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Preparation, characterization and optimization of nanocellulose whiskers by simultaneously ultrasonic wave and microwave assisted

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HIGHLIGHTS

- Nanocellulose whiskers were prepared by ultrasonic/microwave assisted method.
- The yield affected by reaction parameters was studied by single factor tests.
- The reaction conditions were optimized with response surface methodology.
- The acid hydrolysis of cellulose was intensified by ultrasonic and microwave.
- The yield and the crystallinity of the sample is 85.75% and 80%, respectively.

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ABSTRACT

Simultaneously ultrasonic wave and microwave assisted technique (SUMAT), as a method of process intensification, was first applied to the preparation of nanocellulose whiskers (NCWs) from filter paper by sulfuric acid hydrolysis. The effects of temperature, sulfuric acid concentration, and mass of raw material and time on the yield of NCWs were investigated by single-factor experiments, and the preparation conditions were optimized with response surface methodology. The obtained NCWs were characterized by transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction and thermal gravimetry. The results showed NCWs were facilely prepared by using SUMAT. However, some harsh reaction conditions such as high temperature, strong acidity and long time treatment easily induced the reduction of the yield of NCWs. Under the optimal conditions, the yield and the crystallinity of NCWs with the crystal form of cellulose Iα is 85.75% and 80%, respectively.

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1. Introduction

Nanocellulose whiskers (NCWs) exhibit great potential in engineering application such as optical and electronic devices (Mendez and Weder, 2010; Zhou et al., 2011), composite materials (Leung et al., 2011) and molecule biology (Mangalam et al., 2009) due to its low density, high surface area, modifiable surface properties, biocompatible and biodegradability (Brinchi et al., 2013; Duran et al., 2011), etc. It has attracted more and more attention in recent years. Typical preparation procedure of NCWs consists of three stages: pre-treatments of raw materials such as wood, plant, residual biomass and some kind of relatively pure cellulose to obtain cellulose; acid hydrolysis of the obtained cellulose to remove the amorphous regions; sonication treatment to disperse the nanocrystals as a uniform stable suspension (Brinchi et al., 2013). However, the production of NCWs currently is a time-consuming process with low yield, which diminishes its commercial availability. Therefore, preparation intensification of NCWs is significant and essential to improve the production efficiency.

Some assisted technologies such as ultrasonic wave (UW) and microwave (MW) are usually applied to physicochemical treatments of plant fiber materials to acquire high efficiency in virtue of the intensification of the heat and mass transfer. Especially, Moholkar has investigated systematically on the intensification of UW in textile washing in recent years (Moholkar et al., 2003, 2004; Moholkar and Warmoeskerken, 2004). These valuable research works illuminate that the mass transfer of textile treatment can be improved by convective diffusion enhancement in the inter- and intra-yarn pores due to the intense micro-flows near the fiber surface resulting from cavitation effect. In addition, MW can induce heat at molecular level by direct conversion of electromagnetic energy and are helpful in reducing energy consumption and reaction time compared to conventional heating (Cravotto and Cintas, 2007). Since MW can intensify the heat transfer and improve the reaction activity of raw material, meanwhile UW can enhance

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the mass transfer in inter- and intra-fiber pores, it is worth looking forward to the coupling of these two methods in some physicochemical treatments of fiber materials. Nowadays simultaneously UW and MW assisted technique (SUMAT) has been used to some physicochemical processes such as extraction (Zhang and Liu, 2008), reaction (Haque and Jhung, 2011) and chemistry analysis (Domini et al., 2009). In these processes, SUMAT exhibits very high efficiency due to the synergetic effect induced by the heat transfer enhancement of MW and the mass transfer enhancement of UW. Thus, the application of SUMAT in the preparation of NCWs may greatly shorten preparation time and enhance production efficiency by improving acid hydrolysis of cellulose to remove the amorphous regions.

Response surface methodology (RSM) (Box and Wilson, 1951) has been widely applied to the modeling, simulation and optimization of complex processes on the base of statistical design and analysis. This method not only can efficiently achieve optimal conditions at low cost and without carrying out extensive experimental tests, but also can readily realize the relationship between variables and one or more response variables by the visualization of response surface. Recently, RSM is used as a powerful tool in biomass conversion processes (Awad et al., 2013; Guo et al., 2012; Rodrigues et al., 2012; Tian et al., 2011).

In the present study, NCWs were manufactured from filter paper (FP) by acid hydrolysis with SUMAT. In order to explore the intensification mechanism in the preparation process, the effects of reaction temperature, sulfuric acid concentration, and mass of raw material and reaction time on the yield of NCWs were investigated by single-factor experiments. Based on the results of single-factor experiments, the preparation conditions were optimized by RSM. The factors, including reaction temperature, sulfuric acid concentration and reaction time, were chosen as independent variables for a Box–Behnken experimental design; meanwhile mass of raw material was set as fixed value. RSM was used to describe the relationship between independent variables and the yield of NCWs. In addition, the morphology, microstructure and thermal behavior of the obtained NCWs were characterized by several analytical methods.

2. Methods

2.1. Materials

Filter paper (102 #, Φ 125 mm), purchased from Hangzhou special paper Co. Ltd., China, was cut into 10 mm × 10 mm of square slices, and then dried under vacuum at 30 °C for 24 h prior to use. Sulfuric acid and calcium oxide were analytical grade and supplied by Sinopharm chemical reagent Co. Ltd., China.

2.2. Preparation of nanocellulose whiskers

Nanocellulose whiskers were prepared by acid-catalyzed hydrolysis of FP in the reactor (CW2000, Shangshai xintuo analytical instruments Co. Ltd., China) with 40 kHz 50 W UW and 2450 MHz MW assisted simultaneously. The MW power can automatically vary from 10 W to 800 W according to the set reaction temperature. Generally, the high power of MW is only adopted automatically within initial 2 min in the preparation process to heat the reaction mixture from room temperature to the set temperature (55–75 °C) and the low power of MW about 50 W is sufficient to maintain the set temperature according to our previous pre-experiments, although the power cannot be observed from the reactor in auto mode.

Briefly, 2 g slices of FP was mixed with 56 mL 50% (w/w) sulfuric acid solution and then loaded into the reactor. After a set reaction time, the resultant was diluted with deionized water and purified with centrifugation at 6000 r min^{-1} for 7 min. The purified process was repeated at least three times to remove the acid. The collected supernatant fluid was vaporized to recycle sulfuric acid. The residue was diluted with deionized water and then adjusted pH to neutrality by 0.1 mol L^{-1} CaO aqueous solution. The neutral suspension was centrifugalized for four times as the above mentioned conditions. Finally the milky NCWs suspension was obtained. An amount of the NCWs suspension was dried up to constant weight at 105 °C and the yield of NCWs was calculated according to the formula (1):

$$\text{Yield } (\%) = \frac{M_1 \times M_3}{M_2 \times M_0} \times 100\% \quad (1)$$

where M_0 is the mass of FP; M_1 is the mass of NCWs dry powder; M_2 is the mass of the NCWs suspension sample used to acquire the dry powder; M_3 is the total mass of NCWs suspension obtained in the final preparation.

2.3. Optimization of preparation conditions for nanocellulose whiskers

The Box–Behnken experimental design of Response surface methodology was employed for the optimization of NCWs preparation with software Design-Expert (Trial Version 7.0.0, Static Made Easy, Minneapolis, Minnesota, USA). Based on single-factor experiments, the three independent variables involved their levels were chosen as follow: reaction temperature X_1 (67 °C, 70 °C and 73 °C); sulfuric acid concentration X_2 (47%, 50% and 53%); reaction time X_3 (1.0 h, 1.5 h and 2.0 h). The detailed plan is shown in Table 1. The experimental design consisted of 17 experiments, including 12 factorial experiments (replicated 3 times for each factorial experiment) and another 5 replicated at the central point to estimate the pure error sum of squares.

2.4. Characterization of samples

The microphology of NCWs was observed with JEM-1010 transmission electron microscopy (TEM) (JEOL Ltd., Japan) at 200 kV accelerating voltage. A droplet of diluted NCWs suspension (1%, w/w) under optimal preparation conditions was put on a Cu-grid covered with a thin carbon film and the excess liquid was removed by blotting with a piece of filter paper.

FP and the NCWs powder obtained under the optimum preparation condition both were characterized by Fourier transform infrared (FT-IR), Thermal gravimetry (TG) and Wide-angle X-ray diffraction (WAXRD), respectively. FT-IR spectra of samples were measured using a Nicolet 380 spectrometer (Thermo Electron Co., USA) at ambient conditions. Samples were ground with KBr (1:100, w/w) and pressed into transparent pellets. The spectra were collected in the transmittance mode from 400 cm^{-1} to 4000 cm^{-1} at a 4 cm^{-1} resolution. TG experiments of the samples were performed using a NETZSCH STA 449 F3 Jupiter® simultaneous thermal analyzer under heated from room temperature to 600 °C at 10 °C min^{-1} with a flow N_2 of 30 mL min^{-1} as protecting gas. WAXRD patterns of samples were obtained using a X'Pert Pro MPD diffractometer with Ni-filtered Cu Kα radiation (Philips Co., Holland) at the scan rate of 0.2 s^{-1} in a 2θ range of 10–90°. The crystallinity index (CrI) of samples was calculated from the X-ray diffraction patterns according to the following equation:

$$\text{CrI} = \frac{I_{200} - I_{\text{am}}}{I_{200}} \quad (2)$$

where I_{200} is the overall intensity of the peak at 2θ about 22.6° and I_{am} is the intensity of the baseline at 2θ about 18° (Segal et al., 1959).

Table 1
Box–Behnken experimental design and the yield of nanocellulose whiskers.

No.	Variables levels			Yield of nanocellulose whiskers, *Y* (%)		
	X_1 (°C)	X_2 (%, w/w)	X_3 (h)	Experimental	Standard deviation	Predicted
1	0 (70)	1 (53)	1 (2.0)	77.98	1.26	77.24
2	0 (70)	−1 (47)	−1 (1.0)	44.46	1.17	45.20
3	−1 (67)	−1 (47)	0 (1.5)	61.06	0.89	60.92
4	0 (70)	1 (53)	−1 (1.0)	74.37	1.21	74.18
5	0 (70)	−1 (47)	1 (2.0)	57.17	0.94	57.36
6	0 (70)	0 (50)	0 (1.5)	79.35	0.73	78.67
7	−1 (67)	1 (53)	0 (1.5)	80.18	1.05	80.97
8	1 (73)	0 (50)	−1 (1.0)	59.21	1.07	59.26
9	0 (70)	0 (50)	0 (1.5)	79.09	0.73	78.67
10	0 (70)	0 (50)	0 (1.5)	77.53	0.73	78.67
11	−1 (67)	0 (50)	−1 (1.0)	60.75	1.36	60.15
12	−1 (67)	0 (50)	1 (2.0)	70.67	0.98	70.62
13	0 (70)	0 (50)	0 (1.5)	79.01	0.73	78.67
14	1 (73)	−1 (47)	0 (1.5)	53.59	0.86	52.80
15	0 (70)	0 (50)	0 (1.5)	78.39	0.73	78.67
16	1 (73)	0 (50)	1 (2.0)	63.42	1.04	64.02
17	1 (73)	1 (53)	0 (1.5)	81.46	0.78	81.60

Mass of filter paper: 2 g.

3. Results and discussion

3.1. Effect of reaction temperature on the NCWs yield

Reaction temperature is an important factor that could influence the hydrolysis of cellulose. The yield of NCWs affected by reaction temperature is shown in Fig. 1(a). Reaction temperature maintained by self-adjusting MW was set at 55 °C, 60 °C, 65 °C, 70 °C, 73 °C and 75 °C, respectively. Other reaction parameters were: sulfuric acid concentration 50%, mass of FP 2.0 g and reaction time 1 h. Fig. 1(a) indicates that the yield of NCWs increases first and then decreases, and reaches the maximum value about 67% at 70 °C with increasing reaction temperature. High temperature means that high power of MW is adopted automatically by the reactor, which can enhance the reaction activity of cellulose in FP. Moreover, the mass transfer in intra-fiber pores of wet FP is also intensified with the rise of temperature due to the increase of the diffusion coefficient of H^+ in aqueous solution. However, the temperature is so high (>70 °C) that cellulose should be excessively hydrolyzed into glucose monomers, which reduces the yield of NCWs. Therefore, the reaction temperature of 70 °C was considered to be optimal reaction temperature owing to its higher yield of NCWs in this experiment.

3.2. Effect of sulfuric acid concentration on the NCWs yield

Generally, higher sulfuric acid concentration can enhance the hydrolysis degree of cellulose, including amorphous component and crystalline component of cellulose. In addition, amorphous component of cellulose is more easily decomposed in the presence of acid catalyst than crystalline component of cellulose due to their disorder microstructure. Thus, the hydrolysis degree of amorphous cellulose rises with acid concentration increasing and benefits to the production of nanocrystalline cellulose. However, the

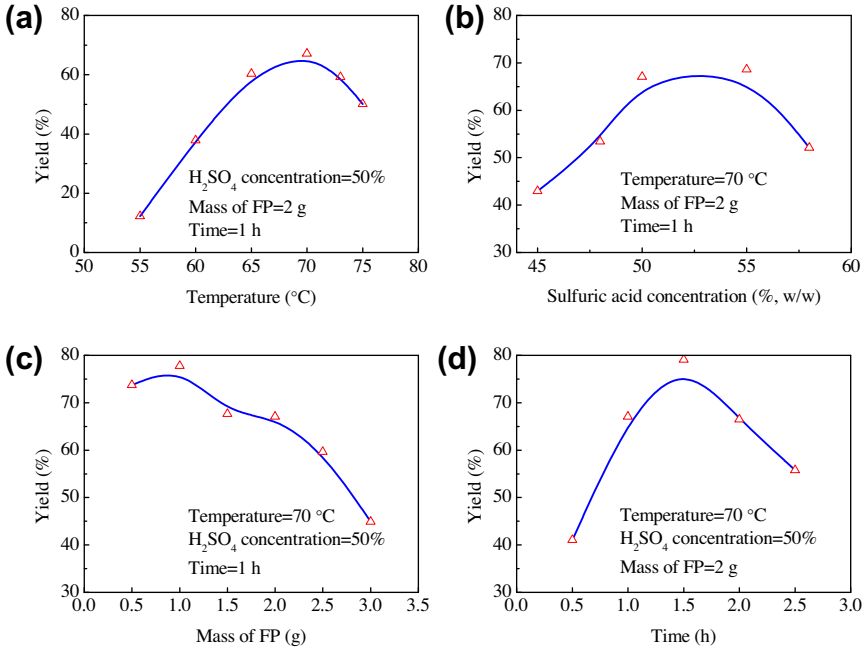

Fig. 1. The effects of (a) reaction temperature; (b) sulfuric acid concentration; (c) mass of FP; (d) reaction time on the yield of NCWs.

crystalline component of cellulose is gradually hydrolyzed with acid concentration further increasing, which often leads to lower yield of nanocrystalline cellulose. In order to find an optimal sulfuric acid concentration, the effect of sulfuric acid concentration on the yield of NCWs was investigated and shown in Fig. 1(b), while other reaction conditions were set as follow: reaction temperature 70 °C, mass of FP 2.0 g and reaction time 1 h.

Fig. 1(b) shows that when sulfuric acid concentration increases from 45% to 50%, the yield of NCWs increases due to the hydrolysis of amorphous component of cellulose, and the maximum yield can be obtained at sulfuric acid concentration of 50%. Although the yield still keeps up at sulfuric acid concentration of 55%, it is observed that the suspension liquid of NCWs becomes slight gray, suggesting that the NCWs start charring on this condition. The reason for this phenomenon may be that the synergetic effect between MW and UW wave comes into being in the preparation process of NCWs and significantly accelerates hydrolysis of cellulose into glucose monomers and even carbonization. Thereby, sulfuric acid concentration of 50% was adopted in the optimization of NCWs preparation.

3.3. Effect of mass of FP on the NCWs yield

Fig. 1(c) shows that the effect of mass of raw material on the yield of NCWs, while other reaction conditions were set as follow: reaction temperature 70 °C, sulfuric acid concentration 50% and reaction time 1 h. In Fig. 1(c), when mass of FP increases from 0.5 g to 3.0 g, the yield of NCWs initially increases and then gradually decreases, and reaches the maximum value about 78% at 1.0 g. The reduction of the yield may be mainly due to the weakness of ultrasonic cavitation with increasing the dosage of FP. In addition, when the dosage of FP is more than 2.0 g, a few slices of FP cannot be immersed completely in sulfuric acid solution, which also leads to the reduction of the yield.

On the other hand, the output of NCWs increases with the dosage of FP increasing from 0.5 g to 2.0 g. For example, the output of NCWs at 2 g of FP dosage is 1.34 g and almost twice that at 1 g of FP dosage (0.78 g). Moreover, high output means not only the reduction of time and energy consumption in the preparation process of NCWs, but also the decrease of waste acid solution. Hence, considering the balance between output and yield, 2.0 g of FP was chosen as a suitable loading of feedstock in the present work.

3.4. Effect of reaction time on the NCWs yield

A reaction time also presents a significant effect on the yield of NCWs, which is shown in Fig. 1(d). The other three factors (reaction temperature, sulfuric acid concentration, mass of FP) were fixed at 70 °C, 50% and 2.0 g, respectively.

From Fig. 1(d), the yield of NCWs rises quickly from 41% to 67% when reaction time increasing from 0.5 h to 1.0 h. The mass transfer resistance gradually decreases and the specific surface of FP increases with reaction time increasing owing to the breakdown of the net structure of FP and even the enlargement of the inter- and intra-fiber pores, which results from the acid hydrolysis of more and more cellulose under the synergy between MW and UW. In turn, the enhancement of mass transfer can further improve the hydrolysis of cellulose. Thus, this indicates that synergetic effect between MW and UW can play an important role in accelerating the preparation of NCWs. On the other hand, it is observed that the yield reaches the maximum value of 79% at 1.5 h, and then decreases when reaction time further increases owing to the hydrolysis of crystalline cellulose. Therefore, reaction time of 1.5 h was chosen in the optimization of preparation conditions.

3.5. Statistical analysis and model fitting

The experimental yield of NCWs and their standard deviations according to the factorial design are listed in Table 1. The results showed that the yield ranges from 44.46% to 81.46%, their standard deviations distributes between 0.73% and 1.36% and the maximum yield is found in conditions of X_1 = 73 °C, X_2 = 53% and X_3 = 1.5 h. The yield and three independent variables are related by the following second-order polynomial equation:

$$Y = 78.67 - 1.87X_1 + 12.21X_2 + 3.81X_3 + 2.19X_1X_2 - 1.43X_1X_3 - 2.28X_2X_3 - 4.79X_1^2 - 4.81X_2^2 - 10.37X_3^2 \quad (3)$$

where Y is the yield of NCWs; X_1, X_2 and X_3 are the independent variables for reaction temperature, sulfuric acid concentration and reaction time, respectively.

Table 2 shows that analysis of variance for the response surface model. The model F-value of 306.33 indicates the model is highly significant, and the model P-value of less than 0.0001 illuminates that model terms are also significant. Furthermore, the determination coefficient (R^2) of the model (0.9975) is close to 1, with no significant lack of fit ($P > 0.05$). This means that the regression model represents the true relationship between the responses and the independent variables within the range of experimental variables. (Borges et al., 2011; Li et al., 2011). Therefore, it can be confirmed from the above analysis that the response surface model is adequate for the optimization of preparation conditions in the present work.

In Table 2, the linear terms (X_1, X_2 and X_3) and the quadratic terms (X_1^2, X_2^2 and X_3^2) are significant ($P < 0.006$), indicating that the yield of NCWs was affected significantly by the three variables. What is more, all the interaction terms (X_1X_2, X_1X_3 and X_2X_3) are significant at the level of $P < 0.05$, which maybe results from the present of the synergetic effect between MW and UW in the preparation process of NCWs using SUMAT.

3.6. Optimization of preparation conditions

To investigate the effect of three independent variables on the yield of NCWs and obtain the optimal preparation conditions, the three-dimensional response surface and contour plots were constructed according to Eq. (3) and shown in Fig. 2. Generally, 3-D response surface plots show the combined effects of two variables on response as other variables are kept at level zero. Elliptical plots imply that the interaction between the variables is significant and circular contour plots mean that the interaction between the variables is not important (Dehghani et al., 2010).

Fig. 2(a) shows that the yield of NCWs increases with the increase of reaction temperature from 67 °C to 73 °C at same sulfuric acid concentration, and the yield gradually enhances with the increase of sulfuric acid concentration from 47% to 53% at constant temperature. Additionally, the partial elliptical contour plot obtained suggests the presence of the significant interaction between sulfuric acid concentration and reaction temperature. Fig. 2(b) exhibits a clear peak of the response, indicating the yield of NCWs increases first and then decreases with the increase of reaction temperature and reaction time, respectively, which is in accord with the results of the single factor experiment. At the same time, the contour plot is close to a circle shape, which suggests relative mild interaction between reaction temperature and reaction time. Fig. 2(c) shows that when reaction time prolongs from 1 h to 2 h at same sulfuric acid concentration, the yield of NCWs increases first and then decreases. It can be seen that the yield gradually increases as sulfuric acid concentration rising from 47% to 53% at same reaction time.

Table 2
Analysis of variance for response surface quadratic model.

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*P*-value
Model	2093.68	9	232.63	306.33	<0.0001
X_1	28.05	1	28.05	36.94	0.0005
X_2	1193.41	1	1193.41	1571.47	<0.0001
X_3	115.90	1	115.90	152.62	<0.0001
$X_1 X_2$	19.14	1	19.14	25.20	0.0015
$X_1 X_3$	8.15	1	8.15	10.73	0.0136
$X_2 X_3$	20.70	1	20.70	27.26	0.0012
X_1^2	96.69	1	96.69	127.32	<0.0001
X_2^2	97.37	1	97.37	128.25	<0.0001
X_3^2	452.74	1	452.74	596.17	<0.0001
Residual	5.32	7	0.76		
Lack of fit	3.18	3	1.06	1.99	0.2577
Pure error	2.13	4	0.53		

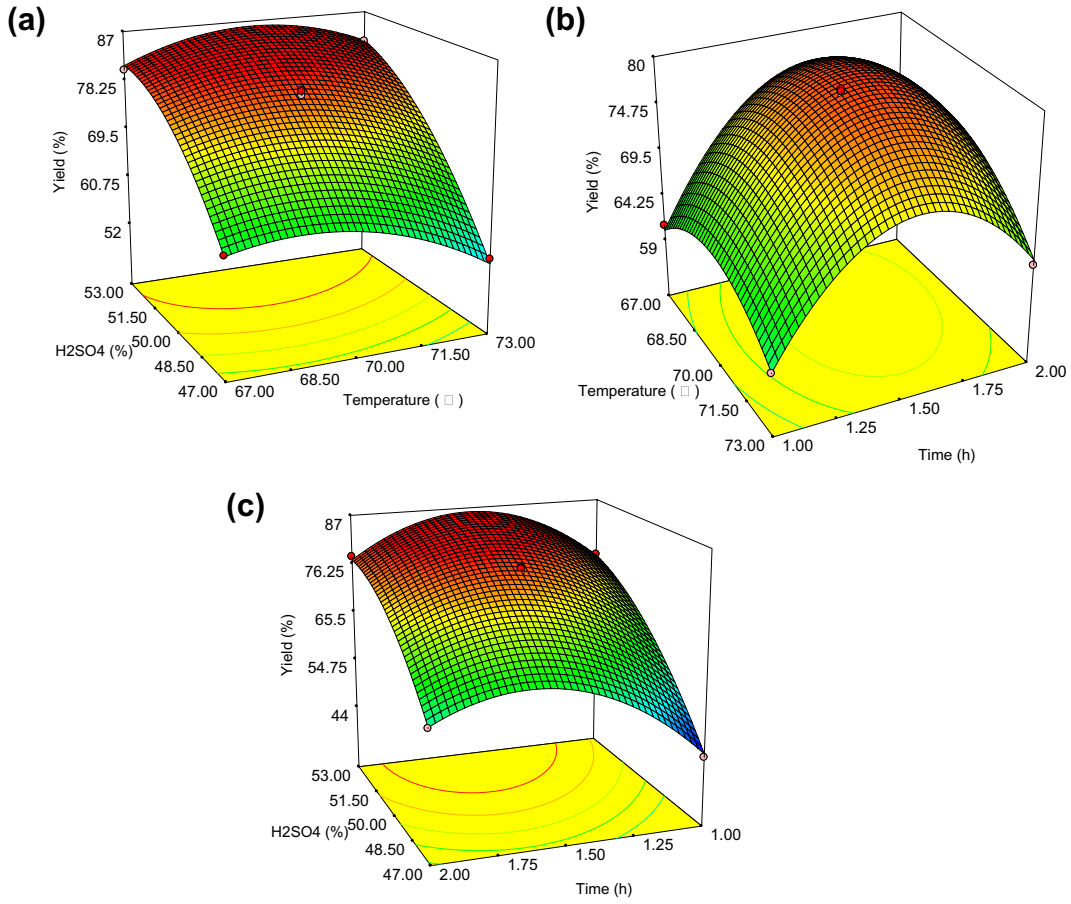

Fig. 2. Response surface and contour plots of (a) sulfuric acid concentration and reaction temperature; (b) reaction temperature and reaction time; (c) sulfuric acid concentration and reaction time.

Obviously, the contour plot shows elliptical, indicating the presence of the significant interaction between sulfuric acid concentration and reaction time.

Moreover, the optimum preparation conditions were obtained, namely, reaction temperature 70.06 °C, sulfuric acid concentration 53% and reaction time 1.54 h. Under these optimal conditions, the maximum yield of NCWs of 86.14% was predicted by the response surface model.

3.7. Verification of predictive model

Taking operability into consideration, the optimum preparation conditions were modified as follow: reaction temperature 70 °C, sulfuric acid concentration 53% and reaction time 1.5 h (Table 3). Three parallel experiments were carried out under the modified conditions to test the validation of the model. The mean yield of

Table 3
Predicted and experimental value of response at the optimum conditions.

	Temperature (°C)	H_2SO_4 concentration (%, w/w)	Time (h)	Yield of NCWs (%)	Standard deviation
Optimum conditions	70.06	53.00	1.54	86.14 (predicted)	–
Modified conditions	70	53	1.5	85.75 (actual)	0.96

NCWs is 85.75% with a standard deviation of 0.96% under the modified conditions and very close to the predicted value (Table 3), which indicates that the model is adequate for the preparation process of NCWs using SUMAT. In addition, the optimal yield of NCWs is higher than that reported in other literatures (Tang et al., 2011, 2013) ranging from 70% to 80%, which suggests the lower hydrolysis degree of cellulose into glucose monomers in our present research.

3.8. Characterization of FP and NCWs

To confirm the size of NCWs, a dilute suspension was observed using TEM and is shown in Supplementary Fig. S1(a). It can bee seen from Fig. S1(a) that the width of NCWs is estimated to be less than 100 nm and in nanometer scale. However, their length distributes between 200 and 500 nm which is close to that of submicrometer fiber.

In Supplementary Fig. S1(b), FTIR spectrum of NCWs do not significantly differ from that of raw material FP, suggesting that the molecular structure of cellulose was unchanged by acid hydrolysis using SUMAT. The broad band in the range from 3700 cm^{-1} to 3000 cm^{-1} is indicative of O–H stretching vibrations and the peak at 2900 cm^{-1} is attributed to C–H stretching vibrations. The peak at 1430 cm^{-1} can be assigned to bending of the –C-6CH_2–. Other absorption peaks observed from 1800 cm^{-1} to 600 cm^{-1} are related to the deformation, wagging and twisting modes of the anhydroglucopyranose unit, which is consistent with previous studies (Lu and Hsieh, 2010). The native cellulose Iα and Iβ have different O–H stretching and out-of-plane bending bands because of their different hydrogen-bonding strength. The peak of O–H stretching at 3270 cm^{-1} and that of O–H out-of-plane bending at 710 cm^{-1} are simultaneously observed in the spectra of FP and NCWs, indicating that they both are cellulose Iα type (Wada et al., 2003; Lu and Hsieh, 2010). The main differences in the FTIR are the stronger absorption peaks in NCWs, illuminating that the NCWs powder has abundant surface functional groups of cellulose because of higher ratio surface area than that of the raw material.

WAXRD patterns of FP and NCWs were obtained in order to study their crystalline behavior, and are shown in Supplementary Fig. S1(c). These patterns show diffraction peaks at $2\theta = 15°$, 16° and 22.6°, assigned to $(1\,0\,\bar{1})$, (1 0 1) and (2 0 0) lattice plane, respectively. It indicates that FP and NCWs are both typical cellulose Iα structure. However, compared with the pattern of FP, the peaks of NCWs strengthen and sharpen, suggesting the reduction and removal of amorphous component of cellulose with acid hydrolysis treatment using SUMAT. The crystallinity of cellulose calculated according to Eq. (2) increases from 77% for raw material FP to 80% for NCWs. This increase of crystallinity after acid hydrolysis has been reported in previous researches (Kaushik and Singh, 2011; Filson and Dawson-Andoh, 2009).

Supplementary Fig. S1(d) shows TG curves of original FP and NCWs obtained under the optimum preparation condition. The weight loss (<120 °C) is due to the evaporation of water in these samples. However, the thermal decomposition behavior of NCWs in the high temperature range (>200 °C) is different from FP as shown in the TG curves. Comparing with FP, the sample of NCWs exhibits lower initial decomposition temperature and a wider degradation temperature range from 322 °C to 372 °C, which may be caused by the introduction of acid sulfate groups in the preparation process. This is also consistent with the previous reports (Roman and Winter, 2004; Wang et al., 2007). It can be seen from Fig. S1(d), the residue weight of NCWs (18.82%) is higher than that of FP, which results from the acid hydrolysis of the amorphous cellulose in the preparation process.

MW radiation induces heat at molecular level by direct conversion of the electromagnetic field into heat, which enhances reactive capability of lignocellulosic biomass (Bu et al., 2012). In addition, ultrasonication is an effective way to remove the disordered region of cellulose to make amorphous cellulose more susceptible to acid hydrolysis (Kontturi and Vuorinen, 2009; Tang et al., 2013). Based on the analysis results of TEM, FTIR, TG and WAXRD, it is clearly shown that synergetic effect between MW and UW in SUMAT mainly intensifies the acid hydrolysis of the amorphous cellulose of FP and can improve the production of nanoscale cellulose fragments.

4. Conclusion

The presence of synergetic effect between UW and MW can intensify acid hydrolysis of cellulose, but the yield of NCWs decreases under some hash reaction conditions such as high temperature, strong acidity and long treatment time. At the optimum condition of temperature 70 °C, sulfuric acid concentration 50%, mass of raw material 2 g and reaction time 1.5 h, the yield and the crystallinity of NCWs is 78% and 80%, respectively. The research of SUMAT in this paper can promote the facile and efficient manufacture of biomass nanomaterials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.07.047.

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