CELLULOSE CHEMISTRY AND TECHNOLOGY

SONO-CHEMICAL PREPARATION OF CELLULOSE NANOWHISKERS FROM *LUFFA CYLINDRICA* FIBERS OPTIMIZED BY RESPONSE SURFACE METHODOLOGY

YANDAN CHEN,[*] QIAOMEI WU,[*] XIAOLIN AI,[*] MINGJIE HUANG[**] and QILIN LU[*]

[*]*College of Materials Engineering, Fujian Agriculture and Forestry University,*
Fuzhou 350002, China
[**]*College of Life Sciences, Fujian Agriculture and Forestry University, Fuzhou 350002, China*
✉ *Corresponding author: Y. Chen, fjaucyd@163.com*

Received March 10, 2016

An attempt to optimize the sono-chemical processing for cellulose nanowhiskers (CNWs) from *Luffa cylindrica* has been reported. Response surface methodology was applied to describe the influence of sulfuric acid concentration, temperature and sonication time on the yield of CNWs using the Box–Behnken experimental design. The sulfuric acid concentration of 62 wt%, temperature of 51 °C, and sonication time of 46 min were the optimal conditions for preparing CNWs *via* low-intensity ultrasound-assisted acid hydrolysis. The CNW yield reached 93.6% at the optimal combination of parameter settings and the value was well within the range predicted by the model, while the yield was only 72.1% in the absence of ultrasonic treatment. TEM observation revealed that CNWs obtained from ultrasound-assisted hydrolysis and conventional hydrolysis was very similar in rod-like micro-morphology with widths and lengths of 10-20 and 100-300 nm, respectively. XRD analysis indicated that both CNW samples presented cellulose I crystal structure with a Segal crystallinity index of 68.7% for ultrasound-assisted hydrolysis and 73.4% for conventional hydrolysis. These results suggest that low-intensity ultrasound-assisted acid hydrolysis could be a recommendable option for the high-yield production of uniform nanosized CNWs from *Luffa cylindrica* with high crystallinity and good dispersion stability at industrial level.

Keywords: cellulose nanowhiskers, *Luffa cylindrical*, ultrasound-assisted acid hydrolysis, optimization, response surface methodology

INTRODUCTION

Nanocelluloses, an outstanding renewable nano-sized material largely derived from various lignocellulosic biomass, are drawing a tremendous level of attention as shown by the continuously increasing number of scientific contributions (papers and patents) that describe various aspects of nanocrystalline cellulose (NCC) involving processing, chemical modification of surfaces, NCC-containing nanocomposites and self-assembly of suspensions.[1-3] The diversity of nanocellulose types mainly depends on the cellulosic source and processing conditions, and the nomenclature has not been standardized as described by Moon *et al*.[4] The term nanocrystalline celluloses (NCC), also known as cellulose nanocrystals (CNCs), cellulose nanowhiskers (CNWs), whiskers, or nanofibrils, are a rigid rod-like fibrous form of cellulose produced by the acid hydrolysis of plant (or animal or bacterial) based cellulose, with lateral dimensions ranging between 3-30 nm.[2,5] Despite the abundant availability of raw materials, NCC is not commercially available because the production is time consuming and the yield is low. One main challenge in the field is thus related to an efficient NCC separation from the natural resource through optimization of the acid hydrolysis or through implementation of new processes, aiming at saving time and at obtaining higher yields, and at using milder reaction conditions.[1] In connection with the emerging concept of 'green chemistry', recent emphasis has been increasingly given to develop non-conventional chemistry mainly based on a combination of chemical and physical treatments (such as sono-chemical approach) to intensify the isolation efficiency of nanocelluloses.[6-8]

Luffa cylindrica (LC) is a fast-growing, long-season, warm-climate vine plant that is native to the Asian tropics – it is commonly called luffa, but is also known as Chinese loofah, vegetable sponge, and dishcloth gourd. The matured fruit, when dried and peeled, reveals a fibrous, spongy skeleton so downright useful in areas such as daily household cleaning materials, stuffing and packing materials, biotechnology and bioengineering applications in biofuel production, cell immobilization scaffold, wastewater treatment, and use in plant, animal, and human cell culture, which are ascribed to its characteristics of high porosity (79-93%), very low density (0.02-0.04 g/cm^3), high specific pore volume (21-29 cm^3/g) and remarkable mechanical properties.[9-12] The luffa plant is thus now cultivated as a cash crop throughout the tropics due to its increasing economic importance. Moreover, fibers extracted from *Luffa cylindrica* have been recently studied as a new potential powerful source for nanocellulose preparation due to its high cellulose content (>60%).[13,14] However, no data on the yield of NCC obtained from LC fibers is accessible in the known literature, and there are no reports dedicated to a systematic investigation of optimizing the hydrolysis conditions by an experimental factorial design matrix carried out for LC-based NCC preparation. Furthermore, there have been few studies touching upon the improvement of NCC yield based on simultaneous assistance of low-intensity ultrasonic radiation during the whole process of acid hydrolysis, although many investigators have applied ultrasonication to disperse the NCC product after acid hydrolysis of cellulose.[1,15] Since NCC yields have an important impact on the final cost of its broad range of potential applications, more studies are necessary to optimize the NCC extraction process to achieve higher yields. Mild ultrasonic treatment has been proposed as successful assistance for acid hydrolysis to acquire improved yields as well as more homogeneous morphology of NCC.[8,16,17]

Therefore, the present work mainly aims at determining the optimal conditions for the maximum yield of cellulose nanowhiskers (CNWs) *via* sulfuric acid hydrolysis synchronously assisted with low-intensity ultrasonication by response surface methodology (RSM). Based on the Box–Behnken experimental design (BBD), a regression model was developed, and the optimum conditions to attain the highest yield of CNWs were predicted. Moreover, a comparative study on the CNWs yield, morphological and structural characteristics of CNWs prepared in the presence or absence of ultrasonic treatment was carried out.

EXPERIMENTAL

Materials

Natural sponge-like luffa strips were purchased from Luohe Huahui Loofah Sponge Product Processing Factory, Henan, China. The as-received luffa strips were washed several times with deionized water and then dried at 100 °C for 24 h. Afterwards, the dried luffa strips were cut into pieces and milled, until fine particulate fibers were obtained for further use. All reagents were of analytical grade and used as received. The chemical compositions, *i.e.* lignin, α-cellulose, hemicellulose, ethanol–benzene extractables, and ash content of the raw fibrous LC, were measured in accordance to the corresponding TAPPI standards, and averaged values from three tested samples were obtained as follows: 9.4% for lignin, 61.3% for α-cellulose, 23.3% for hemicellulose, 1.3% for extractives, and 2.1% for ash.

Extraction of *Luffa cylindrica* cellulose fibres (LCF)

The KOH-$NaClO_2$ system was applied to purify *Luffa cylindrica* fibres (LCF). Briefly, the as-dried LC powder was first extracted in a Soxhlet apparatus with a 2:1 (v/v) mixture of benzene/ethanol for 6 h.

Afterwards, lignin in the samples was removed using an acidified $NaClO_2$ solution (1.4 wt%) at 75 °C for 1 h. The bleaching treatment was performed five times, resulting in holocellulose fibers. Next, the bleached fibers were treated with 2.0 wt% potassium hydroxide at 90 °C for 2 h to remove hemicelluloses. To obtain highly purified cellulose, the samples were again treated with an acidified sodium chlorite solution at 75 °C for one hour and then treated with 5.0 wt% potassium hydroxide at 90 °C for 2 h. Finally, the residue was further treated with 1.0 wt% hydrochloric acid solution at 80 °C for 2 h and then thoroughly washed with distilled water, resulting in highly purified LCF.

Preparation of cellulose nanowhiskers (CNWs) via ultrasound-assisted sulfuric acid hydrolysis

In a typical procedure, 2.0 g of the highly purified LCF was hydrolyzed by 62 wt% H_2SO_4 solution (w/w, 1:10 g/ml) in a common ultrasonic bath with an output power of 250 W (KQ-250DB, Kunshan ultrasonic instrument Co., Ltd., China, 40 kHz) at 50 °C for 45 min under continuous mechanical stirring. The hydrolysis process was stopped by adding 10-fold cold distilled water. Removal of excess acid was achieved by centrifugation/washing process at 9000 rpm for 10 min until the suspension became turbid. The cloudy supernatant, containing nanowhiskers, was collected and the residual sediment was repeatedly subjected to ultrasonication and centrifugation cycles to obtain additional nanowhiskers. The supernatants collected were dialyzed against distilled water until a pH of 6-7 was reached. The obtained product was denoted as UH-CNWs. To investigate the effect of ultrasonication, a control sample prepared following the same procedures as described for UH-CNWs, but without ultrasonic exposure during hydrolysis, was named as H-CNWs.

Calculation of CNW yield

A known volume of the CNW suspension was dried by vacuum freeze drying for 48 h and the yield of CNWs was calculated according to the following equation:

$$Yield(\%) = \frac{(m_2 - m_1) \times V_1}{m_3 \times V_2} \times 100 \qquad (1)$$

where V_1 is the total volume of the CNW colloidal suspension collected; V_2 is the specified volume of the CNW suspension being dried; m_1 is the mass of the weighing bottle; m_2 is the gross mass of the weighing bottle and the as-dried CNW powder; m_3 is referred to the initial mass of the purified LCF used for preparation. The final result for each sample was obtained as the average of three runs of measurements.

Experimental design for optimization

The yield of CNWs derived from the purified LCF *via* ultrasound-assisted sulfuric acid hydrolysis was optimized by response surface methodology (RSM) combined with Box–Behnken experimental design (BBD). On the basis of our preliminary findings, three important independent variables, including sulfuric acid concentration (X_1), temperature (X_2) and sonication time (X_3) were studied to optimize CNW yield, and each variable was set at the three levels, as listed in Table 1. Seventeen experimental runs were conducted, including five replicates at the center point to estimate the pure error sum of squares. All the experiments were carried out at random, in order to minimize the effect of unexplained variability in the observed responses due to systematic errors.

The Design-Expert software (Trial Version 7.0.0, Static Made Easy, Minneapolis, Minnesota, USA) was used for regression and graphical analysis of the data obtained. The optimization process involves studying the response of the statistically designed combinations, estimating the coefficients by fitting them in a mathematical model, predicting the response of the fitted model and validating the adequacy of the model. After selecting the most accurate model, the analysis of variance (ANOVA) was used to investigate the statistical significance of the regression coefficients by conducting the Fisher's F-test at 95% confidence level.

Characterization

The morphology of CNWs was observed with JEM-2010 transmission electron microscopy (TEM) (JEOL Ltd., Japan) at 80kV accelerating voltage. A droplet of diluted CNW suspension was deposited on a carbon-coated Cu-grid and the excess liquid was removed by blotting with a piece of filter paper. To enhance the contrast, the nanocrystals were negatively stained with 2 wt% phosphotungstic acid solution for 1 min and then dried at room temperature. For X-ray diffraction (XRD), data were collected with an X'Pert Pro MPD X-ray diffractometer with Co tube at 40 kV and 30 mA. The crystallinity index (*CrI*) of the cellulose was calculated using Eq. (2):[18]

$$CrI = [(I_{002} - I_{am})/I_{002}] \times 100 \qquad (2)$$

In this equation, I_{am} represents the minimal diffraction intensity of the amorphous region at a 2θ angle between 21° and 22°, and I_{002} is the maximum lattice diffraction intensity at a 2θ angle between 26°and 27°.[19]

Table 1
Independent variables and their levels used in BBD

Variables	Codes	Levels		
		−1	0	1
Sulfuric acid concentration (wt%)	X_1	60	62	64
Temperature (°C)	X_2	40	50	60
Sonication time (min)	X_3	35	45	55

RESULTS AND DISCUSSION

Model development and statistical analysis

According to the experimental plan, the codified and actual values of the three important factors, together with response values and observed results were depicted in Table 2. Based on fitting the data to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA results, using the Design Expert software, it was revealed that the quadratic polynomial model as expressed in Eq. (3) was the most suitable for the yield of CNWs:

$$Y = 91.52 - 4.44X_1 + 9.48X_2 + 4.22\,X_3 - 11.6X_1X_2 + 0.57X_1X_3 - 7.23X_2X_3 - 8.71X_1^2 - 11.09X_2^2 - 3.49X_3^2 \qquad (3)$$

With analysis of variance (ANOVA), the adequacy of the regression equation and the multiple regression coefficients with respective P values gained by the least squares technique were summarized in Table 3. All of the linear and quadratic coefficients were highly significant ($P < 0.0001$) except the significant interactive term of X_1X_3 ($0.01 < P < 0.05$). The accuracy of the model was also checked by the multiple correlation coefficient R^2 value of 0.9988 and the lack-of-fit p-value of 0.0994, which indicate that the proposed regression model for the CNW yield is satisfactory and adequately fits with the experimental results.

RSM analysis of experimental results

Response surface methodology (RSM) is considered as the faster and less laborious technique, as it requires minimum experimental runs for optimizing complex processes on the base of statistical design and analysis.[20]

Table 2
BBD matrix of factors and the responses to the yield of nanocellulose whiskers

Run no.	Variables levels			Yield of NCWs, Y (%)	
	X_1 (%)	X_2 (°C)	X_3 (min)	Experimental	Predicted
1	-1(60)	-1(40)	0(45)	45.73	46.20
2	1(64)	-1(40)	0(45)	78.28	78.29
3	-1(60)	1(60)	0(45)	88.37	88.36
4	1(64)	1(60)	0(45)	74.52	74.05
5	-1(60)	0(50)	-1(35)	71.63	71.23
6	1(64)	0(50)	-1(35)	78.91	78.97
7	-1(60)	0(50)	1(55)	78.59	78.53
8	1(64)	0(50)	1(55)	88.15	88.55
9	0(62)	-1(40)	-1(35)	56.08	56.01
10	0(62)	1(60)	-1(35)	89.03	89.44
11	0(62)	-1(40)	1(55)	79.32	78.91
12	0(62)	1(60)	1(55)	83.34	83.41
13	0(62)	0(50)	0(45)	91.16	91.52
14	0(62)	0(50)	0(45)	91.27	91.52
15	0(62)	0(50)	0(45)	91.66	91.52
16	0(62)	0(50)	0(45)	91.87	91.52
17	0(62)	0(50)	0(45)	91.66	91.52

Table 3
Analysis of variance for response surface quadratic model

Source	Sum of squares	DF	Mean square	F-value	*P*-value [a]
Model	2739.97	9	304.44	1449.72	<0.0001
X_1	157.89	1	157.89	751.84	<0.0001
X_2	719.15	1	719.15	3424.55	<0.0001
X_3	142.38	1	142.38	678.02	<0.0001
X_1X_2	538.24	1	538.24	2563.06	<0.0001
X_1X_3	1.30	1	1.30	6.19	0.0417
X_2X_3	209.24	1	209.24	996.37	<0.0001
X_1^2	319.48	1	319.48	1521.35	<0.0001
X_2^2	517.68	1	517.68	2465.16	<0.0001
X_3^2	51.38	1	51.38	244.67	<0.0001
Residual	1.47	7	0.21		
Lack of fit	1.12	3	0.37	4.21	0.0994
Pure error	0.35	4	0.088		
R^2	0.9995				
Adj R^2	0.9988				

[a] $P < 0.01$ highly significant; $0.01 < P < 0.05$ significant; $P > 0.05$ not significant

A three-dimensional response surface graph and a two-dimensional contour plot can be plotted using the linear, quadratic and interaction terms demonstrated in the second order polynomial model, which is helpful to further examine the interactions of the observed factors and determine the optimum levels of each factor required for the highest response.[21,22]

The response surfaces for the effects of the independent variables on the yield of CNWs were drawn as three-dimensional plots of two factors, while the other variable constant was held at the zero level. Each response surface plot shown in Figure 1 exhibits a peak of the response, suggesting the maximum value of the response can be achieved within the experimental design boundaries studied.[23] The yield of CNWs was found to be a function of the linear and quadratic effects of sulfuric acid concentration, temperature and sonication time as demonstrated in Eq. (3). The linear effects were positive, except the sulfuric acid concentration, whereas all the quadratic effects ($P < 0.001$) were negative, except the interaction effect between sulfuric acid concentration and sonication time, which explained the observed nature of the curved surfaces, as shown in Figure 1. On the whole, the yield of CNWs increases first and then decreases with the increase of sulfuric acid concentration, temperature and sonication time, respectively, as a result of the multiple effects of the independent variables investigated in this case. The results obtained in this work are generally similar with those of previous reports.[7,23] Besides, the clear partial elliptical contour plots obtained in Figure 1 imply that the interaction between the variables is significant.[23,24]

Determination and experimental validation of the optimal conditions

The optimal values of each factor for the highest yield of CNWs were figured out based on the numerical analysis of Design-Expert software. The sulfuric acid concentration of 62 wt%, temperature of 51 °C, and sonication time of 46 min were found as the optimum conditions, under which the maximum yield of CNWs was predicted as 93.20%. To validate the model, a confirmatory experiment at these specific conditions was carried out in triplicate and was compared with the predicted result. The average yield of CNWs observed was 93.6% based on the initial weight of purified LCF, which is in good agreement with the predicted value from the regression model, thereby validating the optimization protocol. In contrast, the yield found for H-CNWs prepared under the identical conditions, in the absence of ultrasonication, was only 72.1%. As far as we know, the optimal yield of CNWs in our present work is higher than the accessible data ranging from 21% to 86% in previous publications related to the isolation of CNWs by sulfuric acid hydrolysis process.[1,7,25,26] According to the previous studies, low-intensity ultrasonication was believed to generate an unfocused ultrasonic beam to facilitate the acid hydrolysis process of cellulose under a fairly mild non-selective acoustic cavitation effect.[8,27] As a consequence, the resulting moderate mechanical shearing forces could be generally favorable to a rational bond cleavage of cellulose chains into whiskers with nano-scale lengths instead of excessive hydrolysis into glucose monomers. The highest yield of CNWs obtained in this work may consequently be accounted for the minimum degradation of luffa-based cellulose into soluble sugars under the proposed process of sulfuric hydrolysis coupled with mild ultrasonic treatment for manufacture of CNWs.

Morphological and structural characteristics of the as-prepared CNWs

Figure 2a-b shows the TEM images of UH-CNWs and H-CNWs samples with estimated diameters ranging from 10 nm to 20 nm and length distribution between 100 nm and 300 nm, similar to that observed in previous studies.[13,16] Both types of CNWs had rod-like shapes with subtle differences in morphologies and dimensions, except for the more remarkable aggregation of H-CNWs prepared *via* the conventional hydrolysis procedure without integration of ultrasound radiation. This suggested that low-intensity ultrasonic treatment may have boosted the grafting of negatively charged sulfate groups on the surface of CNWs due to the effect of acoustic cavitation, to produce a more stable colloidal dispersion despite its limited impact on the morphology characteristics of CNWs generated during the acid-catalyzed hydrolysis process.

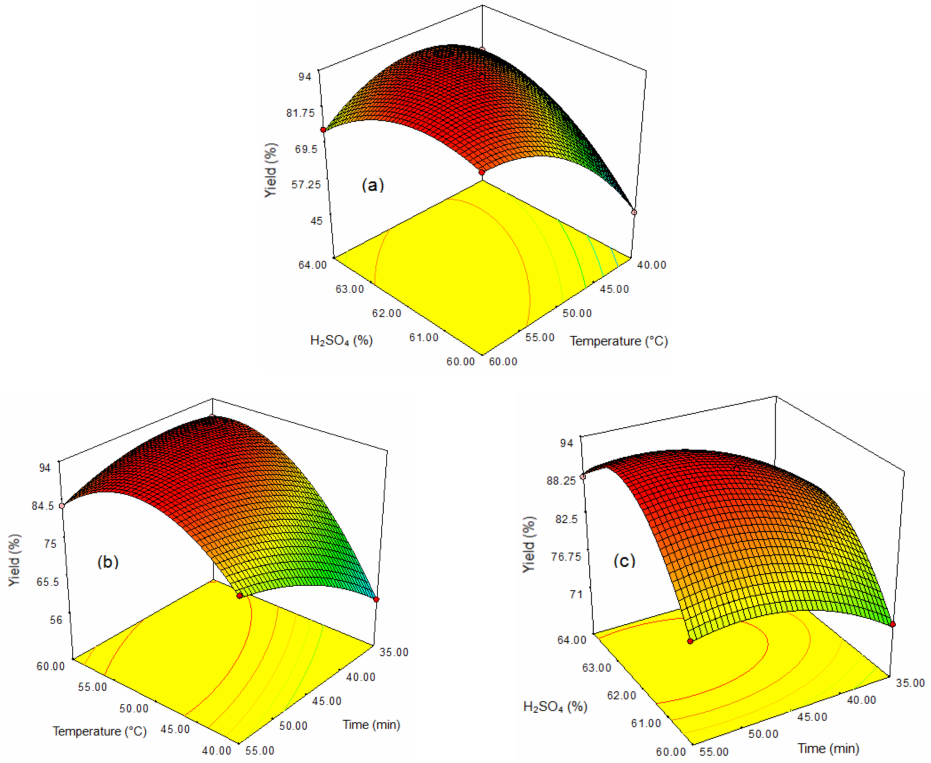

Figure 1: Response surfaces for the yield of CNWs, as a function of sulfuric acid concentration, temperature and sonication time (the value of the missing independent variable in each plot was

kept at the centre point)

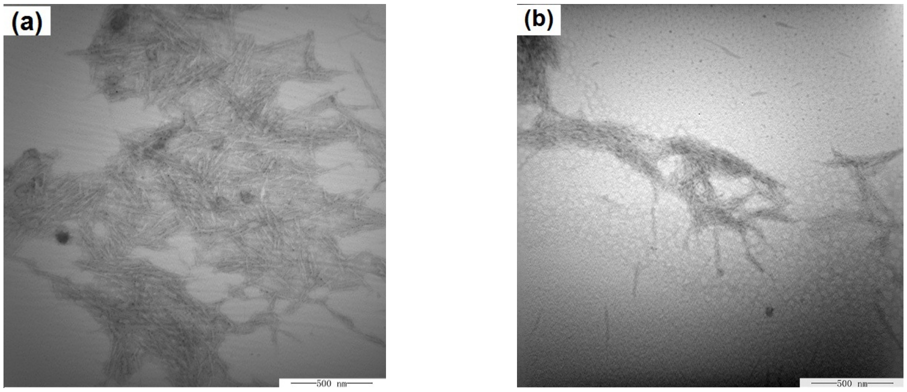

Figure 2: TEM images of UH-CNWs (a) and H-CNWs (b)

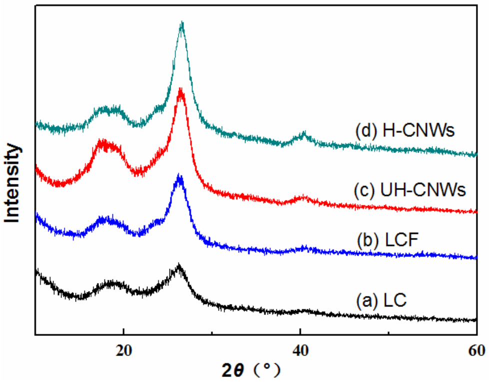

Figure 3: XRD patterns of LC (a), LCF (b), UH-CNWs (c) and H-CNWs (d)

Figure 3 shows the X-ray diffraction profiles of LC, LCF, UH-CNWs and H-CNWs. All samples had similar diffraction patterns with three typical cellulose I peaks at 2θ = 17.5°, 19.1° and 26.4°, indicating that the native cellulose I crystal structure was preserved after the delignification and nanofibrillation processes. The XRD of the original LC exhibited the broadest and least defined XRD peaks with the lowest crystallinity index (*CrI*) of 54.2%, whilst the crystallinity of LCF, UH-CNWs and H-CNWs was calculated as 67.9%, 68.7%, and 73.4%, respectively. The increase in the degree of crystallinity for LCF, compared to that of LC, can be explained by the removal of amorphous hemicelluloses and lignin during chemical treatment. Notably, UH-CNW was found to possess a slight decrease in crystallinity in comparison with H-CNW obtained by conventional sulfuric acid hydrolysis, implying that both amorphous and crystalline domains in cellulose may become susceptible to acid hydrolysis under ultrasonic exposure due to the non-selective ultrasonication effect.[27] Moreover, some lattice defects generated on the surface of cellulose crystallites, resulting from the powerful shock waves created by the sudden collapse of the ultrasonic cavitation bubbles,[28] could also be supposed to have negative impact on the crystallinity of NCWs in the ultrasonic-assisted hydrolysis process. A similar decrease of crystallinity with *CrI* values ranging from 61.9% to 73% for NCWs produced from different cellulosic sources using high-intensity ultrasonication has also been observed in previous reports.[27,29] However, marginal increases of the crystallinity (within 5%) of NCWs produced *via* ultrasonic-assisted sulfuric acid hydrolysis when compared to the NCWs generated in the same manner, but without ultrasonication, have also been found in the recently reported literature.[8,16]

At present, it is generally accepted that both micro-morphology and crystallinity characteristics of the resultant nanocelluloses depend largely not only on the hydrolysis conditions,[30] but also on the different origins, with wide variations in proportions of crystalline and amorphous regions found in their native celluloses.[31,32] For this reason, this aspect would require further investigation. Additionally, a remarkably superior crystallinity of 96.5% for luffa-based whiskers prepared by conventional sulfuric acid hydrolysis has been reported by Siqueira *et al.*,[13] which may be explained by the rather high intrinsic crystallinity (81.3%) of the raw LC fibers in comparison with the *CrI* value of only 54.2% for the untreated LC used in this work.

CONCLUSION

Optimization by RSM based on BBD was successfully employed for luffa-based NCW manufacture *via* low-intensity ultrasound-assisted sulfuric acid hydrolysis. ANOVA and statistical parameters indicated that the experimental data corresponding to the NCWs yield showed a good fit to a quadratic model. The sulfuric acid concentration of 62 wt%, temperature of 51 °C and sonication time of 46 min were determined as the optimal conditions for the maximum yield of 93.6% for NCWs in this case. The superiority of ultrasound-assisted acid hydrolysis procedure for preparing NCWs, as compared to the conventional hydrolysis under the same conditions of sulfuric acid concentration, temperature and time, was evaluated in terms of the yield as well as the micromorphology and crystallinity characteristics of the NCWs. The results obtained in present study indicated that low-intensity ultrasound-assisted acid hydrolysis can be a promising method in practice for isolating cellulose nanowhiskers with improved yield, satisfactory crystallinity, uniform size distribution, together with good dispersion stability.

ACKNOWLEDGEMENTS: This work was financially supported by the National Natural Science Foundation of China (No. 31000276 and 31170520), Fundamental Research Funds for Distinguished College Young Scholars of Fujian Province, China (No. JA11071 and No. JA12088). We also gratefully acknowledge the financial funding from the Incubation Program for Distinguished Young Scholars of FAFU Science Foundation (No. xjq201208).

REFERENCES

[1] L. Brinchi, F. Cotana, E. Fortunati and J. M. Kenny, *Carbohyd. Polym.*, **1**, 154 (2013).

[2] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors *et al.*, *Angew. Chem. Int. Ed.*, **50**, 5438 (2011).

[3] M. B. Habibi Najafi and R. Farhoosh, *Food Chem.*, **155**, 319 (2014).

[4] R. J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Younblood, *Chem. Soc. Rev.*, **40**, 3941 (2011).

[5] S. J. Eichhorn, *Soft Matter.*, **7**, 303 (2011).

[6] W. Chen, H. Yu and Y. Liu, *Carbohyd. Polym.*, **2**, 453 (2011).

[7] Z. Lu, L. Fan, H. Zheng, Q. Lu, Y. Liao *et al.*, *Bioresour. Technol.*, **146**, 82 (2013).

[8] Y. Tang, S. Yang, N. Zhang and J. Zhang, *Cellulose*, **1**, 335 (2014).

[9] I. O. Oboh and E. O. Aluyor, *Afr. J. Agr. Res.*, **8**, 684 (2009).

[10] M. Iqbal and A. Saeed, *Process Biochem.*, **2**, 148 (2007).

[11] A. Saeed and M. Iqbal, *Biotechnol. Progr.*, **3**, 573 (2013).

[12] J. Shen, X. Y. Min, X. Huang, S. Zhou and D. Ruan, *J. Mech. Behav. Biomed.*, **15**, 141 (2012).

[13] G. Siqueira, J. Bras and A. Dufresne, *BioResources*, **2**, 727 (2010).

[14] N. Follain, S. Belbekhouche, J. Bras, G. Siqueira, S. Marais *et al.*, *J. Membrane Sci.*, **427**, 218 (2013).

[15] D. Bondeson, A. Mathew and K. Oksman, *Cellulose*, **2**, 171 (2006).

[16] W. Li, R. Wang and S. Liu, *BioResources*, **4**, 4271 (2011).

[17] P. B. Filson and B. E. Dawson-Andoh, *Bioresour. Technol.*, **100**, 2259 (2009).

[18] L. Segal, J. J. Creely, A. E. Martin and C. M. Conrad, *Text. Res. J.*, **10**, 786 (1959).

[19] J. P. Moraisa, M. de F. Rosa, M. de S. de Souza Filho, L. D. Nascimento, D. M. do Nascimento *et al.*, *Carbohyd. Polym.*, **91**, 229 (2013).

[20] J. Azmir, I. S. M. Zaidul, M. M. Rahman, K. M. Sharif, F. Sahena *et al.*, *Ind. Crop. Prod.*, **52**, 405 (2014).

[21] Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, **6**, 3479 (2010).

[22] B. Hong, L. Chen, G. Xue, Q. Xie and F. Chen, *Cellulose*, **3**, 2157 (2014).

[23] L. Tang, B. Huang, W. Ou, X. Chen and Y. Chen, *Bioresour. Technol.*, **23**, 10973 (2011).

[24] K. Dehghani, A. Nekahi and M. A. M. Mirzaie, *Mater. Des.*, **31**, 1768 (2010).

[25] M. A. Henrique, H. A. Silvério, W. P. Flauzino Neto and D. Pasquini, *J. Environ. Manag.*, **121**, 202 (2013).

[26] W. Y. Hamad and T. Q. Hu, *Can. J. Chem. Eng.*, **88**, 392 (2010).

[27] W. Li, J. Yue and S. Liu, *Ultrason. Sonochem.*, **3**, 479 (2012).

[28] P. Cintas and J. L. Luche, *Green. Chem.*, **3**, 115 (1999).

[29] W. Chen, H. Yu, Y. Liu, P. Chen, M. Zhang *et al.*, *Carbohyd. Polym.*, **4**, 1804 (2011).

[30] S. Beck-Candanedo, M. Roman and D. G. Gray, *Biomacromolecules*, **2**, 1048 (2005).

[31] M. K. M. Haafiz, A. Hassan, Z. and Inuw I. M. Zakaria, *Carbohyd. Polym.*, **103**, 119 (2014).

[32] A. Mandal and D. Chakrabarty, *Carbohyd. Polym.*, **3**, 1291 (2011).