

Rapid Removal of Perfluoroalkyl Substances from Water by Quaternized Amine-Functionalized Nanocellulose/Deacetylated Chitin Composite Aerogel

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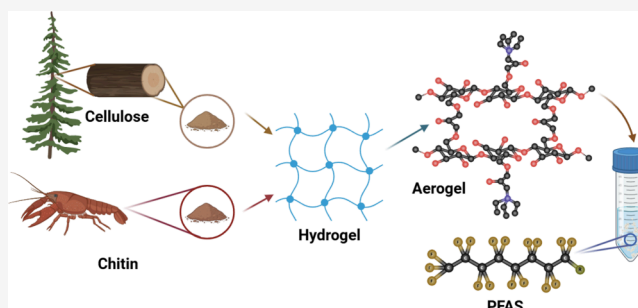
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ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants, and many chemical adsorbents have recently been utilized for their removal. In this study, we synthesized a quaternary amine-modified (QA-CNF/DAC) composite aerogel by simultaneous cross-linking and amination of two most abundant natural polymers: cellulose nanofiber (CNF) and deacetylated chitin (DAC). The characterization results confirmed successful modification of aerogel by yielding a high surface area and quaternized amine content of 64.5 m²/g and 0.598 mmol/g, respectively. The aerogel exhibited high adsorption capacities of 269.76 mg/g for perfluorooctanesulfonate at pH 6.78 and 83.20 mg/g for perfluorohexanoic acid at pH 4.1, with rapid equilibrium times of 0.5 and 3 min, respectively. Adsorption followed pseudo-second order kinetics and the Freundlich model, indicating multilayer exothermic interactions on a heterogeneous aerogel surface. The aerogel retained performance when tested over multiple cycles, showing high stability and reusability. These findings demonstrate that QA-CNF/DAC aerogel is sustainable and cost-effective material for efficient PFAS remediation.

KEYWORDS: nanocellulose, deacetylated chitin, perfluoroalkyl substances, aerogel, adsorption



1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are highly fluorinated compounds. They are considered emerging contaminants due to their widespread use in commercial and industrial products, resulting from their ability to repel both water and oil.¹ PFASs, such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are most prevalent in the environment. Due to their strong carbon–fluorine bonds, PFAS compounds exhibit extremely high thermal and chemical stability. They also have a hydrophobic fluorinated alkyl chain at one end and a hydrophilic functional group at the other end.^{2,3} This unique combination of chemical and thermal stability, along with hydrophilic–lipophilic moieties, resulted in PFAS being widely manufactured for large-scale industrial applications, including the production of paper, textiles, pesticides, leather, medical aids, oil, food packaging, cosmetics, paints, inks, nonstick cooking utensils, surfactants, firefighting foams, and various other waterproof products.⁴ Over the past few decades, PFAS have been widely detected in the environment, existing in almost all aquatic matrices, including drinking water, surface water, and groundwater. Consequently, they pose a threat to both the environment and human health.

In the United States, PFAS contamination has been detected at nearly 1,400 sites, including drinking water sources that serve up to 110 million Americans.⁵ According to a report by

the Center for Disease Control and Prevention, almost all people (>99%) had PFAS in their blood serum, with a detection frequency of 60% for five different PFAS compounds when tested.⁶ Once ingested, these substances can bioaccumulate in the human body and cause immunotoxicity, as well as several types of cancer, including liver, kidney, and testicular cancer.⁷ In 2024, the Environmental Protection Agency (EPA) updated regulations for six PFAS substances. The maximum contamination level for long-chain PFAS, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), is set at 4 ppt. At the same time, for GenX, a short-chain alternative molecule for PFOS, it is established at 10 ppt.^{8,9} Many states in the US have enacted regulations that are lower than the federal values for various PFAS molecules, referred to as Lower Health Advisory.^{9,10} In response to environmental and human health concerns, a campaign was initiated to phase out long-chain PFAS (>C6) in favor of short-chain PFAS (C4–C6). Later, short-chain PFAS were

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recognized as being more mobile, less hydrophobic, and more hydrophilic, with a lower adsorption potential.¹¹

In recent years, various studies have suggested several methods for treating PFAS-contaminated water, including physical, chemical, and biological treatment methods.¹² Commonly used treatment methods, such as biological processes, oxidation, and disinfection using chlorine or UV irradiation, are often ineffective for removing PFAS.¹³ Due to their simplicity and effectiveness, membrane-based in-flow purification techniques are widely used nowadays.¹⁴ However, the requirement for high operating pressures (10–80 bar) and membrane fouling remain issues associated with this technique.¹⁵ Ion exchange resins and reverse osmosis have been demonstrated to be effective methods for removing PFAS to a minimal level. However, these methods are more costly and not energy-efficient.^{16,17} Several technologies are currently available for removing PFASs from water; however, adsorption remains the most established and cost-effective process.⁴ Adsorbents such as granular carbon (GC), activated carbon (AC), covalent organic frameworks (COFs), metal-organic frameworks (MOFs), and clay minerals have demonstrated their effectiveness in PFAS removal due to their high surface area and porosity. However, they have significant deficiencies, including slow adsorption kinetics, low affinity for short-chain PFAS, and reduced efficiency in removing PFAS in the presence of natural organic matter, which competes for adsorption sites.¹⁸ The challenges outlined above emphasized the urgent need to develop more efficient adsorption materials for removing PFAS that do not perpetuate environmental persistence and are therefore sustainable and biodegradable.

Biopolymers, such as cellulose, chitin, chitosan, and alginate, possess large quantities of surface functional groups that can be modified through chemical or physical cross-linking to enhance surface charge, facilitating the adsorption of anionic PFAS molecules.¹⁹ Cellulose stands out as the most promising biopolymer due to its natural abundance, low cost, and biodegradability.²⁰ Chitin, the third most abundant natural polymer on Earth, is hydrophobic and can be converted to chitosan through the deacetylation of its acetyl groups. Chitosan is a strong cationic polymer because it contains amino pendant groups. This cationic property enables the synthesis of various derivatives with different degrees of deacetylation, thereby facilitating the creation of a diverse range of modified adsorbents.²¹ Materials containing amine functional groups have shown superior and rapid removal of the anionic short-chain and branched PFAS structures.²² Both natural and synthetic aminated materials exhibited superior adsorption capacity and kinetics. However, the sustainable approach of generating adsorbents from renewable resources, specifically ones that can be regenerated and then biodegraded at the end of their usable lifetimes, is favorable.²³

Cellulosic nanomaterials (CN) have been successfully tested for removing various types of water contaminants, including PFAS. For example, poly(ethylenimine)-functionalized cellulose microcrystals (PEI-f-CMC) showed good selectivity and adsorption capacity toward 22 different PFAS at environmentally relevant concentrations.²⁴ In another study, cellulose fibers functionalized with cationic amines (quaternized wood pulp) removed more than 80% of the most prevalent PFOS and PFOA within seconds at environmentally relevant concentrations.²⁰ Quaternized cellulose and cotton-based adsorbents were successfully utilized to remove both short- and long-chain PFAS efficiently.^{3,25} A quaternized cellulose-

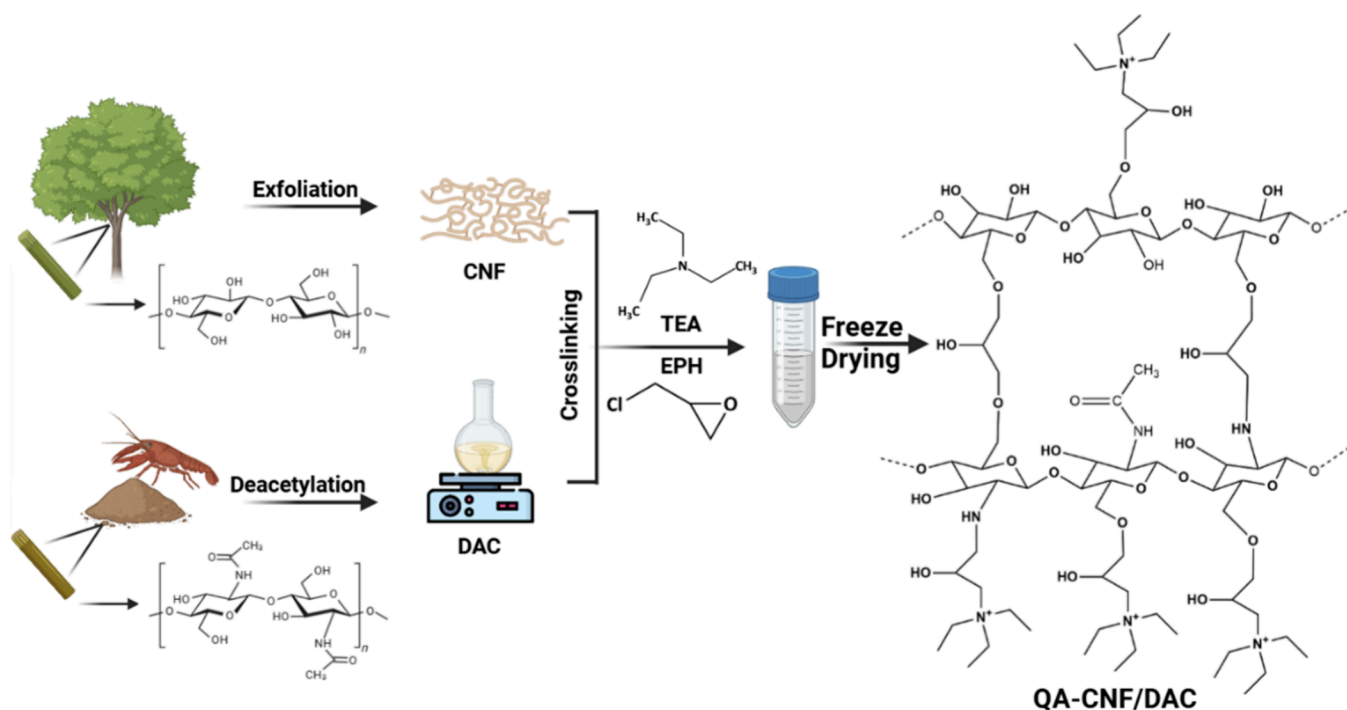
functionalized polymer resin (QC-CMPS) demonstrated exceptional selective capability for PFAS removal in real environmental water matrices, achieving over 99% removal efficiency at an initial concentration of 1000 ppt.²⁶ In another study, chitosan-based ethylene glycol hydrogels achieved higher adsorption capacities; however, these materials required longer equilibrium times (up to 24 h) and were primarily tested at relatively high PFAS concentrations, thereby limiting their practical utility.²⁷

In our previous study, we developed a novel and straightforward method for the self-assembly of cellulose nanofibers (CNF) and partly deacetylated chitin nanofibers for the preparation of highly effective and versatile biohybrid aerogel for water purification.²⁸ The prepared aerogel exhibited different charge behaviors at various pH levels due to the presence of quaternized amine cation ($-NR_3^+$) on the surface. As the adsorption mechanism of PFAS removal depends mainly on the electrostatic interactions with the charged groups on the sorbent surface, we believe that a highly positively charged (cationic) aerogel would efficiently adsorb both short, branched, and long-chain PFAS via the electrostatic interaction. Therefore, this study focused on synthesizing a novel, green, sustainable, and cost-effective quaternized amine-nanocellulose/deacetylated chitin (QA-CNF/DAC) composite aerogel. This dual biopolymer network was specifically designed to enhance the efficacy of CNF in removing both long- and short-chain PFAS across a range of concentrations under environmentally relevant conditions. Our primary objective was to achieve CNF/DAC surface functionalization through quaternized amination with triethylamine, aiming to increase the surface positive charge and enhance the electrostatic interaction between anionic PFAS molecules and cationic aerogel, thereby addressing critical gaps in previously reported findings.

2. EXPERIMENTAL SECTION

Materials. The practical grade powder of chitin from shrimp shells (poly(1→4)- β -N-acetyl-D-glucosamine), hydrochloric acid (HCl, 37%), Heptadecafluorooctanesulfonic acid potassium salt (98%, molecular formula $C_8F_{17}KO_3S$, MW = 538.22 g/mol), and ammonium acetate (98%, MW = 77.08) were all purchased from Sigma-Aldrich. Mechanical grade cellulose nanofiber (CNF, 3% aqueous slurry) was obtained from the Process Development Center at the University of Maine. Sodium hydroxide pellets (NaOH, 99%), sodium chloride (NaCl) reagent grade, silver nitrate ($AgNO_3$, 99.9%), and triethylamine (TEA, 99%) were purchased from Thermo Fischer Chemicals. Epichlorohydrin (EPH, 99%, MW = 92.52 g/mol, empirical formula C_3H_5ClO) was obtained from Acros Organics. Undecafluorohexanoic acid, high grade (>98%, molecular formula $C_6HF_{11}O_2$, MW = 214.05, S.G = 1.76), was obtained from TCI. HPLC-grade water (ACS reagent grade) was purchased from Ricca Chemical Company USA, while methanol, ultrapure (>99.8%), HPLC-grade, was obtained from Alfa Aesar for LC/MS analysis of PFAS samples. ISA, 5 M sodium nitrate ($NaNO_3$), and a 1000 ppm silver standard were purchased from Cole-Palmer. A silver sulfide electrode was obtained from Environmental Express for quaternized amine content analysis. All experiments were conducted using polypropylene labware, including beakers, volumetric flasks, and measuring flasks, which were purchased from Corning. Additionally, 50 mL centrifuge vials and pipette tips were procured from Fisher Scientific, and 1.5 mL sample

Scheme 1. Synthetic Pathway of Quaternized Amine-Cellulose Nanofiber/Deacetylated Chitin (QA-CNF/DAC) Composite Aerogel



vials were obtained from Eppendorf. For filtration, 13 mm diameter syringe filters with 0.22 μm PTFE hydrophobic outer ring were purchased from Labfill, while 5 mL/cc disposable syringes were obtained from BH Supplies.

Synthesis of the Quaternized Amine-Functionalized QA-CNF/DAC Aerogel. The QA-CNF/DAC aerogel was prepared by chemically cross-linking partially deacetylated chitin and regenerating cellulose nanofibers in the following steps.

Preparation of Deacetylated Chitin. Four g of chitin (shrimp shell) was dispersed in 100 mL of 33% NaOH solution and heated at 90 $^{\circ}\text{C}$ for 3.5 h under constant stirring. The mixture was diluted to 300 mL with DI water and centrifuged for 20 min at room temperature, after which the precipitates were redispersed in DI water and centrifuged again. Deacetylated chitin precipitates were separated from the supernatant and washed with DI water under vacuum filtration until a neutral pH was achieved. The retentate was redispersed in 600 mL of DI water, and the pH was adjusted to 3 with 0.1 M HCl. It was blended for 20 min using a Vitamix mechanical blender and then cooled. The solution's pH was adjusted to a range of 7–8 using the required volume of NaOH (0.1 M). The solution was blended for 20 min and subsequently cooled using an ice bath. This blending and cooling process was repeated to achieve a finer-grained deacylated chitin. Then this solution was centrifuged and washed several times until it reached neutral pH.²⁸

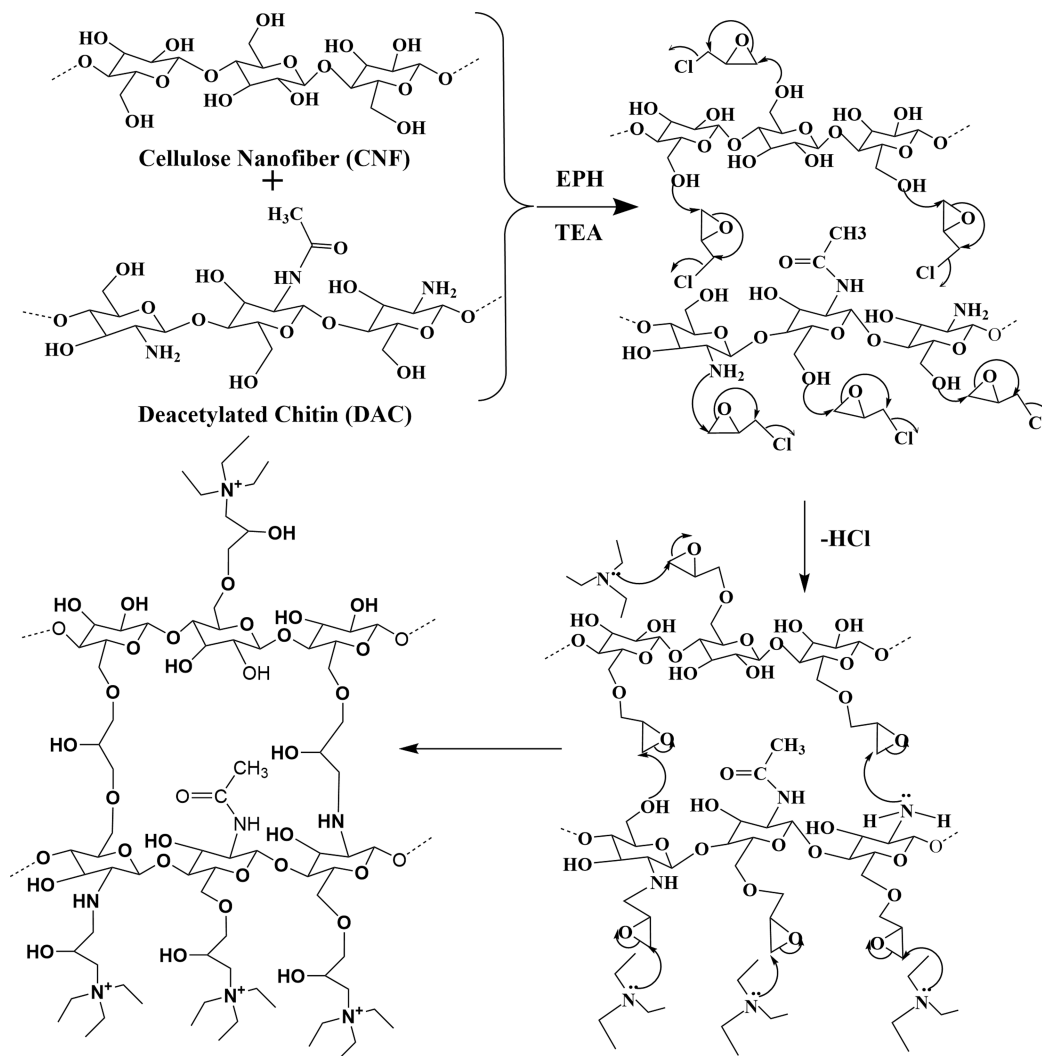
Regeneration of Cellulose Nanofibrils. A 10 g amount of NaOH was dissolved in 100 mL of a 3% aqueous slurry of cellulose nanofibrils in a beaker, and the mixture was dispersed using a mechanical stirrer. The mixture was then placed in a cooling bath at -5°C and continuously stirred until it became transparent. It was subsequently diluted, and the pH was adjusted to 7 using 0.1 M HCl, then blended with a Vitamix blender. The mixture was then filtered several times and

centrifuged at approximately 4150 rpm for 30 min to obtain a cellulose nanofibril gel.²⁹

Synthesis of QA-CNF/DAC Aerogel. The synthesis pathway of aminated-cellulose nanofiber/deacetylated chitin (Am-CNF/DAC) composite aerogel is shown in Scheme 1. In a 250 mL volumetric flask, 0.330 g of cellulose nanofibrils (CNF) and 0.165 g of deacetylated chitin (DAC) in a 2:1 ratio were dispersed in 50 mL of DI water. Fourteen mL of triethylamine (TEA) was added to the reaction mixture, followed by the dropwise addition of 7.8 mL of epichlorohydrin (EPH). The mixture was stirred and refluxed at 80 $^{\circ}\text{C}$ for 24 h continuously. Subsequently, the mixture underwent multiple washes with DI water until the pH reached 7, followed by filtration. The obtained hydrogel was freeze-dried for 48 h to yield the aerogel. A similar procedure was performed using different ratios of CNF and DAC (1:1 and 1:2) to synthesize the aerogel.

Proposed Mechanism for the Synthesis of QA-CNF/DAC Aerogel. The reaction between cellulose nanofiber (CNF) and deacetylated chitin (DAC), using triethylamine (TEA) and epichlorohydrin (EPH), is shown in Scheme 2. It involves a series of steps that lead to the quaternized amination and cross-linking of the two biopolymers. Initially, the hydroxyl group at C-6 of CNF and DAC, as well as the amine group at C-2 of DAC, react with the epoxide ring of EPH, forming an ether intermediate and releasing HCl. Meanwhile, the hydroxyl or amine group on the deacetylated chitin chain attacks the other end of the epoxide ring, resulting in cross-linking between OH-OH and OH-NH₂. TEA, which is a base and acts as a nucleophile, attacks the other terminal of the epoxide ring through nucleophilic substitution, leading to ring opening. This process introduces quaternized amine groups into cellulose and chitin. The free hydroxyl groups on CNF and DAC further react with epichlorohydrin through epoxide ring opening, resulting in extensive cross-linking.

Scheme 2. Synthesis Mechanism of QA-CNF/DAC Composite Aerogel



QA-CNF/DAC Aerogel Characterizations. The quaternized amine content on the surface of QA-CNF/DAC composite aerogel was determined by conducting conductometric titration using a silver/sulfide electrode and an Oakton PC2700 conductivity meter. A 5 mM solution of silver nitrate (AgNO_3) was loaded into the buret. In a 150 mL beaker, 100 mg of aerogel was dispersed in 100 mL of deionized water under constant stirring, followed by the addition of 2 mL of an ion strength adjuster (ISA), specifically 5 M NaNO_3 . 0.2 mL of AgNO_3 solution was added dropwise into the beaker at regular intervals. The Ag^+ ion concentration was monitored after each addition until no further change in concentration was observed. The total volume of AgNO_3 used was plotted against the concentration of silver ions. The total amine content was calculated using the following formula:

$$\text{Quaternized amine content (mmol/g)} = \frac{M \times V \times 1000}{m} \quad (1)$$

Where M is the molarity (mol/L), and V (mL) is the volume of AgNO_3 used, and m (g) is the amount of adsorbent used for analysis.

The point of zero charge (PZC) of the QA-CNF/DAC (2:1) aerogel was determined using the pH drift method.

Briefly, 15 mL of a 0.01 M NaCl solution was placed into 20 mL plastic vials. The initial pH of the solutions was adjusted from 2 to 12 with an interval of 2 using appropriate amounts of 0.1 M NaOH or 0.1 M HCl (initial pH). Subsequently, 10 mg of the aerogel was added to each vial, and the mixtures were shaken on a mechanical shaker (250 rpm) at room temperature for 24 h. After equilibration, the pH of the solutions was measured again (final pH). The initial and final pH values were plotted, and the PZC was determined from the graph.

An elemental analyzer (Exeter Analytical, Inc., CE-440) was used to analyze the hydrogen, carbon, and nitrogen content in the presence of helium (He). The combustion temperature was set at 900 °C, while the reduction temperature was set at 700 °C. The samples were prepared using tin capsules (6 mm × 2.9 mm) enclosed within a nickel sleeve (7 mm × 5 mm). The functional groups of the QA-CNF/DAC composite aerogel were investigated through Fourier-transform infrared (FTIR) spectroscopy. The analysis was performed in attenuated total reflectance (ATR) mode on a PerkinElmer Spectrum Two spectrometer, covering the 400–4000 cm^{-1} range, with an average of 10 scans at a 4 cm^{-1} resolution. A thermogravimetric analyzer (TA Instruments SDT Q600 series) was employed for thermogravimetric analysis. The

ramping temperature was set at 10 °C/min to 800 °C. Nitrogen gas was purged at a flow rate of 100 mL/min. The QA-CNF/DAC (2:1) composite aerogel surface morphology was determined by an FE-SEM (JEOL JSM-6500F, Tokyo, Japan). Aerogel samples were sputter-coated with 15 nm platinum by EMS150T ES sputter coater and imaged at a five keV accelerating voltage. The surface area and pore structure of the QA-CNF/DAC composite aerogels were evaluated using a QuantaChrome Autosorb iQ gas sorption analyzer (Model: ASIC0500-5, USA). The sample was loaded into a 6 mm sample cell and degassed at 70 °C for 5 h to remove any adsorbed contaminants. Nitrogen adsorption–desorption isotherms were then recorded at 77.35 K using liquid nitrogen. The data were analyzed using the ASiQwin 3.01 software to determine specific surface area, pore volume, and pore size distribution.

PFAS Analysis. A Finnigan LCQ Deca XP mass spectrometer coupled with a Surveyor MS Pump Plus and Autosampler was used to analyze PFOS and PFHxA. The physical properties and chemical structures of the analyzed PFAS are listed in Table S1. The LC/MS system was tuned using 1000 mg/L standard solutions of each contaminant, delivered with a 500 μ L Hamilton syringe. Chromatographic separation was achieved on a Nova-Pak C18 analytical column (3.9 $\times$ 150 mm, 4 μ m, 60 Å) with a corresponding guard column maintained at 50 °C. A binary solvent system comprising 5 mM ammonium acetate in water (A) and 5 mM ammonium acetate in methanol (B) was employed at a flow rate of 200 μ L/min (Table S2). The gradient began with 80% A and 20% B, transitioning to 5% A and 95% B within 3 min and was maintained until the end of each run (12 min for PFOS, 10 min for PFHxA) as shown in Figures S1 (d) and S2 (d), respectively. Mass spectrometric detection was performed in negative electrospray ionization (ESI) mode using selected reaction monitoring (SRM). For PFOS, the parent ion was m/z 499.00 with a collision energy of 3.0, while for PFHxA, the parent ion was m/z 313.00 with 0.0 collision energy. Both analytes used an isolation width of 1.0 and 3.0 m/z , respectively, an activation Q of 0.250, and an activation time of 30 ms. The retention times for PFOS and PFHxA were 9.25 and 8.5 min, respectively (Table S3). External standards at concentrations of 50, 200, 400, 600, 800, and 1000 ppb were used to calibrate PFOS and PFHxA. Based on these concentrations, calibration curves were plotted using their respective LC/MS analysis protocols. The coefficient of determination (R^2) values were found to be 0.996 for PFOS and 0.998 for PFHxA as shown in Figures S1, S2 (a–c), demonstrating the method's excellent linearity and sensitivity.

PFAS Adsorption Experiments. Preliminary adsorption studies were conducted to determine the optimal (QA-CNF/DAC) composite aerogel ratios (1:1, 1:2, and 2:1) for adsorption. Five mg of each adsorbent aerogel was added to 10 mL of solutions containing either 50 mg/L PFOS or 21 mg/L PFHxA, and the samples were shaken for 2 h. After the adsorption period, the solutions were filtered and analyzed using LC/MS. The removal efficiency of QA-CNF/DAC aerogel was calculated using the following equation:

$$\% \text{removal} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (2)$$

Where C_0 (mg/L) is the initial concentration, C_e (mg/L) is the concentration of PFOS and PFHxA at equilibrium.

Effect of the pH. The influence of pH on the adsorption capability of the QA-CNF/DAC (2:1) aerogel was evaluated by adding 5 mg of adsorbent to 10 mL of 50 mg/L PFOS or PFHxA solutions at room temperature. All the experiments were conducted in 15 mL polypropylene linerless cap bottles. Before adding the adsorbent, the pH levels of each PFOS or PFHxA solution were adjusted to 2, 4, 6, 8, 10, and 12 by using suitable amounts of 0.1 M HCl or 0.1 M NaOH. The samples were placed on a shaker and continuously agitated with a mechanical shaker at 250 rpm for 1 h for PFOS and 2 h for PFHxA. Afterward, the adsorbed mixtures were filtered using a 0.22 μ m syringe filter. All adsorption experiments were performed with three replicates, and all samples were analyzed before and after adsorption using the LCQ Deca XP LC/MS system.

Adsorption Kinetics. Adsorption kinetic studies were conducted to investigate the effect of contact time on the removal of PFOS and PFHxA by QA-CNF/DAC. Adsorption experiments were conducted under the conditions described in the previous sections. Adsorption studies for PFOS were performed at initial concentrations of 10, 30, and 50 mg/L for up to 15 min. In contrast, PFHxA experiments were conducted at concentrations of 1, 10, and 30 mg/L for up to 120 min under constant shaking (250 rpm). The solutions were filtered through a syringe filter at each specified time interval, and the filtrates were analyzed using LC/MS. The adsorption capacity of QA-CNF/DAC aerogel was determined using the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (3)$$

where C_0 (mg/L) and C_t (mg/L) are the PFOS and PFHxA concentrations (mg/g) before and after adsorption, respectively, V (L) is the adsorbate solution volume, and m (g) is the dry mass of QA-CNF/DAC. Pseudo-first order and pseudo-second order adsorption kinetic models were fitted to the adsorption kinetics data by using eqs 4 and 5.^{30,31}

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \quad (5)$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, q_t (mg/g) is the adsorption capacity at time t , k_1 (min^{-1}) is the pseudo-first order rate constant, and k_2 (g/mg.min) is the pseudo-second order rate constant.

Adsorption Isotherm. Adsorption isotherm experiments were carried out by adding 5 mg of QA-CNF/DAC aerogel to 10 mL of contaminant solution (PFOS or PFHxA) in separate vials. Before aerogel addition, all contaminant solutions were pre-equilibrated at the desired temperatures (15, 30, and 45 °C) using a water bath. After addition, all the vials were placed in an oil bath at the desired temperature under constant shaking (250 rpm). All the experiments were conducted at pH 7.5 for PFOS and pH 4.1 for PFHxA, with a fixed contact time of 15 min. The initial PFOS concentrations were varied from 20 to 300 mg/L (20, 40, 60, 80, 100, 150, 200, 250, and 300 mg/L), while PFHxA concentrations ranged from 10 to 250 mg/L. After adsorption, the solution was filtered and analyzed using LC/MS analysis. The equilibrium adsorption data were fitted to both the Langmuir and the Freundlich isotherm

models to evaluate the adsorption mechanism by using the following equations:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (6)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

where C_e (mg/L) is the adsorbate solution concentration at equilibrium, q_e (mg/g) is the equilibrium adsorption capacity, q_m (mg/g) is the maximum adsorption capacity, b is the Langmuir adsorption constant related to adsorption energy, K_f (mg/g)·(L/mg)^{1/n} and n are the Freundlich adsorption constants which indicate the capacity and intensity of the adsorption, respectively.²⁹

Adsorption Thermodynamics. Adsorption thermodynamic studies were conducted at three different temperatures, 15, 30, and 45 °C, for a 150 mg/L and 60 mg/L solution of PFOS and PFHxA, respectively, to evaluate the effect of temperature on the internal energy of the adsorbates. The obtained values were analyzed using Van't Hoff equations:

$$\Delta G = -RT \ln K_e^\circ \quad (8)$$

$$\ln K_e^\circ = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

$$K_e^\circ = \frac{(1000 \cdot K_{\text{isotherm}} \cdot \text{molecular weight of adsorbate}) \cdot [\text{Adsorbate}]^\circ}{\gamma} \quad (10)$$

Where R is the gas constant (8.314 J K⁻¹), ΔH is the change in enthalpy (kJ mol⁻¹), ΔG is the standard free energy change (kJ mol⁻¹), and ΔS is the change in entropy (J mol⁻¹ K⁻¹), and K_e° is the distribution coefficient. In eq 10, γ denotes coefficient of activity, K_{isotherm} represents K of isotherm model fitted, and $[\text{Adsorbate}]^\circ$ is unitary standard concentration of the adsorbate (1 mol/L).³²

Reusability Study. The reusability of the QA-CNF/DAC aerogel for removing PFOS and PFHxA was assessed through multiple adsorption–desorption cycles. Initially, 50 mL of an 80 mg/L PFOS solution and a 50 mg/L PFHxA solution were used, with 25 mg of aerogel for adsorption. Each cycle was conducted with a contact time of 60 min. 0.5 M NaCl in a 45/55% methanol/water solution was used for regeneration. After each cycle, the adsorbent was collected using a Fischer Scientific Accuspin 3R centrifuge, followed by two times washing with regeneration solution and three to four times with deionized water. All samples, before and after adsorption and following regeneration, were analyzed using LC/MS. Desorption percentage was calculated using the following equation:

$$\% \text{Desorption} = \left(\frac{q_{\text{desor}}}{q_{\text{sorb}}} \right) \times 100 \quad (11)$$

Where q_{desor} (mg/g) is the desorption capacity of the adsorbent material, and q_{sorb} is the adsorption capacity of the adsorbent material after desorption of PFAS.

RESULTS AND DISCUSSION

Optimization of QA-CNF/DAC Aerogel Synthesis. The total amine content of the QA-CNF/DAC aerogel is a key

factor influencing its effectiveness for adsorbing PFAS. The total amine content on the surface of QA-CNF/DAC composite aerogels was measured by conductometric titration as shown in Table 1 and Figure 1a. The results show that the

Table 1. Surface Charge Densities of Am-CNF/DAC Aerogels

samples	AgNO ₃ volume (mL)	amine content (mmol/g)
DAC	5.60	0.280
QA-CNF/DAC (1:1)	10.2	0.510
QA-CNF/DAC (2:1)	11.96	0.598
QA-CNF/DAC (1:2)	15	0.750

highest amine content was observed with (1:2), measuring 0.750 mmol/g. This may be due to the presence of an amine group on the second carbon of the partially deacetylated chitin, in addition to the quaternized amine group. Next was (2:1) with 0.598 mmol/g, and then (1:1), which had the lowest quaternized amine functionalization at 0.510 mmol/g. These results were compared with a study by Kopac et al., who examined the trimethylammonium chloride (TMAC) content of CNF by varying the concentrations of TMAC and CNF. They reported that using 1 mol of TMAC with CNF yielded an amine content of 0.40 mmol/g.³³ So, these findings confirm that increasing the TEA concentration increases the amine content in the composite aerogels.

The point of zero charge (PZC) for the QA-CNF/DAC (2:1) composite aerogel was measured as shown in Figure 1b. At a pH of 5.1, there was no net charge, as the initial and final pH values were the same before and after adding the QA-CNF/DAC composite aerogel. It can be inferred that below this pH value, the surface of the adsorbent is likely to be protonated and positively charged, while above this pH value, the aerogel surface is expected to be negatively charged due to deprotonation. Therefore, it can be predicted that the adsorption of PFAS on the aerogel surface will be pH dependent.

The quaternized amination of CNF and DAC was confirmed using combustion elemental analysis, as presented in Table 2. The nitrogen content in QA-CNF/DAC aerogel variants with ratios of (1:1), (1:2), and (2:1) was 4.29%, 5.29%, and 3.54%, respectively. These values were higher than those of pristine CNF (0.41%) and quaternized CNF (0.57%), but lower than pristine DAC (7.94%) and quaternized DAC (5.00%), except in the (2:1) variant. The relatively higher nitrogen content in the (1:2) aerogel may be attributed to the greater proportion of DAC, which contains -NH₂ groups at the C-2 position of the glucosamine units. However, it can be inferred from the results that after quaternization with triethylamine, the final product had a significant increase in nitrogen content. The QA-CNF/DAC (2:1) variant exhibited the highest surface area (64.546 m²/g) among all aerogels and, consequently, was the focus of our adsorption studies.

FTIR analysis of QA-CNF/DAC was conducted to examine the cross-linking between QA-CNF and QA-DAC. As shown in Figure 2a, the peak appeared at 1439 cm⁻¹, which is more prominent in QA-CNF/DAC (2:1) spectra and represents the symmetric vibrations of the triethyl group of the quaternary ammonium.^{34,35} The peak at 1648 cm⁻¹ is attributed to the vibration of the quaternary C–N bonds,^{23,29} and it could be carbonyl functional groups of the acetyl group bonded to -NH- (amide I) present at the C-2 position on DAC.³⁶ The peak at

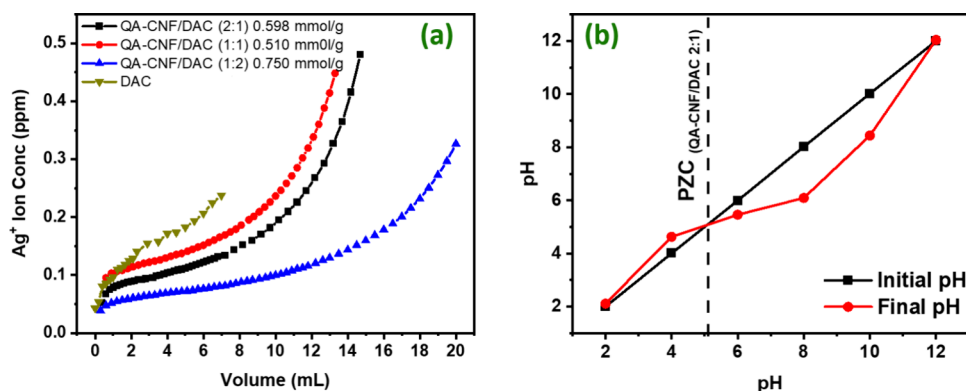


Figure 1. (a) Conductometric titration curves, (b) Point of Zero Charge of QA-CNF/DAC composite aerogel.

Table 2. Elemental Analysis and Surface Area of Synthesized Aerogels

sample	elemental analysis				surface area (m ² /g)
	%C	%H	%N	%R	
CNF	39.96	6.58	0.41	53.05	34.386
DAC	42.16	7.25	7.48	43.11	41.063
QA-CNF	42.55	6.59	0.57	50.29	37.747
QA-DAC	44.25	7.33	5.00	43.41	63.308
QA-CNF/DAC (1:1)	47.45	7.85	4.29	40.42	28.499
QA-CNF/DAC (1:2)	46.43	8.00	5.29	40.27	19.473
QA-CNF/DAC (2:1)	45.66	7.97	3.54	42.84	64.546
regenerated QA-CNF/DAC (2:1)	43.07	6.93	3.42	46.58	61.066

2884 cm⁻¹ confirms the symmetric stretching vibrations of C–H bonds of the ethyl group in the quaternary ammonium.^{37,38}

This peak appears broader and more pronounced in the composite aerogel due to the contribution from both CNF and DAC.¹⁹ The sharp and intense peaks at 1050 cm⁻¹ in all the samples are assigned to the pyranose ether bond.³ Therefore, these findings confirm the successful amination and cross-linking between QA-CNF and QA-DAC.

As shown in Figure 2b, in the TGA all aerogels experienced approximately a 10% rapid weight loss up to 100 °C, likely due to dehydration or moisture loss, whether physically adsorbed or bound water.²⁴ No significant weight loss was observed from 100 to 200 °C. However, TGA curves showed maximum weight loss of about 60%, 85%, and 80% around 250 °C, 350 °C, and 250–370 °C for QA-DAC, QA-CNF, and QA-CNF/DAC aerogels, respectively.³⁹ The maximum weight loss of composite aerogel was caused by the cleavage of attached QA groups at 250 °C and breakdown of ether and amine cross-linkages formed by EPH at 270–300 °C. The glycosidic bond

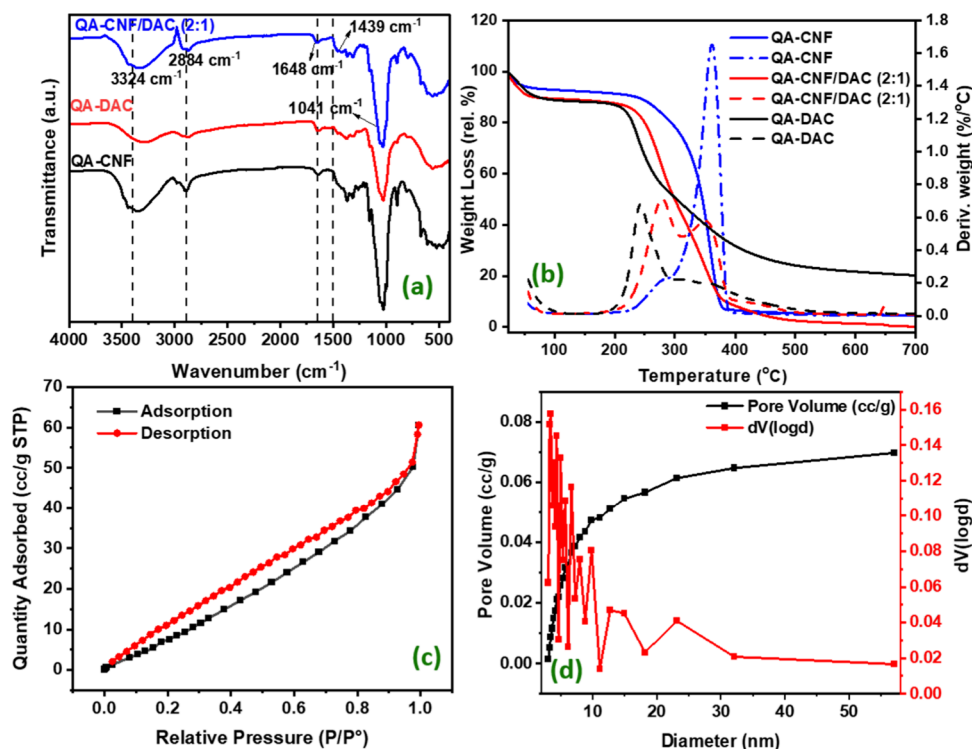


Figure 2. (a) FTIR spectrum, (b) TGA thermograph, (c) adsorption–desorption isotherm, and (d) BJH pore size distribution of QA-CNF/DAC composite aerogel.

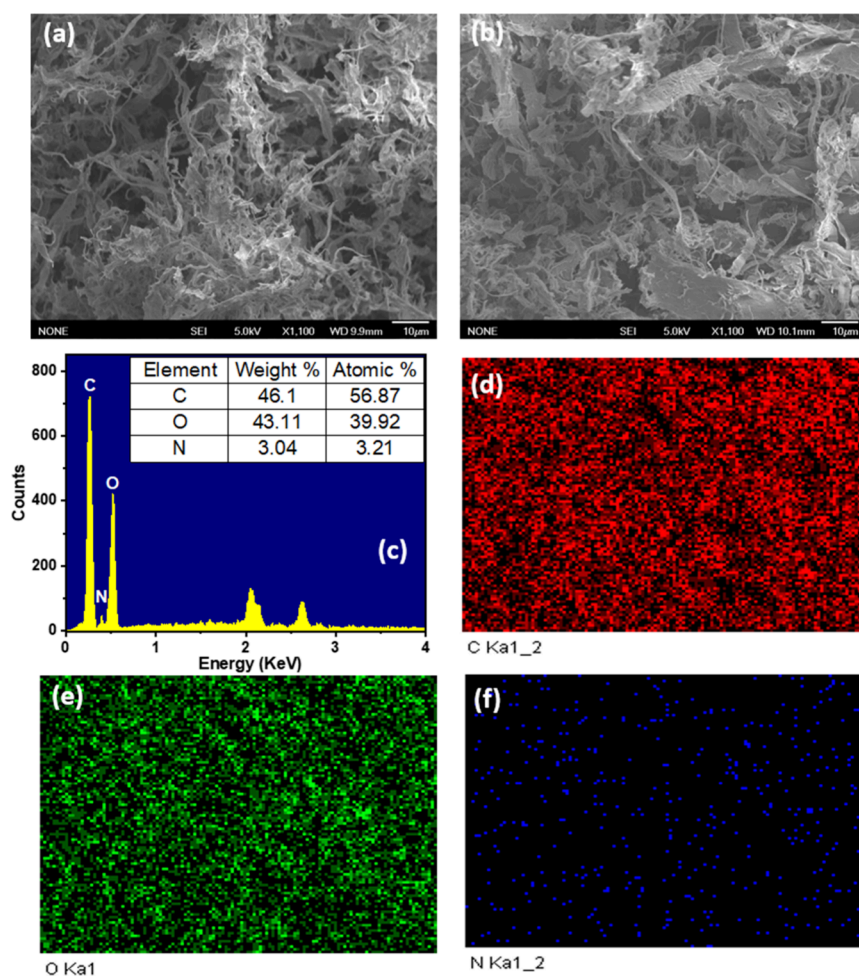


Figure 3. (a, b) Fe-SEM micrograph and (c–f) electron image and EDS of QA-CNF/DAC composite aerogel (2:1).

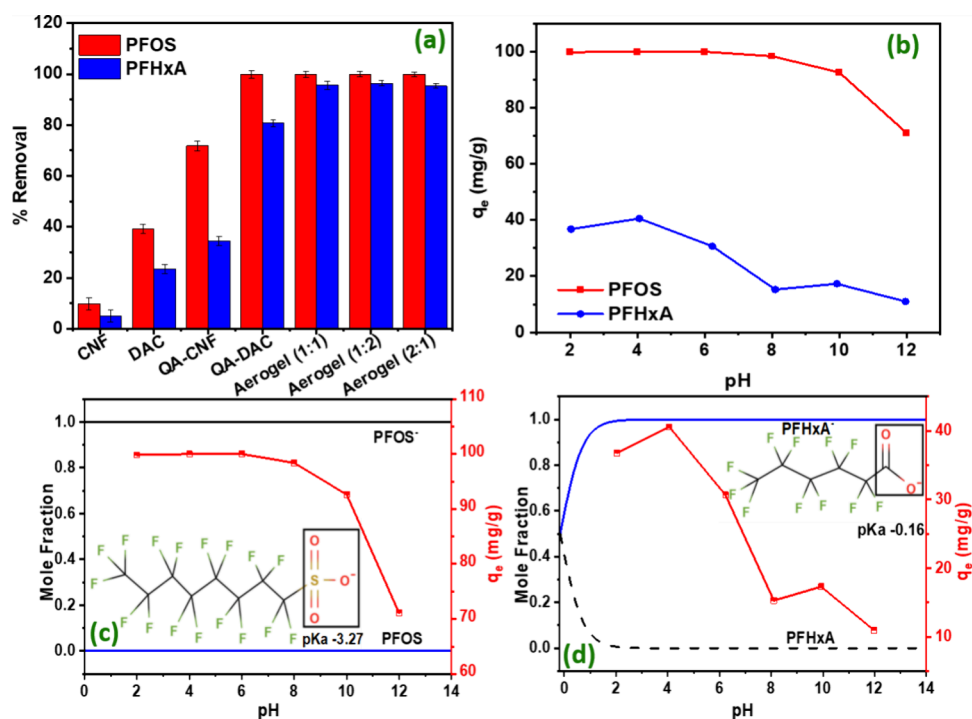


Figure 4. (a) Preliminary adsorption study for PFOS and PFHxA, (b) effect of pH on PFOS and PFHxA removal, (c) pH speciation curve for PFOS, and (d) pH speciation curve for PFHxA.

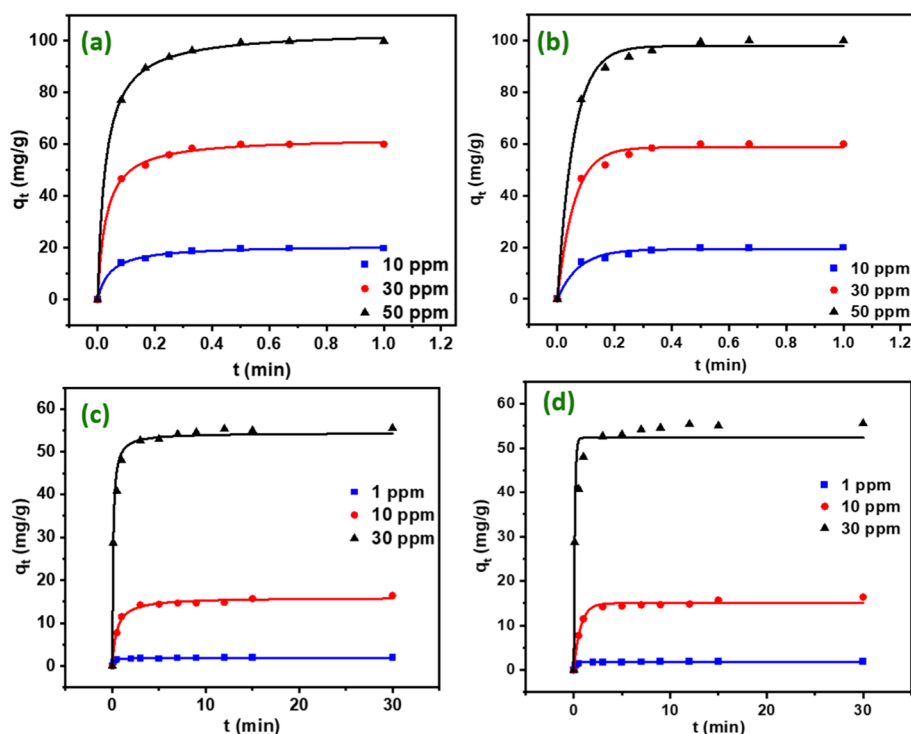


Figure 5. Adsorption kinetics curves of PFOS and PFHxA using QA-CNF/DAC at room temperature: (a) PFOS pseudo-first order nonlinear fit, (b) PFOS pseudo-second order nonlinear fit, (c) PFHxA pseudo-first order nonlinear fit, and (d) PFHxA pseudo-second order nonlinear fit.

between glucose and N-acetylglucosamine monomers decomposes at 350 and 270 °C, respectively.⁴⁰ The differential curves reveal a shift in the peak of decomposition for the DAC portion of the QA-CNF/DAC to higher temperatures. This may be the result of its intertwined and cross-linked nature. From 400 to 800 °C, no additional weight loss was observed for QA-DAC, QA-CNF, and QA-CNF/DAC aerogels, indicating complete conversion to char. These TGA results confirm the stability of the composite aerogel over a broad range of temperatures and the intermediate decomposition temperature of QA-CNF/DAC.

Figure 2c illustrates that the adsorption–desorption isotherm of the QA-CNF/DAC (2:1) composite aerogel displays a Type IV isotherm with an H3 hysteresis loop, which is characteristic of mesoporous materials having plate-like pores.⁴¹ As shown in Table 1, the QA-CNF/DAC (2:1) variant showed the highest surface area (64.546 m²/g) among all aerogels. These results are closely relevant to a study reported by Zhang et al. They synthesized a biohybrid aerogel (BHA) through the self-assembly of TEMPO-oxidized CNF and partially deacetylated chitin. However, the BHA aerogel showed a lower surface area (54 m²/g) compared to the QA-CNF/DAC aerogel developed in this study (64.54 m²/g), despite both aerogels having similar pore size distributions. The higher surface area of the QA-CNF/DAC aerogel is due to the extensive quaternization of the aerogel with triethylamine during cross-linking, which improved the overall porosity and structural integrity of the network.²⁸ Figure 2d presents the BJH pore size distribution, revealing a dominant pore diameter of 3.282 nm with several sharp peaks in the 3–20 nm range. This indicates a multimodal mesoporous structure with total pore volume of 0.081 cc/g.²⁹

The SEM images, as presented in Figure 3(a) and (b), illustrate the porous, fibrous morphology of the QA-CNF/

DAC composite aerogel, highlighting a well-developed three-dimensional interconnected network of CNF and DAC with long, hairy fibers in the form of grooves, characterized by a rough surface that facilitates surface accessibility and diffusion pathways.^{42,43} The EDX spectrum, as shown in Figure 3 (c–f), confirms the elemental composition of the composite, with prominent peaks corresponding to carbon (C), oxygen (O), and nitrogen (N). The presence of nitrogen, with an atomic percentage of 3.21%, confirms the presence of the -NR₃⁺ group on the aerogel surface. Elemental mapping images (e–f) show uniform distributions of C (56.87%) (red), O (39.925%) (green), and N (3.21%) (blue) throughout the aerogel surface, indicating homogeneous dispersion of the components and confirming effective integration of aminated CNF and DAC.

Adsorption Studies. A preliminary adsorption study was conducted to determine the maximum adsorption capacities of pristine CNF, DAC, QA-CNF, QA-DAC, and QA-CNF/DAC composite aerogels (1:1, 1:2, and 2:1) for PFOS and PFHxA adsorption. As shown in Figure 4a, all QA-CNF/DAC composite aerogels variants demonstrated excellent adsorption performance, removing over 99% of PFOS. Similar results were observed for PFHxA, with a maximum adsorption of about 96% across all instance variants. Pristine CNF and DAC exhibited PFOS removal efficiencies of 9.76% and 39.26%, respectively, while PFHxA removal was nearly half of the PFOS removal for both polymers. Based on these preliminary results and characterization data, the QA-CNF/DAC (2:1) variant was selected for all subsequent adsorption experiments. Its higher surface area and the potential to use more cellulose motivated this selection, as cellulose is the primary component of the composite. It is the most abundant natural polymer on Earth and is cost-effective compared to other natural polymers, such as chitin, alginate, and cyclodextrins. Therefore, we

Table 3. Adsorption Kinetic Parameters for PFOS and PFHxA Removal at 25°C

models	C_0 (mg/L)	PFOS			PFHxA		
		10	30	50	1	10	30
pseudo-first order	K_1 (1/min)	13.44343	17.19845	17.61079	3.90429	1.43499	8.72268
	q_e (mg/g)	19.22566	58.67797	97.82423	1.84141	15.0213	52.32566
	R^2	0.98145	0.99132	0.99553	0.96964	0.98484	0.9403
pseudo-second order	K_2 (g/mg/min)	1.09123	0.54149	0.34051	3.36791	0.13442	0.1961
	q_e (mg/g)	20.93179	62.58057	104.07365	1.90533	15.94826	54.41334
	R^2	0.99575	0.99853	0.99963	0.98671	0.99109	0.98523

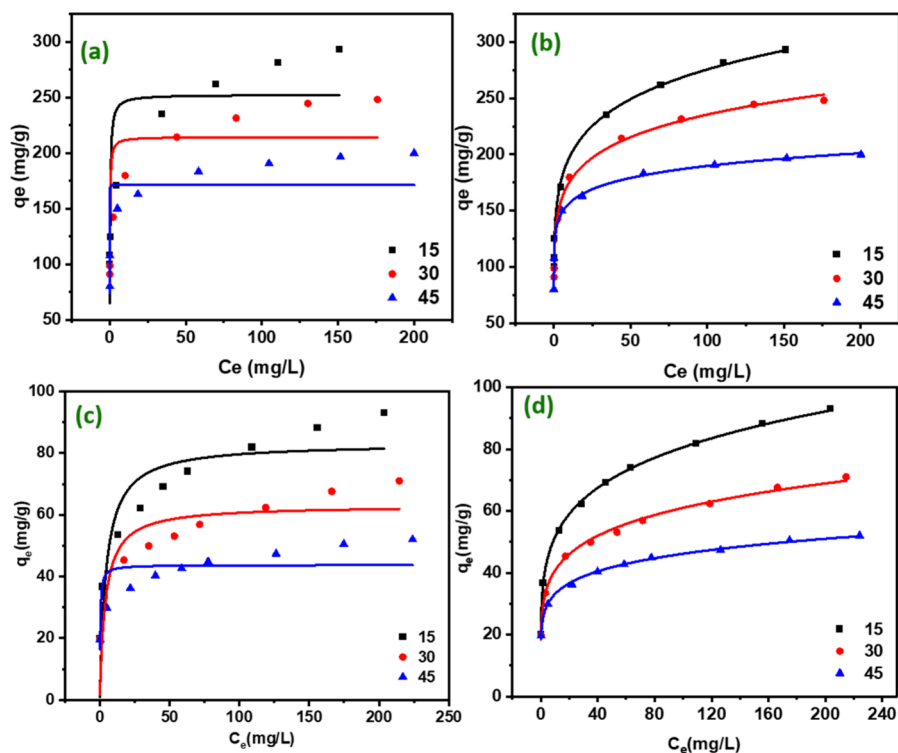


Figure 6. Adsorption kinetics curves of PFOS and PFHxA using QA-CNF/DAC at different temperatures: (a) PFOS Langmuir nonlinear fit, (b) PFOS Freundlich nonlinear fit, (c) PFHxA Langmuir nonlinear fit, and (d) PFHxA Freundlich nonlinear fit.

prioritized using a more sustainable and economically feasible material in our studies.

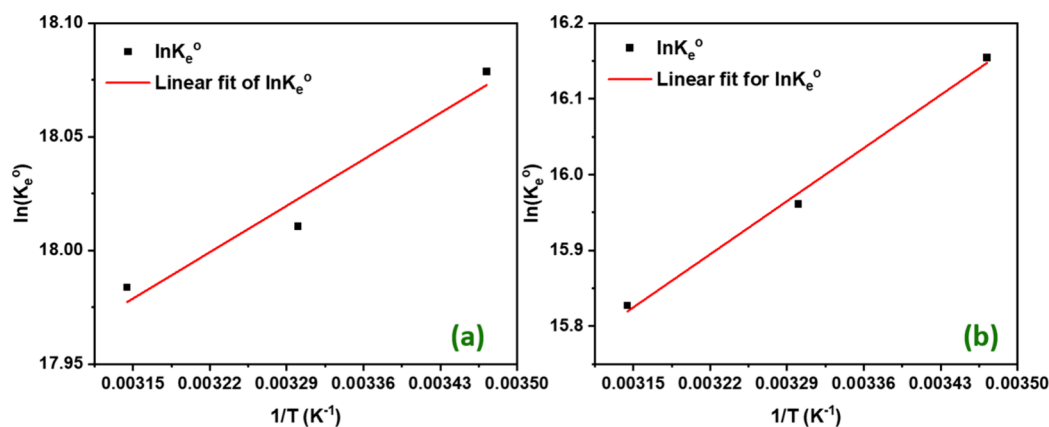
Figure 4b shows the pH-dependent adsorption behavior of QA-CNF/DAC aerogel for PFOS and PFHxA. PFOS shows a consistently high adsorption capacity (~ 100 mg/g) across pH 2–8, then declines at alkaline pH (8–12), while PFHxA exhibits moderate adsorption (~ 40 mg/g) at acidic pH (2–6), which gradually decreases above pH 4 in alkaline conditions. The pH speciation curve shown in Figure 4c indicates that PFOS mainly exists in an anionic form across most pH levels. This explains its strong adsorption performance under acidic to neutral conditions and a slight decrease at higher pH. The speciation of PFHxA (Figure 4d) indicates that it also exists in anionic form at all pH levels, with higher adsorption occurring around pH 4, just before the aerogel surface becomes positively charged. When pH reaches 6, adsorption drops because both the adsorbate and adsorbent carry negative charges, resulting in minimal interaction.

Adsorption Kinetics. The impact of contact time on PFOS and PFHxA adsorption was examined at various initial concentrations. As shown in Figure 5 (a, b), the adsorption of PFOS onto the QA-CNF/DAC composite aerogel was rapid, reaching equilibrium within 30 s. In contrast, the adsorption

process for PFHxA, shown in Figure 5 (c, d), was slower than that of PFOS, reaching equilibrium in 3 min. The results were best fitted with the Pseudo-second order (PSO-2) kinetic model for both PFAS molecules, exhibiting maximum correlation coefficient (R^2) values at all concentrations. For PFOS, the R^2 values were 0.99575, 0.99853, and 0.99963 at concentrations of 10, 30, and 50 mg/L, respectively (Table 3). The corresponding adsorption capacities (q_e) were 20.93, 62.58, and 104.07 mg/g, indicating a significant increase in adsorption capacity with increasing adsorbate concentration. PFHxA also exhibited excellent fit with PSO-2 kinetic model across all tested concentrations, with high R^2 values of 0.98671, 0.99109, and 0.98523 at 1, 10, and 30 mg/L, respectively. The adsorption capacities (q_e) were determined to be 1.91, 15.95, and 54.41 mg/g, respectively, and were consistently greater than the values predicted by the Pseudo-first order (PSO-1) kinetic model, as presented in Table 3. Despite the effective adsorption performance, the q_e values for PFHxA were nearly half of those recorded for PFOS. This difference is mainly due to the shorter C–F chain of PFHxA. Although this fluorocarbon chain length does not directly participate in chemical bonds, it affects the kinetics of chemisorption by changing molecular orientation, surface affinity, and interaction

Table 4. Langmuir and Freundlich Isotherm Model Values for PFOS and PFHxA Removal at Initial Concentration from 20 to 140 (mg/L) and Three Different Temperatures (15, 30, and 45 °C)

models	temp (°C)	PFOS			PFHxA		
		15	30	45	15	30	45
Langmuir	K_1 (L/mg)	3.98602	7.32582	269.75996	0.22336	0.25319	3.03174
	$q_{\max}$ (mg/g)	269.75996	214.42702	171.36017	83.19943	63.05883	43.76847
	R^2	0.797	0.7515	0.55697	0.78841	0.72627	0.62747
Freundlich	K_F ([mg g ⁻¹ (Lmg ⁻¹) ^{1/n}])	142.01986	132.67047	129.15697	33.01845	27.21359	23.80321
	N	6.88768	8.04414	11.97194	5.15933	5.70325	6.95462
	R^2	0.99054	0.99386	0.99859	0.9989	0.99622	0.99776

**Figure 7.** Linear diagram of the Van't Hoff equation to calculate the thermodynamic parameters: (a) PFOS and (b) PFHxA.**Table 5.** Thermodynamic Factors Estimated for the PFOS and PFHxA Adsorption at Various Temperatures

adsorbate	T (°C)	K_e^0	$\ln K_e^0$	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ .K ⁻¹)
PFOS	15	71028392.58	18.08	-43.29	-2.42	141.84
	30	66352482.16	18.01	-45.37		
	45	64595275.41	17.98	-47.55		
PFHxA	15	10369444.22	16.15	-38.68	-8.32	105.34
	30	8546427.94	15.96	-40.21		
	45	7475398.10	15.83	-41.84		

strength at the adsorbent interface, which leads to relatively weaker interactions with the adsorbent.^{44,45} The superior fit with the PSO-2 model indicates that chemisorption likely occurs through electrostatic interactions between the surface-active protonated amine (NR_3^+) groups of the functionalized aerogel and the negatively charged functionalities on PFAS molecules, specifically the sulfonate (SO_3^-) group in PFOS and the carboxylate (COO^-) group in PFHxA. These findings suggest that the chemical interaction between the adsorbate (PFAS) and the surface functionalities on the adsorbent (aerogel) determines the rate-limiting step.²⁹

Adsorption Isothermal Studies. The effect of temperature on the adsorption behavior of PFOS and PFHxA by the QA-CNF/DAC composite aerogel was investigated at 15, 30, and 45 °C. Adsorption isotherm models (Langmuir and Freundlich) were used to evaluate the adsorption results. The results for both PFAS molecules best fit the Freundlich model across all reported temperatures, as shown in Figure 6 (a-d). The maximum adsorption capacities were observed at 15 °C, with values of 269.76 mg/g for PFOS and 83.20 mg/g for PFHxA. At lower temperatures (15 °C), the K_f value was higher compared to that at higher temperatures, indicating that adsorption is more favorable at lower temperatures due to stronger interactions between the adsorbate and the

adsorbent.^{46–48} This typical adsorption behavior indicates that the process is mainly exothermic and favored at lower temperatures. More PFOS adsorption was observed compared to PFHxA adsorption because larger molecules are more likely to adsorb due to increased interaction opportunities. Sulfonate groups generally adsorb more from water than carboxylates due to their different charge distributions.⁴⁷ The R^2 values for the PFOS adsorption data fitted to the Freundlich isotherm were above 0.99 at 15, 30, and 45 °C, respectively, which were higher than those for the Langmuir isotherm ($R^2 = 0.55–0.79$), as mentioned in Table 4. Similarly, the R^2 values for PFHxA adsorption fitted to the Freundlich model were consistently 0.99 across all tested temperatures, while the Langmuir model yielded lower R^2 values ranging from 0.63 to 0.79. This type of adsorption supports the heterogeneous multilayer adsorption mechanism favored by physisorption.^{47,48} Additionally, all PFAS molecules exhibited Freundlich n values greater than 1, indicating nonparallel adsorption on the aerogel surface, which increases the potential of multilayer adsorption interactions.⁴⁶

Adsorption Thermodynamics. Adsorption thermodynamics were performed for PFOS and PFHxA at 15, 30, and 45 °C. Thermodynamics parameters, i.e., ΔG° , ΔH° , and ΔS° , were calculated using eqs 8, 9, and 10 from a linear plot of $1/T$

versus $\ln(K_{eq})$, as shown in Figure 7 (a, b). ΔG° for PFOS was -43.29 to -47.55 kJ mol^{-1} , while for PFHxA, the value of ΔG° was between -38.68 to -41.84 kJ mol^{-1} at 15, 30, and 45 $^\circ\text{C}$, indicating spontaneous adsorption, as all the values for Gibbs free energy were less than zero.^{49,50} The value for ΔH° was -2.42 and -8.32 kJ mol^{-1} for PFOS and PFHxA, respectively, as mentioned in Table 5. The negative ΔH° values observed for both PFAS molecules confirm that the adsorption process is exothermic. Moreover, the relatively low magnitude of ΔH° suggests that the interaction is mainly driven by physisorption rather than chemisorption.⁵¹ The value of entropy, ΔS° (141.84 and 105.34 $\text{J mol}^{-1}\text{K}^{-1}$) for PFOS and PFHxA, respectively, means there was significant interaction between PFAS and the adsorbate surface. As a result, the adsorbed PFAS molecules at solid–liquid interface increase the randomness of the system by the end of the process.

Adsorption Mechanism. The adsorption process of PFOS and PFHxA onto the QA-CNF/DAC composite aerogel was investigated using appropriate adsorption models. The adsorption mechanism was evaluated based on which models best fit the experimental data. This approach indicated that the initial stage, PFAS removal was mainly driven by chemisorption, facilitated by electrostatic interaction between the quaternized amine groups ($-\text{NR}_3^+$) on the aerogel's heterogeneous surface and the negatively charged functional groups sulfonate ($-\text{SO}_3^-$) in PFOS and carboxylate ($-\text{COO}^-$) in PFHxA. This was followed by physical multilayer adsorption through hydrophobic interactions between the fluorocarbon (C–F) chains of PFAS molecules and the hydrophobic regions of the cross-linked polymeric chains, specifically the C–H bonds in the glucose monomers of cellulose and the acetyl groups in the N-acetyl-D-glucosamine units of chitin. However, since PFHxA is a short-chain PFAS, literature suggests that it has lower hydrophobicity compared to long-chain PFAS, resulting in less adsorption for PFHxA.^{46,52} Thus, it can be concluded that the adsorption behavior observed in our study involved an interplay of chemical and physical sorption, supported by the heterogeneity of the aerogel surface. Overall, the hydrophobic–hydrophobic interaction was the dominant mechanism, well supported by electrostatic interactions as illustrated in Figure 8. Noncovalent hydrophobic interactions are the primary mechanism for PFAS removal.⁵³ The sp^3 hybridization of C–F bonds in PFAS molecules⁵⁴ which have three lone pairs on the fluorine atoms, increases steric and

electrostatic hindrance against nucleophile attack on the carbon–fluorine tail. This imparts a hydrophobic nature, especially in PFOS. The nonpolar and hydrophobic C–F bonds do not interact with water molecules and tend to adopt energetically unfavorable conformations orientations.^{53,55,56} To achieve stability, these bonds interact with hydrophobic regions of QA-CNF/DAC aerogel, which behave similarly in water, resulting in hydrophobic interactions.⁵⁷ The electrostatic interactions involving the electronegative F atoms are generally weak;^{58,59} therefore, they do not significantly contribute to such interactions. They generally occur between the functional acid head groups of PFOS and PFHxA (which are anionic) and charged cationic sites on the QA-CNF/DAC aerogel.⁶⁰

Literature Comparisons. Table 6 summarizes the adsorption behavior of various materials cited in the literature. The QA-CNF/DAC composite aerogel exhibited exceptional adsorption times of 30 s for PFOS and 3 min for PFHxA, which are significantly faster than the equilibrium times reported in the studies listed in Table 6.^{26,61,62} The prepared aerogel in this study gives maximum adsorption capacities of 255.97 and 83.20 mg/g under environmentally relevant conditions. As the adsorption reaction was spontaneous, this aerogel does not require any energy input to initiate the process. Various adsorbents, such as quaternized cellulose-based hydrogels, aerogels, MOFs, and COFs with surface modifications, were evaluated to compare the removal performance of QA-CNF/DAC aerogel. The adsorption capacities of the adsorbents listed in Table 6 varied widely; He et al. reported a very high adsorption capacity of 8307.1 mg/g for PFOS using COF-functionalized chitosan. However, they conducted adsorption studies at very high initial concentrations (1–1000 mg/L), which are not representative of environmental levels.⁶³ In a recent study, Ilango et al. developed a PEI-functionalized chitosan/glutaraldehyde aerogel (GTH-CTNPEI), which removed a mixture of 12 PFAS at environmentally relevant levels (10 $\mu\text{g/L}$ each) with maximum adsorption capacity approaching 12,133 mg/g . This performance was mainly due to hydrophobic interactions, strengthened by electrostatic attraction, although their contribution was minimal.¹³ In a subsequent study, they reported that the same aerogel was processed into ~ 9 mm flakes, enabling $>99\%$ removal of all PFAS, including short-chain compounds, i.e., GenX, within 10 h, while maintaining efficiency across four regeneration cycles. These findings emphasize that synergistic functionalization and morphology optimization can dramatically enhance both capacity and kinetics.⁶⁴ In contrast, our QA-CNF/DAC aerogel excels in ultrafast adsorption kinetics (seconds to minutes), under environmentally relevant conditions, which are considerably faster than those reported in previous studies, as mentioned in Table 6. The combination of rapid kinetics, sustainable raw materials (cellulose and chitin), and high efficiency at realistic PFAS concentrations underscores the practical value of the present work.

Reusability Study. The adsorption efficiency of QA-CNF/DAC was tested over four consecutive adsorption–desorption cycles for PFOS and PFHxA, as shown in Figure 9. In the first cycle, PFOS shows a nearly 100% adsorption rate, while PFHxA demonstrates a slightly lower adsorption efficiency of about 85%. As the number of cycles increases, a gradual decrease in adsorption efficiency is observed for both contaminants, with PFOS remaining around 90% and PFHxA dropping to 75% by the fourth cycle. The decline in

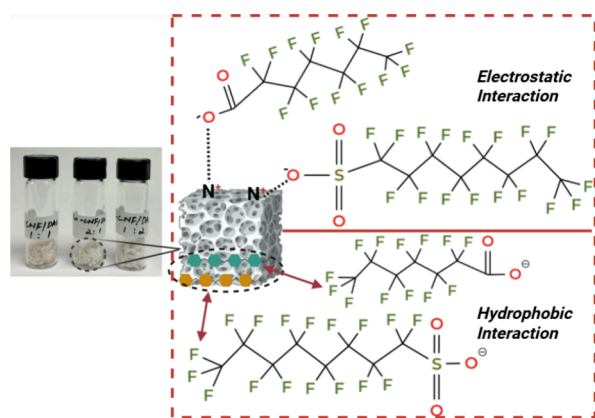


Figure 8. Adsorption mechanism for PFOS and PFHxA removal.

Table 6. Comparison of QA-CNF/DAC Aerogel Efficacy for PFAS Removal with Reported Studies

adsorbents	dose (mg/L)	target PFAS	C_0 (mg/L)	sorption time (h)	isotherm	adsorption capacity (mg/g)	removal %	reference
QA-CNF/DAC aerogel	500	PFOS	10–50	<0.0167	Freundlich	269.76	99%	this study
QC-CMPS	500	PFHxA	10–30	<0.050	Freundlich	83.20	90%	26
		PFOS	0.001	2		46	95%	
		PFOA				35		
		PFBS				68		
NW-101	50	GenX			Langmuir	31		26
		PFOA	10–50	0.1167		698.4	90%	
		PFOA	0.1	24			91%	
		PFOS					95%	
UiO-66-(F) ₄ -OS	400	GenX			Langmuir		34%	62
		PFOA						
		PFOS						
		GenX						
CTN-ethylene glycol hydrogel	1000	PFOA	50–900	24	Freundlich-Langmuir	1275.9	98%	27
quaternized wood pulp	10	PFOA, PFOS	~0.0025	24	Langmuir	763	80%	20
						605		20
PEI-f-CMC	20–50	PFOA	0.01–0.1	15–24	Freundlich	2.32	85%	24
quaternized cotton	100	PFOA, PFOS	190	4	Langmuir	128.36	95%	25
				12		165.04	98%	25
				4		6177.1	88.4%	65
CTN/F-COF	100	PFOA, PFOS, GenX	1–1000	4	Langmuir	8307.1		65
						4603.3		65
						456	99%	66
PEI-glycidyl trimethyl ammonium modified pine bark	400	PFOA	200	24	Freundlich			
ALGPEI-3 & GTH-CTNPEI aerogels	100	PFNA, PFDA, PFOS, 2-N-EtFOSAA, PFHxA, PFHpA, PFBS, GenX	0.01	24	Freundlich	3045	long chain hydrophobic: 99%	19
						12133	short chain hydrophilic: 70–90%	19
quaternized nanocellulose (QNC)		PFOS	1–50	0.01–0.25		559	95%	3
	32	PFOA	1–50	0.01–0.25	Langmuir	405	90%	3
	320	PFBA	1–100	0.01–0.25		319	95%	3
		PFBS	1–250			121	95%	3

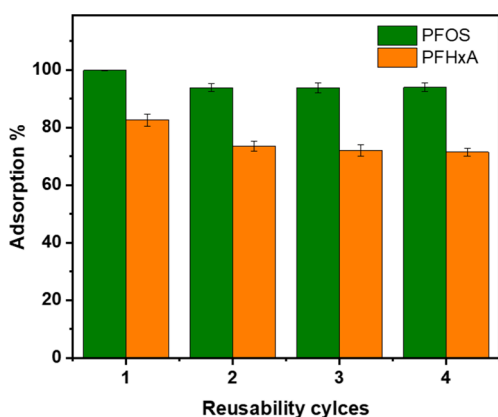


Figure 9. Reusability study for PFOS and PFHxA removal.

adsorption efficiency of QA-CNF/DAC aerogel over multiple cycles may be due to loss of aerogel during washing and regeneration or saturation of active functional groups. This study demonstrated that our prepared aerogel can effectively remove both long- and short-chain PFAS multiple times. Even after four adsorption–desorption cycles, the QA-CNF/DAC aerogel maintains a strong capacity for PFAS removal. To further assess the long-term stability and structural integrity of the regenerated aerogel, conductometric titration, elemental

analysis, and BET surface area measurements were performed. As shown in Figure S3, the regenerated aerogel retained 0.4875 mmol/g of quaternary amine groups, which although slightly lower than that of the pristine aerogel. It could be due to material loss during repeated regeneration and washing cycles. Elemental analysis confirmed that there was no significant loss of the active functional groups throughout four regeneration cycles, as evidenced by consistent elemental composition values (C: 43.07%, H: 6.93%, N: 3.42%), much closer to pristine aerogel % composition (N: 3.54%). In addition, surface area analysis confirmed the retention of similar surface area (61.06 m²/g) along with a mesoporous structure having pore diameters in the range (2–20 nm). These results are better and comparable to those reported in previous studies.^{26,61,62,67} This aerogel has promising potential to be developed into a ready-to-use material for tackling emerging PFAS contaminants in water.

Future Work. The QA-CNF/DAC aerogel demonstrated exceptionally rapid adsorption across both environmentally relevant and high contaminant concentrations. The synthesis involves a simple, green, and sustainable approach under moderate reaction conditions, utilizing two of the most abundant and inexpensive natural biopolymers. The adsorption results highlight the strong potential of this aerogel to be scaled up for membrane fabrication with high flux rates through

appropriate modifications, thereby advancing it toward a ready-to-use technology. However, successful scale-up requires further investigation, including potential optimization for membrane casting processes. Additional research should also address strategies to enhance the adsorption capacity of cellulose nanofibers for short-chain PFAS, as well as safe and sustainable disposal methods for spent aerogels. Finally, a comprehensive cost analysis of the production process is essential to evaluate its economic feasibility to support future commercialization as a cost-effective and reliable solution for industrial applications.

CONCLUSIONS

This study successfully synthesized a novel quaternized amine-functionalized cellulose nanofiber/deacetylated chitin (QA-CNF/DAC) composite aerogel using an environmentally friendly and sustainable method for the efficient removal of PFAS from water. The cross-linking and quaternized amination of two natural polymers were carried out using epichlorohydrin as a cross-linker and triethylamine, resulting in a mesoporous, heterogeneous, highly functionalized aerogel with a high amine content (0.598 mmol/g), surface area (64.5 m²/g), and favorable physicochemical properties. The aerogel demonstrated high adsorption capacities for both long-chain (PFOS) and short-chain (PFHxA) PFAS molecules, with $q_{\max}$ values of 269.76 mg/g and 83.20 mg/g, respectively, with rapid adsorption equilibrium times of just 30 s and 3 min. The adsorption process involved chemisorption through electrostatic interaction between quaternized amine groups ($-NR_3^+$) of the aerogel and the anionic acid head functional groups of PFOS and PFHxA, as described by pseudo-second order kinetics. The adsorption isotherm studies showed that the process closely followed the Freundlich adsorption isotherm, indicating multilayer adsorption between the PFAS hydrophobic chain and the aerogel matrix at lower temperatures through weak physical interactions. Thermodynamic results showed that the adsorption was spontaneous, as indicated by negative ΔG° values ranging from -43.29 to -47.55 kJmol⁻¹ for PFOS and -38.68 to -41.84 kJmol⁻¹ for PFHxA. The ΔH° was negative for both PFAS molecules, suggesting an exothermic physisorption process. A reusability study over four consecutive cycles showed no significant decline in adsorption capacity, demonstrating the aerogel's durability and strong potential for sustained PFAS removal. Overall, the QA-CNF/DAC composite aerogel shows a promising, cost-effective, and sustainable approach for the rapid and efficient removal of both short- and long-chain PFAS molecules from contaminated water under environmentally relevant conditions. Its biodegradability and reusability highlight its potential as a practical solution for PFAS remediation. In the future, such materials could be used to develop ready-to-use technology for field applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.5c00881>.

Additional details about properties of PFOS and PFHxA, operating and calibration conditions of LC/MS for detection and quantification of PFOS and PFHxA, along with their detection peak spectra, mobile phase gradient, calibration curves, and statistical analysis of adsorption

studies; additional data for regenerated QA-CNF/DAC aerogel characterizations (PDF)

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Author Contributions

The manuscript was written with contributions from all authors, and all authors have approved the final version. Credit: M.H. was in charge of conceptualization, investigation, methodology, writing-original draft; I.E. was in charge of conceptualization, methodology, resource gathering, and writing-review and editing; G.S. performed funding acquisition and writing-review and editing; and E.B.H. performed conceptualization, funding acquisition, project administration, resource gathering, supervision, and writing-review and editing. CRediT: **Muhammad Hamza** conceptualization, investigation, methodology, writing - original draft; **Islam Elsayed** conceptualization, methodology, resources, writing - review & editing; **Gregory T. Schueneman** funding acquisition, writing - review & editing; **El Barbary Hassan** conceptualization, funding acquisition, methodology, project administration, resources, supervision, writing - review & editing.

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Notes

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