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Biochemical softening of cotton plant stalk for production of pulp and paper

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ABSTRACT : In India cotton plant stalk is treated as waste. Cotton plant stalk is rich in cellulose. The biochemical pre treatment completely replaces the conventional thermo mechanical pulping process. The cocktail of enzymes in the active system elaborated mostly by anaerobic microorganisms assisted by the presence of aerobic flora are responsible for softening the lignocellulose complex. The paper produced will be comparatively cheaper and will help in the proper utilization of this agrowaste.

Key words : Biopulp, cotton plant stalk, paper

Cotton plant stalk is a byproduct of cotton cultivation and is available at around 30 million tonnes annually in India. It is being used as fuel by the rural people to a limited extent, while the bulk of the stalk is treated as waste. This could be of use as raw material for many useful purposes. Therefore, attempts were made to develop technology using cotton plant stalk for the preparation of particle boards, binderless boards (Chaubal *et al.,* 2011) for growing edible mushrooms. In addition, a process has been developed to prepare various grade of pulp and paper from cotton plant stalk. The different types of papers produced from cotton plant stalk had properties *on par* with those produced from hard wood. To, the pulp maker, lignin is the unwanted ingredient that creates most problems during pulping. Delignification is the foremost goal of pulping. Delignification is achieved by mechanical action alone or by thermal and mechanical action, chemical and mechanical action or by complete chemical action.

All these pulping processes consume intensive amount of energy. The chemical used for the degradation of lignin result in environmental pollution on a large scale. Thus, new methods to reduce both energy requirement and pollution outputs are being searched continuously. A process has been developed for the preparation of pulp through biological softening of lignocellulosic raw materials by anaerobic treatment (Khandeparkar *et al.*, 1993).

Biotechnology promises new approach for the pulp and paper industry. Practical application of biodelignification is removal of lignin by microorganism in pulping, hold a great promise for future use in the industry (Kirk *et al.*, 1994). In view of this, biotreatment to lignocellulosic materials for softening appears to be more attractive, economical and ecologically safe. Pulp and paper preparation employing biochemical pre treatment and post treatment under anaerobic condition replacing the conventional process is carried out under this study.

MATERIALS AND METHODS

Cotton plant stalk (*Gossypium hirsutum*) was procured from Central Institute for Cotton Research, Nagpur. All the chemicals used were of analytical reagent grade. Methods used for analysis were TAPPI standard test methods under standard conditions. The instruments used for evaluating the various physical properties of pulp and paper are canadian standard freeness tester, bursting strength tester, universal tensile tester, elmendorf tearing tester, MIT double fold endurance tester.

Preparation of biopulp :

Pre treatment : The cotton stalk chips (100 g) were open boiled at 100^0C with sodium hydroxide (1 - 4%) on the weight of the material

keeping material to liquor ratio 1:10 for 30 min. The cooked material was washed with tap water and then subjected to anaerobic treatment.

Anaerobic treatment : Cotton stalk chips were subjected to 1, 2, 3 and 4 weeks of anaerobic treatment. The microbial consortium contains both aerobic and anaerobic organisms given below (Table 1).

Table 1. Anaerobic and organisms

	Aerobic	Anaerobic
Bacteria	*Bacillus* *Enterobacter* *Pseudomonas* *Acinetobacter* *Beijerinckia*	*Clostridium* *Methanomicrobium* *Methanothrix* *Desulfotomaculum*
Fungi	*Erwinia* *Aspergillus* *Penicillium*	Blue green and green algae, Rumenfungi, protozoa and Phototrophicbacteria are also present
Actinomycetes	*Streptomyces* *Nocardia*	
Yeast	*Pichia*	

Post alkali treatment : The biologically treated cotton stalk chips were washed thoroughly with water and then given a post alkali treatment by boiling the digested material with 1 per cent sodium hydroxide on the weight of the material keeping material to liquor ratio 1:10 for 30 min and washed thoroughly with water.

Biopulp : The biochemically softened cotton plant stalk was converted into pulp by refining in a disc refiner and beating in a valley beater for (30-80 min.) to get the pulp of desired freeness *i.e.* 250 canadian standard freeness. The pulp was screened on a flat screen to remove the fibre bundles, which was dried in an oven and weighed as rejects. The prepared pulps were evaluated for unscreened yield, screened yield, rejects per centage and beating time.

Bleaching of biopulp : Fifty of pulp was bleached by employing a three step bleaching cycle, namely i) Chlorination ii) Alkali Extraction and iii) Hypochlorite. The bleached pulp was washed thoroughly with water till free of chlorine followed by a treatment with 1 per cent solution of sodium metabisulfite (an anti chlorine agent) for 30 min and washed thoroughly. The details of the bleaching conditions are given in Table 2.

Preparation of paper sheet : Standard paper sheets of 60 ± 1 g/m^2 were prepared from unbleached and bleached pulps on a British Standard sheet making machine. The paper sheets were dried in air, and then conditioned at 65 per cent R. H. and 27^{0}C for 2 h and were evaluated for various properties such as burst factor, tear factor, breaking length, folding endurance, brightness etc. as per TAPPI Standard test methods.

RESULTS AND DISCUSSION

The properties of the unbleached and bleached pulp prepared are given in Table 3. The unscreened yield of the pulps showed a gradual decrease with an increase in the concentration of alkali employed in the pretreatment, that is, 1 to 4 per cent NaOH, as well as with the duration of the anaerobic treatment from 1 to 4 weeks. The unscreened yield decreased from a level of 85 per cent (1 per cent NaOH in 1 week) to 49 per cent (4 per cent NaOH in 4 weeks). However, the pulps showed a gradual improvement in quality as indicated by the decreasing trend in the reject per centage and improvement in brightness levels. The reject per centage decreased from 16 per cent (1 per cent NaOH in 1 week) to almost traces when the concentration of alkali as well as the period of treatment was increased to 4 per cent and 4 weeks of anaerobic treatment, respectively. The screened yield varied from 69 per cent (1per cent NaOH in 1 week) to 49 per cent (4 per cent NaOH in 4 weeks). The degree of softening due to biological treatment can be evaluated indirectly from the time required for beating the pulp to the same level of freeness *i. e.* (250 ± 1 CSF). The beating time gradually decreased from a level of 73 min for pulp (1 per cent NaOH in 1 week) to 30 min for pulp (4 per cent NaOH in 4 weeks); clearly

Table 2. Details of bleaching conditions of biopulp

Step I Chlorination stage	
Hypochlorite as available Cl_2 added (% on pulp)	5.0
Consistency (%)	10
Temperature (^0C)	45
Time (min)	60
Sulfamic acid (H_3NSO_3) (%) on pulp.	0.05
Final pH	8.0
Hypochlorite as available Cl_2 consumed (%)	5.0
Step II Alkali extraction stage	
NaOH added (% on pulp)	1.2
Temperature (^0C)	55
Consistency (%)	5
Time (min)	60
Final pH	8.9
Step III Hypochlorite stage	
Hypochlorite as available Cl_2 added (% on pulp)	2.0
Consistency (%)	10
Temperature (^0C)	45
Time (min)	90
Sulfamic acid (H_3NSO_3) (%) on pulp.	0.07
Final pH	7.9
Hypochlorite as available Cl_2 consumed (%)	2.0
Total Cl_2 added and consumed (% on pulp)	7.0

indicating a direct relationship between the degree of softening, alkali concentration and duration of anaerobic treatment. Lower the concentration of alkali used in the pretreatment, longer will be the period of anaerobic treatment to get good quality pulp. Similarly, by use of higher concentration of alkali in the pretreatment, the duration of anaerobic treatment can be brought down.

The bleached pulp yield decreased from 60 to 41 per cent while, the brightness improved from 56 to 78 per cent. Similarly, for unbleached pulp the brightness varies from 31 to 55 per cent, when the concentration of alkali used in the pretreatment increased from 1 to 4 per cent, and the period of treatment from 1 to 4 weeks. The properties of unbleached and bleached paper sheets showed a gradual improvement with increase in the concentration of chemicals used in the pretreatment as well as with the duration of anaerobic treatment. Similarly, on bleaching, the paper sheets showed improvement in strength properties such as burst factor, breaking length, tear factor and number of double folds, as compared to unbleached paper due to better

Table 3. Properties of biopulp prepared from cotton plant stalks

Treatment	Unscre-ened yield (%)	Scree-ned yield (%)	Rejects (%)	Refining (no. of passes)	Beating time (min)	Free-ness (CSF)	Bright-ness unbleached (%)	Blea-ched yield (%)	Brightness bleached (%)
NaOH (1%)	87	69	18	2	80	250±1	28	61	55
NaOH (1%) + 1 week*	85	69	16	2	73	250±1	31	60	56
NaOH (1%) + 2 weeks*	80	67	13	2	65	250±1	35	58	62
NaOH (1%) + 3 weeks*	75	65	10	2	57	250±1	35	58	65
NaOH (1%) + 4 weeks*	69	62	7	2	50	250±1	41	55	71
NaOH (2%)	83	68	15	2	73	250±1	30	58	57
NaOH (2%) + 1 week*	78	64	14	2	69	250±1	33	55	59
NaOH (2%) + 2 weeks*	70	59	11	2	61	250±1	38	52	64
NaOH (2%) + 3 weeks*	65	57	8	2	53	250±1	45	50	69
NaOH (2%) + 4 weeks*	60	55	5	2	40	250±1	49	48	73
NaOH (3%)	78	65	13	2	65	250±1	35	56	57
NaOH (3%) + 1 week*	70	61	9	2	60	250±1	38	53	60
NaOH (3%) + 2 weeks*	65	58	7	2	56	250±1	43	50	67
NaOH (3%) + 3 weeks*	58	54	4	1	43	250±1	48	47	71
NaOH (3%) + 4 weeks*	50	48	2	1	37	250±1	52	45	79
NaOH (4%)	74	63	11	1	62	250±1	35	52	61
NaOH (4%) + 1 week*	68	59	9	1	50	250±1	39	47	64
NaOH (4%) + 2 weeks*	57	54	3	1	41	250±1	46	44	68
NaOH (4%) + 3 weeks*	52	50	2	1	35	250±1	50	43	73
NaOH (4%) + 4 weeks*	49	49	Traces	1	30	250±1	55	41	78

CSF = Canadian Standard Freeness * Anaerobically treated followed by 1percent post alkali treatment

fibrillar bonding. The residual lignin present in the unbleached pulps generally interferes with the fibrillar bonding and thereby, results in the formation of paper having poor strength properties. During bleaching, maximum delignification takes place, resulting in better fibrillar bonding during paper formation, resulting in better strength properties of paper.

The properties of paper sheets prepared from biologically softened cotton plant stalks are given in Table 4. The strength properties of both the bleached and unbleached papers showed a gradual improvement with increase in the concentration of alkali employed in the pretreatment as well as with the duration of anaerobic treatment. These results confirm the findings of Balasubramanya *et al.,* (2006).

In the case of unbleached paper, the burst factor improved gradually from 4.8 to 31.6, breaking length from 1210 to 3480 m, tear factor from 62 to 117, double fold from 2 to 78., while brightness improved from 31 to 55 per cent when the concentration of alkali was increased from 1 to 4 per cent and the duration of anaerobic treatment extended from 1 to 4 weeks. Nagarkar *et al.,* (2012) reported the similar findings for burst factor, breaking length, tear factor and double fold for unbleached kraft paper prepared by chemical process using 16 per cent kraft liquor.

In the case of bleached paper, the burst factor improved gradually from 6.9 to 38.2, breaking length from 1422 to 3746 m, tear factor from 79 to127, double fold from 5 to 95 No., while brightness improved from 56 to 78 per cent when the concentration of alkali was increased from 1 to 4 per cent and the duration of anaerobic treatment extended from 1 to 4 weeks.

The quality of paper produced using lower concentration of alkali and shorter period of anaerobic treatment was inferior. Being hard material, cotton stalks require higher concentration of alkali and longer period of digestion (Balasubramanya *et al.*, 2006). The properties of paper sheets produced by biochemical process were compared with the ones produced by employing chemical process, the paper sheets produced using 4 per cent alkali

Table 4. Properties of paper made from biologically softened cotton stalks (CSF = 250 ± 1)

Treatment	GSM	Burst factor		Breaking length (m)		Tear factor		Double folds (no.)		Brightness (%)	
	(g/m^2)	UB	B	UB	B	UB	B	UB	B	UB	B
NaOH (1%)	60 ± 1	4.0	5.8	1150	1323	45	56	2	5	28	55
NaOH (1%) + 1 week*	60 ± 1	4.8	6.9	1210	1422	62	79	2	5	31	56
NaOH (1%) + 2 weeks*	60 ± 1	5.6	7.8	1900	2170	88	102	11	19	35	62
NaOH (1%) + 3 weeks*	60 ± 1	7.3	9.3	1980	2002	90	107	13	30	35	65
NaOH (1%) + 4 weeks*	60 ± 1	9.4	12.1	2160	2323	96	110	21	20	41	71
NaOH (2%)	60 ± 1	4.1	6.2	1810	2068	81	96	4	10	30	57
NaOH (2%) + 1 week*	60 ± 1	9.8	14.1	2170	2309	84	98	5	10	33	59
NaOH (2%) + 2 weeks*	60 ± 1	10.1	14.8	2210	2349	91	113	28	41	38	64
NaOH (2%) + 3 weeks*	60 ± 1	12.8	15.6	2380	2537	106	128	30	35	45	69
NaOH (2%) + 4 weeks*	60 ± 1	16.6	19.5	2410	2634	134	155	48	63	49	73
NaOH (3%)	60 ± 1	6.0	8.2	1980	2259	72	83	8	14	35	57
NaOH (3%) + 1 week*	60 ± 1	9.7	14.6	2320	2523	72	87	20	29	38	60
NaOH (3%) + 2 weeks*	60 ± 1	10.3	14.8	2150	2389	98	123	31	41	43	67
NaOH (3%) + 3 weeks*	60 ± 1	16.4	19.5	2415	2634	133	155	55	63	48	71
NaOH (3%) + 4 weeks*	60 ± 1	15.3	20.61	2370	2637	137	158	58	65	52	77
NaOH (4%)	60 ± 1	6.8	8.5	2440	2645	73	87	16	24	35	61
NaOH (4%) + 1 week*	60 ± 1	16.1	20.1	2810	3335	117	127	24	34	39	64
NaOH (4%) + 2 weeks*	60 ± 1	22.0	26.5	3190	3463	89	102	26	37	46	68
NaOH (4%) + 3 weeks*	60 ± 1	23.9	28.2	3360	3602	88	102	67	85	50	73
NaOH (4%) + 4 weeks*	60 ± 1	31.6	38.2	3480	3746	117	127	78	95	55	78

UB = Unbleached* Anaerobically treated followed by 1percent post alkali treatment B= Bleached GSM, sq. mt

pretreatment followed by 1 week anaerobic treatment and 1 per cent post alkali treatment had properties *on par* with those prepared by chemical process.

Therefore, the most ideal cooking conditions that can be recommended for adoption in respect of cotton stalks can be pretreatment with 4 per cent alkali followed by 1 week anaerobic treatment and 1 per cent post alkali treatment. Chemical and energy requirements: energy and chemical requirement for pulping of 100 kg of cotton plant stalk both by chemical process as well as by anaerobic treatment is studied. The study clearly indicated that the thermal energy required in chemical pulping of cotton plant stalks is 221.03 MJ/day, electrical energy required is 15 KWh/day and the chemical requirement is 16 kg. While the corresponding values for anaerobic processes are very low i.e. 115.34 MJ/day, 3-5 KWh/day electrical energy and only 5 kg of chemicals.

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