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Enhancing *Pinus pinaster* Wood Durability Through Citric Acid Impregnation

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Abstract: Citric acid (CA), a naturally occurring compound in fruits, mainly citrus, has gained attention for its eco-friendly potential in wood modification. Through esterification, citric acid reacts with wood polymers to form bonds that improve adhesion, dimensional stability, and durability while reducing moisture absorption and susceptibility to decay. This study evaluated the efficacy of CA as an eco-friendly wood treatment. Wood samples were treated with solutions at varying concentrations (5%, 10%, and 15%) and assessed for dimensional stability, mechanical properties, biological resistance, and ecotoxicity. CA treatments significantly improved dimensional stability, with higher concentrations yielding greater weight percent gain (WPG) and anti-swelling efficiency (ASE). Biological tests demonstrated exceptional termite resistance, with no survival and minimal mass loss in treated samples at higher concentrations. Similarly, fungal resistance improved, as citric acid inhibited fungal growth. Ecotoxicity tests showed relatively low phytotoxicity, with some decrease in germination indices (GI) at higher CA concentrations. These findings highlight CA as a sustainable wood treatment for enhanced durability and biodegradation resistance in construction and outdoor applications.

Keywords: bending strength; citric acid; esterification; *Pinus pinaster*; toxicological analysis; wood treatment; sustainability

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1. Introduction

The construction and furniture industries' demand for sustainable materials is driving research into eco-friendly alternatives [1]. Conventional wood treatments often rely on chemical preservatives, raising environmental and health concerns [2] This has led to a growing interest in bio-based approaches to wood modification, aiming to enhance wood properties while minimizing ecological impact. CA is a substance that occurs naturally in a variety of fruits and vegetables, especially citrus fruits. Although it is widely known for its properties associated with acidity and flavor and is widely used pharmacologically in cosmetic products, e.g., as an acidifier, a pH stabilizer in beverages, and in blood thinners, among others, it is interesting to note that CA can play a surprising and ecological role in the modification and binding of wood, although the scarcity of scientific studies on the subject is great.

Persistent environmental concerns have driven the development of new, ecological wood modification technologies to replace conventional preservative treatments. These techniques aim to improve wood performance without compromising environmental sustainability [3]. A relatively recent approach in wood modification involves the use of aromatic polycarboxylic acid compounds. These compounds were previously used

to achieve crosslinking in cellulose [4], and given that cellulose is a major component of wood, they were also applied to wood. It was found that 1,2,3,4-butanetetracarboxylic acid (BTCA) was the most efficient crosslinking agent with the ability to form a greater amount of chemical bonds with cellulose compared to CA. This is due to the fact that CA has the ability to form only two ester bonds with cellulose [5]. However, BTCA is a costly chemical compared to CA, which is generally more accessible and cost-effective, as it can be obtained from both natural and synthetic sources.

In the process of modifying wood with polycarboxylic acids, a chemical reaction called esterification is used: a chemical reaction between acid (carboxylic acid) and alcohol (or other OH groups) that eventually results in ester and water. It is important to consider that the polycarboxylic acids used must have three or more acid groups capable of reacting with the hydroxyl groups of the cell wall polymers. CA, with its molecular structure that contains three carboxyl groups, is particularly interesting, as it allows at least two esterification reactions to occur when it interacts with the polymers present in the wood cell wall. These reactions not only improve adhesion and binding properties but also make CA an excellent binding agent [6].

The reaction process between wood and CA involves a two-step esterification, in which the formation of an anhydride initially occurs, followed by the reaction of this cyclic anhydride with the hydroxyl groups present in the wood, resulting in the formation of ester bonds [7]. A study conducted by Fang et al. [8] provided a detailed quantitative analysis of the crosslinking reaction process and reaction parameters, such as the degree of esterification, the proportion of carbonyl, and the degree of crosslinking, between polycarboxlic acid and wood components by means of Fourier transform infrared spectroscopy (FTIR). The results of this study indicated that the crosslinking esterification reaction process between polycarboxylic acid and wood follows a specific pattern. First, the hydroxyl groups of the carboxylic groups in polycarboxylic acid are dehydrated, forming an anhydride. Next, a nucleophilic substitution reaction occurs, in which the hydroxyl groups of the wood and the cyclic anhydride combine to form an ester.

One of the first studies on the use of CA was presented by Katović et al. [9], who studied alternative agents for chemical modification of wood. The authors reported a reduction in moisture absorption and a 40% decrease in wood swelling of small wood blocks when treated with CA, suggesting that the modification of wood with these compounds may offer advantages in terms of durability and resistance to environmental changes. The biological durability of beech wood modified by CA was studied by Despot et al. [10], who concluded it was significantly increased. A weight percentage gain (WPG) of 6.1% resulted in an eight-time increase of biological durability against brown rot fungus *Poria placenta* in comparison to un-modified controls. Vukusic et al. [7] studied spruce and beech wood treated with two different polycarboxylic acids, BTCA and CA; the results showed that the tensile strength of samples treated with CA was higher than that of samples treated with BTCA. Therefore, despite the advantages of BTCA in terms of the amount of carboxylic groups available, the choice between BTCA and CA as a wood modifier and binder may depend on the specific characteristics of the process and the material to be modified [6]. Šefc et al. [11] investigated the use of two catalysts, sodium hypophosphite (NaH_2PO_2) and sodium dihydrogen phosphate (NaH_2PO_4), both at a concentration of 6.5% and combined with a 6.9% CA solution. They reported ASE values of about 54% in fir wood (*Abies alba* Mill.) and about 40% in beech (*Fagus sylvatica* L.) cured at temperatures of 140 °C, 160 °C, and 180 °C. The compression strength parallel to the grain of wood modified with CA was reported by Šefc et al. [12] under various curing regimes and compared to unmodified wood. The results showed that the average compression strength parallel to the grain was maintained following modification. For fir wood, the compression strength even improved

after modification. These findings suggest that wood modified with CA is suitable for applications where maintaining or enhancing compression strength is as important as achieving improved durability and dimensional stability.

However, it is important to note that CA treatment can have a negative impact on the brittleness of the treated wood. A significant loss in impact strength was observed with or without the addition of sodium hypophosphite (SHP) [13]. This decrease in impact strength can make treated wood more susceptible to damage from impact forces. Also, findings suggest that CA modification negatively impacts the adhesive properties of beech wood. A decrease in bond strength was observed in modified wood bonded with PVAC glue compared to unmodified wood. The results showed that the modified samples failed to meet the minimum requirements of EN 204 [14] for PVAC-bonded wood. Consequently, further research is needed to explore alternative adhesives and assess the suitability of modified wood for gluing applications [15].

In recent years, CA has been used in conjunction with several polyalcohols/sugars, such as glycerol [16,17], sorbitol [18–23], and glucose [24], which are known to increase crosslinking, avoiding leaching.

The use of CA is considered to be a wood modification procedure if the impact on the environment is lower than that of untreated wood. A study that investigated the environmental impacts of *Pinus contorta* wood treated with CA and glycerol through a life cycle assessment showed promising results. It was found that the life expectancy of treated wood was 2.8 times longer than that of untreated wood. In addition, in relation to environmental impact categories such as land occupation and impact on respiratory organics, citric acid-modified wood demonstrated an 80% lower and 44% lower environmental impact, respectively, compared to untreated wood [16]. It is relevant to highlight that these evaluations were conducted based on the premise that both treated and untreated boards have a life expectancy of 20 years. However, it has become evident that citric acid-modified wood is more environmentally friendly than untreated wood only when the life expectancy of treated boards reaches 55 years, which is five times longer than that of untreated wood boards [16].

The aim of this study was to comprehensively evaluate the efficacy of CA as an eco-friendly wood treatment, focusing on its potential to enhance the properties of maritime pine wood sustainably while reducing the reliance on conventional and potentially harmful chemical treatments. This study aimed to evaluate the efficacy of CA as an eco-friendly wood treatment, focusing on its potential to sustainably enhance the properties of maritime pine wood.

2. Materials and Methods

2.1. Impregnation of Samples

The wood specimens were prepared from a piece of *Pinus pinaster* and cut into four different sizes, each tailored for a specific test. The first sample type, used for the dimensional stability test, measured 20 × 20 × 20 mm (radial × tangential × axial). The second type measured 10 × 10 × 30 mm for termite exposure tests. The third type had dimensions of 10 × 5 × 30 mm for fungal exposure tests. The fourth type was cut to 20 × 20 × 260 mm for bending strength and stiffness tests.

All wood specimens were impregnated with predetermined CA solutions prepared in three concentrations (5%, 10%, and 15% w/w).

Samples were oven-dried at 100 °C for 48 h to record initial mass and dimensions and then impregnated under vacuum in a Kitasato flask. After impregnation, they were air-dried (approximately 20 °C 65% RH) for 72 h and cured at 140 °C for 10 h. Final

measurements and weights were recorded. The weight percent gain due to the treatment was determined by Equation (1) using ten replicates.

$$WPG\ (\%) = \frac{(M_m - M_0)}{M_0} \times 100 \quad (1)$$

2.2. Dimensional Stability Test

The samples were immersed in a thermostatic bath containing sterilized distilled water maintained at 20 °C. Measurements and weighing were conducted after 2 h and 24 h of water saturation. Following this, the samples were dried in an oven at 100 °C for 24 h. Additional measurements and weighing were performed after drying. This process was repeated twice for each specimen to ensure consistent results. On average, five replicates were used for the tests.

The dimensional stability studies of untreated and treated specimens were conducted based on the swelling coefficient (*S*) and anti-swelling efficiency (*ASE*), as defined by Equations (2) and (3), respectively [25].

$$S\ (\%) = \frac{(L_2 - L_1)}{L_1} \times 100 \quad (2)$$

where L_2 is the dimension (or volume) of the saturated specimen (mm or mm^3), and L_1 is the dimension (or volume) of the dried specimen (mm or mm^3).

$$ASE\ (\%) = \frac{(S_u - S_m)}{S_m} \times 100 \quad (3)$$

where S_u is the swelling coefficient of the untreated specimen, and S_m is the swelling coefficient of the treated specimen.

2.3. Mechanical Bending Strength Test

The mechanical bending strength test is a widely used method to evaluate the strength and behavior of materials under surface-applied loads that cause bending deformation. Its main purpose is to assess a material's ability to withstand bending forces and deformations without fracturing. This test was performed according to the EN 408:2010 [26] standard, with some modifications.

In the test, samples were subjected to a centrally applied load at a constant rate of 400 kgf/min along the tangential direction and radial face until rupture. As the load was gradually applied by the universal testing machine, the specimens bent, creating internal stresses. The extent of deformation was recorded relative to the applied load.

Data on applied load and deformation were collected to construct a load–deformation curve, enabling analysis of key mechanical properties such as bending strength and elasticity.

These parameters were determined using a three-point bending test on a Servosis Universal testing machine. Ten replicates were used for each test. The modulus of elasticity (*MOE*) and modulus of rupture (*MOR*) were calculated according to Equations (4) and (5), respectively, from NP 619—Static Bending Test [27].

$$MOE\ (\mathrm{MPa}) = \frac{\Delta F \times L^3}{\Delta x \times 4 \times b \times h^3} \quad (4)$$

where $\Delta F/\Delta x$ is the slope of the elastic zone (N/mm), L is the arm length (210 mm for all specimens), b is the width (mm), and h is the height (mm).

$$MOR\ (MPa) = \frac{F_{max} \times L}{2 \times b \times h^{(10/6)}} \quad (5)$$

where F_{max} is the maximum rupture load (N).

2.4. Termites and Decay Fungi Test

Wood samples were exposed to subterranean termites in a controlled environment at UPB.LNEC, following EN 118:2013 [28] standards. Termites were confined to the wood surface inside a glass tube, with a substrate to support colony development, for 8 weeks (Figure 1). *Pinus silvestris* was used as control.

Figure 1. Termite durability tests according to EN 118:2013 [28].

The samples were maintained at 24–26 °C and relative humidity (RH) > 75%. The termite colonies were inspected daily to monitor gallery openings and the construction of chimney structures that could serve as escape routes. Additionally, these inspections aimed to maintain the appropriate substrate moisture level and record any mold development.

At the end of the test, the moisture content, theoretical dry mass (*TDM*), theoretical mass loss (*TML*), corrected mass loss (*CML*), and survival rate (*SR*) were calculated using the following Equations (6)–(10). Five samples were used for each variable.

$$Moisture\ content\ (\%) = \frac{(M_s - M_l)}{M_l} \times 100 \quad (6)$$

where M_s is the wet mass of the specimen after the test (g), and M_l is the dry mass of the specimen after the test (g).

$$TDM = M_m - (M_m \times MC) \quad (7)$$

where M_m is the dry mass of the specimen after treatment and before testing (g) and MC is the moisture content specific to each cellulosic matrix.

$$TML = TDM - M_l \quad (8)$$

$$CML\ (\%) = \frac{TML}{TDM} \times 100 \quad (9)$$

$$SR\ (\%) = \frac{N_f}{N_i} \times 100 \quad (10)$$

where N_i is the initial number of termites (150 per sample), and N_f is the number of surviving termites.

Termite attack was visually assessed and classified according to EN 118:2013 [28] (Table 1).

Table 1. Classification of Termite Attack Severity According to EN 118:2013 [28].

Grade	Description
0	No attack.
1	Attempted attack with superficial erosion.
2	Light attack with erosion around 1 mm deep in a limited area or a single tunnel up to 3 mm deep.
3	Moderate attack with erosion less than 1 mm deep over more than 1/10 of the surface or 1–3 mm in a smaller area or an isolated deep tunnel.
4	Severe attack with erosion 1–3 mm deep over more than 1/10 of the surface or deep tunnels forming cavities.

Wood samples were exposed to *Rhodonia placenta* rot fungi at UPB.LNEC under EN 113 [29] standards (Figure 2).

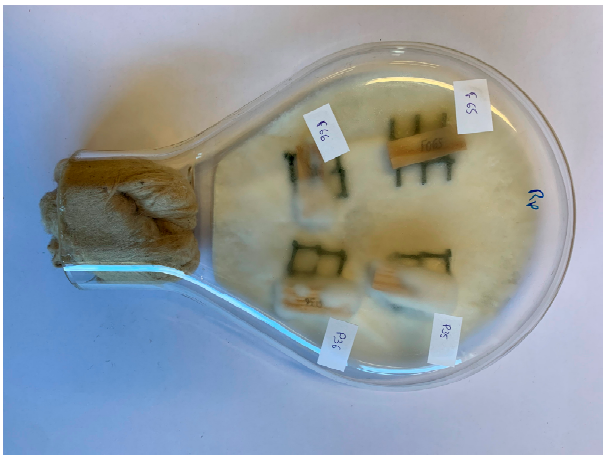

Figure 2. Fungi durability tests according to EN 113 [29].

The fungus was cultivated in a malt medium, and sterilized samples were placed in *Kolle* flasks on stainless steel mesh to avoid contact with the medium. Flasks were sealed with sterile cotton for airflow and kept at 22 ± 2 °C and 70% ± 5% humidity for 16 weeks. After exposure, samples were cleaned, stabilized for moisture, and assessed for moisture content and corrected mass loss using predefined equations. Ten samples were used for each variable.

2.5. Toxicological Test

This study followed EN 84:2020 [30] standard using 20 × 20 × 20 mm wood samples treated with CA at various concentrations (0%, 5%, 10%, and 15%). Samples were vacuum-immersed and leached for 14 days with regular water replacements.

The germination test was conducted to assess ecotoxicity by evaluating the inhibition of germination in *Lactuca sativa* seeds exposed to leachates. A 1 mL aliquot of each leachate solution was pipetted onto filter paper in a Petri dish, on which 20 *Lactuca sativa* seeds were placed. The dishes were incubated at 22 °C for 7 days. After incubation, the germination rate as well as the lengths of radicles and hypocotyls were measured. The Radicle Growth Index (*RGI*) and Germination Index (*GI*) were calculated using Equations (11) and (12), respectively, to quantify the effects of growth and germination inhibition.

$$RGI = \frac{CRA}{CRC} \tag{11}$$

where CRA is the radicle length in the sample, and CRC is the radicle length in the control.

$$GI\ (\%) = RGI \times \frac{SGA}{SGC} \times 100 \quad (12)$$

where SGA is the number of germinated seeds in the sample, and SGC is the number of germinated seeds in the control.

3. Results and Discussion

3.1. Weight Percent Gain (WPG)

The weight percent gain was determined after the curing step and in relation to the initial dry mass without any leaching procedure. Table 2 shows the effect of different concentrations of CA on the weight percent gain of samples. For the CA-treated samples, the WPG increased with higher CA concentrations: at 5% CA, the weight gain was 6.48%; at 10% CA, it rose to 16.38%; and at 15% CA, it reached 24.29%.

Table 2. Variation of weight percent gain with CA percentage ± Std dv.

Sample	5% CA	10% CA	15% CA
Weight percent gain (%)	6.48 ± 0.28	16.40 ± 0.42	24.30 ± 5.11

Šefc et al. [11] used two different catalysts at 6.5%, sodium hypophosphite (NaH_2PO_2) and dihydrogen phosphate (NaH_2PO_4), with a 6.9% solution of citric acid, and WPG values were reported for beech (*Fagus sylvatica* L.) and fir (*Abies alba* Mill) at 140 °C, 160 °C, and 180 °C. On average, the weight percent gain for sodium hypophosphite catalyst was higher for fir wood, with values ranging from 14.9% to 17.9%, while those for beech wood ranged from 7.8% to 9.7%. Even though the concentration used was 5%, the WPG with *Pinus pinaster* was similar to beech wood and smaller than that observed for fir. In another study, Feng et al. [13] reported a weight percent gain (WPG) of 36% for poplar wood (*Populus adenopoda* Maxim.) after modification with 20% CA solution using sodium hypophosphite (SHP) as catalyst (5%). The study found that SHP significantly catalyzed the reaction, enhancing the wood's stability and water resistance.

3.2. Dimensional Stability

Figure 3 presents the tangential swelling of untreated and CA-treated wood at 5%, 10%, and 15% concentration along the three wet and dry cycles (I, II, and III of 24 h each). All the treatments with CA decreased wood swelling, and higher CA concentrations led to higher decreases in swelling. Even though there was a loss of efficiency along the wet and dry cycles, treated wood still performed better than untreated wood after the three cycles. After the first cycle, tangential swelling was about 8.0% for untreated wood and was reduced to about 6.5%, 4.4%, and 3.5% for treatments using 5%, 10%, and 15% CA, respectively. After three wet and dry cycles, untreated wood presented 9.0% tangential swelling and treated woods 7.1%, 5.8%, and 5.0% for treatments using 5%, 10%, and 15% CA. The results shows that after three cycles, all the different treatment concentrations still performed better than untreated wood. Similar behavior was observed for the radial direction, where radial swelling decreased proportionally to the amount of CA in the wood. Overall, radial swelling was lower than tangential swelling, as expected. Therefore, no significant changes were observed in wood anisotropy.

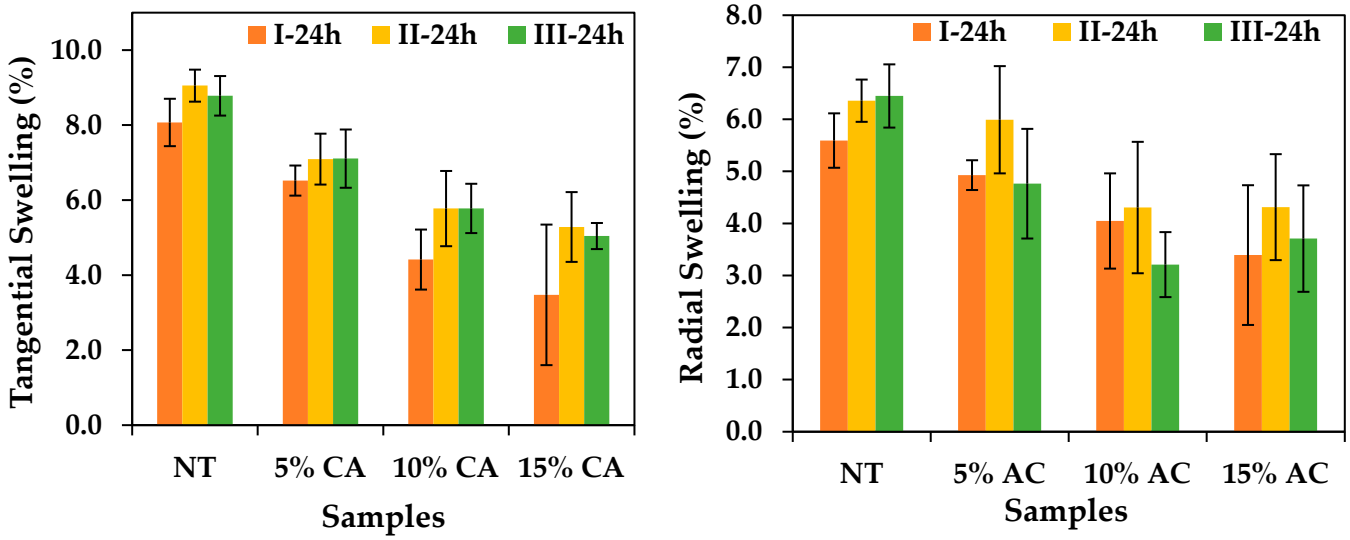

Figure 3. Average percentage of tangential and radial swelling for the different samples.

In order to better understand the improvements on dimensional stability, anti-swelling efficiency (ASE) was determined by comparing the swelling of treated and untreated wood. After the first wet and dry cycle, the tangential ASE was 19%, 45%, and 57% for treatments using 5%, 10%, and 15% CA, corresponding to a significant improvement in wood dimensional stability even at a low concentration of CA (Figure 4). After three cycles, the ASE still was 19%, 34%, and 43%, which means that even though there was some decrease in efficiency, the improvements were still significant. Similarly for the radial direction, after three cycles, the radial ASE was 26.1%, 50.2%, and 42.5% for 5%, 10%, and 15% CA solutions.

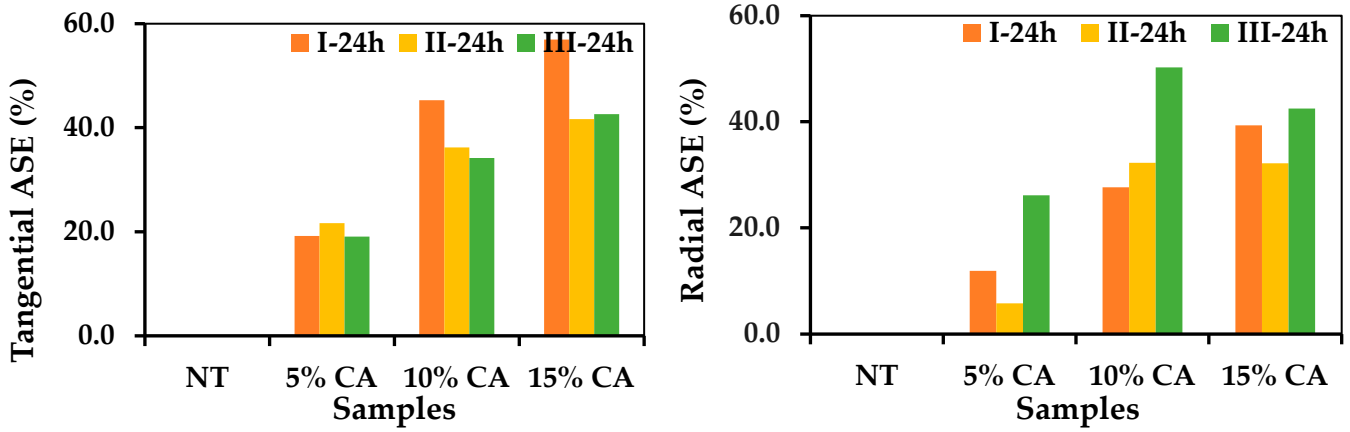

Figure 4. Anti-swelling efficiency (ASE) of tangential and radial swelling for the different samples.

Šefc et al. [11] reported that using a 6.9% CA solution with sodium hypophosphite (NaH_2PO_2) as a catalyst, the average anti-swelling efficiency (ASE) was approximately 54% for fir wood and 40% for beech wood. Similar ASE improvements were observed for both wood species when sodium dihydrogen phosphate (NaH_2PO_4) was used as the catalyst. Comparing these values with the 5% CA solution, the treatment seemed to perform better for fir and beech wood. Nevertheless, these values are comparable to the 10% CA solution. Similar results were presented before by Katović et al. [9] for the same species but with a swelling reduction of approximately 40% for both species.

Figure 5 shows water absorption (%) for untreated (NT) wood and wood treated with CA at concentrations of 5%, 10%, and 15% under different cycles (I, II, and III) and soaking

times of 2 h and 24 h. For untreated wood, water absorption was the highest, reaching approximately 70% after 24 h (I-24 h), which highlights its natural susceptibility to moisture. The 2 h absorption (I-2 h) was also significantly high. In relation to treated wood, higher levels of CA impregnation led to higher reductions in water adsorption. Similar results were presented before [7,11].

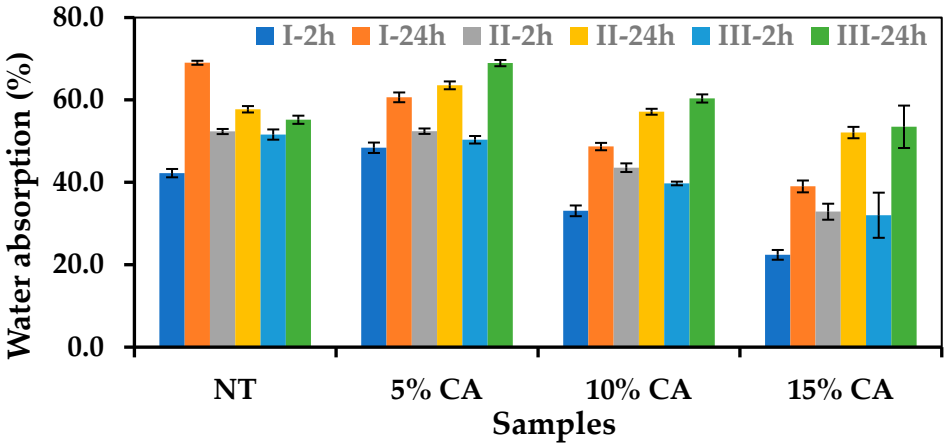

Figure 5. Water absorption of citric acid-treated maritime pine wood (2 and 24 h, per cycle).

For wood treated with 5% CA, water absorption decreased compared to untreated wood, particularly under cycle I, showing moderate water resistance. However, cycles II and III showed higher water absorption after 24 h, indicating that this lower CA concentration was less effective for prolonged exposure. With 10% CA treatment, there was a noticeable reduction in water absorption, especially for the first two cycles. This suggests improved water resistance compared to the 5% CA treatment, particularly for shorter soaking times of 2 h. Nevertheless, prolonged exposure of 24 h still showed some water uptake. At 15% CA treatment, the lowest water absorption was observed across all cycles. The first cycle, in particular, performed the best for both 2 h and 24 h soaking times, indicating that higher CA concentrations significantly reduce the wood's hygroscopicity. Overall, water absorption decreased with increasing CA concentration, with 15% CA being the most effective in enhancing water resistance. The first cycle produced the best results. However, further optimization might still be required to improve water resistance during prolonged exposure.

The results show that wood treated with CA had a greater difference between water absorption in 2 h and 24 h compared to untreated wood. This behavior can be at-tributed to the reduction in wood wettability caused by the treatment, as evidenced by the decrease in water absorption at higher concentrations of CA (15%).

3.3. Mechanical Bending Strength

Figure 6 shows the variation of the bending strength and bending stress (MOE) for the different CA concentrations. The results show that CA decreased the bending strength of wood and that this decrease was proportional to the amount of citric acid in wood. The bending strength decreased from the 402 MPa of untreated wood to 353 MPa, 304 MPa, and 278 MPa for 5%, 10%, and 15% CA solutions, corresponding to a 12%, 24%, and 31% decrease, respectively. On the other hand, the treatment increased wood elasticity by more than 30%. While the stress–strain curves reveal an increase in MOE (indicated by a steeper slope), they also show no plastic deformation following the elastic deformation stage, resulting in immediate rupture and a reduction in bending strength in citric acid-treated wood. These results demonstrate a considerable improvement in the elasticity of treated wood compared to other impregnations systems. For example, Esteves et al. [31] obtained

just a 13% MOE increase for paraffin-impregnated wood. Several authors have reported that when polycarboxylic acids are combined with polyols like D-sorbitol and sucrose, the addition of these polyols can effectively reduce the crosslinking density of the resulting material [19,21,22,32]. This reduction in crosslinking contributes to improved flexibility and helps mitigate brittleness. Despite these changes, the material retains its water resistance and benefits from enhanced mechanical properties, particularly in terms of the modulus of rupture, which indicates improved strength and durability under stress [32].

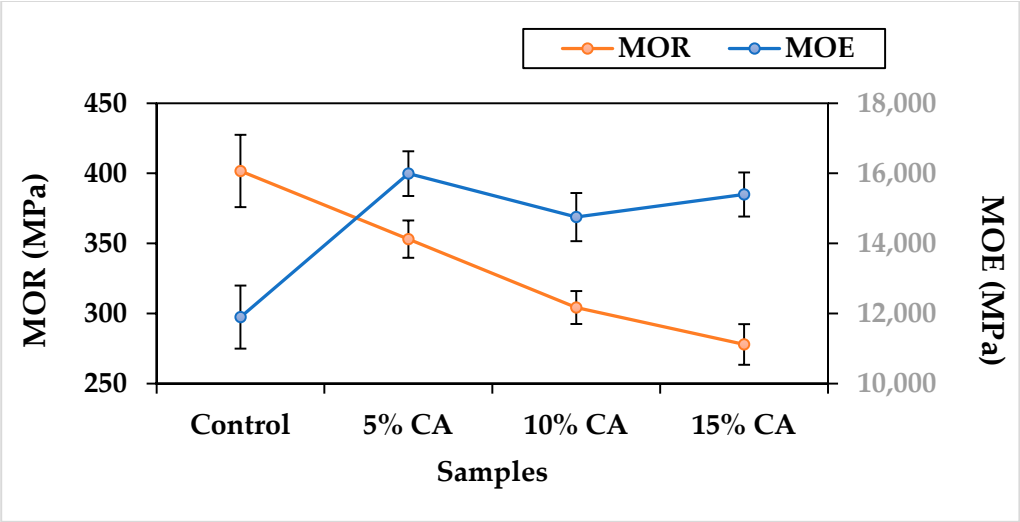

Figure 6. Variation of the bending strength for the different samples.

3.4. Termites and Decay Fungi

The termite resistance test is essential for validating wood treatments, assessing their effectiveness in preventing termite infestations, and ensuring structural stability. It also supports sustainability by reducing the need for frequent material replacement, thus minimizing environmental impact and promoting resource efficiency.

In the experiment conducted to evaluate the durability of wood samples against termite attack, the wood specimens were treated and tested according to the guidelines set forth in EN 113 [29], which provides a standard method for assessing the resistance of wood to biological degradation by termites. Figure 7 shows the tested samples after the 8-week exposure to termites.

Figure 7. Wood samples after the 8-week exposure to termites. From left to right: 10% CA, 5% CA, 15% CA, untreated, and control.

The test involved two sets of wood samples, untreated or CA-treated wood, alongside the control samples. The control samples used were samples from *Pinus silvestris* wood. The

untreated wood and the control samples showed significant evidence of termite infestation. Upon examination, multiple termite galleries were observed throughout the samples, indicating active feeding and tunneling by the termites. These galleries were often extensive, suggesting a high level of damage to the wood as a result of termite activity. In contrast, the wood samples impregnated with CA exhibited a stark difference. No termite galleries were visible on these treated samples, indicating that the CA treatment effectively inhibited termite feeding behavior. The absence of galleries suggests that the CA treatment either repelled the termites or created an environment that was unsuitable for termite survival and feeding, thus preserving the integrity of the wood.

Table 3 presents the results for the control group (untreated wood *Pinus sylvestris* samples, serving as a reference for comparison) and the untreated group (wood samples from the same batch as the treated ones), and 5%, 10%, and 15% represent the percentage of CA used in treated samples.

Table 3. Moisture content, corrected mass loss, survival and attack and their standard deviation (±).

	Control	Untreated	5% CA	10% CA	15% CA
Moisture content (%)	36.4 ± 9.8	40.0 ± 25.4	74.7 ± 9.2	67.5 ± 7.9	57.1 ± 3.3
Corrected mass loss (%)	8.4 ± 4.5	5.5 ± 3.1	0.6 ± 0.5	4.3 ± 0.4	5.7 ± 1.7
Survival (%)	67.1 ± 11.9	61.7 ± 35.1	1.5 ± 3.3	0.0 ± 0.0	0.0 ± 0.0
Attack	4 ± 0	3.4 ± 1.34	0.8 ± 0.8	0.4 ± 0.5	0.0 ± 0.0

The analysis of termite resistance revealed that the attack level decreased proportionally with higher CA concentrations. Samples treated with a 5% CA solution had an average attack level of 0.8, while those treated with a 15% solution showed complete resistance (attack level of 0.0). Untreated samples displayed small or no resistance to termites, with an attack level of 3.4; nevertheless, this attack level and the corresponding mass loss were influenced by the mortality of 100% in one of the samples from the C1 colony since the attack level was 4 for the remaining untreated samples. In treated samples, termite mortality began within the first week, with 0% survival for samples treated at higher CA concentrations. Even a 5% CA solution was highly effective, showing attack levels between 0 and 1 and average mass loss below 1%.

Compared to previous studies, these results are promising. Esteves et al. [31] found that paraffin-impregnated *Pinus pinaster* wood, while less susceptible than untreated wood (attack level of 3), still suffered termite damage, with a termite survival rate of 48%—higher than in CA-treated wood. Thermally treated wood performed even worse, with attack levels like the untreated wood and multiple termite galleries observed, highlighting the limited effectiveness of thermal treatment.

Mass loss was lowest at 5% CA (0.6%), indicating minimal degradation at this concentration. However, at 10% and 15% CA, mass loss was higher, approaching levels similar to the untreated group. Nevertheless, mass loss does not reflect the resistance to termite attack and is often misleading, and this is the reason for determining the attack level. Survival rate decreased sharply with CA treatment. At 5% CA, survival was almost zero (1.5%), and it was completely eliminated (0%) at 10% and 15% CA.

This results were better than those presented before for wood (*Melaleuca cajuputi*; Myrtaceae) treated with CA by dipping in 50%, 25%, and 15% CA solutions for 15 s and by impregnation of 6%, 3%, and 1.5% CA under vacuum for 1 h against *Coptotermes gestroi* Wasmann, where at only 6% impregnation, the mass loss was around 11% [33].

Given that the global economic impact of termites is estimated at USD 40 billion annually, with subterranean termites responsible for 80% of this damage [34], the use of toxic termiticides has raised health and environmental concerns, driving the search for alternatives. These results indicate that CA could be a viable, eco-friendly alternative to conventional termiticides for wood protection.

The wood decay fungi resistance test is as crucial as the termite resistance test for evaluating the effectiveness and durability of treated wood, particularly for outdoor applications. This assessment is essential to ensure compliance with standards and regulations and provide protection against biological degradation by fungi, which poses a significant threat to wood's structural integrity. In the fungal resistance tests, the brown rot fungus *Rhodonia placenta* was used, with treated samples and controls placed on each experimental plate. The results of the decay fungi resistance tests are presented in Table 4.

Table 4. Moisture content and corrected mass loss for untreated wood and CA-impregnated wood by *Rhodonia placenta* fungi.

	Untreated		**5% CA**		**10% CA**		**15% CA**	
	NT	**T.NT**	**5**	**T.5**	**10**	**T.10**	**15**	**T.15**
Moisture content (%)	58.85 ± 33.63	51.15 ± 13.00	119.03 ± 8.89	34.82 ± 8.27	117.11 ± 8.98	43.51 ± 20.59	110.32 ± 7.94	33.83 ± 5.57
Corrected mass loss (%)	4.96 ± 8.30	18.86 ± 9.25	1.15 ± 0.58	3.57 ± 2.55	2.45 ± 1.29	2.50 ± 1.53	0.73 ± 1.36	2.39 ± 2.05

Untreated wood (NT) presented a mass loss of 4.96%, while the test sample (T.NT) showed a higher mass loss of 18.86%. For 5% CA-treated wood, the corrected mass loss was minimal at 1.15, with a slight increase to 3.57% in the test sample (T.5). Similarly, for 10% CA-treated wood, mass loss was 2.45% and remained comparable in the test sample (T.10) at 2.50%. For 15% CA-treated wood, the corrected mass loss was the lowest across all samples, at 0.73%, with only a slight increase to 2.39% in the test sample (T.15). The results indicate that CA leaching from the treated wood into the culture medium effectively inhibited fungal growth, preventing substantial mass loss. Consequently, only the control samples, which were placed next to untreated specimens, exhibited a mass loss greater than 5%. This can be confirmed by the high moisture content in treated samples, indicating CA leaching, as leached acid was measured as water. Despite reduced mass loss in controls due to fungal inhibition, the mass loss in treated samples was still lower than that in controls.

Overall, the mass loss values indicate that CA treatment results in minimal degradation, with the test samples confirming the stability of this approach.

CA impregnation decreased the moisture content in treated wood. The lower moisture content may reduce the availability of moisture that fungi need to grow and cause decay. Nevertheless, since fungi require moisture levels around 20–25% to thrive [35–37], values over 30% should be enough to allow their growth. Nevertheless, the lower moisture content in CA-treated wood may lead to slower decay rates and result in the treated wood showing less decay compared to untreated wood with higher moisture content.

3.5. Toxicological Analysis

The ecotoxicity test for treated wood is essential for ensuring environmental safety and promoting sustainable material use by assessing its impact on soil and plant growth. It identifies potential adverse effects on seeds and seedlings, safeguarding ecosystem integrity. The germination index, which measures seed germination and radicle growth, serves as a sensitive indicator of toxicity, helping validate the effectiveness of wood treatments and their minimal leaching of harmful substances. This test supports environmentally responsible practices by evaluating the overall impact on plant development.

Table 5 shows the germination index for the different samples, highlighting significant differences influenced by the treatment concentration

Table 5. Variation in Germination for Untreated and CA-Treated Wood with 5%, 10%, and 15% Concentrations.

	Control	Untreated	5% AC	10% AC	15% AC
Germination Index (%)	-	68.4	59.3	63.2	26.8
Average germinated seeds (0/20)	19.4	14.6	13.8	17.4	17.2
Sprouted seeds (%)	97	73	69	87	86
Average radicle (mm)	34.89	31.72	29.10	24.58	10.55
Average hypocotyl (mm)	27.94	30.02	31.51	28.99	26.88
Root growth index	-	0.96	0.83	0.70	0.30

The table presents data on the impact of different concentrations of CA treatment on seed germination. The parameters evaluated include germination index (GI), average number of germinated seeds, percentage of germinated seeds, average radicle length, average hypocotyl length, and the radicle growth index. The control group was used as a reference, indicating optimal germination conditions without any treatment interference. Treatments with 5% and 10% CA reduced the GI to 68.4% and 59.3%, respectively, suggesting a moderately negative effect. At 15% CA, the GI dropped significantly to 26.8%, indicating elevated toxicity at higher concentrations. Nevertheless, compared with untreated wood, the negative effect is not very pronounced.

The average number of germinated seeds was highest in the control group (19.4 out of 20), demonstrating nearly complete germination. For untreated wood, the average decreased to 14.6 seeds, reflecting some inhibition. With 5% CA, the average number of germinated seeds dropped further to 13.8, indicating stronger inhibition. At 10% CA, the average increased to 17.4 seeds, suggesting partial recovery, similarly to 15% CA with 17.2 germinated seeds. The percentage of germinated seeds followed a similar pattern. The control group achieved 97% germination, while untreated wood exhibited 73%. The treatment with 5% CA resulted in 69% germination, indicating further reduction. At 10% CA, the percentage increased to 87%, showing slight improvement. However, at 15% CA, germination remained at 86%, still lower than the control.

Radicle length was most affected by the treatments. The control group exhibited the longest radicles (34.89 mm), indicating healthy growth. For untreated wood, the average radicle length decreased to 31.72 mm, reflecting moderate inhibition. With 5% CA, the radicle length dropped further to 29.10 mm, showing stronger inhibition. At 10% CA, the radicle length was slightly lower at 24.58 mm, and at 15% CA, the radicle length dropped sharply to 10.55 mm, reflecting severe inhibition of root development.

Hypocotyl length was also reduced by the treatments but to a lesser extent than the radicle. In the control group, the hypocotyl length was 27.19 mm. For untreated wood, the length increased to 30.0 mm, while at 5% CA, it increased further to 31.5 mm. At 10% CA, the hypocotyl length decreased slightly to 29.0 mm, and at 15% CA, the length also decreased to 26.9 mm.

In summary, the results show that CA treatments and also untreated wood negatively affect seed germination and early growth, with higher concentrations of CA leading to greater inhibition. Germination rates and radicle development are particularly sensitive, with the radicle being more affected than the hypocotyl. These findings suggest that while CA may have beneficial effects in specific contexts, its use should be carefully controlled to avoid detrimental impacts on seed germination and early seedling growth.

The number of germinated seeds was higher for 10% and 15% CA concentrations but with small radicles. In some cases, CA has been shown to stimulate seed germination, especially in seeds that are dormant or have a hard seed coat [38]. It was also shown that CA increased germination of okra (*Abelmoschus Esculentus* L.) plants under salinity stress [39].

Nonetheless, the role of CA in mitigating the environmental impact of wood treatments is noteworthy. Studies such as those by Essoua et al. [16] and Cahyono [40] have emphasized the small environmental footprint of CA-treated wood, pointing out its potential as a sustainable alternative to conventional biocides.

4. Conclusions

The present study demonstrated that citric acid (CA) effectively enhances the physical, mechanical, and biological properties of wood. Increasing the CA concentration resulted in higher weight percent gains (WPG), improved dimensional stability, reduced water absorption, and enhanced resistance to termites and fungi. However, this also led to a decrease in bending strength, although the elasticity of the wood was improved. The weight percent gain increased from 7.5% at 5% CA concentration to 21.7% at 15% CA, indicating effective impregnation. Dimensional stability was also enhanced, with anti-swelling efficiency (ASE) values of 53.4% at 15% CA. However, ASE decreased over five wet–dry cycles, dropping to 30.4% for 15% CA, although it remained superior to untreated wood. Water absorption decreased from 91.2% for untreated wood to 31.5% at 15% CA after 24 h of immersion. Mechanical testing revealed a decrease in bending strength from 97.4 MPa for untreated wood to 62.1 MPa at 15% CA, while the modulus of elasticity (MOE) increased from 10.3 GPa (untreated) to 13.9 GPa (15% CA). This indicates enhanced elasticity but also increased brittleness. Compared to other impregnation systems, CA-treated wood showed a 35% improvement in elasticity at the highest concentration.

CA treatment significantly enhanced resistance to termite attack, with no galleries observed on treated samples. Mortality rates for termites increased from 10% (untreated) to 100% at 15% CA, achieving complete resistance. In fungal decay tests, mass loss decreased from 34.7% (untreated) to 3.2% at 15% CA against the brown rot fungus *Rhodonia placenta*, demonstrating effective protection.

Ecotoxicity tests revealed that CA treatment affects seed germination and early growth. Germination rates decreased from 94% (untreated) to 52% at 15% CA. Radicle length was significantly impacted, decreasing from 27.6 mm (untreated) to 11.3 mm at 15% CA, while hypocotyl length showed a smaller decrease from 36.4 mm to 29.7 mm. Despite these effects, CA demonstrated a lower environmental impact compared to conventional wood preservatives.

Overall, CA proves to be an effective and eco-friendly treatment for enhancing wood properties, particularly for improving dimensional stability, water resistance, and biological durability. However, the reduction in bending strength and the impact on seed germination highlight the need for balanced optimization to maximize benefits while minimizing drawbacks.

Future studies could explore the synergistic effects of combining citric acid with other eco-friendly additives, such as sugars like sorbitol, to further enhance wood properties and decrease leaching. Investigating the optimal ratios and treatment conditions for such combinations could open new avenues for sustainable wood modification.

Overall, citric acid treatment, especially at higher concentrations, emerges as a promising, environmentally responsible method for wood modification, delivering improved performance while aligning with sustainability goals.

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