

Supporting Information

Amine-Site Accessibility and Low-Temperature Deep-Vacuum Regeneration of Biomass-Derived Porous Carbons for Direct Air Capture

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S1. Loading-dependent CO₂ breakthrough curves

Figure S1 presents the loading-dependent breakthrough profiles for the TEP and PEI series. The TEP series shows a progressive delay in breakthrough up to the 30-40% loading region, followed by little additional benefit at the highest loading. The PEI series shows a weaker loading benefit and earlier performance loss at higher nominal loading. These profiles complement the mean adsorption capacities reported in Figure 2 of the main text.

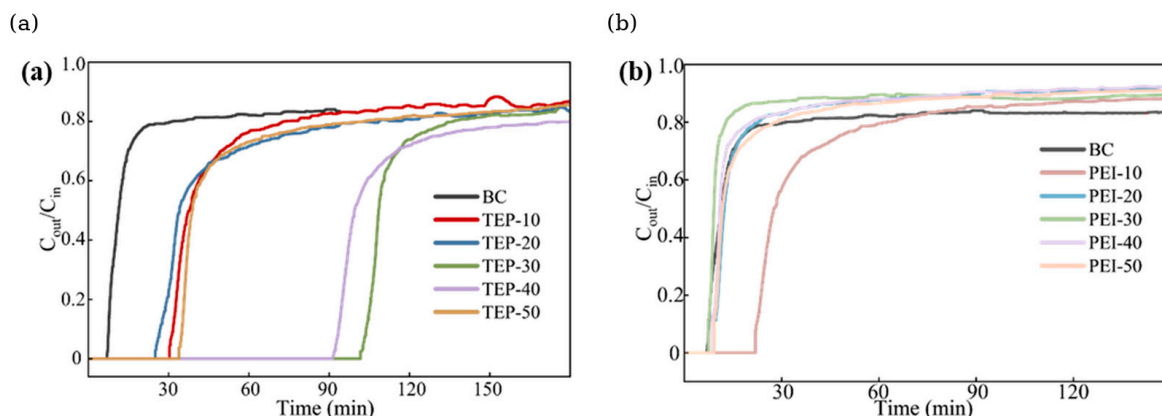


Figure S1. CO₂ breakthrough curves of amine-functionalized porous carbons at different loadings: (a) TEP series and (b) PEI series.

S2. Thermogravimetric validation of the TEPA loading

Thermogravimetric analysis (TGA) was performed for BC and TEP-30 as an independent mass-based check of the amine inventory. At approximately 120 °C, BC and TEP-30 retain 93.08% and 94.32% of their initial masses, respectively. The absence of additional low-temperature mass loss for TEP-30 relative to BC does not indicate a large selective TEPA-loss event during one short 110 °C conditioning step.

At 550 °C, the residual masses of BC and TEP-30 are 91.32% and 68.57%, respectively. The composite therefore shows 22.75 percentage points of additional mass loss relative to BC. Using the

BC residual to correct for support mass loss gives an apparent TEPA loading of approximately 24.9 wt%, reasonably consistent with the 22.58 wt% loading obtained independently from the nitrogen balance. Because support devolatilization and TEPA volatilization/decomposition overlap, this result is treated as semi-quantitative validation rather than an exact component-specific mass balance.

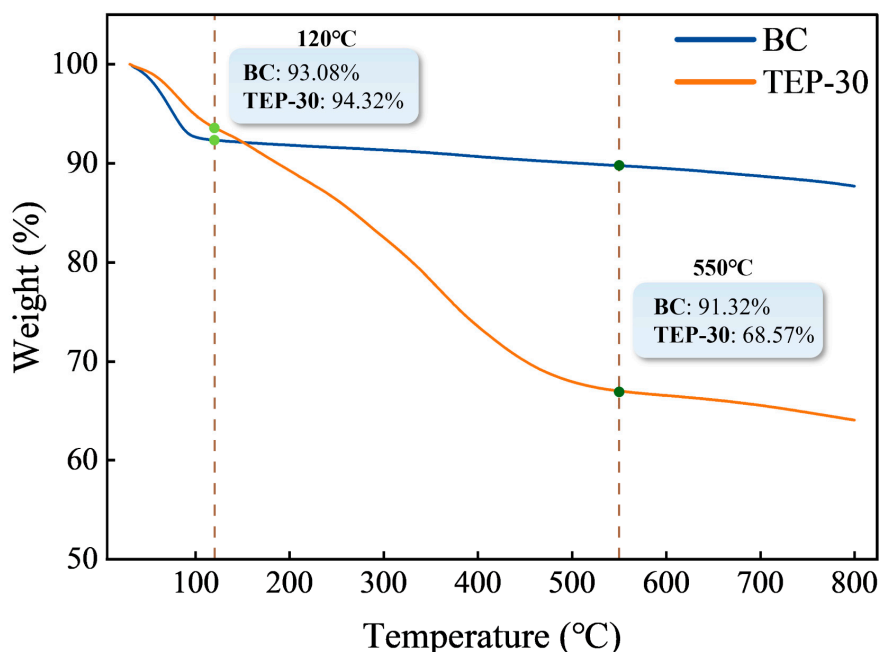


Figure S2. TGA curves of BC and TEP-30 used as an independent check of the TEPA inventory.

S3. Nitrogen-normalized CO₂ uptake

To avoid treating amine-mass-normalized uptake as a direct measurement of accessible reactive sites, the dynamic capacities were additionally normalized by the measured nitrogen content. TEP-30 gives approximately 0.063 mol CO₂ per mol N, compared with 0.0137 mol CO₂ per mol N for PEI-30. TEP-40 gives approximately 0.0558 mol CO₂ per mol N, compared with 0.00945 mol CO₂ per mol N for PEI-40. The nitrogen-normalized comparison therefore shows higher nitrogen-normalized uptake for the TEPA-containing samples under the present fixed-bed conditions without assigning a molecular adsorption stoichiometry.

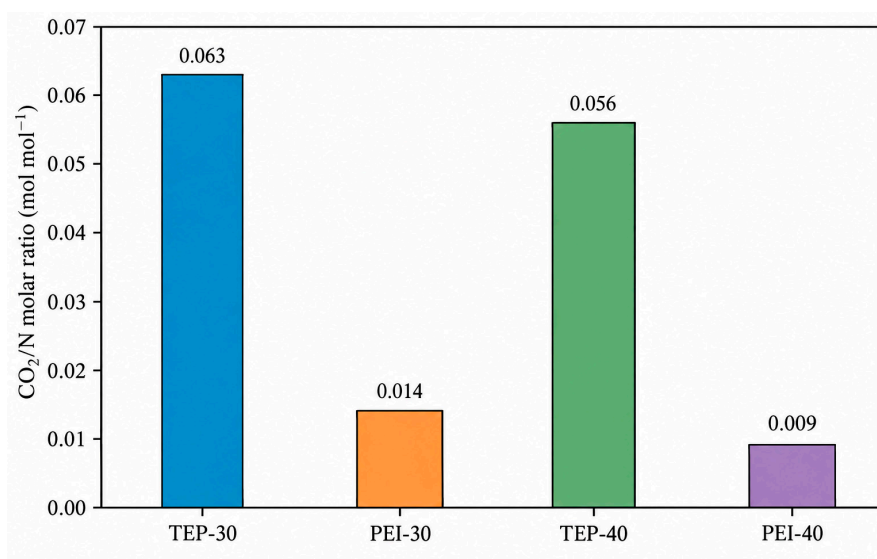


Figure S3. Nitrogen-normalized CO₂ uptake calculated from the measured nitrogen contents and dynamic adsorption capacities.

S4. Repeated humidity experiments

The humidity series was repeated for TEP-30 under 0%, 1.2%, 2.2%, and 3.2% H₂O. Among the tested conditions, 1.2% H₂O produced the longest breakthrough delay, while the benefit decreased at 2.2% and 3.2% H₂O.

The nonmonotonic response is consistent with a limited beneficial humidity window: modest hydration can increase the effective participation of the amine-containing phase, whereas larger water loading can occupy free volume and increase transport resistance in the confined amine phase (Zhang et al., 2017; Hua et al., 2024; Zhao et al., 2024; Holmes et al., 2023). The present data do not identify individual adsorbed species, so this explanation is treated as a reaction-transport interpretation rather than a confirmed molecular mechanism.

For the humidity comparison, condition-specific inlet CO₂ concentrations were used in the uptake calculation and all curves were integrated over the same 0-120 min interval after gas stabilization. The outlet gas passed through a moisture-drying unit before CO₂ analysis.

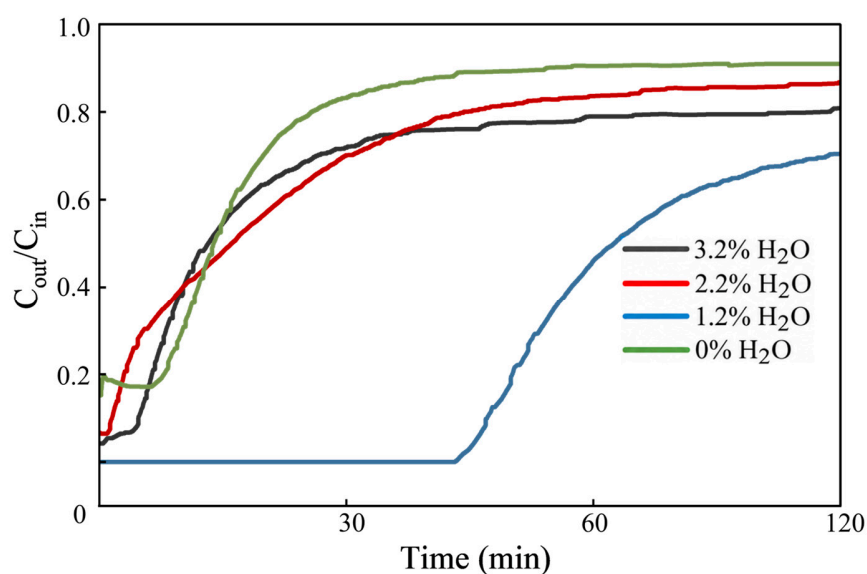


Figure S4. Breakthrough curves of TEP-30 at inlet H₂O concentrations of 0%, 1.2%, 2.2%, and 3.2%.

S5. Capacity-based cyclic functional retention

For TEP-30, capacity retention was used to quantify the loss or recovery of CO₂-capture function across regeneration cycles without equating capacity decline directly with physical amine mass loss. For repeated 110 °C regeneration, the capacity decreased from the initial 0.39 mmol g⁻¹ to 0.14, 0.11, and 0.09 mmol g⁻¹, corresponding to apparent retentions of approximately 36%, 28%, and 23%. Under 80 °C/500 Pa regeneration, the adsorption capacities were 0.18, 0.24, 0.25, and 0.20 mmol g⁻¹ over four cycles, corresponding to approximately 46%, 62%, 64%, and 51% of the 0.39 mmol g⁻¹ initial reference capacity.

The comparison supports improved short-term cyclic retention under 80 °C/500 Pa regeneration relative to repeated 110 °C treatment. Capacity retention is a functional metric and is not interpreted as direct physical amine retention.

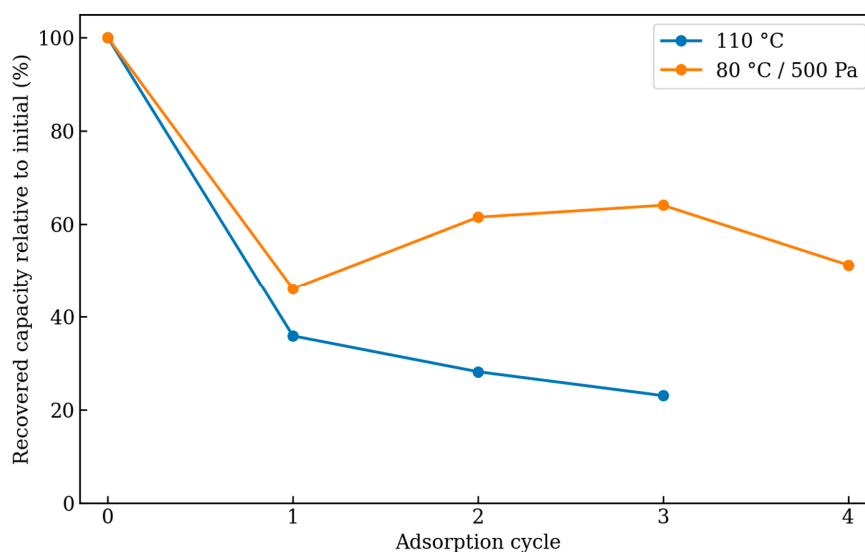


Figure S5. Capacity-based apparent functional retention of TEP-30 during repeated 110 °C regeneration and 80 °C/500 Pa regeneration.

S6. Experimental repeatability and uncertainty reporting

The adsorption-capacity measurements used for quantitative comparison were independently repeated three times using freshly prepared specimens. Figure 2 of the main text reports mean capacities with error bars, while the breakthrough profiles in Figure S1 are representative curves.

N₂ physisorption is used as structural characterization rather than as a repeated performance metric. Average pore size is treated as a model-derived mean descriptor of the N₂-accessible structure.

S7. Porous-carbon preparation and amine impregnation

The porous-carbon support was prepared as follows. Bamboo precursor was dried at 105 °C for 12 h, carbonized at 800 °C for 1 h under N₂ (100 mL min⁻¹; 5 °C min⁻¹), mixed with KOH at a char:KOH mass ratio of 1:1, and activated at 600 °C for 1 h under N₂ (10 °C min⁻¹).

For amine impregnation, TEPA or PEI was dissolved in 20 mL ethanol and stirred for 30 min, porous carbon was added at the target loading, and the suspension was stirred at 30 °C for 3 h. The product was vacuum-dried at 65 °C for 12 h.

S8. Fixed-bed configuration and gas handling

The fixed-bed adsorption system used a 1.00 g adsorbent charge in a 10 mm-ID pressure-rated column, giving an approximately 35 mm bed height. Gas flow was controlled by 0-500 mL min⁻¹ mass-flow controllers; N₂ was supplied at 200 mL min⁻¹ for pretreatment/regeneration and simulated air at 150 mL min⁻¹ for adsorption. Pressure was controlled by a downstream back-pressure regulator and monitored with a 0-0.6 MPa pressure transducer. Outlet CO₂ was measured by an NDIR analyzer (0-5000 ppm); zero and 500 ppm span checks were performed before each test series.

Dry simulated air was specified as 500 ppm CO₂, 20.9 vol% O₂, and balance N₂. Humidity was generated by wet/dry gas mixing at 30 °C to obtain 1.2%, 2.2%, and 3.2% H₂O. Each humidity setting was stabilized for 20 min before adsorption, and the humid outlet stream passed through the moisture dryer before CO₂ analysis.

S9. Calculation, characterization, and regeneration-metric definitions

Mass-flow-controller set points were treated as standard volumetric flow rates referenced to 25 °C and 101.325 kPa; therefore $V_m = 24.47 \text{ L mol}^{-1}$ was used on the same basis. The pressurized in-bed volumetric flow was not combined with a standard-state molar volume.

N₂ adsorption-desorption measurements were conducted at 77 K. BC was degassed at 300 °C for 6 h, whereas amine-loaded samples were degassed at 75 °C for 4 h to limit amine loss. BET area was obtained by multipoint BET analysis, micropore volume by the t-plot method, and pore-size distributions by an NLDFT carbon slit-pore model. TGA used approximately 5-10 mg sample heated from about 30 to 800 °C at 10 °C min⁻¹ under N₂.

Adsorption capacity denotes uptake in a given adsorption step; recovered adsorption capacity denotes uptake measured after regeneration; capacity retention is recovered capacity divided by the

initial capacity. The term regeneration efficiency is used only when a desorbed/adsorbed CO₂ ratio is explicitly calculated.

S10. Contextual literature comparison

Reported DAC capacities depend strongly on feed composition, humidity, temperature, amine loading, test mode, and regeneration protocol. Table S1 therefore provides operating context for representative sorbents and is intended for comparison of test conditions rather than performance ranking.

Table S1. Contextual comparison of representative DAC sorbents and test conditions. Current main-manuscript reference numbers are used where applicable; SI-only sources are identified by author and year. NR indicates information not reported in the cited summary.

Source	Sorbent	Amine/loading	CO ₂ feed	Humidity	T (°C)	Test mode	Capacity (mmol g ⁻¹)	Regeneration/cycling
Kulkarni et al. (2023)	Hierarchical silica	TEPA, 70 wt%	400 ppm CO ₂ /He	Dry; 50±3 % RH	30	Simulated DAC	5.20 dry; 5.88 humid	TSA; 10 cycles
Kulkarni et al. (2024)	Hierarchical silica	Aminosilane, 70 wt%	400 ppm CO ₂ /He; indoor air	Dry; 50±3 % RH	30	Simulated + indoor DAC	1.54 dry; 2.08 humid (HST-70)	TSA; 5 simulated-air + 10 indoor-air cycles
[14]	KOH-activated bamboo biochar	No amine; KOH/char 1:1	Ambient air	2.7% and 67.1% RH	Room T	Fixed-bed ambient DAC	0.0517	TSA at 70 °C; 50 humidity cycles
[15]	Activated carbon	TEPA, 70 wt%	DAC condition	NR	NR	Quick/complete capture modes	1.25	Economic/process comparison
[16]	Aminated activated-carbon paper	PEI; post-impregnated	400 ppm CO ₂	Dry in reported static uptake	20	Static + structured contactor	0.46	NR in abstract
Sujan et al. (2019)	Polymer/silica fiber	PEI-800	Ambient -air-level CO ₂	Dry and humid	Ambient	Breakthrough fiber module	NR in abstract	Vacuum-assisted desorption demonstrated

Darunte et al. (2016)	MIL-101(Cr)	TREN or PEI-800	Simulated air	Humidity examined	Ambient	DAC adsorption/cycling	Loading-dependent	Temperature-swing cycling; PEI more stable than TREN
This work	Bamboo-derived porous carbon	TEPA or PEI, 10-50 wt% nominal	500 ppm CO ₂ /simulated air	Dry; 1.2-3.2 vol% H ₂ O	30	Fixed-bed breakthrough	0.39 max dry (TEP-40)	Thermal/vacuum/coupled regeneration; subsequent regeneration tests used TEP-30

References cited only in the Supporting Information

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