Optimization of Alkali Pretreatment Conditions for Wax Removal from Bamboo Culm

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Appropriate chemical reagents were selected for removing the wax layer of bamboo culm, and optimal treatment conditions with the selected agents were determined in this study. Solutions of potassium carbonate, potassium hydroxide, sodium carbonate, and sodium chloride, along with their mixtures with 1% sodium dodecyl sulfate, were tested for efficacy of wax removal on culms of giant timber bamboo (*Phyllostachys bambusoides* S. *et* Z.), hachiku bamboo (*Phyllostachys nigra* var. *henosis* Stapf), and moso bamboo (*Phyllostachys pubescens* Mazel). Of the tested reagents, the mixture of potassium hydroxide and sodium dodecyl sulfate showed the best capability. The effects of varying concentrations of the selected reagents and reaction times at 90 °C were investigated by response surface methodology (RSM). Quadratic regression models representing the degree of wax removal at various treatment conditions were determined. The coefficients of determination of the fitted models were greater than 0.98, meaning that the models were highly accurate in predicting the degree of wax removal. According to the fitted models, the optimal conditions of potassium hydroxide concentration, sodium dodecyl sulfate concentration, and reaction time were 5.08%, 3.6%, and 63 min, respectively. The use of an RSM model offers considerable flexibility for practical uses because it allows multiple solutions with any desired level of wax removal.

Keywords: Bamboo; Wax layer; Alkali pretreatment; Optimization; Response surface methodology (RSM)

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INTRODUCTION

Bamboo is a non-wood material with strong historical and traditional use in Korea and other Asian countries. It has been widely used for everyday items such as mats, furniture, and handicrafts, but the advent of mass-produced synthetic plastics in the early 1970s greatly decreased the use of bamboo. Recently, however, the decrease in wood supply has stimulated research on value-added utilization of bamboo, due to its fast growth and high renewability. There are chemical treatments for protecting the green color of fresh bamboo (Chang and Wu 2000a, 2000b; Chang and Yeh 2000, 2001; Chang *et al*. 2001, 2002a; Wu *et al*. 2002, 2004; Chung *et al*. 2005; Wu *et al*. 2005; Chung *et al*. 2008, 2009, 2011) and preservative treatments for extending its service life (Lee *et al*. 2001; Möller and Mild 2019). Bamboo-based composites such as bamboo particleboard and bamboo oriented strand board (Sumardi *et al*. 2007; Semple *et al*. 2015; De Almeida *et al*. 2017; Chung and Wang 2018) are important examples of value-added utilization of bamboo.

A natural siliceous wax layer on the bamboo surface prevents liquid from penetrating the bamboo, decreasing the performance of chemical treatments and the bond strength of bamboo composites. Therefore, surface treatments to remove the wax layer are a prerequisite for the various value-added utilizations of bamboo. The water-wettability of the bamboo surface is improved most effectively by irradiation with a hydrogen ion beam (Wada *et al*. 2003). However, among the available methods for removal of the wax layer, soaking with an aqueous alkali solution is widely used as a simple and economical pretreatment method. Bamboo samples have been pretreated at 80 °C with 2% potassium hydroxide (KOH) containing 3% surfactant for 30 min (Chang *et al*. 2002b), and Chang *et al*. (2002a) pretreated bamboo samples at 80 °C in 4% potassium carbonate (K_2CO_3) and 1% surfactant mixtures for 30 min to remove the wax layer on the outer surfaces. Chang and Yeh (2001) pretreated bamboo samples at 80 °C with a mixture of 2% KOH and 3% sodium lauryl sulfate ($NaC_{12}H_{25}SO_4$) as an anionic surfactant for 30 min for removing waxes.

This study was performed to select appropriate chemical reagents for removing the wax layer on bamboo culm and to suggest optimal treatment conditions with the selected agents. Response surface methodology (RSM) was used to find the optimized conditions for the wax removal treatment, and the flexibility of the RSM model for practical purposes was discussed.

EXPERIMENTAL

Materials

Three-year-old giant timber bamboo (*Phyllostachys bambusoides* S. *et* Z.), hachiku bamboo (*Phyllostachys nigra* var. *henosis* Stapf), and moso bamboo (*Phyllostachys pubescens* Mazel) were harvested from the bamboo forest in southern Korea. The fresh bamboo culms were cut into strips with dimensions of 100 mm (longitudinal) × 20 mm (tangential) and stored at 20 °C until their moisture contents (MC) reached approximately 12%. All reagents used were of analytical grade and purchased from Sigma-Aldrich.

Methods

Selection of reagent for wax removal

Wax removal efficiency was evaluated for 3% solutions of potassium carbonate (K_2CO_3), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), sodium chloride (NaCl), and their mixtures with 1% sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) as a surfactant. Five samples per treatment combination were put into beakers, and each of the prepared solutions (1 L) was added into them. The sample to solution ratio was approximately 1:20. The contents were heated at 90 °C for 1 h and then carefully rinsed with distilled water. The samples were conditioned to 12% MC after the treatment. The wax removal efficacies of the tested chemicals were evaluated by the change in the contact angle of water upon an outer surface of the sample. A 10-µL water droplet was placed on the bamboo sample surface with a micropipette, and the contact angle was measured at ambient conditions by a contact-angle meter (OCA25, Dataphysics Instruments GmbH, Filderstadt, Germany) at 0 s and 20 s after it was placed onto the bamboo surface (Kwok and Neumann 1999).

Determination of optimal treatment conditions

With the reagent selected, a series of experiments was designed to find the optimized treatment conditions for wax removal from giant timber bamboo; 15 different combinations were set according to a 2^3 factorial central composite design (Table 1). All experiments were performed at 90 °C, and each treatment had five replicates. Each variable was coded by Eq. 1 to simplify the statistical analysis:

$$C = [R - \{\max(R) + \min(R)\} / 2] / [\{\max(R) - \min(R)\} / 3] \quad (1)$$

where C is the coded value, and R is the actual value.

The experimental design consisted of eight equally spaced points: one point on a circle of radius √2, one point in the design center, and six points on a circle of radius 1.5. Although a point with radius 2 offers more precise results for modeling, the value of 1.5 instead of √2 was chosen to provide easy control of the treatment variables in this experiment. The set of six points on a circle of radius 1.5 allows for efficient estimation of pure quadratic terms (Myers and Montgomery 1995).

Table 1. 2^3 Factorial Central Composite Design of Wax Removal Experiment

Actual Variables			Coded Variables		
Chemical (%)	Surfactant (%)	Time (min)	Chemical (%)	Surfactant (%)	Time (min)
2	1	20	-1	-1	-1
6	1	20	+1	-1	-1
2	3	20	-1	+1	-1
6	3	20	+1	+1	-1
2	1	60	-1	-1	+1
6	1	60	+1	-1	+1
2	3	60	-1	+1	+1
6	3	60	+1	+1	+1
4	2	40	0	0	0
1	2	40	-1.5	0	0
7	2	40	+1.5	0	0
4	0.5	40	0	-1.5	0
4	3.5	40	0	+1.5	0
4	2	10	0	0	-1.5
4	2	70	0	0	+1.5

Statistical analysis

Statistical analysis was performed using SAS/Graph® software (Version 6.1, SAS Institute Inc., Cary, NC, USA). The quadratic RSM model was determined at the 0.05 significance level, and three-dimensional response surface plots and contour plots were made using the fitted model.

RESULTS AND DISCUSSION

Selection of Reagent for Wax Removal

The measured contact angles of the bamboo samples treated with 3% solutions of potassium carbonate, potassium hydroxide, sodium carbonate, and sodium chloride, along with their mixtures with 1% sodium dodecyl sulfate, are shown in Table 2. The lowest initial contact angle was observed in samples treated with the mixture of potassium hydroxide and sodium dodecyl sulfate, followed by samples treated with the potassium hydroxide. Treatment with the mixture of potassium hydroxide and sodium dodecyl sulfate decreased the initial contact angle from 72.8° to 52.6°, 68.8° to 48.7°, and 69.8° to 45.7° in giant timber bamboo, hachiku bamboo, and moso bamboo, respectively. This result indicates that the wax layer of the bamboo epidermis was considerably removed by pretreatment with the mixture of potassium hydroxide and sodium dodecyl sulfate, regardless of bamboo species. In the samples treated with the mixture of potassium hydroxide and sodium dodecyl sulfate, the initial contact angle decreased by 5° to 10° in the first 20 s after wetting. The other reagents were not effective for removing the wax layer, as the initial contact angles of the treated samples were similar to those of the untreated samples for both hachiku bamboo and moso bamboo, although the initial contact angle slightly decreased in giant timber bamboo. In these cases, the contact angle was independent of wetting time for all bamboo species tested; that is, the contact angle was almost constant in the wetting period between 0 s and 20 s. Based on these results, the mixture of potassium hydroxide and sodium dodecyl sulfate was selected as the chemical combination for wax removal from the bamboo epidermis for further research. The highest wax removal performance of potassium hydroxide is attributed to its highest alkalinity. The pH of potassium carbonate, potassium hydroxide, sodium carbonate, and sodium chloride solutions were 11.5, 13.6, 11.5, and 6.4, respectively. The alkalinity of other reagents might be not enough to cause considerable wax removal from bamboo species. An increase in alkali concentration was known to perform wax removal from bamboo species better (Wong *et al*. 2010).

Table 2. Contact Angles of a Water Droplet on the Outer Surface of Bamboo *

	Giant Timber Bamboo		Hachiku Bamboo		Moso Bamboo	
Chemical	$\theta_{0\text{ sec}}$ (°)	$\theta_{20\text{ sec}}$ (°)	$\theta_{0\text{ sec}}$ (°)	$\theta_{20\text{ sec}}$ (°)	$\theta_{0\text{ sec}}$ (°)	$\theta_{20\text{ sec}}$ (°)
Control	72.8 (1.5)	72.2 (1.9)	68.8 (1.0)	69.4 (1.3)	69.8 (1.7)	69.4 (1.4)
PC	68.2 (3.1)	68.1 (2.7)	72.5 (1.8)	72.4 (1.6)	71.9 (2.6)	71.5 (2.6)
PC + S	66.3 (1.3)	65.9 (1.2)	72.3 (1.1)	72.3 (1.2)	70.1 (1.0)	69.5 (1.7)
PH	61.4 (5.1)	56.8 (5.5)	58.2 (4.6)	51.8 (5.8)	61.5 (3.8)	59.6 (2.6)
PH + S	52.6 (6.2)	46.2 (8.6)	48.7 (6.2)	39.2 (5.6)	45.7 (6.6)	40.9 (5.8)
SCA	67.6 (1.7)	67.2 (1.8)	71.8 (1.7)	72.2 (1.3)	69.9 (2.5)	69.7 (2.5)
SCA + S	65.7 (2.5)	65.5 (2.4)	69.6 (1.7)	69.3 (1.6)	68.4 (4.0)	68.0 (3.6)
SCL	63.9 (3.3)	63.9 (3.0)	69.3 (1.8)	69.4 (1.7)	70.9 (1.4)	70.9 (1.3)
SCL + S	65.9 (2.8)	66.1 (2.7)	67.7 (1.2)	66.6 (0.9)	69.1 (2.4)	68.8 (2.2)

* Values represent the mean of five replicates, and values in parenthesis represent the standard deviation. $\theta_{t\text{ sec}}$ – contact angle after *t* seconds, PC – potassium carbonate, PH – potassium hydroxide, SCA – sodium carbonate, SCL – sodium chloride, and S – surfactant

Determination of Optimal Treatment Conditions

The differences in the contact angle before and after treatment were determined for 15 different treatment conditions using the mixtures of potassium hydroxide and sodium dodecyl sulfate as shown in Table 3.

Table 3. Differences of Contact Angles of Water Droplet on the Bamboo Surface for Various Treatment Conditions

Actual Variables			Coded Variables			Difference of Contact Angles (°) *
KOH (%)	Surfactant (%)	Time (min)	KOH (%)	Surfactant (%)	Time (min)	
2	1	20	- 1	- 1	- 1	2.34
6	1	20	+1	- 1	- 1	1.72
2	3	20	- 1	+1	- 1	3.47
6	3	20	+1	+1	- 1	8.23
2	1	60	- 1	- 1	+1	7.63
6	1	60	+1	- 1	+1	12.37
2	3	60	- 1	+1	+1	12.75
6	3	60	+1	+1	+1	18.82
4	2	40	0	0	0	16.17
1	2	40	- 1.5	0	0	4.31
7	2	40	+1.5	0	0	9.30
4	0.5	40	0	- 1.5	0	7.57
4	3.5	40	0	+1.5	0	17.43
4	2	10	0	0	- 1.5	2.73
4	2	70	0	0	+1.5	16.37

* The values represent the differences of the contact angles before and after the treatment.

The efficiency of wax removal tended to increase with increases of the concentrations of potassium hydroxide and sodium dodecyl sulfate and of reaction time. The initial contact angles were used to fit the quadratic RSM model. Equation 2 describes the differences of the contact angles on the bamboo surface in terms of the coded factors,

$$Y_1 = 5.635 + 5.674\,x_1 + 8.598\,x_2 + 14.230\,x_3 - 7.774\,x_1^2 - 5.215\,x_3^2 \qquad (2)$$

where Y_1 is the difference in contact angle (°) before and after the treatment, x_1 is the coded KOH concentration, x_2 is the coded surfactant concentration, and x_3 is the coded reaction time.

For practical applications, the equation should be in terms of the actual variables. Equation 3 describes the RSM model representing the differences in contact angles in terms of the actual variables,

$$Y_2 = -36.405 + 18.385\,a + 8.598\,b + 0.3315\,c - 1.9435\,a^2 - 0.01304\,c^2 \qquad (3)$$

where Y_2 is the difference in contact angle (°) before and after the treatment, a is the KOH concentration (%), b is the surfactant concentration (%), and c is the reaction time (min).

The fitted models had a coefficient of determination (R^2) greater than 0.98, meaning that they were highly accurate in reflecting the degree of wax removal. The equations showed that the concentration of potassium hydroxide affected the wax removal the most, followed by the surfactant concentration and reaction time. No interaction effect of the reagent concentrations and reaction time on wax removal was found at the 0.05 significance level.

The optimal values of potassium hydroxide concentration, sodium dodecyl sulfate concentration, and reaction time determined from the fitted RSM model were 5.08%, 3.6%, and 63 min, respectively. However, multiple solutions could be obtained for any desired level of wax removal by using the RSM surface plots (Figs. 1 to 3). The contour graphs can be applied for simultaneous optimization of several responses. The contour lines represent the same degree of wax removal, and any combination of potassium hydroxide and sodium dodecyl sulfate can be chosen as an optimized solution.

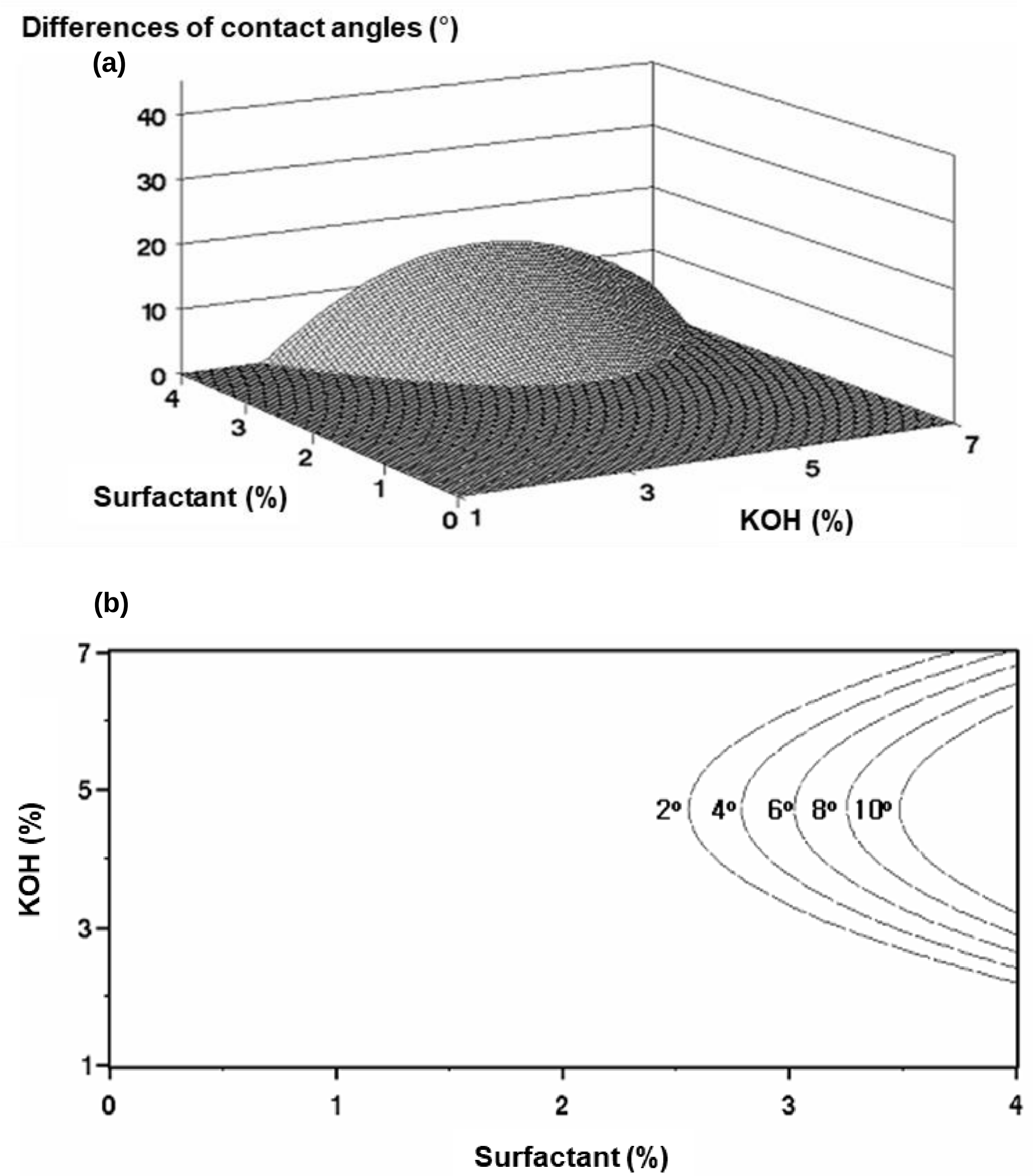
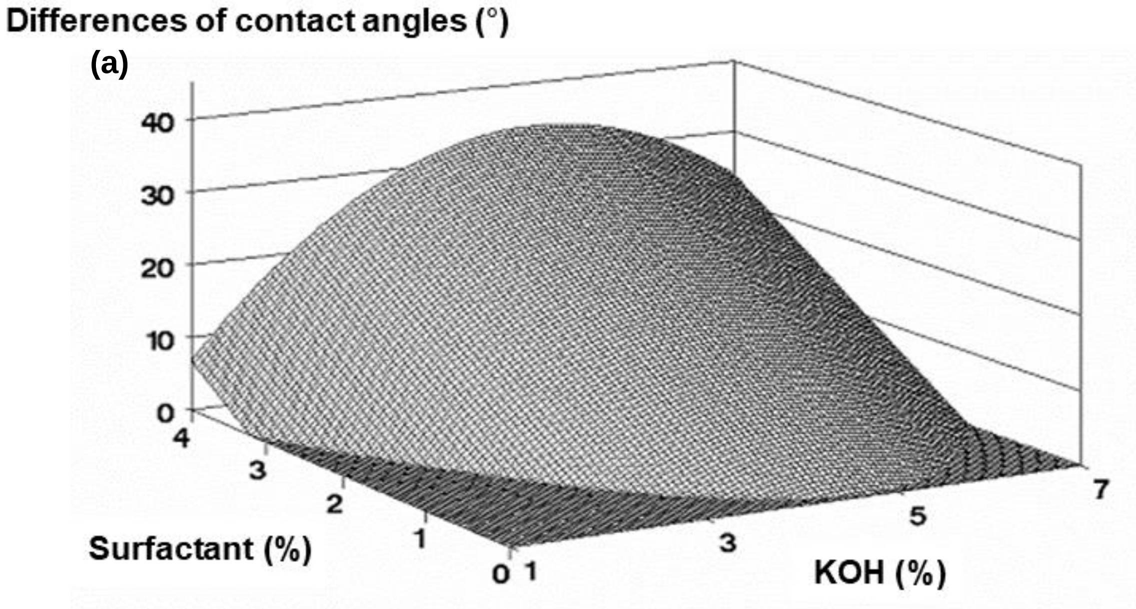


Fig. 1. Difference in contact angle of water droplet on bamboo surface before and after treatment when the reaction time is 20 min: (a) three-dimensional response surface plot and (b) contour plot



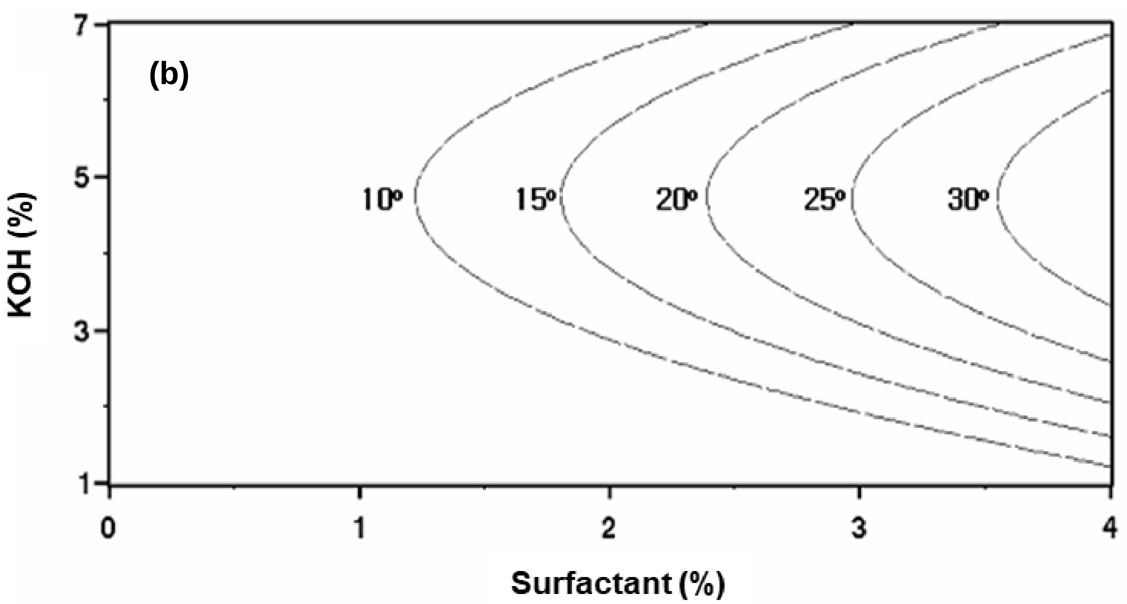


Fig. 2. Difference in contact angle of water droplet on bamboo surface before and after treatment when the reaction time is 40 min: (a) three-dimensional response surface plot and (b) contour plot

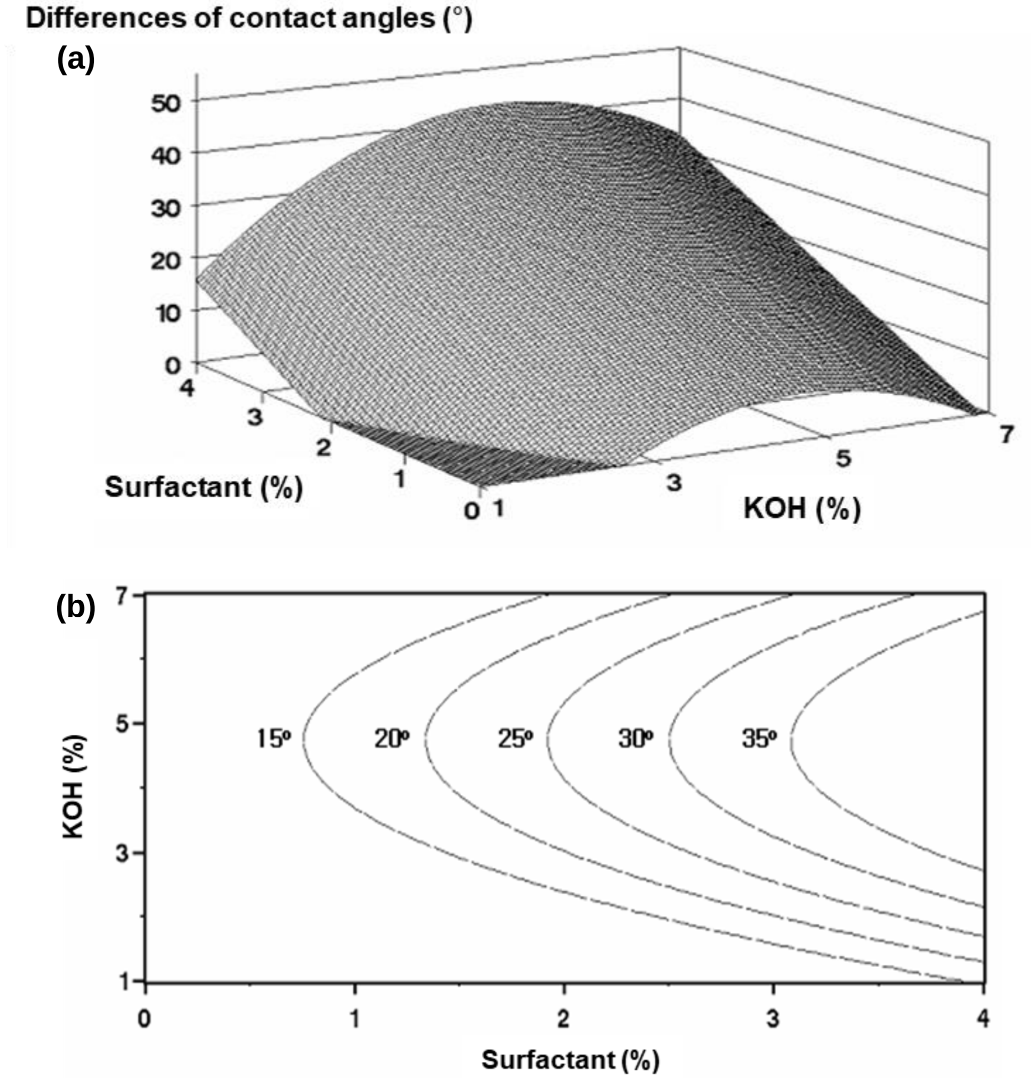


Fig. 3. Difference in contact angle of water droplet on bamboo surface before and after treatment when the reaction time is 60 min: (a) three-dimensional response surface plot and (b) contour plot

CONCLUSIONS

1. Among the various chemicals tested, the mixture of potassium hydroxide and sodium dodecyl sulfate was the most effective for removing wax from the bamboo culms.
2. According to the fitted RSM model for determining the optimal treatment conditions, the concentration of potassium hydroxide affected the wax removal the most, followed by surfactant concentration and reaction time. No interaction effect of the reagent concentrations and reaction time on wax removal was found.
3. The optimal values of potassium hydroxide concentration, sodium dodecyl sulfate concentration, and reaction time determined from the fitted RSM model were 5.08%, 3.6%, and 63 min, respectively. Simultaneous optimization of several responses offers considerable flexibility in controlling treatment variables for practical purposes.

ACKNOWLEDGMENTS

This study was conducted with the support of Technology Development Program for Agriculture and Forestry and of 'Forest Science & Technology Projects (Project No. S121010L110000)' provided by the Korea Forest Service.

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Article submitted: June 23, 2020; Peer review completed: Peer review completed: Aug. 23, 2020; Revised version received and accepted: Sept. 4, 2020; Published: September 11, 2020.
DOI: 10.15376/biores.15.4.8202-8211