

Scalable and Sustainable Cellulose Xerogels for High-Capacity Enrichment of Per- and polyfluoroalkyl Substances

Qinyu Wang^{a b c}, Zhonghao Chen^{a c}, Kemeng Wang^{a c d}, Ke Wang^{a c d}, Zhugen Yang^e, Yanyan Zhang^{a c d}, Lei Wang^{a b c *}

^a Research Center for Industries of the Future, Westlake University, 600 Dunyu Road, Hangzhou, Zhejiang 310024, China

^b Zhejiang Key Laboratory of Low-Carbon Intelligent Synthetic Biology, School of Engineering, Westlake University, Hangzhou, Zhejiang 310030, China

^c Institute of Advanced Technology, Westlake Institute for Advanced Study, Hangzhou, Zhejiang 310024, China

^d Key Laboratory of Coastal Environment and Resources of Zhejiang Province, School of Engineering, Westlake University, Hangzhou, Zhejiang 310030, China

^e Faculty of Engineering and Applied Science, Cranfield University, Cranfield, MK43 0AL, UK

*Corresponding author:

Lei Wang

Email address: wang_lei@westlake.edu.cn

Tel: +86-0571-85278909

Mailing address: School of Engineering, Westlake University, Hangzhou 310030, China

Abstract

The phase-out of long chain per- and polyfluoroalkyl substances (PFAS) in the global fluorochemical industry has accelerated the adoption of alternatives (short/ultra-short chain and ether-bond-containing compounds). The persistent residues of conventional long chain PFAS and the unclear environmental fate of alternatives pose a dual pollution challenge to traditional water treatment processes. Herein, we develop a scalable and closed-loop strategy to produce aminated cellulose xerogel (CNPK) via ambient drying process. The hierarchical network of xerogel demonstrates excellent mechanical properties with a maximum compressive strength of 1.96 MPa, guaranteeing structural integrity under complex conditions in wastewater treatment. The xerogel exhibits superior adsorption capacities for six representative PFAS: 3.26 g/g HFPO-TrA, 1.82 g/g PFOA, 2.14 g/g HFPO-DA, 1.27 g/g PFHxA, 1.02 g/g PFBA and 1.01 g/g PFPrA, correlating with its hierarchical porous network that facilitates mass transport and the microenvironment that optimizes adsorbent-PFAS interactions. Its ability to absorb PFAS is several times greater than its own weight, and orders of magnitude higher than that of traditional adsorbents. Mechanism investigations further reveal that hydrogen bonding, electrostatic interactions and hydrophobic effects are major contributors to adsorption. Interestingly, enhanced kinetics and affinity for short/ultra-short chain PFAS in mixed systems are observed compared to single systems, with PFBA and PFPrA being almost completely removed. These are due to the preferential capture of long fluorocarbon chains that accelerates the adsorption of short chain compounds by providing new anchor points through F $\cdots$ F interactions. Moreover, the xerogel demonstrates good enrichment in the proof-of-concept filter column and achieves removal rates of more than 95% for short /ultra-short chain species, and over 82%-99% removal efficiencies for six PFAS through 5 continuous cycles. After the use, the spent xerogel can be dissolved and reproduced. The life cycle assessment (LCA) further highlights the carbon footprint for adsorption of short/ultra-short chain PFAS as 66.69-67.14 kg CO₂eq/kg PFAS using our xerogel, lower than those of most carbon-based adsorbents (61.85-2757.49 kg CO₂eq/kg PFAS). Overall, the proposed strategy of xerogel addresses the urgent issue of PFAS contamination through reconciling high-capacity enrichment with circular economy principles.

Keywords: Cellulose xerogel; Ambient pressure drying; PFAS enrichment; Adsorption mechanism; Life cycle assessment

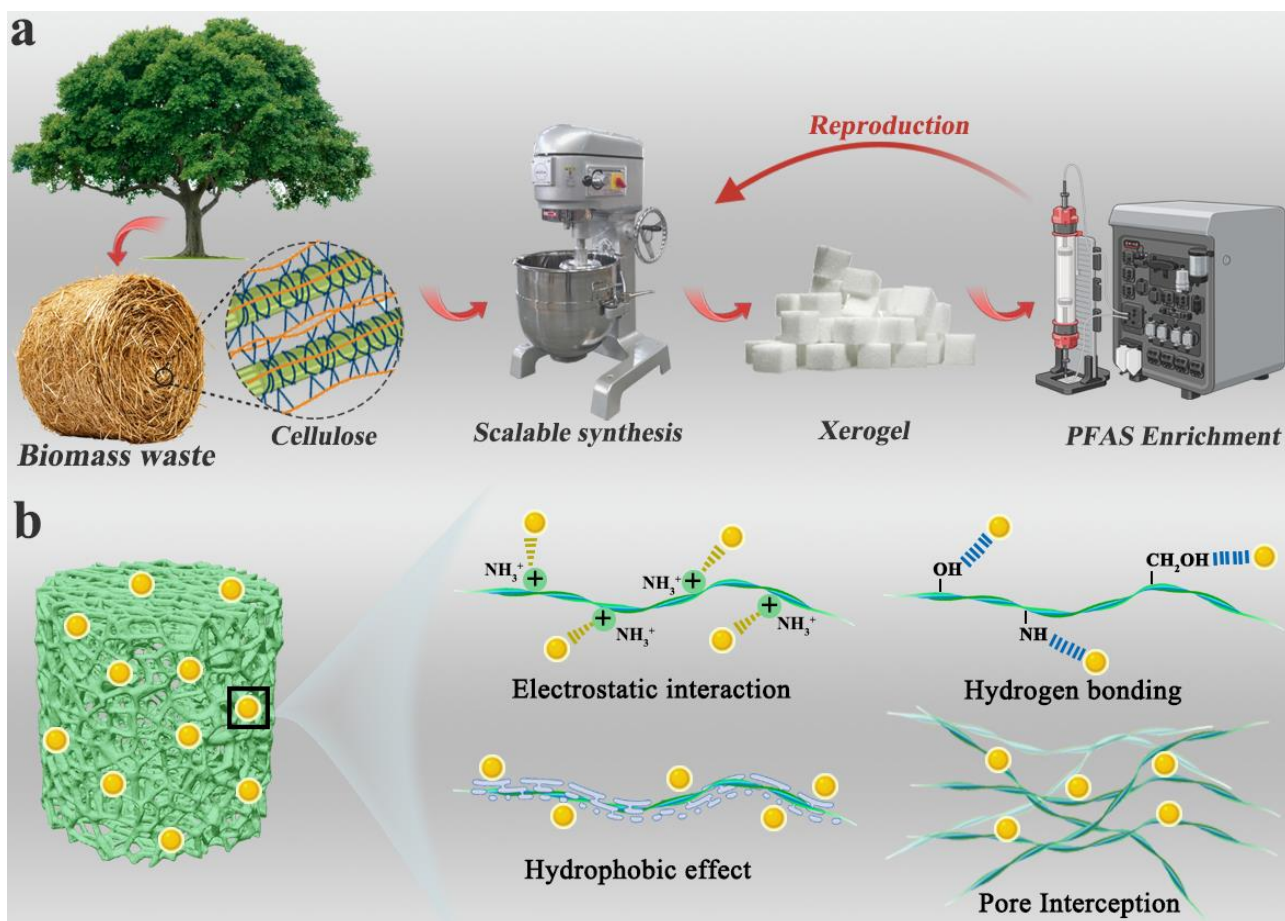
Introduction

Per- and polyfluoroalkyl substances (PFAS), a class of synthetic fluorinated organic compounds with superior chemical stability and amphiphobic properties, have been widely used in over 200 industrial sectors¹⁻³. Due to their environmental persistence and bioaccumulation^{4,5}, long chain PFAS (e.g. perfluorooctanoic acid (PFOA)) have been listed for restriction under the Stockholm Convention on Persistent Organic Chemicals. However, emerging substitutes such as ether-bond-containing PFAS (e.g. hexafluoropropylene oxide trimer acid (HFPO-TrA), hexafluoropropylene oxide dimer acid (HFPO-DA)) and short/ultra-short chain PFAS (e.g. perfluorohexanoic acid (PFHxA), Heptafluorobutyric acid (PFBA), perfluoropropionic acid (PFPrA)) are still currently in use^{6,7}, despite restrictions likely to cover a broader range of PFAS in the future⁸⁻¹⁰. In China, fluorine-related industries such as fluorochemical production, textile and electroplating generate process water and wastewater after treatment that contain various concentrations of PFAS ranging from ng/L to mg/L^{10,11}. Data shows that a mega fluorochemical industrial park in Shandong, China, discharged up to 9.45 tons of PFOA and 6.30 tons of HFPO-DA/-TrA in 2021¹². Their release into the environment poses a risk of contamination and therefore requires prevention through effective technologies.

Enrichment technology could be a promising approach to remove PFAS in wastewater or to concentrate PFAS for further effective treatment¹³⁻¹⁵. Adsorption materials such as granular activated carbon (GAC), anion exchange resins (AER) and metal organic frameworks (MOF) have been used to remove PFAS effectively from wastewater, but their large-scale application still remains challenging due to their costly, unsustainable production process, low stability and poor adsorption of short chain PFAS¹⁶⁻¹⁸. Recent developed Perfluoropolyethers (PFPE)-modified polystyrene ion exchangers show excellent performance in removing PFAS from drinking water and landfill leachate^{1,19}. However, long-term environmental stability assessments of PFPE and appropriate end-of-life treatment strategies are lacking, posing potential challenges for regulatory compliance and ecological sustainability. Therefore, the development of sustainable enrichment materials with excellent adsorption capacity, kinetics, stability, scalability, recyclability is essential.

Cellulose, derived from the most abundant renewable resource lignocellulosic biomass is biodegradable and rich in functional groups, making it an excellent feedstock for producing enrichment materials for PFAS^{20,21}. Aerogels made from cellulose and lignin, have been used as microorganism host for adsorption and bioremediation of PFOA and PFOS, achieving adsorption capacities of 3529 mg/g and 4151 mg/g, with equilibrium times of 30 h and 45 h²². However, aerogels production is usually energy intensive (e.g., freeze drying or supercritical CO₂ drying) and suffers from low mechanical stability and poor adsorption performance for less hydrophobic or shorter chain PFAS.

To address these challenges, we synthesize a cellulose nanofiber (NFC)-polyethyleneimine (PEI) xerogel (CNPK) crosslinked with silane coupling agent (KH560). The production process takes place under ambient pressure, enabling adsorption materials of various sizes to be produced on a large scale (**Scheme 1a**). The NFC/KH560 backbone is supposed to provide structural integrity and hydrophobic sites, while the high-density amine groups from PEI introduce strong electrostatic interactions and hydrogen bonding for PFAS adsorption (**Scheme 1b**). Moreover, spent xerogels after multiple cycles can be dissolved and reproduced, establishing a "make-use-reproduce" close-loop strategy.



Scheme 1 (a) Manufacturing of CNPK xerogel via ambient pressure drying. (b) Hypothesized PFAS enrichment mechanisms.

Results

Synthesis and characterization of xerogel

As illustrated in **Fig. 1a**, a scalable synthesis approach for CNPK xerogel is designed including preparation via homogenization, freezing, solvent exchange and ambient pressure drying. NFC (substrate), PEI (functional polymer), and KH560 (crosslinking agent) spontaneously assemble into a hydrogel during the homogenization process. The nucleophilic epoxy-amine coupling between PEI and KH560 forms beta-amino alcohol bridges^{23,24}, while the silanol (Si-OH) produced by KH560 hydrolysis connects with NFC to form a crosslinked network²⁵. Hydrogel is then frozen to create ice-templated macropores, after which solvent exchange and ambient pressure drying are performed.

The spectroscopic signatures of CNPK composites, as revealed by comparative FT-IR analysis (**Fig. 1b** and **Fig. S1**), demonstrate successful chemical reactions among three components: (i) NFC (C-O-C stretching at 1023 cm^{-1}), (ii) KH560 (Si-O-Si asymmetric vibration at 1157 cm^{-1}) and (iii) PEI (N-H deformation at 1458 cm^{-1})²⁶⁻²⁸. The attenuation of the 1300-1560 cm^{-1} bands and the broadening of the peak at 902 cm^{-1} confirm the nucleophilic ring-opening reaction between the amine of PEI and the epoxy groups of KH560²⁹. In addition, a decrease in the NH bending strength with an increasing KH560 content is observed from the local magnified area. Raman analysis (**Fig. 1c**) further confirms the crosslinking, showing the reduced intensity for CH₂ shear (1301 cm^{-1}) and NH in-plane bending vibrations (1456 cm^{-1}) of PEI³⁰. KH560 typically hydrolyzes to form active silanols that covalently bond with -OH of NFC and amines of PEI, accompanied by self-condensation to form Si-O-Si bridges. With weight concentrations of KH560 increase from 1% in CNPK-1 to 5% in CNPK-5, the enhanced formation of its self-condensation oligomers leads to a more obvious self-limiting cross-linking structure, thereby reducing the incorporation efficiency of PEI due to steric hindrance.

Furthermore, the loading of KH560 has a significant effect on the structure of xerogel. While the loading is low (CNPk-1), both the longitudinal and transverse structures show obvious collapse (**Figs. S2a, b**). High magnification images visualize the rough wrinkles on the channel wall surface, suggesting that inadequate PEI crosslinking leads to poor interfacial compatibility with NFC and pore wall collapse during solvent exchange and ambient drying. Increasing in the loading of crosslinker could transit the xerogel morphology to a more homogeneous state with improved regularity and thickness (**Figs. S2c, d** for CNPK-2, **Figs. S2e, f** for CNPK-3). However, when the crosslinker loading is high (CNPk-5), the cellular network encounters structural disruption (**Figs. S2g, h**), probably due to the competitive self-condensation of the silanol groups of excess KH560³¹⁻³³. CNPK-4 shows the most desired morphology (**Figs. 1d, e**) and can be processed to size-tunable (**Fig. 1f**), low-density (**Fig. S4**), and light weight xerogel that can withstand a load of 40 times its own weight (**Fig. S5**).

High compressive strength and superior elasticity are key features that enable xerogel to withstand dynamic hydraulic shocks and long-term mechanical stress in water treatment applications. The loading of KH560 significantly affects the mechanical properties of the xerogel. As illustrated in **Fig. 1g**, xerogels with different crosslinker concentrations maintain fully closed hysteresis loops at 60% strain, indicating excellent elastic recovery capability. Increasing the crosslinker concentration enhances compressive strength from 0.28 MPa (CNPk-1) to 0.92 MPa (CNPk-4), followed by a significant decrease for CNPK-5 (0.59 MPa). Results reflect that the controlled incorporation of

KH560 ($\leq 4\%$) into xerogel improves the elasticity and compression modulus. These are due to the formation of synergistic interfacial hydrogen bonding and covalent crosslinking with NFC and PEI^{34,35}. However, excessive siloxane aggregation can lead to phase separation, resulting in a relaxed network structure and compromised mechanical integrity³⁶. As shown in **Fig. 1h**, the load-bearing performance of CNPK-4 shows a steep increase in stress under incremental strain loading, with the stress reaching 1.96 MPa at 80% strain, exceeding the reported range for cellulose-based aerogels (0.020-0.782 MPa, **Table S3**). In addition, stress retention after 10 cycles at 60% strain is 53.4% (**Fig. 1i**), and the shape memory property of the xerogel allows it to quickly recover its original morphology after compression (**Video S1**). While conventional cellulose-based aerogels often suffer from plastic deformation or permanent damage to the pore structure under cyclic compression due to insufficient crosslinking or single network architecture, our CNPK xerogel has an elastic-rigid double network formed by multi-level networks, where stress is dissipated by the elastic deformation of PEI chains, while the rigid NFC/KH560 chains inhibit structural collapse.

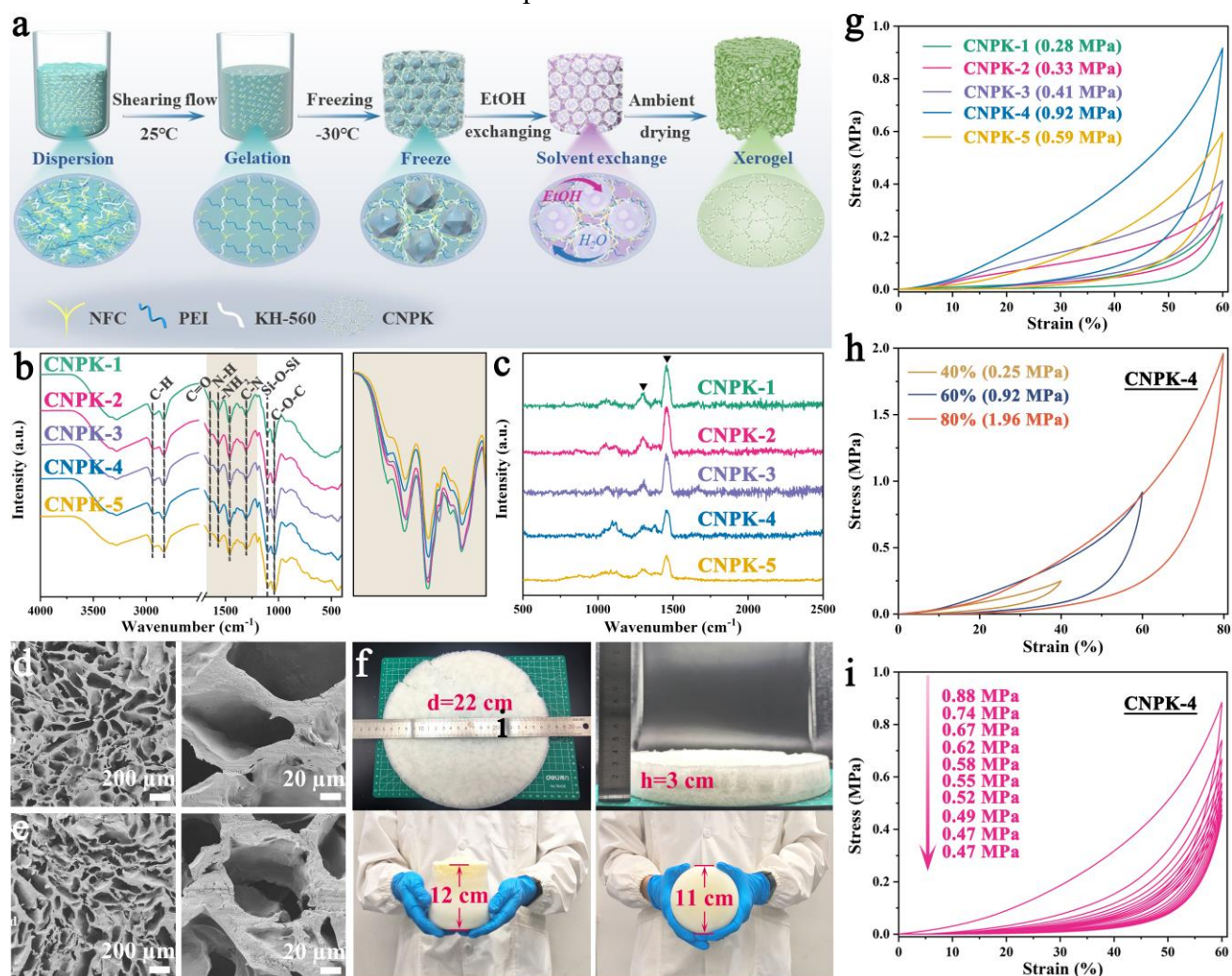


Fig. 1 Synthesis, composition and mechanical characterization of CNPK xerogels. (a) Schematic illustration of the xerogel fabrication. (b) FTIR and (c) Raman spectra of CNPK1-5 xerogels (CNPK-1, CNPK-2, CNPK-3, CNPK-4 and CNPK-5 indicate weight concentrations of KH560 in a cellulose solution of 1%, 2%, 3%, 4%, and 5%, respectively). (d) Longitudinal and (e) transverse SEM images of CNPK-4 xerogel. (f) Scalable production of xerogel demonstrated by dimensional tuning and shape design. (g) Stress-strain curves of CNPK1-5 xerogels under 60% strain.

stress. (h) Mechanical responses of CNPK-4 xerogel across incremental strain levels (40-80%). (i) Cyclic compression stability of CNPK-4 xerogel at 60% strain.

PFAS enrichment performance of xerogel

The enrichment performance of xerogels is evaluated using six PFAS including PFOA (traditional long chain), HFPO-TrA and HFPO-DA (emerging alternatives to PFOA), as well as PFHxA, PFBA and PFPrA (typical short/ultra-short chain PFAS) (PFAS structures are shown in **Fig. S9**). As shown in **Fig. 2a**, CNPK-4 demonstrates exceptional pH adaptability for PFAS with $C \geq 8$, maintaining relatively stable removal efficiencies all above 95% across a large pH range of 3-7. Zeta potential analysis reveals the persistent cationic surface charge (+30.1 mV to +21.9 mV) of CNPK-4 across pH 3-7 due to the abundant protonated amino groups (**Fig. S10**), ensuring its strong interactions with PFAS. Meanwhile, the nonpolar carbon chains of NFC and the alkyl chains in KH560 exhibit adsorption affinity to the perfluorinated groups of long chain PFAS through hydrophobic effects. While CNPK-4 exhibits a significant decrease in adsorption of PFAS with $C \leq 6$ at $\text{pH} > 3$ due to the loss of the protonated amino groups of CNPK-4 and the weakening of hydrophobic effects of PFAS, as indicated by their lower n-octanol/water partition coefficients ($\log K_{ow}$, 1.47 for PFPrA, 2.14 for PFBA, 5.55 for PFOA, **Fig. S11**)¹¹. According to the pH-modulated adsorption differential analysis (see SI for method details), the contribution of electrostatic attraction to adsorption of six PFAS species varies: 3.4% for HFPO-TrA, 23.0% for PFOA, 67.0% for HFPO-DA, 70.2% for PFHxA, 89.2% for PFBA and 83.9% for PFPrA. This reveals that adsorption might be governed by multiple mechanisms. As shown in **Fig. 2b**, the adsorption capacities for PFAS with $C \geq 6$ are not sensitive to the concentration of KH560 at pH 3 owing to synergistic effects of electrostatic and hydrophobic binding sites of xerogels. In contrast, short/ultra-short chain species ($C < 6$) exhibit obvious dependent with increasing KH560 content, attributed to the progressive formation of enhanced binding sites through KH560-derived silanized crosslinking networks³⁷. Considering the superior mechanical property and adsorption performance of CNPK-4, it is selected as the adsorption material for further investigation.

To assess the adsorption capacity, **Fig. 2c** presents the adsorption isotherms of individual PFAS onto CNPK-4, accompanied by nonlinear fittings using the Langmuir and Freundlich equations. The higher coefficient of determination (R^2) for the fitting of Langmuir equation compared to the Freundlich equation (**Table S5**) suggests that monolayer adsorption is the predominant mechanism^{38,39}. The fitting data of the Langmuir model show the adsorption capacities in the following ordered: HFPO-TrA (3.26 g/g) > HFPO-DA (2.14 g/g) > PFOA (1.82 g/g) > PFHxA (1.27 g/g) > PFBA (1.02 g/g) > PFPrA (1.01 g/g). This reflects the xerogel's ability to capture PFAS is several times greater than its own weight. Compared to widely used adsorbents such as activated carbon (1.2-172.6 mg/g) and resins (10.8-1209.1 mg/g), our xerogel demonstrates exceptional capacity and broad-spectrum applicability, as illustrated in **Fig. 2d** and **Table S6**.

To assess adsorption dynamics, kinetic studies are carried out in both single and mixed PFAS systems. The xerogel demonstrates ultrafast capture kinetics for PFAS with $C \geq 6$ in both systems, achieving over 98% removal efficiency within 10 min (**Fig. 2e**). In contrast, short/ultra-short chain compounds ($C < 6$) require prolonged equilibration times of 120 min in the single system with reduced efficiencies of 93.7% (PFBA) and 86.0% (PFPrA) (**Fig. 2f**). However, the xerogel exhibits notable

improvements in capturing PFBA and PFPrA in mixed systems, reducing the equilibrium time by 50% and enhancing removal efficiencies to 98.4% for PFBA and 93.4% for PFPrA. It can be hypothesized that PFAS ($C \geq 6$) adsorbed on the xerogel surface provide new anchoring points driven by $F \cdots F$ interactions, whereas shorter species ($C < 6$) maintain monodisperse states owing to excellent diffusivity and limited hydrophobicity, as proved by the final step of MD simulation in presentation mode (**Figs. S14**). This difference leads to synergistic adsorption behavior in mixed PFAS systems, where the rapid binding of long chain PFAS to the xerogel alters the surface characteristics of the xerogel by increasing its fluorine content and subsequently facilitating the capture of short/ ultra-short chain compounds via $F \cdots F$ interactions. This unique adsorption stage was also supported by a recent study that long-chain PFAS aggregation driven by hydrophobic interactions provides new adsorption sites³⁸. Kinetic analysis using both pseudo-first-order and pseudo-second-order equations (**Fig. S15, Table S7**) suggests that electrostatic, hydrophobic and charge-assisted hydrogen bonding (CAHB) interactions govern the adsorption process under acidic conditions^{22,40,41}.

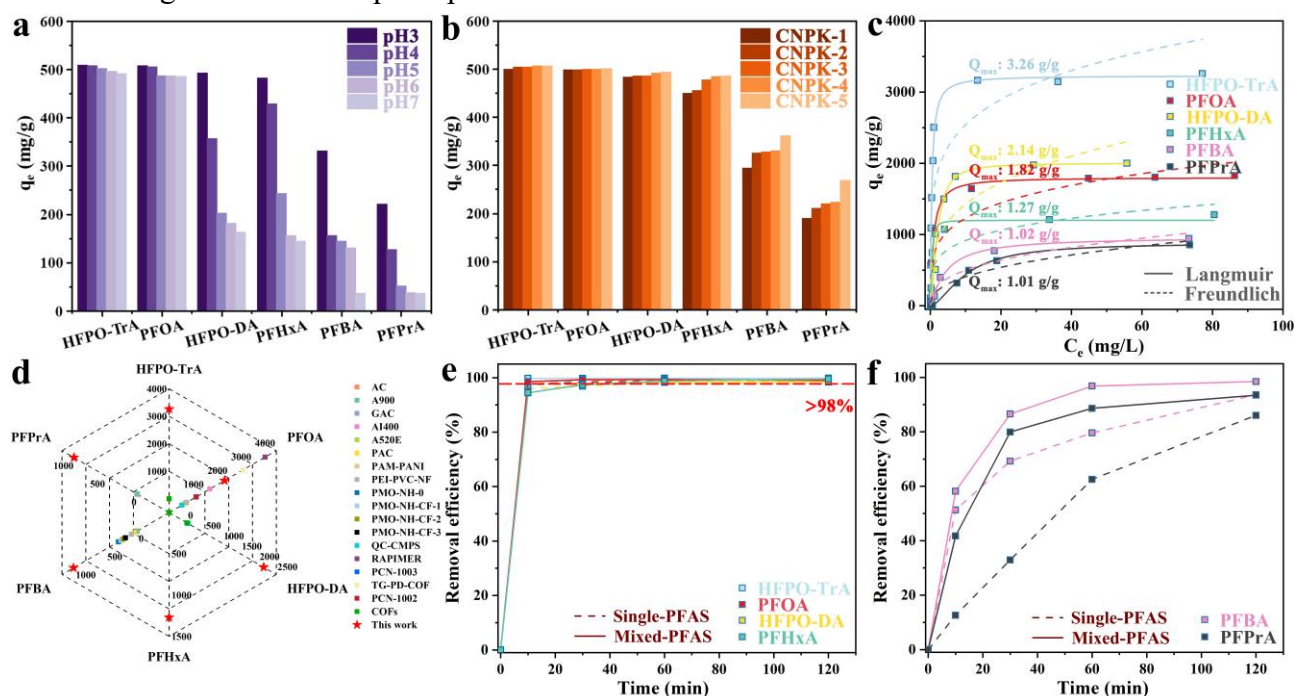
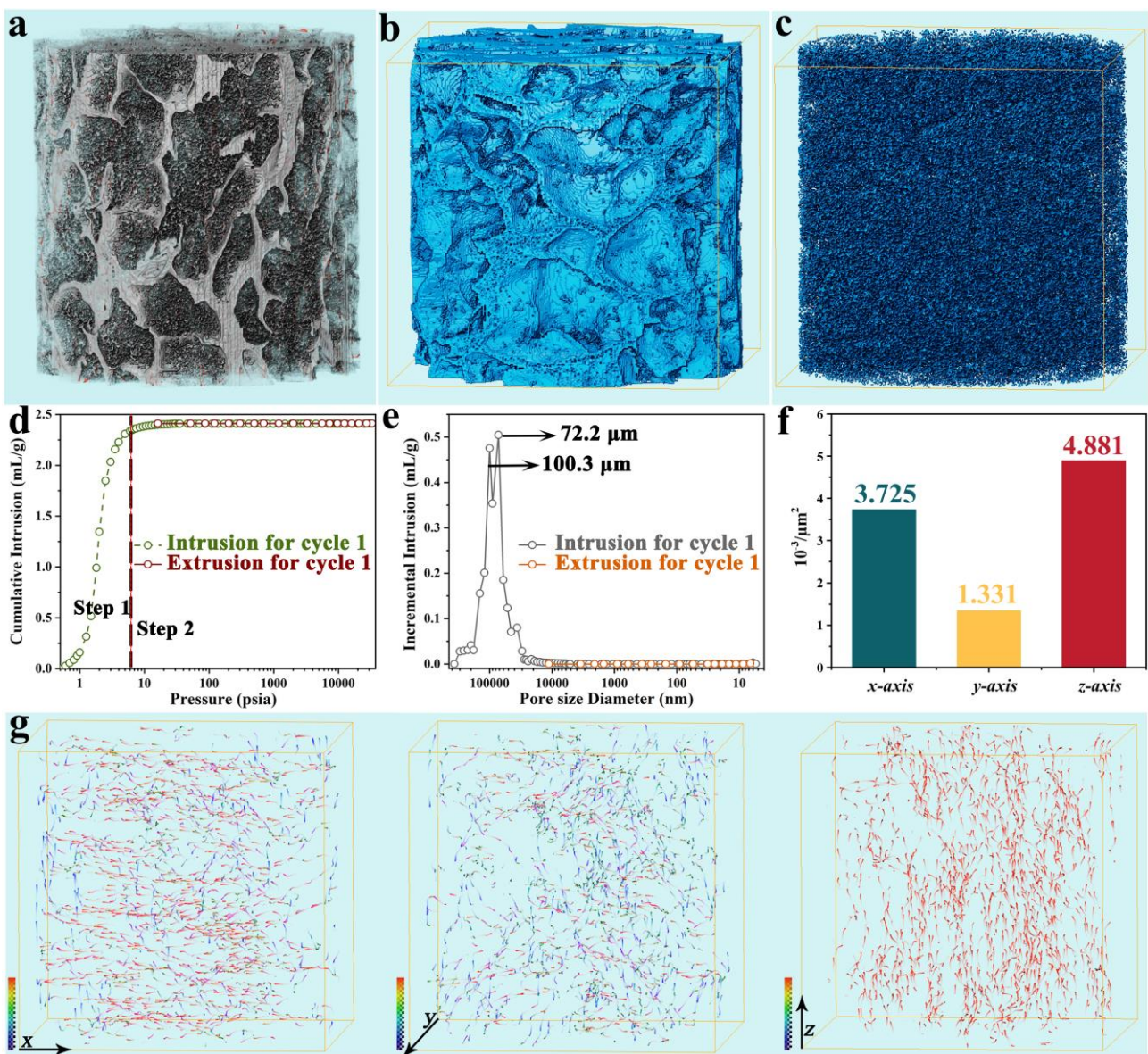


Fig. 2 Adsorption performance of PFAS on CNPK xerogel. (a) pH-dependent adsorption efficiency of CNPK-4 (PFAS: 50 mg/L; adsorbent: 0.1 g/L). (b) Effect of different content of crosslinker on adsorption of PFAS (PFAS: 50 mg/L; adsorbent: 0.1 g/L; pH: 3). Adsorption isotherm analysis with (c) Langmuir/Freundlich model fitting (adsorbent: 0.1 g/L; pH: 3). (d) Comparison of adsorption capacities for PFAS between CNPK and other adsorbents. Evaluation on the removal efficiency of xerogel for PFAS with $C \geq 6$ (Fig. 2e) and PFAS with $C < 6$ (Fig. 2f) in single and mixed systems (pH: 3; PFAS: 100 μ g/L; adsorbent: 1 g/L).

Multi-scale mechanism investigation

The excellent adsorption performance of our xerogel could be attributed to its characteristics: (1) the presence of a hierarchical porous network, integrating interconnected pores of varying sizes, facilitates efficient mass transport and provides sufficient contact area; (2) the deliberate tailoring of the microenvironment, balancing polar and hydrophobic characteristics, significantly optimizes the interactions between the adsorbent surface and the PFAS molecules, thereby boosting adsorption

223 capacity. The 3D porous architecture of CNPK-4 xerogel, visualized via Micro-CT, exhibits a
 224 hierarchical anisotropic pore network optimized for PFAS adsorption (**Fig. 3a and Video S2**). Fluid
 225 dynamics simulations confirm efficient mass transport with permeability of 1.92 mm/s (**Videos S3-**
 226 **S4**), allowing PFAS to rapidly access the hydrophilic-hydrophobic microporous regions. With an 84.96%
 227 channel interconnection ratio (**Figs. 3b, c**) and 80.77% porosity (validated by MIP, **Figs. 3d, e**), the
 228 structure enables rapid, multidirectional diffusion of PFAS-contaminated water through interconnected
 229 microchannels with an average pore size of 4.36 μm (**Table S8**). Crucially, anisotropic permeability
 230 is greatest along the z-axis due to cryogenically induced longitudinal channels (see **Figs. 3f, 3g**). This
 231 minimizes flow resistance while maximizing contact between the PFAS and the adsorption sites. Thus,
 232 the architecture constructed by balancing high connectivity (>84%) and controlled wall thickness (~ 20
 233 μm , **Fig. S17**) contributes to the high adsorption efficiency and overcomes limitations of traditional
 234 adsorbents (e.g., pore blockage, slow kinetics).



235
 236 **Fig. 3 The structural advantages of CNPK-4 xerogel in PFAS enrichment.** (a) 3D reconstruction of the
 237 CNPK-4 xerogel characterized by Micro-CT. Quantitative analysis of (b) interconnected and (c) isolated pore
 238 volumes calculated from 3D structural models. (d) Mercury intrusion porosimetry (MIP) characterizing porosity

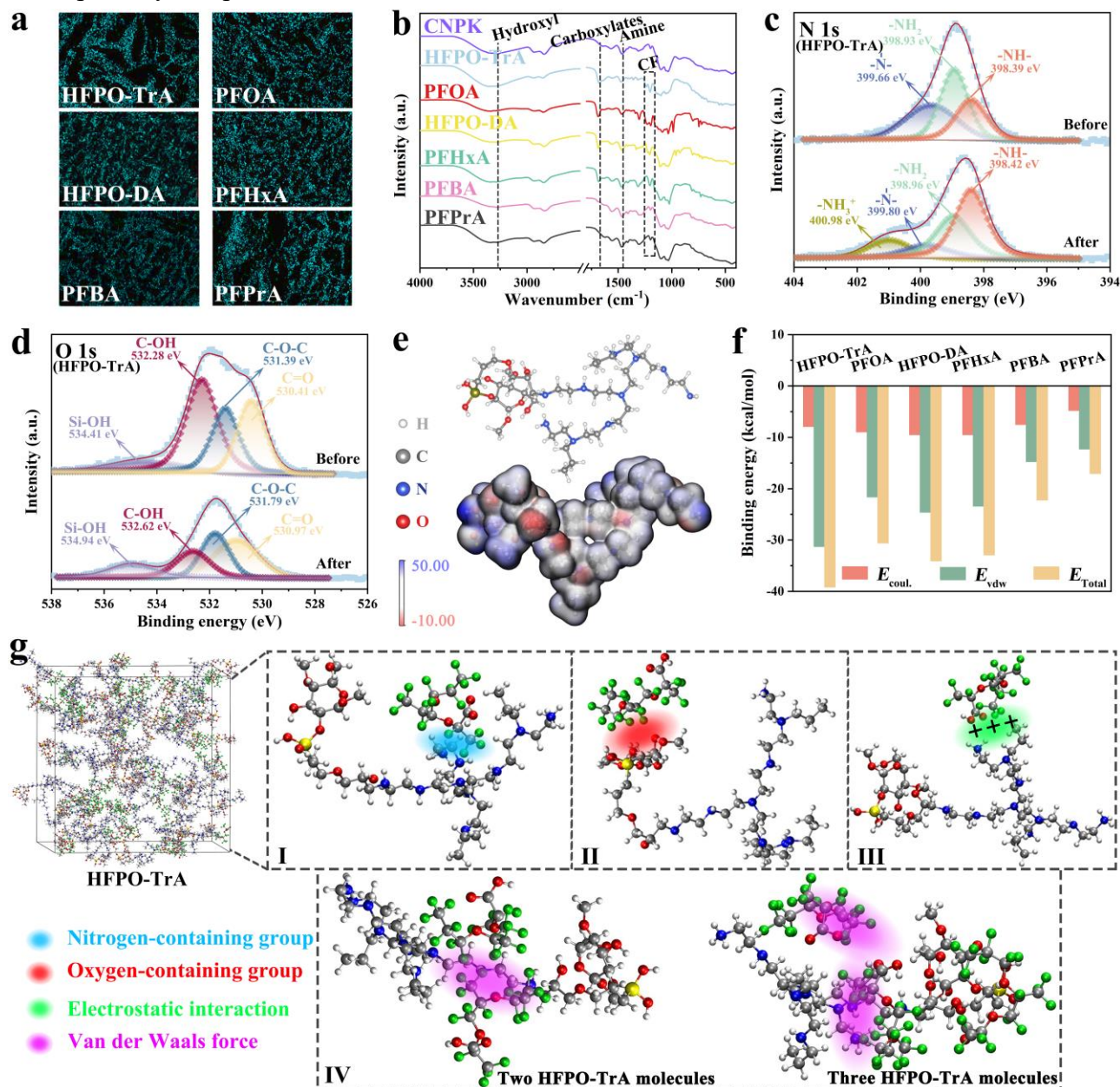
characteristics. (e) Pore size distribution of CNPK-4 obtained from porosity analysis. (f) Permeability coefficients determined from directional flow simulations. (g) Fluid dynamics simulations visualizing flow streamlines in three orthogonal directions, where red and blue represent high and low flux.

To verify the proposed mass transport mechanism, SEM-EDS mapping after adsorption (**Fig. 4a**) demonstrates homogeneous F element distribution throughout the xerogel network channels. This uniformity directly confirms the structural advantage of highly accessible adsorption sites (hydroxyl, amino and hydrophobic microdomains) and validates the efficient diffusion and binding of PFAS enabled by the hierarchical anisotropic pore architecture. Mechanistic investigation using FTIR spectra explains the interfacial interactions governing PFAS adsorption on CNPK-4 (**Fig. 4b**). The 39 cm^{-1} red shift at 3300 cm^{-1} and the attenuation of the vibration peak intensity at 1458 cm^{-1} confirm that the weakly acidic PFAS can interact with O–H and N–H in the xerogel⁴². Notably, the CF_3 and CF_2 vibrational features of PFAS appear in the spectral region of $1202\text{--}1241\text{ cm}^{-1}$ ^{43,44}. In addition, adsorption of carboxylate PFAS species induces upward shift to 1676 cm^{-1} in the asymmetric carboxylate peak of the xerogel, with peak intensity enhancement of long chain PFAS^{45,46}.

High-resolution N 1s XPS deconvolution (**Fig. 4c**) after adsorption shows obvious changes in nitrogen-related binding energies. Peaks corresponding to the N= , –NH and –NH_2 groups systematically shift toward higher binding energies, indicating that the lone pair on unprotonated amines coordinate with electron-deficient regions on PFAS molecules, resulting electron density redistribution around nitrogen centers⁴⁷. Furthermore, a new peak appears at $\sim 400.98\text{ eV}$, attributed to –NH_3^+ groups, suggesting that primary amines readily accept protons (H^+) for protonation, enhancing their electrostatic binding with PFAS²¹. Following PFAS adsorption, the binding energy and peak area of the oxygen-containing functional groups in the xerogel change markedly (**Fig. 4d**), where the oxygen atoms act as electron donor, forming hydrogen bonds with the fluorine atoms of PFAS. Additionally, it contributes to charge-assisted hydrogen bonding (CAHB) by bridging with the carboxylate head group of PFAS²⁰.

We further determine the contribution of different sites on the xerogel based on electrostatic potential (ESP) mapping of CNPK-0.4. As shown in **Fig. 4e**, blue regions (nitrogen-containing groups) correspond to protonated electrophilic regions, indicating preferential electrostatic anchoring sites for PFAS headgroups. The red regions (oxygen-containing groups) suggest hydrogen-bonding propensity, while the gray-white regions (alkyl chains) highlight the hydrophobic interaction via van der Waals (vdW) forces⁴⁸. To quantitatively assess the adsorption forces, we conduct MD simulations for various PFAS under acidic conditions, with protonated –COOH groups modeled to reflect dominant species. **Fig. 4f** indicates the interfacial energetics between CNPK and PFAS, revealing vdW interactions as the dominant binding driver, with the calculated energies are -31.26 , -21.62 , -24.60 , -23.42 , -14.72 and -12.28 kcal/mol for HFPO-TrA, PFOA, HFPO-DA, PFHxA, PFBA and PFPrA, respectively. Since hydrophobic effects generally arise from vdW forces, the gradual shortening of the perfluoroalkyl chain reduces the matching of silane chains in KH560 and the hydrophobic microdomains in NFC crystallites for vdW interactions, thereby influencing the overall hydrophobic contribution. The integration of PEI within the xerogel framework introduces pronounced coulombic electrostatic effects, as quantified by binding energies with -7.90 , -8.96 , -9.48 , -9.48 , -7.50 , and

279 -4.78 kcal/mol for HFPO-TrA, PFOA, HFPO-DA, PFHxA, PFBA and PFPrA, respectively. Thus, the
 280 chain-length dependent attenuation of the coulombic and vdW forces directly leads to the decrease of
 281 the total binding energy for short/ultra-short chain PFAS (Table S9). Taking HFPO-TrA as an example,
 282 the optimized system snapshot, shown in Fig. 4g, visually demonstrates the contribution of nitrogen-
 283 containing groups and oxygen-containing groups of CNPK in the adsorption process and demonstrates
 284 the micelle/semi-micelle adsorption mechanism driven by vdW forces. Therefore, the high adsorption
 285 capacity of CNPK-4 xerogel arises from the strong synergy among multiple interaction mechanisms
 286 (hydrogen bonding, electrostatic interactions and hydrophobic effects) combined with physical
 287 interception by its open network structure.



288
 289 **Fig. 4 Systematic evaluation of PFAS enrichment mechanisms on CNPK xerogel.** (a) SEM-EDS elemental
 290 mapping of F elements adsorbed on the xerogel. (b) FTIR spectral comparison pre-/post-adsorption. Deconvoluted
 291 XPS spectra of xerogel after HFPO-TrA adsorption: (c) N 1s, (d) O 1s. (e) DFT-derived electrostatic potential surface
 292 of CNPK-4. (f) Comparative adsorption energies for six PFAS via MD simulations. (g) MD-optimized adsorption

configurations for HFPO-TrA: (I) nitrogen-containing groups driven; (II) oxygen-containing groups driven; (III) electrostatic dipole interactions; (IV) Van der Waals force.

Regeneration, performance in real contaminated water and reconstruction of xerogel

To evaluate practical applicability, cyclic adsorption and regeneration of CNPK-4 are performed in simulated wastewater. As shown in **Fig. 5a**, after five consecutive cycles, high removal efficiencies for HFPO-TrA (98.1%), PFOA (99.5%), HFPO-DA (92.7%), PFHxA (92.6%), PFBA (86.8%) and PFPrA (82.5%) still maintain. Structural (**Fig. S18**) and mechanical (**Fig. S19**) stability analyses show excellent durability of the xerogel after five cycles. Additionally, the chemical resistance to various solvents is assessed by immersion testing (**Fig. S20**) and the dimensional integrity preservation can be maintained after 60 days. After cyclic reuse, we also develop reconstruction technologies to recycle xerogels via alkaline-mediated dissolving, filtration and reproduction processes of new xerogel (**Fig. 5d**). As shown in **Figs. 5e-g**, the reconstituted xerogel maintain the adsorption capacity with losses of 1-10% only across various PFAS concentrations. This circular strategy overcomes the common costly disposal for used absorbent (e.g., pyrolysis) or 'downcycling' of aerogels, synergistically reduce resource consumption and hazardous waste disposal.

To develop a more robust technology in the realistic environment, we integrate GAC and our CNPK as a two-stage system (**Fig. 5b**) for full-spectrum PFAS adsorption. **Fig. 5c** illustrates that the GAC single-column results in a high interception rate (93%-99%) for PFAS with $C \geq 6$ in simulated wastewater containing PFAS, organic matter and heavy metal salts, mimicking landfill leachate (**Table S10**)¹. However, GAC exhibits poor adsorption performance for short/ultra-short chain compounds like PFBA and PFPrA, with the removal rates rapidly dropping to 63.7% and 49.9%. In contrast, the two-stage GAC-CNPK system achieves removal rates exceeding 95% for all PFAS species, in which the GAC column serves as a pretreatment unit removing complex substrates while CNPK effectively adsorb short chain PFAS, demonstrating a promising and practical strategy for PFAS containing wastewater treatment.

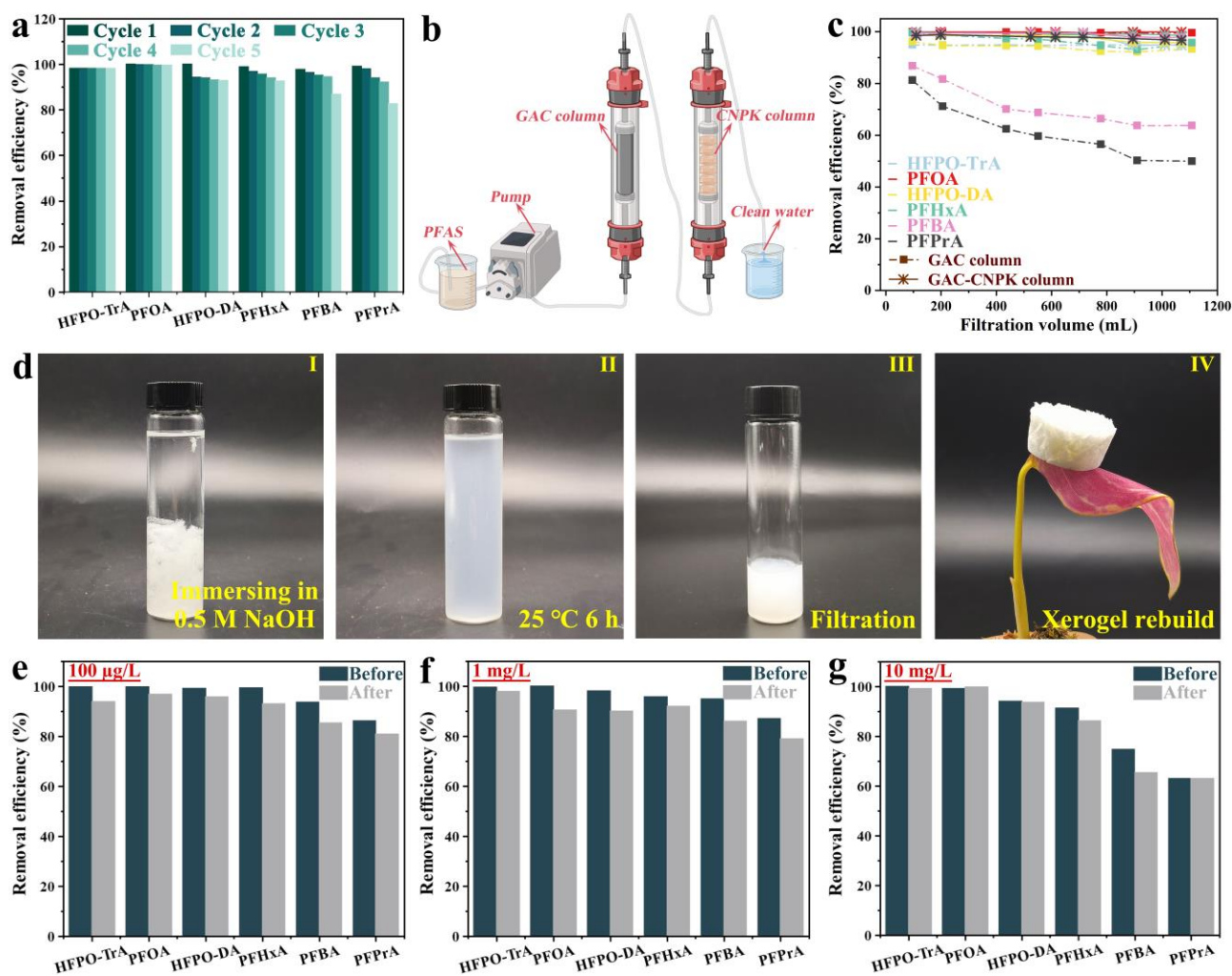


Fig. 5 Practical application exploration (a) Cyclic adsorption-regeneration performance over 5 cycles (pH: 3; PFAS: 1 mg/L; adsorbent: 5 g/L). (b) Schematic diagram of GAC-CNPK two-stage series system. (c) Fixed-bed breakthrough curves of GAC-CNPK two-stage series system for six PFAS mixtures in simulated wastewater (adsorbent: 2 g per column; per PFAS: 100 µg/L; flow rate: 2 mL/min). (d) Alkaline degradation (0.5 M NaOH) and sustainable regeneration protocol. Comparison of the adsorption capacities of the raw xerogel and xerogel after regeneration for six PFAS: (e) 100 µg/L, (f) 1 mg/L, (g) 10 mg/L (pH: 3, adsorbent: 1 g/L).

Environmental impact of xerogel

A cradle-to-gate life cycle assessment (LCA) is conducted to evaluate the environmental impact of CNPK xerogel production. The assessment framework involves process stages including cellulose raw material procurement, xerogel synthesis, energy/material inputs integration and waste management (Fig. 6a). As quantified in Figs. 6b, c, the global warming potential (GWP) for producing 1 kg of CNPK xerogel is 67.84 kg CO₂eq/kg, with PEI (87.64%) and thermal energy consumption (9.98%) as the major contributors. PEI production relies on petrochemical feedstocks and energy-intensive polymerization processes, contributing significantly to the GWP and other environmental impacts (Fig. S21). Owing to the biogenic carbon sequestered in cellulose derived from agricultural waste, carbon credits can offset the overall GWP value. Due to less energy used in our process, this value is much lower than other biobased cryogel produced via conventional technologies (freeze-

drying and supercritical CO₂ drying, 56.0-454.0 kg CO₂eq/kg) or other ambient-pressure process (56.3-141.0 kg CO₂eq/kg), primarily due to the consumption of solvents such as ethanol and methanol⁴⁹. Specifically, when compared with studies where chitin/chitosan cryogels used for PFAS removal, our xerogel exhibits advantages in not only environmental impacts (GWP, FATEP, MATEP, TEP, POCP, AP, and EP) but also inherent properties such as compressive strength, porosity, adsorption capacity and kinetics (**Fig. 6d**).

Furthermore, the GWP of xerogel for adsorbing 1 kg of PFAS (considering material production but not the disposal of used material) is evaluated and compared with that of other conventional carbon-based adsorbents. For long-chain PFOA (**Fig. 6e**), xerogel exhibits a comparable GWP (37.12 kg CO₂eq/kg PFOA) with that of GAC (20.50 kg CO₂eq/kg PFOA) and PAC (19.17 kg CO₂eq/kg PFOA). Whilst xerogel demonstrates significant advantages for short/ultra-short chain PFAS, with GWPs of 66.69 kg CO₂eq/kg PFBA (**Fig. 6f**) and 67.14 kg CO₂eq/kg PFPrA (**Fig. 6g**). These GWPs are considerably lower than those of most carbon-based adsorbents (61.85-2757.49 kg CO₂eq/kg PFAS) due to higher adsorption capacity of our xerogel the fact that less material is used. Moreover, the xerogel shows competitive environmental performance for PFBA and PFPrA across other life cycle impact categories (ADP (fossil), HTP, FATEP, MATEP, TEP, POCP, AP, and EP) (**Tables S15-17**).

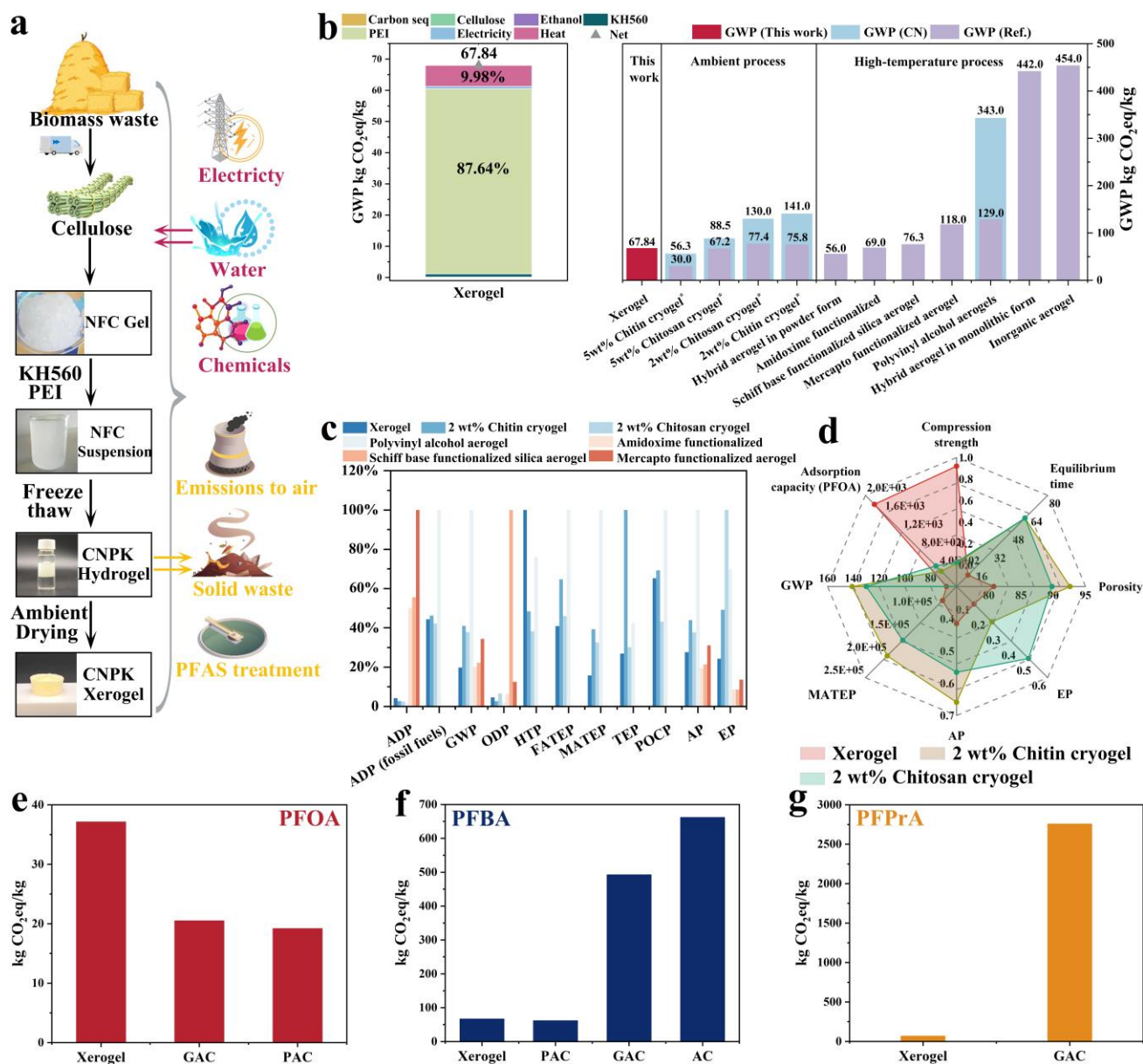


Fig. 6 Life cycle assessment (LCA) of xerogel for PFAS remediation applications. (a) Cradle-to-gate system boundary of xerogel production and application. (b) GWP analysis of 1 kg xerogel production and comparison with other gel materials (* Refers to the gel materials for PFAS removal). The purple columns show values derived from literature, while the blue columns show results adjusted using Chinese-sourced energy. (c) Comparison of other environmental impacts of xerogel and related gels for wastewater treatment applications under Chinese energy. (d) A systematic comparative analysis between the CNPK xerogel and existing cryogel-based adsorbents, including enrichment capacity, compressive strength, equilibrium time, porosity, and environmental impact assessment metrics (GWP, MATEP, AP, EP). GWP of 1 kg PFAS enriched by xerogel or by other carbon-based materials: (e) PFOA; (f) PFBA; (g) PFPrA.

Conclusion

To be preparing for tightening regulations of PFAS use and emissions, this research develops a scalable synthesis strategy to produce an aminated cellulose xerogel under ambient environment, with an excellent structural stability (maximum compressive strength of 1.96 MPa) and exceptional adsorption capacities of for six PFAS (3.26 g/g HFPO-TrA, 1.82 g/g PFOA, 2.14 g/g HFPO-DA, 1.27

g/g PFHxA, 1.02 g/g PFBA and 1.01 g/g PFPrA), outperforming conventional adsorbents such as GAC and AER, even for short/ultra-short chain PFAS like PFBA and PFPrA. These are due to the combined effects of excellent mass transfer and abundant adsorption sites of our material. Micro-CT analysis reveals an anisotropic hierarchical pore structure with 84.96% connectivity, which supports the rapid PFAS diffusion and ensures effective adsorption site contact, thus preventing the pore blockage issues in conventional adsorbents. MD simulations reveal the interfacial energy contributions of van der Waals and Coulomb forces between xerogel and PFAS are major contributors to adsorption. Furthermore, our xerogel has excellent recyclability and retains 82-99% of its adsorption capacity after five cycles of regeneration, and can be reproduced towards the end of its life. The LCA quantifies the carbon footprint of short/ultra-short chain PFAS enrichment as 66.69-67.14 kg CO₂eq/kg PFAS. This is significantly lower than that of most carbon-based adsorbents (61.85-2,757.49 kg CO₂eq/kg PFAS), owing to the higher adsorption capacity of our xerogel. Overall, using renewable feedstocks, we develop a scalable fabrication technology to achieve superior PFAS enrichment. This offers a promising and sustainable way of tackling the environmental challenge posed by the emerging contaminant PFAS.

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Competing interests

The authors declare no competing interests.

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Wang, Qinyu; Chen, Zhonghao; Li, Xinrui; Wang, Kemeng; Wang, Ke ...

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