

NaOH/Urea Swelling Treatment and Hydrothermal Degradation of Waste Cotton Fiber

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Abstract: In this study, waste cotton fabric was used as cellulose raw material and pretreated in aqueous NaOH/urea solution system to investigate the effect of NaOH/urea pretreatment solution on the hydrolysis of cotton fiber. The cotton fiber was pretreated with different conditions of aqueous NaOH/urea solution, and the pretreated cotton fiber was hydrolyzed under the same conditions as the original cotton fiber. The results of characterization analysis showed that water retention value of pretreated cotton fiber was higher than that of unpretreated sample. Moreover, the cotton fiber presented both a convoluted structure and a coarser surface, XRD results suggested that the crystallinity degree of cellulose decreased dramatically, more cellulose II appeared, and the hydrogen bond is broken. Among the different pretreatment conditions, the pretreatment effect was the best when the reaction temperature was 0°C, the solid-liquid ratio was 2:50, and the NaOH/urea ratio was 7:12. The hydrolysis experiments of pretreated and unpretreated cotton fibers showed that when the hydrothermal temperature was 230°C, the heat preservation was 2 h, and the hydrochloric acid concentration was 5 wt. %, the glucose yield reached 29.99%. H⁺ could catalyze the hydrolysis of cotton fiber more effectively due to damage to crystal structure and hydrogen bonds.

Keywords: Waste cotton fibers; NaOH/urea; pretreatment; hydrolyze; recycling and reusing

1 Introduction

With the rapid development of economy and the improvement of living standards, the use cycle of clothing and household textiles is shortened year by year. The output of waste textiles is also increasing [1]. It is estimated that by 2020, the world will produce 100 million tons of waste textiles every year [2], whereas the comprehensive utilization rate is only 10%–15% so far. The most important natural fiber in textile is cotton fiber, and the main component of cotton fiber is cellulose [3], which can be hydrolyzed into micro molecular oligosaccharides and glucose [4,5]. In addition, cellulose can also be depolymerized to organic acids such as formic acid [6,7]. It is reported that polyols [8] and furans [9,10] can be prepared through biomass depolymerization of cellulose, which undoubtedly provides a direction for the reuse of waste cotton fabrics. However, due to the strong crystal structure and high chemical stability of natural



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cellulose [11], the hydrolysis process is difficult and inefficient, which hinders the degradation and reuse of waste cotton fabrics [12].

In recent years, in order to reduce the crystallinity of cellulose and improve the hydrolysis efficiency of cellulose under mild reaction conditions, many cellulose pretreatment technologies have been developed, which can be divided into chemical and physical methods. The chemical method involves pretreating cellulose by using concentrated acids such as phosphoric acid and sulfuric acid. Although the purpose of decrystallization is achieved, the large-scale use of acid causes strong corrosion of equipment and generates acid residue as waste. The physical method mainly involves solvent pretreatment. Cellulose can be dissolved in ionic liquids at 80°C [13]. This method has the advantages of non-volatilization, good chemical stability, thermal stability, and strong solubility. However, ionic liquids cause environmental problems and unnecessary by-products [14]. Also, the high cost and long-term uncertain biological toxicity of ionic liquids limit their large-scale applications [6]. In recent years, NaOH/urea solution system was found to be a new cellulose pretreatment solvent with low cost and no pollution. The mechanism involved in this pretreatment is that alkali hydrate can penetrate the amorphous region of cellulose, destroy the adjacent crystalline region, make cellulose swell, and reduce the crystallinity of cellulose. In addition, the addition of thiourea or urea components can trap free water and prevent the interaction between cellulose chains through hydrogen bonds [15]. For example, Wang et al. pretreated cotton fibers with NaOH/urea to different degrees and used the different fiber samples to prepare cellulose acetate. It was found that the substitution degree was improved compared with untreated cotton fibers [16]. However, the solubility of cellulose in NaOH/urea is related to the polymerization degree of cellulose. When the polymerization degree of cellulose is higher than 800, its solubility is less than 20% [17]. The polymerization degree of cotton fiber is above 2000, thus it cannot be completely dissolved and can only be inflated. In this study, waste cotton fiber was used as the research object for pretreatment with NaOH/urea solution. The pretreated samples were characterized and their properties were compared with the untreated samples. Furthermore, the changes in cotton fiber in the hydrolysis process after pretreatment were investigated to promote the recycling and reuse of cotton waste fabric.

2 Materials and Methods

2.1 Materials

In this case, waste cotton fabric was kindly provided by Shanxi Gefulan Textile Co., Ltd. (China). All fiber samples were cut into small pieces ($\sim 2 \times 2 \text{ cm}^2$), cleaned with water, air dried, and preserved in a desiccator for use. NaOH, urea and HCl of analytical grade were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (China). Glucose assay kits were obtained from Perkin Elmer, USA. Distilled water for the experiments was prepared in the laboratory.

2.2 Pretreatment of Cotton Fiber

NaOH/urea were measured out in different proportions (mass fraction) and added into a beaker. The solution was precooled in a constant low-temperature water bath (the aqueous ethylene glycol coolant used, DCW-2006, Xi'an Bilang Biotechnology Co., Ltd. [China]) for 10 minutes. A certain amount of waste cotton fabric was added immediately into this precooled solution with mechanical stirring for 10 minutes. Subsequently, the generated fiber/solution mixture was squeezed to remove the cellulose solution. Then, the reactants were washed for 2–3 times and kept in distilled water at ambient room temperature until no residual chemicals could be detected in the waste water. Finally, the reactants were oven-dried in a vacuum oven at 60°C for 6 h and stored for further processing.

2.3 Hydrolysis of Cotton Fiber

In the hydrolysis procedure, 1 g of raw cotton fiber and pretreated cotton fiber respectively were added into hydrochloric acid solution with various mass fractions. Then, the mixture was placed in a muffle furnace

and sealed. The filling degree of reaction kettle was 60%. The reaction products were taken out and centrifuged to separate the solid and liquid phase products. The solid phase products were washed by ethanol and distilled water for several times and then placed in a drying box to be dried at 120°C for 4 h. Then they were cooled naturally to room temperature, weighed, bagged and tested.

3 Characterization of Cotton Fiber

3.1 Water Retention Value

The water retention value (WRV) of fiber was determined by centrifugal method. First, 1.5 g of pretreated cotton fiber (absolutely dry) was measured out and then added into a centrifugal tube with enough deionized water. It was soaked completely for 10 min. Then, the test tube was placed into the centrifuge and subjected to centrifugation for 15 min at the speed of 3000 rpm. After removing the free water in the fiber, it was placed into a weighing bottle and weighed. Finally, the fiber was oven-dried at (105 ± 1°C) to constant weight and weighed after cooling to room temperature. The WRV for each sample was calculated according to the following Eq. (1):

$$W = \frac{M_1 - M_0}{M_0} \times 100\% \quad (1)$$

where M_0 and M_1 are the dry and wet weights of the cotton fiber, respectively.

3.2 FTIR

FTIR analysis was conducted using an FTIR-1730 spectrometer (PE, USA) over the range of 4000–400 cm^{-1} and at a resolution of 2 cm^{-1} over 20 scans. The sample for FTIR analysis was ground, mixed with dried potassium bromide powder, and compressed into a tablet.

3.3 XRD

The XRD patterns were obtained using an X-ray diffractometer (Y-2000, Dandong, China) equipped with Cu $K\alpha$ radiation at the operational conditions of 35 kV and 25 mA. The data were collected in the 2θ range of 5–40° with an interval of 0.04°.

The crystallinity of cotton fiber (CI) was calculated using the peak height in the XRD pattern, as shown in Eq. (2):

$$CI = (I_{200} - I_{am}) / I_{200} \times 100\% \quad (2)$$

where I_{200} is the intensity of major diffraction peak at $2\theta = 22.7^\circ$ corresponding to 200 plane on the surface of the crystal lattice (20.1° for cellulose II); I_{am} is the intensity of the diffraction peak at $2\theta \approx 18^\circ$ caused by the amorphous cellulose part between the lattice surfaces 101 and 002 [18]. High CI value indicates high degree of crystallization of cellulose I or II.

3.4 SEM

The surface morphology of samples was analyzed using a scanning electron microscope (FESEM; JSM-6700F, JEOL, Tokyo, Japan).

The surface of dried sample was coated with gold and then observed with an accelerating voltage of 7 kV.

3.5 HPLC

The hydrolyzed products of cotton fiber were characterized by high performance liquid chromatography (HPLC, PerkinElmer, USA) with a refractive index detector (RID). SH1011 chromatographic column (Shodex, Japan) was used for the separation. The mobile phase was 5×10^{-3} mol H_2SO_4 solution and the flow rate was 0.5 mL/min. The sample injection volume was 10 mL and the column temperature was 50°C.

4 Results and Discussion

4.1 Effects of Different Degrees of NaOH/Urea Preconditioning on Water Retention Value of Cotton Fiber

The pretreatment conditions are shown in [Tab. 1](#). Water retention value (WRV) is the main indicator of the swelling degree of cellulose. The reason for fiber swelling lies in the polar hydroxyl groups contained in the molecular structure of cellulose and hemicellulose and the polar attraction between water molecules [19]. Water molecules enter the amorphous zone of cellulose, which increases the distance between the molecular chains of cellulose, and causes fiber deformation and swelling. It was found that the WRV of cotton fiber after NaOH/urea aqueous solution preconditioning was significantly increased. The WRV and loss rate of cotton fiber after pretreatment with different NaOH/urea aqueous solutions are shown in [Fig. 1a](#). When the NaOH/urea concentration was 6:14, the WRV was the lowest. However, when the NaOH/urea concentration was 7:12, the WRV was as high as 25.34%, after which it gradually decreased. This is because when the NaOH content in the system remained constant, the amount of alkali cellulose generated was basically unchanged, and the synergistic effect of small urea molecules had a corresponding efficiency upper limit. On the other hand, the excessive alkali content led to the complete infiltration of cellulose by alkali metal ions. Consequently, the number of hydration ions decreased and the WRV decreased. It should be noted that the amorphous part of cotton fiber contains cellulose macromolecules with relatively low polymerization degree, which can be dissolved in the NaOH/urea aqueous solution system, resulting in loss of the solid-phase cotton fiber. However, the fiber loss rate remained stable at around 10% under different pretreatment conditions.

Table 1: Pretreatment conditions of cotton fiber

Sample	NaOH/urea (mass fraction)	T (°C)	Solid/liquid	Fiberloss rate (%)	WRV (%)
1	6:14	-15	2:50	11.38	16.71
2	7:12	-15	2:50	12.53	25.34
3	7:14	-15	2:50	12.31	20.78
4	8:12	-15	2:50	13.07	20.82
5	8:14	-15	2:50	11.01	18.47
6	7:12	5	2:50	13.41	25.27
7	7:12	0	2:50	10.61	27.37
8	7:12	-5	2:50	11.87	20.82
9	7:12	-10	2:50	12	22.34
10	7:12	0	2:30	10	19.84
11	7:12	0	2:40	11.5	21.07
12	7:12	0	2:60	9	17.43
13	7:12	0	2:70	7.5	15.64

In addition, the temperature of pretreatment system had a significant effect on cotton fiber swelling. When the system was at 0°C, the WRV reached 27.37% ([Fig. 1b](#)), but the fiber loss rate was low and the WRV showed a downward trend. However, when the temperature dropped to -5°C, the WRV gradually increased and the solubility of cotton fiber also increased correspondingly. This is because the swelling of cellulose in alkali solution is one of the few swelling processes with negative temperature coefficient [19]. Thus, the swelling of cellulose can be increased by lowering the temperature of the NaOH/urea

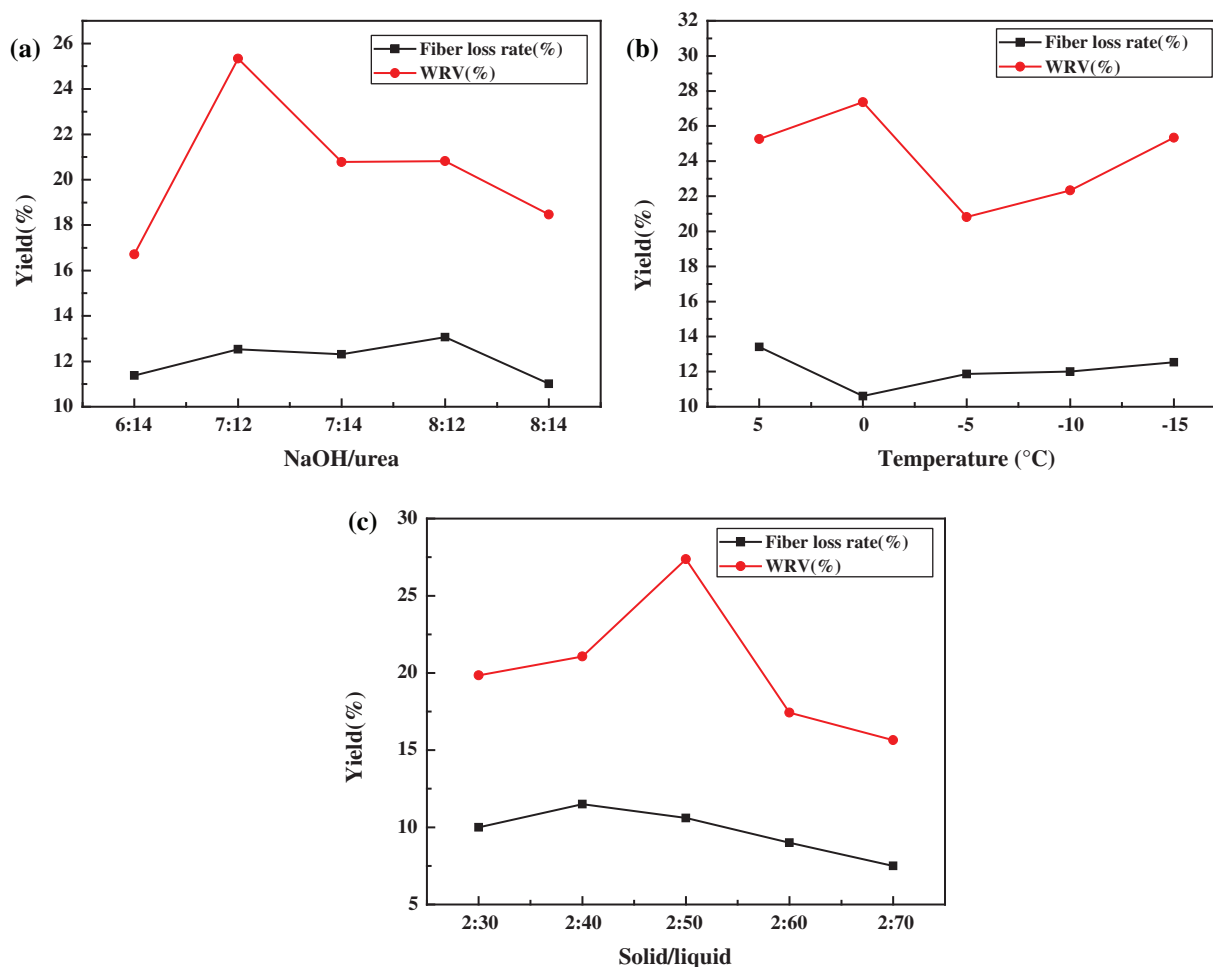


Figure 1: Effects of NaOH/urea ratio (a), reaction temperature (b), and solid/liquid ratio (c) on the fiber loss rate and WRV of pretreated cotton fiber. Reaction conditions: (a: -15°C , 2:50; b: $7:12$, 2:50; c: 0°C , 7:12)

aqueous solution. By studying the solid-liquid ratio of the pretreatment system, it was found that cotton fibers had different WRVs at different solid-liquid ratios (Fig. 1c). When the solid-liquid ratio was 2:50, the WRV was the maximum value of 27.37%. To summarize, the optimal pretreatment conditions for cotton fiber were: reaction temperature of 0°C , solid-liquid ratio of 2:50, and NaOH/urea ratio of 7:12.

4.2 Effect of Pretreatment on the Surface Morphology of Fibers

Fig. 2 shows the morphology and structure of cotton fibers after different degrees of pretreatment. As seen from the image, the untreated cotton fibers presented long crystal beams on the surface, were smooth, flat and straight, and had a complete surface structure (Fig. 2a). After different degrees of NaOH/urea preconditioning, the surface morphology of cotton fiber changed significantly. Uneven surface of cotton fiber was observed with increased torsion and increased surface area (Figs. 2b–2j). Figs. 2b–2d shows the SEM images of cotton fiber after pretreatment with different NaOH/urea ratios. When the NaOH/urea ratio was 7:12, the fiber presented a helix shape with rough surface. Moreover, cracks and folds were observed, which were the most serious damages. Figs. 2b–2g shows the SEM images of pretreated cotton fiber at different temperatures. As can be seen, the cotton fiber surface showed torsion and curling, and even breakage. It indicates that NaOH/urea solution caused a certain degree of corrosion

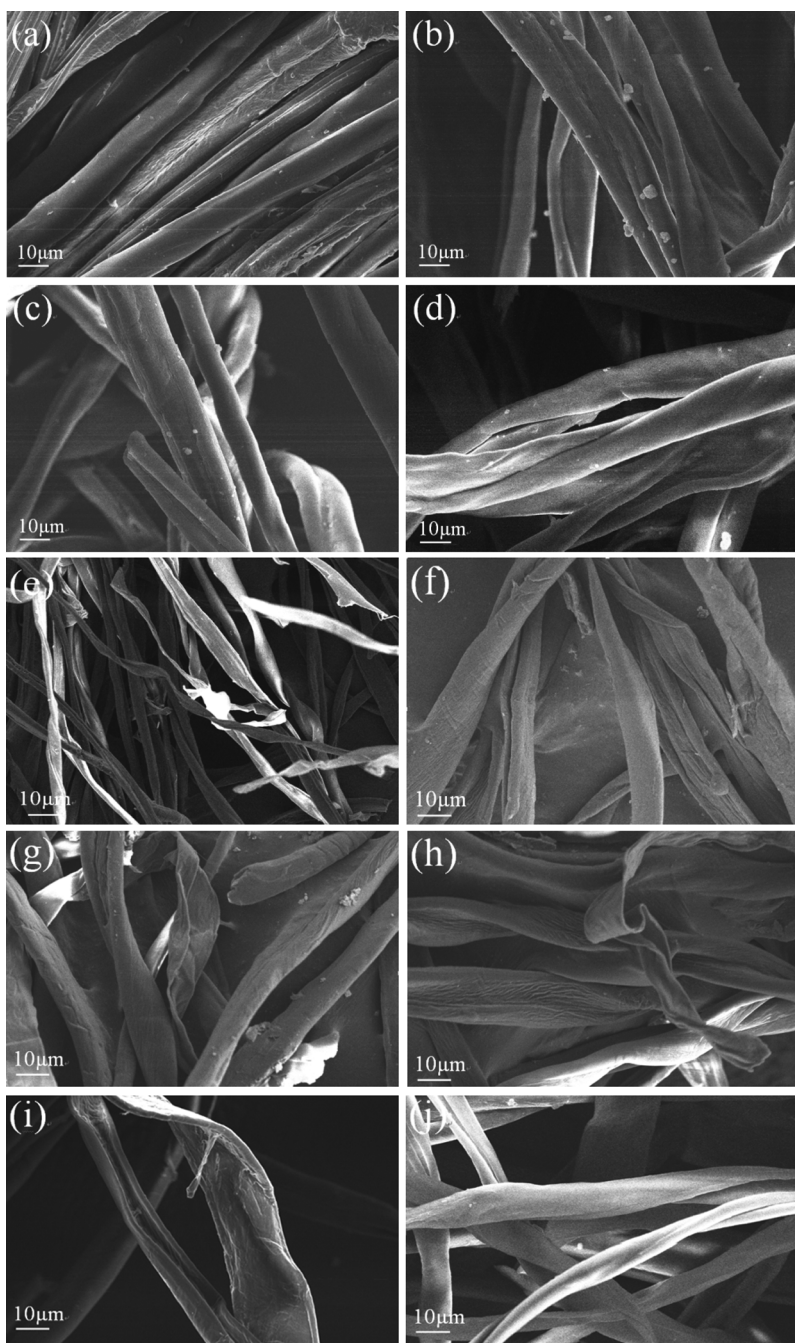


Figure 2: SEM images of cotton fibers without pretreatment (a), and with pretreatment using aqueous NaOH/urea solution and with different NaOH/urea ratios (b: 7:12; c: 7:14; d: 8:12), and different temperatures (e: 0; f: -5°C ; g: -10°C), and different solid:liquid ratios (h: 2:30; i: 2:40; j: 2:50; k: 2:70)

on the surface of cotton fiber. According to the comparison of Figs. 2e, 2h–2j, when the solid-liquid ratio was 2:50, the change in cotton fiber morphology was most obvious. All these changes are beneficial to increase the surface area of cotton fiber, improve the accessibility and enhance the hydrolysis reactivity [20].

4.3 Effect of Pretreatment on the Crystallization Properties of Fibers

In order to analyze the crystal structure of cotton fiber before and after pretreatment, X-ray diffraction was performed on the samples. As seen from the XRD pattern in Fig. 3, the diffraction peaks at 2θ of 14.7° , 16.8° , 22.7° and 34.8° corresponded to the crystal layers of (1-01), (101), (200) and (004), respectively, which are the characteristic crystal peaks of typical cellulose I (Fig. 3a). The cotton fibers after NaOH/urea pretreatment with different conditions presented obvious diffraction peaks at $2\theta = 12.1^\circ$ and 20.1° , which were characteristic diffraction peaks of cellulose type II (Figs. 3b–3f). This suggests that a series of structural changes occurred in the cellulose chain after NaOH/urea pretreatment of cotton fiber [10]. Cellulose I is natural cellulose while cellulose II is formed by dissolving and regeneration. Intensity of cellulose I is higher than that of cellulose II. It should be noted that after the pretreatment, the cotton fiber also showed obvious diffraction peak at $2\theta = 22.7^\circ$, which is the characteristic peak of cellulose I. It shows that cellulose I and cellulose II crystals coexisted after the pretreatment of cotton fiber, this is mainly due to reaction time was short, which was not enough to convert cotton fiber from cellulose I completely into cellulose II in NaOH/urea pretreatment system. In addition, the crystallinity of raw cotton fiber was 78.3%, and crystallinity of the pretreated cotton fiber was only 54.9% (according to the height method [type 2]) when the conditions were: temperature of the entire system at 0°C , the solid-liquid ratio at 2:50, and NaOH/Urea of 7:12. These results demonstrate that pretreatment process can reduce the crystallinity of cotton fiber and change the fiber crystal form, thus improving the cotton fiber reaction.

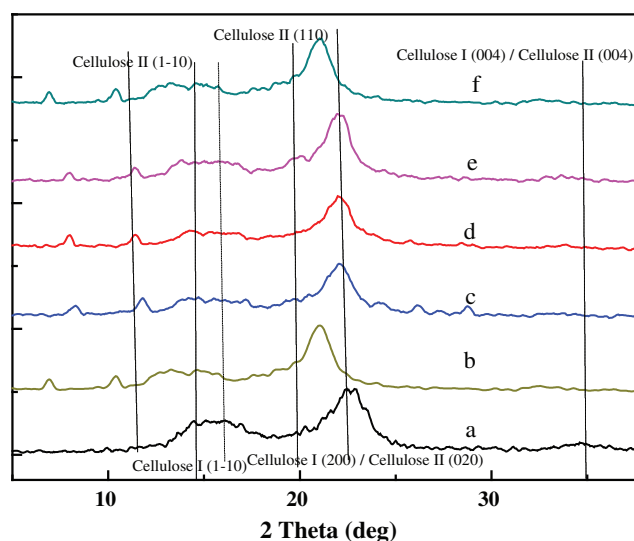


Figure 3: XRD patterns of cotton fibers without pretreatment (a) and after pretreatment using aqueous NaOH/urea solution under the following conditions (b) -15°C , 7:12, 2:50; (c) -10°C , 7:12, 2:50; (d) 0°C , 7:12, 2:50; (e) 0°C , 7:12, 2:30; (f) 0°C , 7:12, 2:70

4.4 Effect of Pretreatment on the Chemical Structure of Fibers

As can be seen from Fig. 4, the derivative functional group formed by NaOH/urea solvent system was $-\text{CONH}_2$. The peaks in $1200\text{--}1400\text{ cm}^{-1}$ region (designated as the C–H deformation vibrations, the O–H bending vibration and the CH_2 shimmy motion) are related to crystallinity rather than lattice type [21]. Compared with the raw cotton, the intensity of peaks for cotton fiber after pretreatment became significantly weaker, which also indicates that the crystallinity was decreased. The peaks at 3411 cm^{-1} for the pretreated cotton fiber were shifted to a higher wavenumber (around 3455 cm^{-1} , blue shift) and their intensity was slightly decreased. This implied that the hydrogen bonds of fiber were broken and their

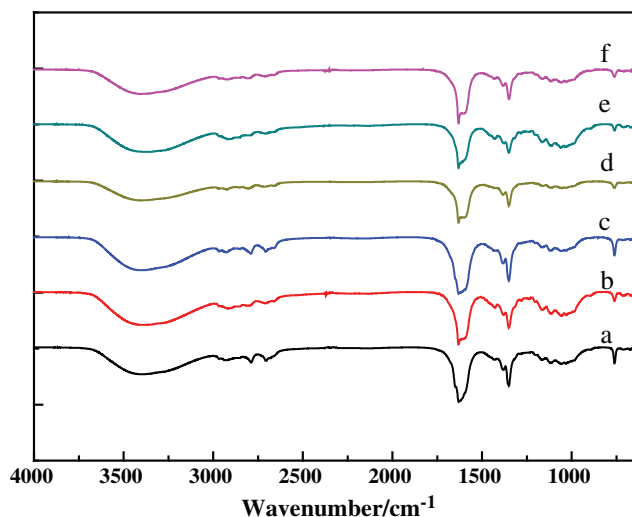


Figure 4: FTIR spectra of cotton fibers without pretreatment (a) and after pretreatment using aqueous NaOH/urea solution with the following conditions (b) -15°C , 7:12, 2:50; (c) -10°C , 7:12, 2:50; (d) 0°C , 7:12, 2:50; (e) 0°C , 7:12, 2:30; (f) 0°C , 7:12, 2:70

association degree decreased after the pretreatment. In particular, the peak intensity was the weakest for the sample pretreated at the reaction temperature of 0°C and NaOH/urea ratio of 7:12.

4.5 Effect of Pretreatment on Cotton Fiber Hydrolysis

The untreated and pretreated cotton fibers were respectively added to 5 wt.% hydrochloric acid solution and reacted at 230°C for 5 h. The yield of glucose from cotton fiber hydrolysis is shown in Fig. 5a. The primary hydrolyzed product of cotton fiber was glucose, which is easy to decompose in high-temperature aqueous solution. Therefore, with the extension of reaction time, the yield of glucose from both samples showed a trend of first increasing and then decreasing. However, the hydrolysis efficiency of cotton fiber was improved greatly after pretreatment. The hydrolysis rate reached 6.40% at 0.5 h and reached a peak of 29.99% at 2 h. Moreover, the untreated cotton fiber reached the maximum hydrolysis rate of only 16.00% at 2.5 h. This was mainly due to the rapid dynamic self-assembly of cellulose macromolecules in cotton fiber after NaOH/urea pretreatment to form hydrogen bond keyed clathrate. This caused the fibers to be evenly dispersed in water system, and resulted in the decrease in cotton fiber crystallinity and partial hydrogen bond damage. These factors promoted the hydrolysis efficiency of cotton.

Fig. 5b shows the glucose yield curve of cotton fiber before and after pretreatment at 5 wt.% hydrochloric acid concentration for 2 h in the reaction temperature range from 160°C to 260°C . As observed in the figure, pretreatment was beneficial to reduce the decomposition temperature of cotton fiber. The untreated cotton fiber generated a large amount of glucose at 180°C , while glucose was produced from pretreated cotton fiber at 160°C , indicating that pretreatment can significantly reduce the initial hydrolysis temperature of cotton fiber. With the increase in temperature, the glucose yield of pretreated cotton fiber increased rapidly, reaching a peak of 29.99% at 230°C , and then began to decrease due to the accelerated decomposition rate of glucose. The glucose yield of untreated cotton fiber was 16.80% at 260°C , indicating that the pretreatment process could significantly improve the hydrolysis efficiency of cotton fiber.

Fig. 5c shows the glucose yield curve of cotton fiber before and after pretreatment at the reaction temperature of 230°C , heat preservation for 2 h and hydrochloric acid concentration of 1–5.5 wt.%. It can be seen that the yield of glucose from cotton fiber hydrolyzed by pretreatment was higher than that from

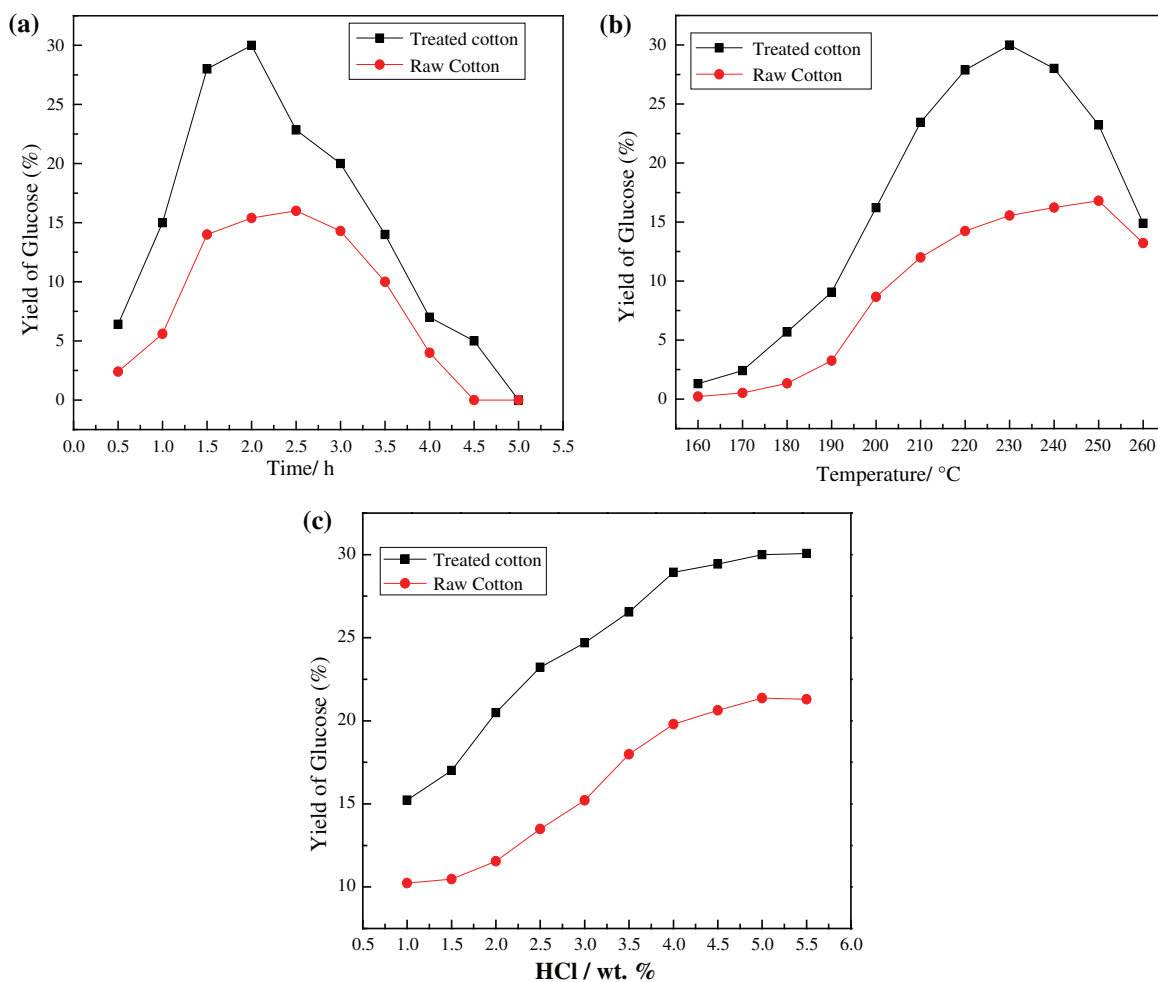


Figure 5: Effects of reaction time (a), reaction temperature (b), H^+ ions concentration (c) on glucose production from untreated and pretreated cotton fibers. Conditions: (a: 230°C, 5wt.%; b: 2h, 5wt.%; c: 230°C, 2h)

the untreated cotton fiber with the same acid concentration. Moreover, for the cotton fiber after pretreatment, glucose yield increased rapidly when the concentration of acid was 1.5–4 wt. %, whereas the glucose yield of untreated cotton fiber increased faster in the acid concentration range of 2–4.5 wt. %. The results showed that H^+ could catalyze the hydrolysis of cotton fiber more effectively due to some crystal structure and hydrogen bond damages.

5 Conclusions

Herein, the effects of NaOH/urea pretreatment on the structure and properties of waste cotton fibers were investigated. It was found that the NaOH/urea system had a weak effect on the dissolution of cotton fibers, but it could cause full swelling of the cotton fibers. The water retention value of the cotton fibers after pretreatment with NaOH/urea aqueous system was 27.37%, when the temperature was 0°C, the solid-liquid ratio was 2:50, and the NaOH/urea ratio was 7:12. Moreover, it was observed that the surface structure of cotton fiber was damaged, the crystallinity was reduced, and some internal cellulose crystal forms were changed after pretreatment. The hydrolysis efficiency of cotton fiber after pretreatment was significantly improved. When the hydrothermal temperature was 230°C, the heat preservation was 2 h,

and the hydrochloric acid concentration was 5 wt.%, the glucose yield reached 29.99%. The results indicated that H^+ could catalyze the hydrolysis of cotton fiber more effectively due to some damage to the crystal structure and hydrogen bonds. The proposed pretreatment system can be potentially used as a high value method to utilize waste cotton fabrics.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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