EXTRACTION AND CHARACTERIZATION OF NATURAL CELLULOSE FIBERS FROM REED STRAW: MORPHOLOGICAL, MICROSTRUCTURAL AND THERMAL PROPERTIES

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As an available resource rich in cellulose, agricultural residues have attracted a lot of interest for textile and other applications. Herein, reed straw fiber was obtained from a typical agricultural waste – reed straw – by an alkali-oxygen one-bath process. The effects of the amount of sodium hydroxide and hydrogen peroxide, the treatment temperature and time on the degumming rate were discussed. The optimum technological parameters of the alkali-oxygen one-bath process were found as follows: the dosage of sodium hydroxide was 35 g/L, the dosage of hydrogen peroxide – 30 mL/L, treatment temperature – 85 °C and cooking time – 2 h. Under these conditions, the degumming rate achieved was 54.30%. The prepared fiber will be considered as a promising and sustainable raw material for the textile industry and other applications.

Keywords: alkali-oxygen method, cellulose fiber, degumming rate, lignin, microstructure, reed straw

INTRODUCTION

Gaseous emissions from field burning have a negative impact on the atmosphere, significantly contributing to particulate matter in the atmosphere.[1] The main burning material is crop straw. Straw field burning, therefore, affects human health and global climate change, being both a regional and a global environmental burden.[2,3] Retaining straw on the farm after the harvest is a sustainable and cleaner management practice. The efficient use of crop residues must be affordable and appropriate for an environment, where sustainable and clean production can be achieved. In this context, cleaner production means the efficient use of straw resources, without resorting to open burning.[4,5]

Straw fiber can be used in many papermaking grades, such as sustainable copy and packaging paper tissue, towels, and molten fiber application solutions.[6] Reed straw as a widely distributed, easily accessible and natural intermediate product contains high amounts of cellulose. Besides the study of cellulose extraction from reed straw and other crop straws, their recycling has also been investigated using special methods for crop straw recycling.[7-9] Straw is still in its infancy as a major intermediate product in the natural ecological cycle for straw recycling. It is necessary to reconceptualize the position and the role of straw in the establishment of an artificial ecological cycle system.[10]

To extract the cellulose fibers, a process called degumming is used. On the premise of ensuring fiber fineness, the associated impurities in common biomass fibers should be removed as much as possible. However, a small amount of pectin and lignin should still be retained as bonding points between the fibers to ensure the length of the fiber bundle. The degumming process has been improved over time and is today the most common chemical extraction process to

obtain cellulose fiber, applied worldwide to bast fiber materials. Currently, the main degumming methods include physical degumming, chemical degumming, and biological degumming.[11] Among them, chemical degumming is less time-consuming.[12] Zhou *et al*. degummed flax fibers using Fenton reagent and hydrogen peroxide, which largely improved the quality of the degummed fibers, but also resulted in some loss of fracture strength.[13]

Herein, we report a novel method for the separation of cellulose fibers from reed straws by an alkali-oxygen one-bath process. Various factors, such as the amount of sodium hydroxide and hydrogen peroxide, treatment temperature and time, which may have an effect on the degumming results are discussed. The reed straw fibers, before and after degumming, were also analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The raw materials used in this study were natural mature reed straws (considered as control) collected from the garden of Wuhan Textile University (Fig. 1). 98% sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), 30% hydrogen peroxide (H_2O_2), and other chemicals of laboratory grade were purchased from Aladdin Chemical Regent Inc., Shanghai, China. All the chemicals were used as received, without further purification.

Extraction of reed straw fiber

The reed straw was cut into strips, with the length of 3 cm and width of 0.2 cm, and dried for 20 h at 75 °C in a water bath (DU-30G Thermostat water bath, Shanghai Precision Instrument Co., Ltd., China), followed by degumming by the alkaline-oxygen method (20, 25, 30 g/L NaOH; 20, 25, 30 mL/L H_2O_2; temperature 85, 90, 95 °C; treatment time 2, 2.5, 3 h, respectively, and the bath ratio of 1:50). The sample was then washed at room temperature for 5 min and oven-dried (DHG-9030 air drying oven, Shanghai Yiheng Instrument Co., Ltd., China) at 80 °C for 24 h.[14,15] The degumming process was shown in Figure 1.

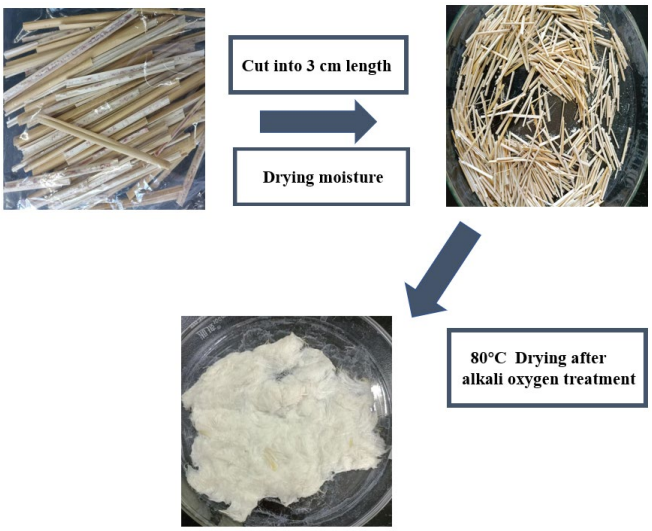

Figure 1: Degumming process of reed straw fibers

Calculation of degumming rate

The degumming rate of reed straw fibers was calculated by the following formula:[15]

$$\text{Degumming rate} = \frac{W_a - W_b}{W_a} * 100\% \quad (1)$$

where W_a and W_b are the weights of samples before and after degumming, respectively.

Chemical composition analysis

The cellulose, hemicelluloses and lignin contents of the fiber samples were determined by chemical analysis according to the literature reported.[15] The content of cellulose, hemicelluloses, lignin and pectin was determined for five replicated samples and the average values with standard deviation were reported.

Scanning electron microscopy (SEM)

The samples were observed before and after the treatment by the alkaline-oxygen bath method using a scanning electron microscope (JSM-6510 LV, JEOL, Japan). Prior to SEM evaluation, the samples were coated with a thin layer of gold by a plasma sputtering device to avoid charging effects.

X-ray diffraction (XRD) measurement

The crystallinities of the reed straw fiber, before and after the treatment, were determined by a (D/max-2550pc, RIGAKU) X-ray diffractometer. The experimental conditions were as follows: Cu Target Ka radiation (X-ray wavelength 0.154 nm), tube voltage of 40 kV, tube current of 30 mA for scanning, diffraction direction θ-2θ linkage scanning mode, scanning angle of 10-50° and scanning speed of 5°/min.

Fourier transform infrared spectroscopy (FTIR)

The sample, before and after the alkaline-oxygen bath treatment, was well ground with KBr particles and then analyzed on a Fourier transform spectrometer (Nicolet iS50, Thermo Fisher, USA). The instrument has a recording range of 4000-500 cm^{-1} and a resolution of 4 cm^{-1}, with 16 scans for each sample.

Thermogravimetric analysis (TGA)

The samples were analyzed for thermal properties using a differential thermogravimetric analyzer (TGA 209 F1 Libra). Each sample weighed 5.0 mg and was subjected to a nitrogen flow rate of 50 mL/min, heating rate of 10 °C/min in the temperature range of 20-600 °C.

RESULTS AND DISCUSSION

Degumming process for reed straw fibers

The effects of various factors on the degumming were investigated through several single-factor experiments, followed by orthogonal experiments to determine the best process conditions for optimum degumming. Finally, the range of factors is shown in Table 1, and the results of degumming reed fibers are presented in Table 2. It can be concluded that the R-values are R_C, R_D, R_B, and R_A in a descending order, and the effects of single factors, such as temperature, time, NaOH concentration, and H_2O_2 concentration, are in a decreasing order, and the larger the R-value, the greater the effect of this factor.

Table 1
Level of orthogonal factors in degumming experiment of reed straw fibers

Levels	Factors			
	A NaOH (g/L)	B H_2O_2 (mL/L)	C Temperature (°C)	D Time (h)
1	20	20	85	2.5
2	25	25	90	3
3	30	30	95	3.5

Table 2
Orthogonal design and test data of reed straw fiber degumming

	A	B	C	D	Test index
					Degumming rate (%)
1	①	①	①	①	53.66
2	①	②	②	②	50.20
3	①	③	③	③	43.55
4	②	①	②	③	49.72
5	②	②	③	①	45.89
6	②	③	①	②	48.22
7	③	①	③	②	43.55
8	③	②	①	③	54.86
9	③	③	②	①	53.20
k_1	49.13	48.98	52.25	50.92	
k_2	49.94	50.31	51.04	47.32	
k_3	50.53	48.32	44.33	49.38	
R	1.40	1.99	7.92	3.60	
Optimal scheme	$A_3B_2C_1D_1$				

Table 3
Chemical composition of reed straw fiber before and after treatment

Sample	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Control	34.97±1.21	26.74±0.84	27.73±0.62
Treated	69.67±2.12	10.87±0.67	6.50±0.21

The larger range value of one factor would have greater influence on the experimental results. The R values for A (NaOH), B (H_2O_2), C (Temperature) and D (Time) were 1.40, 1.99, 7.92 and 3.60, respectively. It was noticed that soaking temperature (D) displayed a relatively higher influence than soaking time (C). Additionally, the concentration of H_2O_2 (B) helped comparatively more in regulating the degumming performance than that of NaOH (A). The optimal scheme of the orthogonal experiment is $A_3B_2C_1D_1$, which means 35 g/L NaOH, 30 mL/L H_2O_2, treatment time 2 h, bath ratio 1:50, and temperature 85 °C. The degumming rate of 54.30% was achieved under these optimized process conditions.

Chemical composition analysis

As can be seen from Table 3, reed straw mainly contains cellulose, hemicelluloses, lignin, *etc*. The cellulose content in the control reed straw is low, the mass fraction being of 34.97%. The lignin and hemicellulose contents are high, with a total mass fraction of about 54.47%. The cellulose content after the alkaline-oxygen treatment (69.67%) was significantly higher than that of the control. However, after the treatment, the lignin content decreased, which is attributed to lignin oxidation in the presence of hydrogen peroxide, which was easily dissolved in the alkaline solution.[16] The results showed that alkoxide methods can successfully resolve the tangled structures of cellulose, hemicelluloses and lignin, and finally extract cellulose

Morphological structure

Figure 2 shows the SEM images of (a) control and (b) treated reed straw fibers. As shown in Figure 2 (a), there were grooves and cracks on the surface of the reed straw fiber before the treatment, while the knots on the surface of the reed straw fiber (Fig. 2 (b)) were obviously reduced after the treatment. Moreover, the gum was basically removed from the fiber surface and the surface became smooth. This shows that the reed straw fiber is actually a fiber bundle formed by combining several single fibers, and its appearance is similar to that of ramie fiber.[16] The surface of reed straw fiber before the treatment had grooves and cracks. The surface structure of reed straw fibers facilitates the transfer of moisture, which means that fabrics made of reed straw fibers would have excellent moisture permeability.

Crystalline structure

Figure 3 shows the X-ray diffraction patterns of the reed straw and reed straw fiber. It can be seen that the reed straw fiber treated by degumming shows some kind of crystalline structure, and the analysis shows the main diffraction peaks at 2θ = 15.6, 21.7 and 34.7, corresponding to (110), (200) and (040) crystal plane peaks, respectively, indicating a typical cellulose type crystal structure.[17,18]

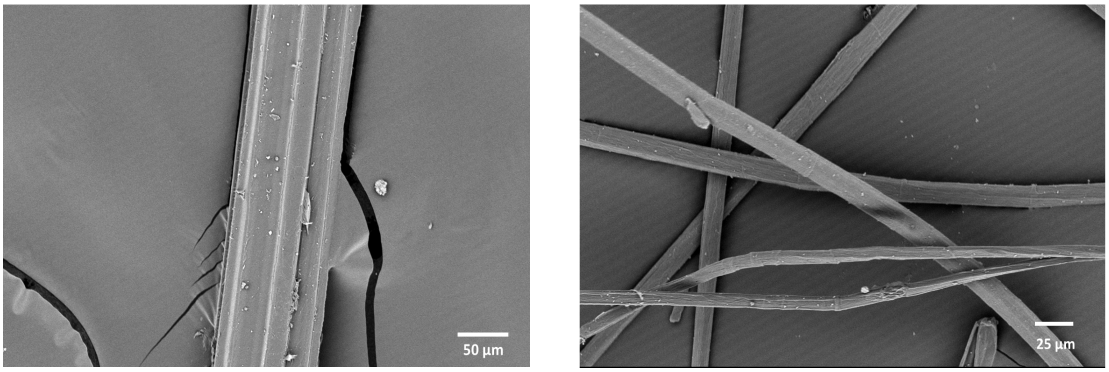

Figure 2: SEM images of (a) control and (b) reed straw fibers

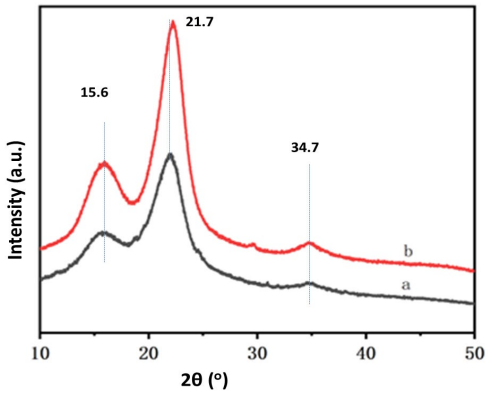

Figure 3: X-ray diffraction patterns of (a) reed straw and (b) reed straw fiber

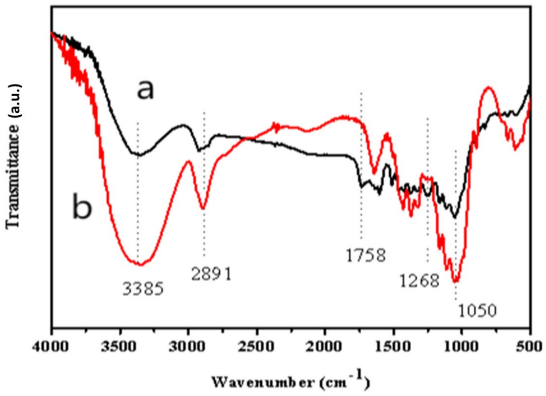

Figure 4: FTIR spectra of reed straw fibers before (a) and after (b) the treatment

The results show that, after degumming, the crystallinity of reed straw fiber reached 51.84%, while before the treatment the crystallinity of the reed straw fibers was 43.53%. This improvement in the crystalline region of the reed straw fibers after the degumming process was attributed to the increase in the proportion of the crystalline region, owing to the removal of lignin, hemicelluloses, pectin and water solutes from the fiber matrix.

Infrared spectroscopy analysis

Figure 4 displays the infrared spectra of the reed straw fiber before (a) and after (b) the treatment. The FT-IR spectra of the reed straw fibers exhibit all the characteristics of cellulose. The strong absorption band at 3385 cm^{-1} corresponded to the stretching vibration of the -OH group, whose strength increased due to the increase in the cellulose content after degumming. The existence of the methyl group was confirmed by the presence of a typical peak at 2891 cm^{-1}. Another peak at 1050 cm^{-1} attributed to the stretching vibration of the C-O group in C-O-C confirmed the presence of cellulose. The absorption peak at 1758 cm^{-1} contains the C=O group in the acetyl group, which is a characteristic peak of hemicelluloses, and its absorption peak at 1268 cm^{-1} is the C-O in the aromatic ring stretching vibration, which is the characteristic peak of lignin.[19] The peaks of reed straw fiber after degumming are reduced in both places, indicating that the hemicellulose and lignin content of reed straw fiber is lower after alkali-oxygen degumming. Further, compared to the spectrum of untreated reed straw, it can be seen in Figure 4 that the intensity of characteristic peaks of cellulose in the degummed reed straw fibers increased, indicating an increment in the cellulose content after degumming.[20] The infrared spectral results showed that the reed straw contained cellulose, while most of the hemicelluloses and lignin were removed after degumming by the alkali-oxygen bath method.[21] The results are well consistent with the findings of XRD and chemical composition.

Thermal performance

As can be seen from Figure 5, the test fibers obtained after alkali-oxygen degumming present three weight loss points. The first weight loss was recorded in the temperature range of 30-150 °C, considering the weight of the fiber relative to the untreated one before the reduction of about 5%, as a result of the evaporation of water from the internal region of the fiber with a rising temperature.[22] The second weight loss occurred in the temperature range of 200-375 °C. This can be explained by the fact that with a gradually increasing temperature, the decomposition point of some constituents in the internal fiber is reached, and as the temperature continues to increase, the constituents in the fiber gradually cleave, resulting in weight loss. The third weight loss is recorded in the temperature range of 380-600 °C. The decomposition temperature of the reed straw fiber is quite low, starting from 200 °C. The untreated reed straw fiber continues decomposing after both cellulose and hemicelluloses are decomposed completely after 375 °C. Degumming can remove the components with lower decomposition temperature, and thus, the treated reed straw fiber has higher temperature ranges for the significant stages of weight loss, due to the higher crystallinity of the material, *i.e.*, the higher thermal stability of the fiber.[23]

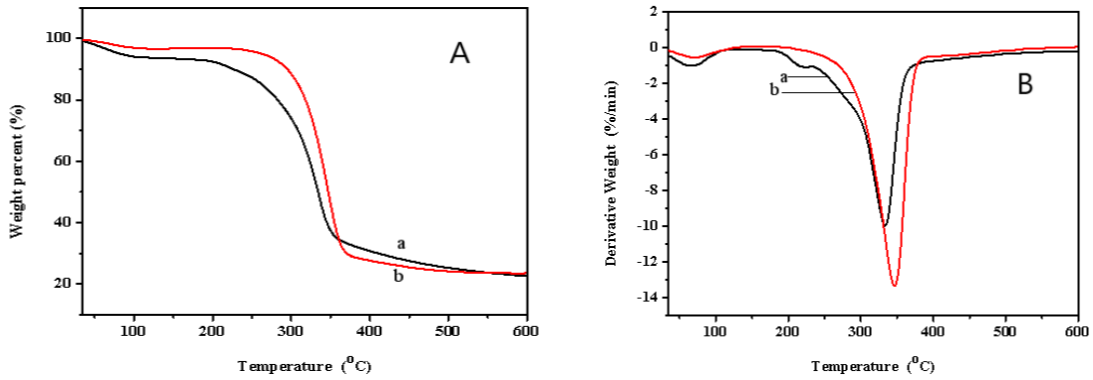

Figure 5: TG (A) and DTG (B) curves of (a) untreated reed straw and (b) treated reed straw fibers

CONCLUSION

In this study, orthogonal design of experiment was used to study the effects of different concentrations of sodium hydroxide and hydrogen peroxide, treatment time and bath liquid ratio on the degumming effect of reed straw, and the optimal scheme was found with the parameters: sodium hydroxide – 35 g/L, hydrogen peroxide – 30 mL/L, 85 °C, 2 h and bath ratio of 1:50. SEM images showed that the surface of the untreated reed straw was uneven, revealing the presence of colloidal particles. Meanwhile, after degumming, the fibers presented a smooth surface due to the removal of most of the pectin and other impurities. XRD analysis indicated that the prepared fiber was cellulose type I and had a crystallinity of 51.84%. The main component of the reed fiber after degumming is cellulose, since most of the hemicelluloses, lignin and impurities have been removed. The results showed that the degumming by the alkali-oxygen bath method was effective in removing most of the non-cellulose components. The reed straw fibers showed intact single fibers and good properties for textile applications. This study can provide a reference for straw management and reuse, as well as for the application of thus-obtained reed straw fibers in the textile field.

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REFERENCES

[1] L. Siim, Y. Patrik and H. Leena, *Renew. Energ.*, **124**, 18 (2018), https://doi.org/10.1016/j.renene.2017.09.050
[2] L. Guo and J. Zhao, *Arab. J. Geosci.*, **14**, 1357 (2021), https://doi.org/10.1007/s12517-021-07797-7
[3] P. A. Seglah, W. Yang, H. Wang, Y. Bi, K. Zhou *et al.*, *J. Clean. Prod.*, **261**, 121191.2 (2020), https://doi.org/10.1016/j.jclepro.2020.121191
[4] X. E. Cao, *Anal. Chem.*, **93**, 15804 (2021), https://doi.org/10.1021/acs.analchem.1c04794
[5] E. Uitterhaegen, J. Parinet, L. Labonne, T. Merian, S. Ballas *et al.*, *Compos. Part A Appl. Sci. Manuf.*, **113A**, 256 (2018), https://doi.org/10.1016/j.compositesa.2018.07.038
[6] Y. Li, S. Yan, Z. Li, S. Xiong, S. Yang *et al. J. Mater. Chem. A*, **10**, 16224 (2022), https://doi.org/2022/ta/d2ta04566d
[7] Z. Xue, W. Cheng, L. Wang and G. Song, *KSCE J. Civ. Eng.*, **25**, 3320 (2021), https://doi.org/10.1007/s12205-021-2263-3
[8] H. Milan, F. Katarina and K. Tatiana, *Chem. Select*, **4**, 6061 (2019), https://doi.org/10.1002/slct.201900562
[9] W. Shuai, N. Chen and B. Li, *Biomass Bioenerg.*, **92**, 46 (2016), https://doi.org/10.1016/j.biombioe.2016.06.002
[10] M. Krstic, Z. Maksimovic, S. Ibrić, T. Bakic, J. Prodanovic *et al.*, *Cellulose Chem. Technol.*, **52**, 580 (2018), https://www.cellulosechemtechnol.ro/pdf/CCT7-8(2018)/p.577-588.pdf
[11] L. Zheng, Y. Du and J. Zhang, *Bioresour. Technol.*, **78**, 90 (2001), https://doi.org/10.1016/S0960-8524(00)00154-1
[12] J. Lojewska, P. Miskowiec, T. Lojewski and L. M. Proniewicz, *Polym. Degrad. Stab.*, **88**, 513 (2005), https://doi.org/10.1016/j.polymdegradstab.2004.12.012

[13] L. Ye, J. Zhang, J. Zhao, Z. Luo, S. Tu *et al*., *J. Anal. Appl. Pyrol*., **114**, 178 (2015), https://doi.org/10.1016/j.jaap.2015.05.016
[14] Y. Cui, M. Jia, L. Liu, R. Zhang, L. Cheng *et al*., *Text. Res. J*., **88**, 11 (2017), https://doi.org/10.1177/0040517517703601
[15] Z. Li and C. Yu, *J. Text. Inst*., **106**, 1261 (2015), https://doi.org/10.1080/00405000.2014.985889
[16] F. M. Pelissari, P. J. A. Sobral and F. C. Menegalli, *Cellulose*, **21**, 430 (2014), https://doi.org/10.1007/s10570-013-0138-6
[17] M. A. Martins, E. M. Teixeira, A. C. Corrêa, M. Ferreira and L. H. C. Mattoso, *J. Mater. Sci*., **46**, 7860 (2011), https://doi.org/10.1007/s10853-011-5767-2
[18] M. M. Ibrahim, W. K. Zawawy and Y. Juttke, *Cellulose*, **20**, 2416 (2013), https://doi.org/10.1007/s10570-013-9992-5
[19] S. A. Ovalle-Serrano, C. Blanco-Tirado and M. Y. Combariza, *Cellulose*, **25**, 7863 (2018), https://doi.org/10.1007/s10570-017-1599-9
[20] B. H. McDonagh and G. Chinga-Carrasco, *Polymers*, **12**, 2416 (2020), https://doi.org/10.3390/polym12112538
[21] M. M. Kabir, H. Wang, K. T. Lau and F. Cardona, *Appl. Surf. Sci*., **276**, 23 (2013), https://doi.org/10.1016/j.apsusc.2013.02.086
[22] H. Celebi and A. Kurt, *Carbohyd. Polym*., **133**, 293 (2015), https://doi.org/10.1016/j.carbpol.2015.07.007
[23] F. Fan, M. Zhu, K. Fang, J. Xie, Z. Deng *et al*., *Cellulose*, **28**, 8386 (2021), https://doi.org/10.1007/s10570-021-04090-4