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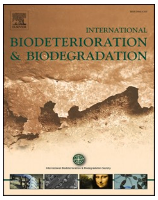

Assessment of glutaraldehyde and formaldehyde for enhancing decay resistance and reducing caffeine leachability in Scots pine wood

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ABSTRACT

Caffeine-treated wood is valued for its decay resistance, but caffeine high leachability under outdoor conditions significantly reduces its long-term effectiveness. This study aimed to mitigate the leachability of caffeine-impregnated Scots pine wood by incorporating either formaldehyde or glutaraldehyde. The treatments were evaluated using standard leachability analysis (EN 84), decay resistance testing (EN 113), mass spectrometry, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and mechanical testing. Leaching tests revealed that caffeine-glutaraldehyde-impregnated wood exhibited the lowest mass loss after leaching (3.30 ± 0.15%), outperforming caffeine-treated (6.18 ± 0.15%) and caffeine-formaldehyde-treated (5.94 ± 0.13%) specimens, indicating superior caffeine fixation. ATR-FTIR spectroscopy showed that characteristic caffeine bands diminished following leaching, confirming caffeine leachability. However, caffeine-glutaraldehyde-treated samples exhibited less pronounced spectral changes compared to caffeine-formaldehyde-treated samples. Mass spectrometry further corroborated these findings, detecting higher caffeine content in glutaraldehyde-treated wood than in caffeine-only specimens after leaching test. Decay resistance tests demonstrated that caffeine-glutaraldehyde-treated wood retained high resistance to fungal decay both before and after leaching. Mechanical tests revealed that the modulus of rupture (MOR) was preserved post-leaching only in caffeine-glutaraldehyde-treated samples. These findings highlight the effectiveness of low concentrations of glutaraldehyde in reducing caffeine leachability, thereby enhancing the decay resistance and durability of treated wood, making it a promising approach for outdoor applications.

1. Introduction

Wood, as a renewable material, has experienced a resurgence in popularity. The demand for sustainable building materials has led to innovations in wood construction and engineering, allowing wood to compete with current construction materials such as concrete and steel. Wood is highly regarded building material for its strength-to-mass ratio, making it an excellent choice for construction, furniture, and various consumer goods. It is also an insulating material, which helps reduce energy consumption in buildings (Asdrubali et al., 2017). Moreover, wood products can be recycled and reused, enhancing their environmental credentials (Ormondroyd et al., 2016). The main drawback of wood as a material is its susceptibility to decay, discoloration, and dimensional instability. However, a small portion of naturally durable wood species possesses sufficient resistance to decay, offering enhanced longevity in certain applications. Various preservation chemicals and wood modification methods (Papadopoulos et al., 2008; Sandberg et al., 2017) have been used to slow down the degradation caused by decay fungi and mitigate other degradation issues. Due to health awareness and environmental concerns, the use of some commercial preservation treatments has been declined or avoided, such as creosotes (Hiemstra et al., 2007) and chromated copper arsenate (CCA) has been significantly restricted within the European Union (Liu et al., 2018). Additionally, restriction on CCA usage have been implemented in the Unites States and Canada. New copper-based preservatives have been used as replacements, but these may not provide a permanent solution to all the related problems, such as toxicity of treated product and leachability of metal salts. Some of these preservatives include copper azole (CA),

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alkaline copper quaternary (ACQ), micronized copper (MCQ), copper dimethyl-dithio-carbamate (CDDC), ammoniacal copper citrate (CC), and Cu-HDO (bis-(N-cyclohexyldiazeniumdioxy)-copper) (Cao and Kamdem, 2004; Lin et al., 2009). As the utilization of wood is expected to grow (FAO, 2022) and with the introduction of more rigorous regulations, finding and fixing novel bio-based preservatives is poised to present a substantial contemporary challenge in the field of wood science.

Biobased wood preservatives, such as coffee waste extracts (Barbero-López et al., 2018), monoterpenes (Zhang et al., 2016), propolis extracts (Woźniak et al., 2020), mistletoe extractives (Yildiz et al., 2020), tannins (Tomak and Gonultas, 2018; Da Silveira et al., 2017), and hydrothermal liquefaction liquids from spent mushroom and tomato residues (Barbero-López et al., 2024), have demonstrated promising properties as decay inhibitors. However, their water solubility often leads to leaching in outdoor applications, limiting their long-term effectiveness. Despite their potential, none of these biobased products have been commercialized, primarily due to challenges such as insufficient durability under weathering conditions, high production costs, and regulatory hurdles. Additionally, the use of industrial wood side-streams has potential in wood preservation. Barbero-López et al. (2022) (Barbero-López et al., 2022) showed that the Norway spruce log soaking pit water contains promising components, such as phenolics, that could be used in wood preservation. Previous studies have also investigated various methods to reduce the leaching of different chemicals from wood, but this remains a significant limitation for their widespread use. For instance, caffeine has been fixed through thermal modification (Kwaśniewska-Sip et al., 2019), whereas tannins have been fixed using thermal, oil, and geopolymers treatments as a second step (López-Gómez et al., 2022, 2025). Other studies have focused on fixing boric acid in wood using tannins and examining its fire and mechanical properties (Thevenon et al., 2009; Tondi et al., 2012, 2015). The approval of the biobased formulations in the EU is a costly and brings a lot of complexity. However, caffeine-based wood preservatives may have potential due to caffeine's well-documented antifungal properties, safety profile and its widespread use in various industries. This familiarity could ease some regulatory concerns. Additionally, the environmental benefits of caffeine, particularly when effectively fixed in wood, align with the EU's sustainability goals. The economic feasibility of using caffeine for wood protection is promising but requires further exploration. While its cost currently presents challenges, advancements in extraction methods and the potential integration of waste streams from the coffee industry could enhance its viability for large-scale commercial application.

Caffeine has been found to have biocidal efficacy against wood-destroying fungi, molds, and insects, making it a promising compound for wood protection (Tondi et al., 2015). But its high leachability is also well known. Broda et al. (2018) (Broda et al., 2018) used aminosilane to reduce the leachability of caffeine from wood, suggesting that caffeine, when combined with other agents, can enhance the durability of wood, and reduce its leachability. The proposed solutions appear to work by promoting chemical interactions between caffeine and the wood matrix, potentially forming more stable complexes that resist leaching. This makes caffeine a potential candidate for use in wood preservative products where leaching is a concern. However, further research, methods and testing are needed to fully evaluate the effectiveness of caffeine in terms of leachability and long-term durability as a wood preservative in different applications.

Formaldehyde and glutaraldehyde are commonly used in the wood industry in adhesives and coating for their fast curing and good performance (Grinins et al., 2022; Hussin et al., 2022). Due to concerns about formaldehyde emissions, there has been a growing interest in low concentration formaldehyde treatments or substitution with lignin derived phenolics (Cavdar et al., 2008). A study on soy-based adhesive cross-linked by phenol-formaldehyde-glutaraldehyde (PFG) resin showed that it can be used to prepare a low-formaldehyde adhesive with good water resistance (Bennett et al., 2022; Arias et al., 2021). Other investigations focused on reducing formaldehyde emissions from wood-based products through various methods. These include the use of additives like urea, ammonia, ammonium salts, tannin, and wood bark to act as formaldehyde scavengers (Saito et al., 2021), as well as the development of non-formaldehyde, bio-based adhesives to replace traditional formaldehyde-based adhesive systems in wood-based panels (Antov et al., 2020; Saud et al., 2021). On the other hand, glyoxal, glutaraldehyde, furfural, 5-hydroxymethylfurfural, and dimethoxyethanal are among the promising alternatives to formaldehyde (Solt et al., 2019). Studies have shown that glutaraldehyde-modified cassava starch, without formaldehyde, can effectively bond particle boards, offering a safer alternative (Akinyemi et al., 2019).

The present study hypothesizes that the addition of low concentrations of formaldehyde and glutaraldehyde will significantly reduce the leachability of caffeine while maintaining acceptable biodegradation resistance and mechanical properties, making it suitable for use in class 3.2 applications (exterior, above ground, unprotected from the weather).

2. Materials and methods

2.1. Wood specimens

Specimens measuring 40 × 10 × 5 mm^3 were extracted from Scots pine (*Pinus sylvestris*) sapwood sourced from the Kerimäki sawmill in Finland. The wood had an average of 3–5 tree rings per cm and a density of approximately 450–500 kg/m^3. There were 58 replicates per treatment. The specimens were cut with their longitudinal faces parallel to the grain direction and ensured to be defect-free.

2.2. Chemical impregnation

The treatments used were as follows—caffeine at a concentration of 3, with a 2% concentration previously reported as effective (Šimůnková et al., 2021), formaldehyde diluted to 0.5% concentration in Milli-Q water, glutaraldehyde also diluted to 0.5% concentration in Milli-Q water, and combination of caffeine at 3% with either formaldehyde at 0.5% or glutaraldehyde at 0.5%.

Caffeine ($C_8H_{10}N_4O_2$), 99% pure, was purchased from Sigma Aldrich, while formaldehyde solution (37%, stabilized with 10–15% methanol) and glutaraldehyde solution (25%) were purchased Merck Life Science Oy, Espoo.

The specimens underwent impregnation using the Bethell full-cell process, involving an initial vacuum of 15 kPa for 20 min at 20 °C, followed by a pressure increase to 1000 kPa for 60 min at 20 °C. Chemical retention was determined by comparing the oven-dried mass (at 103 ± 2 °C) before and after the treatment. Untreated wood specimens were used as controls.

The chemical retention (kg/m^3), mass loss due to leaching (%), and the chemical loss due to leaching (kg/m^3) were reported, as given by Eqs. (1)–(3).

$$\text{Chemical retention } (kg/m^3) = (M_1 - M_0) / V \tag{1}$$

where M_1 (kg) is the dry mass after the impregnation, M_0 (kg) is the dry mass before the impregnation, and V the volume of the sample (m^3).

$$\text{Chemical loss due to leaching } (kg/m^3) = (M_b - M_a) / V \tag{2}$$

where M_b (kg) is the dry mass after the impregnation, M_0 (kg) is the dry mass after the leaching test, and V the volume of the sample (m^3).

$$\text{Mass loss due to leaching } (\%) = [M_0 - M_1] / M_0] \times 100 \tag{3}$$

where M_0 (kg) is the dry mass after impregnation and M_1 (kg) is the dry mass after leaching exposure.

2.3. Leaching test

Randomized half of the specimens in each treatment were exposed to a leaching test following the European standard EN 84 (CEN, 1997) (EN 84, 1997). The specimens underwent immersion in Milli-Q water at a ratio of 1:5 (v/v) for a duration of 14 days, with the water being replaced nine times throughout this period. Initial water changes occurred at 24 and 48 h, followed by seven additional changes over the subsequent 12 days, with intervals ranging from 24 to 72 h. Following leaching, the specimens were oven-dried at 103 ± 2 °C until a constant mass was achieved. The dry mass before and after the leaching test was then compared.

2.4. Decay test

The decay test was performed following a modified version of the standard mini-block procedure in the European norm EN 113 (2021) (), as previously done by Barbero-López et al. (2022) (Barbero-López et al., 2021). The growth media were prepared by combining 4% malt powder and 2% agar in Milli-Q water, followed by autoclaving (120 °C, 15 min). Subsequently, 25 mL of liquid culture medium was dispensed into each Petri dish (Ø 90 mm, 15 mm height) under sterile conditions.

In this experiment, sixteen replicates of each treatment (eight leached and eight non-leached) were exposed to two different brown-rot fungi: *Gloeophyllum trabeum* (strain BAM 115) and *Coniophora puteana* (strain BAM 112), purchased from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany). The inoculation procedure was conducted under sterile conditions, with a plug (Ø 5.5 mm) of actively growing fungus placed at the center of each dish. Following inoculation, the Petri dishes were sealed with parafilm and maintained in a growth chamber at 65 ± 5% relative humidity (RH) and a temperature of 22 ± 2 °C. In each Petri dish, four wood specimens from the same treatment—two leached and two non-leached specimens—were exposed to the fungus once the mycelium had fully covered the entire surface of the culture medium. Control specimens were used to prove the virulence of the fungi. All wood specimens utilized in the experiment underwent autoclaving (120 °C for 15 min) and were maintained in a sterile condition within a laminar flow hood before being introduced into the Petri dishes containing fungi. Additionally, a high-density polyethylene (HDPE) plastic mesh was placed inside each Petri dish to prevent direct contact between the wood and the growth medium. The sealed Petri dishes were placed in a growth chamber maintained at 22 ± 2 °C and 65 ± 5% relative humidity (RH) for a duration of 16 weeks. Later, the dry mass of the wood specimens was measured at 103 ± 2 °C and compared with their initial dry mass before exposure to decay, allowing the calculation of the mass loss (wt-%) attributed to the fungi.

The mass loss was evaluated following equation (4):

$$\textit{Mass loss } (\%) = (M_0 - M_1) \,/\, M_0 \tag{4}$$

where M_1 (g) represents the dry mass (103 ± 2 °C) after decay exposure and M_0 (g) represents the dry mass (103 ± 2 °C) before decay exposure.

2.5. Mechanical test

The three-point bending test was performed to determine the modulus of elasticity (MOE) and modulus of rupture (MOR) on a Zwick Roell Material Testing Machine Z050, following a modified version of DIN 52186 (DIN 52186, 1978), previously reported by López-Gómez et al. (2025) (López-Gómez et al., 2025). Before testing, the specimens were conditioned at a temperature of 20 ± 2 °C and a relative humidity of 65 ± 5% until they reached a constant mass. Sixteen replicates of each treatment (eight leached and eight non-leached) with dimensions of 40 × 10 × 5 mm^3 were used to calculate the MOR and MOE. The following equations were used:

$$\textit{MOE (GPa)} = d\sigma \,/\, d\varepsilon \tag{5}$$

$$\textit{MOR (MPa)} = 3\,PL \,/\, 2bd^{2} \tag{6}$$

In equation (5), $d\sigma$ is the stress and $d\varepsilon$ is the strain, referring to the slope in the elastic range of the material. In equation (6), P is the maximum load (N), L is the distance between supports for the beam (mm), b is the sample width (mm), and d is the sample thickness (mm).

2.6. Infrared (IR) spectroscopy

The Scots pine sapwood's surface was analyzed using a Vertex 70 (Bruker, Leipzig, Germany) Fourier transform infrared (FTIR) spectrometer, equipped with a single reflection diamond attenuated total reflectance (ATR) accessory and a RT-DLaTGS detector. The data was recorded within a spectral range of 4000-400 cm-1 with 16 scans at a resolution of 2 cm-1. OPUS 6.5 software (Bruker, Leipzig, Germany) was used in the data acquisition and post-processing.

2.7. Mass spectrometry

Chemical composition of the wood samples was analyzed using a high-resolution Bruker timsTOF PRO (1st generation) quadrupole time of flight mass spectrometer. The instrument was equipped with a combination of atmospheric pressure chemical ionization (APCI) source and a direct insertion probe (DIP) accessory by Bruker, enabling analysis of solid samples with minimal sample preparation. A small piece (0.6 ± 0.1 mg) cut from the wood sample was placed in a pre-baked glass capillary (Hirschmann melting point tube), which was then closed with a quartz filter (Pallflex Tissuquartz 2500QAT-UP) and inserted into the ion source. Next, the APCI vaporizer temperature was stepwise increased from 150 °C to 350 °C with 50 °C steps within 7 min (Fig. 1). The MS measurements were conducted in a positive ion mode using the following source parameters: a capillary voltage of 4000 V, a corona current of 4000 nA, a nebulizer pressure of 2.0 bar, a dry gas flow of 5.0 L/min and a dry gas temperature of 200 °C. The ion transfer parameters (a multipole RF of 120 V_{pp}, a collision RF of 400V_{pp}, a transfer time of 100 μs, and a pre-pulse storage of 8 μs) were adjusted to enable efficient detection of ions in a m/z range of approximately 100–500.

The mass spectrometer was externally calibrated with a polystyrene standard prior to the measurements, and the instrument was controlled with Bruker otofControl 6.2 software. The obtained data was treated semi manually in a targeted manner using Bruker DataAnalysis 5.1 software. Compounds were identified based on their accurate masses and obtained molecular formulae. Averaged mass spectra obtained within a time frame of 4.0–7.0 min of the temperature program, corresponding to 300−350 °C, were used in the compositional characterization. Each sample was measured in triplicate.

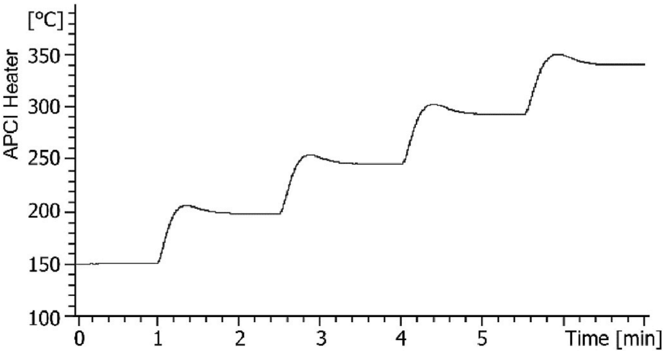

Fig. 1. The APCI heater temperature program used in the DIP-MS analysis of wood samples.

2.8. Statistical analysis

Statistical analysis was conducted using the R statistical software. Mean and standard error values were calculated for each of the evaluated properties. Subsequently, an analysis of variance (ANOVA) was carried out, and Tukey's range test was used as a post-hoc analysis to compare the different treatments.

3. Results

3.1. Toxicity comparation

The toxicity values according to regulation (EC) No. 1907/2006 are shown in Table 1. Formaldehyde had the highest oral toxicity value with a LD_{50} of 100 mg/kg. Glutaraldehyde exhibited a lower toxicity level with an LD_{50} of 200 mg/kg, followed by Caffeine with an LD_{50} of 367.7 mg/kg. Celcure C4 displayed the lowest oral toxicity with an LD_{50} of 1350 mg/kg.

The inhalation data indicated that both Formaldehyde and Glutaraldehyde are highly toxic, with LC_{50} values of less than 0.57 mg/l over a 4-h exposure period for vapor and dust/mist, respectively. Caffeine, with an LC_{50} of 4.94 mg/l for aerosol, showed considerably lower toxicity via inhalation. No inhalation toxicity data was available for Celcure C4.

The dermal exposure results showed that Formaldehyde again had significant toxicity with an LC_{50} of 270 mg/kg. Glutaraldehyde presented lower values of dermal toxicity with an LC_{50} of 1000 mg/kg, while Caffeine exhibited the lowest dermal toxicity with an LC_{50} of 2000 mg/kg. No dermal toxicity data was available for Celcure C4.

3.2. Leaching and infrared (IR) spectroscopy

The values for the chemical retention and mass loss due to leaching are presented in Table 2. The results indicate that the treatments involving caffeine, caffeine with glutaraldehyde, and caffeine with formaldehyde exhibited the highest retention levels, with retention values above 24 (kg/m^3). This contrasts with the glutaraldehyde and formaldehyde treatments alone, which showed retention values below 2 (kg/m^3).

After the leaching test, differences in mass loss were observed among the treatments. The caffeine and the caffeine with formaldehyde treatment experienced the highest mass loss, with values around 6 %. Conversely, the mass loss for the caffeine with glutaraldehyde treatment was significantly lower than other caffeine-related treatments. The control, glutaraldehyde and formaldehyde treatments exhibited the lowest values in mass loss due to leaching.

The wood specimens were characterized using ATR-FTIR (Fig. 2). Absorbance spectra before and after the leaching test were compared to evaluate the effects of leaching and the presence of caffeine. The spectrum of caffeine-treated wood exhibited specific bands corresponding to vibrational modes of caffeine. However, many of these bands overlapped significantly with those of wood, particularly in the 1450–1600 cm^{-1} region (associated with C=C stretching) and the 2800–3000 cm^{-1} region (linked to C-H stretching).

The most distinct and prominent bands for caffeine were observed in the 1650–1750 cm^{-1} range, corresponding to the stretching vibration of C=O bonds (Paradkar and Irudayaraj, 2002). In this region, non-leached specimens treated with caffeine, caffeine with glutaraldehyde, and caffeine with formaldehyde all showed increased absorbance, confirming the presence of caffeine. However, after the leaching test, the absorbance decreased, indicating partial loss of caffeine. Among the leached specimens, the wood impregnated with caffeine with formaldehyde exhibited a lower absorbance compared to those treated with caffeine and caffeine with glutaraldehyde. It is worth noting that glutaraldehyde also contains C=O groups in its structure. The intensity in this region in glutaraldehyde treated wood, however, is low, as the spectra do not show any significant increase due to overlapping with the wood structure.

Table 1
Safety data sheet in accordance with regulation (EC) No. 1907/2006. Lethal concentration (LC) and Lethal dose (LD).

	LD_{50} Oral	LC_{50} Inhalation	LC_{50} Dermal
Formaldehyde	100 mg/kg	- 4h - <0.57 mg/l - vapor	270 mg/kg
Glutaraldehyde	200 mg/kg	- 4h - <0.57 mg/l - dust/mist	1000 mg/kg
Caffeine	367.7 mg/kg	–4 h–4.94 mg/l - aerosol	2000 mg/kg
Celcure C4	1350 mg/kg	–	–

Table 2
Dry retention values after impregnation treatment (kg/m^3), mass loss due to leaching (%), and Chemical loss due to leaching (kg/m^3). Values are presented as mean ± standard error (n = 64 for chemical retention and n = 32 for mass loss due to leaching).

Treatment	Chemical retention (kg/m^3)	Mass loss due to leaching (%)	Chemical loss due to leaching (kg/m^3)
Control	–	1.3 ± 0.09	5.87 ± 0.28
Caffeine	24.41 ± 0.2	6.18 ± 0.15	28.88 ± 0.27
Glutaraldehyde	0.95 ± 0.13	1.31 ± 0.06	5.32 ± 0.24
Formaldehyde	1.98 ± 0.12	1.80 ± 0.10	7.41 ± 0.30
Caffeine + Glutaraldehyde	26.97 ± 0.20	3.30 ± 0.15	15.10 ± 0.26
Caffeine + Formaldehyde	24.04 ± 0.25	5.94 ± 0.13	25.10 ± 0.33

3.3. Mass spectrometry

The chemical composition of the wood samples was semi-quantitatively evaluated by means of temperature-programmed direct mass spectrometry (Fig. 3). Caffeine was readily detected in the corresponding wood samples using DIP-MS, with the formation of both radical cation ($C_8H_{10}N_4O_2^{+\bullet}$) and protonated molecule ($C_8H_{11}N_4O_2^{+}$) observed. Based on the combined abundance of $M^{+\bullet}$ and $[M+H]^+$ ions proportioned to the sample mass, the amount of caffeine before leaching was the same, regardless of the inclusion of glutaraldehyde. Expectedly, the DIP-MS study indicated that leaching of the samples significantly decreased their caffeine content. The intensity of signals assigned to caffeine was reduced to approximately 10 and 20% of its original value, on average, in the cases caffeine and caffeine-glutaraldehyde samples, respectively. The DIP-MS analysis also indicated the presence of glutaraldehyde in all samples impregnated with it, although the abundance of $C_5H_9O_2^{+}$ ions was relatively low.

3.4. Decay test

The decay test findings, presented in Table 3, indicated that the mass loss in untreated specimens exposed to both fungi exceeded 20%, with the exception of the non-leached wood specimens exposed to *C. puteana*. Caffeine with glutaraldehyde treatment increased the decay resistance against *G. trabeum* and *C. puteana*, having the lowest mass loss. The mass loss of non-leached caffeine treated specimens were significantly lower compared to control in both fungi (0.8 ± 0.2% and 0.2 ± 0.1%), contrary to the leached specimens exhibiting mass losses of 12.9 ± 1.8% and 14.3 ± 1.1% respectively. The application of glutaraldehyde treatment yielded an improvement in the decay resistance at the same level as caffeine treatment prior to leaching. Nonetheless, there was an increase of mass loss after leaching test in both fungi. The non-leached specimens treated with formaldehyde exposed to *C. puteana* reduced the mass loss as the caffeine treatment, contrary to the leached exposed to *C. puteana* and both leached and non-leached exposed to *G. trabeum*, that decays as untreated samples.

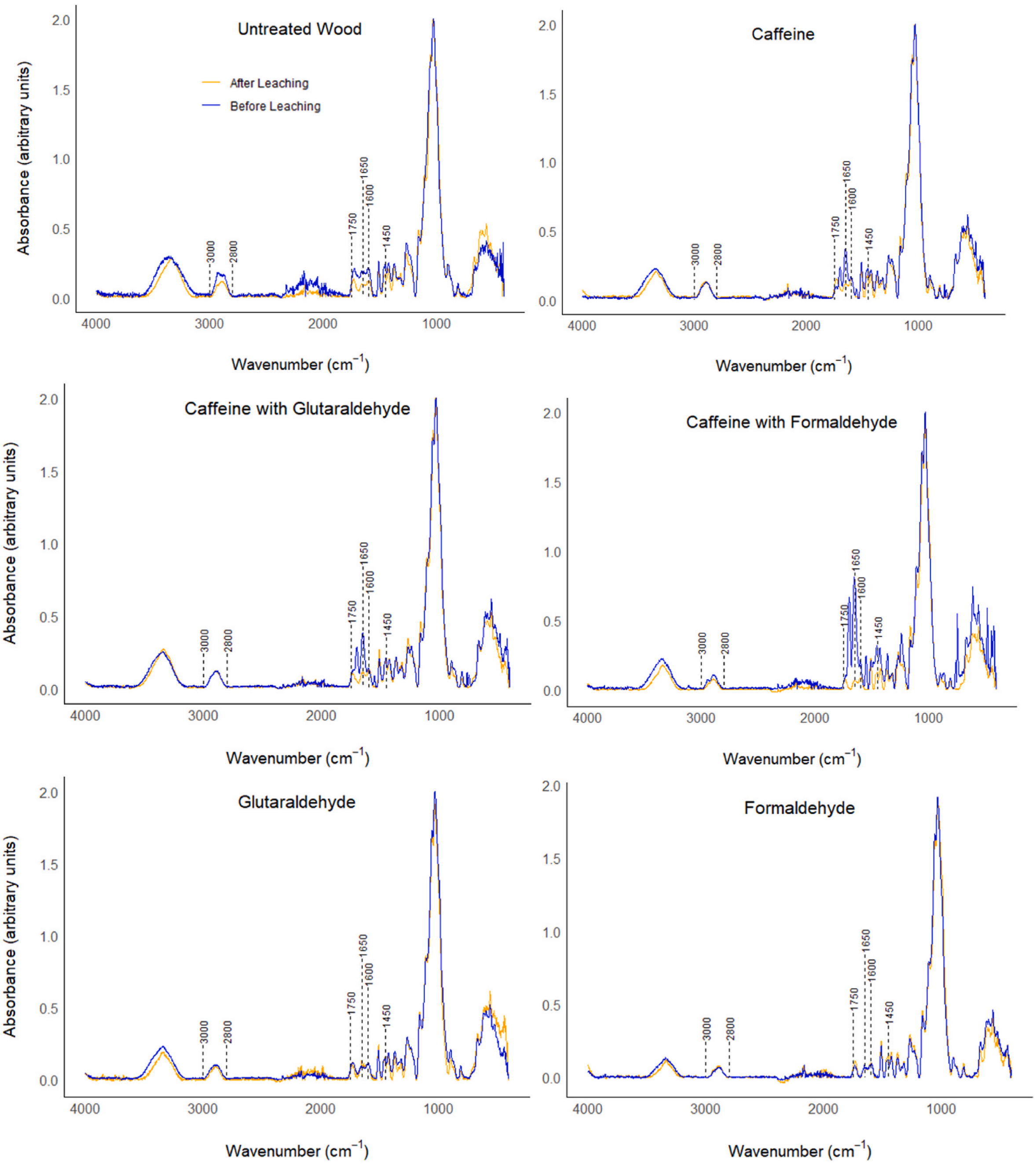

Fig. 2. ATR-FTIR spectra of the untreated wood, caffeine, caffeine with glutaraldehyde, caffeine with formaldehyde, glutaraldehyde, and formaldehyde treatments. The blue lines represent the spectra before the leaching test and the orange lines after the leaching test. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

In the case of combination treatments, caffeine with glutaraldehyde demonstrated superior performance compared to caffeine with formaldehyde and caffeine treatments after the leaching test. The caffeine-formaldehyde-impregnated wood had a decay resistance comparable to untreated specimens when exposed to *G. trabeum* after the leaching test with a mass loss value of 21.6 ± 2.6%.

On the other hand, the caffeine with formaldehyde treatment obtained a decay resistance as high as caffeine with glutaraldehyde treatment when exposed to *C. puteana* after the leaching test. The non-leached specimens of caffeine with glutaraldehyde and caffeine with formaldehyde treatments exposed to both fungi did not exhibit significant difference compared to caffeine treatment.

The wood specimens exposed to *G. trabeum* without a leaching test, and treated with the following treatments—caffeine, caffeine with glutaraldehyde, and caffeine with formaldehyde—achieved a durability class of DC 1 (EN 350) (EN 350, 2016). In contrast, the glutaraldehyde treatment resulted in a durability class of DC 2 (EN 350), while the formaldehyde treatment yielded a durability class of DC 4 (EN 350). The wood specimens exposed to *C. puteana* without a leaching test, and treated with the following treatments—caffeine, glutaraldehyde, formaldehyde, caffeine with glutaraldehyde, and caffeine with formaldehyde—achieved a durability class of DC 1 (EN 350).

3.5. *Mechanical test*

The three-point bending test (Table 4) revealed minor differences

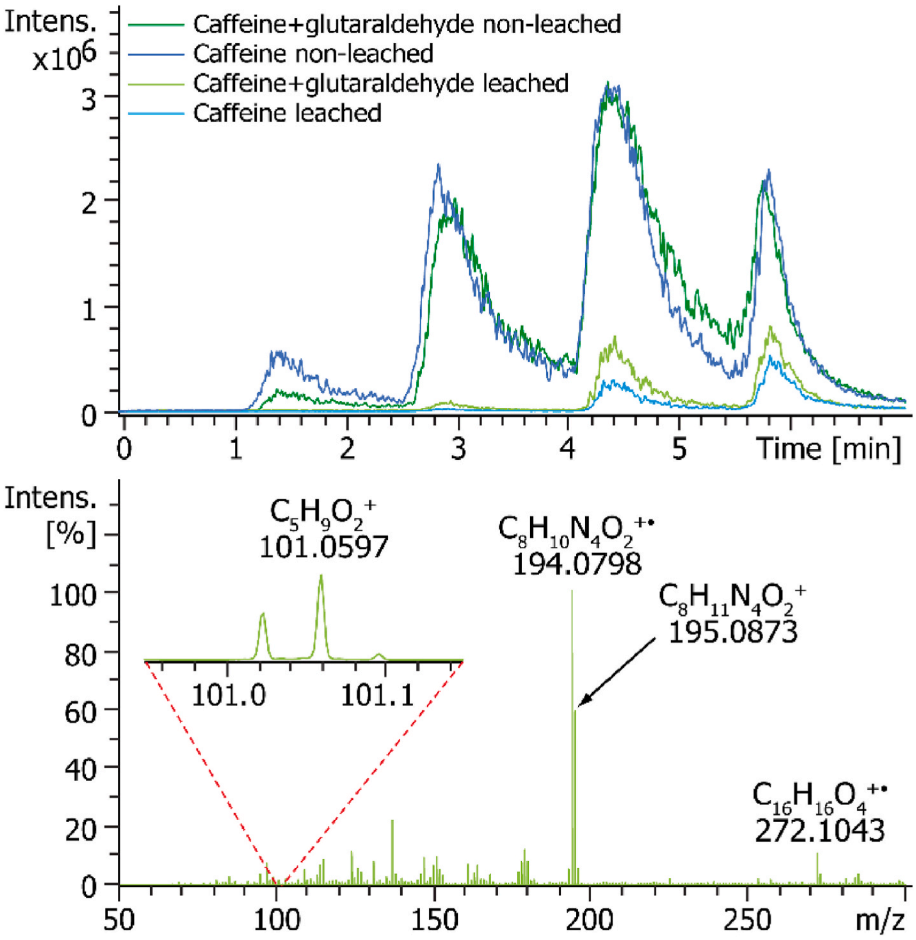

Fig. 3. Temperature-programmed DIP-MS analysis of wood specimens impregnated with caffeine and glutaraldehyde, before and after leaching. The top panel presents extracted ion chromatograms of m/z 194.0798 ($C_8H_{10}N_4O_2^{+\bullet}$; caffeine) and the bottom panel shows an exemplary averaged mass spectrum of leached caffeine + glutaraldehyde sample obtained within the time frame of 4.0–7.0 min (300−350 °C).

Table 3

Specimens mass loss due to *G. trabeum* and *C. puteana*. Results are presented as mean ± standard error (n = 8). Different letters indicate significant differences between treatments based on Tukey's range test.

Treatment	Mass loss due to decay (%)			
	G. trabeum		*C. puteana*	
	Leached	Non-leached	Leached	Non-leached
Control	20.0 ± 3.6^{a}	19.4 ± 3.8^{a}	21.9 ± 2.7^{a}	16.3 ± 1.2^{a}
Caffeine	12.9 ± 1.8^{ab}	0.8 ± 0.2^{b}	14.3 ± 1.1^{ab}	0.2 ± 0.1^{b}
Glutaraldehyde	8.5 ± 4.0^{ab}	3.8 ± 1.8^{b}	4.7 ± 2.6^{bc}	2.0 ± 1.1^{b}
Formaldehyde	17.0 ± 5.2^{ab}	18.9 ± 6.7^{a}	19.4 ± 7.9^{ab}	3.2 ± 0.8^{b}
Caffeine + Glutaraldehyde	4.3 ± 3.0^{b}	0.8 ± 0.1^{b}	0.3 ± 0.7^{c}	0.1 ± 0.3^{b}
Caffeine + Formaldehyde	21.6 ± 2.6^{a}	1.5 ± 0.2^{b}	4.6 ± 1.7^{bc}	0.3 ± 0.1^{b}

Table 4

The MOE and MOR of the leached and non-leached wood samples. Results are presented as mean ± standard error (n = 8). Different letters indicate significant differences between treatments based on Tukey's range test.

Treatment	MOE (GPa)		MOR (MPa)	
	Leached	Non-leached	Leached	Non-leached
Control	3.6 ± 0.3	3.9 ± 0.4	83.8 ± 6.3^{ab}	93.4 ± 7.8^{ab}
Caffeine	3.9 ± 0.4	4.1 ± 0.3	85.9 ± 8.6^{ab}	100.4 ± 5.8^{ab}
Caffeine + Glutaraldehyde	4.1 ± 0.3	4.0 ± 0.3	103.9 ± 6.4^{a}	109.5 ± 7.4^{a}
Caffeine + Formaldehyde	3.9 ± 0.2	3.6 ± 0.3	86.2 ± 4.2^{ab}	91.3 ± 5.15^{ab}
Glutaraldehyde	3.1 ± 0.2	3.9 ± 0.3	71.0 ± 4.8^{ab}	92.5 ± 5.4^{ab}
Formaldehyde	3.0 ± 0.2	3.8 ± 0.3	63.6 ± 4.0^{b}	77.7 ± 6.3^{b}

between treatments. The MOR of the non-leached specimens treated with caffeine with glutaraldehyde exhibited the highest value among all the treatments, while the specimens treated with only formaldehyde showed the lowest value. A similar pattern was observed with the MOR of the leached specimens, where formaldehyde treatment yielded the lowest value, the caffeine with glutaraldehyde treatment yielded the highest value, and the remaining treatment did not differ from the control. The MOR of the caffeine with glutaraldehyde treatment showed no significant differences before and after leaching test.

In contrast, the MOE did not show any significant differences among the treatments compared to the control specimens, in either the leached or non-leached groups.

4. Discussion

The retention values for caffeine, caffeine with glutaraldehyde, and caffeine with formaldehyde treatments analyzed were like those of commercial wood preservatives, such as CCA for exterior use (12–30 kg/m^3) and ACQ for exterior use (10-25 kg/m^3) (Breslin and Adler-Ivanbrook, 1998; Lebow et al., 1999; Ross, 2010). After the leaching test, caffeine-impregnated wood and caffeine-formaldehyde-impregnated wood exhibited the highest mass loss, suggesting that these treatments were more susceptible to leaching. In contrast, the mass loss of caffeine-glutaraldehyde-impregnated wood showed the lowest leaching value. This indicates that the addition of glutaraldehyde enhances the fixation of caffeine to wood.

In the FTIR analysis the most well-defined and prominent bands associated with caffeine were observed in the 1650–1750 cm^{-1} region, as overlapping with wood components in other regions highlights the limitations of this technique. Nevertheless, within this region, the spectra confirmed the presence of caffeine. After the leaching test, wood specimens treated with caffeine-formaldehyde exhibited a lower absorbance compared to those treated with caffeine alone or caffeine combined with glutaraldehyde. This suggests that the addition of glutaraldehyde enhances caffeine retention more effectively than formaldehyde. However, no significant differences in absorbance were observed between caffeine-impregnated wood and wood treated with caffeine-glutaraldehyde after the leaching test.

To further explore the caffeine content in the caffeine-glutaraldehyde wood samples, a semi-quantitative analysis was conducted using temperature-programmed direct mass spectrometry. The findings demonstrate the capability of temperature-programmed DIP-MS to evaluate the chemical composition of treated wood samples, including the detection and semi-quantification of specific compounds like caffeine. The same approach has been previously used in the chemical fingerprinting of semivolatile compounds from wood samples (Shroff et al., 2024). Furthermore, Grönlund et al., 2024 (Grönlund et al., 2024) recently reported that DIP-MS could also hold the potential for the quantitative analysis of additives directly from plastic samples. The consistent caffeine levels across untreated samples prior to leaching suggest that the impregnation process was uniform. However, the significant reduction in caffeine content after leaching underscores caffeine's susceptibility to being leached from wood when exposed to water (Kwaśniewska-Sip et al., 2021). Interestingly, the inclusion of glutaraldehyde substantially mitigated caffeine leaching, as evidenced by the higher post-leaching caffeine signal intensities in samples containing both compounds. This enhanced retention may be attributed to potential chemical interactions between glutaraldehyde and caffeine, such as hydrogen bond or stabilization effects, which could fortify the wood matrix and inhibit caffeine dissolution.

The low abundance of glutaraldehyde-derived ions ($C_5H_9O_2^+$) suggests that the compound is retained in the wood in small quantities. Despite this, its presence appears to influence caffeine retention, thus improving the antifungal properties of wood. These findings highlight the complex interactions between caffeine and the other chemical agents used in the treatments. The results suggest potential pathways for improving the fixation of caffeine treatments by carefully selecting and combining specific agents. Further research is needed to fully understand the mechanisms behind these interactions and to optimize formulations for enhanced performance. Given the simplicity of the treatment process, which utilizes standard Bethel impregnation process, there is strong potential for this treatment to be scaled-up and applied on an industrial scale.

In the decay test, wood treated with caffeine and glutaraldehyde demonstrated the lowest mass loss both before and after the leaching test against both fungi. Its performance was comparable to that of current wood preservatives, achieving a durability class (DC) 1 rating without leaching exposure for both fungi. After leaching, the treatment maintained a DC2 rating against *G. trabeum* and a DC1 rating against *C. puteana*. These findings align with previous research on wood modification with glutaraldehyde (Xiao et al., 2012). The high mass loss observed after the leaching test of caffeine-treated wood when exposed to *G. trabeum* and *C. puteana* demonstrates the high leachability of caffeine from wood, consistent with both the leaching and in IR results and corroborated by previous research (Simunkova et al., 2021; Woźniak et al., 2022). Concerning the combined treatments, the leached specimens treated with caffeine-formaldehyde decayed at the same level as control when exposed to *G. trabeum*, whereas the non-leached specimens did not decay. These findings are consistent with the leachability of caffeine from wood when formaldehyde is added, not enhancing its fixation. However, the performance is dependent on the concentration of the preservatives. Previous research demonstrated the decay resistance of alkaline copper quaternary (ACQ-C) and copper azole (CA-C) treatments at various concentrations against *Trametes versicolor* and *G. trabeum*, revealing variation contingent upon the concentration (Ma et al., 2013). The decay performance of some of these preservatives have been reported in previous research in terms of mass loss due to the fungi, such as MCQ (4.23 ± 0.45%), ACQ (12.99 ± 1.98%), and CCA (3.21 ± 2.90%) treatments against *G. trabeum* (Kartal et al., 2015), and copper-based treatment against *C. puteana* resulting in a mass loss of 0.1 ± 0.2% before leaching and 0.3 ± 0.4 after leaching (Barbero-López et al., 2021).

Considering the similar performance of copper-based treatments compared to caffeine with glutaraldehyde treated wood, it is important to consider its potential as a wood preservative, as wood treated with copper-based preservatives must undergo a decontamination process prior to disposal (Janin et al., 2011). In addition, the effectiveness of the caffeine and glutaraldehyde combination in woods of different tree species should be assessed, as the effectiveness of some preservatives can vary depending on the species (López-Gómez et al., 2022). It is important to highlight that, according to EN 113, mass losses lower than 3% from the non-leached specimens exposed to *C. puteana* are considered insignificant, as the control did not reach a minimum mass loss of 20%. On the other hand, the non-leached specimens treated with caffeine with glutaraldehyde, as well as caffeine with formaldehyde, exhibited a mass loss of less than 3% when exposed to *G. trabeum*, while the control group showed a mass loss of 20%, indicating good performance according to the EN113 standard. Similarly, the leached specimens treated with caffeine with glutaraldehyde demonstrated comparable resistance when exposed to *C. puteana*. Improved decay resistance of caffeine with glutaraldehyde and caffeine with formaldehyde treatments, compared to the other treatments after leaching, is attributed to the fixation of caffeine.

Glutaraldehyde treatment has some challenges, such as concerns about toxicity as shown in Table 1. However, it serves as a practical demonstration that the fixation of caffeine in wood can be enhanced by adding glutaraldehyde, resulting in improved performance, particularly in terms of decay resistance.

Caffeine-glutaraldehyde-impregnated wood exhibited the highest MOR values both before and after the leaching test, indicating low chemical leachability. This increase in MOR may be attributed to caffeine's ability to fill micro-voids and pores, thereby densifying the wood and reducing internal weaknesses. Additionally, caffeine might reinforce the wood matrix, enhancing stress distribution and overall strength. Previous studies have shown that caffeine does not influence the MOE of various woods, including *P. sylvestris* (Pánek et al., 2021), which aligns with our findings. Additionally, while glutaraldehyde modification has been reported to enhance the mechanical properties of wood (Xiao et al., 2010), our study found no significant differences in MOE compared to control samples. In contrast, wood specimens treated with formaldehyde exhibited a decrease in MOR. This aligns with earlier studies that reported a significant reduction in mechanical properties when formaldehyde is used (Crespo-Gutiérrez et al., 2018).

Our primary objective in this study was to assess the leachability of caffeine when treated with glutaraldehyde and formaldehyde, focusing on the leachability dynamics rather than evaluating the long-term environmental impact of these substances. The concentration of these compounds in our experiments was kept low and controlled to establish a baseline for their effectiveness in this scientific context. Glutaraldehyde can potentially act as a linking agent by bridging the hydroxyl groups of wood and caffeine molecules through hydrogen bonding and weak dipolar interactions. Although the exact reaction pathway was beyond the scope of this study, the enhanced stability of caffeine observed after leaching suggests that these interactions are likely facilitated by the bifunctional nature of glutaraldehyde. Further research is needed to confirm these mechanisms and to assess whether the balance between performance and environmental risks is acceptable. While formaldehyde and glutaraldehyde are recognized for their significant toxicity, the risk of substantial exposure from treated wood in outdoor applications, such as cladding, is minimal. Nonetheless, it remains important to consider the potential ecotoxicity, safety implications, and proper disposal of wood treated with these chemicals, even though it is generally not classified as hazardous waste.

The efficacy of caffeine-based products may be enhanced by increasing the concentration, as higher levels of active compounds could improve fungal inhibition. However, the fixation efficiency may be inherently limited by the finite number of reactive sites within the wood structure, which restricts the extent of chemical binding or interaction.

This study demonstrates the promising potential of using caffeine in combination with glutaraldehyde as a wood preservative. The results demonstrate enhanced fixation of caffeine to wood using glutaraldehyde, although it exhibits significant toxicity. Given the proven effectiveness of this methodology, further research into alternative bonding agents with lower toxicity would be highly beneficial for optimizing the process. By establishing glutaraldehyde effectiveness, this study provides a foundation for exploring safer alternatives to enhance the applicability of caffeine as a wood preservative.

5. Conclusion

Glutaraldehyde treatment effectively reduced the leachability of caffeine from wood while enhancing decay resistance and retaining mechanical properties after the leaching test. In contrast, formaldehyde treatment showed less favorable results, particularly regarding leachability reduction and decay resistance against *G. trabeum* after leaching. These findings confirm the hypothesis that glutaraldehyde treatment offers significant improvements in caffeine retention and, consequently, in wood durability.

CRediT authorship contribution statement

Yeray Manuel López-Gómez: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Ville H. Nissinen:** Writing – review & editing, Methodology, Formal analysis. **Aitor Barbero-López:** Writing – review & editing, Validation, Methodology. **Martti Venäläinen:** Writing – review & editing, Validation, Methodology. **Antti Haapala:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization.

Declaration of competing interest

Authors declare no conflict of interest in publishing this manuscript.

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Data availability

Data will be made available on request.

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