

COMPARATION OF DIFFERENT ENVIRONMENT-FRIENDLY ANTI-MILDEW AGENTS ON BAMBOO

HUI GUO, CAIJUAN ZHANG, XINJIE ZHOU, SHUOWANG, LILI YU
TIANJIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
CHINA

HUI LI^{1,2}

¹HUBEI ACADEMY OF FORESTRY, CHINA

²HUBEI MUFUSHAN MOUNTAIN BAMBOO FOREST ECOSYSTEM
RESEARCH STATION, CHINA

ZHI-BIN YANG
HUBEI ACADEMY OF FORESTRY
CHINA

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ABSTRACT

Four kinds of environmental anti-mildew agents (boric acid/borax, 3-iodo-2-propynyl-butyl-carbamate (IPBC), sodium tetrafluoroborate/didecyl dimethyl ammonium chloride (NaBF₄/DDAC), tebuconazole) were used to treat bamboo with different concentrations respectively. The optimal concentration of each anti-mildew agent and the comparison of the anti-mildew capacity were evaluated with *Aspergillus niger*, *Trichoderma viride* and *Penicillium citrinum*, respectively. The results showed that the optimal anti-mildew agent concentrations of boric acid/borax (F1), IPBC (F2), NaBF₄/DDAC (F3) and tebuconazole (F4) were 3.0%, 1.5%, 0.5% and 0.4%, respectively, and the average control efficacy of the three test molds was 73.15%, 92.03%, 88.43% and 98.67%, respectively. The order of anti-mildew capability of these four anti-mildew agents with their optimal concentrations was F4 > F2 > F3 > F1.

KEYWORDS: Bamboo, anti-mildew agent, control efficacy.

INTRODUCTION

Bamboo is one kind of natural biomass materials, which is widely used in the furniture, papermaking, textile, building structure, decoration and other fields because of its fast growth rate, high strength, good toughness, easy processing, large output and so on (Zheng et al. 2021, Chen et al. 2019). China's bamboo resources are abundant, which has greatly alleviated the current situation of timber shortage. However, as a biomass material, some nutrients such as starch, protein, sugar and fat are also very rich in bamboo, which provide nutrient conditions for the growth and reproduction of the microorganisms, which make the bamboo attacked easily by the mildew molds and decay fungi in the process of processing, transportation and use (Liu et al. 2019, Li et al. 2015, Huang et al. 2014). As a result, the quality of bamboo is reduced, the appearance is damaged, the mechanical properties are reduced, and the service life is shortened, which seriously affect the use value and economic value of bamboo and bamboo based products. Therefore, the anti-mildew treatment of bamboo is of great significance to the development of bamboo and the bamboo industry.

The traditional anti-mildew treatment of bamboo was mainly to impregnation or immersion of the anti-mildew agents to inhibit or kill the molds. Traditional bamboo anti-mildew agent systems mainly include fumigant, tar, oil-soluble, water-soluble and gas (Yu et al. 2016, Li et al. 2016). Liu et al. (2017) used four different anti-mildew agents to treat moso bamboo, and the experimental results showed that the control effectiveness of moso bamboo treated with glutaraldehyde was more than 90%, and citric acid and sucrose compound treatment had a certain anti-mildew effect on *Aspergillus niger*. Wu et al. (2019) studied the synergistic effects of mesoporous aluminosilicate with Cu-B-P anti-mildew agents, and found the anti-mildew performance of bamboo were improved by preparing mesoporous aluminosilicate film on the surface of bamboo fibers. Sun et al. (2012) studied the mildew resistance of moso bamboo treated with a combination of chitosan-copper complex (CCC) and propiconazole (PPA), and the better synergistic effects on the mildew resistance of bamboo.

Although the traditional anti-mildew agents of bamboo have efficient anti-mildew performance, some disadvantages such as high toxicity and poor environmental safety has been found and proved in these systems (Zhao et al. 2019, Huang 2018). Nowadays, the anti-mildew treatment technology of bamboo has focus on exploring a new type of bamboo anti-mildew agent with environmental protection, low toxicity and high efficiency (Zhang et al. 2021, Wang et al. 2018). Inorganic nanomaterials play an important role in many fields, and now they have been gradually applied into the field of bamboo. Many researchers have applied Ag, ZnO, CuO, TiO₂ and other nanomaterials with low toxicity and strong bactericidal ability in the anti-mildew treatment of bamboo. Pandoli et al. (2016) treated bamboo with silver nanoparticle colloid solution, and didn't find any fungal colonies on the surface of the bamboo after exposed outdoors for 5 months. Chen et al. (2018) prepared ZnO/PMHS coatings on the surface of bamboo by hydrothermal synthesis method and polymethylhydrosiloxane (PMHS) hydrophobic modification method. The test results showed ZnO/PMHS coating had displayed excellent anti-mildew performance, which indicated that nano-ZnO and PMHS had good synergistic effect on bamboo antimildew capacity.

Boric acid / borax has the characteristics of rich resources, low price, low toxicity to human body, easy to soak wood and so on, and has obvious anti-corrosion properties (Huang 2018). 3-iodo-2-propargyl-butyl-carbamate (IPBC) is a new type of anti-mildew fungicide, which has been widely used in paint, wood, leather, cosmetics and other fields, and it has a good effect on wood-rot fungi and molds with low toxicity and high efficiency (Gottscheetal et al. 2017). Gobakken et al. (2008) added IPBC to acrylic paint to treat wood, which not only obtained good antibacterial properties, but also improved water absorption and photodegradation. Borate preservatives have good antiseptic effect in bamboo wood treatment. The combination of borates and quaternary ammonium compounds (QACs) reduces the leaching of boron in borate treated wood. When QACs combined with some borates, such as dodecyl dimethyl ammonium chloride (DDAC) and sodium tetrafluoroborate (NaBF_4), which forms insoluble quaternary ammonium borates (QABs) via anion exchange reactions, the anti-loss property of boron was improved, and then the anti-mildew property of bamboo was improved. (Pernak et al. 2006, Xue et al. 2006). Triazole compounds are mainly used in the production of agricultural fungicides, and they also have excellent control effects on some bamboo discoloration bacteria and have certain anti-loss properties (Xi et al. 2013).

In this study, the effects of four kinds of anti-mildew agents including boric acid/borax, IPBC, NaBF_4 /DDAC and tebuconazole on bamboo were studied to determine the optimal concentration for each agent, and compare the anti-mildew capacity of agents. The aim is to provide suitable anti-mildew protection for bamboo and promote its wide and safe application.

MATERIALS AND METHODS

Materials

Bamboo slices were cut into $50 \times 20 \times 2$ mm, and the moisture content was conditioned to 2% in order to perform the screening experiment of bamboo anti-mildew agent. One kind of environment-friendly anti-mildew aqueous solution (boric acid / borax) and three kinds of environment-friendly anti-mildew organic solutions (IPBC, NaBF_4 /DDAC and tebuconazole) were used to treat bamboo with different concentrations as Tab. 1 showed. Six replicates were adopted in each anti-mildew treatment.

Tab. 1: Anti-mildew agents.

Type	Anti-mildew ingredients	Proportion of anti-mildew agents	Concentration of anti-mildew agent (wt%)
F1	boric acid/borax	1 : 1	1.0
		2 : 2	2.0
		3 : 3	3.0
		4 : 4	4.0
F2	IPBC	—	0.5
	1.0		
	1.5		
	2.0		
F3	NaBF_4 /DDAC	0.5 : 0.5	0.5
		1 : 1	1.0
		1.5 : 1.5	1.5
		2 : 2	2.0

F4	Tebuconazole		0.1
			0.2
			0.3
			0.4

Anti-mildew agent treatment of bamboo

The bamboo specimens were immersed into different anti-mildew solutions as Tab. 1 showed at room temperature for 24 h. After anti-mildew immersion, the specimens were taken out, and wiped off the extra solution on the surface, and then dried in the hot air drying chamber at $(20 \pm 2)^\circ\text{C}$ and relative humidity $(65 \pm 5)\%$ to reach the constant weight. Then the specimens were performed the anti-mildew performance test in the laboratory.

Anti-mildew performance test of treated bamboo

According to GB/T 18261: 2013, *Aspergillus niger*, *Trichoderma viride* and *Penicillium citrinum* were selected as the test molds to evaluate the anti-mildew capabilities of bamboo treated with different anti-mildew agents, and the potato agar medium (PDA) was prepared as the growth culture of these test molds. Then the specimens were sterilized at 100°C for 30 min. After sterilization, the specimens were cooled and transferred to the aseptic console. Under aseptic condition, two replicates were placed in the same plate, in which the medium was full of mycelium, then the Petri dish was covered with a lid and sealed with a sealing film. Finally, it was cultured in a biochemical incubator with suitable temperature and humidity for 28 days.

After 28 days of inoculation culture, the surface infection areas of the specimens were carefully observed and the infection values were recorded. The classification standard of the specimens affected by molds were evaluated according to Tab. 2. The control efficacy could be calculated by Eq. 1, and the comprehensive control effect was taken as the average value of the three fungi control effects.

Tab. 2: Evaluation standards of infection value.

Infection value	Infection area of sample	Discoloration degree of sample
0	No hyphae or mildew on the sample surface	Normal surface color
1	Surface infected area $< 1/4$	Only a few discolored spots on the surface
2	Surface infected area $1/4-1/2$	Surface obvious discoloration, continuous discoloration area up to $1/3$
3	Surface infected area $1/2-3/4$	Continuous color change area over $1/3$
4	Surface infected area $> 3/4$	Surface discoloration area $> 3/4$

Percentages of the average prevention and control effectiveness of the six replicates were calculated using Eq. 1:

$$E = \left(1 - \frac{D_1}{D_0}\right) \times 100\% \quad (1)$$

where: E is the control efficacy (%), D_1 is the average infection ratio of samples treated with anti-mildew agent, and D_0 is the average infection ratio of the untreated control sample.

RESULTS AND DISCUSSION

Effect of boric acid/borax anti-mildew agent on bamboo

As Fig. 1 showed, the control effect of boric acid/borax compound anti-mildew agent on different types of molds were obviously different, and its control effect on *Aspergillus niger* and *Penicillium citrinum* was more significant. With the gradual increase of the concentration of boric acid/borax anti-mildew agent, its control effect on *Aspergillus niger* and *Penicillium citrinum* gradually increased until reaching 100%, but the control effect on *Trichoderma viride* decreased sharply. At the same concentration of anti-mildew agent, the resistance of boric acid/borax to *Aspergillus niger* and *Penicillium citrinum* was about the same, but the resistance to *Trichoderma viride* was significantly weaker than the former two kinds of molds.

The average control efficacy of boric acid/borax anti-mildew agent against these three kinds of mildew molds varied obviously with the concentration increased. As can be seen from the Fig. 1, when the concentration of anti-mildew agent increased from 1.0% to 3.0%, the average control efficacy increased obviously, while when the concentration exceeded 3.0%, the average control efficacy began to decrease, which showed that the addition of boric acid/borax was beneficial to improve anti-mildew capability of bamboo in a certain concentration range. The experimental results were consistent with the results of the study of Pei et al. (2014), who showed that the boric acid/borax solution had a positive effect on the improvement of the mold resistance of particleboard.

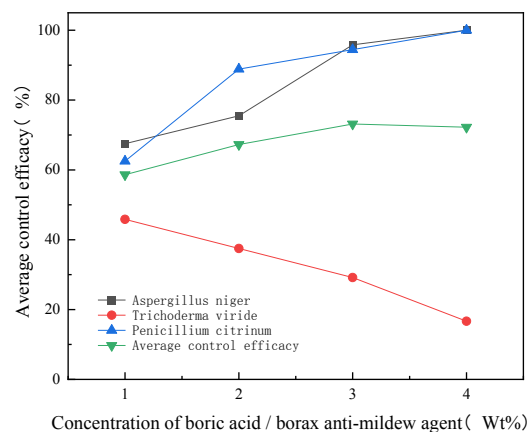


Fig. 1: Control effect of different concentrations of boric acid/borax anti-mildew agent on bamboo.

Effect of IPBC anti-mildew agent on bamboo

From Fig. 2, the effect of IPBC concentration on the control of different types of molds varied greatly. With the increase of IPBC concentration, its control effect on *Penicillium citrinum* was not obvious, even at lower concentrations, it could achieve 100% control efficacy, while the control effect of *Aspergillus niger* and *Trichoderma viride* would increase significantly until it reached 100%. When the IPBC concentration was below 1.5%, the resistance of IPBC to *Aspergillus niger* was slightly greater than that of *Trichoderma viride*. When the concentration increased to 1.5%, the control effect of *Aspergillus niger*, *Trichoderma viride* and *Penicillium*

citrinum all reached and maintained at 100%, which indicated that a certain concentration of IPBC could have excellent resistance to these three kinds of molds. The results were the same as that obtained by Han et al (2021). They studied the anti-loss property of IPBC anti-mildew agent in *Pinus massoniana*, *Pinus radiata* and *Phyllostachys pubescens* treated wood, and showed better anti-mildew performance in the treated wood. As can be seen from the Fig. 2, the average control efficacy of mold gradually increased to 100% with the increase of the concentration of anti-mildew agent, and maintained at the level of 100%.

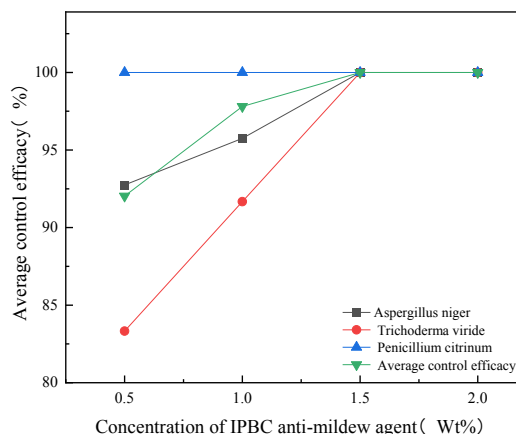


Fig. 2: Control effect of different concentrations of IPBC anti-mildew agent on bamboo.

Effect of NaBF₄/DDAC anti-mildew agent on bamboo

Fig. 3, the concentration of NaBF₄/DDAC has obvious differences in the control efficacy of different types of molds. Its control effect on *Aspergillus niger* and *Trichoderma viride* was significant effective, while the control effect on *Penicillium citrinum* was very limited, especially when the concentration of anti-mildew agent increased to 3.0%, the control effect of *Aspergillus niger* gradually increased to 100% and stabilized at 100%, the control effect of *Trichoderma viride* had always reached 100%, while the control effect of *Penicillium citrinum* was decreasing sharply. When the concentration of anti-mildew agent was less than 1.5%, the resistance of NaBF₄/DDAC to *Trichoderma viride* was better than that of *Aspergillus niger*, while the resistance to *Penicillium citrinum* would have the worst performance.

From the trend of the average control effectiveness of mold with the change of the concentration of anti-mildew agent, it could be seen that the concentration of anti-mildew agent had little effect on it. The results were similar to the research results of Zhao et al. (2019). The anti-biological deterioration performance and anti-loss performance of bamboo after treatment were significantly improved, and it increased with the increase of the molar ratio of DDAC in the impregnation solution, especially the control effect of *Aspergillus niger* was up to 100%. As observed from Fig. 3, when the concentration of NaBF₄/DDAC was 0.5%, the comprehensive anti-mildew performance of bamboo against these three molds achieved the optimal effect.

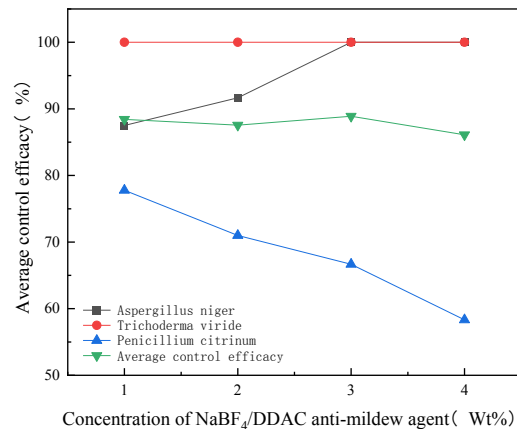


Fig. 3: Control effect of different concentrations of NaBF₄/DDAC anti-mildew agent on bamboo.

Effect of tebuconazole anti-mildew agent on bamboo

From Fig. 4, the change of tebuconazole concentration had a significant effect on the control efficacy of different types of molds. With the increase of the concentration of tebuconazole, its control effect on *Aspergillus niger*, *Trichoderma viride* and *Penicillium citrinum* showed a gradual increase trend. While the concentration was below 0.3%, tebuconazole had the strongest resistance to *Penicillium citrinum*, and the resistance to *Trichoderma viride* was better than that of *Aspergillus niger*. When the concentration of the anti-mildew agent was more than 0.3%, its resistance to *Aspergillus niger* began to be better than that of *Trichoderma viride*. But when the concentration was 0.4%, the control effect was similar to that of *Penicillium citrinum* (close to 100%).

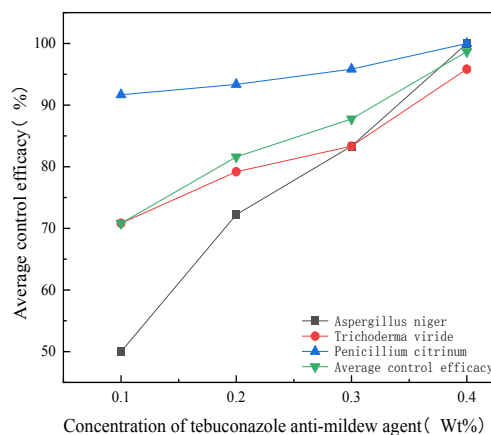


Fig. 4: Control effect of different concentrations of tebuconazole anti-mildew agent on bamboo.

The average comprehensive control effectiveness of these three molds increased significantly with the increase of the concentration of tebuconazole anti-mildew agent. The results are similar to the research of He et al. (2022). Their research showed that tebuconazole had a stronger inhibitory effect on the mycelium growth of anthracnose with the increase of solution concentration.

Comparison of anti-mildew capabilities of different anti-mildew agents on bamboo

The optimal anti-mildew capabilities obtained from these four types of anti-mildew agents on bamboo were compared in Fig. 5. It can be seen that the order of anti-mildew performance under the better concentration is tebuconazole (F4), IPBC (F2), NaBF₄/DDAC (F3) and boric acid/borax (F1). As observed from the comparison result, tebuconazole had the best control effect on molds, with an average control efficacy of 98.67%, followed by anti-mildew agents IPBC and NaBF₄/DDAC, in which the control efficacy was 92.03% and 88.43%, respectively, and the lowest control effectiveness was observed in the bamboo treated with boric acid/borax anti-mildew agent (73.15%).

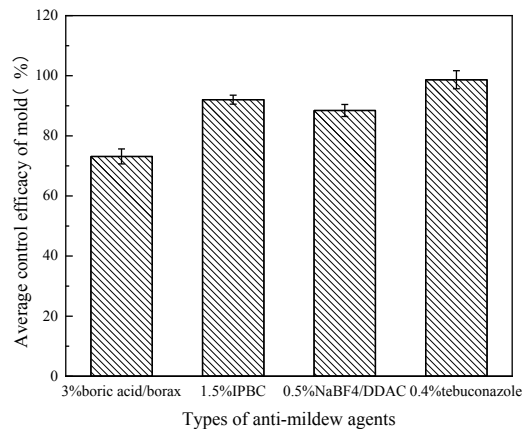


Fig. 5: Comparison of the average control effect of different anti-mildew agents on bamboo.

mildew type	F1	F2	F3	F4	Blank control
Aspergillus niger					
Trichoderma viride					
Penicillium citrinum					

Fig. 6: Actual prevention and control effect diagram.

Fig. 6 showed the actual control effect of 3% boric acid/borax, 1.5% IPBC, 0.5% NaBF₄/DDAC, 0.4% tebuconazole and blank control specimens on bamboo against these three types of molds (*Aspergillus niger*, *Trichoderma viride* and *Penicillium citrinum*). It can be seen

that the bamboo surface of the control group is completely covered with mycelium, while the surfaces of the bamboo treated with all of these three anti-mildew agents could be observed less or no mycelium growth.

CONCLUSIONS

Four different environmental anti-mildew agents of boric acid/boric acid (F1), IPBC (F2), NaBF₄/DDAC (F3) and tebuconazole (F4) were selected to treat bamboo with different concentrations. The optimal concentrations of F1, F2, F3 and F4 were 3.0%, 1.5%, 0.5% and 0.4%, respectively, and the average control effectiveness of the three test molds was 73.15%, 92.03%, 88.43% and 98.67%, respectively. There were also some differences in the sensitivity of the same anti-mildew agent to different molds. The anti-mildew agent F1 had obvious control effect on *Aspergillus Niger* and *Penicillium citrus*, F2 had obvious control effect on these three kinds of mold, F3 had obvious control effect on *Aspergillus niger* and *Trichoderma viride*, and F4 had obvious control effect on *Aspergillus niger* and *Penicillium citrinum*. The order of anti-mildew capability of each anti-mildew agent with better concentration was F4 > F2 > F3 > F1.

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HUI GUO, LILI YU*
TIANJIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
FACULTY OF LIGHT INDUSTRY SCIENCE AND ENGINEERING
NO. 9, 13TH STREET, BINHAI NEW AREA
P.O. BOX 546, TIANJIN
P.R. CHINA

*Corresponding author: yulilucky@tust.edu.cn

HUI LI^{1,2*}
¹HUBEI ACADEMY OF FORESTRY
WUHAN 430075, HUBEI
P. R. CHINA
²HUBEI MUFUSHAN MOUNTAIN BAMBOO FOREST ECOSYSTEM
RESEARCH STATION
XIANNING 437100, HUBEI
P. R. CHINA

*Corresponding author: 827231442@qq.com

ZHI-BIN YANG*
HUBEI ACADEMY OF FORESTRY
WUHAN 430075, HUBEI
P. R. CHINA
*Corresponding author: 176785765@qq.com