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Quality Improvement of Rayon Grade Bamboo Pulp by Modified Bleaching

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ABSTRACT

The presence of high silica in bamboo hinders the use of this material for production of rayon grade pulp. Research has been carried out to overcome this deficiency and improve quality of rayon grade pulp with the modification in pulping and bleaching process. Effect of acid boosted water prehydrolysis, sulphuric acid pre-treatment of unbleached pulp, chlorination stage at lower pH and treatment of bleached pulp with SO_2 water were evaluated. Acid boosted water prehydrolysis of chips reduces prehydrolysis time by 50 minutes as compared to water prehydrolysis. Treatment of unbleached pulp with sulphuric acid reduces ash, acid insoluble, silica, calcium and iron contents of the pulp by 56, 31, 82, 84 and 60% respectively. The addition of acid, increase in kappa factor in C_D stage and combination of both were effective in removing silica in the pulp. Treatment of final bleached pulp with SO_2 water removes silica to a great extent and improves optical properties of the pulp as compared to H_2SO_4 or PAA. Pretreatment of the pulp with acid and modification in the bleaching process can reduce silica substantially and improve the quality of rayon grade bamboo pulp.

***Keywords**: Bamboo, silica, prehydrolysis, pulping, bleaching, rayon grade pulp.*

1. INTRODUCTION

Rayon grade pulp is conventionally produced from softwood or mixed hardwoods like casuarina, subabul and eucalyptus etc., which contain very little ash and silica. Bamboo is an important raw material grown in Asian continent. But it contains very high silica, acid insolubles, calcium and iron as compared to softwoods and hardwoods. Production of dissolving grade pulp from bamboo is difficult with conventional pulping and bleaching methods due to the presence of high silica and pentosan.

Silica in the bamboo varies from 0.5 to 3.0% depending on the climate and species. Bamboo species

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produced in north-east region of India contains lower amount of silica as compared to the bamboo produced in central part of India. Several studies have been conducted worldwide to remove silica from the bamboo pulp, like strong acid hydrolysis of cellulosic and hemicellulosic materials (1), use of ethanol in prehydrolysis stage (2) and use of sodium carbonate in prehydrolysis stage (3) etc., but none of the above methods could be commercially exploited.

Recently there is an increased demand of viscose fibre made from bamboo. Bamboo fibre is termed "breathing" fabric as this fibre has special structures and natural "hollow" in the horizontal cross- sections. It has the characteristic of touching soft, dressing comfortably, smooth, good drapability and feeling cool etc. Additionally, the wearability and strength of this fabric are all very good. Viscose fiber of bamboo is used in the knitted underwear, T-shirt, the bed clothes woven by machine (4). The present paper deals with acid prehydrolysis and modification in the bleaching sequence for producing rayon grade pulp of acceptable quality from bamboo.

2. MATERIALS AND METHODS

Bamboo chips of species *Bambusa vulgaris* collected from central part of India were air dried and kept in the polythene bags to attain uniform moisture content which was determined as per the Tappi Test Method T 210 cm-03 before further processing of the chips.

For proximate chemical analysis of bamboo, sample was prepared as per Tappi test method T 257 cm-02 and T 264 cm-97. Hot water solubility, 1% NaOH solubility and Klason lignin of bamboo was determined as per Tappi test method T 207 cm-99, T 212 om-02 and T 222 om-02 respectively. Cellulose, hemicelluloses and holocellulose content of the bamboo were determined as per methods; Updegroff 1969, Deschatelets 1986 and Wise 1946 respectively. Ash and silica of raw material were determined as per Tappi test methods T 211 om-85 and T 244 om-88 respectively. DCM extractives, methanol solubility and total extractives of raw materials were determined as per Tappi test method T 204 cm-97 and T 264 cm-97 respectively.

Prehydrolysis and kraft pulping of bamboo chips was carried out in the series digester consisting six bombs of 2.5 l capacity each, rotating in an electrically heated polyethylene glycol bath. For hydrolysis, the temperature was increased from ambient to 170 ℃ in 90 min, maintained at this temperature for 90 or 140 min. Prehydrolysis liquor was drained from the bombs, and chips were further processed for kraft pulping. The pulping conditions like time, temperature, bath ratio and sulphidity were maintained similar for all the experiments. Maximum cooking temperature was 167 ℃. The temperature during pulping was increased from ambient to 167 ℃ in 90 min and maintained at this temperature for 200 min. The unbleached pulp was screened in laboratory Somerville screen with 0.15 mm slot width. Screened unbleached pulp was cleaned in the laboratory centricleaner. The centricleaned pulp was tested for kappa number, yield, brightness and viscosity as per Tappi test methods T 236 om-99, T 412 om-02, ISO 2470 and Tappi T 230 om-04 respectively. The unbleached pulp of kappa number ~15 were bleached with $C_DE_{OP}HDE_P$ sequence followed by SO_2 treatment in the laboratory. Bleached pulps were characterized for brightness, CIE whiteness, L*a*b* values, yellowness and post color number using Technibrite Brightness Meter (Model TB 1c). Low molecular weight carbohydrates (hemicelluloses and degraded cellulose) were analysed by extracting the pulp with 10, 18 and 21.5% sodium hydroxide solution at 25°C for 1 h as per Tappi T 235 cm-00. Alpha cellulose and rayon yield of bleached pulp was determined using same methods. Bleaching experiments were performed under constant conditions as indicated below:

Particular	C_D-Stage	E_{OP}-Stage	H-Stage	D-Stage	E_P-Stage
Consistency (%)	3.0	10.0	10.0	10.0	10.0
Temperature (℃)	amb	70	40	75	75
Time (min.)	45	120	120	180	120

3. RESULTS AND DISCUSSION

3.1 Proximate chemical analysis

Results of proximate chemical analysis show that *Bambusa vulgaris, Melocanna baccifera* and *Dendrocalamus strictus* contains 1.65, 0.51 and 3.0% silica respectively. *Bambusa vulgaris* has 27.0% lignin, 51.1% cellulose and 21.0% hemicelluloses. Detailed results of the proximate chemical analysis of different species of bamboo are given in Table 1.

3.2 Prehydrolysis and kraft pulping

To reduce silica in the pulp, prehydrolysis of the bamboo chips was carried out with conventional water prehydrolysis as well as with water prehydrolysis boosted with sulfuric acid. pH of acid boosted prehydrolysate was 3.4 whereas the same was 3.6 with water only. It was found that sulphuric acid in prehydrolysis stage reduced pre-hydrolysis time by 50 min compared to prehydrolysis with water without affecting pulp properties and silica. There was no adverse impact of acid prehydrolysis on other pulp properties. Conditions of prehydrolysis and results thereof are given in Table 2.

Table 1. Proximate chemical analysis of bamboo

Parameter	*Bambusa vulgaris*	*Melocanna baccifera*	*Dendrocalamus strictus*
Hot water solubility (%)	3.50	4.19	3.37
1% NaOH solubility (%)	19.23	20.25	19.21
Methanol solubility (%)	2.95	4.09	2.59
A-B extractives (%)	1.45	2.40	0.94
DCM extractives (%)	0.58	0.59	0.43
Cellulose (%)	51.10	52.78	52.80
Hemicelluloses (%)	21.00	23.20	21.80
Klason lignin (%)	27.00	25.30	27.30
Holocellulose (%)	71.61	75.53	71.09
Ash (%)	3.35	2.42	4.40
Silica (%)	1.65	0.51	3.00

Table 2. Prehydrolysis and kraft pulping of bamboo

Parameter	Water prehydrolysis boosted with H_2SO_4	Water prehydrolysis
Sulphuric acid used (%)	0.3	--
Time to max. temp.(min)	120	120
Time at max. temp.(min)	90	140
pH of hydrolyses water	3.4	3.6
Screened pulp yield (%)	32.6	32.5
Screen rejects (%)	0.2	0.2
Kappa number	14.5	15.2
Free alkali as Na_2O (g/l)	8.97	8.43
Pentosan in pulp (%)	3.1	3.1

Bath ratio: 1:3, prehydrolysis temperature: 170°C, AA in cooking: 19%, sulphidity: 22.6%.

Kraft pulping of prehydrolyzed bamboo chips was conducted with 19.0% active alkali as Na_2O. Unbleached pulp of kappa number 14.5 and 15.2 was obtained respectively with acid boosted and normal water prehydrolysis respectively. 3.1% pentosan in unbleached pulp in both the cases was obtained. Results of pulping of bamboo are given in Table 2.

3.3 Bleaching

Unbleached pulps produced with acid boosted and water prehydrolysis were bleached with $C_DE_{OP}HDE_P$ sequence followed by SO_2 treatment. Acid treated pulps showed slightly better bleaching response as impurities like acid insoluble and silica in the acid treated pulp was lower as compared to water prehydrolysis pulp. Bleaching of pulp made with both acid boosted and water prehydrolysis with conventional sequence of $C_DE_{OP}HDE_P$ showed high level of ash, acid insoluble and silica in the pulps. However final brightness, whiteness and pentosans, iron and calcium content were within the acceptable limit (Table 3). Results of bleaching of bamboo are given in Table 4.

Table 3. Acceptable limit of impurities in rayon grade pulp

Parameter	Value
Pentosan (%)	~3.0
Ash content (%)	0.06-0.08
Acid insoluble (ppm)	< 160
Silica (ppm)	80-120
Calcium (ppm)	40-60
Iron (ppm)	20-40

Final pulp brightness +90%, CIE Whiteness +80.

Table 4. Bleaching of bamboo pulps

Parameter	Acid treated	Control
Kappa number	14.5	15.2
C_D stage		
Kappa factor	0.22	0.22
E_{OP} stage		
NaOH/ H_2O_2 added (%)	2.3/0.5	2.3/0.5
H stage		
Hypo added (%)	1.5	1.5
D stage		
ClO_2 added (%)	0.9	0.9
Brightness (% ISO)	87.8	87.3
E_P stage		
NaOH/ H_2O_2 added (%)	0.7/0.5	0.7/0.5
Brightness (% ISO)	88.8	88.1
SO_2 treatment		
Final brightness (% ISO)	90.5	89.6
Whiteness (% CIE)	82.3	80.2
Ash (%)	0.1	0.11
Acid insoluble (ppm)	274	308
Silica (ppm)	158	160
CaO (ppm)	45	50
Iron (ppm)	30	40
Pentosan (%)	2.75	2.9

3.4 Analysis of ash at different stages of bleaching

Pulp from different stages of the bleaching was analysed for ash, acid insoluble, silica, calcium and iron content to observe the efficiency of silica removal in each individual stage. Results showed that silica removal was more in the acidic stage of bleaching process. Results of ash analysis of pulp at different stages of bleaching are given in Table 5.

3.5 Modifications in bleaching sequence

3.5.1 Acid pretreatment of pulp

Acid treatment prior to bleaching is reported for

Table 5. Ash and other metallic impurities in pulp at different stages of bleaching

Parameter	Unbld	C_D stage	E_{OP} stage	H stage	D stage	E_P stage	Final pulp
Ash (%)	2.92	1.45	1.17	1.24	0.58	0.49	0.11
Acid insoluble (ppm)	14880	9915	5640	6360	3990	2945	890
Silica (ppm)	2390	1785	1145	1545	960	710	320
CaO (ppm)	3584	1190	1120	1960	462	168	56
Iron (ppm)	250	75	50	50	37	25	12

paper grade pulps to decrease brightness reversion and chlorine/chlorine dioxide consumption (5-9). The effect of acid pretreatment of unbleached pulp was studied to reduce the silica content in pulp, as silica removal was found to be higher in the acidic bleaching stages.

3.5.1.1 Effect of acid dose on different pulp properties

Different dosages of sulphuric acid; 5, 10, 15 and 20 kg/t of unbleached pulp were used in the acid pre treatment of pulp. Acid dose of 20 kg/t was found to be most effective in removal of silica in the pulp. Effect of acid dosage on ash, acid insoluble, silica, calcium and iron content is shown in Fig. 1.

3.5.1.2 Effect of duration of acid treatment on different pulp properties

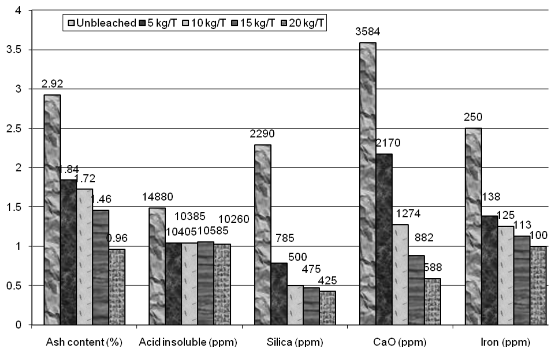

Fig. 1. Effect of acid dose on pulp properties.

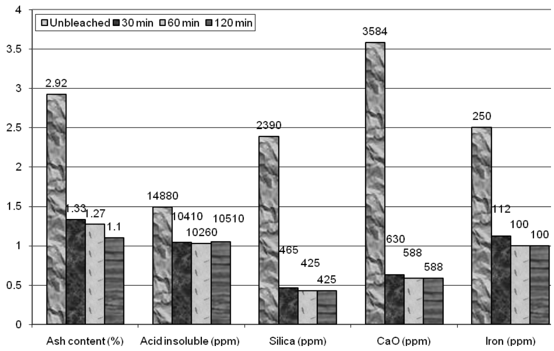

Fig. 2. Effect of duration of acid treatment on pulp properties.

Unbleached bamboo pulp was treated with 20 kg/t of acid dosage for 30, 60 and 120 minute retention time. 60 minutes duration was found to be effective in removal of silica in pulp. Effect of duration of treatment on ash, acid insoluble, silica, calcium and iron in the pulp is shown in Fig. 2.

3.5.1.3 Effect of temperature during acid treatment on different pulp properties

Unbleached bamboo pulp was treated with 20 kg/t of acid dosage for retention time of 60 min at 40^{o}C, 50^{o}C and 60^{o}C temperature. Treatment temperature of 40^{o}C was found optimum. Effect of temperature during acid treatment on ash, acid insoluble, silica, calcium and iron content of the pulp are shown in the Fig. 3.

3.5.1.4 Optimized conditions for acid treatment of pulp

On the basis of experiments on acid pretreatment, the conditions are optimized which are given in Table 6.

Table 6. Optimized conditions for acid treatment

Parameter	Value
Chemical (H_2SO_4) dosage (%)	2.0
Treatment time (min)	60
Treatment temperature (℃)	40
Consistency (%)	5

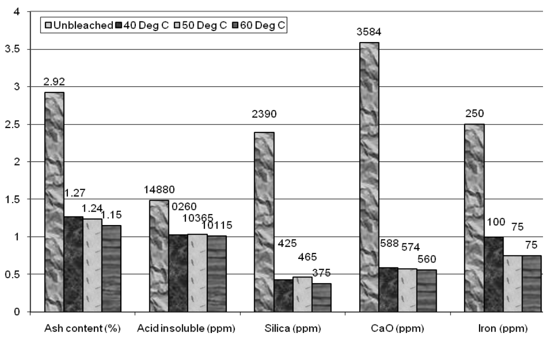

Fig. 3. Effect of temperature during acid treatment on pulp properties.

Table 7. Properties of the pulp after post bleaching treatments.

Parameter	SO_2 water	H_2SO_4	PAA
Brightness, %	89.7	89.0	88.3
CIE whiteness	78.9	78.1	77.6
Ash content (%)	0.064	0.099	0.132
Acid insoluble (ppm)	506	654	753
Silica (ppm)	205	281	336
CaO (ppm)	45	76	152
Iron (ppm)	32	36	42

Treatment time: 60 min, initial pH 2.0

3.5.2 Effect of pH in C_D stage

pH of C_D stage was varied from 2.2 to 1.6 to see its effect on removal of silica in pulp. Silica content was lowest at pH 2.0 in the pH range of 2.2 to 1.6. Effect of pH in C_D stage on ash, acid insoluble, silica, calcium and iron in the pulp are shown in Fig. 4.

3.5.3 Effect of kappa factor (KF)

Kappa factor in C_D stage was increased from 0.22 to 0.25 and 0.28 to see its effect on removal of silica in pulp. Reduction in silica was higher when kappa factor was 0.25 as compared to that of 0.22, whereas not much difference was observed in the silica content and other properties of the pulp at kappa factor 0.25 and 0.28. Effect of kappa factor on acid insoluble, silica, calcium and iron content of the pulp is shown in the

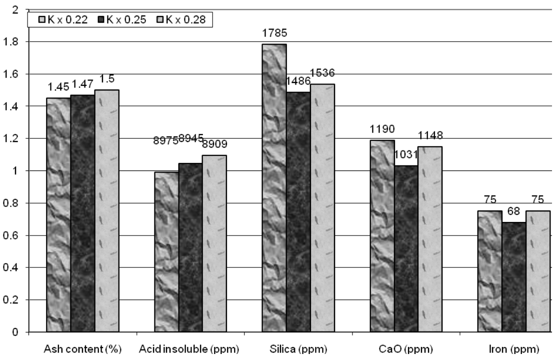

Fig. 5. Effect of kappa factor on pulp properties.

Fig. 5.

3.5.4 Effect of variation of pH in D stage

pH in D stage was varied from 3.0 to 4.0 to see its effect on removal of silica in pulp. By varying the pH in D stage insignificant difference was observed in the silica in the pulp and its other properties. Effect of variation in pH of D stage on ash, acid insoluble, silica, calcium and iron content of the pulp are shown in the Fig. 6.

3.5.5 Post bleaching treatment

A few other chemicals were applied on the final bleached pulp like sulfuric acid and per acetic acid (PAA) to see its effect on removal of silica in pulp. It is reported that use of per acetic acid at ambient

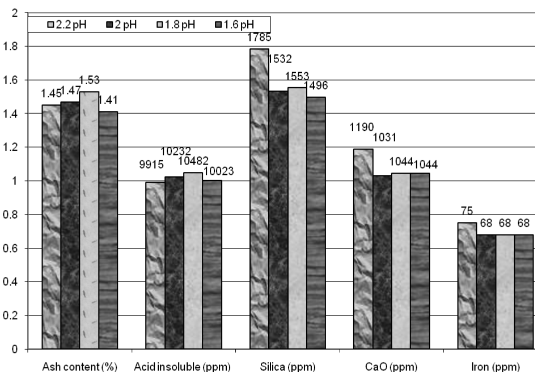

Fig. 4. Effect of pH in C_D stage on pulp properties.

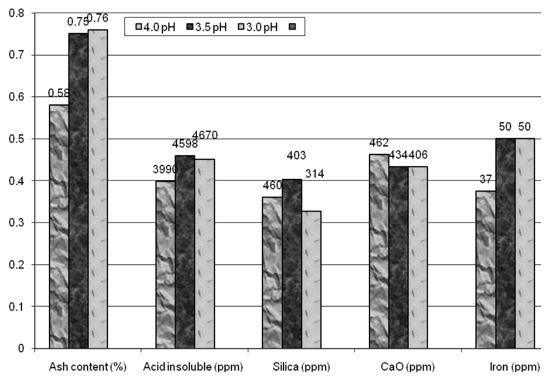

Fig. 6. Effect of variation in pH of D stage on pulp properties.

temperature increased the final pulp brightness by 1.0-1.5 points and whiteness by 2.0-3.5 points (10). Treatment of final bleached pulp with SO_2 water or H_2SO_4 was more efficient as compared to PAA treatment in the removal of silica and improving optical properties of the pulp. SO_2 water was more effective compared to H_2SO_4. Properties of the pulp after post bleaching treatments are given in Table 7.

3.6 Implementation of modifications in bleaching sequence

Unbleached bamboo pulp was bleached with the modified bleaching sequence; C_D stage was carried out at pH 2.0 with kappa factor of 0.25, with and without acid pretreatment of the unbleached pulp and compared with conventional bleaching sequence. By pre-treating the pulp with acid and varying the process conditions of bleaching, rayon grade pulp was obtained with more than 90% ISO brightness, 80 CIE whiteness, 0.07% ash, acid insolubles below 160 ppm, silica 100-110 ppm, calcium 28-40 ppm and iron 25 ppm. α -cellulose and rayon yield of the pulp improved from 94.7 to 95.3% and 96.9 to 97.2% respectively with the acid treatment of pulp and modified bleaching. Results in detail are given in Table 8.

4. CONCLUSIONS

Use of sulphuric acid in prehydrolysis stage reduces prehydrolysis time from 140 minutes to 90 minutes. It marginally improves bleachability of the pulp.

Treatment of unbleached pulp with sulphuric acid reduces ash, acid insoluble, silica, calcium and iron. Addition of acid, increase in kappa factor in C_D stage and their combination are effective in removing silica from the pulp.

Treatment of final bleached pulp with SO_2 water removes silica to a great extent and improves optical properties of the pulp.

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Table 8. Properties of bamboo pulp

Particular	CBS	All Mod.	A – all Mod.
Brightness (% ISO)	89.5	90.0	90.2
CIE whiteness	79.9	80.2	80.7
ASTM yellowness	5.5	5.4	5.3
Ash (%)	0.11	0.07	0.07
Acid insoluble (ppm)	300	160	150
Silica (ppm)	175	110	100
CaO (ppm)	49	42	28
Iron (ppm)	37.5	25	25
Hemicelluloses and degraded cellulose	5.3	4.7	4.7
α- Cellulose (%)	94.7	95.3	95.3
Rayon yield (%)	96.9	97.2	97.2

CBS – C_D E_{OP} H D E_P (SO_2)
All Mod. – C_D (pH-2.0, KF-0.25) E_{OP} H D E_P (SO_2)
A-all Mod. – A C_D (pH-2.0, KF-0.25) E_{OP} H D E_P (SO_2)

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