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## Research Article

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# Citrate-Regulated Fe(III)-Tannic Acid Assembly for Processable and Recoverable Self-Bonding Fiberboards

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Abstract Conventional fiberboards rely on synthetic resin adhesives that can limit material recovery and raise formaldehyde and volatile organic compound (VOC) concerns. Dynamic metal-polyphenol networks offer an adhesive-free route, but Fe(III)-tannic acid systems are difficult to process because strong coordination can trigger premature aggregation before the network reaches fiber interfaces. Here, we investigate a citrate-containing Fe(III)-tannic acid formulation for self-bonding fiberboards. KOH/TEMPO activation increased fiber carboxylate content from 0.202 to 0.657 mmol g<sup>-1</sup>, and citrate maintained low-turbidity precursors at pH 2.4-2.8, whereas the no-citric-acid control aggregated strongly. Across density-matched P0, P1, P2, P2a, and P3 boards, Full boards reached 44.2 MPa modulus of rupture (MOR) and 1.200 MPa internal bond strength (IB), exceeding both No-CA controls (33.5 MPa and 0.830 MPa) and CA-only controls (35.0 MPa and 0.950 MPa). Full boards also reduced 24 h thickness swelling to 13.2%, compared with 20.8% for No-CA and 20.0% for CA-only boards. Full boards showed lower total volatile organic compound (TVOC) emissions than No-CA controls (126 vs 247 μg m<sup>-3</sup>) and lower 336 h Fe release in the leaching screen (0.810 vs 2.860 mg L<sup>-1</sup>); both Fe(III)-tannic acid groups were below the commercial urea-formaldehyde high-density fiberboard (UF-HDF) comparator for formaldehyde in the same audit. Interfacial characterization and recovery tests defined mechanistic and recovery boundaries, while screening inventory data identified likely hotspots without making a comparative life-cycle assessment (LCA) claim. These results frame citrate-containing Fe(III)-tannic acid chemistry as a controllable assembly and disassembly strategy for recoverable self-bonding fiberboards.

**Keywords** Cellulose fiberboard; Metal-polyphenol network; Tannic acid; Citric acid; Self-bonding composite; Recovery

**Abbreviations** CA: citric acid; EDX: energy-dispersive X-ray spectroscopy; FeTA: Fe(III)-tannic acid; FTIR: Fourier-transform infrared spectroscopy; IB: internal bond strength; LCI: life-cycle inventory; MOR: modulus of rupture; SEM: scanning electron microscopy; TA: tannic acid; TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl; TVOC: total volatile organic compounds; VOC: volatile organic compound; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

## Introduction

Wood- and bamboo-based fiberboards are widely used in furniture, interior decoration, packaging, and engineered panels because they can combine processability, dimensional stability, and cost-effective mechanical performance (Antov et al. 2021a; Antov et al. 2021b). Conventional high-density fiberboard and related wood-panel manufacture, however, still relies heavily on synthetic thermosetting adhesives such as urea-formaldehyde and phenol-formaldehyde resins (Wibowo et al. 2021; Hemmilä et al. 2017; Gonçalves et al. 2021). These adhesives are effective bonding agents, but their formaldehyde/VOC emission profile and irreversible cured networks create persistent environmental and recovery challenges (Xu et al. 2022; Wang et al. 2024; Arias et al. 2020; Hussin et al. 2022). Binderless and bio-based adhesive strategies have therefore been widely explored, yet reviews of self-bonding fiberboards and sustainable wood adhesives still identify the simultaneous achievement of high internal bonding, dimensional stability, low emissions, and practical recyclability as a central unresolved problem (Zhang et al. 2015; Hussin et al. 2022).

Recent work has shifted the field from simply replacing petrochemical adhesives to engineering the fiber interface itself. Binderless fiberboard studies show that intrinsic lignocellulosic bonding can be activated by thermal, enzymatic, fungal, or chemical pretreatments, while newer wood and bamboo studies demonstrate that oxidation, lignin mobility, and in situ interfacial chemistry can turn biomass fibers into active bonding units (Zhang et al. 2015; Wu et al. 2024; Meng et al. 2023; Ju et al. 2024). In the most directly related supramolecular fiberboard work, Na-TA and metal-polyphenol routes use oxidized fiber surfaces, polyphenols, and metal ions to build dynamic inter-fiber networks that support low-odor or recyclable boards with high internal bonding and improved water resistance (Yu et al. 2026a; Yu et al. 2026b). Related bamboo-based materials further show that hydrogen bonding, van der Waals interactions, and metal-carboxylate coordination can work together to provide strong and recoverable interfaces (Fu et al. 2025; Wang et al. 2025). These studies establish the promise of dynamic interfacial bonding, but they also make a simple "another metal-polyphenol fiberboard" claim insufficient.

Fe(III)-tannic acid chemistry offers a particularly attractive but difficult route. Fe(III)-TA complexes and metal-phenolic networks are well known for rapid aqueous assembly, strong coordination, pH-responsive disassembly, and versatile interfacial film formation (Ejima et al.

2013; Kim et al. 2017; Fan et al. 2015; Lin et al. 2024). Spectroscopic and chemometric studies also show that FeTA complexation depends strongly on pH, Fe oxidation state, stoichiometry, and the heterogeneous structure of commercial tannic acid (Fu and Chen 2019; Berto and Alladio 2020). This chemistry is useful for surface functionalization and coating, including tannic-acid immobilization followed by in situ iron complexation on wood fibers (Huang et al. 2020). However, the same fast coordination that makes FeTA useful at interfaces can be problematic in macroscopic fiberboard manufacture: if complexation proceeds too early in the precursor, it may favor bulk aggregation rather than uniform fiber impregnation. For fiberboard applications, the unresolved challenge is therefore not only how to form FeTA interactions, but how to control when and where they form.

Citric acid provides a plausible way to regulate this timing, but it is not a chemically inert additive. In wood science, citric acid has been studied as a green modifier and binder because its carboxyl groups can form ester-linked and hydrogen-bonded interactions with wood components under suitable molding or hot-pressing conditions (Lee et al. 2020; Ando and Umemura 2020; Umemura et al. 2012; Umemura et al. 2013). Citric-acid-containing tannin or sucrose adhesive systems further show that acid chemistry can affect natural adhesive curing and particleboard performance (Zhao et al. 2015; Zhou et al. 2025). In a FeTA system, the intended role of citric acid is therefore tested as part of a citrate-containing FeTA formulation rather than assumed to be a standalone adhesive replacement. Drawing on FeTA pH-dependent coordination, metal-phenolic buffering, and MPN disassembly literature, citrate may act as a competitive carboxylate regulator that buffers acidity, moderates Fe(III)-TA complexation, delays premature aggregation, and provides an acidic recovery handle (Fu and Chen 2019; Berto and Alladio 2020; Chen et al. 2021; Liao et al. 2024).

Here, we investigate a citrate-containing FeTA dynamic supramolecular formulation as an interfacial bonding strategy for self-bonding fiberboards. Activated fibers were prepared by KOH/TEMPO oxidation to introduce carboxylate anchoring sites, following the broader logic of oxidation-assisted interfacial bonding in recent adhesive-free and supramolecular fiberboard studies (Yu et al. 2026a; Ju et al. 2024). FeTA precursors with and without citric acid were screened for pH-dependent stability, and density-matched boards were prepared by hot pressing blank, activated-only, No-CA, CA-only, and Full formulations. Board-level strength and water resistance were evaluated alongside SEM/EDX, FTIR, XPS, leaching, VOC/formaldehyde,

recycling, and screening LCI analyses. The central hypothesis is that the citrate-containing FeTA formulation can widen the processing window of FeTA, support more uniform retained Fe-containing interfacial assembly during hot pressing, and provide a recovery handle without relying on conventional synthetic resin adhesives.

The contribution of this study is therefore deliberately bounded. It does not claim that Fe(III) should rank above Na<sup>+</sup> or Ca<sup>2+</sup> across fiberboard systems, because those routes already provide strong benchmarks for low-odor or recyclable supramolecular boards (Yu et al. 2026a; Yu et al. 2026b; Fu et al. 2025). It also does not treat citric acid alone as a newly discovered wood adhesive, since citric-acid-based wood bonding has an established literature (Lee et al. 2020; Umemura et al. 2012; Ando and Umemura 2020). Instead, this study tests whether a citrate-containing FeTA coordination system can become more controllable, auditable, and recoverable in a fiberboard context. This framing places the work between metal-phenolic network chemistry, self-bonding biomass composites, and circular wood-panel design.

## **Materials and methods**

### **Study design and sample matrix**

This study tested whether a citrate-containing Fe(III)-tannic acid formulation could regulate a fast-aggregating coordination system into a processable and recoverable interfacial network for self-bonding fiberboards. The measured experimental design compared five density-matched board groups: untreated fiberboards without supramolecular additives (P0, Blank), KOH/TEMPO-activated fiberboards without additives (P1, Activated-only), activated fiberboards treated with tannic acid and FeCl<sub>3</sub>·6H<sub>2</sub>O but without citric acid (P2, No-CA control), activated fiberboards treated with citric acid but without tannic acid or FeCl<sub>3</sub>·6H<sub>2</sub>O (P2a, CA-only control), and activated fiberboards treated with tannic acid, FeCl<sub>3</sub>·6H<sub>2</sub>O, and citric acid (P3, Full board). Simplified in-house anchor formulations comprised a Na-TA board (P4) and a Ca-TP board (P5) prepared under the present pressing/density window; these groups were reported descriptively and were not treated as full reproductions of the published Na-TA or Ca-TP benchmarks.

The independent statistical unit was the hot-pressed board, not the number of specimens cut from the same board. The performance analysis used n = 5 independent boards for each density-

matched P0, P1, P2, P2a, and P3 group. Separate specimens or boards were assigned to characterization, leaching, VOC, and recycling workflows with the replicate structures described in the corresponding Methods sections. P4 and P5 were three-board exploratory anchor groups and were reported descriptively. Density matching was applied to the five-group P0/P1/P2/P2a/P3 board matrix by using the same nominal board geometry, oven-dry fiber basis, target density, conditioning window, and exclusion rules. Specimens cut from the same board were first averaged to board-level values before group-level comparison. P4 and P5 were evaluated for MOR and IB only.

To close the citric-acid-only attribution gap, an activated-fiber + citric-acid-only board group (P2a, CA-only control) was prepared using the same activated fibers, board geometry, target density, mat-moisture window, conditioning, and hot-pressing cycle as P3. P2a contained citric acid at the P3 dosage while omitting tannic acid and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Five independent P2a boards were tested for MOR, IB, 24 h thickness swelling, and 24 h water absorption using the same board-level averaging and density-matching rules used for the P0, P1, P2, and P3 groups.

Table 1 Experimental groups and evidence roles

| Group | Short name      | Formulation role                                                               | Use in analysis                         |
|-------|-----------------|--------------------------------------------------------------------------------|-----------------------------------------|
| P0    | Blank           | Untreated fibers; no supramolecular additives                                  | Density-matched blank control           |
| P1    | Activated-only  | KOH/TEMPO-activated fibers; no FeTA additives                                  | Activation control                      |
| P2    | No-CA control   | Activated fibers + TA + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; no CA      | FeTA/no-citrate control                 |
| P2a   | CA-only control | Activated fibers + CA only; no TA or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ | Board-level CA-only attribution control |
| P3    | Full board      | Activated fibers + TA + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + CA         | Primary FeTA-CA formulation             |
| P4    | Na-TA anchor    | Simplified in-house Na-TA formulation                                          | Exploratory benchmark                   |
| P5    | Ca-TP anchor    | Simplified in-house Ca-polyphenol formulation                                  | Exploratory benchmark                   |

## Fiber moisture correction and activation

The raw bamboo-fiber lot (batch bamboo-fiber-lot-A; batch metadata recorded for supplier, size fraction, and receipt condition) was first moisture-corrected on an oven-dry basis. Three subsamples of 1-2 g were dried at 105 °C to constant mass, and all subsequent formulation quantities were calculated from the oven-dry fiber mass. Fibers were then pretreated with 2 wt% KOH at a liquid-to-solid ratio of approximately 25:1 at 90 °C for 2 h. The KOH-treated fibers were washed with deionized water until the filtrate reached pH 7-8, and the wet mass, appearance, and recovery yield were recorded.

Carboxylate-rich anchoring sites were introduced using a pH 6.8 TEMPO oxidation system. For a 20 g oven-dry fiber batch, the reaction mixture contained 220 mL phosphate buffer, 0.032 g TEMPO, 2.825 g NaClO<sub>2</sub>, and 0.64 mL NaClO, with reaction at 60 °C for 12 h. During oxidation, pH, temperature, color, and reaction time were recorded. The oxidized fibers were washed until the conductivity approached the background value, then sampled for carboxylate titration, FTIR, XRD, and SEM. Activation batches used for board manufacture met the locked gate for carboxylate content, yield, dispersibility, and morphology.

### **Precursor formulation and stability screening**

Precursor screening was used to determine whether citrate delayed premature Fe(III)-TA aggregation under acidic processing conditions. Seven vial conditions were tested: Full precursors at nominal pH 2.4, 2.8, 3.0, and 4.0; a No-CA precursor matched to the Full pH 2.8 condition; an Fe+CA control without tannic acid; and a tannic-acid-only control. Each condition was prepared in triplicate. For the Full precursor, citric acid or citrate buffer was dissolved first, FeCl<sub>3</sub>·6H<sub>2</sub>O was added until fully dissolved, pH was adjusted to the target value, and tannic acid was added last. For the No-CA control, FeCl<sub>3</sub>·6H<sub>2</sub>O and tannic acid were combined at matched volume and pH to mirror the Full pH 2.8 condition. The Fe+CA and tannic-acid-only controls were used to interpret precursor stability and were not treated as board-level controls. At 0, 10, 30, 60, 120 min, and 24 h after tannic acid addition, the pH, visual dispersion state, OD600 or turbidity, UV-Vis spectra, and standardized photographs were recorded. The 24 h samples were inverted five times to assess redispersibility. Visual scores were defined as 0 for visually clear or uniformly dispersed, 1 for haze, 2 for flocculation, and 3 for sedimented or hard aggregates.

### **Board impregnation, mat conditioning, and hot pressing**

For each board, activated fibers were weighed separately and treated as an independent batch. The Full board precursor was prepared immediately before use by dissolving citric acid first, adding FeCl<sub>3</sub>·6H<sub>2</sub>O, adjusting pH to approximately 2.8, and adding tannic acid last. The default 200 × 200 × 3 mm board formulation used 120.0 g oven-dry fiber, 1.92 g tannic acid, 0.96 g FeCl<sub>3</sub>·6H<sub>2</sub>O, and 0.68 g citric acid. The matched No-CA control used the same tannic acid and FeCl<sub>3</sub>·6H<sub>2</sub>O masses but omitted citric acid. The P2a CA-only control used the same citric-acid

dosage as the Full formulation (0.68 g for  $200 \times 200 \times 3$  mm boards) while omitting tannic acid and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . For  $150 \times 150 \times 3$  mm boards, the corresponding oven-dry fiber mass was 67.5 g, with 1.08 g tannic acid, 0.54 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and 0.38 g citric acid for the Full formulation; the P2a scale-down used the same 0.38 g citric-acid dosage without tannic acid or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The precursor was added to fibers in five spraying or dropwise passes. After each pass, the mat was mixed for 3-5 min to reduce local FeTA-rich aggregates. The treated fibers were dried at 50-60 °C with intermittent turning until the dry-basis mat moisture content reached 15-18%, then sealed and equilibrated for 12-24 h. Before hot pressing, the actual fiber mass, precursor pH, spray-pass count, mat moisture content, color uniformity, and any visible hard aggregates were recorded. Boards were hot pressed at 160 °C under a target board-surface pressure of 8 MPa for 10 min. The pressing cycle included staged venting at approximately 1.5, 3, and 5 min, followed by holding at target pressure until the total pressing time reached 10 min. Boards were cooled under pressure to below 60 °C before demolding. Front, back, edge, and defect photographs were taken immediately after demolding, and defects such as blistering, edge delamination, local scorching, center cracking, or density mismatch were recorded. Representative photographs of the prepared board groups are provided in Online Resource 1 (Supplementary Fig. S1).

### **Density, mechanical properties, and water resistance**

Boards were conditioned at 20-25 °C and 60-65% relative humidity for 24-48 h. Board density was calculated from conditioned mass and measured dimensions. Thickness was measured at five positions, and boards with density or thickness variation outside the locked exclusion criteria were retained as process records rather than used for mechanism claims. Mechanical and water-resistance testing followed the locked board-level analysis plan. Bending (MOR) specimens were cut to  $150 \times 50$  mm, and IB and water-resistance specimens were cut to  $50 \times 50$  mm. Each board contributed one or two bending specimens, one or two IB specimens, and two water-resistance specimens; specimen-level values were averaged to board-level values before statistical analysis. MOR was measured by three-point bending, with the support span, loading-nose geometry, and final crosshead speed recorded from the machine log. IB was measured on  $50 \times 50$  mm specimens using bonded loading blocks; loading-block dimensions, adhesive type, curing conditions, and loading rate were recorded with the platform log before

analysis. For 24 h water absorption and thickness swelling, specimens were fully immersed in deionized water at room temperature using a GB/T 17657-2022/EN 317-inspired screening protocol rather than a formal standard claim. Specimens were removed after 24 h, gently blotted, and immediately reweighed and remeasured. Failure mode was photographed and classified for each specimen.

For statistical analysis, multiple specimens from the same board were averaged to obtain a single board-level value. Group means, standard deviations, one-way ANOVA, Tukey post hoc comparisons, and pairwise interpretation were reported after density matching had been confirmed across the P0/P1/P2/P2a/P3 board matrix. Density was therefore treated as a gatekeeping check for interpreting activation, FeTA chemistry, CA-only bonding, and the citrate-containing Full formulation rather than compaction alone.

## **Spectroscopic and morphological characterization**

The interfacial-network hypothesis was tested by combining FTIR, XRD, SEM/EDX, and XPS. The characterization set included raw fibers, activated fibers, P1 board, No-CA board, Full board, leached Full board, and recovered Full fibers. Samples were cut from predefined board positions and labelled with surface or cross-section orientation.

FTIR was used to monitor carboxylate, phenolic, aromatic, and hydrogen-bonding regions. XRD was used to assess whether activation or hot pressing caused substantial changes in cellulose crystallinity. SEM was performed on fracture cross-sections to examine fiber contact, inter-fiber voids, and interface density. EDX mapping was used to compare Fe distribution between No-CA and Full boards using a consistent ROI-selection and background-thresholding workflow; the number of maps, board positions, magnification, coating condition, and ROI criteria were reported with the figure or supporting table. XPS was used to quantify surface C, O, Fe, and Cl and to resolve Fe 2p, O 1s, and C 1s components associated with coordination and residual salts. Raw spectra, fitting parameters, residuals, magnification, coating condition, and sampling position were retained as source files.

## **Leaching and VOC/formaldehyde audit**

Leaching was designed as an environmental-retention screen rather than a formal EN 84 test. The primary leaching-kinetics comparison used No-CA and Full board specimens from three

independent boards immersed in deionized water at fixed liquid-to-solid ratios. Leachates were sampled at 24, 72, 168, and 336 h. At each time point, leachate color, pH, conductivity, and photographs were recorded. Filtered aliquots were acidified for ICP-OES Fe analysis, and unacidified aliquots were retained for UV280, total phenol, or TOC analysis. Fe release was reported both as  $\text{mg L}^{-1}$  and as normalized loss relative to initial board Fe content. Exploratory P4 and P5 anchor boards were included only as 336 h normalized Fe-loss endpoint screens when material was available; these values were treated as contextual and were not pooled with the primary P2-P3 leaching-kinetics comparison. VOC and formaldehyde testing was conducted as an emission audit rather than an inference from resin-free formulation. The screen shown in Fig. 6 included P0, P2, P3, P4, P5, and a commercial UF-HDF comparator, with triplicate measurements for each displayed group. Samples were conditioned under matched conditions, cut to platform-required dimensions, sealed immediately in clean aluminum-laminate bags or platform-specified containers, and submitted for formaldehyde, TVOC, benzene, toluene, xylene, acetaldehyde, acetic acid, furfural, and related VOC analysis. The emission screen was interpreted with reference to HJ 571-2010 and GB/T 39600-2021 where applicable to the platform workflow. Detection limits, chromatograms, storage time after pressing, sample sealing conditions, platform method number, chamber or bag configuration, and sample loading factor were retained as source records for the VOC/formaldehyde claims.

### **Citric-acid-assisted disassembly and repressing**

Recovery experiments tested whether citric acid functioned as a disassembly trigger rather than merely as a formulation additive. P3 board pieces from at least three independent boards were cut to 5-10 mm pieces and treated under four conditions: hot water at 90 °C, 0.1 M citric acid at 60 °C, 0.1 M citric acid at room temperature, and 0.05 M citric acid at 60 °C. The solid-to-liquid ratio was fixed at 1:20, and the suspension was stirred at 200 rpm. Photographs were taken every 30 min for up to 4 h. Recovered fibers were collected by sieving, washed, briefly neutralized with approximately pH 8  $\text{NaHCO}_3$  solution, washed to near-neutral filtrate pH, and dried or conditioned for repressing. Recovered fibers were repressed under the original board pressing conditions either without additional precursor (C0), with 50% replenishment of the Full precursor (C50), or with 100%

replenishment as a full-replenishment check. The 50% and 100% replenishment levels were defined relative to the original Full formulation solids while preserving the TA/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /citric-acid mass ratio. MOR, IB, and thickness swelling retention were calculated relative to the original Full board, and absolute MOR/IB values were also back-calculated or reported when the original denominator was fixed.

## **Life-cycle inventory**

The sustainability analysis was limited to transparent screening life-cycle inventory construction rather than a full comparative life-cycle assessment (LCA). The functional unit was 1 m<sup>3</sup> of high-density fiberboard at 1000 kg m<sup>-3</sup>. Inventory categories included dry fiber mass, tannic acid,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , citric acid, KOH, TEMPO,  $\text{NaClO}_2$ ,  $\text{NaClO}$ , buffer salts, water, ethanol, drying energy, hot-pressing energy, washing water, wastewater, recovery chemicals, and board yield. Screening-level carbon estimates were treated as directional hotspot information only; no comparative LCA claim was made without verified emission-factor sources, system boundaries, data-quality grading, allocation rules, database choices, and sensitivity analysis.

## **Results**

### **Fiber activation generated interfacial anchoring sites**

Figure 1 establishes the activated fiber substrate before the introduction of FeTA-CA chemistry. The carboxylate content increased from  $0.202 \pm 0.005$  mmol g<sup>-1</sup> in raw fibers to  $0.657 \pm 0.051$  mmol g<sup>-1</sup> after KOH/TEMPO activation. The corresponding yield remained  $88.3 \pm 1.4\%$ , and the crystallinity index changed only modestly from  $59.2 \pm 1.7\%$  to  $57.4 \pm 0.1\%$ . These values indicate that the activation step increased the density of carboxylate anchoring sites without severe fiber loss or obvious crystallinity collapse.

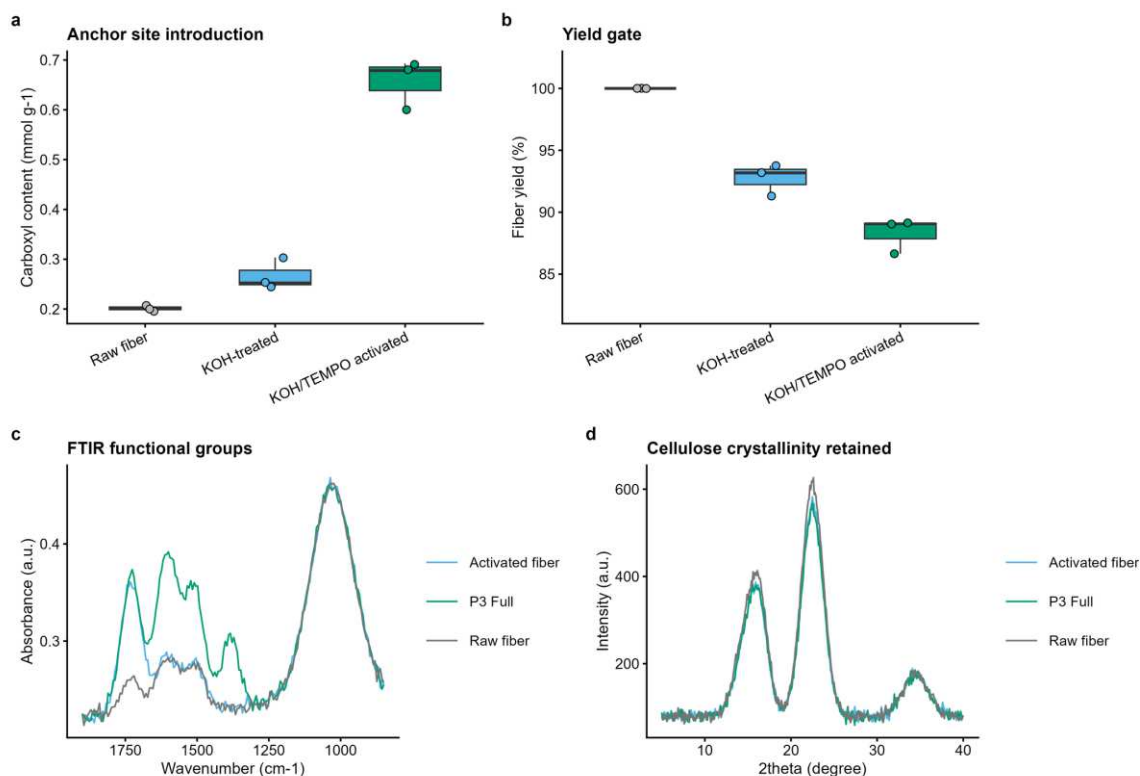


Fig. 1 Fiber activation and substrate characterization. KOH/TEMPO activation increased carboxylate availability while retaining fiber integrity, providing anchoring sites for subsequent Fe(III)-tannic acid assembly.

### Citrate suppressed premature Fe(III)-TA aggregation in the precursor

Figure 2 tests whether citrate suppresses premature Fe(III)-TA aggregation before the precursor contacts activated fibers. Full precursors at pH 2.4 and pH 2.8 retained low turbidity through 24 h, with 24 h OD600 values of  $0.072 \pm 0.016$  and  $0.112 \pm 0.008$ , respectively, and a visual score of 0. The pH 3.0 Full condition showed a mild haze, whereas pH 4.0 showed clear instability. By contrast, the No-CA precursor matched to the pH 2.8 condition reached an OD600 of  $1.334 \pm 0.006$  at 24 h and a visual score of 3, indicating visible sedimentation or hard aggregation. The two single-component precursor controls remained stable over the same 24 h window. Fe+CA and TA-only controls showed low OD600 values of  $0.052 \pm 0.009$  and  $0.030 \pm 0.014$ , respectively, with visual scores of 0 and retained redispersibility. The contrast with the No-CA Fe(III)-TA precursor indicates that rapid turbidity and sedimentation required the combined presence of Fe(III) and tannic acid in the absence of citrate regulation, rather than Fe/citrate or tannic acid alone.

This pattern places the practical processing window at approximately pH 2.4-2.8. These results indicate that the relevant formulation effect is not simple additive inclusion, but delayed Fe(III)-TA aggregation within a pH-dependent processing window before impregnation and hot pressing.

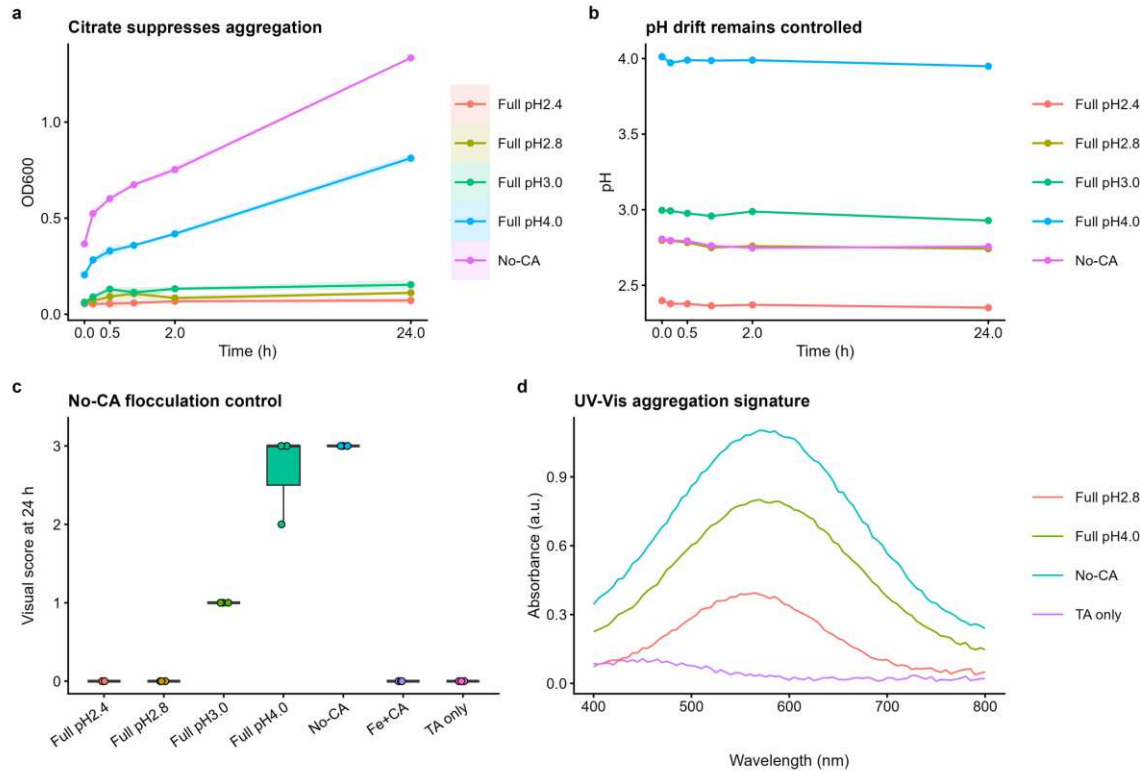


Fig. 2 Citrate-containing precursor stability. Full precursors at pH 2.4-2.8 retained low turbidity through 24 h, whereas the No-CA control showed visible aggregation and high OD600.

# Density-matched Full boards improved mechanical and water-resistance performance

Figure 3 tests whether precursor regulation translated into board-level function while explicitly including the CA-only attribution control. The density analysis confirmed matching across P0, P1, P2, P2a, and P3. The mean densities of P0, P1, P2, P2a, and P3 were  $0.994 \pm 0.005$ ,  $0.995 \pm 0.006$ ,  $0.996 \pm 0.006$ ,  $0.994 \pm 0.004$ , and  $0.995 \pm 0.006$  g cm<sup>-3</sup>, respectively; density ANOVA showed no group effect ( $F(4,20) = 0.109$ ,  $p = 0.978$ ), and Tukey HSD did not separate any density group. This confirms that the performance comparisons were not driven by systematic compaction differences.

Under these matched-density conditions, the blank P0 boards reached MOR, IB, 24 h thickness swelling, and water absorption values of  $18.5 \pm 0.6$  MPa,  $0.350 \pm 0.011$  MPa,  $33.0 \pm 1.5\%$ , and  $76.0 \pm 2.3\%$ , respectively. KOH/TEMPO activation alone improved the P1 boards to  $26.5 \pm 0.9$  MPa MOR,  $0.610 \pm 0.019$  MPa IB,  $25.0 \pm 1.1\%$  TS, and  $61.0 \pm 2.3\%$  WA. The No-CA P2 boards reached  $33.5 \pm 1.0$  MPa MOR,  $0.830 \pm 0.025$  MPa IB,  $20.8 \pm 1.2\%$  TS, and  $53.5 \pm 3.4\%$  WA. The P2a CA-only boards reached  $35.0 \pm 1.3$  MPa MOR,  $0.950 \pm 0.026$  MPa IB,  $20.0 \pm 1.0\%$  TS, and  $50.0 \pm 1.0\%$  WA. The Full P3 boards reached  $44.2 \pm 1.0$  MPa MOR,  $1.200 \pm 0.033$  MPa IB,  $13.2 \pm 0.2\%$  TS, and  $33.2 \pm 1.5\%$  WA.

ANOVA detected group effects across P0, P1, P2, P2a, and P3 for MOR ( $F(4,20) = 493.8$ ,  $p < 2.00 \times 10^{-16}$ ), IB ( $F(4,20) = 927.8$ ,  $p < 2.00 \times 10^{-16}$ ), TS ( $F(4,20) = 211.0$ ,  $p = 4.76 \times 10^{-16}$ ), and WA ( $F(4,20) = 240.5$ ,  $p < 2.00 \times 10^{-16}$ ). Tukey letters ranked MOR as P3 a > P2a/P2 b > P1 c > P0 d. IB separated all five groups as P3 a > P2a b > P2 c > P1 d > P0 e. For TS and WA, where lower values indicate better water resistance, the letters were P3 a < P2a/P2 b < P1 c < P0 d. P3 exceeded P2a for MOR ( $p = 2.33 \times 10^{-11}$ ) and IB ( $p = 3.61 \times 10^{-12}$ ), and showed lower TS ( $p = 5.99 \times 10^{-8}$ ) and WA ( $p = 1.77 \times 10^{-9}$ ). P2a and P2 did not differ significantly for MOR ( $p = 0.144$ ), TS ( $p = 0.788$ ), or WA ( $p = 0.143$ ), but P2a had higher IB than P2 ( $p = 1.04 \times 10^{-6}$ ).

The P0-to-P1-to-P2/P2a-to-P3 sequence separates the contributions of fiber activation, FeTA addition, CA-only bonding, and the citrate-containing FeTA formulation under matched density. Activation alone provided a measurable but incomplete improvement. CA-only treatment narrowed the gap relative to No-CA mainly through IB, but it did not account for the Full board response. The Full formulation produced the strongest and most water-resistant board in this five-group matrix, supporting the combined FeTA-CA formulation rather than a CA-only explanation. Representative hot-pressed board photographs are provided in Online Resource 1 (Supplementary Fig. S1) as visual process records.

Simplified in-house Na-TA (P4) and Ca-TP (P5) anchor formulations provide context under the present pressing and density window but do not replace the primary P3 versus P2/P2a comparison. P4 and P5 reached MOR values of  $38.8 \pm 0.9$  and  $40.9 \pm 1.8$  MPa and IB values of  $1.028 \pm 0.039$  and  $1.092 \pm 0.020$  MPa, respectively. These values were closer to P3 than to P2/P2a and slightly below P3 in the same in-house workflow, but P4 and P5 used three boards and were not included in the five-group P0/P1/P2/P2a/P3 ANOVA/Tukey comparison; they are

therefore reported descriptively as exploratory benchmark values rather than as primary statistical comparators.

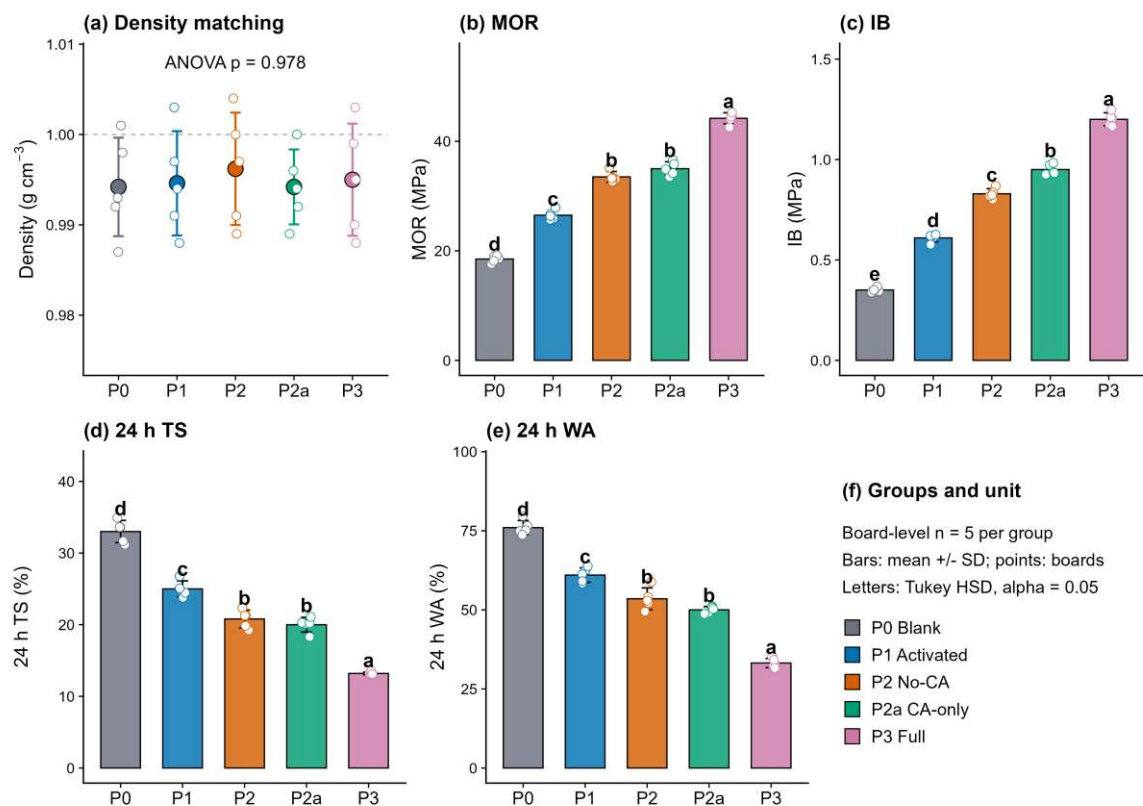


Fig. 3 Density-matched board-level performance with CA-only control. Density is shown as mean  $\pm$  SD with individual board points. MOR, IB, 24 h thickness swelling (TS), and 24 h water absorption (WA) are shown as mean  $\pm$  SD bars overlaid with independent board-level points ( $n = 5$  boards per group). Letters indicate Tukey HSD groups within each metric; lower TS and WA indicate better water resistance.

## Interfacial characterization tested network homogeneity and retention

Figure 4 summarizes SEM/EDX distribution and retention. The characterization panels show a strong contrast between the No-CA and Full boards. The SEM/EDX summary reports a Fe-map coefficient of variation of 77.0% in the No-CA control and 15.1% in the Full board, consistent with local Fe-enriched domains in the absence of citrate and a more homogeneous retained Fe-containing interfacial state in the Full board.

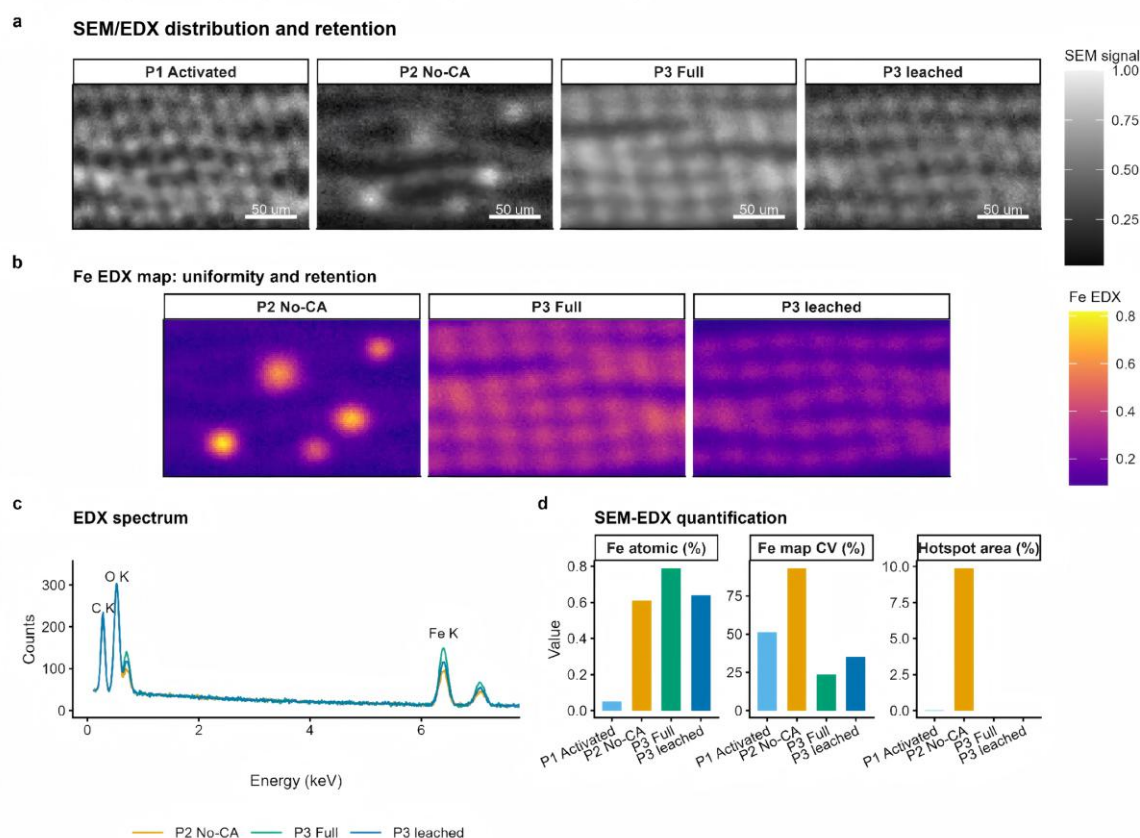


Fig. 4 SEM/EDX distribution and retention. Cross-section morphology, Fe-EDX maps, spectra, and quantification show more homogeneous retained Fe signal in the Full board than in the No-CA control.

Figure 5 summarizes FTIR and XPS evidence for coordination-associated interfacial states. FTIR and XPS tables indicate higher coordination-associated descriptors in the Full board, including a higher O1s coordinated component and a stronger carboxylate/Fe-associated FTIR index. These data provide convergent evidence rather than isolated proof from any single technique. SEM/EDX directly describes Fe distribution, FTIR tracks changes in carboxylate, phenolic, and hydrogen-bonding environments, XPS tests surface Fe and O states, and leached-board characterization evaluates retained signatures after water exposure. Together, these measurements support a more homogeneous retained Fe-containing interfacial state consistent with FeTA/carboxylate assembly, but they do not by themselves establish the exact coordination structure or bulk network architecture.

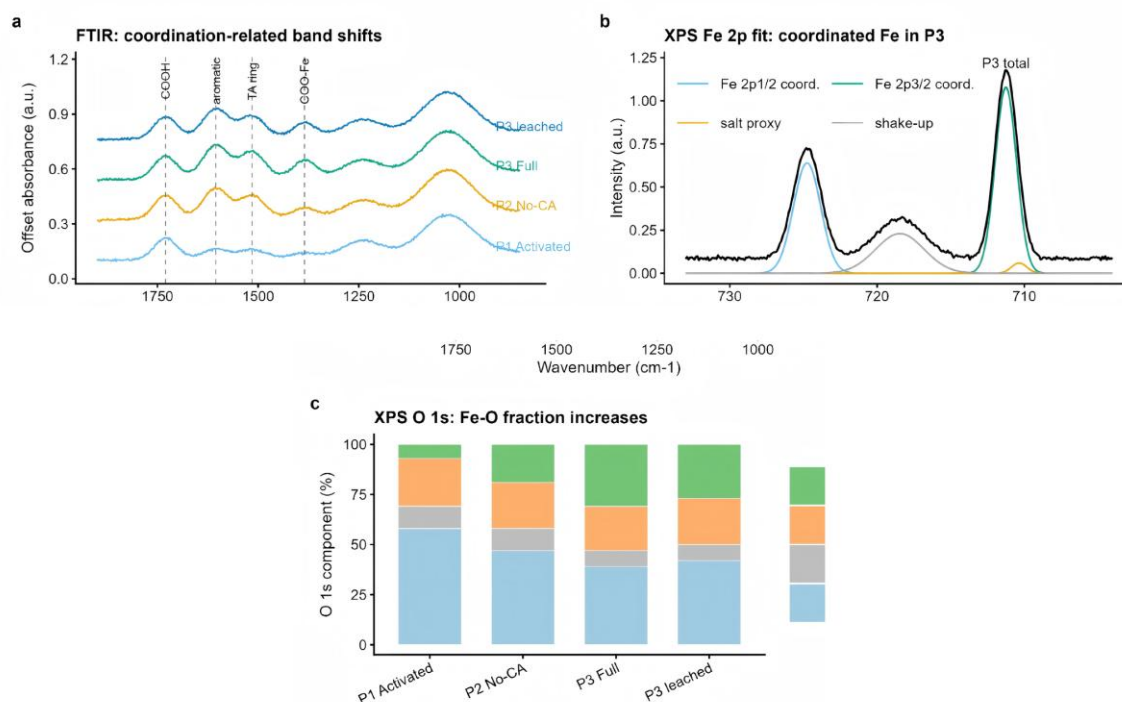


Fig. 5 Spectroscopic evidence for coordination-associated interfacial states. FTIR and XPS summaries support coordination-associated changes in the Full board while preserving the boundary that no single technique proves the exact bulk network architecture.

## Leaching and VOC audits constrain the environmental claim

Figure 6 frames the environmental evidence as an audit rather than a promotional sustainability claim. In the primary P2-P3 leaching screen, after 336 h the Full board released less Fe and less total phenolic material than the No-CA control. Mean Fe concentration decreased from  $2.860 \pm 0.288 \text{ mg L}^{-1}$  in P2 to  $0.810 \pm 0.050 \text{ mg L}^{-1}$  in P3, and total phenol decreased from  $2.970 \pm 0.217 \text{ mg L}^{-1}$  to  $1.192 \pm 0.139 \text{ mg L}^{-1}$ . The P2-P3 Tukey p values at 336 h were  $2.68 \times 10^{-4}$  for Fe and  $2.84 \times 10^{-4}$  for total phenol, supporting improved FeTA retention during the water-exposure screen. The P4 and P5 anchor endpoints shown in Fig. 6b are retained only as contextual normalized-loss screens and are not used to revise the primary P2-P3 leaching conclusion. Representative P2 and P3 leachate time-course photographs are provided in Online Resource 1 (Supplementary Fig. S2); quantitative leaching conclusions are based on ICP-OES Fe analysis and total phenol assays.

The VOC/formaldehyde screen gives the same section a second audit dimension. The No-CA P2 board showed formaldehyde and TVOC values of  $0.029 \pm 0.007 \text{ mg m}^{-3}$  and  $247 \pm 13 \text{ } \mu\text{g m}^{-3}$ , respectively. The Full P3 board showed corresponding values of  $0.016 \pm 0.002 \text{ mg m}^{-3}$  and  $126 \pm 11 \text{ } \mu\text{g m}^{-3}$ , while the commercial UF-HDF comparator showed  $0.091 \pm 0.011 \text{ mg m}^{-3}$  formaldehyde and  $415 \pm 36 \text{ } \mu\text{g m}^{-3}$  TVOC. Across P2, P3, and the commercial comparator, formaldehyde and TVOC showed group effects (ANOVA  $p = 4.91 \times 10^{-5}$  and  $1.45 \times 10^{-5}$ , respectively). P3 had lower TVOC than P2 (Tukey  $p = 0.0016$ ) and the commercial comparator ( $p = 1.12 \times 10^{-5}$ ). The P3-P2 formaldehyde difference was numerical in this triplicate comparison ( $p = 0.182$ ), whereas both FeTA groups were below the commercial comparator in the same audit. The P0/P4/P5 values in Fig. 6c are contextual screening comparators, not evidence for a universal ranking among anchor systems.

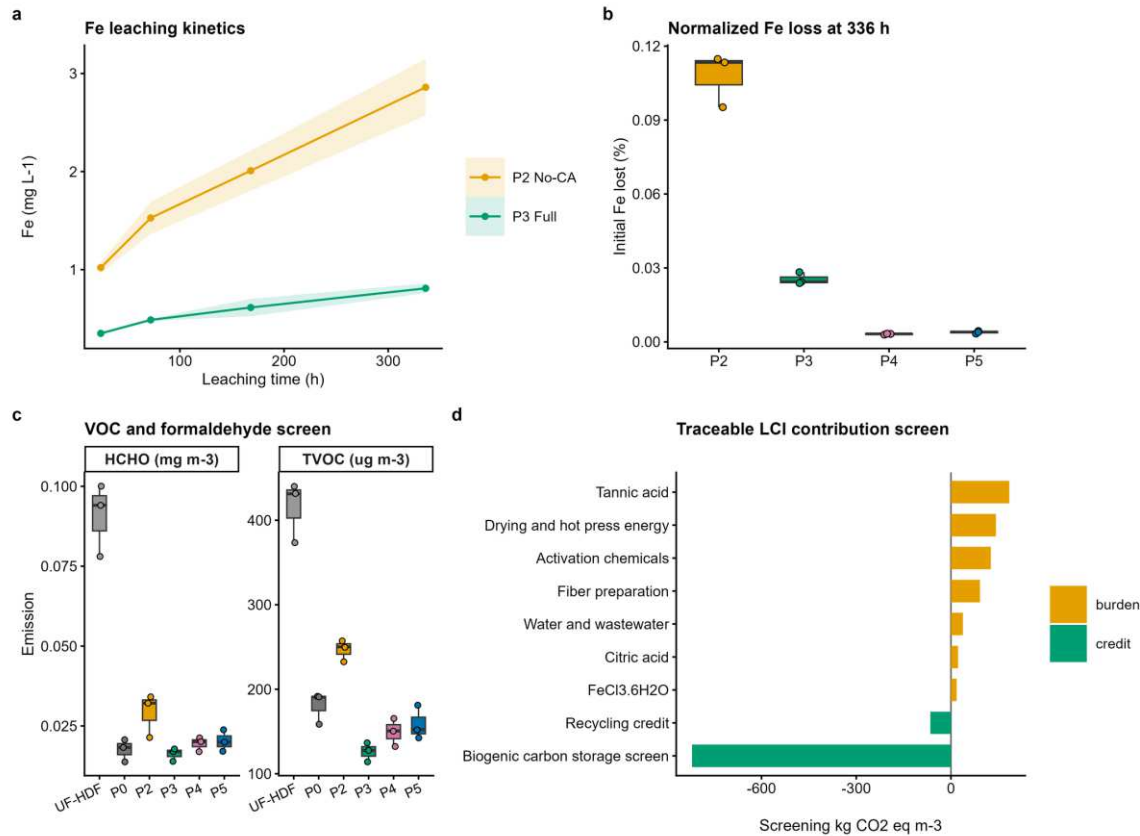


Fig. 6 Environmental audit evidence. Leaching, VOC/formaldehyde, and screening inventory results are reported as measured audit outcomes rather than inferred from resin-free formulation alone. P4/P5 anchor data are contextual screens only, and the LCI panel is a hotspot-oriented screening inventory rather than a comparative LCA claim.

## **Citric acid promoted disassembly and repressing, with liquid-phase loss as a trade-off**

Figure 7 tests the recovery pathway. 0.1 M citric acid at 60 °C produced higher disassembly and recovered-fiber yield than hot water at 90 °C after 240 min. Disassembly increased from  $62.1 \pm 3.1\%$  under hot water to  $91.1 \pm 1.7\%$  under 0.1 M citric acid at 60 °C (Tukey  $p = 1.47 \times 10^{-4}$ ), and recovered yield increased from  $53.1 \pm 2.3\%$  to  $83.4 \pm 1.3\%$  ( $p = 4.45 \times 10^{-5}$ ). Repressing results also favored citric-acid recovery. At cycle 4 with 50% precursor replenishment, CA60 C50 retained  $75.1 \pm 2.8\%$  of MOR and  $73.5 \pm 0.5\%$  of IB, whereas hot-water C50 retained only  $26.7 \pm 1.8\%$  of MOR and  $21.3 \pm 0.6\%$  of IB. The cycle-4 C50 Tukey  $p$  values were  $1.89 \times 10^{-5}$  for MOR retention and  $9.37 \times 10^{-14}$  for IB retention. Using the original Full-board means as the denominator, the cycle-4 C50 values correspond to approximately 33.0 MPa MOR and 0.879 MPa IB for CA60 C50, compared with approximately 11.7 MPa MOR and 0.254 MPa IB for hot-water C50.

The same data also identify a quantified trade-off. At 240 min, the citric-acid recovery liquid contained more Fe than the hot-water recovery liquid ( $2.077 \pm 0.044$  versus  $0.359 \pm 0.011$  mg  $L^{-1}$ ; Tukey  $p = 5.02 \times 10^{-10}$ ). That observation is part of the mechanism and environmental balance rather than a peripheral defect: if citric acid reopens coordination crosslinks, it may also increase Fe transfer into the recovery liquid. The remaining question is whether the process can control, recover, or manage this transfer.

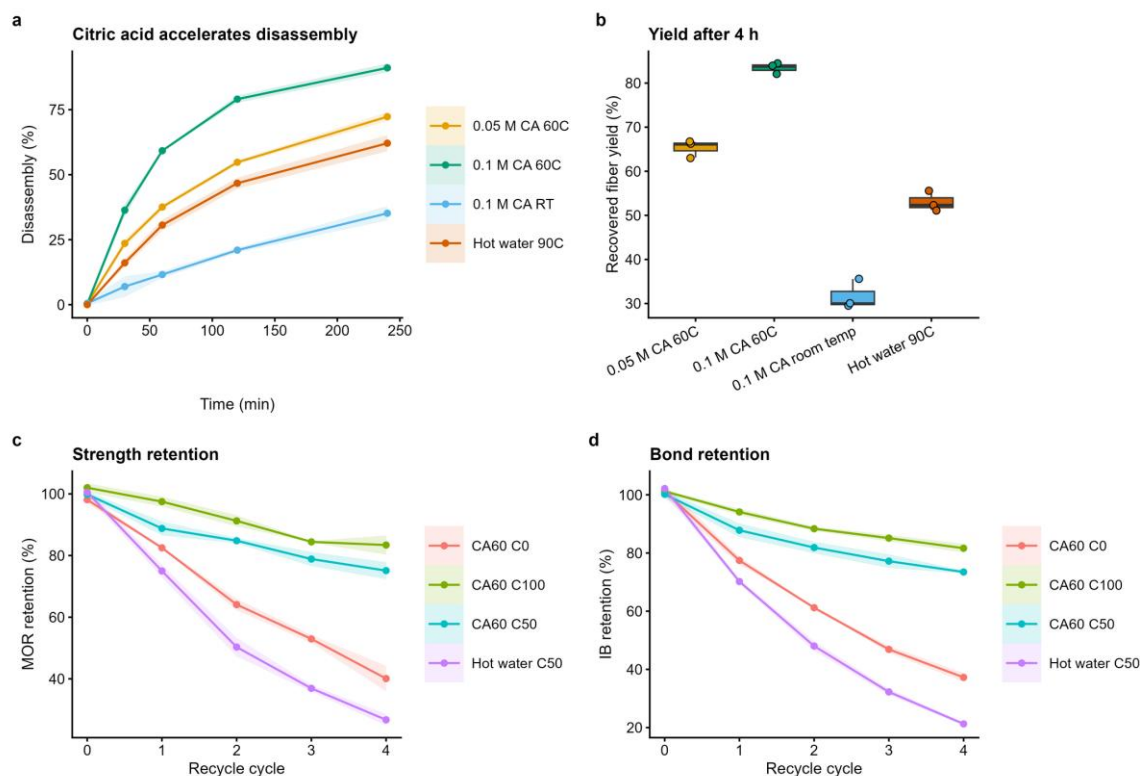


Fig. 7 Citric-acid-assisted disassembly and repressing. Citric acid at 60 °C improved disassembly and recovered-fiber repressing relative to hot water, while increasing liquid-phase Fe transfer.

## Screening LCI defines inventory boundaries

The screening LCI defines inventory boundaries rather than comparative sustainability. The inventory table lists the functional unit, chemical inputs, activation and pressing energy, water/wastewater streams, recovery inputs, data-quality labels, and provisional burden/credit categories. The screening inventory identified likely hotspots, but no comparative LCA claim was made. Any GWP comparison remains tied to a verified LCA model, emission-factor sources, allocation choices, and sensitivity analysis.

435 Table 2 Concise evidence summary and interpretation boundaries

| Evidence block         | Key finding                                                                                                                                                                | Boundary retained in the manuscript                                                                                                                  |
|------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| Activation             | Carboxylate content increased from $0.202 \pm 0.005$ to $0.657 \pm 0.051$ mmol g <sup>-1</sup> ; yield was $88.3 \pm 1.4\%$ .                                              | Activation supplies anchoring sites but is not treated as the whole bonding mechanism.                                                               |
| Precursor stability    | Full pH 2.8 precursor OD600 at 24 h was $0.112 \pm 0.008$ ; No-CA was $1.334 \pm 0.006$ .                                                                                  | Citrate delays FeTA aggregation within a pH window; it is not a passive additive.                                                                    |
| Board performance      | P3 exceeded both P2 and P2a under density-matched conditions (MOR $44.2 \pm 1.0$ MPa; IB $1.200 \pm 0.033$ MPa).                                                           | Supports the combined FeTA-CA formulation, not a CA-only explanation or universal Fe superiority.                                                    |
| Leaching/VOC/LCI audit | P3 showed lower 336 h Fe release than P2 ( $0.810 \pm 0.050$ vs $2.860 \pm 0.288$ mg L <sup>-1</sup> ) and lower TVOC ( $126 \pm 11$ vs $247 \pm 13$ µg m <sup>-3</sup> ). | Environmental claims remain audit outcomes; P4/P5 and LCI are contextual screens, and formaldehyde is benchmarked against the commercial comparator. |
| Recovery               | 0.1 M citric acid at 60 °C increased disassembly to $91.1 \pm 1.7\%$ and cycle-4 C50 MOR retention to $75.1 \pm 2.8\%$ .                                                   | Recovery is a pathway, not complete closed-loop recyclability, and is paired with quantified liquid-phase Fe transfer.                               |

436 **Discussion**

437 The main result to defend is not that Fe(III) is inherently better than Na<sup>+</sup> or Ca<sup>2+</sup> in self-bonding  
438 fiberboards. The more defensible claim is that citrate can make a difficult Fe(III)-TA  
439 coordination system usable by separating the timing of precursor preparation, interfacial  
440 assembly, service retention, and recovery. This distinction matters because prior Na-TA and Ca-  
441 polyphenol fiberboard studies have already shown that metal/polyphenol interactions can provide  
442 adhesive-free bonding and recyclability (Yu et al. 2026a; Yu et al. 2026b). The present FeTA-  
443 CA route therefore needs to justify itself through a regulated processing and recovery window,  
444 not through broad novelty language.

445 The precursor screen provides the first point of mechanistic leverage. Fe(III)-TA chemistry is  
446 attractive because Fe(III) forms strong coordination interactions with phenolic ligands, but that  
447 same strength can produce premature bulk aggregation, color changes, poor dispersion, and  
448 leaching concerns. The precursor data are consistent with citrate suppressing premature Fe(III)-  
449 TA flocculation at pH 2.4-2.8 while leaving the system capable of later network formation. This  
450 interpretation fits the broader metal-phenolic-network literature, in which pH and ligand  
451 environment strongly influence assembly, stability, and disassembly behavior (Ejima et al. 2013;  
452 Chen et al. 2021; Lin et al. 2024). Direct UV-Vis/OD600 tracking and comparison with No-CA  
453 controls define this as a measured processing mechanism rather than a visual observation alone.  
454 The performance results connect precursor regulation to material function but no longer rely on a  
455 missing CA-only control. The key comparison is P3 against both P2 and P2a under matched

density, because density alone can improve MOR, IB, and water resistance in hot-pressed fiberboards, and citric acid alone can also contribute to bonding. The density check extended across all five P0/P1/P2/P2a/P3 groups, and ANOVA/Tukey results showed no group separation for density. This strengthens the interpretation of the performance pattern: activation improves the fiber substrate, FeTA adds a coordination/polyphenol contribution, CA alone contributes measurably to IB, and the Full citrate-containing FeTA formulation reaches the strongest and most water-resistant board in this dataset.

The Na-TA and Ca-TP anchor controls help place the FeTA-CA board within the broader metal/polyphenol fiberboard landscape, but they do not change the main mechanistic comparison. Under the present pressing and density window, the simplified in-house P4 and P5 anchors performed closer to the Full board than to the No-CA and CA-only controls, and P3 was slightly higher than P4/P5 for both MOR (44.2 versus 38.8/40.9 MPa) and IB (1.200 versus 1.028/1.092 MPa). This internal comparison is useful because it used the same fiber lot, pressing window, board geometry, and test workflow. However, P4 and P5 were exploratory three-board groups outside the five-group ANOVA/Tukey comparison, so the result is treated as contextual rather than as proof of mechanical superiority.

The comparison with published Na-TA and Ca-polyphenol benchmarks is stated cautiously. Reported Na-TA low-odor HDF reaches an internal bond strength of approximately 3.1 MPa with an MOR near 49 MPa, and the reported Ca-polyphenol recyclable fiberboard reaches an internal bonding strength of approximately 2.6 MPa with a bending strength near 46 MPa (Yu et al. 2026a; Yu et al. 2026b). The present Full-board MOR falls in the same numerical range (44.2 MPa), but its IB is lower (1.200 MPa). However, the in-house Na-TA anchor itself reached only 1.028 MPa IB under the present workflow, far below the published Na-TA value. This mismatch indicates that raw fiber source, board geometry, thickness, pressing protocol, density window, loading-block geometry, and IB testing conditions all affect absolute IB values across studies. The published Na/Ca values are therefore useful benchmarks but should not overrule the higher-confidence internal comparison. The contribution is a controllable Fe(III)-TA processing and recovery window, not an ultimate IB record and not a universal ranking above Na or Ca systems. The mechanism figures work as convergent evidence rather than single-technique proof. SEM/EDX tests whether Fe distributes homogeneously or concentrates in aggregates; FTIR tracks changes in carboxylate, phenolic, and hydrogen-bonding environments; XPS probes

surface Fe and O coordination-associated states; leached-board characterization tests whether interfacial signatures persist after water exposure; and the CA-only board group tests whether citric acid alone can explain the board-level response. The convergent evidence points toward a more homogeneous retained Fe-containing interfacial state consistent with FeTA/carboxylate assembly in the Full board. It does not uniquely establish the exact FeTA coordination structure, distinguish every Fe-citrate, FeTA, esterification, and hydrogen-bonding contribution, or establish bulk network architecture by itself.

The environmental interpretation remains deliberately bounded. Resin-free or formaldehyde-free formulation does not automatically mean low VOC, low leaching, or low environmental burden. Prior recyclable fiberboard studies have increasingly combined mechanical performance with VOC and LCA information, which raises the evidentiary bar for this manuscript (Yu et al. 2026a; Yu et al. 2026b; Fu et al. 2025). For the FeTA-CA route, Fe and phenolic leaching are not peripheral checks; they are central to whether a Fe-based network can be environmentally defensible. The leaching data are encouraging because P3 releases less Fe and phenolic material than P2, and the interpretation remains tied to ICP-OES calibration, detection limits, and mass-normalized losses rather than concentration values alone.

The recovery data point to a dynamic-network recovery trade-off, summarized schematically in Fig. 8. Citric acid appears to be useful as a disassembly trigger because it can compete for Fe(III) and reopen coordination crosslinks, consistent with the broader concept that chemical triggers can disassemble metal-phenolic networks (Liao et al. 2024). Yet the same mechanism transferred more Fe into the recovery liquid than hot water in the present screen (2.077 versus 0.359 mg L<sup>-1</sup> at 240 min). The Discussion therefore avoids portraying citric-acid recovery as cost-free and instead frames recovery as a controlled exchange: improved disassembly and repressing are valuable only when the analysis quantifies and manages liquid-phase Fe/phenolic losses.

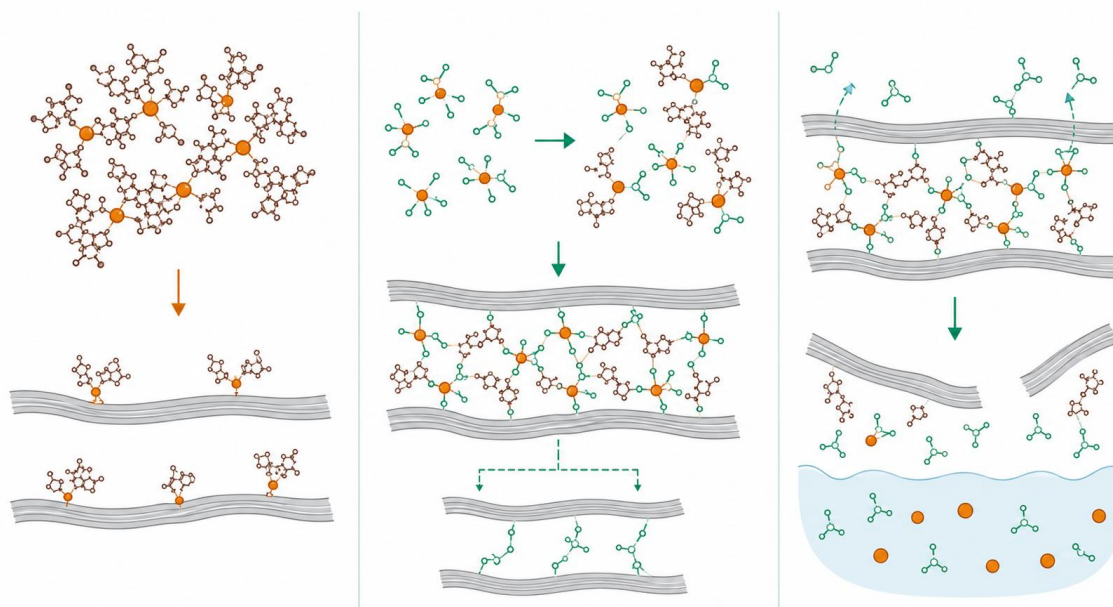


Fig. 8 Schematic FeTA-CA timing and recovery model. The schematic summarizes the proposed interpretation: without CA, Fe(III)-TA can aggregate before uniform fiber-interface assembly; with CA, Fe(III) pre-complexation delays assembly until TA addition and hot pressing; during recovery, excess CA competes for Fe-linked interactions, enabling fiber release while increasing liquid-phase Fe transfer. The figure is conceptual and does not represent direct structural proof.

Compared with citric-acid wood-bonding studies, the present route gives citric acid a measured but bounded role. Citric acid has been widely discussed as a green wood modifier or binder through esterification and crosslinking with wood components (Lee et al. 2020; Ando and Umemura 2020; Umemura et al. 2012; Zhao et al. 2015). The P2a CA-only data show that citric acid alone can increase IB relative to the No-CA FeTA board, so direct CA-fiber bonding cannot be dismissed. Accordingly, FTIR changes near  $1720\text{-}1740\text{ cm}^{-1}$  are assigned cautiously to overlapping ester/carboxyl contributions from CA-fiber esterification, Fe-citrate/carboxylate environments, and FeTA-associated interfacial states rather than to a single Fe-coordination mode. The present data do not quantify the fractional contribution of each process. However, P2a did not explain the Full-board gains in MOR, TS, or WA, and P3 remained statistically better than P2a across all four board-performance metrics. The result is therefore framed as a citrate-containing FeTA formulation in which CA contributes to timing/recovery and may also contribute direct bonding, rather than as absolute proof that coordination timing is the only cause of performance improvement.

Several limitations define the boundary of the contribution. First, the mechanism remains indirect and technique-limited: spectroscopy, microscopy, the CA-only board-level performance control, and leached-board evidence constrain the interpretation but do not replace direct molecular speciation. Second, P2a narrows the attribution gap but does not quantify the microscopic share of esterification, hydrogen bonding, Fe-citrate interaction, and FeTA/carboxylate coordination. Third, long-term durability, repeated wet-dry cycling, and standardized leaching remain open unless performed under a recognized protocol. Fourth, screening inventory construction is not the same as a full LCA. These limitations define the evidentiary boundary of the present work and clarify what the current dataset can and cannot support.

The strongest framing is therefore a regulated dynamic-coordination strategy with explicit boundaries: the citrate-containing FeTA formulation widens the precursor processing window, is consistent with more uniform retained Fe-containing interfacial assembly during hot pressing, reduces Fe and phenolic release during water exposure, and provides a mild chemical handle for recovery with a quantifiable liquid-phase Fe trade-off. The contribution becomes clearest when the manuscript presents these stages as a connected evidence chain rather than as separate claims.

## Conclusions

This study supports a bounded citrate-regulated Fe(III)-tannic acid strategy for self-bonding fiberboards. The evidence chain links fiber activation, precursor stability, density-matched board performance including the CA-only attribution control, interfacial characterization, leaching/VOC auditing, and citric-acid-assisted recovery. The strongest claim is not universal superiority over other metal-polyphenol systems, but the creation of a more controllable FeTA processing and recovery window with explicit environmental and mechanistic boundaries.

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### Competing interests

The author declares that there are no relevant financial or non-financial interests to disclose.

### Author contributions

Ruke Yao: conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing—original draft, and writing—review and editing.

### Data availability

The data supporting the findings of this study are available within the article and its Supplementary Information files. Supplementary process photographs are provided in Online Resource 1. Additional raw data, including board-level measurements, instrumental output files, original uncropped photographs, and data-processing records, are available from the author upon reasonable request.

658 **Ethics approval**

659 Not applicable.

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