

Adsorption Failure and Control Strategies of Hierarchical-Porous Biochar in Dynamic-Humidity Indoor Environments: A Mechanism-Directed Review and Adaptive Control Framework

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Abstract—Indoor adsorption filters operate under relative-humidity (RH) trajectories rather than under a single dry-state condition. This distinction is particularly consequential for hierarchical-porous biochar because its high-affinity micropores and polar surface sites can also serve as loci for water adsorption. The resulting performance loss is often described simply as competitive adsorption, although recent evidence indicates three separable processes: water competition at polar binding sites, confined-water clustering that restricts pore access and intraparticle diffusion, and adsorption – desorption hysteresis that makes a bed’s prior humidity exposure part of its functional state. This review evaluates these processes for volatile organic compounds (VOCs) and formaldehyde (HCHO) in indoor-air-relevant carbon adsorbents, with emphasis on activated biochar and related activated carbons. It synthesises humid co-feed experiments, water-vapour isotherms, fixed-bed breakthrough studies, and routine pore and elemental characterisation published principally from 2020 onward. The evidence shows that pore hierarchy does not itself confer humidity tolerance: ultramicroporosity may maximise dry adsorption potential yet increase sensitivity to confined water, whereas mesopore connectivity can improve access to adsorption domains without independently guaranteeing humid capacity. Surface oxygen, nitrogen functionality and readily obtained surface properties exert conditional effects that depend on target polarity and whether removal is physical capture or reactive transformation. Building on this evidence, the paper proposes a humidity-aware evaluation protocol and a laboratory-scale decision framework that couples material design, RH-path testing, regeneration diagnostics, and sensor-informed operation. The central conclusion is that credible claims of indoor durability require dynamic, mixed-pollutant, cycling evidence with water-state characterisation; dry equilibrium capacity and Brunauer – Emmett – Teller surface area are insufficient proxies for humid service performance.

Keywords—*hierarchical porous biochar, indoor air quality, water co-adsorption, volatile organic compounds, humidity-aware adsorption control*

I. INTRODUCTION

Indoor environments contain pollutant mixtures emitted from furnishings, coatings, cleaning products, combustion, occupant activities, and outdoor-air infiltration. Formaldehyde, aromatic hydrocarbons, oxygenated VOCs, terpenes, and fine particles can coexist while ventilation, source strength, temperature, and humidity change over hours or days [1] [2]. Such variability complicates the

interpretation of nominal filter capacity because the conditions used to create an adsorbent’s dry-state ranking often differ from the conditions experienced by a working indoor filter. Recent indoor-air reviews consistently identify humid, multicomponent operation and reliable regeneration as unresolved limitations of carbon-based purification systems [3] [4].

Biochar is attractive for this application because biomass-derived precursors can be converted into carbon materials with adjustable pore architecture, surface chemistry, and potentially favourable resource profiles. Conventional pyrolysis, activation, and simple nitrogen incorporation can produce a range of pores and surface sites. However, the design objective cannot be reduced to maximising surface area. In a humid airstream, water can occupy adsorption sites, form clusters within restricted voids, alter mass-transfer resistance, induce hysteresis, and influence both desorption and the capacity observed in subsequent cycles. The same polar surface groups that enhance dry uptake of a polar molecule may also increase water affinity. Consequently, a material that appears favourable in dry equilibrium measurements may show early breakthrough or slow uptake after a humidity excursion [5] [6].

This review addresses the following question: how do hierarchical-porous biochar materials lose adsorption function under dynamic humidity, and which material and operational controls are technically defensible? The analysis is deliberately bounded to gaseous VOC and HCHO removal by carbonaceous sorbents in indoor-air-relevant contexts. It distinguishes biochar, activated biochar, and activated carbon where the cited evidence permits, while drawing cautiously on activated-carbon studies to elucidate pore-scale water-adsorbate processes. Particulate filtration, biological aerosol removal, and stand-alone photocatalytic devices are outside the principal scope, except where hybrid designs clarify a control requirement.

The paper is organised as a mechanism-directed review rather than as an experimental research article. Section 2 establishes an evidence framework and reviews the physical origins of humidity-driven failure. Section 3 evaluates pore hierarchy and surface chemistry as conditional design levers. Section 4 develops a reproducible dynamic-humidity evaluation protocol. Section 5 discusses material, regeneration, and system-control strategies. Section 6 defines limitations and a translation agenda. The figures are conceptual syntheses derived from the cited evidence; the

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tables are editable reporting frameworks and do not contain fabricated experimental results.

II. EVIDENCE FRAMEWORK AND FAILURE PHYSICS

A. Why a single RH value is an incomplete description of adsorbent state

A stated RH value is necessary but insufficient to describe a carbon bed because adsorption and desorption pathways can differ. Water-vapour sorption experiments on granular activated carbon and activated carbon fibre showed that the observed hysteresis depended on adsorbent properties and temperature; the authors attributed the hysteresis primarily to hydrogen-bonded cluster formation, cluster-induced micropore filling, and kinetically restricted rearrangement of confined water [7]. Therefore, a bed conditioned from dry air to 60% RH is not necessarily equivalent to a bed returned to 60% RH after a high-humidity excursion. This distinction is central to indoor environments, where the relevant input is a time-dependent RH history rather than a constant laboratory set point.

The literature uses the term pore condensation in some high-humidity carbon studies. That description should not be transferred uncritically across carbon materials. In narrow pores, water aggregation, cooperative filling, and mobility restrictions can produce behaviour that differs from classical capillary condensation in larger mesopores. A rigorous manuscript should consequently report adsorption and desorption branches of water-vapour isotherms, the temperature, the preconditioning sequence, and the pore-size distribution before assigning a mechanistic label [7] [8]. Figure 1 summarises this state-dependent failure pathway.

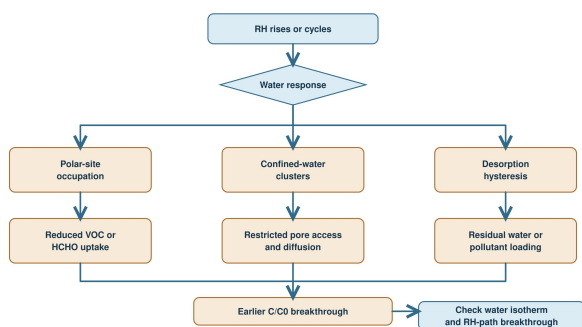


Fig. 1. Humidity-driven adsorption-failure state map for hierarchical porous carbon. The figure is a conceptual synthesis of humid co-adsorption, breakthrough, and water-isotherm evidence [5] [7] [8]. Cluster-induced confined-water filling should not automatically be interpreted as classical capillary condensation.

B. Competitive site occupation

The first failure route is local competition for polar surface sites. A study combining adsorption tests with mechanistic interpretation of HCHO capture by oxygen-rich activated carbons found that water co-adsorption could impede HCHO removal through strong interactions between water and oxygen-containing surface groups, particularly carboxyl-associated sites [8]. This finding does not mean that oxygen functionality is intrinsically detrimental. Oxygenated groups can improve low-pressure interaction with polar adsorbates, but their net benefit is contingent on target polarity, water activity, and the accessibility of the affected sites. The appropriate inference is a dry-state affinity versus humid-state selectivity trade-off, not a universal design rule.

For weakly polar aromatic VOCs, lowering surface oxygen content through conventional preparation and selection of lower-polarity surfaces can improve humid performance in specified adsorbent–pollutant systems. In one controlled study, the authors varied activated-carbon surface polarity while maintaining broadly similar pore properties and demonstrated polarity-dependent competition between water vapour and VOCs [9]. A reported modified activated carbon showed improved selectivity and reuse in a dynamic multicomponent water/VOC challenge [5]; routine preparation should instead prioritise conventional activation and direct humid testing. These results support screening surface polarity as a control lever for selected VOCs; they do not establish that a low-polarity surface is optimal for polar VOCs or reactive HCHO media.

C. Confined-water clustering, pore blockage, and transport limitation

The second failure route is volumetric and kinetic. Water does not merely replace an organic molecule at an isolated site. Under increasing humidity, hydrogen-bonded water clusters can occupy restricted pore volumes and pore mouths, decreasing the accessibility of high-affinity domains and increasing diffusion resistance. Studies of humid toluene adsorption on nitrogen-doped porous biochar reported that greater micropore abundance could slow mass transfer when water was present [10]. HCHO adsorption measurements were interpreted as showing that water clusters can block ultramicropores, while excessively large mesopores lack sufficient confinement for efficient adsorption [11].

These observations motivate a pore-accessibility criterion. The relevant question is not whether a material has the greatest total micropore volume but whether its pore geometry admits the target molecule, resists persistent water occupation, and retains a continuous route for diffusion during RH transients. A study including humid adsorption experiments of toluene under 70% RH identified an optimal slit-pore range near 1.0 nm for the carbon surface examined [12]. This is useful as a bounded hypothesis, not a universal pore-size prescription: the optimum is expected to shift with the target molecule, surface oxidation state, temperature, and RH trajectory.

D. Hysteresis and regeneration-associated memory

The third failure route is history-dependent. If water desorption lags water uptake, a regenerated or dried bed may retain a different distribution of water and pollutants than a pristine bed. Short-cycle studies have documented an initial reuse penalty followed by comparatively more stable later cycles under the reported regeneration conditions [13]. A study of VOC-loaded activated carbon reported residual loading in microporous domains after regeneration, often described as a loading heel [14]; future work can verify its extent with conventional thermal or humid-air cycles. These observations have two implications. First, recovery measured after one cycle should not be equated with durable service life. Second, regeneration must be assessed not only by recovered uptake but also by residual pollutant loading, pressure-drop change, energy demand, and the fate of desorbed compounds. Table I summarises the five failure modes, their evidence boundaries, and routine diagnostic measurements.

TABLE I. EVIDENCE MAP FOR HUMIDITY-DRIVEN ADSORPTION FAILURE

Failure mode	Evidence-supported interpretation	Appropriate boundary statement	Minimum diagnostic measurement
Polar-site competition	Water can bind strongly to oxygenated carbon sites and reduce access of HCHO or polar VOCs to those sites.	Applies to the tested surface chemistry, target, and RH history; it is not a universal penalty of oxygen groups.	Bulk elemental analysis, O/N water isotherm, humid fixed-bed C/C ₀ .
Confined-water clustering	Water clusters can fill or restrict microporous regions and slow VOC access.	Do not equate every humidity effect with simple site replacement or classical capillary condensation.	Adsorption and desorption water-vapour branches, pore-size distribution, humid uptake kinetics.
Transport limitation	Water-affected pore entrances and high micropore fractions can increase intraparticle mass-transfer resistance.	A high dry micropore volume does not by itself demonstrate humid dynamic performance.	Full C/C ₀ curve, simple breakthrough-time comparison, RH-path test.
Hysteretic state	Identical nominal RH values may correspond to different water distributions after different conditioning paths.	RH must be reported with its prior path, duration, and temperature.	Dry-to-humid, humid-to-dry, and RH-cycled preconditioning tests.
Regeneration heel	Residual pollutant or water can alter later cycles even when short-term capacity appears partly recovered.	A few cycles are screening evidence, not proof of long-term durability.	Cycle-by-cycle C/C ₀ curves, desorbed VOC monitoring, and basic post-cycle checks.

III. HIERARCHICAL PORES AND SURFACE CHEMISTRY UNDER HUMIDITY

A. Pore hierarchy is a division of functions

Hierarchical design should be viewed as a division of functions rather than a requirement to maximise each pore class. Micropores provide confinement and much of the adsorption potential at low partial pressure. Mesopores can expose those domains more rapidly and reduce intraparticle resistance. Macropores and interparticle voids are physically plausible contributors to flow distribution and pressure-drop management, particularly in monoliths and pleated media. However, the direct humid VOC/HCHO literature has not yet isolated a universal quantitative macropore effect. Accordingly, macropore connectivity should be presented as a transport-design hypothesis requiring direct pressure-drop and residence-time validation rather than as a demonstrated performance guarantee.

A food-waste-derived nitrogen-doped biochar study linked pore development in a nitrogen-doped carbon to precursor composition and treatment conditions; the resulting hierarchy was associated with toluene-removal behaviour [15]. This supports screening accessible pore structures

obtained through ordinary pyrolysis, activation, and simple nitrogen doping. A microwave-prepared carbon report [16] and a carbon-silica composite report [17] illustrate relationships between porosity, surface properties, and dynamic VOC uptake; future work can verify these relationships using conventionally prepared biochars and routine fixed-bed tests. Together, these reports support the need to characterise both structure and dynamic behaviour; these studies do not justify reducing humid performance to a single BET surface-area value. Figure 2 maps the distinct functions of macro-, meso-, and micropores and their response to humid air.

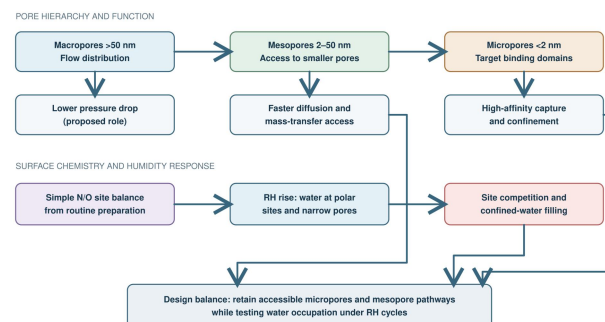


Fig. 2. Pore-function and water-response map for hierarchical porous biochar. Micropores, mesopores, and macropores are assigned distinct functions. The macropore role is a proposed transport-design hypothesis; the micro- and mesopore roles are supported by the cited adsorption and structural studies [10] [11] [15] [17].

B. Surface functionality creates target-dependent trade-offs

Surface chemistry determines whether water, the pollutant, or a reaction intermediate is preferentially stabilised. Oxygen-containing groups may increase low-pressure uptake of polar molecules, yet can also favour water sorption; the effect of oxygen-rich porous carbon on VOC adsorption is correspondingly concentration- and target-dependent [18]. Simple nitrogen incorporation can alter HCHO interactions; reports on resin-derived and polyamine-bearing carbons indicate additional target-dependent processes that should not be assumed for routinely prepared biochar [19] [20] [21]. Where transformation is claimed, parent-compound loss is insufficient evidence of safe removal. Conventional inlet/outlet sampling and a simple carbon balance can screen for possible transformation; claims of a specific reaction pathway require separate verification.

Hydrophobic surface treatments offer a different trade-off. A reported alkylated biochar improved humid VOC adsorption in the studied system [22], but this specialised treatment is not required for a routine screening protocol; future work can verify the surface-polarity effect with conventionally activated biochar and humid breakthrough tests. A separately modified hierarchical carbon improved humid toluene uptake in its test configuration [23]; future work can verify transferability with conventionally prepared samples. These results justify the design proposition of a lower-polarity surface for weakly polar VOCs. They do not justify applying the same surface preference to HCHO, alcohols, or other polar targets without co-fed tests.

C. A conditional design landscape

The material-design objective can be expressed as a three-way balance among adsorption potential, humid accessibility, and transport. Fine pores may offer high

confinement but be vulnerable to water occupancy. Larger micropores may retain confinement while providing more accessible channels. Mesopores can buffer access and support mass transfer, while excessive mesoporosity may reduce confinement at low concentration. Surface polarity adds another axis: polar sites can strengthen a target interaction but also stabilise water. The resulting design landscape is material- and target-specific. Table II compares these pore and surface-chemistry design levers with their principal uncertainties.

TABLE II. HIERARCHY AND SURFACE-CHEMISTRY DESIGN MATRIX

Design lever	Evidence-supported role	Main uncertainty	Humidity-aware design rule
Ultramicropores and small micropores	Provide confined adsorption domains but can become water-sensitive.	No universal lower pore-width threshold is supported.	Match molecular access and test water-affected accessibility instead of maximising total micropore volume.
Larger micropores	Can retain confinement while reducing water-cluster blockage in particular HCHO and aromatic-VOC systems.	Reported optima depend on target, RH, and surface chemistry.	Treat any optimum as target-, chemistry-, and RH-specific.
Mesopores	Facilitate access and may increase uptake rate.	Mesopores alone do not guarantee higher humid equilibrium capacity.	Verify with kinetics and fixed-bed mass-transfer behaviour.
Macropores and voids	May improve flow distribution and pressure drop in simple packed beds.	Quantitative humid-VOC evidence remains sparse.	Measure pressure drop and flow; treat the benefit as a hypothesis until tested.
Oxygen-containing groups	Can promote polar-molecule interactions but often increase water affinity.	Net effect varies with group type and target polarity.	Use humid co-feed data rather than dry adsorption energy alone.
Nitrogen and amine sites	Simple nitrogen doping can change HCHO interactions.	Reactive capture specialised in materials does not establish behaviour in routine biochar.	Compare humid HCHO C/C ₀ outlet products before claiming reaction.
Surface polarity selection	Lower polarity can improve selected aromatic VOC cases under humidity.	May reduce useful polar-site density.	Compare routinely prepared carbons across representative targets and RH paths.

IV. FROM MATERIAL DESCRIPTORS TO DYNAMIC-HUMIDITY EVALUATION

A. Evidence standard for a humidity-resilient claim

A claim of humidity resilience should be stronger than a dry isotherm plus a single humid endpoint. The minimum evidence package should include: (i) BET surface area and a reported pore-size distribution; (ii) elemental analysis for bulk O/N content; (iii) water-vapour adsorption and desorption branches; (iv) controlled fixed-bed breakthrough under defined RH; and (v) post-cycle capacity and basic pore/elemental characterisation. Contact angle can supplement water-vapour measurements but cannot substitute for them because it probes a macroscopic liquid interface rather than confined vapour adsorption.

Testing must record the material and bed state completely. Essential variables include precursor, activation route, particle size or simple bed geometry, sorbent mass, bed depth, gas flow, superficial velocity or empty-bed contact time, temperature, inlet pollutant concentration, co-contaminants, RH, RH sensor location, conditioning duration, and breakthrough definition. A result reported only as “high-humidity performance” is not comparable unless the RH path and bed geometry are specified. Dynamic filter studies of indoor carbon-based filters reinforce the importance of pollutant mixture, inlet concentration, velocity, particle size, and bed thickness for breakthrough behaviour [24].

B. A protocol based on RH paths instead of fixed points

A robust protocol should include a dry baseline, an RH-up step, an RH-down step, and at least one RH-cycling sequence. The humid stress point should be selected relative to the intended application, not merely chosen for convenience. Single compounds are useful for mechanistic diagnosis, but mixed challenges are required before asserting indoor applicability because water competition varies across aromatic, oxygenated, carbonyl, and terpene VOCs. The source stream should explicitly identify whether formaldehyde, toluene, limonene, alcohols, or a defined mixture is used.

The core output should be the complete normalised breakthrough curve, C/C₀, not an isolated terminal capacity. Predefined endpoints such as t₁₀, t₅₀, or t₉₀ can be reported when the concentration threshold is stated. The analysis should also retain pressure drop, water uptake or desorption where feasible, and an uncertainty estimate based on independent replicate beds. The protocol should not claim an experimental result until those measurements have actually been made. Figure 3 sets out the corresponding RH-path test sequence and minimum laboratory data package.

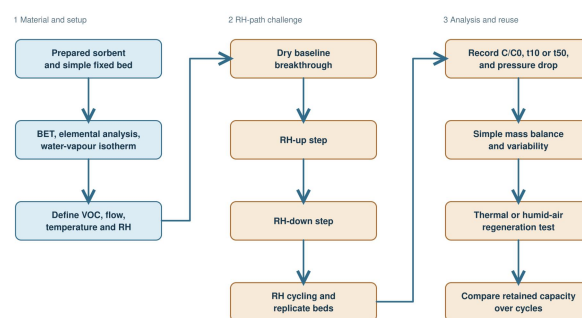


Fig. 3. Dynamic-humidity evaluation protocol and minimum data package. This figure is a proposed experimental framework. It does not represent completed experiments or a validated device benchmark.

C. Data processing and model validation

Model use is most defensible when it is attached to observable mechanisms. Simple mass balances and complete C/C₀ breakthrough curves should be analysed separately under dry and defined humid conditions. Compare measured breakthrough time and integrated uptake over RH-up and RH-down tests without fitting an unverified multivariable service-life model. Published dynamic filter work illustrates why reversibility matters under changing inlet concentrations [25]; future work can verify this behaviour with conventional fixed-bed experiments.

The purpose of data analysis is not to create an artificially precise service-life number from incomplete inputs. Instead, it should identify when the filter has entered a state in which humidity, pollutant loading, or flow conditions make a pre-specified control action appropriate. A reproducible study should report the breakthrough threshold, integration interval, replicate variability, and the observed response to stated RH, airflow, and inlet-concentration changes. Table III consolidates the test conditions, interpretation limits, regeneration checks, and control inputs.

TABLE III. DYNAMIC-HUMIDITY TEST AND CONTROL SPECIFICATION

Item	Required report or experiment	Interpretation permitted	Interpretation not permitted
Bed and gas conditions	Mass, dimensions, media geometry, flow, velocity or EBCT, temperature, carrier gas, inlet concentration, RH, and RH measurement location.	Comparison across fully defined operating states.	Indoor applicability inferred from an incomplete dry isotherm.
Humidity protocol	RH matrix, humid stress condition, adsorption and desorption RH paths, and preconditioning history.	Identification of RH- and path-specific performance.	A single nominal RH as a complete definition of water state.
Challenge chemistry	Single targets followed by relevant mixtures; explicit target polarity and concentration.	Target-specific selectivity and failure analysis.	Transfer of one-VOC performance to all indoor mixtures.
Dynamic endpoints	Full C/C ₀ curves, predeclared breakthrough threshold, uptake/time, ΔP , and uncertainty estimate.	Dynamic capacity and mass-transfer comparison.	Ranking by BET area or static capacity alone.

Item	Required report or experiment	Interpretation permitted	Interpretation not permitted
Cycling and regeneration	Per-cycle capacity, thermal or humid-air regeneration conditions, treatment time or energy, retained loading, and basic post-cycle checks.	Short-term recovery and failure-mode screening.	Long-term durability or safe regeneration from a few cycles.
Control inputs	Ordinary inlet/outlet VOC readings, RH and temperature; measured flow and pressure drop where available.	A laboratory decision rule based on stated C/C ₀ and RH thresholds.	Universal thresholds or safety assurance from a low-cost total-VOC proxy alone.

V. CONTROL STRATEGIES ACROSS THE FILTER LIFE CYCLE

A. Material-level controls

The evidence supports three practical material-level strategies, each with a defined caveat. First, choosing a less polar surface can reduce water competition for selected non-polar or weakly polar VOCs; specialised treatments reported in the literature require conventional laboratory verification [5] [22] [23]. Second, a controlled population of accessible larger micropores may preserve confinement while avoiding the most severe water-cluster restriction observed in ultramicroporous domains [11] [12]. Third, connected mesopores may shorten intraparticle diffusion paths. These three strategies can be compared with ordinary pyrolysis or activation batches and fixed-bed humid breakthrough tests before any more elaborate architecture is considered.

The choice of control must begin with pollutant chemistry. A hydrophobic aromatic-VOC filter may underperform for HCHO if it removes the polar or reactive sites responsible for HCHO interaction. Conversely, a highly polar HCHO sorbent may exhibit rapid humid deactivation if water occupies the same functional domains. A rational material programme therefore screens at least one weakly polar aromatic, one oxygenated VOC, and HCHO where the intended application requires broad-spectrum control. It also differentiates between physical adsorption and chemical transformation.

B. Regeneration as a compound-specific operation

Regeneration is not a generic reset. Humid, VOC-free air enhanced in situ toluene desorption from activated-carbon filter media in one indoor-relevant study, while limonene responded differently under the same general concept [26]. This contrast demonstrates that humidity can be both a disturbance during adsorption and a possible off-line desorption actuator. It also underscores the risk of downstream rebound if regenerated compounds are not contained or treated.

Conventional low-temperature thermal and VOC-free humid-air regeneration should be compared by recovered capacity, retained capacity over repeated cycles, energy or treatment time, pressure-drop change, and capture of desorbed VOCs. A specialised regeneration study reported residual micropore loading [14]; future work can verify this observation with conventional laboratory cycles. Humid-air regeneration and formaldehyde-adsorbent thermal-treatment

studies support short-cycle comparison with thermal treatment but do not demonstrate multi-month indoor lifetime [13] [27]. A responsible deployment claim should therefore specify the number of cycles tested and avoid extrapolating an early-cycle recovery ratio into a lifetime estimate.

C. Humidity-aware sensing and adaptive operation

Fixed calendar replacement is poorly matched to a filter whose adsorption state depends on pollutant load, humidity history, temperature, and airflow. Figure 4 proposes a laboratory-scale decision rule using ordinary temperature/RH probes and inlet/outlet VOC readings, with measured flow and pressure drop where available. Predefined C/C₀ and RH thresholds can prompt continued operation, inspection or replacement, or an independently tested off-line thermal or humid-air regeneration cycle.

An industrial sensor-management study illustrates the potential value of monitoring while also showing drift, cross-sensitivity, and dependence on operating conditions [28]. Those lessons are relevant to indoor biochar filters, but the operating thresholds cannot simply be transferred from industrial exhaust to occupied buildings. Low-cost VOC readings should be treated as comparative proxies, checked periodically against a standard measurement where available, and interpreted alongside RH and temperature. Mixture-specific thresholds require validation before use outside the laboratory.

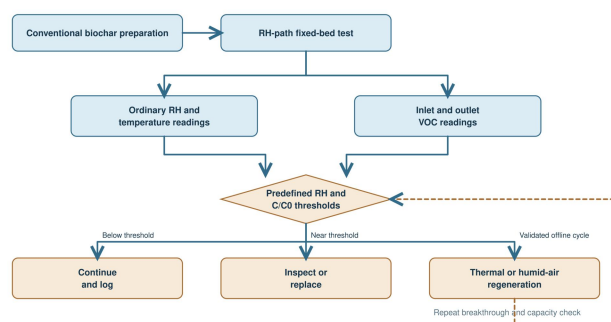


Fig. 4. Proposed humidity-aware control architecture for hierarchical-biochar filters. The system integrates material design, RH-path testing, failure diagnosis, adaptive operation, and multi-cycle validation. It is a proposed framework that requires target-device calibration and chemical-specific field validation.

D. Hybrid adsorption–oxidation systems

Hybrid systems may address the saturation limitation of adsorption, but they introduce a stricter evidence requirement. An adsorbent can concentrate pollutants near photoactive or catalytic sites; however, a reduction in the parent VOC does not establish complete mineralisation or absence of harmful intermediates. Non-carbon indoor filters that combine adsorption and photocatalytic destruction provide useful adjacent evidence for the architecture, but they should not be cited as proof of carbon/biochar performance [29]. Future work can first verify such coupling in a simple bench test with inlet/outlet VOC measurements and readily measurable byproducts; broader oxidation or safety claims require separate product analysis and energy accounting.

E. Sustainability and scale-up

Biochar’s potential resource advantages do not eliminate the value of a transparent bench-scale comparison. At a

minimum, report precursor and activation inputs, heating and washing steps, measured pressure drop, regeneration time or energy, and replacement frequency for the tested media. Published life-cycle comparisons between biomass-derived biochar and activated carbon are informative at the material-production level, but they do not by themselves answer which filter delivers a defined clean-air duty with the lowest impact [30]. A feasible screening basis is VOC mass captured before a defined breakthrough point per mass of prepared sorbent, accompanied by simple input and energy records; a full service-level assessment can follow when reliable field data become available.

VI. DISCUSSION, LIMITATIONS, AND TRANSLATION AGENDA

The principal contribution of this review is to reframe humidity tolerance as a coupled material–state–operation problem. The reviewed evidence makes clear that hierarchical porosity is not inherently protective. A material can possess a desirable dry pore-size distribution and still fail under humidity because water changes both energetic selectivity and pore accessibility. Conversely, humidity may support a specified regeneration operation or a material-specific reactive pathway. These apparently contradictory observations are not inconsistent; they reflect different adsorbates, surface chemistries, RH histories, and performance definitions.

The review also identifies an evidence imbalance. Many reports provide dry isotherms, BET area, or a single humid capacity, whereas fewer provide RH-up/RH-down water isotherms, full fixed-bed curves under controlled humidity, representative mixtures, and post-cycle characterisation. The field requires less reliance on generic claims that “higher surface area” or “more micropores” improve indoor adsorption. It requires more explicit reporting of the conditions under which the measured advantage appeared and the material state after humidity cycling.

Three limitations delimit this manuscript. First, the primary evidence base includes activated carbons as well as activated biochars. Activated carbon is used here to elucidate pore-scale mechanisms, not as evidence that every biochar behaves identically. Second, several mechanistic papers apply high-RH or single-pollutant stress conditions. Their findings are useful for causal analysis but should not be translated directly into occupied-building service life. Third, mechanistic explanations inferred from the literature remain provisional until conventional RH-path water-isotherm and fixed-bed tests verify their relevance to the particular biochar.

A practical research agenda follows. Future experiments should couple water-vapour adsorption/desorption branches to RH-path fixed-bed challenges. They should include low-concentration, dynamic emissions; representative mixtures; airflow variation; multi-cycle regeneration; pressure-drop tracking; and post-aging structural and chemical characterisation. Simple mass balances and C/C₀ curves should be compared across measured RH trajectories. Laboratory control can use ordinary temperature/RH and VOC readings with stated decision thresholds. A transparent bench-scale comparison of preparation inputs, energy, pressure drop, and captured VOC can guide later service-level assessment.

VII. CONCLUSION

Hierarchical-porous biochar can be a promising platform for indoor gaseous-pollutant control, but performance under dynamic humidity cannot be inferred from dry capacity, surface area, or pore volume alone. The evidence supports three distinct humidity-driven failure mechanisms: competition at polar sites, confined-water clustering that blocks pore access and slows diffusion, and hysteresis that makes humidity history part of the sorbent state. Pore hierarchy and surface chemistry provide useful control levers, but their benefits are conditional on target polarity, RH path, and whether removal is physical capture or reactive transformation.

The most defensible strategy is therefore an integrated one: design accessible micropores and connected mesopores, control surface polarity with the target mixture in mind, evaluate beds over RH paths rather than a single RH point, quantify regeneration-associated residual loading, and operate filters with humidity-aware monitoring. The proposed protocol and laboratory-scale decision framework provide a transparent basis for future experiments. Claims of durable indoor performance should await validation in mixed-pollutant, low-concentration, cycling, and representative indoor conditions.

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COMPETING INTERESTS

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