Preparation and characterization of Salix Psammophila cellulose and Mic-cellulose under the pretreatment of two kinds of acid

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Abstract. The pretreatment of salix psammophila (SP) with HNO₃-ethanol and HC1-ethanol, followed by the treatment with sodium chlorite and KOH, were investigated to obtain SP cellulose. Microcrystalline cellulose was prepared by hydrochloric acid hydrolysis from cellulose treated with nitric acid. The cellulose was characterized by FTIR, XRD, TG, SEM and DSC. The yield of cellulose pretreated with nitric acid and hydrochloric acid were 38.89% and 35.14%, respectively. Infrared spectroscopy showed that lignin and hemicellulose were separated from the extracted cellulose. The SEM photos showed that the width of the extracted cellulose was 5.71 μm and 6.92 μm respectively. XRD analysis showed that the crystallinity of the two groups was 54.13% and 60.86%, respectively. TG analysis showed that the amount of residue showed an increasing trend, and the residual amount extracted from cellulose was 6.67% and 7.90% respectively. In the SEM image of microcrystalline cellulose, a slender structure with a crystallinity of 59.32% was proposed, which had better thermal stability than cellulose.

1. Introduction
Cellulose is a long-chain polymer made up of pyranoid glucose residues connected by glucosidic bonds, which accounts for a large proportion in biomass. Natural cellulose has high degree of polymerisation and weight average molecular weight[1]. Because of the existence of a variety of substances in the biomass, it cannot be directly applied, so it needs a certain treatment to extract cellulose. Due to different extraction methods and raw material sources, the extracted cellulose has different conditions.

As for the extraction process, it can be divided into different stages. First of all, the biomass was pretreated to remove most components. Common pretreatment technologies include ionic liquid, acid pretreatment[2], alkali pretreatment[3,4], the high-pressure cooking method[5], enzyme pretreatment, etc. Then, for hemicellulose, KOH or NaOH is commonly used to remove hemicellulose by breaking glycoside bonds and acetyl groups in hemicellulose molecules[6]. Finally, the lignin in the components can be removed by bleaching, so that the colour of the extracted cellulose is closer to white. Sodium chlorite[7], hydrogen peroxide[8] etc. There are commonly used for bleaching. The processing order in extraction varies from person to person.

Salix Psammophila, a plant of the genus Salix, distributed in the northwest of China. It is one of the main plants for windbreak and sand fixation. The chemical composition of Salix Psammophila...
powder was determined as follows: ash content was 4.53%, benzoyl alcohol extract was 2.49%, cellulose content was 36.95%, comprehensive cellulose content was 71.92%, lignin content was 24.77% \[9-10\]. On the one hand, the extracted cellulose can be used to prepare microcrystalline cellulose \[11\]; on the other hand, it can be hydrolysed by acid \[12\], mechanically treated \[13\] and oxidised \[14-16\] to prepare nano-cellulose. It is also used in the synthesis of polymer materials such as resin or hydrogel \[17,18\], as well as biomedicine \[19\], heavy metal treatment \[20\], and composite materials \[21\].

2. Materials and method

2.1. Materials
The Salix Psammophila used in this study were collected from Kabuki desert in ordos, China. After water cleaning, drying and crushing, take 100-120 powder for reserve. Nitric acid, Hydrochloric acid (sinopiate chemical reagent co., LTD.); Anhydrous ethanol (Tianjin kemao chemical reagent co., LTD.); Potassium hydroxide (Tianjin damao chemical reagent factory), Glacial acetic acid (Tianjin fuchen chemical reagent co., LTD.); Sodium chlorite (Alighting reagent co., LTD.), the above drugs are pure analysis. All reactants are analysis grade and are used without pretreated.

2.2. Methods

2.2.1. Cellulose extraction from Salix Psammophila
10 g dried Salix Psammophila powder was heated in 80 ℃ distilled water (1:60 g/mL) for 1 h and filtered to remove impurities and some water-soluble components. After washing, the Salix Psammophila was pretreated with HNO₃-ethanol and HCl-ethanol, use magnetic stirring at a certain temperature and time, the pretreated plant materials were neutralized by washing with deionized water until reaches pH=7, then dry at 105 ℃ to constant weight, the samples were named as HNO₃-ethanol-SP and HCl-ethanol-SP. The dried HNO₃-ethanol-SP and HCl-ethanol-SP were then added to a 7.5 wt% solution of sodium chlorite (1:20 g/mL) and use glacial acetic acid to adjust pH=3~4, at 75 ℃ for 3 h, washing with deionized water and anhydrous ethanol, then dried at 60 ℃ to constant weight, the samples were named Bleached-SP. The dried Bleach-SP was placed in a solution of 10% KOH (1:20 g/mL), and the reaction was performed with magnetic stirring at 75 ℃ for 2 h. The product was washed with deionized water and anhydrous ethanol, and dried at 60 ℃. The sample was named SP-C.

2.2.2. Preparation of MCC
The preparation of Salix Psammophila microcrystalline cellulose referred to the paper of Ahmed Fouzi Tarchoun et.al \[22\]. Briefly, HNO₃-ethanol pretreatment Cellulose was hydrolyzed by 8 wt% HCl solution (1:20 g/mL) at 90 ℃ for 1.5 h. After that, large quantities of distilled water were added into the reaction beaker to stop the hydrolysis, filtered and oven-dried for 24 h at 60 ℃. The sample was named SP-Mic-C, the microcrystalline cellulose extracted on the basis of cellulose is more white in color.

3. Analyticals

3.1. Calculation of yield of cellulose extraction process
The yield of cellulose products was estimated by the weighing method, and each experiment was repeated three times and its average value was taken:

\[
\text{Cellulose Yield(\%) = \frac{m_{\text{Now}}}{m_{\text{Winitial}}} \times 100\%}
\]

Where Now is the weight of cellulose at the current stage of treatment, and Winitial is the weight of the initial material.

3.2. Scanning electron microscopy (SEM)
Scanning electron microscopy (Hitachi 4800) was used to observe the changes of the sample surface during the process from raw material to cellulose, operated at accelerating voltage of 10 kV, a small
amount of samples were placed on conductive adhesive, then gold sprayed, and their morphology was observed.

3.3. Fourier transform infrared spectroscopy (FTIR)
The infrared spectrum was measured by Perkin Elmer 65. The experimental parameters ranged from 4000-600 cm\(^{-1}\), the cumulative number of scans was 32, and the resolution was 1 cm\(^{-1}\).

3.4. X-ray diffraction (XRD)
XRD was carried out in the X-ray diffractometer (Empyrean X-ray diffractometer). The test condition was Cu Ka, radiation, the generator voltage was 40 kV and the current was 40 mA. \(2\theta = 5^\circ \sim 80^\circ\), The step length was 0.017\(^\circ\), and the counting time was 4.5 min. The crystallinity index sample was calculated by the siegel equation.

\[
CrI = \frac{I_2 - I_1}{I_2} \times 100 \%
\]

Where \(I_2\) is the crystalline peak intensity around \(2\theta=20^\circ\) and \(I_1\) is the amorphous intensity of the background scattered measure around \(2\theta=18^\circ\).

3.5. Thermo gravimetric analysis (TGA)
The TGA experiment was carried out on the HCT-1 integrated thermal analyzer. The sample was analyzed in N\(_2\) atmosphere with pressure of 0.3 Mpa, flow rate of 20 mL/min, heating rate of 10\(^\circ\)/min and temperature range of 25~800\(^\circ\)C.

3.6. Differential scanning calorimetry (DSC)
DSC curves were obtained using a DSC700 differential scanning calorimeter, The samples were analysed in N\(_2\) atmosphere, the pressure was 0.1 ~ 0.2 Mpa, the flow rate was 20 mL/min, the heating rate was 20 \(^\circ\)/min, and the heating range was 25~ 480 \(^\circ\)C.

4. Results and discussion

4.1. The appearance of cellulose during the extraction

![Fig 1. Photograph of extracted cellulose](SP-C(HNO3) SP-C(HCl) SP-Mic-C)

The cellulose extracted by different pretreatment is also different. The luster of cellulose extracted by HNO\(_3\) pretreatment is slightly darker than that of HCl pretreatment, and its hand feel is rougher than that of hydrochloric acid pretreatment. Microcrystalline cellulose compared with the two cellulose has a finer and closer to Snow White.
4.2. Calculation of yield of the cellulose extraction process

Table 1. The yield of extraction process of cellulose

| Sample          | Yield (%) | Sample          | Yield (%) |
|-----------------|-----------|-----------------|-----------|
| HNO₃-ethanol-SP | 45.25     | HCl-ethanol-SP  | 49.60     |
| Bleached-SP     | 42.19     | SP-C            | 38.89     |
| SP-Mic-C        | 32.95     | Sp-C            | 35.14     |

Table 1 shows the yield of cellulose relative to the raw material in the extraction process. After acid pretreatment, more than half of the hemicellulose and lignin in the raw material were removed, and the yield was 45.25%, 49.60%, respectively. The residual lignin was removed by sodium chlorite bleaching, and the yield was 42.19% and 41.64%, respectively. After HCl treatment, the biomass structure is more loose, which can be seen from the SEM behind, so the removal effect of lignin is more sufficient than that of nitric acid pretreatment. The yield of microcrystalline cellulose was 32.95%, which was basically the same as that of microcrystalline cellulose extracted by Katakojwala[23]. The yield of the three methods was 30±2%, 34±2% and 32±2% respectively.

4.3. Scanning electron microscopy (SEM)

SEM of SP, HNO₃-ethanol-SP, Bleached-SP, SP-C, SP-Mic-C and HCl-ethanol-SP, Bleached-SP, SP-C are presented in Fig 2. The average diameter of cellulose was determined by Nano Measurer 1.2. The surface of the raw material was smooth without cell wall dissection and fibrosis. When after acid pretreatment, SP surface structure has a significant fibrosis. The cell wall was damaged and a certain amount of lignin and hemicellulose was removed, because of the different types of acid, the sample sizes obtained after pretreatment are also greatly different. Then, by comparing the two species Bleached-SP treated with sodium chlorite, both Bleached-SP had obvious fold marks on the surface, indicating that the removal of lignin caused certain changes in the surface structure, and its diameter was 8.68 μm and 9.98 μm. On the one hand, KOH can remove hemicellulose from the biomass, on the other hand, it can produce a certain degree of swelling effect on the generated cellulose. The two species SP-C treated with KOH have smaller diameters than Bleached-SP, because the removal of hemicellulose destroys the structure and produces SP-C with shorter diameters. Because of HCl hydrolyzed, resulting in a smaller cellulose structure than that of HNO₃ hydrolysed. This is because, in the high-temperature environment of hydrochloric acid, the glucose bonds in the amorphous region of cellulose were firstly broken, and then gradually transferred to the crystalline region of cellulose, so that part of the crystalline region was still hydrolysed.
Table 2. The average diameter of the sample

| Sample             | The average diameter (μm) |
|--------------------|---------------------------|
| HNO₃-ethanol-SP    | 13.25                     |
| Bleached-SP       | 8.68                      |
| SP-C              | 5.71                      |
| SP-Mic-C          | 5.26                      |
| HCl-ethanol-SP    | 13.39                     |
| Bleached-SP       | 9.98                      |
| SP-C              | 6.92                      |

4.4. Fourier transform infrared spectroscopy (FTIR)

FT-IR spectra of SP, Bleached-SP, SP-C, and SP-Mic-C fiber obtained from HNO₃-ethanol and HCl-ethanol pretreatment are depicted in Fig 3. The peaks at 3330-3350 cm⁻¹ correspond to the stretching vibrations O-H in cellulose [24]. The peak near 2900 cm⁻¹ is C-H stretching vibrations, they come from methyl, methylene and submethyl. The bond 1740 cm⁻¹ ascribed to the stretching vibration peak of the carbonyl group, Carbonyl derived from biomass components of lignin and hemicellulose, near the bond at 1510 cm⁻¹ is the benzene ring of carbon-carbon double bond vibration in lignin, through the processing of sodium chlorite, 1735 cm⁻¹ near the absorption peak is reduced, but still exist, but after alkali treatment, 1735 cm⁻¹ near the absorption peak of disappear, above shows that through a series of processing, SP to removal of hemicellulose and lignin. The peaks at 1377 cm⁻¹ is C=H bending vibration. The peaks at 1050 cm⁻¹ and 897 cm⁻¹ is characteristic absorption peaks of cellulose, it are respectively referred to the C-O stretching vibration and C-H swing vibration of cellulose.

![Fig 3. FTIR spectra of samples under two different pretreatment conditions](image)

4.5. X-ray diffraction (XRD)

XRD analysis of different samples is shown in Fig 4. The samples of cellulose under different treatment conditions, the peaks occurred near 2θ=16°, 22°, 34°, which were cellulose 101 020 040 crystallographic. After a series of treatments, the crystalline shape of cellulose did not change, are the type I of cellulose [22]. However, the crystallinity showed a trend of increased gradually. Acid pretreatment could not only partially release hemicellulose and lignin from biomass components, but
also hydrolyse cellulose to some extent, thus increasing crystallinity. The cellulose prepared by hydrochloric acid pretreatment has higher crystallinity than that prepared by HNO$_3$. This is because HCl hydrolyses cellulose more than HNO$_3$. At the same time, with the help of SEM, the cellulose after hydrochloric acid pretreatment was smaller than that after HNO$_3$ pretreatment, which further explained the change of apparent structure of cellulose with the increase of crystallinity.

Table 3. The crystallinity of samples under two different pretreatment conditions

| Sample          | CrI (%) | Sample          | CrI (%) |
|-----------------|---------|-----------------|---------|
| SP              | 29.27   | SP              | 29.27   |
| HNO$_3$-ethanol-SP | 56.39   | HCl-ethanol-SP  | 54.30   |
| Bleached-SP     | 58.62   | Bleached-SP     | 42.27   |
| SP-C            | 54.13   | SP-C            | 60.86   |
| SP-Mic-C        | 59.32   |                 |         |

4.6. Thermo gravimetric analysis (TGA)

The fig 5. (a,b) shows the thermogravimetric graph of the samples during the cellulose extraction process. All the samples had a small weight loss at the initial stage, which was due to the evaporation of water in the samples. For biomass, the degradation of hemicellulose between 210-310 °C is generally interpreted as hemicellulose, and the degradation of cellulose is around 315-380 °C. Lignin degradation occurs in all stages of pyrolysis [26]. About DTG, the small peak near 540°C is the oxidation decomposition peak of residual carbon. As for the raw materials, due to the gradual decline of non-cellulose components, the pyrolytic weight loss of subsequent treated samples is relatively obvious. Through different treatments, the amount of sample residue at each stage gradually increased, indicating the enhancement of thermal stability and indirectly indicating the improvement of cellulose purity. At 700 °C, the residue of HNO$_3$ pretreatment was 3.65%, 5.41%, 6.67% and 7.20% respectively, while that of HCl pretreatment was 2.85%, 7.98% and 7.90% respectively.

The Fig 5. (e,f) shows the different thermal degradation of cellulose in the process of energy change. The endothermic peak corresponds to the evaporation and heat absorption of water at nearly 110 °C, and then a longer thermal equilibrium phase. All samples had an endothermic peak between 350 °C and 400 °C, indicating the degradation and degradation of cellulose lattice.
Fig 5. TGA (a,b), DTG (c,d) and DSC (e,f) curves of samples under two different pretreatment conditions

5. Conclusion
In this experiment, cellulose and microcrystalline cellulose were extracted from Salix Psammophila. After pretreatment with ethanol nitrate and ethanol hydrochloric acid, the yield of cellulose reached 38.89% and 35.14%, and that of microcrystalline cellulose was 32.22%. It was observed from scanning electron microscope that the structure of Salix Psammophila was destroyed and obvious fiber structure was produced. The hemicellulose and lignin in the samples have been removed by FTIR analysis. This has laid a foundation for a series of experiments to be carried out through Salix Psammophila.

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