Supplemental file for:

Adsorption of trace perfluorooctanoic acid on corn stover-based lignin amine by synergy of electrostatic and hydrophobic interactions

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SUPPLEMENTARY NOTES

Supplementary Note 1 | The formulas of removal rate and adsorption capacity of PFOA by CSLA:

The removal rate of CSLA towards PFOA (R, %) and the mass of PFOA adsorbed by unit mass of CSLA at desired time (q_t, mg/g) and equilibration time (q_e, mg/g) were calculated according to the following equations (1–3):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

Where C_0, C_t and C_e (mg/L) denote the initial, immediate and final PFOA concentrations, respectively; V (L) stands for the volume of the PFOA solution used, and m (mg) presents the weight of CSLA.

Supplementary Note 2 | Measurement and analysis:

This study used scanning electron microscopy (SEM, Hitachi Regulus 8100, Japan) and energy dispersive X-Ray spectrometer (EDS, Ultim Max 65, UK) to observe the surface morphology and element weight ratio of CSLA; the element content analysis and valence state calibration of CSLA were performed by X-ray photoelectron spectroscopy (XPS, Thermo fisher Nexsa G2, USA); fourier transform infrared spectroscopy (FTIR, Thermo Fisher Scientific Nicolet iS5, USA) was used to evaluate types of surface functional groups and chemical bonds of CSLA in KBr flake; the surface potentials were determined by a Nano particle potential analyzer (Zetasizer Nano S90, Malvern, UK); thermal stability of CSLA was measured using thermal gravimetric analyzer (TGA, TA TGA 550, USA); the surface area and porosity analyzer (BET, Micromeritics 3FLEX, USA) was used to gauge the specific surface area of CSLA.

The concentration of PFOA in the solution was measured by High-Performance Liquid Chromatography Mass Spectrometry (U3000/TSQ quantum). The instrument test conditions of Liquid Chromatography are as follows: the mobile phase is 5 mmol/L ammonium acetate aqueous solution and acetonitrile (30:70, V/V); the injection volume is 1 μL; the column temperature is 40°C; the flow rate is 0.15

mL/min. The mass spectrometer used the anion mode HESI ion source. The scanning conditions were: the ion source temperature was 350°C; the ion source voltage was 3000 V, the ion transport tube temperature was 350°C; the sheath gas pressure was 35 bar; the auxiliary gas pressure was 10 bar.

SUPPLEMENTARY FIGURES

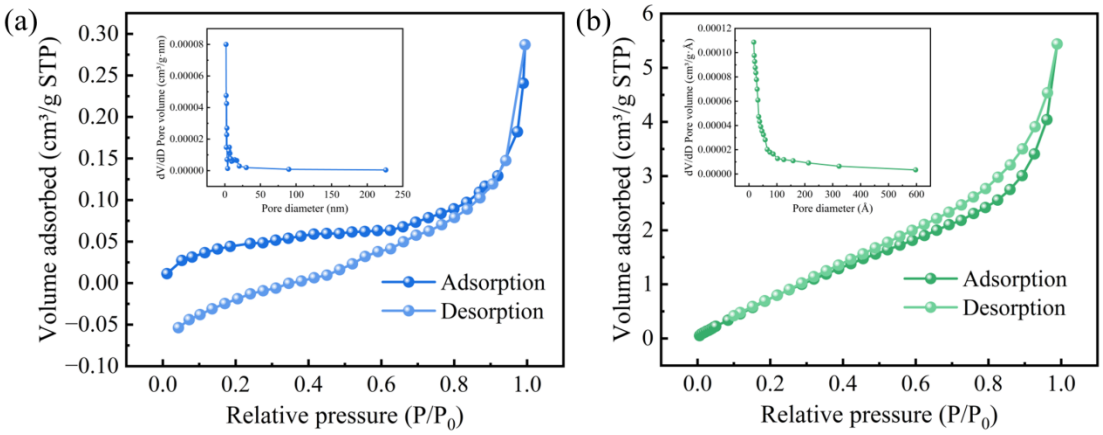

Fig. S1. The N_2 adsorption-desorption isotherms of (a) lignin and (b) CSLA.

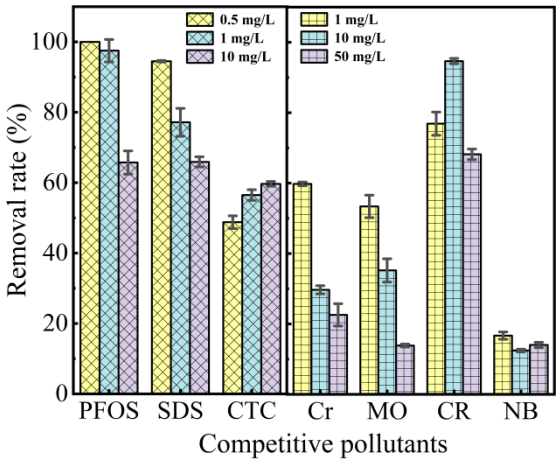

Fig. S2. Removal rate of competitive pollutants by CSLA

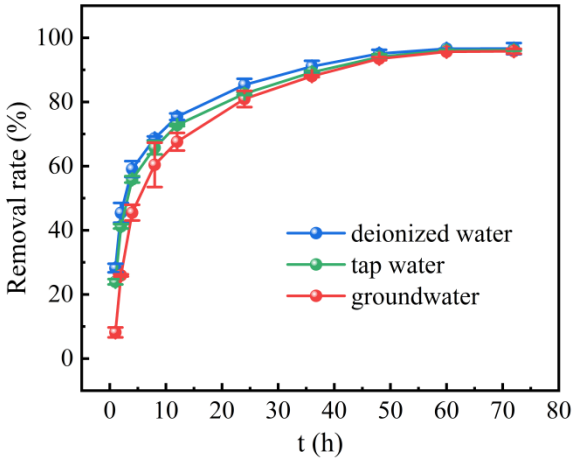

Fig. S3. The adsorption of PFOA on CSLA in actual water.

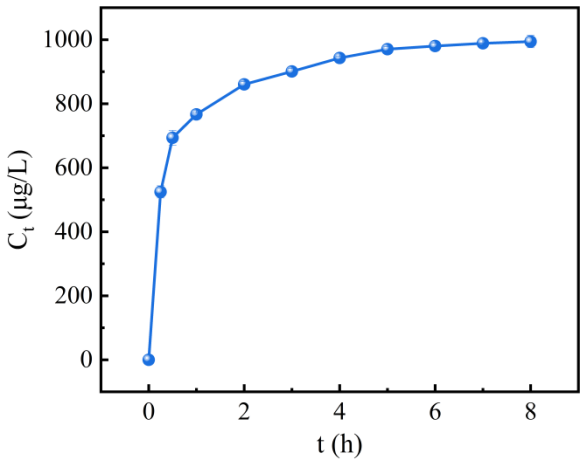

Fig. S4. Desorption efficiency experiment.

The react conditions of the adsorption test are: the initial concentration of PFOA was 1000 μg/L, the volume of PFOA solution was 50 mL, and the addition amount of CSLA was 5 mg. In order to obtain the desorption efficiency of PFOA by the mixed solution of 1% NaCl and 70% methanol, the adsorbed and dried CSLA was added to 50 mL mixed solution for desorption. The concentration of PFOA in the mixed solution was monitored during the desorption process, and it was found that the desorption equilibrium was reached after 6 h. The concentration of PFOA in the mixed solution at desorption equilibrium was 994.05 μg/L, and the desorption rate reached 99.41%, indicating that the mixed solution of 1% NaCl and 70% methanol has a good desorption effect on PFOA.

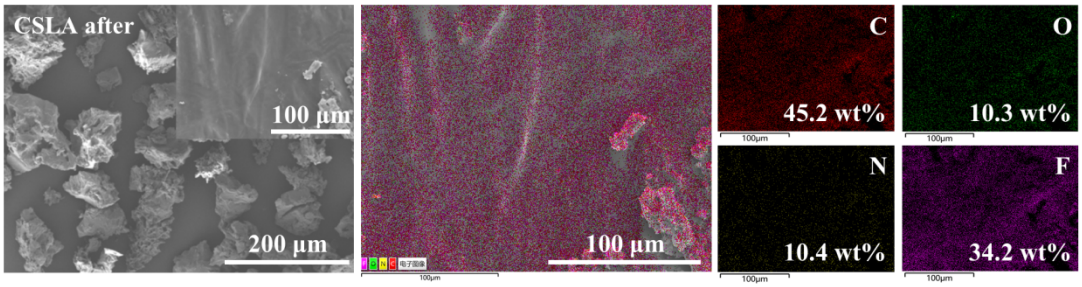

Fig. S5. The SEM-EDS images of PFOA adsorbed CSLA.

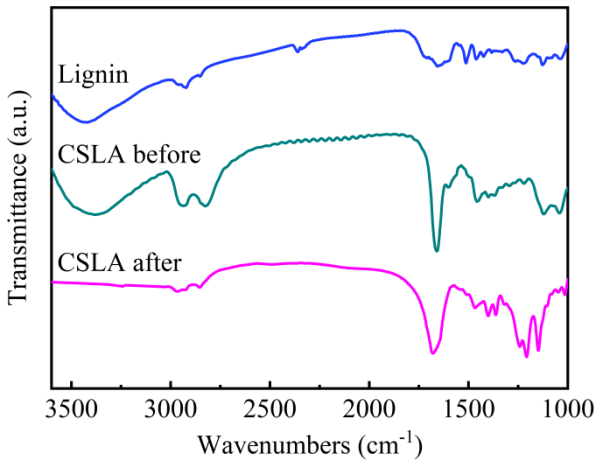

Fig. S6. Complete FTIR spectra of lignin and CSLA before and after adsorption of PFOA.

SUPPLEMENTARY TABLES

Table S1. Adsorption kinetic models.

Model	Nonlinear equation	Parameters
Pseudo-first-order	$q_t = q_e(1 - e^{-k_1 t})$	q_e and q_t (mg/g) are the adsorbed amount at an equilibrium concentration (C_e, mg/g) and a predetermined time (t, h) k_1 (h^{-1}) is the rate constants.
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	k_2 (g/(mg·h)) is the rate constants for the pseudo-second order.
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t)$	α (mg/(g·h)) is the initial rate constant, β (mg/g) is the desorption constant.
Intra-particle diffusion	$q_t = K_i t^{1/2} + C_i$	K_i (mg/(g·$h^{0.5}$)) is the adsorption rate constants of intra-particle diffusion model and C_i is the constant for film thickness of the intra-particle diffusion model.

79 Table S2. Adsorption isotherm models and adsorption thermodynamics equation.

Model	Nonlinear equation	Parameters
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	q_{max} (mg/g) is the maximum adsorption capacity of the adsorbent, q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the adsorbate concentration at equilibrium, K_L (L/mg) is the constant for the affinity between the adsorbate and the adsorbent.
Freundlich	$q_e = K_F C_e^{1/n}$	K_F (mg/g)·(L/mg)$^{1/n}$ is the Freundlich constant, n is a dimensionless Freundlich intensity parameter.
Adsorption thermodynamics	$\Delta G^0 = -RT \ln \frac{q_e}{C_e}$ $\Delta G^0 = \Delta H^0 - T\Delta S^0$	R is the universal gas constant (8.314 J/mol·K), T is the absolute temperature (K), q_e (mg/g) is the adsorption capacity at equilibrium, and C_e (mg/L) is the adsorbate concentration at equilibrium. The values of ΔS^0 and ΔH^0 were obtained from the intercept and slope of the line that was plotted by ΔG^0 versus T.

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81 Table S3. The parameters of adsorption kinetics models and intra-particle diffusion model.

Parameters	PFOA solution (μg/L)		
	250	500	1000
Pseudo first-order			
q_e (mg/g)	4.74	9.49	19.33
k_1 (h^{-1})	0.87	0.63	0.16
R^2	0.9175	0.9648	0.9387
Pseudo second-order			
q_e (mg/g)	4.91	9.91	20.16
k_1 (h^{-1})	0.32	0.10	0.01
R^2	0.9902	0.9764	0.9891
Elovich			
α (mg/(g·h)	10191.80	873.96	56.68
β	2.93	1.11	0.39
R^2	0.8154	0.7870	0.9627
Intra-particle diffusion			
K_1 (mg/(g·$h^{1/2}$))	1.04	3.55	6.29
C_1 (mg/g)	2.26	1.42	-0.56
R^2	0.8976	0.9751	0.9862
K_2 (mg/(g·$h^{1/2}$))	0.23	0.43	1.34
C_2 (mg/g)	3.81	7.67	10.04
R^2	0.9490	0.9905	0.9794
K_3 (mg/(g·$h^{1/2}$))	0.03	0.09	0.17
C_3 (mg/g)	4.60	8.98	17.87
R^2	0.9652	0.9830	0.9945

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Table S4. The parameters of adsorption isotherm models and adsorption thermodynamics.

	T	283 K	293 K	303 K
Langmuir	q_{max} (mg/g)	426.87	654.11	1018.10
	K_L (L/mg)	0.07	0.10	0.22
	R^2	0.9970	0.9942	0.9911
Freundlich	K_F (mg/g)(L/mg)$^{1/n}$	51.10	95.78	219.86
	n	1.93	1.99	2.02
	R^2	0.9941	0.9940	0.9881
Thermodynamics	ΔG^0 (kJ/mol)	-10.56	-15.08	-18.12
	ΔH^0 (kJ/mol)		96.22	
	ΔS^0 (kJ/(mol·K))		0.38	

85 Table S5. Concentrations of contaminants in CSLA leaching solution.

Samples	Mass concentration / $mg \cdot L^{-1}$	Standard / $mg \cdot L^{-1}$
Cl^-	0.05224	50[a]
Formaldehyde	0.07903	0.9[b]

86 a Category I standard of *Standard for groundwater quality* (GB/T 14848-2017)

87 b Standard limits for specific projects of centralized drinking water surface water sources of

88 *Environmental quality standards for surface water* (GB 3838-2002)

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Table S6. Comparison of PFOA adsorption on different adsorbents.

Material	C_0 (μg/L)	T (K)	pH	R (%)	q_e[a] (mg/g)	q_{max}[b] (mg/g)	Reference
calcium-based MOF	10	-	7.0	72.00	0.0038	0.061	[1]
MWNTs	100	297	6.5	65.00	0.00094	0.0035	[2]
Alumina	100	297	4.3	-	0.0049	0.014	[3]
Carbon nanotube sponge	100	297	-	75.00	1.52	-	[4]
Boehmite	200	297	7.0	-	0.027	0.19	[5]
AE-APTMS@ gFe_2O_3	1000	297	-	65.00	3.30	12.06	[6]
MOF (In_2O_3-400)	20000	297	4.6	-	25.45	-	[7]
CS_MBC	50000	297	3.5	63.42	158.55	517.00	[8]
PEI-PVC NF	100000	297	7.0	51.20	175.01	223.36	[9]
CSLA	250	293	6.0	99.03	4.95	654.11	This study
	500			99.31	9.93		
	1000			98.45	19.69		

a The q_e is the saturated adsorption capacity obtained from the adsorption kinetics experiment.

b The q_{max} is the maximum adsorption capacity of the material obtained by Langmuir model fitting in the adsorption isotherm experiment.

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