IMPROVING THE BLEACHABILITY OF WHOLE COTTON STALK CHEMIMECHANICAL PULP WITH DEPECTINIZATION AGENTS

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The effects of pretreatment agents on pectin removal and chemical compositions in cotton stalk bark were studied. The results showed that the reaction rates of the depectinization agents reacting with calcium pectinate were $V_{Na_2C_2O_4} > V_{Na_5P_3O_{10}} > V_{NaOH}$. The ratio of pectin removal reached 53.73% after pretreatment with 3% sodium oxalate. When the parameters of precondition were 3% sodium oxalate, 90 ^oC, and bleaching with 6.5% NaOH and 11% H_2O_2, the brightness of chemimechanical pulp from whole cotton stalk reached 76.18% ISO.

Keywords: Whole cotton stalk; Chemimechanical pulp; Pectin; Brightness

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INTRODUCTION

Cotton stalk is one of the non-wood resources used for pulping and papermaking in China. It has advantages such as high annual output, a centralized production area, and low price (Tang *et al*. 2005; Wang *et al*. 2006). Whole cotton stalk can be divided into cuticle tissue, phloem, and xylem from exterior to interior. The chemical compositions, plant properties, and fiber morphologies of each part differ greatly (Nie and Hu 2003), as do the pulping properties of each part. The fiber in the bark of the cotton stalk is soft and slender, while the fiber in the xylem is similar to aspen.

However, the brown pectin, which exists largely in the bark, and which carries a large number of transition metal ions, can cause bleaching agents to decompose. The cotton stalk bark accounts for 30% of the total weight of the whole cotton stalk, and it accumulates more than 57% pectin (Kirci 1997). Pectin leads to a high dirt count and low applicability, so unbleached whole cotton stalk pulp is mostly used to produce low-grade paper such as brown paper and corrugating medium. It can be observed that the main challenge of pulping with whole cotton stalk is in improving its bleachability and reducing the dirt count. In a word, the key technique is the treatment of cotton stalk bark.

Infrared absorption spectroscopy was used to represent the structure of calcium pectinate in this experiment. The most efficient depectinization agent was selected by means of comparing the rate of degradation of calcium pectinate. In the preimpregnation stage, sodium hydroxide and sodium oxalate were added to cotton stalk bark directly, leading to the removal of a large quantity of pectin and chromophoric substances. Thus, the consumption of bleaching agents in the follow-up bleaching treatment was reduced, and the bleachability performance and brightness of the final pulp were enhanced effectively.

EXPERIMENTAL

Materials

The cotton stalks were obtained from a paper mill in Shandong province, China. The cotton stalks were cut into lengths of 20 to 40 mm, then washed and dried at room temperature. The depectinization agents used in this experiment were sodium oxalate and sodium hydroxide.

Methods

Determination of the metal ion content in cotton stalk by flame atomic absorption spectrometry (FAAS)

Before measurement of the content of trace elements by flame atomic absorption spectrometry (Wang *et al*. 2006), a nitration treatment was conducted. The operating conditions of the FAAS are presented in Table 1.

Table 1. The Working Condition of FAAS

Element Name	Wave Length (nm)	Spectrum Pass Band (nm)	Lamp Current (mA)	Acetylene/Air
Fe	248.3	0.2	12.0	2.2:12.0
Cu	324.8	0.5	6.0	1.8:12.0
Ca	422.7	0.5	10.0	2.3:9.8
Mg	285.2	0.5	8.0	1.8:12.0
Mn	279.5	0.2	10.0	2.0:12.0

Preparation of calcium pectinate gel

3g of pectin were added to 300 mL of pure water while slowly stirring until it became a homogeneous solution. 100 mL (1%) of $CaCl_2$ solution were then added, and the agitation was continued for five minutes. The mixture of calcium pectinate was transferred into a 3000-mL beaker and stirred for another 24 hours. An aliquot of ethyl alcohol was added into the beaker and stirring was continued for half an hour, a procedure in which calcium pectinate precipitates out. The precipitate was removed from the breaker to a watch glass and dried in a vacuum drying oven at 40 ^{o}C for 24 hours.

The reaction rates of depectinization agents

Different depectinization agents of the same dosages were weighed in different beakers, and then 0.0025 g of calcium pectinate were added to each of the beakers. A timer was started. The mixture was agitated for a while. Timing was stopped when the calcium pectinate in each beaker had dissolved completely. The time for the complete dissolution of the calcium pectinate under a different temperature was recorded. The reaction rates of depectinization were represented by the average dissolution rates of calcium pectinate in the corresponding mixtures. The calculation proceeded according to Eq.1.

$$V=C_A/t \quad (1)$$

In Eq.1, V is the average reaction rate (mol·L^{-1}min^{-1}), C_A is the amount of depectinization agents (mol·L^{-1}), and t is the reaction time (min).

The preparation of CTMP and bleaching process

Table 2. The Conditions of Preparation of CTMP and Bleaching Process

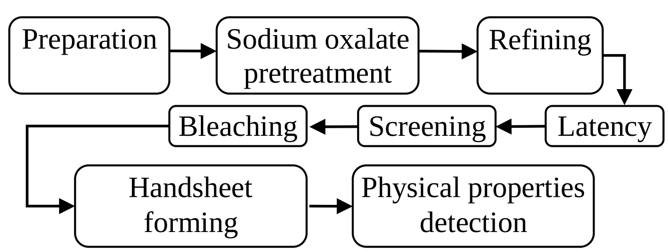
Pretreatment	Temperature /^{o}C	Liquor-to-Cotton Stalk Ratio	Time/min	Method	NaOH/%	0, 0.5, 1.0, 1.5		
	90	3 : 1	40		$Na_2C_2O_4$/%	0, 0.5, 1.0, 1.5		
Impregnation	NaOH/%	2			Na_2SO_3/%	4		
Hydrogen Peroxide Bleaching	Temperature / ^{o}C	Time/min	Pulp Consistency /%	Na_2SiO_3 /%	$MgSO_4$ /%	DTPA /%	NaOH /%	H_2O_2 /%
	80	150	10	3.5	0.1	0.2	1.5	3

Effect of pretreatment on the chemical compositions in cotton stalk bark

The cotton stalk bark was shortened to 20 to 30 mm before being fed into a small tank for preimpregnation. Pretreatment was carried out in a rotating digester with a capacity of 15 L. The parameters of preconditioning were 3% sodium hydroxide (and sodium oxalate), liquor to cotton stalk bark in a ratio of 4:1, a maximum temperature of 90 ^{o}C, and time at the maximum temperature, 30 min. The washed cotton stalk bark was dried at room temperature before being milled into powder. The powder passing through 40 mesh and being retained at 60 mesh was collected for the measurements of chemical components.

Flow chart of preparation and bleaching

The sequence of steps before and after bleaching is laid out in the following diagram:



RESULTS AND DISCUSSION

Metal Ion Contents in Raw Material

The metal ion contents in the raw materials as determined by flame atomic absorption spectrometry are presented in Fig. 1.

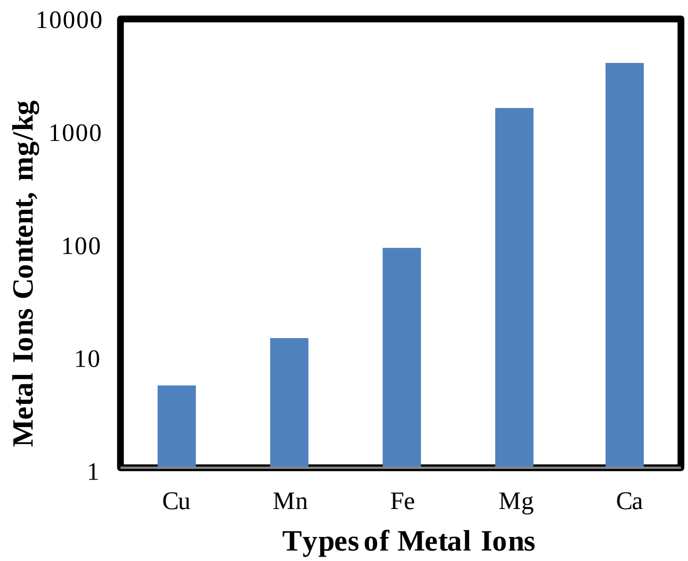


Fig. 1. A comparison of various metal ion contents in whole cotton stalk

As shown in Fig. 1, the metal ions in the cotton stalk were mainly calcium and magnesium ion, and those contents were 4081.71 mg/kg and 1630.20 mg/kg, respectively. Generally, the pectin in cotton stalk presents as insoluble salt of calcium or magnesium pectinate and methyl ester. We know that calcium pectinate is the major form of pectin in cotton stalk. Therefore, the calcium pectinate was selected as the model by which to carry out a mechanistic study of the removal of pectin.

Depectinization Pretreatment to Improve the Bleachability of Whole Cotton Stalk Chemimechanical Pulp

The reaction rates of different depectinization agents

In the experiment, different depectinization agents were selected to dissolve the same dosage of calcium pectinate gel under the same temperature. The amount of time required for the calcium pectinate to dissolve completely was recorded. The dissolution reaction rate of calcium pectinate gel was calculated based on Eq. 1. Figure 2 presents the relationship between the dissolution reaction rate of the calcium pectinate gel and different depectinization agents of different dosages. The depectinization efficiency of different depectinization agents is presented in Fig. 3.

The various straight lines in the figures indicate the higher coefficients of determination and better correlations. The dosages of the depectinization agents were the same, and the reaction rates of the depectinization agents that reacted with the calcium pectinate were $V_{Na_2C_2O_4} > V_{Na_5P_3O_{10}} > V_{NaOH}$. The relationship between the slopes of various straight lines was $K_{Na_2C_2O_4} > K_{Na_5P_3O_{10}} > K_{NaOH}$. In conclusion, with the same dosage of depectinization agents, the increase in reaction rate of sodium oxalate was the highest, followed by sodium phosphate, then sodium hydroxide.

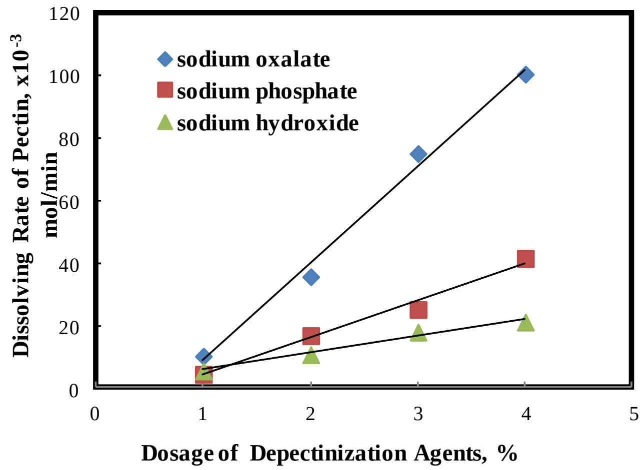


Fig. 2. A comparison of model dissolved reaction rates of different depectinization agents

Figure 3 shows the relationship between the amount of pectin removed and the dosage of depectinization agents. When comparing similar increases in the dosage of different agents, the depectinizing effect of sodium oxalate was more obvious than that of sodium hydroxide. That was because the anion in sodium oxalate made the calcium ion settled down more effectively during the depectinization pretreatment, and thus ensured the subsequent reaction.

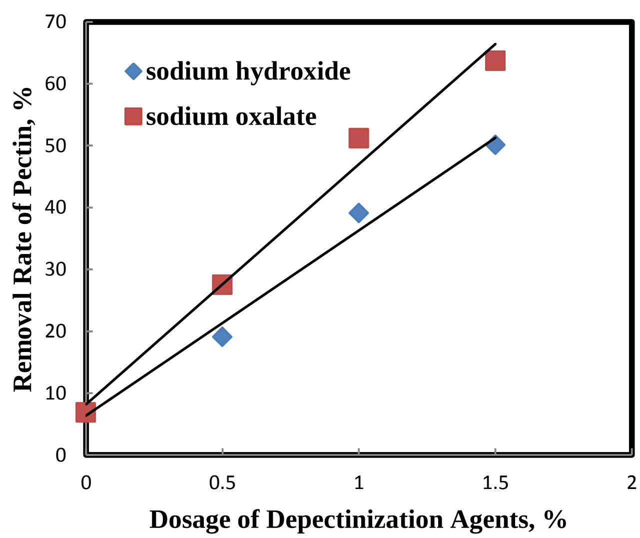


Fig. 3. A comparison of depectinization efficiency of different agents

The relationship between the bleachability and the pectin removal of whole cotton stalk chemimechanical pulp

In the experiment, the cotton stalk bark was pretreated with sodium oxalate and sodium hydroxide, respectively, and the conditions of preparation of CTMP and bleaching process according to Table 2. The relationship between brightness gain and pectin removal is presented in Fig. 4.

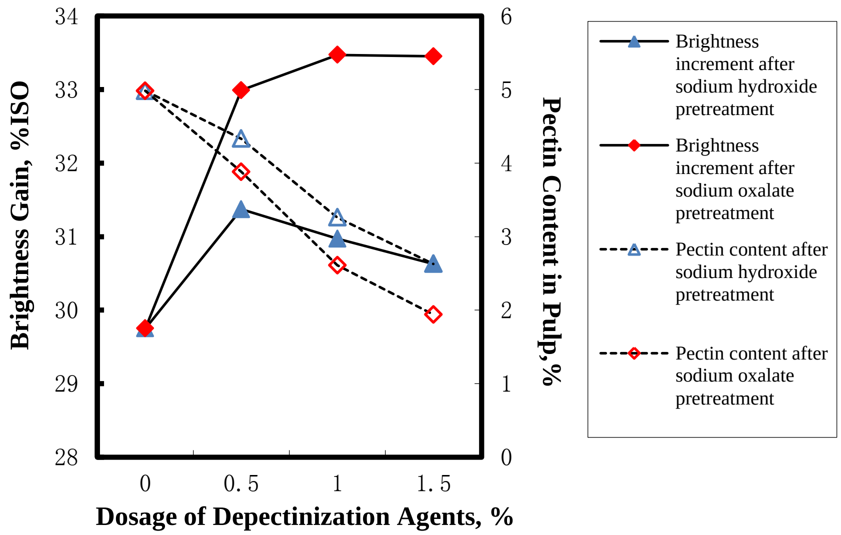


Fig. 4. A comparison of pectin removal and brightness gain

As shown in Fig. 4, sodium hydroxide and sodium oxalate had obvious effects on pectin removal. Moreover, the brightness of the pulp increased significantly with the pectin removal caused by sodium hydroxide (and sodium oxalate), and the enhancement effect of depectinization pretreatment with sodium oxalate on the brightness was greater than that of sodium hydroxide. At this point, it is apparent that the brightness gain and the pectin removal were closely related. Under high doses of sodium hydroxide pretreatment, accompanying the removal of pectin the bleachability improvement of the pulp slowed down, and this might be caused by alkaline blackening (Tian *et al*. 2007). However, the sodium oxalate pretreatment could avoid this problem.

The Effect of Different Depectinization Agents on the Chemical Compositions of Cotton Stalk Bark

The cotton stalk bark was pretreated with sodium oxalate and sodium hydroxide, respectively, and the effects of the different depectinization agents on the chemical compositions in cotton stalk bark were analyzed. The pretreatment process was carried out as explained above, and the results are presented in Table 3.

Table 3. The Effect of Different Depectinization Agents on the Chemical Compositions of Cotton Stalk Bark (%)

Methods	Ash	Benzene - Alcohol Extractives	Cellulose	Holo-cellulose	Acid Accumulator Insoluble Lignin	Acid Accumulator Soluble Lignin	Pentosan	Pectin
untreated	5.44	2.26	35.87	63.85	13.27	1.8	17.40	5.23
NaOH Treated	5.31	1.60	39.93	68.59	13.76	2.2	17.52	4.34
$Na_2C_2O_4$ Treated	4.38	1.37	40.04	70.37	13.92	1.9	14.34	2.42

From Table 3, it can be observed that the contents of ash, benzene-alcohol extractives, and pectin in the cotton stalk bark decreased when the bark was treated with sodium oxalate and sodium hydroxide. Moreover, the sodium oxalate was more effective than the sodium hydroxide. The contents of the pectin and the benzene-alcohol extractive in the cotton stalk bark were obviously higher than in other parts of the cotton stalk. For this reason, plenty of cooking and bleaching chemicals, such as caustic soda, would be consumed in the process of cooking and bleaching. Furthermore, the existence of pectin in the bark caused an obvious color that showed resistance to oxidative degradation. This was the main reason that the bark fiber had lower bleachability. From the data in Table 3, it can be observed that the bark that was pretreated with sodium oxalate improved the brightness of the whole cotton stalk pulp and decreased the dirt count effectively.

The Effect of Different Sodium Oxalate Pretreatment Methods on the Brightness of Whole Cotton Stalk Chemimechanical Pulp

The whole cotton stalk was pretreated with sodium oxalate during the production of chemimechanical pulp. Different sodium oxalate pretreatment methods were carried out, and other parameters of bleaching were 3% Na_2SiO_3, 0.5%$MgSO_4$, 1% DTPA, pulp consistency of 10%, a constant temperature of 90 ^oC, and bleaching time, 2h. The results are presented in Table 4.

Table 4. The Effect of Different Sodium Oxalate Pretreatment Methods on Brightness of Whole Cotton Stalk Chemimechanical Pulp

Samples	$Na_2C_2O_4$%	H_2O_2%	NaOH%	Brightness %ISO
1	3	—	—	28.93
	—	11	6.5	76.18
2	3	7	4.5	44.69
	—	4	2	70.74

The pulp samples 1 and 2 were produced by different pulping methods. In the pretreatment and bleaching stage, the dosages of hydrogen peroxide and sodium hydroxide were kept the same. The final brightness of sample 1 was 76.18% ISO, an increase of 5.44% ISO from sample 2. It is apparent that the sodium oxalate was a more efficient depectinization agent in the pretreatment stage than NaOH and H_2O_2, and had a better effect on the brightness of sample 1.

CONCLUSIONS

The most reasonable model was selected through quantitative and qualitative analysis of whole cotton stalk by modern analysis methods. The effects of depectinization agents such as sodium oxalate and sodium hydroxide on the structure of calcium pectinate gel were studied through the investigation of the solubility of reaction production calcium salts. The relationship between the reaction rates was $V_{Na_2C_2O_4} > V_{Na_5P_3O_{10}} > V_{NaOH}$.

Pectin content was found to be an important factor that affects the bleachability of whole cotton stalk chemimechanical pulp, and the pectin removal contributed to improve brightness of the pulp. Compared with NaOH, $Na_2C_2O_4$ had a better ability to remove pectin and would not cause alkaline blackening, so it was judged to be an ideal depectinization agent.

For cotton stalk bark pretreated with 3% sodium oxalate, the removal rate of pectin reached 53.73％. The experimental effect of bleaching on whole cotton stalk chemimechanical pulp showed that when the parameters of preconditioning were only 3% sodium oxalate, 90 ^oC, and bleaching with 6.5% NaOH and 11% H_2O_2, the brightness of chemimechanical pulp from whole cotton stalk reached 76.18% ISO.

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