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EVALUATION OF COPPERISED CASHEW NUT SHELL LIQUID AND NEEM OIL AS WOOD PRESERVATIVES

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Abstract

An effort has been made to develop eco-friendly wood preservatives using naturally available plant by-products with less toxicity. Copper was incorporated into Cashew nut shell liquid (CNSL) and Neem seed oil. Rubber wood samples were treated with these solutions employing dipping and pressure techniques with different levels. These samples have been evaluated to find out the effectiveness as wood preservatives against decay fungi and termites. The combinations of copper & CNSL and copper & Neem in pressure treatment have resulted in discernibly high protection against wood rotters and termites.

Keywords: Cashew nut shell liquid (CNSL), Neem seed oil, wood preservatives, and rubber wood

Introduction

Wood being ligno-cellulolytic material is liable to degradation due to microbial agencies and termites causing significant losses. Since the supply of wood is limited, it is necessary to protect the wood in service from biological deterioration. From time immemorial, attempts were made by many workers to impart durability by treating the wood with natural and synthetic chemicals (Purushotham, 1970). The conventional wood preservatives although found to be very effective against wood destroying organisms, are said to cause environmental pollution and a few of them are hazardous to animals and human beings (Fisher, 1968; Thompson, 1971; Onuorah, 2000). Over the past few decades, there has been substantial global awareness to develop eco-friendly wood preservatives and those, which do not cause any ill effect on the health of mammals (Onuorah, 2000). There is a continuous search for different methods of bio-control methods for wood preservation.

Green plants act as a reservoir for inexhaustible source of innocuous fungicides/pesticides, which are mammalian non-toxic and easily biodegradable than synthetic chemicals. To develop eco-friendly wood preservatives, many studies have been conducted. Most of the reported work is on extractives from heartwood (Onuorah, 2000; Soni, 1975; Gupta and I.Dev, 1999). However, very few reports are available in which other components of tree like leaves of *Ipomea carnea* (Saxena *et al.,* 2002) and Neem (Swathi *et al*., 2004) possess a number of toxic constituents exhibiting high toxicity against wood-destroying microbes. Efforts have been made by many workers to use these plant products with the amendment of toxic metals and tested for durability against termites or fungi (Jain and Virendra Narayan, 1991; Jain *et al*., 1989 &1997; Purushotham & Tewari, 1961; Indra Dev & Nautiyal, 2004)

In the present study, an effort has been made in this direction to evolve wood preservative, utilizing the vegetable oil with the incorporation of copper as toxic ion. Amending toxic ions in Cashew Nut Shell Liquid (CNSL) which is a natural phenol and

Neem seed oil (contains Azadirachtin) with the incorporation of copper ion, have been evaluated to find out the effectiveness as wood preservatives.

Cashew nut shell liquid (CNSL) is a by-product of cashew industry. It is obtained either by extraction in hot oil or in solvents or by mechanical expulsion from the shells. Cashew nut shell liquid is chiefly used in the preparation of synthetic resins. In addition to its main application in brake lining of motor vehicles, it is used for manufacturing heat and waterproof paints, corrosion-resistant varnishes, insulating enamels and different types of surface coatings. CNSL consists chiefly of naturally produced phenolic compounds-Anacardic acid (about 90%) and Cardol (about 10%). Anacardic acid is a derivative of salicycylic acid, which readily decarboxylates on heating, to obtain anacardol or cardanol. The cardol is a resorcinol derivative having a long unsaturated hydrocarbon chain (Cornelius, 1996). In its natural form, CNSL is reported to accord protection against termites and has water repellency (Lepage and Delelis, 1980). The fishermen are also reported to be using this for protection of boat and fishing nets (Anon, 1948). Such protection is however temporary, as CNSL as such, has not been found effective for the purpose of wood preservation (Purushotham and Tewari 1961). Bagchee (1950) in his toxicity studies of CNSL against wood rotters reported that the activity of fungus and also weight loss was less in CNSL-treated blocks than in untreated ones. Activity of the fungus was decreased with the increase of concentrations of CNSL. Due to its phenolic nature, this product can be used directly as an outstanding preservative for timber and textile against insect and fungus attack (Ohler, 1979).

Neem (*Azadirachta indica*, A. Juss) is popularly known as village pharmacy, as all parts of this plant are used for several types of diseases since centuries. Extract of leaves and seeds exhibit the property of antibacterial, antifungal, antiviral (Tewari, 1992) anti malarial (Chavan *et al*., 1988) etc. Leaf extract also known to inhibit the growth of plant pathogens (Bhatnagar *et al.,* Kurucheve *et al.,* 1997) and wood decay fungi (Swathi Dhyani *et al*). Neem wood is known to be durable against wood rotters (Rao, 1990) and it is used for agriculture implements, construction etc.

Neem oil with the main constituent of Azadirachtin is used as insect repellent, feeding inhibitors, egg laying deterrents, growth retardants, sterilants etc. It has both contact and systemic action on plants for controlling fungal diseases.

Methods and Materials

Preparation of samples: Test samples were prepared from defect-free air-dried rubber wood (*Hevea brasiliensis*). Specimens of 1.9x 1.9 x1.9 cms were prepared to test against decay fungi and test panels of the dimension 15 X 3.81 X0.635 cms were prepared for field test. This sample size is used for accelerated field test.

Preparation of preservatives: Incorporation of copper for CNSL was done as per Sharma *et al* , 1964 with some changes. Crude Cashew nut shell liquid was dissolved in kerosene and refluxed over a heating mantle using water condenser to prevent evaporation of kerosene. The CNSL solution with kerosene was continuously stirred; keeping copper oxide in perforated hollow wanes of a stirrer, for 48 hours to obtain copperised CNSL. The copper content in the prepared solution was estimated as per IS 2753 part I (Anon, 1991), was found to be 5.26 %. This solution was diluted to 5 times W/W by using kerosene, and used for treating the test samples. The copper content in the diluted solution was also estimated.

Neem oil was incorporated with 20% copper naphthenate by thorough mixing by constant stirring and was diluted with kerosene to 5 times **W/W**. Copper content in the prepared solution was 4 %.

Treatment procedure

Fungus test samples: One set of test samples of the size 1.9x 1.9 x1.9 cms was treated by dipping for one hour. Another set of samples was subjected to pressure treatment by adopting full cell process, following the treatment schedule of 15 minutes with initial

vacuum of 56 cms of mercury followed by a pressure of 10 psi for 30 minutes and final vaccum of 56 cms of Hg for 5 minutes (15'/ 10/ 30'/5').

Field Test samples: Test samples of the size 15 X 3.81 X0.635 cms were dipped independently for three durations - 24, 48 and 96 hrs. Another set of samples was subjected to pressure treatment by adopting full cell process, following the treatment schedules of 15 minutes initial vacuum of 56 cms of mercury followed by a pressure of 10 psi for 30 minutes and final vaccum of 56 cms of Hg for 5 minutes (15'/ 10/ 30'/5'). The initial vacuum, the treatment time and final vacuum were kept constant with the change of pressure to 20 psi (15'/ 20/ 30'/5') and 40 psi (15'/ 40/ 30'/5'). Treatment procedures were same for both CNSL - Copper combination and Neem oil - Copper combination. There were following 12 treatments for each combination, and in total, there were 24 treatments.

1. Dipping treatment – CNSL alone – 24 hrs
- 48 hrs
- 96 hrs
- CNSL +Cu – 24 hrs
- 48 hrs
- 96 hrs

2. Pressure treatment CNSL alone - 10 psi
- 20 psi
- 40 psi

CNSL + Cu - 10 psi
- 20 psi
- 40 psi

Treatment combinations were same as above, for neem oil and neem + Cu combination.

After each treatment, the samples were weighed and absorption of preservatives was calculated for each specimen individually. Cu content was assessed individually where necessary. 15 samples were taken for each treatment.

Fungus test: The fungal resistance of the treated blocks was tested as per Indian Standard No.4873 (Anon,1968) using *Corilous versicolor* L.ex. Fr. FRI 165 (white-rot) and *Polyporus meliae Undrew* FRI 836 (brown-rot fungi). Six matched replicates were taken from each treatment and for each fungus. Untreated blocks were taken as controls. Treated and control test blocks were kept for conditioning in incubators at 70% relative humidity and 24^0C to attain constant weight (initial weight) and then these blocks were subjected to accelerated laboratory test employing malt agar method (Anon 1968).

After 16 weeks, test blocks were withdrawn from the cultured bottles. These blocks were carefully brushed off the fungal mats, then dried in warm air, again conditioned, and weighed to obtain constant weight (final weight). Percentage of weight loss was calculated for each block after fungal exposure.

Field Test (Test Yard)

Treated and untreated test panels were installed in test yard as per Indian Standard (No.4833-1968). Ten matched replicates were taken from each treatment. Termite activity and percentage of damage to the test panels was recorded at the intervals of three months by visual observation. Specimens were reinstalled in their respective positions after each inspection. The knife test or sound test was carried out when necessary to determine the extent of decay or destruction due to fungal or termite attack, till the sample was destroyed. Percentage of deterioration and increase in durability were calculated with reference to the control samples.

Results and Discussion

Absorption: Table-1 shows the mean absorption value of different treatments and percentage of copper in each treated block (fungus test blocks). On an average, absorption is 4 times more in pressure-treated blocks as compared to dip treatment blocks. The percentage of Cu in CNSL combinations is around 0.02- 0.048, whereas in Neem combinations, it is "between" 0.012 - 0.033. The percentage of copper alone treated blocks is around 0.01. The copper content in treated blocks is within the permissible limit of toxicity.

Table-2 shows the mean absorption value of different treatments of copperised CNSL and CNSL alone (test yard specimens). Minimum absorption of 23.98 kg/m^3 of CNSL was found in the 24 hrs dipping treatment and maximum of 42.37 kg/m^3 copperised CNSL was obtained in 10 psi pressure treatment. The percentage of copper in CNSL combinations is around 0.27-0.44, where as in neem combinations, it is between 0.36 - 0.48. Rate of absorption increased with the increase in duration of dipping in dipping treatment where as in pressure treatment, absorption was maximum (42.37 kg/m^3) at 10 psi and increase in pressure did not help in increasing absorption. As rubber wood is highly permeable, it reached the maximum absorption at 10 psi pressure itself. Further increase in the pressure did not improve the level of absorption.

Table-3 shows the mean absorption value of different treatments of copperised neem oil and neem oil alone (test yard specimens). In neem oil minimum absorption of 45.1 kg/m^3 of neem oil was found in the 24 hrs dip treatment and maximum of 83.7 kg/m^3 neem oil was obtained in 40 psi pressure treatment. Rate of absorption is proportional to the treatment time in dipping and increase of pressure in pressure methods.

The absorption of neem oil is more compared to the absorption of CNSL; this may be due to the less viscosity of neem oil when compared to CNSL.

Decay resistance: The decay resistance of treated wood samples against specific brown and white rotter was analysed by the weight loss. The weight loss in treated and control

blocks is shown in figure-1. White rot is generally more virulent than brown rot fungi in hard wood species (Eaton and Hale, 1993), and relative virulence in rubber wood was not exceptional. In untreated blocks, weight loss of 65% was observed in samples exposed to white rot as compared to that of 43 % in samples exposed to brown rot fungus. Weight loss in all treated samples are less when compared to control. But, copper alone treated blocks has not improved over combined effect. Pressure treated blocks are better than dip treated blocks. Among the dipping treatment, copperised neem oil and CNSL treatments have given complete protection against both the rotters. The combined treatment has resulted in discernibly high protection against wood rotters. Neem oil and CNSL- alone treatment also showed better performance than control. But these treatments could not bring the complete protection against the wood decay fungi.

In case of pressure treated blocks, the virulence of both fungi reduced drastically to less than 10 % irrespective of treatment. The effect of combined treatment with copper has resulted in discernibly high protection against wood rotters. Treatment which showed less than 10% of weight loss of test blocks, can be considered as effective treatment and this treated wood can be grouped under 'high resistance class'(Bakshi,1967). This classification of resistance is done only for comparison with natural resistance of durable species as per ASTM (Anon, 1981) and Bakshi (1967). Except for the dipping treatment of CNSL or neem oil alone, other treatments have shown the weight loss less than 10%. All these treatments can be taken as effective treatments for the rubber wood. CNSL or neem oil dip treatment showed the weight loss around 25% which is far better than control. The same chemicals with pressure treatment have given a good protection against wood decay fungi. This shows that improved absorbance of chemicals helped in protecting the test samples against wood decay.

Field exposure trials: Table-4 shows the percentage of destruction by termites in untreated and treated (CNSL and copperised CNSL) test panels exposed in the test yard. The untreated panels were damaged up to 40% within 3 months and completely destroyed (100%) within 6 months of exposure. It can be seen from the figure that treated test panels are almost sound up to 9 months of exposure

irrespective of treatment. In case of CNSL treated panels (both dip and pressure treated), destruction was observed from 12 months onwards and destroyed around 70 to 100% within 24 months. Whereas in copperised CNSL dip treatment, panels were sound up to 15 months and started deteriorating after that and reached 40% in 24 months. But, pressure treated copperised CNSL panels are very sound up to 24 months of exposure. After that stakes are showing the symptom of superficial attack. The panels are still under observation, which further may give detailed result at a later stage. Since, the specimens are thinner in size, the rate of depletion of preservative will be higher due to various causes and also that the rate of attack of specimens would be approximately proportional to the volume surface area ratio of specimens. The deterioration of the thinner veneer specimens is roughly about four times more than the standard specimens (Sharma et al., 1964).

From the test yard experiment, it can be concluded that an average increase in life due to treatment as compared to untreated samples are minimum 4-5 times more in CNSL- alone treatment and 7-8 times more in copperised CNSL treatment (Figure-2). Impregnation of CNSL into rubber wood helps in protection against termites to some extent. But, incorporating copper helped in improving the durability significantly in rubber wood.

Neem oil and copperised neem oil treated test panels are intact in the field without any symptom of destruction after 9 months of installation. Untreated samples are already destroyed in 6 months of duration. The panels are still under observation, which further may give detailed result at a later stage.

Rubber wood without any treatment is highly susceptible to fungi and termites. In the present study, treatment to rubber wood offered protection against decay fungi and termites. Very low concentration of copper (0.4%) with the help of plant products has given good protection. Hence, both CNSL+Cu and Neem + Cu can be taken as good preservatives. This observation confirms with that of John *et al*, 1964, where he has proved the bio-cidal efficacy of CNSL. Because of its versatile chemical nature, it

however offers a number of possibilities to get modified and it has been found very reactive to Copper and Zinc (Purushotham and Tewari, 1961). With the proven effectiveness against termites and fungi, copperised CNSL and copperised neem oil can be taken as low cost eco- friendly preservatives.

A more detailed study to fix the effective absorption level of CNSL and copper that are most toxic to fungi and termites and to better define the adequate levels of treatment, is now under way.

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Table-1. Absorption of preservative and % of Cu in test samples of different treatment (for fungal exposure)

Treatment Methods	Treatment Combinations	Absorption* (kg/m3)	Cu %*
Dip treatment	CNSL alone	2.00	
	CNSL + Cu	1.87	0.02
	Neem oil	1.95	-
	Neem oil + Cu	1.61	0.012
	Cu alone	1.31	0.01
Pressure treatment	CNSL alone	4.24	-
	CNSL + Cu	4.55	0.048
	Neem oil	3.54	-
	Neem oil + Cu	4.17	0.033
	Cu alone	3.95	0.032

*Average value of 10 replicates

Table-2. Absorption of CNSL and % of Cu in test samples of different treatment (CNSL combinations –for test yard samples)

Treatment Methods	Treatment Combinations	Durations/Level	Absorption* (kg/m3)	Cu %*
Dip treatment	CNSL alone	24 hrs	23.98	-
		48hrs	30.63	-
		96hrs	35.39	-
	CNSL + Cu	24 hrs	26.18	0.27
		48hrs	31.08	0.33
		96hrs	38.83	0.41
Pressure treatment	CNSL alone	10psi	33.92	-
		20psi	38.2	-
		40psi	32.49	-
	CNSL + Cu	10psi	42.37	0.44
		20psi	41.56	0.44
		40psi	41.6	0.44

*Average value of 10 replicates

Table-3. Absorption of neem oil and % of Cu in test samples of different treatment (Neem combinations - for test yard samples)

Treatment Methods	Treatment Combinations	Durations/Level	Absorption* (kg/m^3)	Cu %*
Dip treatment	Neem alone	24 hrs	51.03	-
		48hrs	55.07	-
		96hrs	55.46	-
	Neem + Cu	24 hrs	45.1	0.36
		48hrs	49.73	0.4
		96hrs	59.93	0.48
Pressure treatment	Neem alone	10psi	68.23	-
		20psi	79.0	-
		40psi	83.7	-
	Neem + Cu	10psi	51.2	0.41
		20psi	59.26	0.47
		40psi	54.63	0.43

*Average value of 10 replicates

Table-4. Effect of treatments of CNSL and its combinations in test yard

Duration in months	Damage level (%) in different treatments *												
	Dip treatment (in hrs)						Pressure treatment (psi)						Control
	CNSL			CNSL + Cu			CNSL			CNSL + Cu			
	24	48	96	24	48	96	10	20	40	10	20	40	
3	0	0	0	0	0	0	0	0	0	0	0	0	40
6	0	0	0	0	0	0	0	0	0	0	0	0	100
9	0	0	0	0	0	0	0	0	0	0	0	0	--
12	30	20	15	0	0	0	20	15	10	0	0	0	--
15	50	30	30	0	0	0	20	25	25	0	0	0	--
18	70	40	40	30	20	10	50	60	60	10	12	12	--
21	80	80	70	40	30	20	60	65	60	10	10	15	--
24	100	80	75	46	40	25	65	65	70	15	15	15	--

* The mean values of 10 samples

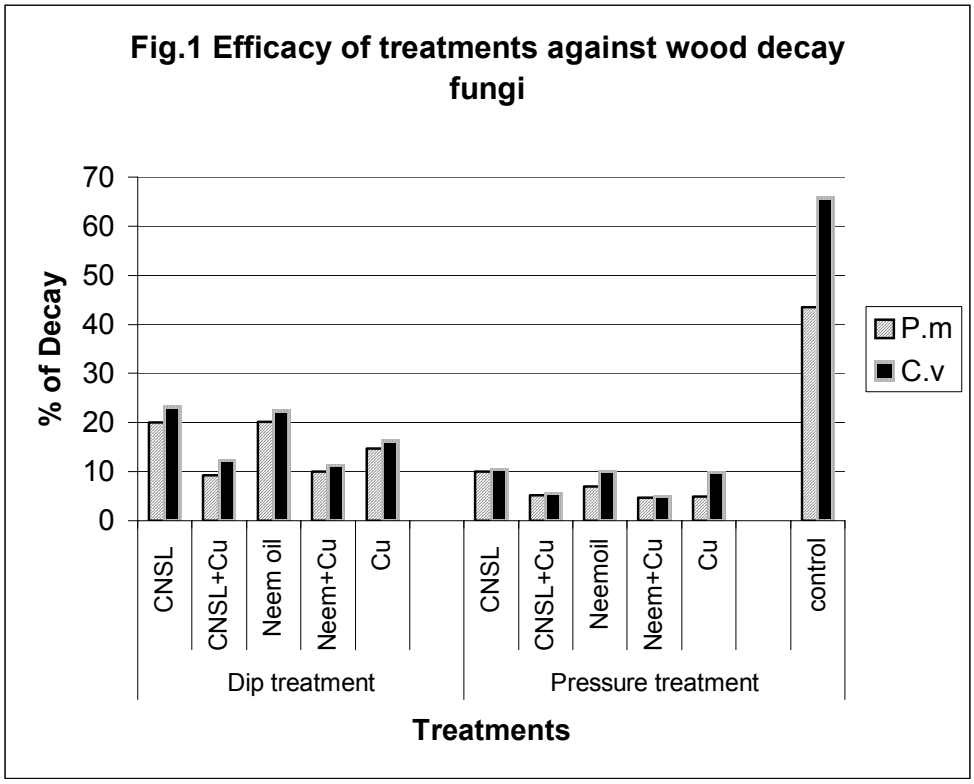
Fig.1 Efficacy of treatments against wood decay fungi
70
60
50
40
30
20
10
0
% of Decay
P.m
C.v
CNSL
CNSL+Cu
Neem oil
Neem+Cu
Cu
CNSL
CNSL+Cu
Neemoil
Neem+Cu
Cu
control
Dip treatment
Pressure treatment
Treatments

Fig 2: Increase in life due to treatment as compared to untreated samples