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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.

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).