Production of Cellulose From Bamboo Shoot Shell Using Hydrothermal Technique

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The preparation and characterization of purified cellulose from bamboo shoot shell were studied using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The preparation of cellulose fiber included extraction of cellulose from bamboo shoot shell by treatment with 5% NaOH and 4% H₂O₂, and purification of cellulose fiber using hydrothermal technique. The result showed that cellulose has been successfully extracted at a 32.56% yield by the 5% NaOH / 4% H₂O₂ treatment, and the purified cellulose was produced using autoclaving at the temperature of 120°C and pressure at 0.1 MPa for 2 h 5 min, with the % recovery of purified cellulose around 94.08. Bamboo shoot shell and cellulose sample were further characterized using FTIR technique. It was found that the 5% NaOH / 4% H₂O₂ treatment eliminated lignin and hemicellulose from bamboo shoot shell but did not affect cellulose. The hydrothermal technique did not affect the destruction of the cellulose structure as well. Comparison of the SEM image showed that cellulose was separated into individual microfibers after the 5% NaOH / 4% H₂O₂ treatment while the SEM image of purified cellulose was the small thread-like fibers with smoother surface. Therefore, hydrothermal treatment can be performed for purification of cellulose.

Key Words
Cellulose, Bamboo shoot shell, Hydrothermal

1. Introduction

Bamboo shoots are common food that can be used in a variety of dishes. It consists of the edible shoot part and the shell which are inedible. There are many food products that use bamboo shoot as raw material such as pickled bamboo shoot, canned bamboo shoot, and dried bamboo shoot. In 2019, Thailand generated 422.1 million THB from exporting canned bamboo shoots around the world, resulting in a large quantity of bamboo shoot shells in the industry. In General, bamboo shoot shells, outer part of bamboo shoot, are considered as industry waste. People usually burned or buried to eliminate the bamboo shoot shell, leading to environmental problem.

Bamboo shoot shell contains many valuable organic compounds. He et al. (2013) studied the chemical composition of bamboo shoot shell, and found that bamboo shoot shell had cellulose 22.96%, hemicellulose 13.73%, lignin 10.55%, moisture 8.80% and ash 0.51%. Bamboo shoot shell has higher amount of cellulose than other organic compounds. Therefore, it is an interesting material to produce cellulose fiber. Cellulose is a main component of plant cell wall structure. It can be used for many purpose because of its properties such as renewability, biodegradability, inexpensiveness, light weight and abundance. Cellulose can be used to improve the quality of baked products, used as raw materials in the production of ethanol, and used as reinforcing fibers in composite materials, etc.

There are many researchers who are interested in methods to produce cellulose. Jiang and Hsieh (2015) studied two different routes to isolate cellulose by using acidified sodium chlorite and chlorine-free sodium hydroxide on tomato peels, and found that sodium hydroxide removed more non-cellulosic mass than sodium chlorite. Hiasa et al. (2014) compared two treatments to produce purified cellulose from mandarin peels, between multi-
step treatment using 3 chemicals and single step treatment using hydrochloric acid with hydrothermal process and found that hydrothermal treatment had more ecological and economic advantages than multistep treatment.

This research aims to study the extraction and purification of cellulose using hydrothermal technique which relied on subcritical water to make high purity cellulose, and studied the characterization of purified cellulose derived from bamboo shoot shell.

2. Methodology

2.1 Materials

Materials employed in this study were bamboo shoot shell (Thysostachys siamensis) from Ban Prong Wai school in Kanchanaburi (Thailand), ethanol (C₂H₅OH, 95% solution, AR grade, RCI Labscan, Thailand), hydrogen peroxide (H₂O₂, 30% solution, AR grade, Merck, Germany), nitrogen gas (N₂, Praxair, Thailand), petroleum ether (AR grade, Leonid Chemicals, India), sodium hydroxide (NaOH, pellets, AR grade, Thermo Fisher Scientific, Australia), distilled water (Better Syndicate, Thailand), and Whatman No.1 filter paper (GE Healthcare, USA).

2.2 Isolation of cellulose from bamboo shoot shells

Bamboo shoot shell was dried at 60 °C for 24 h and milled (Hammer mill, JB-40, Jiangyin Baoli Machinery, China) into powder. Then, bamboo shoot shell powder was extracted with petroleum ether using Soxhlet extraction (Soxtherm, S306A7, Gerhardt, Germany) for 2 h to removed wax and oils. The bamboo shoot shell powder after extraction was treated with alkaline peroxide treatment using 5% NaOH at the solid-liquid ratio of 1:30 and the temperature of 90 °C for 5 h, followed by treatment with 4% H₂O₂ at the solid-liquid ratio of 1:20 and the temperature of 45 °C for 6 h, and then freeze-dried (Freeze dryer, CoolSafe 95/55-80 pro, Scanvac, Denmark) for 24 h. Cellulose was stored in desiccator. The yield of cellulose was calculated followed Eq. (1).

\[ \text{yield of cellulose (\%)} \times 100 = \frac{\text{weight of cellulose}}{\text{weight of bamboo shoot shell}} \]  

(1)

2.3 Purification of cellulose using hydrothermal technique

The cellulose from bamboo shot shell was added in distilled water at the solid-liquid ratio of 1:20 and stirred at room temperature for 10 min. The mixture was put in an autoclave reactor. The pressure of autoclave reactor was increased to 0.1-0.3 MPa using nitrogen gas. Then, the hydrothermal process was conducted at 80-120 °C for 1-3 h. The yield of purified cellulose was calculated followed Eq. (2).

\[ \text{yield of purified cellulose (\%)} = \frac{\text{weight of cellulose after hydrothermal}}{\text{weight of bamboo shoot shell}} \times 100 \]  

(2)

2.4 Statistic design of experiments

The conditions of cellulose purification using hydrothermal technique was optimized using Box-Behnken Design (BBD) via Minitab18 program. The variables evaluated were temperature (°C), pressure (MPa), time (h) and the weight of cellulose (g). The response was the % recovery of purified cellulose. The % recovery of purified cellulose was calculated followed Eq. (3). The Box-Behnken design for the purification of cellulose was shown in Table 1.

\[ \text{recovery of purified cellulose (\%)} = \frac{\text{weight of cellulose after hydrothermal}}{\text{weight of cellulose before hydrothermal}} \times 100 \]  

(3)

2.5 Effect of variables on the % recovery of purified cellulose

Effect of variables which are temperature (°C), pressure (MPa), reaction time (h), and the weight of cellulose (g) were observed by calculating the % recovery of purified cellulose before and after hydrothermal process.

2.6 Fourier transform infrared spectroscopy (FTIR)

The chemical characterization of bamboo shoot shell before and after treatments was analysed by FTIR (Invenio-S, Bruker, USA) in the range of 400 cm⁻¹ to 4000 cm⁻¹. FTIR spectra were used to verify chemical change in bamboo shoot shell structure after the alkaline peroxide treatment and after using hydrothermal technique.

2.7 Scanning electron microscopy (SEM)

SEM (FEI: Quanta 250, Thermo Fisher Scientific, Australia) was used for analysing the morphology of bamboo shoot shell and cellulose before and after using hydrothermal technique with an accelerating voltage of 15 kV at 5000x magnification.

Table 1 Experimental design of cellulose purification using hydrothermal technique

| Factor                | Code | Level |
|-----------------------|------|-------|
| Temperature (°C)      | X₁   | 80    | 100 | 120 |
| Pressure (MPa)        | X₂   | 0.1   | 0.2 | 0.3 |
| Time (h)              | X₃   | 1     | 2   | 3   |
| Weight of Cellulose (g)| X₄ | 1     | 3   | 5   |
3. Results and discussion

3.1 Evaluation of experimental results

The optimization of cellulose purification using hydrothermal technique was carried out by a total 27 runs Box-Behnken Design experiment. The four variables are including temperature (X₁), pressure (X₂), reaction time (X₃) and the weight of cellulose (X₄). By considering the analysis of variance and removing the non-significant term (P-value > 0.05) at the 95% of confidence level, the significant factors were used to model the equation predicted the % recovery of purified cellulose as shown in Eq. (4):

\[
\% \text{ recovery} = -34.1 + 0.476X₁ + 33.88X₂ + 50.12X₃
\]
\[+ 5.43X₁^2 - 3.526X₁X₂ - 8.516X₂^2 - 0.1181X₁X₃
\]
\[+ 0.055X₂X₃ - 2.284X₃X₄. \quad (4)
\]

According to the analysis of variance (ANOVA) in Table 2, most of the P-value are very low, indicating that most of the factor influence the % recovery of purified cellulose. Quadratic term of temperature (X₁²) and the weight of cellulose (X₄²), the interaction between temperature and weight of cellulose (X₁X₄), and the interaction between time and weight of cellulose (X₃X₄) is considered to have no effect on the % recovery of purified cellulose, due to the P-value is greater than the significance level. The lack of fit has 0.269 P-value, which indicates that the equation is accurate enough to predicted the % of purified cellulose.

3.2 Evaluation of experimental results

Table 3 shows the optimum condition for purification of cellulose using hydrothermal technique. The optimum condition was verified by repeating the experiment for 3 times, and purified cellulose with 94.08% recovery was obtained. The yield of cellulose from bamboo shoot shell was 34.61%. After the purification of cellulose using hydrothermal process, the yield of purified cellulose was maximum around 32.56%.

3.3 Main effect of variables on the % recovery of purified cellulose

The main effect plot of variables on the % recovery of the purified cellulose is shown in Fig. 1. The main effect plot showed the means of % recovery which were calculate

Table 2 Analysis of variance for the purification of cellulose using hydrothermal technique

| Source         | Degree of Freedom | Adjusted Sum of Squares | Adjusted Mean Squares | F-Value | P-Value |
|----------------|-------------------|-------------------------|-----------------------|---------|---------|
| Model          | 14                | 1072.21                 | 76.58                 | 64.47   | 0.000   |
| Liner          | 4                 | 445.02                  | 111.25                | 93.66   | 0.000   |
| X₁             | 1                 | 197.07                  | 197.07                | 169.47  | 0.000   |
| X₂             | 1                 | 201.31                  | 201.31                | 165.90  | 0.000   |
| X₃             | 1                 | 77.92                   | 77.92                 | 6.56    | 0.025   |
| X₄             | 1                 | 38.84                   | 38.84                 | 32.70   | 0.000   |
| Square         | 4                 | 476.76                  | 119.19                | 100.34  | 0.000   |
| X₁²            | 1                 | 0.79                    | 0.79                  | 0.66    | 0.431   |
| X₂²            | 1                 | 66.30                   | 66.30                 | 55.82   | 0.000   |
| X₃²            | 1                 | 386.77                  | 386.77                | 326.50  | 0.000   |
| X₄²            | 1                 | 4.45                    | 4.45                  | 3.75    | 0.077   |
| 2-Way Interaction | 6               | 150.43                  | 25.07                 | 21.11   | 0.000   |
| X₁X₂           | 1                 | 22.33                   | 22.33                 | 18.79   | 0.001   |
| X₁X₃           | 1                 | 17.56                   | 17.56                 | 14.78   | 0.002   |
| X₁X₄           | 1                 | 0.27                    | 0.27                  | 0.23    | 0.642   |
| X₂X₃           | 1                 | 26.57                   | 26.57                 | 22.37   | 0.000   |
| X₂X₄           | 1                 | 83.45                   | 83.45                 | 70.25   | 0.000   |
| X₃X₄           | 1                 | 0.26                    | 0.26                  | 0.22    | 0.648   |
| Error          | 12                | 14.25                   | 1.18                 | 0.269   |
| Lack-of-Fit    | 10                | 13.39                   | 1.339                 | 3.09    | 0.269   |
| Pure Error     | 2                 | 0.87                    | 0.433                 | 9.10    | 0.057   |

R-squared = 98.69%, Adjusted R-squared = 97.16%

Table 3 Comparison of predicted value and optimal value at optimum level

| Response | Value |
|----------|-------|
| Y        |       |
| Optimum conditions | X₁ = 120°C |
| X₂ = 01 MPa |
| X₃ = 2 h 5 min |
| X₄ = 5 g  |
| Stationary point | Maximum |
| Predicted value (%) | 96.33% |
| Observed value (%) | 96 ± 3 |
using Eq.(4). The effect plot of temperature showed the increasing trendline which indicated that the % recovery of purified cellulose increased as the temperature increased. Cellulose in general are stable against high temperatures 9), and when the temperature increased, pectin and other soluble components could be released from the sample leading to an increase in the cellulose content. Higher fraction of cellulose could be obtained with a less fraction of hemicellulose and pectin contents 10). Hence it resulted in the higher amount of purified cellulose.

The main effect plot of pressure showed the % recovery decreased as the pressure increased. According to Stevulova et al. (2017) 11), cellulose is more resistant against thermal treatment under nitrogen atmosphere when compared to air atmosphere. This experiment used nitrogen gas to increase pressure in hydrothermal process. The main effect plot of time showed the % recovery increased as the time increased. Because cellulose has longer purification period, it increases the % recovery. But as time passes, the % recovery of purified cellulose was decreased, due to the excessive time for degrading cellulose. The main effect plot of cellulose weight showed the % recovery decreased as the cellulose weight increased.

3.4 FTIR analysis

The FTIR spectra of untreated bamboo shoot shell, bamboo shoot shell treated with alkaline peroxide (cellulose), and bamboo shoot shell treated with alkaline peroxide followed by using hydrothermal technique (purified cellulose) were shown in Fig. 2. The FTIR spectrum of untreated bamboo shoot shell (Fig. 2 (a)) showed characteristic peak at 1632 cm⁻¹ from C=O stretching vibration in conjugated carbonyl of lignin and 1238 cm⁻¹ from C-O-C stretching vibration in lignin 12). These peaks disappeared after bamboo shoot shells were treated with alkaline peroxide (Fig. 2 (b)), indicating the complete removal of lignin which led to 32.56% of cellulose yield, corresponding to the work of Jiang and Hsieh (2015) 7) which showed the peaks of non-cellulosic compounds from tomato peels were removed after treatment with 5% NaOH / 4% H₂O₂.

Both spectra of bamboo shoot shell after using alkaline peroxide and after following hydrothermal technique (Fig. 2 (c)) showed the characteristic peaks of cellulose at 3333 cm⁻¹ from O-H stretching vibration, 2893 cm⁻¹ from C-H stretching, 1425-1199 cm⁻¹ from CH₂ and C-H bonds in cellulose, 1159 cm⁻¹ from C-O-C stretching, 1053 cm⁻¹ and 1030 cm⁻¹ from C-O stretching, 996 cm⁻¹ from the 1 → 4 glycosidic linkages and 896 cm⁻¹ from amorphous region in cellulose 13). These peaks showed that the alkaline peroxide treatment can isolate cellulose from bamboo shoot shell. The peak after hydrothermal process was much clearer than before hydrothermal process, indicating that hydrothermal technique can improve the purity of cellulose, corresponding to the work of Hiasa et al. (2014) 8) which showed purified cellulose was obtained after hydrothermal treatment.
3.5 Morphological analysis

The morphological characteristics of bamboo shoot shell, cellulose and purified cellulose are shown in Fig. 3. In Fig. 3 (a), fibers cannot be seen clearly and the rough surface of bamboo shoot shell was from non-cellulosic elements such as lignin, hemicellulose and fat, etc. In Fig. 3 (b), non-cellulosic elements were removed by alkaline peroxide treatment and the bundle of cellulose fibers was separated into individual microfibers. Cellulose after hydrothermal process (Fig. 3 (c)) showed the thread-like cellulose fibers with smoother surface, indicating that the purified cellulose was obtained from this process.

4. Conclusion

Bamboo shoot shells are by-product from bamboo shoot industry, which can be used in the production of cellulose. The NaOH/H₂O₂ treatment eliminated inorganic as well as other organic substances and hydrothermal process was used to yield the purified cellulose around 32.56%. The hydrothermal technique did not affect the destruction of the cellulose structure and further improved the purity of cellulose into ultra-fine white fibers, with the % recovery of purified cellulose around 94.08%.

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