

Characterization and Comparison of Cellulose Extraction from Ginger Stalk by Two Different Chemical Treatments

CanCan Zhou¹, XiaoMing Song¹, Shuai Wang¹, FuShan Chen^{2,*}

1. College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, Shandong Province, 266042, China

2. College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, Shandong Province, 266042, China

Abstract: Agricultural residues are important renewable biomass resources that have not received much research attention. Ginger stalk is a major agricultural waste in China. The extraction of cellulose from ginger stalk would convert this waste into a high value-added product and, simultaneously, contribute to environmental protection. This research studied the characteristics of cellulose extracted from ginger stalk by two different treatments: (i) potassium hydroxide (KOH) treatment and (ii) nitric acid-ethanol (NAE) treatment. The optimal condition for the KOH treatment was obtained, it was at 1 : 30 solid-to-liquid ratio (SLR) for 5 h extraction time with 14 wt% KOH. The optimal condition for the NAE treatment was as follows: 1 : 40 SLR, 4 h extraction time, and a reaction temperature of 90°C. However, the cellulose obtained by NAE treatment was severely degraded than that by KOH treatment. The Fourier-transform infrared (FT-IR) spectroscopy analyses revealed that both treatments successfully dissolved the lignin and hemicellulose. Two treatments showed a higher cellulose yield, and the extracted cellulose had more crystal structure.

Keywords: ginger stalk; cellulose extraction; potassium hydroxide treatment; nitric acid-ethanol treatment

1 Introduction

Cellulose, a major constituent of all plant materials, forms approximately one-third to one-half of all plant tissues and is the most abundant renewable resource on earth^[1-2]. Chemically, cellulose is a linear natural polymer of anhydroglucose units linked at the



CanCan Zhou, master candidate;
E-mail: zhoucancan0907@163.com



*Corresponding author:
FuShan Chen, professor; research interests: paper chemicals, waste water treatment;
E-mail: chen-fushan@263.com

Received: 14 October 2016; accepted: 2 December 2016.

first and fourth carbon atoms by β -glycosidic bonds. It is widely found in various forms in plants, typically interrupted by hemicellulose and surrounded by lignin matrices. Depending on the type of plant, plant tissue contains approximately 40%~55% cellulose, 15%~35% lignin, and 25%~40% hemicelluloses.

In recent years, with the rapid rise in oil price, the decrease of coal reserves and the increasing attention of environmental problems, the valorization of such an inexpensive renewable resource as cellulose has gained increasing attention^[3]. At present, cellulose is used not only in the traditional industries of papermaking, textiles, and plastics, but also in food, daily chemicals, chemical industries, architecture, medicine, oilfield chemistry, biochemistry, agriculture, and other fields. For example, cellulose is increasingly used as reinforcement materials in thermoset and thermoplastic polymeric matrices, because it has the unique characteristics of renewability, low density, and high specific strength^[4].

Ginger belongs to the Zingiberaceae family and is a commonly used spice and medicinal product^[5]. It is considered as the most important member among the other 1400 species of the Zingiberaceae family. Today, ginger is mostly cultivated in the subtropics and tropics, where it plays an important role in both agricultural and economic systems. In China, ginger is cultivated on approximately 2 million hectares of land every year. Because of its low price, sweet smell, and other benefits, it can be widely used in daily life^[6]. Ginger also contains volatile oil, dietary fiber, and other healthy compounds. The volatile oil can promote blood circulation, increase the appetite, and bring other health benefits^[7]. Gingerols can inhibit the body's absorption of cholesterol, promote blood circulation, relieve pain, induce sweating, warm the stomach to stop vomiting, and eliminate edema when ginger is used as a raw material for soft candy^[8].

Ginger stalk similar to the underground tubers, can be used as a natural renewable resource^[9]. At present, researchers have mostly focused on the tubers, while studies devoted to the above ground portion of

the ginger stalk are rare^[10-12]. Ginger stalk is a major agricultural waste in China. Most ginger residues are abandoned directly in the field to metamorphose into waste, without regard for the surrounding environment. Because the ginger stalk shares the pungent smell of the ginger root, if remains unused, it can cause a significant waste of resources and environmental pollution. To help mitigate the waste disposal problem, agricultural residues can potentially be processed to environmentally sustainable products, such as papers^[13]. Stalk appears as a natural fiber composite, consisting of cellulose (cellulose content of ginger stalk is 39.5 wt%), hemicellulose and lignin^[14]. The content of each component can be determined by specific methods^[15].

This work focused on the characterization and comparison of cellulose extraction from ginger stalk by potassium hydroxide (KOH) and nitric acid-ethanol (NAE) treatments. The study provides a basis for further comprehensive development and utilization of the material.

2 Experimental

2.1 Materials and equipment

The ginger stalk used in this study was collected from the Shandong Province in eastern China. Potassium hydroxide (KOH) was procured in the analytically pure form. NAE solution was prepared using ethanol (C₂H₅OH, 99.9 wt%) and nitric acid (HNO₃, AR). Microcrystalline cellulose (MCC, AR) was received from the Chengdu area of the Industrial Development Zone. Fourier-transform infrared (FT-IR) spectra were recorded using a TENSOR27 FT-IR spectrometer (Bruker Optics, Germany) in the range of 500~4000 cm⁻¹. Scanning electron microscopy (SEM) images were taken on a JSM-6700F scanning microscope (Japanese Electronics, Japan). Phase transformation analysis of the samples was conducted by X-ray diffraction (XRD) using a Scintag XDS 2500 power diffractometer (Japanese Electronics, Japan). Thermogravimetric (TG) analysis and derivative thermogravimetric (DTG) analysis of the samples were carried out on a Pyris Diamond TG/DTG analyzer (STA449C/3/F, German). Water used in

the experiments was purified by a water purification system.

2.2 Preparation of ginger stalk

Fresh ginger leaves were removed and the stalks were cut into small pieces ca. 2 cm. The ginger stalk was washed 3~4 times with deionized water. Then, the ginger stalk was squeezed and the remaining ginger stalk residue was dried in air for approximately two weeks to promote chlorophyll degradation, followed by drying in an oven at 80°C for 8 h.

2.2.1 KOH treatment

First, 5 g of ginger stalk was pretreated at 50°C and a solid-to-liquid ratio (SLR) of 1 : 30 for 2 h with 5% KOH (w/w) solution to dissolve the hemicelluloses and silica^[16]. Afterward, the pretreated sample was treated with KOH solutions of 8%~18% at 100°C for 5 h to dissolve the lignin and remaining hemicelluloses, then filtered and washed with lots of water until the filtrate reached a pH value of 7.0. The sample was filtered again, and then hot air-dried at 80°C. The final mass was obtained and used to calculate the cellulose mass.

2.2.2 NAE treatment

To begin with, 5 g of ginger stalk was added to a flask, then the NAE solutions with different SLR (1 : 10~1 : 60) were added. The flask was fitted with a reflux condenser tube and heated to a certain temperature. Then, the sample was washed and rinsed with NAE solution until the liquid became colorless. Finally, it was washed several times with ethanol until the filtrate reached a pH value of 7.0, then filtered and air-dried. The final mass was obtained and used to calculate the cellulose mass.

2.2.3 Crystallinity index calculation

The crystallinity index (CrI) of each sample was calculated by using the following empirical equation (1)^[17]:

$$\text{CrI} = \frac{I_{200} - I_{\text{am}}}{I_{200}} \times 100\% \quad (1)$$

where I_{200} was the peak intensity at the (200) plane

($2\theta=22.6^\circ$) and I_{am} was the minimum intensity in the valley between peaks at the (200) and (110) planes ($2\theta=18.7^\circ$).

3 Results and discussion

3.1 Effects of different KOH treatment conditions on cellulose extraction from ginger stalk

Fig.1 showed the effects of different KOH treatment conditions on the amount of cellulose extracted from the ginger stalk. Under the condition in Fig.1a, with an increase in KOH concentration, the sample mass was decreased. When the treatment was performed with the 14% KOH solution, the mass of sample reached the minimum amount (2.16 g), which meant that the purity of cellulose came to the maximum value. In order to prevent excessive degradation of cellulose, the optimum dosage of KOH was 14% (Fig.1a). Under the condition in Fig.1b, a significant reduction in the sample mass was obtained as the extraction time increased up to 5 h. At this point, the aromatic compounds, lignin, hemicellulose, resin acids, pigments, and other substances of the ginger stalk were almost entirely removed. In this case, the highest-purity cellulose was obtained (Fig.1b). Under the condition in Fig.1c, the sample mass decreased with the increased SLR. When the SLR exceeded 1 : 30, hemicellulose and lignin were removed and the sample mass underwent almost no further change with greater dilution. Therefore, the optimum SLR was 1 : 30 (Fig.1c).

3.2 Effects of different NAE treatment conditions on cellulose extraction from ginger stalk

Fig.2 illustrated the influence of different NAE treatment conditions on the amount of cellulose extracted from the ginger stalk. Under the condition in Fig.2a, it could be noted that the sample mass decreased with the increased SLR. When the SLR exceeded 1 : 40, the aromatic compounds, lignin, hemicellulose, resin acids, pigments, and other substances of the ginger stalk were almost entirely removed, so the sample mass was no longer significantly changed and the extraction of cellulose was 2.48 g. Therefore, the SLR of 1 : 40

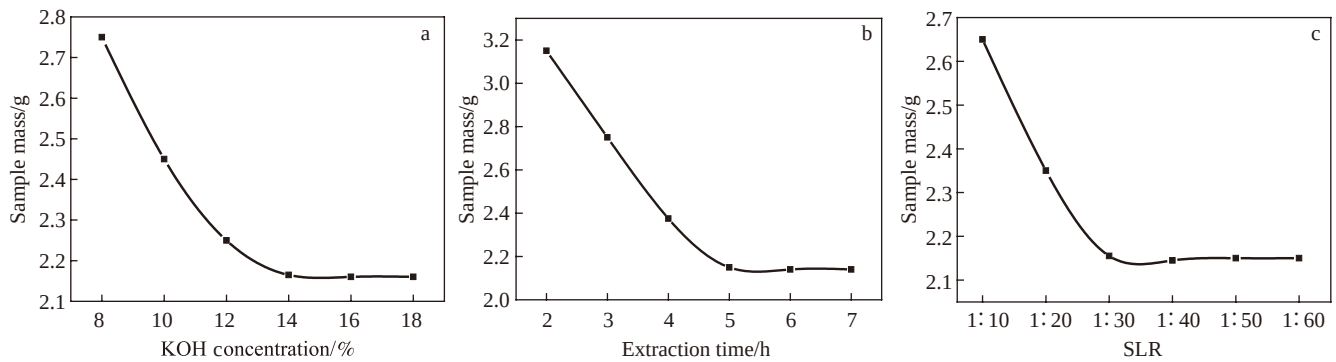


Fig.1 Effects of KOH concentration at 5 h extraction time and 1 : 30 SLR (a), extraction time at 14% KOH and 1 : 30 SLR (b), SLR at 5 h extraction time and 14% KOH (c) on the extraction of cellulose from ginger stalk

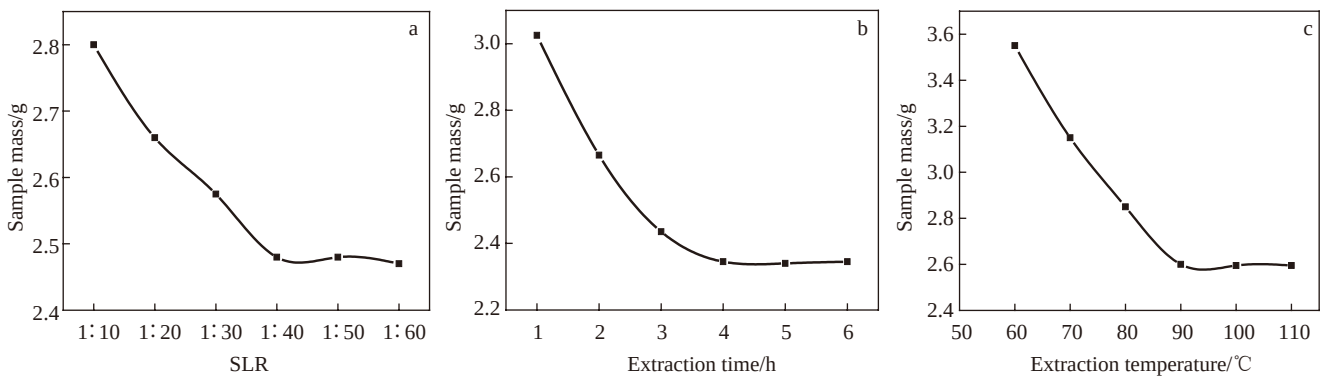


Fig.2 Effects of SLR at 4 h extraction time and 90°C extraction temperature (a), extraction time at 1 : 40 SLR and 90°C extraction temperature (b), extraction temperature at 1 : 40 SLR and 4 h extraction time (c) on the extraction of cellulose from ginger stalk

was chosen as the most suitable condition (Fig.2a). In addition, under the condition in Fig.2b, the sample mass was decreased with increasing the extraction time up to 4 h before leveling off. This indicated that 4 h was the optimum extraction time (Fig.2b). Under the condition in Fig.2c, with the increase of the extraction temperature, the sample mass gradually decreased and then remained unchanged as the extraction temperature exceeded 90°C. Therefore, the optimum extraction temperature was 90°C (Fig.2c).

3.3 FT-IR analysis

FT-IR spectroscopy is an appropriate technique to establish the chemical structure of the samples^[18]. Fig.3 depicted the FT-IR spectra of the ginger stalk cellulose, MCC and the celluloses extracted by KOH and NAE treatments.

In all spectra, a peak near 3200~3400 cm^{-1} could be observed. This corresponded to the O—H stretching vibration of —OH groups in the cellulose molecules, as

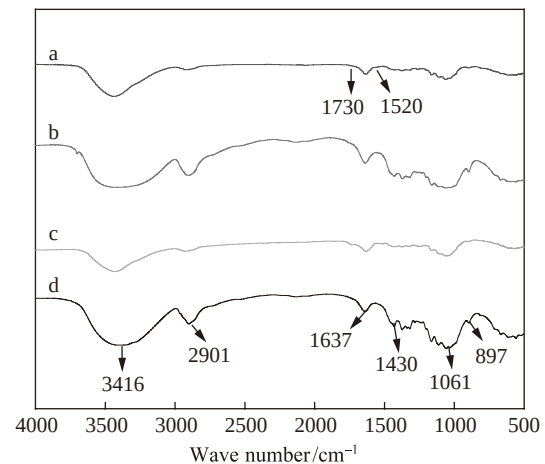


Fig.3 FT-IR spectra of ginger stalk cellulose (a), MCC (b), cellulose extracted by NAE treatment (c), and cellulose obtained by KOH treatment (d)

well as to the intermolecular and intramolecular hydrogen bonds presented in water and lignin structures^[19-20]. It was suggested that the peak was narrower or higher intensity for cellulose, which demonstrated that the cellulose specimens extracted by the NAE (Fig.3c) and

KOH (Fig.3d) treatments contained more —OH groups than the ginger stalk cellulose (Fig.3a). The smaller shoulder peak at 1730 cm^{-1} in the spectrum from the ginger stalk cellulose corresponded to the carbonyl ($\text{C}=\text{O}$) stretching vibration, which might be correlated to the aliphatic esters found in hemicelluloses and lignin^[21]. The spectra also clearly verified the sequential and complete removal of lignin (1520 cm^{-1} , aromatic skeletal vibrations) and hemicellulose (1730 cm^{-1} , carbonyl stretching) (Fig.3c and Fig.3d), compared to the ginger stalk cellulose (Fig.3a). The MCC FT-IR spectrum (Fig.3b) showed the characteristic peaks of pure cellulose. As observed in Fig.3b, Fig.3c, and Fig.3d, the FT-IR spectra were quite similar to each other, especially in the region between 1520 cm^{-1} and 1730 cm^{-1} . This meant that high-purity cellulose was obtained by both chemical treatments.

3.4 XRD analysis

XRD analysis was performed to demonstrate the effects of the chemical treatments on the crystallinity of the samples. Fig.4 presented the XRD patterns of the ginger stalk cellulose and the celluloses obtained by the NAE and KOH treatments.

As could be seen from Fig.4, all samples exhibited two sharp diffraction peaks at 16.5° (2θ , plane 110) and 22.6° (2θ , plane 200), which were characteristic of the I structure of cellulose. In the patterns of the celluloses obtained by the two chemical treatments, the peak intensities at 16.5° and 22.6° increased significantly and became sharper, especially at the diffraction peak of 22.6° . The crystallinity index (CrI) for the ginger

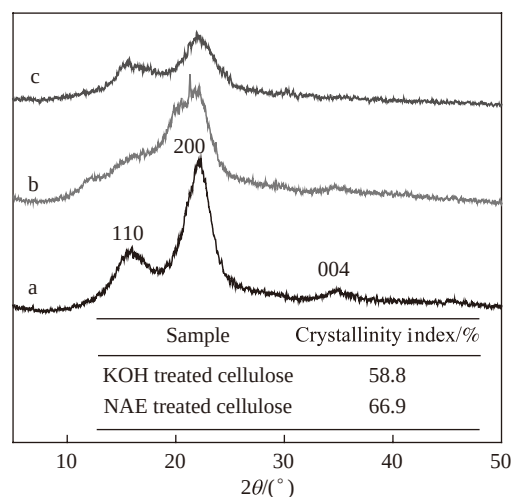


Fig.4 XRD spectra of cellulose extracted by NAE treatment (a), cellulose obtained by KOH treatment (b), and ginger stalk cellulose (c)

stalk cellulose was 46.8%, whereas it was significantly lower for the KOH and NAE celluloses at 58.8% and 66.9%, respectively. The diffraction intensity of the ginger stalk (Fig.4c) at 2θ was lower than those of the celluloses obtained by NAE (Fig.4a) and KOH (Fig.4b) treatments. This suggested that, during the extraction process, the ginger stalk lignin and hemicellulose were effectively removed, which improved the crystallinity of the samples^[22].

3.5 SEM analysis

Fig.5 showed the micrographs of the ginger stalk cellulose, KOH treated cellulose, and NAE treated cellulose. The differences among them were observed based on the surface morphology.

The original ginger stalk cellulose had a very smooth surface, as shown in Fig.5a. After the KOH treatment,



Fig.5 SEM micrographs of the ginger stalk cellulose (a), cellulose extracted by KOH treatment (b), and cellulose extracted by NAE treatment (c)

the cellulose surface seemed to become rougher and covered with grooves (Fig.5b). The cellulose subjected to the NAE treatment presented an even rougher surface, with many grooves and deep cracks (Fig.5c). These results suggested that the cellulose obtained by NAE treatment was severely degraded than that by KOH treatment.

3.6 Thermal analysis

TG and DTG curves of the celluloses extracted by the NAE and KOH treatments, as well as the ginger stalk cellulose, were illustrated in Fig.6.

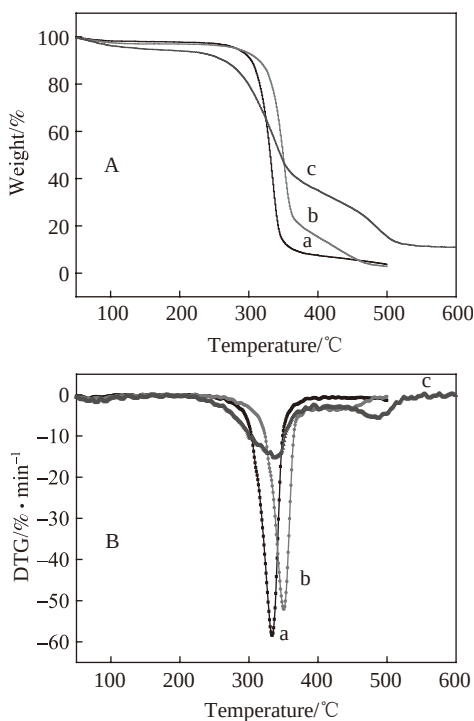


Fig.6 TG (A) and DTG (B) curves of cellulose obtained by NAE treatment (a), cellulose extracted by KOH treatment (b), and ginger stalk cellulose (c)

As noted from the TG and DTG curves displayed in Fig.6, all samples exhibited a similar mass loss in the low temperature (<100°C) range because of the evaporation of absorbed water. With temperature increasing, the samples exhibited different mass loss behaviors. For the cellulose samples, the different production processes conferred different thermal decomposition behaviors. Both treatments contributed to a prominent pyrolysis process. As shown in Fig.6, they had a pronounced decomposition onset at 298°C

and 315°C for the NAE (Fig.6a) and KOH (Fig.6b) celluloses respectively. The ginger stalk cellulose (Fig.6c) presented a lower stability (decomposition onset at approximately 100°C) than the celluloses extracted by NAE and KOH treatments. Thus, with the removal of lignin, hemicellulose, and other non-crystalline components of ginger stalk, the thermal stability was improved.

4 Conclusions

The extraction of cellulose from ginger stalk using the two chemical processes of KOH and NAE treatments was performed successfully. Both processes resulted in the removal of non-cellulosic components, as indicated in the FT-IR spectra. The optimal condition for the KOH treatment was found to be the following: 14% KOH, 5 h extraction time, and solid-to-liquid ratio (SLR) of 1 : 30. The optimal condition for the NAE treatment was as follows: SLR of 1 : 40, 4 h extraction time, and 90°C extraction temperature. The cellulose extracted by the KOH treatment presented the advantage of lower degradation compared to the cellulose obtained by the NAE treatment.

Acknowledgments

The authors greatly appreciate the financial support from the National Basic Research Program of China (Grant No.2014CB460610), National Science Foundation of China (Grant Nos.2157061214 and 21406126), Department of Education of Shandong Province (Grant No.J14LC11).

References

- [1] Mandal A, Chakrabarty D. Isolation of Nanocellulose from Waste Sugarcane Bassage (SCB) and Its Characterization[J]. Carbohydrate Polymers, 2011, 86: 1291-1299.
- [2] Sun J X, Sun X F, Zhao H, et al. Isolation and Characterization of Cellulose from Sugarcane Bagasse[J]. Polymer Degradation and Stability, 2004, 84: 331-339.
- [3] Li C G, Zhou W Y, Tian W. Study on Extraction of Cellulose and Removal of Hemicelluloses and Lignin from Bagasse[J]. Chinese Agricultural Science Bulletin, 2011, 27(4): 316-320.
- [4] Ochi S. Mechanical Properties of Kenaf and Kenaf/PLA Composities[J]. Mechanical of Materials, 2008, 40: 446-

- 452.
- [5] Wang Y, Li D W. Progress of Ginger[J]. Chinese Medicine, 2006, 15: 62-63.
 - [6] Chen G F, Guo W L, Meng Q. Ginger chemical analysis[J]. Amino Acids and Biological Resources, 2002, 24(2): 5-7.
 - [7] Wu P, Luo H B, Li H, et al. Development of Health Wine ginger[J]. Liquor-Making Science & Technology, 2008 (12): 94-96.
 - [8] Zhang B Y. The Manufacture of Ginger Soft Candy[J]. Modern Food Science and Technology, 2006, 22(4): 175-176.
 - [9] Fan Z X. Study on the Inhibition of Ginger Extract against Food coliform bacteria[D]. Shijiazhuang, Hebei Normal University, 2015.
 - [10] Wu J F, Zhang X M. Advances in materials research ginger flavor[J]. Food and Fermentation Industries, 2005, 31(4): 100-104.
 - [11] Li Y T, Liu Y S. Supercritical CO₂ extraction of volatile oil and ginger GC-MS analysis[J]. Food Research and Development, 2009, 30(3): 21-125.
 - [12] Wang L, Yan D H, Chen J Y. Advances in technology and ginger extract[J]. Chinese Journal of Information on Traditional Chinese Medicine, 2006, 13 (11): 96-98.
 - [13] Mazhari Mousavi S M, Hosseini S Z, Resalati H, et al. Papermaking potential of rapeseed straw, a new agricultural-based fiber source[J]. J Clean Prod, 2013, 52: 420-424.
 - [14] Zhao M M, Jiang M, Zhou Z W. Several straw component analysis[J]. Materials Review, 2011, 25 (8): 122-125.
 - [15] Dai C. Herb cellulose extraction, dissolution studies and film-forming properties[D]. Qingdao, China University of Petroleum, 2011.
 - [16] Wang L H, Wang Y L, Zhao X S. Comparative Study of Straw Cellulose Extraction[J]. Chinese Agricultural Science Bulletin, 2013, 29 (20): 130-134.
 - [17] Segal L, Creely J J, Martin A E, et al. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer[J]. Textile Research Journal, 1959, 29(10): 786-794.
 - [18] Zuluaga R, Putaux J L, Cruz J, et al. Cellulose Microfibrils from Banana Rachis: Effect of Alkaline Treatments on Structural and Morphological Features[J]. Carbohydrate Polymer, 2009, 76: 51-59.
 - [19] Tawakkal I S M A, Talib R A, Abdan K, et al. Optimisation of Processing Variables of Kenaf Derived Cellulose Reinforced Polylactic Acid[J]. Asian Journal of Chemistry, 2010, 22(9): 6652-6662.
 - [20] Brígida A I, Calado V M, Gonçalves L R, et al. Effect of chemical treatments on properties of green coconut fiber[J]. Carbohydr Polym, 2010, 79: 832-838.
 - [21] Romanzini D, Ornaghi Junior H L, Amico S C, et al. Preparation and characterization of ramie-glass fiber reinforced polymer matrix hybrid composites[J]. Mater Res, 2012, 15: 415-420.
 - [22] Ping L, You L H. Preparation and characterization of cellulose nanocrystals from rice straw[J]. Carbohydrate Polymers, 2012, 87: 564-573. PBM