Eco-Friendly Preservation of Bamboo Species: Traditional to Modern Techniques

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The continuous depletion of forests calls for the astute usage of existing resources. Fungi and termites cause serious damage to biomass under storage and service conditions. Various protective treatments with high amounts of toxic chemicals are used by the wood and bamboo industry. Efforts are being made the world over to develop environmentally friendly preservatives for wood and bamboo species. Recent research highlights the potential and effectiveness of traditional practices and procedures, mainly water leaching technique and smoke treatment. Under laboratory conditions, the service life of treated blocks were found to be at a par with commercial chemical preservative treated blocks. Various plant extracts and oil-based formulations, such as organic acids, essential oils, and eco-friendly chemical-based preservatives, are in the stage of development. The bio-efficacy of such preservatives is measured in terms of the improvement in resistance to fungi and termites. However, much work still needs to be done to completely determine the efficacy of many of these newly developed preservatives and techniques. The present paper discusses an overview of the developments in the field of environment-friendly biomass preservatives.

Keywords: Bamboo preservation; Plant extracts; Durability; Fungal attack; Termites attack; Bamboo treatment

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INTRODUCTION

The experience of modern development, especially related to the deteriorating status of the environment and human health, is now sufficiently indicative of its inherent non-sustainability. The continuous increase in the human population, coupled with the modern lifestyle, has generated a huge demand for wood and wood-based products in the service sector, causing severe deforestation. Hence, to achieve sustainable development, environmental issues (*i.e.*, issues concerning the relationship between humans and nature), along with other dimensions of SD, have to be given due attention. Bamboo, a unique creation of nature, assumes great significance in this context. The short life span (one to three years) under storage conditions of bamboo culms because of insect-pest infestation is one of the biggest constraints on the utilization of bamboo in the housing sector.

Brown-rot fungi such as *Oligoporus placenta* and white-rot fungi such as *Trametes versicolor*, as well as bacteria and subterranean termites, deteriorate bamboo culms in storage, often one or more of these organisms attacking the culms in succession. It has been found that untreated bamboo has a service life of only two to five years. The environmental and human health hazards of conventional chemical preservatives are well known (Schultz *et al.* 2007; Xu *et al.* 2013).

The present paper discusses the latest developments in the techniques of preservative impregnation inside biomass culms. The latest developments in the methods of wood cell wall modification, heat treatment, and supercritical fluid extraction techniques are compiled and discussed. The bio-efficacy of such preservatives is measured in terms of improvement in fungus resistance, termite resistance, and field performance. Rigorous field testing is required to license the recommendation of a technique for a biomass species. The present paper provides an overview of the developments in the field of environment-friendly preservation for wood and bamboo species.

NEED FOR ECO-FRIENDLY PRESERVATION TECHNIQUES

Chemical treatment has been considered a solution to enhance the service life of biomass species. The chemicals used by local artisans as well as industry include copper chrome arsenic (CCA), sodium pentachlorophenol, boric acid-borax, Cu/Zn naphenates/ abietates, tebuconazole, IPBC (3-iodo 2- propanyl butyl carbamate), chlorothalonil, isothiozolones, and synthetic pyrethroides, all of which are presented in Table 1.

Severe harmful effect of these chemicals has led to their ban in many countries. The leaching of these chemicals into the soil and water has alarming consequences. Even though biomass culms are treated with CCA, creosote preservatives have been able to extend the service life of bamboo to around 36 years, yet their mammalian toxicity cannot be ignored. The odor of creosote makes it a preservative for outdoor application only. CCA, AAC, and CCB contain arsenic and chromium. The carcinogenicity of chromium and arsenic is a well-known fact. For this reason, effluent containing these preservatives should be treated before disposal (Yen and Chang 2008). PCP is banned for use in most countries. In contrast, triazoles, though they are expensive, are commonly used in plant protection of wood, for example: tebuconazole and propiconazole. Previous studies suggest that the leaching of toxic metals from treated wood merits disposal concerns (Khan *et al*. 2006; Moghaddam and Mulligan 2008). If the concentration of leached metals in waste biomass is higher than threshold or the toxicity limit, it is regarded as hazardous waste. The disposal of chemically treated wood is an onerous task.

Looking at the toxic effects of many of these preservatives, researchers are attempting to develop eco-friendly preservatives (Xu *et al.* 2013). The successful preservation of bamboo culms was defined as the safe storage of a large quantity of culms that could later be used.

The characteristics of an ideal preservative as described by Liese and Kumar (2003) are: (i) toxicity to the target organism (wood and bamboo destroying) and minimum toxicity to the non-target organism, (ii) permanent fixation inside the bamboo culm, (iii) high penetration inside the bamboo tissues, (iv) easy disposal of treated product, and (v) strength of treated culm not affected by preservative impregnation. The outer skin of bamboo is high in silica content. This restricts the flow of preservative into the culm. It is also difficult to penetrate inside the waxy layer of bamboo (Janssen 2000). The absence of ray cells in bamboo also constrains the flow of preservative to only the longitudinal direction. The radial flow of the preservative is hindered due to the refractory nature of bamboo culms. Thin culms can collapse and crack during the treatment process (Liese and Kumar 2003).

Table 1. Commercially Available Preservatives used for Wood/Bamboo Treatment (Liese and Kumar 2003; Evans *et al.* 2007)

Compound	Formula	Average life	Advantages	Disad-vantages
Polyborate	$Na_2B_8O_{13}.4H_2O$	NA	Self-diffusing, effective against fungi, insects, and termites	Highly leachable, not suitable for outdoor applications
CCA (copper, chromium arsenic)	47.5% CrO_3, 18.5% CuO, and 34% As_2O_5	NA	Fixable, broad spectrum biocide	Contains harmful chromium and arsenic
Bis-tri-butyl tin Oxide(TBTO)	$[(CH_3CH_2CH_2CH_2)_3Sn]_2O$	NA	Difficult to leach	Toxic
Creosote	By-product of coal manufacture	24.9 years	Good use of an otherwise undesirable product	Oil-soluble and expensive
Zinx Chloride/ Copper sulphate	$ZnCl_2$/ $CuSO_4$	NA	Hygro-scopic, good fungicide, can retard fire as well	Not effective in outdoor applications, ineffective for termites and insects
Sodium Pentacholorphenate	C_6Cl_5ONa	15.9 years	Effective fungicide	Banned in many countries because of presence of PCP
Copper Chrome-Boron (CCB)	$CuSO_4$:$K_2Cr_2O_7$,H_3BO_3(3:4:1.5)	NA	Fungicide, insecticide	Low fixation, presence of chromium
Ammonical-Copper-Arsenate(ACA)	$CuSO_4$:As_2O_3 (3:1) in ammonia	NA	High fixation	Presence of arsenic makes it toxic
Bis-(N-cyclohexyl-diazeniumdioxide)-copper(Cu-HDO)	$C_{12}H_{22}N_4O_4Cu$	NA	Good fungicide, insecticide	Expensive, toxic to aquatic organisms
Copper Naphthenate	$2(C_{11}H_7O_2).Cu$	29.6 years	Effective against insects and fungi	Should use with superficial treatment
3-Iodo-2-propynyl butylcarbamate-(IPBC)	$CH_3(CH_2)_3NHCO_2CH_2C{\equiv}CI$	NA	Fungicide	Not an effective insecticide

Traditional Preservation of Bamboo

The local bamboo growers preserve bamboo using systems that have been passed down to them according to traditional practices. Documentation and scientific verification of these methods is scant.

Good Harvesting Practices

Liese and Kumar (2003) also reported that the harvesting time affects the durability of bamboo. Durability is affected by the seasons. During the dry seasons, susceptibility to attack by fungi is greater because of the increased starch content. Thus, the right time to harvest is during or after the rainy season. The culms should be cut such that leaves are not removed. Leaves allow for the natural evaporation of free capillary water.

Water Leaching Methods

Submerging the bamboo culms in running or stagnant water helps the villagers to preserve the bamboo. As the culms are lighter than water, weight is put on the culms to submerge them completely in water. The fresh poles are stored for about 3 months in stagnant or flowing water. Starch, carbohydrates, and other water-soluble substances may be fermented or washed out. The duration of dipping varies from species to species. Ashaari and Mamat (2000) have observed the lower starch content of water-leached *B. vulgaris* bamboo species. Slaked lime makes the surface of treated bamboo alkaline. This delays the attack of fungi. Kaur *et al*. (2013) performed a decay resistance analysis of water-leached bamboo samples (weight loss: 9.7%) comparable to CCA-treated bamboo culms (weight loss: 7.3%). Studies have also reported that the remarkable reduction in starch content and the presence of additional amine groups in the treated samples might have contributed towards enhanced fungal resistance. Kaur *et al*. (2016b) reported that the ability of treated samples to resist insect and microbial attack under field conditions only lasted up to six months, which was much better than the control. The water leaching method was found to be incapable of giving complete protection to the culms under field conditions.

Smoke Treatment

Smoke treatment is used in villages to enhance the durability of bamboo species. Bamboo culms are stored in the kitchen over the fireplace. This process of using smoke to prevent insect attack is thousands of years old. Villagers have learned from experience that bamboo culms stored in this way are able to survive insect attack up to several years. However, no scientific data on the smoke treatment process for bamboo species can be found in the literature. It is expected that polycyclic aromatic hydrocarbons, phenols, aldehydes, ketones, organic acids, alcohols, esters, hydrocarbons, and various heterocyclic compounds present in wood smoke are able to improve the durability of wood species. If bamboo culms are fumigated (using their own branches and leaves) for a longer time, they become inedible to insects. The culms are smoked at an air temperature of 50 to 60 °C, which changes the moisture level of the air. The reduction in the water-soluble constituents including starch might help to protect the culms from fungi and insect attacks. Looking at the eco-friendly nature of the process, Hadi *et al*. (2012) reported on the effectiveness of smoke-treated wood against subterranean and dry-wood termite attack. The smoke, a byproduct generated during the pyrolysis process for making charcoal, could potentially be a useful means to increase wood resistance to termite attack. Wood specimens were exposed to smoke for a different duration of time. Sengon and Pulai wood specimens given smoke exposure for three days and Sugi specimens given smoke exposure for 15 days were classified as highly resistant. The most effective duration of smoking for producing high resistance in bamboo is not reported in the literature. ZERI (zero emission research and initiatives) at EXPO Hannover (2000) built an impressive circular roof building from smoke-treated bamboo. Kaur *et al*. (2016a) designed an experimental set up for the smoke treatment of *D. strictus* bamboo samples. Their study highlighted the effectiveness of this simple treatment method. Bamboo culms smoked for 8 hours were inoculated with *P. versicolor* fungi for 12 weeks. The significant reduction of starch (34.5%) and the deposition of a sooty layer of un-burnt carbon particles on the culm were reported to be beneficial for enhancing the service life of the treated product. Investigations of smoked bamboo culms found them to be similar to water-leached bamboo culms. Smoked bamboo samples were found to be non-durable under field conditions (Kaur *et al*. 2016b). Under laboratory conditions water leached and smoke treated bamboo samples showed weight loss of 9.6% and 12.2% respectively. However, these methods were not able to protect bamboo give protection to bamboo under field conditions. Samples were able to withstand the field conditions only up-to six months.

Special Construction Practices

Bamboo houses are traditionally made using special precautions. Various constructional methods have been followed since ancient times to protect bamboo houses. Generally, villagers take care to avoid the direct contact of bamboo culms with the soil and ground. This reduces the uptake of moisture through the soil or air. Bamboo culms are not placed in a cement base on the ground. Houses made at places of high altitude are generally free from termite attacks. Buildings are designed to facilitate unrestricted airflow (Liese and Kumar 2003). Along with this, solutions of tar and lime wash are used as paint and coating on wall (Janssen 2000; Randall 2000). The use of mud-coating to protect the huts of bamboo is also practiced in many parts of Bangladesh (Uddain 2008). Plastering with cement also helps to reduce microbial attack. Investigations into the quantitative effectiveness of these methods, is not reported in the literature.

BOTANICAL EXTRACT-BASED PRESERVATIVES

The traditional methods of the preservation of bamboo are simple, safe, and inexpensive. Field investigations of samples treated using these methods showed the poor durability of traditionally treated bamboo culms when exposed to outdoor conditions, including the combined effect of sun, rain, weathering, and microbial and insect attack. Plant extract-based preservatives have extensive potential, as they are toxic only to the target microorganism or termites and are safe for mammals. Plants and trees possess numerous constituents and extractives such as terpenes, alkaloids, flavonoids, glycosides, stilbenes, esters, phenols, polyphenols, alcohols, and water-soluble substances, which are known for their antibacterial and antifungal properties. These components can be isolated from biomass using non-polar and polar solvents. Schultz and Nicholas (2002) described the need to study the fungus and termite resistance of these extracts and termed it as a highly rewarding research area. The nature and quantity of extractives influence the durability of tree species. The factors that influence the choice of preservatives for industrial application are: the fungal and termite resistance of plant extract-treated products, the optimality of preservative concentration, the duration of biomass treatment/preservation, the fixation ability of the plant extract inside of bamboo or wood culms, and the leaching resistance efficiency. In addition to this, knowledge about the shelf life, heat, and temperature stability of the preservative gives more confidence to the consumer. However large scale production and treatment techniques based on plant extract based preservatives is still in development stage.

Azadirachta indica Extract

Neem oil, with azadirachtin as the major component, is known as an assured insect control agent. Subbaraman and Brucker (2001) added certain binding and bittering agents to enhance the efficacy of neem oil (3 to 40%) as a wood preservative. Dhyani *et al*. (2004) reported neem oil to be effective against wood-decaying fungi. Subsequently, Venmalar and Nagaveni (2005) reported the efficacy of neem seed oil on rubber wood. In untreated blocks, a weight loss of 65% was observed in samples exposed to white rot fungus, compared to 43% in samples exposed to brown rot fungus. In treated blocks, a weight loss of less than 10% was observed. Copper in combination with Neem oil has shown complete protection against both brown and white rot fungi. In field experiments, treated wood samples were found to be resistant through nine months of observation. Islam *et al*. (2009) investigated the antifungal efficiency of neem leaf extract along with copper sulfate and boric acid (NECB) tested on mango (*Mangifera indica*) and rain tree (*Albizia saman*) wood. The wood samples treated with neem leaf extract alone showed high levels of resistance against *S. commune* fungi. Furthermore, copper sulfate and boric acid were added, respectively, to neem leaf extract, to each a produce a 5% (w/w) solution that was able to protect the timber specimens, giving rise to weight losses of 3.3% and 3%, respectively. In field testing for 12 weeks, an average increase by six to seven times the life span of treated blocks as compared to the control was reported. Similarly, Machado *et al*. (2013) observed the effectiveness of neem oil (0.01, 0.1, 1.0, 2.5, and 5.0%) in white spirit against five species of decay fungi and two species of termites. It was suggested that the neem oil could only be useful as a wood preservative by optimizing formulations with new co-biocides. Erakhumen and Ogunsanwu (2009) used hot neem seed oil at the temperature of 60 °C to treat *B. vulgaris* bamboo. The treatment was found to be effective in improving the water resistance, anti-swelling efficiency, and dimensional stability of bamboo.

However, contrary to this, Kaur *et al*. (2014) reported the poor durability of bamboo samples treated with neem oil. Dip- as well as pressure-treated bamboo samples showed weight losses of more than 25%.

Aleurites moluccana

Nakayama and Osbrink (2010) tested oil from the nut of the kukui plant, *Aleurites moluccana*, for termite resistance properties. Oil from mechanically pressed nuts of the Kukui plant, on dilution with acetone, was tested on southern yellow pine wood using a vacuum-pressure infiltration chamber. This study reported the best results against the Formosan termite (*Coptotermes formosanus*) when treated with the oil concentration of 47%. The results also reveal that the oil is not a toxic agent and that the treatment is environment friendly.

Neobalanocarpus heimii

Chengal (*Neobalanocarpus heimii*) timber has a high natural durability and a high extractive content. Yamamoto and Hong (1988) studied the extractives of this tree and tested them against decay fungus. The anti-fungal components of chengal were found to be insoluble in water and only slightly soluble in methanol. Components of chengal extracted with methanol over the course of 12 h produced a weight loss of 9% in wood specimens exposed to *C. versicolor* fungi. Kadir *et al*. (2014) further investigated the termite resistance of the extract of this plant and reported that a 1% level of concentration of this extract was sufficient to cause 100% termite mortality in 25 days of laboratory investigation.

Anacardiumo ccidentalel

Cashew nut shell liquid (CNSL) is a by-product of the cashew industry. It is obtained either by extraction in hot oil or in solvents or by mechanical expulsion from the shells. Venmalar and Nagaveni (2005) evaluated the proficiency of cashew nut shell oil as a wood preservative. Cashew nut shell liquid (CNSL) is chiefly used in the preparation of synthetic resins. CNSL consists of anacardic acid (about 90%) and cardol (about 10%). A very low concentration of copper (0.4%) was reported to provide good protection. In a test of the efficacy of CSNL against white and brown rot fungi, the addition of copper to cashew nut shell oil resulted in a weight loss of less than 10%. The percentage of Cu in CNSL combinations was around 0.02 to 0.048. In field experiments, pressure-treated copperized CNSL panels were observed to be resistant up to 24 months of exposure. The average increase in the life of bamboo in the case of copperized CSNL was 7 to 8 times compared to untreated samples.

Cryptomeria japonica

Cedar oil is a natural termicide, mold inhibitor, and decay preventer for wood. Extract of cedar wood tree is reported to be highly effective at penetrating inside the wood cell walls. Areas treated with cedar oil will create a barrier against insect entry, because of the slow release of aromas. The cedar oil interferes with the pheromone system of termites and ants. Japanese cedar oil is reported to contain some terpenoids, which are termite anti-feedants. Ferruginol, present in cedar oil, provides it with a capacity to deter the growth of termites and fungi (Hemmerly 1970; Adams 2004**)**. Mun and Prewitt (2011) performed a double extraction of *Juniperus virginiana* heartwood using methanol flowed by hexane, chloroform, and ethyl acetate. The extract was able to inhibit the growth of *T. versicolor* as well as *G. trabeum* fungi. The effectiveness of cedar oil as a wood preservative was further demonstrated by soil analyses of treated wood blocks performed by Tumen *et al*. (2013). High level of thujopsene and cedrol were expected to be responsible for the high fungal resistance of extracts of the Ashe juniper wood species. Wood blocks treated with ethanol extract of Ashe juniper exhibited the lowest weight losses of 18.8% and 3.6% against brown and white rot fungi, respectively.

Cinnamomum camphora

Camphor (*C. camphora*) is known for its special aroma and insect-repellent properties. The extract of this plant is well established as antifungal and antibacterial. The performance of this extract as a bamboo preservative was studied by Xu *et al*. (2013). Their investigations highlighted the anti-fungal potential of the extract from leaves of the plant by testing the thermal stability and decay resistance properties of the treated product. Bamboo samples impregnated with resin mixed with camphor leaf extract exhibited weight losses of 6.60% and 5.54% against *P. chrysosporium* and *G. trabeum*, respectively (12-week test). Although the thermal stability of the samples treated with leaf extract was found to be improved above the addition of resin alone, still further improvement in thermal stability is required. Another study showed the effectiveness of extracts obtained from the debarked stem of this tree (Li *et al*. 2013). Wood samples treated with a methanol-extracted solution were able to resist the decay of *G. trabeum* fungi. The details about the field investigations of culms in the field have not been reported in the literature.

Parthenium argentatu

Resin from the Guayule tree is reported to be an anti-feedant for termites and is likely to provide protection to wood (Bultman *et al*. 1991). Bultman *et al*. (1998) extracted flaked guayule shrub extract using acetone-pentane azeotrope. The samples were found to be resistant to attack in the Arizona forest. However, the samples were not able to resist attack in Panama, which was thought to be due to the change in microbial activity in the two places. Nakayama *et al*. (2001) attempted to impregnate the wood with resinous material extracted from organic solvents under 700 kPa pressure using the nitrogen gas for 30 minutes. Resin material, *i.e* acetone extractable material, removed from guayule had shown both insect and microbial resistance properties. The impregnation of resin at 50% concentration into wood had made the wood resistant to termite attack. When the resin content was 97% of the maximum, complete termite mortality was achieved. The activity of both brown rot and white rot were observed to be inhibited by resin extracted from guayule. However, Holt *et al*. (2012) directed studies towards the evaluation of the termite resistance of particleboard made of guayule resin and found its termite resistance properties to be less convincing. No further investigations were performed to utilize this extract as a wood or bamboo preservative.

Nerium oleander

Nerium oleander is one of the world's most poisonous plants and contains numerous toxic compounds (oleandrin and neriine) that are cardiac glycosides. Turkish oriental beech (*F. orientalis* L.) and Scots pine (*P. sylvestris*) were impregnated with a solution. The decay resistance of wood specimens treated with aqueous solutions of *N. oleander* extract was studied. The extract was prepared from oleander leaves and flowers in 96% ethyl alcohol. The effects of the extracts on the developments of *P. placenta* (brown-rot fungi) and *T. versicolor* (white-rot fungi) were ascertained. The most effective dosage of *N. oleander* extract was 0.25%. The lowest weight loss observed for beech wood was 5.02% at a concentration level of 0.25% oleander extract against *T. versicolor* after 3 months of decay exposure (Goktas *et al*. 2007a).

Sternbergia candida

An endemic and poisonous plant of Turkey, *S. candida* is known to possess anti-fungal and anti-bacterial properties. Extract from *S. candida* was able to suppress the attacks of *P. placenta* and *T. versicolor* fungi on wood. The extract from the bulb and leaves of the plant was diluted within 96% ethyl alcohol was used to treat wooden blocks that were exposed to theses fungi for 12 weeks. Dosages of 0.25% and 0.75% were reported to be sufficient to provide desirable protection to the treated wood (Goktas *et al*. 2007b).

Milicia excelsa

Onuorah (2000) evaluated the brown rot (*L. trabea*) and white rot (*P. versicolor*) fungal resistance of *Milicia excelsa* and *Erythrophelum suaveolens*. Various dosages of the extract were dissolved in 60% methanol solutions. The soil block analysis of the wood reported its resistance to fungal attack at concentration levels of 3.0 and 6.0 lb/ft^3. Acetone extract of the tree was found to be resistant to termite attack under field conditions as well. Syofuna *et al*. (2012) investigated the water, hexane, and acetone extract of this tree applied on less durable wood species. The acetone extract-treated wood samples displayed weight losses of less than 10% after seven days in a field installation. The acetone extract of this tree is reported to have potential as a wood preservative.

Peppermint Oil

The decay resistance of peppermint oil and eucalyptus oil and their main components (menthol and eucalyptol, respectively) was reported by Matan *et al*. (2009). Several molds (*Aspergillus niger*, *P. chrysogenum*, and *Penicillium* sp.) and a white-rot decay fungus (*T. versicolor*) were used to study the dip treatment. Peppermint oil and menthol were reported to show higher fungal resistance than eucalyptus oil and eucalyptol. Only peppermint oil at the MIC was capable of providing complete protection from mold growth on rubberwood for up to 12 weeks at storage conditions of 25 °C and 100% RH. Both peppermint oil and eucalyptus oil at the MICs showed moderate resistance to fungal decay and high resistance to termite attack.

Valonia Oak

Sen *et al*. (2009) combined extract from the leaf of the Sicilian sumac (*Rhuscoriaria* L.), valonia oak (*Quercus macrolepis* Kotschy), and bark of the Turkish pine with various chemicals like boric acid, borax, aluminum sulfate, and copper sulfate to impregnate wood, using a full-cell pressure process at 1 bar vacuum (30 min) to 8 bar pressure (60 min), followed by 15 min at atmospheric pressure. The results of the wood decay analysis using a white-rot fungi, *T. versicolor*, and a brown-rot fungi, *G. trabeum*, showed that treated unbleached wood blocks displayed high antifungal activity, with weight losses less than 10%. The addition of aluminium sulphate (1%) had a positive effective on the reduction of leaching.

Table 2. Plant Extracts Investigated for Wood/Bamboo Preservation

Formulation	Fungal resisatnce	Termite resistance	Comments
Guayule (Nakayama *et al*. 2000)	Weight loss: 4.64%	NA	An acetone-extracted guayule was strongly anti-fungal.
Neem leaves extract with copper sulphate and boric acid	Weight loss: negligible (Islam *et al*. 2009)	Weight loss: 3-5% (Islam *et al*. 2009)	Wood treated with this extract was sound in the field through 9 months of investigations.
Neem seed oil with sodium chloride	NA	Weight loss: 0% (Himmi *et al*. 2013)	Neem seed oil dissolved into methanol and a 5% NaCl solution extracted with petroleum ether imparted complete resistance to termite attack when applied to rubber wood.
Neem oil	Weight loss: 25% (Kaur *et al*. 2014	Weight loss: 100% in field (Kaur *et al*. 2016b)	Neem seed oil was ineffective at protecting bamboo under laboratory as well as field conditions.
Neem seed oil with copper oxide	Weight loss: 5-7% (Venmalar and Nagaveni 2005)	NA	Neem oil alone gave good protection to rubber wood from fungal attack.
Nerium oleander	Weight loss: 6.33% (Gotaks *et al*. 2007)	NA	An ethanol extract of powdered leaves and flowers impregnated into wood imparted fungal resistance.

Chengal wood	Weight loss: 9% (Yamamoto and Hong 1988)	Termite mortality: 100% (Kadir *et al*. 2014)	The solution was effective at causing complete termite mortality.
Cashew nut shell oil	Weight loss<10% (Venmalar and Nagaveni 2005)	Sound in field till 24 months (Venmalar and Nagaveni 2005)	Wood samples impregnated with this solution showed on average a 7 to 8 times increase in service life.
Cedar wood oil	Weight loss: 3-19% (Tumen *et al*. 2013)	NA	Detailed investigations on the field performance of treated wood is not available in the literature
Cinnamomum camphora	Weight loss: 5.5-6.6%	NA	Field investigations are required for the same.
Nerium oleander	Weight loss: ~ 5% (Goktas *et al*. 2007a)	NA	Ethyl alcohol extract of leaves and flowers was highly effective against fungi.
Camphor Leaves extract	Weight loss: 6.6% (Xu *et al*. 2013)	NA	A mixture of camphor leaf with melamine-modified UF resin mixture was an effective bamboo preservative.

The study indicated the positive effect of adding 1% boric acid or borax on the retention of valonia oak and sumac leaf extracts, but not *P. brutia* bark extracts. Interestingly, it was observed that the addition of more than 3% mineral salts had a negative effect on the fixation of all three extracts. No investigation on the termite resistance of the extract was performed.

Essential Oils

The use of essential oils and their derivatives in the pharmaceutical, healthcare, food, and packaging industries has prompted researchers to explore their effectiveness as green preservatives for bamboo and wood. Various insecticidal, anti-fungal, and antibacterial components present in essential oils provide them with certain advantages as wood preservatives. Being renewable products, they are environment-friendly.

Kartal *et al*. (2006) evaluated the essential oils present in cinnamaldehyde. It was found that the cinnamic acid present in cinnamaldehyde was effective against white rot fungus. All the essential oil-treated wood samples showed weight losses of less than 10% when exposed to termites. Further, Yen and Chang (2008) reported the effects of catechin, quercetin, and eugenolto cinnemaldehyde on the basis of their antifungal index. A combination of three mechanisms of antifungal properties have been suggested, namely alteration of the cell wall, interference with cell wall synthesis, and the addition of radical anti-oxidation.

Mohareb *et al*. (2013) investigated the *in vitro* as well as *in vivo* antifungal activity of eighteen Egyptian plant essential oils, including the oils of *C. sempervirens*, *C. limon*, *T. occidentalis*, *S. molle*, and *A. monosperm*, on the protection of wood. The essential oil of *A. monosperma* exhibited the highest inhibitory effect, with EC50 values of 31 mg/L-1 and 53 mg/L-1 against *H. apiary* and *G. lucidum* fungi, respectively. A solution of cassia oil at 15.0% was reported to be the best fungicide, sustaining a negligible mass loss after 3 weeks of fungal exposure. In recent studies, it has been well established that essential oil-treated wood samples are durable against fungal attack.

Panek *et al*. (2014) reported on the fungal and mold resistance of beech wood treated with ten types of essential oils. Though tea tree, thyme, sage, and lavender essential oils were not able to provide sufficient protection to the wood, they were found to inhibit fungal growth better than the control samples. Oregano, thyme, sweet flag, and clove oil-treated beech wood samples were able to resist the attack of *C. puteana* fungi, sustaining a weight loss of less than 1%. These essential oils were found to be susceptible to attack by white rot fungi. Recently, Salem *et al*. (2016) reported the protection efficiency of essential oils from the leaves of *Pinus rigida* (wood) and *Eucalyptus camaldulensis* Dehnh. against mold fungi. *Eucalyptus camaldulensis* leaves were found to be ineffective at controlling mold fungal growth on wood samples. L-a-pinene, aterpineol, borneol, and fenchyl alcohol applied to *P. rigida* wood helped the treated wood to resist the mold fungi attack up to three months under laboratory conditions.

Although these investigations highlighted the potential of essential oils as bamboo and wood preservatives, none of these studies evaluated the termite and outdoor performance of the treated product. The questions of termite resistance and the service life of treated culms in the field require detailed investigation. The direction of future investigations could involve applying large-scale production protocols to investigate the treatments reviewed above. In addition to this, the heat sensitivity and non-stability of the active constituents of various essential oils need to be addressed to promote their use as an effective wood preservative.

ECO-FRIENDLY CHEMICAL TREATMENTS

There has been considerable recent interest in the development of environmentally friendly, non-toxic chemical-based preservatives in order to protect wood and bamboo from deterioration. The properties of wood, such as easy impregnation inside the biomass cells and deeper and more homogenous uptake makes them an attractive alternative to commercially available toxic chemical-based preservatives. In addition, a few studies have demonstrated the use of certain waste products like industrial effluents as potential preservatives.

Bio-Oil

Pinewood, pine bark, oak wood, and oak bark were pyrolyzed. Bio-oils or pyrolytic oils were fractionated to obtain lignin-rich fractions consisting mainly of phenols and neutrals. The pyrolytic lignin-rich fractions, and complete bio-oils fractions were tested using one brown rot fungus (*G. trabeum*) and one white rot fungus (*T. versicolor*). The lignin-rich fractions showed greater fungal inhibition compared to bio-oils when impregnated at the 10% concentration level. While bio-oils show some effectiveness against both brown and white rot fungi, they were not nearly as effective as commercial biocides. However, they may not be very useful as additives to biocide formulations. These bio-oils were also found to be leachable. Thus, more work is required to reduce their leachability, for instance by the addition of copolymers and other additives (Mohan *et al*. 2008; Temiz *et al*. 2010). Temiz *et al*. (2013) obtained bio-oil by pyrolysis of giant cane at 450 to 525 °C. The anti-fungal decay resistance of this specimen was observed for 16 weeks of exposure. The negligible weight loss of the bio-oil treated samples (less than 3%) showed bio-oil's high potential as a wood preservative. The results of the termite resistance analysis of the treated samples were found to be encouraging, with complete termite mortality after 4 weeks of investigations.

Effluents from Paper Mill and Wood Vinegar

The effluent of paper mill contains a large amount of organic waste. Tripathi and Chand (2005) used black liquor from the soda craft process diluted with water to treat wood. Exterior and ground contact samples showed no growth of fungus when treated with 1% liquor + 3% $CuSO_4$ and 5% liquor + 3% $CuSO_4$, while untreated samples showed 85% growth. The treated samples were shown to be protected under extremely humid conditions for up to 9 months. High humidity promotes the growth of fungus as compared to normal conditions. The results showed that the effluent of paper industry waste could be successfully used as a wood preservative. Interestingly, Sulaiman *et al*. (2005) and Velmurugan *et al.* (2009) described wood vinegar made from bamboo and broad-leafed trees as an antifungal preservative used for treating wood. Furthermore, Salim *et al*. (2013) showed the effectiveness of wood vinegar as an anti-sapstain against mold fungal growth. The studies described the volatile components of wood vinegar as responsible for enhancing the protection from decay. The *P. densiflora* wood dip treated in wood vinegar was durable against decay fungus for up to three weeks under laboratory conditions. Recently, Durmaz *et al*. (2015) studied the anti-fungal resistance of Scots pine sapwood treated with Kraft black liquor using a vacuum impregnation process. A weight loss of 5% kraft liquid was reported for the samples treated at concentrations of 0.35 % and 0.15% following six weeks of exposure to *Coniophora puteana* and *Poria placenta* fungi, respectively.

Nanoparticle Impregnation

Matsunaga *et al*. (2008) investigated the scope of nanoparticle impregnation inside wood cell walls. It was expected that the nanoparticle impregnation of the preservative inside the wood cell wall would make the wood less prone to insect attack. SEM analysis suggested that copper particles were large in size. The challenge of introducing copper particles into the wood cell wall can be overcome by the use of copper carbonate nanoparticles. Dispersions of copper-carbonate nano- and microparticles were examined. A non-uniform distribution of copper particles in the cell walls was achieved, with delivery of bioactive components only into the parenchyma wood cell walls. It was suggested that the copper particles were too large to penetrate into the nano-capillary network of the cell walls. The copper within the cell walls was found to be at a lower level than that in conventionally treated wood. The impregnation of the wood cell was further improved upon by the work of Matsunaga *et al*. (2012) using nano-particles (2 to 4 nm). The spectra of specimens impregnated with nano-particles showed no significant changes in their relative peak intensities of lignin and carbohydrates after exposure to *T. versicolor*.

Wax Impregnation

Kurt *et al*. (2008) used different kinds of hot molten waxes to improve the hardness of wood. The ray cells of wood act inhibit the wax to completely impregnate the wood cell wall. Based on visual observation, paraffin wax provided wood with maximum durability. The use of pine wax was associated with the maximum mortality rate for termites. The termite resistance of the leached samples was found to be less than that of unleached samples. Wax-treated wood was found to susceptible to leaching. In addition to this, Lesar and Humar (2010) used montan wax, polyethylene, ethylene copolymer, and oxidized polyethylene wax to improve the performance of beech (*Fagus sylvatica*) and Norway spruce (*Pinus abies*) wood tested against white rot, brown rot, and blue stain fungi. Polyethylene wax was reported to be the best solution against staining fungi, with samples treated with this wax sustaining a weight loss of only 1.7% against *T. versicolor* fungi. Although the water sorption of the treated samples was reduced, the treated wood samples were not found to be weak against blue stain and mould fungi.

Organic acids

There are various organic acids reported in literature with effectiveness against these micro-organisms and providing improved service life to the treated culms. Certain acids including acetic acid (widely known as preservative in food industry), formic acid (preservative in livestock feed), and propionic acid (preservative in feed and grain storage) have been investigated to reveal their potential as wood preservatives. Schmidt (2006) observed the effectiveness of formic acid and propionic acid to reduce the discoloration of wood because of bacterial attack. Sun *et al*. (2011) found hydrochloric acid effective to protect wood. Citric acid, formic acid, propionic acid, and sorbic acid inhibit the mould growth on bamboo species (Tang *et al*. 2009). Further, acetic acid (10%) and propionic acid (10%) were observed to completely protect bamboo from fungal colonization (Tang *et al.* 2012). Recently, Bahmani *et al.* (2016) observed inhibition of fungal growth by wood samples impregnated with the solution of acetic acid (5%) and propionic acid (5%).

Complexes to Reduce Boron Leaching

Boric acid preservative is associated with the disadvantage of leaching under outdoor conditions. A few investigations have suggested locking the boric acid inside the wood using different approaches. Tetra-hydroxyborate ions produced by the hydration of boric have demonstrated the ability to provide wood with resistance against decay. Obanda *et al*. (2008) have reviewed the research in the field of boron fixation and classified all strategies that have been employed into fifteen categories. Use of oil, polymerization and modification of wood cells, and organic and inorganic complexes of boron are a few of the major methods used in various laboratories. Among these reported methods, wood treated using envelope treatment was reported to perform the best. This includes air-seasoning with diffusible borates, diffusion storage, air-seasoning, and finally treatment with creosote.

A composition of three chemicals (copper sulphate, zinc chloride, and sodium borate) has been used to develop an environment friendly preservative (Tripathi *et al*. 2005). The formulation was found to be amorphous, water insoluble, and soluble with the help of co-solvents. A fixation study of ZiBOC in Chir and Poplar found aqueous leachabilities of only 23.6, 13.1, and 12.1% for copper, zinc, and boron in chir and 53.5, 6.5, and 5% in poplar. Analyses showed that a 0.50% concentration of salt (3.13 kg/m^3) completely protected the poplar completely against both fungi. The laboratory effectiveness of the solution was demonstrated by the weight losses of wood blocks treated with 0.2% (1.39 kg/m^3) and 0.1% (0.68 kg/m^3) concentrations of salt were able to provide complete protection against against white and brown rot fungi.

The boron compounds disodium octa-borate tetrahydrate, boric acid, and borax are used as insecticides for wood. Borates are also stomach poisons against termites. Boron compounds enter a glassy state when heated. The solubility of boric acid in water is about 5%. However, when mixed with borax, the solubility of boric acid markedly increases. This is an excellent preservative for protecting wood indoors because it is highly soluble in water. Wood treated with a 2% boric acid solution showed almost complete protection from fungi (Hashemi *et al*. 2010). A few studies have been reported in the literature involving boric acid and the thermal treatment of wood. Kartal *et al*. (2008) studied the effects of incorporating boric acid and di-sodium octa-borate along with heat treatment to decrease the loss in modulus of elasticity (MOE) because of heat treatment. Similarly, Percin *et al*. (2015) observed that boric acid treatment before heat treatment was useful to a great extent in reducing the mechanical strength losses, including modulus of elasticity, bending strength, tensile strength, and compressive strength. In an attempt to reduce the leaching of boric acid from wood cells, Akong *et al*. (2015) prepared a hydrogel based on N-tert-butyloxycarbonyl amino acid, benzotriazol-1yloxy, tris (dimethylamino) phosphonium hexafluorophosphate, triethylamine, and amino group along with borax powder to provide wood with full protection against leaching.

The antibacterial and enzyme inhibition properties of tannins were used to inhibit the wood rotters. The latest development in the use of tannin impregnation to improve wood properties started with Yamaguchi *et al*. (2002), who investigated three types of tannin solutions, namely mimosa tannin (MT), resorcinolated tannin (RMT), and catecholated tannin (CMT). An ammonia aqueous solution, tannin solution, and $CuC1_2$ aqueous solution were mixed in different proportions. The pressure treatment was applied at pressures up to 9.3 kg/cm and was maintained for 30 minutes. On the third day, the mortality of the termites was 100% for CMT- and $CMTNH_3$-exposed termites. Contact toxicity tests revealed that most of the tannin-ammonia-copper solutions did not have contact toxicity because the termites had eaten the treated cellulose pellets and remained alive. Wood eating-damage tests indicated that the tannin-ammonia copper agents offered a high level of protection against termites. The eating-damage tests, which were conducted after 21 days, revealed that none of the solutions except RMT were able to give complete protection. Thevenon *et al*. (2009) examined the protective effects of other tannin formulations on wood. Tondi *et al*. (2013) used boric acid and a hexamine solution to dissolve tannin powder. Vacuum-impregnated wood samples were tested with the above solutions for fungi and termite resistance. The observed weight losses were less than 3%, which showed the effectiveness of the solutions at imparting fungal and termite resistance to the wood.

Hydrogel Impregnation

The efficacy of using organosilicon compounds (silanes and siloxanes) to protect masonry, textiles, ceramics, *etc*., has been investigated in the context of wood by Palanti *et al*. (2012). A water-based active emulsion of methoxy-terminated dimethyl phenylsiloxane (DMS) and N-octyltrieth oxysilane (n-OTES) in different proportions and a micro-emulsion of polydimethylsiloxane (PDMS) and triethoxysilane (TES) and 60% w/w active macro-emulsion of polydimethylsiloxane (PDMS) were investigated; only the N-octyltriethoxysilane (n-OTES) was included for the analysis of anti-fungal activities. The decay resistance analyses showed a weight loss of 10.9% when using a 100% w/w active micro-emulsion of polydimethylsiloxane (PDMS) and triethoxysilane (TES). The Percentage Weight Gain (PWG) following treatment was found to be related to the durability. As PWG increased, the weight loss due to fungal exposure decreased, and thus implied improved durability. The study found that the PTMS-treated beech (2.75 to 14% PWG) was poorly protected against *T. versicolor*.

Table 3. Eco-Friendly Chemicals for Enhancing the Durability of Wood/Bamboo

Eco-friendly formulations	Fungi and termite resistance	Field testing	Observations
Bio-oil	Excellent decay resistance when not leached. Activity is lost on leaching.	NA	Highly durable under laboratory conditions. Fixation studies of bio-oils need to be addressed.
Paper mill effluent	Provide complete protection with no weight loss on fungal resistance analysis	No insect attack in field up to 9 months of installation.	Fixation studies need detailed investigation.
Tannin copper complex	High-level protection of tannin-ammonia copper agents against termites	NA	Fungal resistance not reported. Level of copper needs to be monitored.
ZiBOC	Provides 100% protection against various fungi	NA	Solution showed encouraging results under lab conditions, field investigations are required to be investigated
N-N-(1,8-naphthalyl) hydroxylamine(NHA-Na)	The termite mortality can be improved by addition of better fixing agents.	Pine wax showed maximum mortality rate.	No weight loss of unleached samples was observed.

N-N-(1,8-Naphthalyl) Hydroxylamine (NHA-Na)

Kartal and Imamura (2004) studied the combined fungicidal properties of copper, boron, and ammonium salts as a means of enhancing the durability of wood. Both the fungal and termite resistances of different treatments were investigated. Various combinations of copper sulfate pentahydrate, boric acid, and N’-N-(1,8-naphthalyl) hydroxylamine (NHA-Na) were examined. *T. versicolor* was reported to be a more depredating fungi than *Fomitopsis palustris*. Ammonium salts were found to be effective against both kinds of fungi. The addition of copper salt to boric acid was reported to improve the fungal resistance of wood. In unleached samples, the boric acid treatment was assessed to be completely resistant to termite attacks. However, upon leaching with water, a tremendous increase in termite attacks was observed in the study. Of all the leached samples, the boric acid and copper combination showed the best termite mortality (65%). Further work is needed to improve the termite mortality.

However, these studies did not incorporate the effects of combined treatment on the fungal and termite resistance of the biomass species.

CONCLUSIONS

1. The preservation and treatment of both bamboo and wood species is essential. A key focus is required to develop good weathering properties and environmentally benign, economical, and effective preservatives that give reliable performance and ensure that the treated product can be easily and safely disposed of at the end of its service life.
2. Traditional bamboo preservation methods such as water leaching and smoke treatment are absolutely safe, economical, and environmentally friendly. However, scientific data regarding their effectiveness and the mechanisms involved is very limited in the literature. Laboratory investigations of traditional treatments (*e.g.*, water leaching, smoking) have shown the potential of these treatments as potent fungicides under laboratory conditions. For the longer-duration protection of bamboo, chemical treatment has been considered a viable solution. For bamboo culms and palm wood environment-friendly organic acid have been used successfully.
3. For the development of environmentally acceptable preservatives, for instance plant-based preservatives, there is much research and development needs to be done. The studies on the efficiency of eco-friendly preservatives have been limited to the laboratory only.
4. Very limited data is available regarding the efficacy of wood preservatives used for bamboo. In the past decade, research on non-toxic preservatives has advanced remarkably. Recent research has demonstrated that eco-frienldy chemicals such as bio-oil, hydrogels, and boron complexes, are very efficient in improving the service life of wood/bamboo culms. Their scale up studies for industrial units need detailed investigations.

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