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Preparation and Characterization of Nanocellulose from *Poria Cocos* Residues

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Abstract

In this paper, the pharmaceutical residue of *Poria Cocos* was used as the extraction object of nanocellulost, and three deep cosoluble solvents (DES), formic acid/choline chloride (Fa/Cc), lactic acid/choline chloride (La/Cc) and oxalate/choline chloride (Oa/Cc), were used to treat the pharmaceutical residue of *Poria cocos* in coordination with ultrasonic treatment technology, and the nanocellulost was extracted. The nanocellulose extracted from the medicinal residue of *Poria Cocos* was determined and characterized. The results showed that the highest extraction yield was 96.8±0.2%, and the lowest extraction yield was 10.0±0.1%. The crystallinity of nanocellulose extracted from the residues was about 85.0%. The extraction yield of cellulose was different with different solvent pretreatment, different temperature and different time. Finally, the optimal extraction process was Fa/Cc, the temperature 110 ℃ and the time 2 h of pretreatment of nanocellulose, the yield was 96.8±0.2%, the nanocellulose suspension particle size was small and the crystallinity was high.

Keywords

***Poria Cocos* residue; Low eutectic solvent; Nano-crystalline cellulose; Particle size; Crystallinity; Micromorphology.**

1. INTRODUCTION

Nanocellulose is a kind of biodegradable renewable cellulose extracted from natural cellulose [1-3]. China is rich in traditional Chinese medicine resources, *Poria cocos* is one of the most edible and medicinal Chinese medicine in China, it will produce a lot of Chinese medicine residue every year [4]. *Poria cocos* contains a lot of cellulose and can be used to prepare nanocellulose [5, 6]. With the increasing demand for nanocellulose, in order to improve the utilization rate of medicinal residue of *Poria cocos*, increase the added value of medicinal residue, so that *Poria cocos* can not only be used in pharmacology and medicine, but also increase the yield of nanocellulose [7, 8].

In this paper, *Poria* residue was used as the extraction object of nanocellulose. Fa/Cc, La/Cc and Oa/Cc, respectively, to obtain the coarse fiber of *Poria cocos* residue, and then Oa/Cc was used to retreat the coarse fiber, the reacted cellulose solid was prepared into a suspension with deionized water, and the suspension was subjected to ultrasonic treatment. Finally, the nanocellulose extracted from the medicinal residue of *Poria cocos* was determined and characterized.

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2. EXPERIMENT

2.1. Preparation of deep eutectic solvent (DES)

Weigh the corresponding molar ratio of choline chloride (Cc), formic acid (Fa), lactic acid (La) and oxalic acid (Oa), respectively, into the conical bottle, placed in the corresponding temperature of the water bath magnetic stirring, stirring the solution fully reaction until the formation of transparent liquid [9]. Three kinds of DESs were obtained: formic acid/choline chloride (Fa/Cc), lactic acid/choline chloride (La/Cc) and oxalate/choline chloride (Oa/Cc) (Table 1).

Table 1. Synthesis of DES

Hbond donor	Hbond Acceptor	Molar Ratio	Temperature (℃)	Time (min)
Choline Chloride (Cc)	Fa	1：2	30	2
	La	1：2	80	1
	Oa	1：1	60	2

2.2. Preparation of nanocellulose

In this experiment, the herb residue of *Poria cocos* was crushed and passed through a 60-mesh sieve, and 9 groups of 4 g each of the herb powder were pretreated with three kinds of DESs, Fa/Cc, La/Cc and Oa/Cc, respectively. After the pretreatment, G3 funnels were used to filter while hot, and 1, 4 dioxane aqueous solution with a volume ratio of 4:1 was used to wash the solid until the liquid was colorless or clear. After rinsing with deionized water, the residual dioxane solution was washed away and the coarse fiber of poria residue was obtained.

The crude fiber of *Poria cocos* residue was dried at 60℃, and the crude fiber of 9 groups of Poria cocos residue was reprocessed by Oa/Cc. 5 times 80℃ deionized water was added to the solution after the reaction, stirred to regenerate the cellulose, filtered through a G4 funnel, and washed the solid with deionized water. The washed solid is added to 400 mL deionized water to form a suspension. Each DESs treated suspension is treated by ultrasonic generator.

2.3. Characterization

The changes of chemical functional groups corresponding to the absorption peaks of nanocellulose prepared by Thermo Scientific Nicolet iS50 Fourier transform infrared spectroscopy were analyzed. The samples were in the form of suspended solution and were taken by KBr tablet method. The nano-cellulose was dried and the XRD of the sample and raw material were analyzed by X-ray diffractometer.

3. RESULTS AND ANALYSIS

3.1. Yield of Nanocellulose under different DES Treatments

During Fa/Cc pretreatment, the nanocellulose yield prepared by F-3 was the highest, which was 96.8±0.2%, while the nanocellulose yield prepared by F-2 was the lowest, which was 10±0.1%. It can be seen that under the pretreatment with this low eutectic solvent, low treatment temperature and short treatment time will affect the nanocellulose yield, which can be seen from the total yield and suspension yield [10].

The suspension state of Fa/Cc pretreated suspensions was good, but the yield range was different, and the yield of extracted nanocellulose was relatively unstable. La/Cc pretreatment, and the yield were similar in both groups, L-3 the rate of 66.7%, the rate of L-1 was 67.22%, visible under the eutectic solvent pretreatment, the effects of a time on the yield, the yield of L-2, 95%, and that no suspension, supernatant fluid experiments can be seen, the nanocellulose

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prepared under this condition swelled more seriously, the swelling made the particle volume become heavier, and the cellulose all sank.

The swelling phenomenon also occurred in the other two groups, and the agglomeration phenomenon was also obvious [11]. The yield of nanocellulose extracted from the pretreatment with the low eutectic solvent was relatively unstable, and the high temperature would reduce the yield of cellulose. Oa/Cc pretreatment, 3 groups were extraction yield, but the overall yield is not high, visible under the eutectic solvent pretreatment, treatment time and temperature on the impact of the preparation of nano cellulose. The total yield of O-3 is 43.0±0.1%, and the yield of suspension is 29.5±0.2%.

It can be seen that the particle size under this condition is small, so the suspension state is good. The yield of nanocellulose prepared by this low eutectic solvent pretreatment is relatively stable. F-3 preparation of nano cellulose yield the highest, followed by L-2 preparation of nano cellulose, F-2 preparation of nano cellulose yield the lowest. The yield of nanocellulose prepared by the other two groups of La/Cc pretreatment was higher, and the yield of nanocellulose prepared by the three groups of Oa/Cc pretreatment was moderately lower.

3.2. FTIR of Nanocellulose

When the treatment temperature was 100°C and the treatment time was 2 h, FT-IR analysis was performed on the cellulose extracted from the three groups of *Poria cocos* residue pretreated with Fa/Cc, La/Cc and Oa/Cc low eutectic solvents, and the treatment conditions were referred to as F, L and O, respectively, as shown in Figure 1.

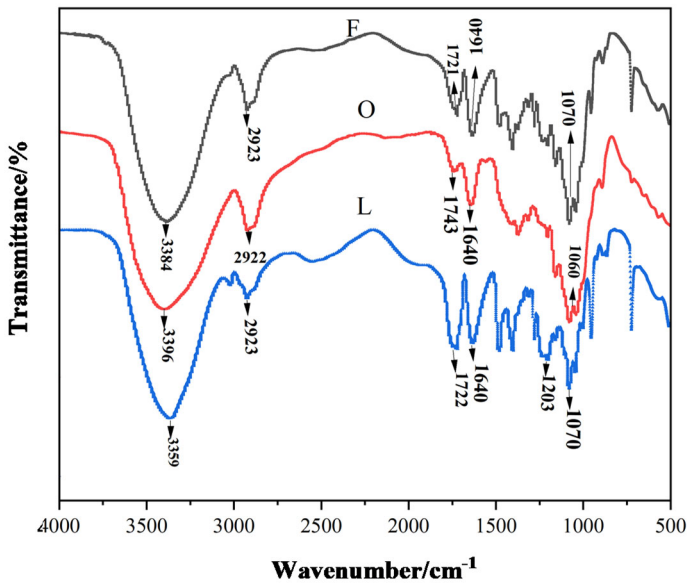

Figure 1. FTIR of nanocellulose with differnt DES treatments (F: Fa/Cc; O: Oa/Cc; L: La/Cc)

The extracted celluloses are basically the same as those of standard nanocellulose, but the absorption peaks are more complex than those of standard cellulose. At the absorption peaks of 3384 cm^{-1}, 3396cm^{-1} and 3359 cm^{-1}, there is O-H absorption peak stretching vibration, and at the absorption peaks of 2923 cm^{-1}, 2922 cm^{-1} and 2923 cm^{-1}, there is C-H, CH_3, -CH_2 absorption peak stretching vibration, which represents the main structure of cellulose. There are C=O absorption peaks from 1721 $cm^{-1}$to 1743 cm^{-1}, and C=O absorption peaks from 1641 $cm^{-1}$to 1663 cm^{-1}. C-O absorption peaks existed from 1039 $cm^{-1}$to 1084 cm^{-1}. In the absorption peaks from 507 cm^{-1} to 513 cm^{-1}, there is a C-C=O absorption peak and in-plane bending vibration. The nanocellulose absorption peak of La/Cc pretreatment at 1203 cm^{-1} was stronger than that of Fa/Cc and Oa/Cc pretreatment, indicating that the cellulose crystal zone was

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destroyed after Fa/Cc and Oa/Cc pretreatment, and the cellulose crystal zone of La/Cc pretreatment was little or not degraded. There was no obvious absorption peak or aromatic nuclear vibration peak from1627 cm^{-1} to 1510 cm^{-1}, indicating a high degree of lignin removal. The absorption peak of nanocellulose prepared by the three groups of low eutectic solvent pretreatment appeared at 1640cm^{-1}, indicating that hemicellulose was effectively removed [12]. The C-OH absorption peak appeared from 1060 cm-^{1}to 1070 cm^{-1}, which is the typical characteristic peak of cellulose [13].

3.3. XRD of Nanocellulose

Figure 2 showed that, La is the XRD pattern of prepared nanocellulost, YL is the XRD pattern of *Poria* raw material, La at 2θ=14.1° and 20.6°, YL at 2θ=15.3° and 21° belong to the diffraction absorption peaks of cellulose (101) and (002) crystal surface, which is a typical type I cellulose diffraction peak [14]. The results showed that the crystal structure and crystal type of the cellulose from *Poria cocos* residue were not damaged after pretreatment with low eutectic solvent, oxalic acid/choline chloride retreatment and ultrasonic treatment, and it was still the type I structure of cellulose, which belonged to the structural configuration of natural cellulose. As can be seen from the figure, the peak value of La was significantly higher than that of YL. The reason is that after the treatment of low eutectic solvent, amorphous areas such as lignin and hemicellulose are removed [15]. The amorphous areas of cellulose are destroyed, more crystalline areas of cellulose are exposed. The peak value of La is increased, indicating that the crystallinity of raw materials is increased after preparation of nanocellulose.

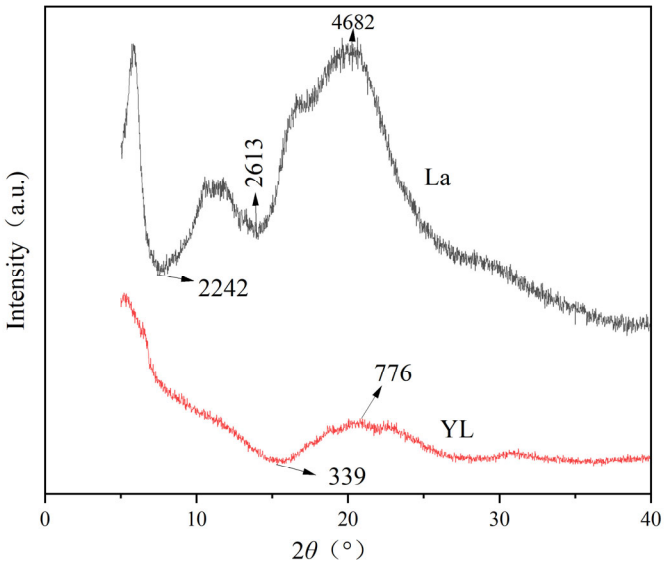

Figure 2. XRD of nanocellulose with La/Cc treatments

4. CONCLUSION

1) The yield of nanocellulose prepared by La/Cc solvent pretreatment was generally higher, while the yield of nanocellulose prepared by Oa/Cc pretreatment was generally lower.

2) FTIR of the nanocellulose from *Poria Cocos* residue were roughly the same as those of the standard nanocellulose. The main composition of cellulose was present, and the lignin and hemicellulose were roughly removed.

3) XRD shows that the prepared nanocellulose has the basic structure of type I cellulose diffraction peak, the amorphous region of cellulose is basically removed, leaving the crystalline region of cellulose, and the crystallinity is high.

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