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Green colour protection of makino bamboo (*Phyllostachys makinoi*) treated with ammoniacal copper quaternary and copper azole preservatives

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Abstract

The objectives of this study were to search for appropriate low-toxicity preservatives to be used as green colour protectors for makino bamboo (*Phyllostachys makinoi*) culms, and to find appropriate conditions and process, especially an alkali-pretreatment-free and a solvent-free process, for treating makino bamboo to achieve green colour protection. The influence of various green colour protection reagents and treatment conditions on the colour of bamboo culms was examined using a colour difference meter. Two water-borne copper-based preservatives, namely ammoniacal copper quaternary compound-type B (ACQ-B) and copper azole (CuAz), were tested as protectors. In addition to heating in a water bath, the ultrasonic heating method was also employed. Results revealed that, without alkali-pretreatment, an excellent green colour protection ($a^* = -11.0$) was obtained when the makino bamboo culms were treated with 2% aqueous ACQ-B solution in a 60 °C water bath for 1 h, and that CuAz has no effect on green colour protection ($a^* = 3.9$) under the same conditions. Compared with conventional heating in a water bath, improvement on the green colour protection can be achieved with a shorter treatment time by using ultrasonic heating. The a^* value of bamboo culms after the treatment with 2% ACQ-B at a 60 °C ultrasonic bath for 15 min was −10.0.

Keywords: Green colour protection; Bamboo; *Phyllostachys makinoi*; Ammoniacal copper quaternary compound-type B (ACQ-B); Copper azole compound (CuAz)

1. Introduction

There are over 1200 varieties of bamboo, most of which are concentrated in Asia. Ninety percent of the bamboo in Asia is found in Southeast Asia [1]. Bamboo is spread in enormous quantities all over the island of Taiwan, from the low-lying coast to 3000 m mountains. Since bamboo naturally thrives in warm, wet climates, the subtropical heat and rain of Taiwan make the perfect environment for bamboo. As a result, there is no shortage of bamboo resources. Of varieties, Taiwan has over 60, including local and imported species [2]. Among them, makino bamboo (*Phyllostachys makinoi* Hayata) is one of the most common and valuable species [3].

In the Sung Dynasty, Su Dong-po, the famous poet had said that we could not live without bamboo and lack of bamboo would be unrefined [4]. It indicates that bamboo plays an important role in daily life from ancient times to nowadays. From this description, it is apparent that bamboo handicrafts are extremely popular and widespread in Taiwan. These bamboo handicrafts, which are present in all aspects of Taiwanese

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daily life, have a multitude of uses. Thus, as we look back on the Taiwanese life and the place of bamboo products in it, it is important that we cherish these processed bamboos as cultural products of a global village with definite historical significance and regional characteristics [3].

Moreover, bamboo fascinates people because of its green colour. However, without any protective or stabilization treatment, bamboo culms are very susceptible to attack by organisms or environment factors, and hence discolour easily [2]. Thus, green colour protection of bamboo has been widely studied in Taiwan during the last decade [5–12]. Numerous studies have reported that several inorganic salts have been proven to be effective green colour protectors for both ma bamboo (*Dendrocalamus latiflorus* Munro) [5–8] and moso bamboo (*Phyllostachys pubescens* Mazel) [9–11]. However, it is very difficult to preserve the attractive green colour of makino bamboo by using any of these protectors. Nevertheless, an appropriate green colour protector, alcohol-borne reagents, and a new one-step treatment process were developed successfully by Wu et al. in a recent investigation [12]. It demonstrated that without alkali-pretreatment, an excellent green colour protection could be obtained when the bamboo culms were treated with this type of protector under proper conditions.

Furthermore, to meet the requirements of industrialization and avoid environmental pollution, keeping the one-step treatment process characteristics without using organic solvents and exploring a low-toxicity preservative with green colour protection functions are imperative. Thus, this study aimed to search for appropriate state-of-the-art preservatives without using alkali-pretreatment for preserving the green colour of makino bamboo culms. The effectiveness of green colour protection using two commercially available low-toxicity copper-based preservatives [13] under different treatment conditions was assessed by a colour difference meter and compared.

2. Materials and methods

2.1. Sample preparation

Three-year-old makino bamboo (*P. makinoi* Hayata) culms were obtained from the experimental forest of National Taiwan University in Nan-Tou County. The bamboo culms were cut into strips with a dimension of 50 mm (longitudinal) × 15 mm (tangential) × 4 mm (radial) and stored at 4 °C in the dark prior to use.

2.2. Chemical treatment

To achieve the protection of the green colour surface, two water-borne copper-based preservatives, including ammoniacal copper quaternary compound-type B (ACQ-B) and copper azole compound (CuAz) were tested as protectors. All reagents were purchased from Acros Organics Co. (Geel, Belgium).

Bamboo specimens were treated with 2% preservatives in a 60 °C water bath for 2 h (alkali-pretreatment-free process) to evaluate the effectiveness of green colour protection by these reagents. Furthermore, to find the most appropriate method and process for treating makino bamboo with water-borne green colour protectors, the effects of various treatment conditions, reagent concentrations (0, 0.5, 1, 2, 4 and 8%), treatment temperatures (25, 60, 80 and 100 °C), and treatment durations (0.5, 1, 2 and 4 h), on the green colour protection of bamboo culms were investigated. Additionally, an ultrasonic treatment method was also used to evaluate the influence of ultrasonic treatment on the colour of bamboo surface. Hence, during the treatment, a water bath was replaced by an ultrasonic bath (Branson PC620, USA; power 180 Watts; output frequency 44 kHz). After treatment, all samples were dried at 60 °C for 12 h before measurement of surface colour and other properties.

2.3. Measurement of surface colour

The colour of bamboo epidermis was measured by a colour and colour difference meter (Dr. Lange Co., Germany) under a D_{65} light source. The tristimulus values X, Y, and Z of all specimens were obtained directly from the colorimeter. From these data, the L^* (value on the white/black axis), a^* (value on the red/green axis), b^* (value on the blue/yellow axis), ΔE^* (the colour difference, $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$) colour parameters were calculated, as established by the Commission Internationale de l'Eclairage (CIE) in 1976 [5].

2.4. Wettability of specimen epidermis

The contact angle of a water bead on the treated surface at ambient conditions was used as the index of wettability. A CA-A type contact-angle meter (Kyowa Kaimenkagaku Co., Japan) was employed for this measurement [10].

2.5. Analysis of variance

All results are expressed as mean ± S.D. ($n = 9$). The significance of difference was calculated by SAS Scheffe's test, and values < 0.05 were considered to be significant.

3. Results and discussion

3.1. Colour variations of makino bamboo treated with water-borne copper-based preservatives

Previous studies revealed that, without alkali-pretreatment, an excellent green colour protection was obtained when the makino bamboo culms were treated with 2% methanol-borne copper chloride ($CuCl_2$). Furthermore, after treatment, the capes of silica on the bamboo surface were still located on the bamboo epidermis [12]. However, using methanol as a treatment solvent could not only be recognized as a hazard to the environment and even to the producer's health, but also increased the cost of equipment required. Hence, developing a one-step treatment process and low-toxic reagents without using organic solvent for protecting the green colour of bamboo culms is imperative. Recently, some studies have revealed that copper-based reagents are good candidates for green colour protectors of bamboo [6,12]. ACQ-B (ammoniacal copper quaternary compound-type B) and CuAz (copper azole) are not only copper-based reagents, but are also two commercially available wood preservatives [14–17]. Thus, ACQ-B and CuAz were selected as feasible green colour protectors in this study, and it was expected that the treated bamboo would have a good green colour protection and a good durability. Colour variations of makino bamboo treated with these two protectors were evaluated by using the CIE LAB colour specifications [5]. In general, the effectiveness of green colour development could be evaluated by examining the a^* value. Comparing a^* values of specimens treated with two types of 2% copper-based preservatives at 60 °C for 2 h (without pretreatment process) shows that 2% ACQ-B ($a^* = -7.9$) was more effective than 2% CuAz ($a^* = 3.9$) (Table 1). This result reveals that CuAz has no effect on green colour protection, but ACQ-B might be a suitable green colour protector. After 2% ACQ-B treatment, the CIE LAB colour parameters L^*, a^*, and b^*, as shown in Table 1, changed from initial 36.0, −5.7, and 19.6 (fresh bamboo) to 54.8, −7.9, and 28.4, respectively. It revealed that an excellent green colour protection could be obtained when makino bamboo culms were treated with 2% ACQ-B in a water bath directly.

Table 1
Surface colour of makino bamboo culms treated with two 2% copper-based preservatives

Specimens	CIE LAB		
	L^*	a^*	b^*
Control[a]	36.0 ± 1.2	−5.7 ± 0.5^B	19.6 ± 1.8
CuAz	44.2 ± 2.5	3.9 ± 2.2^A	21.2 ± 2.7
ACQ-B	54.8 ± 2.1	−7.9 ± 2.5^C	28.4 ± 2.0

The a^* values marked by different letters are significantly different at the level of $P < 0.05$ according to the Scheffe's test.
[a] Fresh makino bamboo.

Copper naphthenate, a solvent-borne preservative, was first tested as a rudimentary green colour protector in 2000 [5]. It was demonstrated that ma bamboo (*D. latiflorus* Munro) treated with copper naphthenate had an acceptable green colour protection. However, it is known that different bamboo species showed the varied green colour performance, even with the same process and reagent used [5–10]. In practice, after 2% copper naphthenate treatment, makino bamboo culms exhibit a slightly green colour protection. Their L^*, a^*, and b^* colour parameters changed from initial 36.0, −5.7, and 19.6 (fresh bamboo) to 57.7, −6.5, and 27.5, respectively [12]. In contrast, the a^* value of 2% ACQ-B treated makino bamboo culms was −7.9, indicating that copper naphthenate-treated makino bamboo specimens had less effective green colour performance. Furthermore, comparison of the cost of two types of solvent used (water for ACQ-B and ethanol/xylene = 1/1 for copper naphthenate) showed that treatment using copper naphthenate was more expensive than using ACQ-B.

Moreover, after ACQ-B treatment, the contact angle of the bamboo surface decreased from an initial value of 84.8° to 67.3°. This result was the same as the makino bamboo culms treated with 2% methanol-borne $CuCl_2$ (68.0°) in 2004 [12]. Thus, it indicates that ACQ-B-treated bamboo culms can also provide good wettability or penetration for subsequent treatments, e.g. coating treatment. Furthermore, after ACQ-B treatment, the treated bamboo has an excellent green colour protection with a lustrous appearance, because the characteristic gloss of its epidermis is similar to that of the fresh bamboo culms. According to the aforementioned results, not only could the ACQ-B treated makino bamboo culms expand their potential utilization, but could also obtain more economic benefits than copper naphthenate-treated ones.

3.2. Influence of treatment conditions on surface colour of makino bamboo culms

The aforesaid results demonstrated that water-borne ACQ-B could be an effective green colour protector for makino bamboo, therefore more detailed treatment conditions were further investigated. First, to understand the influence of ACQ-B treatment temperature on the colour of makino bamboo, four temperatures including 25 °C (room temperature), 60 °C, 80 °C, and 100 °C were examined in this study. The results in Fig. 1 revealed that a^* value decreased when the temperature was raised from room temperature to 100 °C, and a^* values were 4.2 (25 °C), −7.9 (60 °C), −8.5 (80 °C), and −10.3 (100 °C). Although the lowest a^* value was obtained when bamboo culm was

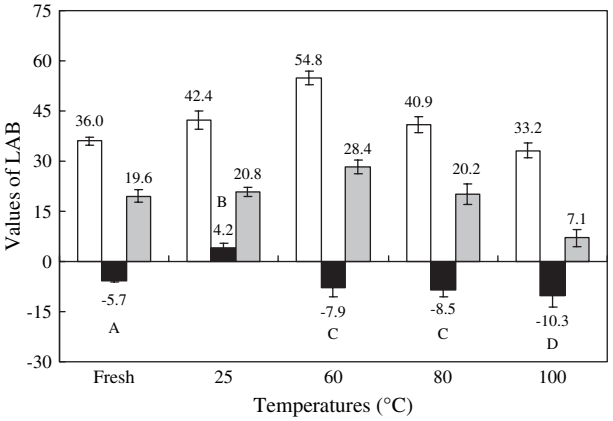

Fig. 1. Changes in colour parameters of makino bamboo culms after treatment with 2% ACQ-B at different temperatures for 2 h (white bars: L^*, black bars: a^*, gray bars: b^*) (a^* value marked by different letters are significantly different at the level of $P < 0.05$ according to the Scheffe's test).

processed at 100 °C, it also had the lowest b^* value, revealing the unnatural blue–green colour. In addition, the a^* values of ACQ-B treated bamboo culms either at 60 °C or at 80 °C showed no statistically significant variation in Schffe's test. Therefore, among the various temperatures used, the most appropriate one for green colour protection treatment of bamboo culms is 60 °C in terms of the cost and the best green colour performance is obtained.

Reducing the treatment time is an important factor for practical applications in the manufacturing process of green bamboo products. Therefore, four different treatment times, including 0.5, 1, 2 and 4 h, were examined for colour protection and the results are shown in Fig. 2. The a^* values of makino bamboo culms treated with 2% ACQ-B at 60 °C for 0.5 and 1 h were −5.1, and −11.0, respectively. However, a^* values increased when the treatment time was more than 1 h. With treatment for 2 and 4 h, the a^* values changed to −7.9 and −7.7, respectively. Hence, taking the production cost into consideration, a treatment time of 1 h would be the best choice for producing bamboo culms with an excellent green colour.

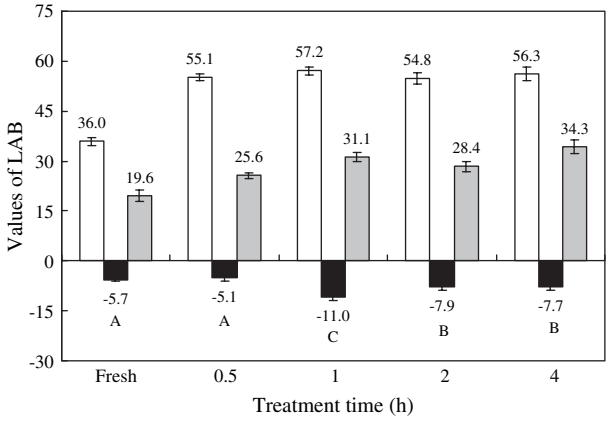

Fig. 2. Changes in colour parameters of makino bamboo culms after treatment with 2% ACQ-B at 60 °C for different times (white bars: L^*, black bars: a^*, gray bars: b^*) (a^* value marked by different letters are significantly different at the level of $P < 0.05$ according to the Scheffe's test).

In addition to 2% of ACQ-B, four other concentrations, 0.5, 1, 4, and 8% were also examined. Table 2 shows the changes of colour parameters on makino bamboo epidermis after treatment with various concentrations of ACQ-B at 60 °C for 1 h. The a^* values of makino bamboo treated with 0, 0.5, 1, 2, 4 and 8% ACQ-B were 3.5, −0.6, −7.5, −11.0, −10.3, and −3.5, respectively. Among these, 2% and 4% of ACQ-B-treated bamboo exhibited the best green colour performance (both bamboos showed no statistically significant variation in Scheffe's test). However, comparison of the colour difference ΔE^* (based on fresh bamboo) of bamboo specimens treated with 2% and 4% ACQ-B showed that the value of 2% ACQ-B treatment was smaller than that of 4%. Accordingly, it is clear that the epidermis of makino bamboo achieves an effective green colour protection after treatment with 2% ACQ-B at 60 °C for 1 h.

In the past alkali-pretreatment was necessary for green colour protection of bamboo culms. In contrast with the traditional two-step treatment, however, the one-step ACQ-B-treated makino bamboo culms ($a^* = -11.0$) have a better green colour performance than two-step ACQ-B-treated specimens ($a^* = -8.6$), as shown in Table 3. Thus, an attractive green colour can be obtained successfully by using a one-step treatment with water-borne copper-based preservative.

3.3. Influence of ultrasonic treatment on colour of makino bamboo culms

Ultrasonic treatment is widely applied to many fields, e.g. natural product extraction [18,19], chemical reactions

Table 2
Changes in colour parameters of makino bamboo culms after treatment with ACQ-B of different concentrations at 60 °C for 1 h

Concentration (%)	CIE LAB			ΔE^*
	L^*	a^*	b^*	
Control[a]	36.0 ± 1.2	-5.7 ± 0.5^{D}	19.6 ± 1.8	0.0
0	60.3 ± 1.5	3.5 ± 1.0^{A}	43.9 ± 3.2	35.2
0.5	45.1 ± 2.6	-0.6 ± 3.3^{B}	23.5 ± 2.7	30.1
1	54.9 ± 3.2	-7.5 ± 2.6^{D}	27.5 ± 2.0	23.1
2	57.2 ± 1.2	-11.0 ± 0.9^{E}	31.1 ± 1.4	26.2
4	51.3 ± 2.3	-10.3 ± 2.9^{E}	26.0 ± 1.9	32.4
8	52.9 ± 2.2	-3.5 ± 2.8^{C}	31.7 ± 3.0	25.9

The a^* values marked by different letters are significantly different at the level of $P < 0.05$ according to the Scheffe's test.

[a] Fresh makino bamboo.

Table 3
Effects of two treatment methods on colour parameters of makino bamboo surface

Treatment process	CIE LAB			Contact angle (°)
	L^*	a^*	b^*	
Control[a]	36.0 ± 1.2	−5.7 ± 0.5^{A}	19.6 ± 1.8	84.8
One-step[b]	57.2 ± 1.2	−11.0 ± 0.9^{C}	31.1 ± 1.4	67.3
Two-step[c]	56.8 ± 1.9	−8.6 ± 2.1^{B}	33.4 ± 2.5	53.4

The a^* values marked by different letters are significantly different at the level of $P < 0.05$ according to the Scheffe's test.
[a] Fresh makino bamboo.
[b] Treated with 2% ACQ at 60 °C for 1 h.
[c] Pretreatment: treated in a mixture of 1% KOH and 1% surfactant at 80 °C for 30 min in a water-bath; green colour protection treatment: pretreated specimens were treated with 2% ACQ at 60 °C for 1 h.

[20], and even food preservation [21]. The results obtained clearly revealed that it was a feasible and reliable method. As discussed above, the best green colour protection was obtained when makino bamboo was treated with 2% ACQ-B in a 60 °C water bath. Thus, in order to understand the influence of ultrasonic treatment on the colour of makino bamboo culms, the same treatment conditions were employed except that the water bath was replaced by the ultrasonic bath. The results in Table 4 demonstrated that, with treatment for 5 min, a green bamboo culm ($a^* = -7.2$) was obtained by using ultrasonic treatment. After 15 min, 30 min, 60 min, and 120 min of treatment, a^* values of bamboo epidermis were −10.0, −8.2, −8.0, and −8.7, respectively. It shows that ultrasonic treatment method endows the makino bamboo culms with an excellent green colour protection and that treatment time can be shortened obviously.

As for the colourfastness of these treated specimens, our preliminary results show that they exhibit an excellent green colourfastness under indoor conditions. After 30 days of indoor exposure, the a^* values of untreated and ACQ-B treated bamboo culms changed from −5.7 and −11.0 to 2.3 and −10.1, respectively. The detailed results will be reported in the future.

Table 4
Effects of treatment time on green colour protection of makino bamboo culms using ultrasonic heating[a]

Treatment time (min)	CIE LAB		
	L^*	a^*	b^*
Control[b]	36.0 ± 1.2	−5.7 ± 0.5^{A}	19.6 ± 1.8
5	56.7 ± 2.1	−7.2 ± 1.9^{B}	25.2 ± 2.4
15	56.8 ± 2.5	−10.0 ± 1.3^{D}	23.9 ± 2.0
30	56.6 ± 2.8	−8.2 ± 1.7^{BC}	25.6 ± 3.1
60	55.7 ± 2.5	−8.0 ± 2.0^{BC}	28.9 ± 3.2
120	57.4 ± 2.4	−8.7 ± 1.8^{C}	32.2 ± 3.5

The a^* values marked by different letters are significantly different at the level of $P < 0.05$ according to the Scheffe's test.
[a] Makino bamboo culms were treated with 2% ACQ solution at 60 °C.
[b] Fresh makino bamboo.

4. Conclusions

Among the various bamboo species in Taiwan, makino bamboo is one of the most popular and valuable species. To preserve its attractive green colour, the alternative treatment approach using water-borne copper-based preservatives was explored successfully in this study. The results obtained demonstrated that the greenish appearance of makino bamboo culms could be preserved when treating with 2% aqueous ACQ-B solution in a 60 °C water bath for 1 h. Its a^* value is −11.0. In addition, compared with conventional heating in a water bath, ultrasonic heating can achieve improvement on the green colour protection within a shorter treatment time. The a^* value of bamboo culms after treatment with 2% ACQ at a 60 °C ultrasonic bath for 15 min was −10.0. This break-through will expand the potential utilization of ACQ-B preservative and also increase the economic value of bamboo products because this novel treatment endows the bamboo culms with a fascinating greenish skin.

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References

[1] Sharma YML. Bamboos in the Asia-Pacific region. In: Lessard G, Chouinard A, editors. Bamboo research in Asia. Ottawa, CA: IDRC; 1980. p. 99–120.
[2] Lu CM. Cultivation and management of bamboo forests. Taiwan: Taiwan Forestry Research Institute; 2001. p. 1–204.
[3] Wu SC. Research and development of the production and utilization of bamboo in Taiwan. For Prod Ind 1982;1:18–24.
[4] Li TS. 20th century Taiwanese bamboo crafts. Taiwan: Artist; 2000. p. 12–8.
[5] Chang ST, Wu JH. Green colour conservation of ma bamboo (*Dendrocalamus latiflorus*) treated with chromium based reagents. J Wood Sci 2000;46:40–4.
[6] Wu JH, Wu SY, Hsieh TY, Chang ST. Effects of copper–phosphorous salt treatment on green colour protection and fastness of ma bamboo (*Dendrocalamus latiflorus*). Polym Degrad Stab 2002;78:379–84.
[7] Chang ST, Wu JH, Yeh TF. Effects of chromated-phosphate treatment process on the green colour protection of ma bamboo (*Dendrocalamus latiflorus*). J Wood Sci 2002;48:227–31.
[8] Chang ST, Wu JH. Stabilizing effect of chromated salt treatment on the green colour of ma bamboo (*Dendrocalamus latiflorus*). Holzforschung 2000;54:327–30.

[9] Chang ST, Yeh TF. Protection and fastness of green colour of moso bamboo (*Phyllostachys pubescens* Mazel) treated with chromium based reagents. J Wood Sci 2001;47:228–32.
[10] Chang ST, Yeh TF. Effect of alkali pretreatment on surface properties and green colour conservation of moso bamboo (*Phyllostacys pubescens* Mazel). Holzforschung 2000;54:487–91.
[11] Chang ST, Yeh TF, Wu JH, Hon DNS. Reaction characteristics on the green surface of moso bamboo (*Phyllostachys pubescens* Mazel) treated with chromated phosphate. Holzforschung 2002;56:130–4.
[12] Wu JH, Chung MJ, Chang ST. Evaluation of the effectiveness of alcohol-borne reagents on the green colour protection of makino bamboo (*Phyllostachys makinoi*). Polym Degrad Stab 2004;83: 473–9.
[13] Permadi P, Groot RC, Woodward B. Alternative wood preservatives for use in Indonesia. Forest Prod J 1998;48(11/12):98–101.
[14] Slahor JJ, Hassler CC, DeGroot RC, Gardner DJ. Preservative treatment evaluation of red maple and yellow-popular with ACQ-B. Forest Prod J 1997;47(4):50–4.
[15] Slahor JJ, Hassler CC, DeGroot RC, Gardner DJ. Preservative treatment evaluation with CCA and ACQ-B of four appalachian wood species for use in timber transportation structures. Forest Prod J 1997;47(9):33–42.
[16] Slahor JJ, Hassler CC, Dawson-Andoh B. The durability of yellow-poplar and red maple treated with ACQ-B. Forest Prod J 2001;51(9):59–62.
[17] Richardson M. Catalyst for change: preservation and timber rules trigger new product development. New Zealand Forest Ind Magazine 2004;35:16–9.
[18] Chang ST, Wang SY, Wu JH. Rapid extraction of epidermis chlorophyll of moso bamboo (*Phyllostachys pubescens*) culm using ultrasonics. J Wood Sci 1998;44:78–80.
[19] Wu JH, Wang SY, Chang ST. Extraction and determination of chlorophylls from moso bamboo (*Phyllostachys pubescens*) culm. J Bamboo Rattan 2002;1:171–80.
[20] Anthony EJ, Jia L, Cyr L, Smith B, Burwell S. The enhancement of hydration of fluidized bed combustion ash by sonication. Environ Sci Technol 2002;36:47–53.
[21] Loske-Mehling AM, Hernandez-Galicia C, Armenta-Ruiz E, Prieto-Calderon FE. Shock wave potential as a food preservation method. Tip Rev Espec Cienc Quimico-Biol 2000;3: 23–30.