFAS-laden biosorbents (Table 6). PFAS recovery from the biosorbents mainly depends on the surface characteristics, such as functional groups, porosity, etc. in addition to the composition of the charged and hydrophobic segments (Ateia et al., 2019a).

From the literature, PFAS anionic head could be desorbed using a solution of Na salts, such as NaCl, whereas a solution of organic solvent (i.e., methanol, ethanol, and acetone) is required to desorb the hydrophobic C-F chain (Liu et al., 2015). For example, Yu et al. (2008) achieved 100 % PFOS recovery from the CTN-based molecularly imprinted polymer (MIP) using 0.5 M NaOH/10 % acetone mixture. The higher removal rate of ~100 % for PFOS was achieved up to five consecutive sorption-regeneration cycles. The adsorbed PFOS can be desorbed easily from the MIPs' surface using the alkaline mixture in which the amino groups in CTN were deprotonated and the electrostatic attraction disappeared.

From Table 6, PEI-f-CMC (Ateia et al., 2018) had the highest reusable capability, i.e., up to eight cycles for PFOA removal at pH 6.5 with environmentally relevant concentrations. Methanol at 100 % was used to elute PFOA from the PEI functionalized CMCs' surface. Although a mixture of 22 PFAS was tested for batch sorption, it is questionable whether the PEI-f-CMC could be reused for all tested PFAS in complex environments given the fact that this sorbent was highly dependent on pH. Removal of PFOA was 85 % and 19.5% at pH 4.4 and 9.5, respectively. Ateia et al. (2019b) achieved 100 % recovery of GenX, PFBA, and PFOA up to six cycles from poly (N-[3 (dimethylamino) propyl] acrylamide, methyl chloride) quaternary hydrogel using 1 % NaCl/methanol (30/70, v/v). Even with lake water samples, the performance of the sorbent was not affected during the six sorption-regeneration cycles.

PEI and quaternary amine functionalized pine bark (PG-PB) could be reusable up to three cycles for PFOA sorption as reported by Ren et al. (2023). The desorption experiments examined the use of different ratios of NaCl, NaOH and methanol. A mixture of 0.05 % NaOH + 20 % methanol was found to be efficient for PFOA desorption from the spent PG-PB. More than 70 % and 85 % of PFOA was recovered from the first and second desorption cycles, respectively. The adsorbed PFOA with PEI via hydrophobic (Zaggia et al., 2016) and electrostatic interactions was recovered by methanol and NaOH respectively, while the quaternary N^+ group bound to PFOA tightly was difficult to desorb and led to decreased removal efficiency in the third cycle (< 80 %). The surface structure and functional groups might also be changed during the long contact time with NaOH due to the dissolution of hemicellulose and lignin (Kim et al., 2016) which could affect the adsorption capability of the regenerated PG-PB.

On the other hand, the regenerability of metal ions coated biosorbents is not promising. As reported by Elanchezhiyan et al. (Elanchezhiyan et al., 2021), although both PFOA and PFOS were recovered from rGO-ZF@CB beads within 2 h using 0.1 M ethanol, significant loss of sorption capacity was observed after each cycle. This is owing to less stability of the recycled rGO-ZF@CB beads and decreased amount of active free sites on the beads' surface for PFAS sorption.

Similarly, the magnetic (Fe_3O_4) carbonized *Calotropis gigantea* fiber (MC-CGF) (Niu et al., 2020) can be reused up to six cycles, but the sudden drop in removal% from 100 to 78 % after the first cycle for both PFOA and PFOS was significant. Zakaria et al. (Zakaria et al., 2023) also observed the drop in PFOS removal% of the regenerated ALG-β-CD/CNTs beads from 91.6 % in the first cycle to 87.6 % in the second cycle and 59.6 % in the fourth cycle. The regenerated beads were also less stable due to washing with 0.1 M HCl.

Cross-linkers assisted biosorbents with the exception of metal ions cross-linked ALG, can retain their structural stability and reasonable removal efficiency after regeneration. Recently, Verma et al. (2022) achieved 100 % recovery of short chain PFBS from GTH cross-linked CTN/β-CD using methanol. The removal efficiency of the regenerated CTN/β-CD decreased slightly from 96.5 to 93.20 % after the first cycle of sorption-regeneration and remained stable in the next three consecutive cycles. Similarly, decafluorobiphenyl (DFB) cross-linked β-CD (Xiao et al., 2017) can be reused up to four cycles for PFOA removal where the amounts of adsorbed and recovered PFOA were very similar (0.5 mg/g) over all four cycles.

Regarding amine functionalized biosorbents, it is unclear whether they can be regenerated and reused. Theoretically speaking, biopolymers containing primary, secondary and tertiary amines are easier to be regenerated because they are readily deprotonated compared to the commercial ion-exchange resins that mostly contain the quaternary N^+ (Maimaiti et al., 2018). The highly hydrophobic bio-based aerogels and cationic N^+ functionalized biopolymers may face difficulties in reuse due to strong binding with PFAS (Harris et al., 2022).

6. Challenges and future perspectives

Biosorbents, mainly sourced from renewable materials possess unique features as being green, renewable, and sustainable. Given the challenges tied to removing different structures of PFAS from water, biosorbents need to be further investigated considering at least these five aspects.

First, further surface modifications of the biopolymers are needed to increase biosorbents' capability in capturing short-chain PFAS, cationic and zwitterionic PFAS. At present, most of the efforts in the field of removing PFAS through adsorption have focused on a few anionic PFAS. This focus considers the fact that several anionic PFAS, such as PFOA, PFOS, PFNA, PFHxS, PFBS, and GenX have been regulated by a few states in the US and may be regulated by the U.S. EPA if the proposed maximum contamination levels (MCLs) are implemented. This attention is rightly oriented given the urgent need of materials and technologies to meet regulatory requirements. However, in light of the fact that these anionic PFAS are oftentimes degradation products of PFAS precursors, more efforts should have been paid to other non-anionic PFAS. Doing so serves the purpose of source control. Otherwise, removal of PFAS will be a forever burden. In addition to the surface modifications listed above, nano, or micro sized clays, COFs, and carbon-based nanostructures could be used to modify the surface for stronger binding with target PFAS.

Second, the physical and chemical stability of the biosorbents in aqueous solution need to be improved to enable their repeated use in concentrating PFAS in water. This can be achieved by grafting biopolymers with appropriate copolymers or cross-linkers as well as developing new and revised synthesis procedures.

Third, it is important to improve the regenerability and reusability of biosorbents. Currently, there is no effective approach to regenerate and reuse them. The choice of a regenerant depends on the surface properties of the sorbents and the desorption mechanism. To remove PFAS molecules from the biosorbent surface, a simple organic solvent rinse can be used, such as with methanol containing NH_4OH, ethanol, or acetone. This process breaks the electrostatic and hydrophobic interactions between the PFAS molecules and the biosorbent surface. To investigate the desorption mechanisms from a molecular interaction perspective, it is necessary to use different tools such as X-ray photoelectron spectroscopy (XPS) analysis and density functional theory (DFT) modeling to determine the sorption location and binding energy of the PFAS with the sorbents' surface.

Fourth, even after repeated use, the spent biosorbent will still need to be disposed of properly at its end of life. Even if the spent sorbent is PFAS-free, its environmental fate still needs to be considered given the fact that most biosorbents are modified by different non-biomolecules.

Fifth, use of biosorbents in practical applications needs to be studied. Currently, the majority of biosorbents are investigated in batch mode. Batch mode suspension test is useful for yielding insights in terms of a sorbent's sorption kinetics and capacity. Results from this mode, however, may not correlate well with those obtained from flow-through column studies. To use biosorbents to replace GAC that has been

widely adopted for PFAS removal, biosorbents, in the form of granules or pellets, must be assessed in columns simulating those with GAC. Until better performance of biosorbents than GAC in flow-through systems is demonstrated, the use of biosorbents has to be limited to suspension systems. While suspension systems still have value in PFAS removal, separating biosorbents from water cost effectively will need to be addressed.

Supplementary information

Physiochemical properties of typical PFAS, cross-linker reaction of ALG and functionalization of modified CEL.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120927.

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