

BIOPULPING AND ITS POTENTIAL TO REDUCE EFFLUENT LOADS FROM BLEACHING OF HARDWOOD KRAFT PULP

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Mixed hardwood chips were treated with lignin-degrading fungi to study the effect of fungal pretreatment on bleaching characteristics of kraft pulp. Pretreated wood chips were subjected to reduced active alkali doses in comparison to untreated chips. Comparable results were obtained for pretreated chips with reduced alkali dose as was obtained with higher dose of alkali in case of untreated chips. Fungal treatment made the process more energy-efficient, and 4.8% less chlorine was consumed in comparison to the control process. Pretreatment with *Ceriporiopsis subvermispora* was responsible for reduction of 4.7% in lignin contents, 14.3% permanganate number, and overall reduction of 15.5 kg/T of Cl₂ consumption. The pollution load in terms of COD and BOD at the C_D stage was reduced by 32.6% and 41.5% respectively, whereas 12% reduction in AOX compounds was observed in effluent of pretreated pulp.

Keywords: Biopulping; Hardwood; Kraft pulp; Lignin degrading fungi; Pollution load

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INTRODUCTION

The pulp and paper industries have been categorized as one of the major sectors that pose a threat to the environment. Economic conditions and environmental pressures have hit the pulp and paper industry hard, and it has been under tremendous pressure to improve the performance related to release of pollutants. Increased environmental concerns are creating pressure for adoption of new, eco-friendly technologies (Dhiman et al. 2009). An integrated pulp and paper process includes the general steps of pulping, bleaching, and paper production. The production of the chemical pulps has been dramatically altered over the past decade in response to new environmental regulations and consumer activism (Sabharwal 1988; Oriaran 1990a).

Two of the most promising technologies for delignification of high lignin pulps are (i) oxygen delignification, and (ii) modification of pulping process through biological means. Use of fungal inoculums prior to pulping offers an attractive opportunity for mechanical wood pulp facilities. This technology could save energy in the refining of mechanical pulp (Shukla et al. 2004). Likewise, in the case of chemical pulping a biological method can be used to facilitate the removal of lignin from wood by modifying lignin for easier extraction in subsequent chemical pulping processes (Castillo et al. 2000; Field 2000).

The use of suitable lignin-degrading fungi can result in saving of electrical energy during mechanical pulping, and paper strength properties also can be improved (Kondo et al. 1996). About 75% of the pulp in the world is produced by the kraft pulping process. This process produces paper with very high strength. However, the process has the disadvantages of being capital and energy intensive, low in yield of production, producing troublesome waste products, and producing byproducts that are of relatively low value (Kondo et al. 1994).

Biotechnology offers a potential solution to many of these problems (Battan et al. 2007). Biopulping, in the form of pretreatment of wood chips prior to conventional pulping, offers the potential for both economic and environmental benefits. Use of white rot fungus (*Phanerochaete sordida* YK624) has been studied to remove lignin in unbleached hardwood kraft pulp and as a bio-bleaching agent (Kondo et al. 1994). Similar results also have been observed with *Phanerochaete chrysosporium*, where reduction in lignin contents was observed (Labosky et al. 1991). However, little work has been done on biokraft and biosulfite pulping (Scott et al. 1996). Two sequential biopulping consortia comprising the USDA Forest Service, Forest Products Laboratory (FPL), and the Universities of Wisconsin and Minnesota have established the technical and economic feasibility of biomechanical pulping (Akhtar et al. 1997, 1998).

In the present investigation the effect of fungal pretreatment on hardwood chips was investigated. Pretreated chips were subjected to reduced active alkali dose with different combinations of cooking conditions. Further effects of pretreatment on consumption of oxidizing chemicals and physical properties of biokraft pulp were also investigated.

EXPERIMENTAL

Fungus Collection and Maintenance

Lignin-degrading fungal cultures of *Ceriporiopsis subvermispota* L-14807-SS-3 were provided by the Thapar Center for Industrial Research and Development, India. The cultures were maintained on potato dextrose agar (PDA) slants at 30 ± 1 °C and glycerated frozen stock at -20 °C.

Pretreatment of Wood Chips

PDA plates were inoculated with selected strains under aseptic conditions. These plates were further used to inoculate liquid media (2.4% of potato dextrose broth; 0.75% of yeast extract) and incubated at 27 ± 1 °C for 12 days. A thick mat was observed on the surface of media due to the growth of fungal culture. Fungal mats were recovered by washing with sterilized saline water on a sterilized Büchner funnel. With the help of a sterilized blender, mycelium was blended to obtain a homogenous suspension. Diluted suspension was used for inoculation of mixed wood chips (moisture content 65%, oven dried basis).

Experiments were conducted with mixed chips of eucalyptus and poplar wood. This combination of wood is the best source of fibrous material for pulp making, and it is being used in many paper mills in India (Messner et al. 1992; Shukla et al. 2004). Wood

chips were dried to adjust the moisture contents to 10–12%, and pretreatment was carried out in a 25 liter aerated bed bioreactor. For fungal pretreatment, 1000 g O.D (oven dry) of sterilized mixed wood chips were used, and about 7.0 mg (dry weight) of the fungal suspension (7 g/ T of wood material) and corn steep liquor (CSL, 0.6% on dry weight basis) were added to the bioreactor and mixed thoroughly with a sterile big spoon.

Wood chips were incubated at 30–35 °C for optimal growth of fungus. The bioreactor was aerated with humidified air at 30 l/ h rate for 3 weeks. The compressed air was passed through a sterilized air filter to avoid any contamination. After incubation, fungus colonized the wood, leading to softening and swelling of fiber walls. Before pulping, fungal treated mixed wood chips were extracted from the bioreactor, weighed, sampled for moisture content, and determination of cellulose, hemicelluloses, holocellulose, and lignin (Table 1) was carried out. The residual lignin content was determined as Klason lignin (TAPPI Method T222), and the cellulose content was determined according to TAPPI Method T249.

Table 1. Effect of Fungal Treatment with *C. subvermispora* I–14807–SS–3 on the Cellulose, Hemicellulose, and Lignin Content of Mixed Wood Chips

Component (%)	Control	Fungal pretreated
Cellulose	42.2	44.5
Hemicellulose	21.3	22.5
Lignin	27.7	26.4
Holocellulose	69.2	70.3
Bulk Density	215	–

Kraft Pulping and Bleaching

Alkaline hydrolysis reactions reduce the molecular weight of the lignin structures and also remove the methoxyl groups, causing formation of phenolate ions. During kraft pulping, the bisulfide ion participates in the ‘blocking’ reaction and inhibits lignin condensation reactions that impair the removal of lignin. In essence, bisulfide ions function as pulping catalyst, and thus speed up the delignification. Pulping at high sulphidity during the kraft process shortens the reaction time compared to pulping with pure sodium hydroxide (soda process) or by pulping at low sulphidity. Thus the viscosity of brown stock is higher because of the reduction in pulping time. This elevated viscosity is often preserved across the bleach plant with modern mills that use predominately ClO₂ as the bleaching agent.

The mixed wood chips were cooked with 16% A.A (Active Alkali) and reduced alkali as Na₂O with 21.5% sulphidity, with a wood-to-liquor ratio of 1:3 at 160 °C for 120 minutes (Table 2). Physical and strength properties of the unbleached pulp were observed after cooking (Table 3). The most extensively used bleaching sequence, C_DE_{OP}D₁D₂ (C_D–chlorine and chlorine dioxide; E_{OP}–extraction with oxygen and hydrogen peroxide; D₁ and D₂–chlorine dioxide) was followed for kraft pulp.

Table 2. Effect of Cooking Schedule and Active Alkali Dose on the Properties of Kraft Pulp

Particular	Unit	Control (16% AA ^c)	Pretreated		
			16% AA ^c	14% AA ^c	12% AA ^c
Sulphidity	%	21.5	21.5	21.5	21.5
Bath ratio	1:3	1:3	1:3	1:3	1:3
Maximum temp.	°C	160	160	160	160
Cooking schedule					
Time to 100 °C	Minute	20	20	20	20
Venting time		10	10	10	10
Time for 100 to 130 °C		30	30	30	30
Time at 130 °C		60	45	50	60
Time for 130 to 160 °C		60	60	60	60
Time at 160 °C		120	100	110	120
Kappa Number		21.0	18.0	20.1	
Screened yield	%	48.9	48.6	48.7	48.8
Pulp properties					
Unbleached brightness	% ISO ^a	38.9	41.5	41.4	39.0
Viscosity	Cps ^b	18.4	18.8	18.9	19.5

a – International Standard Organization; b – Centipoises; c – Active alkali dose (%)

Table 3. Strength Properties of Biokraft Pulp after Pretreatment with *C. subvermispora*

Parameter	Unbleached			
	Control	Pretreated		
	16% AA ^a	16% AA ^a	14% AA ^a	12% AA ^a
Wetness (°SR)	31	32	31	30
PFI mill beating time (Min.)	37	29	34	38
Tensile index (Nm/g)	43.8	49.8	53.5	55.1
Breaking length (m)	4450	4980	5260	5325
Burst index (kN/g)	2.2	2.9	3.1	3.7
Tear index (mNm ² /g)	6.0	6.3	7.16	7.46
Double fold (No.)	8.0	12.0	13.4	14.5

a – Active alkali dose (%)

The unbleached pulp was stored under refrigeration at a consistency of 30% after removal of the free liquor. Three experiments were designed with different doses of Cl₂ at the C_D stage. The chlorination stage was carried out in close lid plastic containers by applying a kappa factor of 0.25 for calculation of Cl₂ dose (Table 4).

The E_{OP} stage was carried out in six bomb autoclaves heated in an oil bath at 70±1 °C after adding the required caustic 25 kg/ T and hydrogen peroxide 5 kg/ T. After maintaining the temperature (70±1 °C), the pressure of oxygen was adjusted to 5.0 kg/cm² for initial 30 min, which was then reduced to 2.5 kg/ cm² for the remaining 90 min.

The D₁ and D₂ bleaching stage treatments were carried out in plastic bags with different dose of chlorine dioxide (ClO₂) to achieve the same brightness as the control and to observe the improvement in pulp properties with same Cl₂ dose (Table 4). The final pH was maintained by the addition of diluted H₂SO₄ before the addition of ClO₂.

Table 4: Bleaching of Biokraft Pulp of Mixed Wood Chips with *C. subvermispora*

Particulars	Control	Pretreated		
	16% AA ^a	16% AA ^a	14% AA ^a	12% AA ^a
C_D Stage				
Kappa No.	21.0	18.0	20.1	21.4
Kappa Factor	0.25	0.25	0.25	0.25
Total Chlorine (%)	5.25	4.5	5.0	5.35
Cl ₂ : ClO ₂	90:10	90:10	90:10	90:10
Residual Chlorine (%)	0.025	0.030	0.035	0.01
CD: Brightness ISO (%)	38.9	39.8	39.2	39.0
COD (mg/l)	2108	1420	1750	2086
BOD (mg/l)	650	380	510	630
Colour (Pt. Co. Unit)	1650	1102	1335	1520
E_{OP} Stage				
NaOH (%)	2.5	2.5	2.5	2.5
H ₂ O ₂ (%)	0.5	0.5	0.5	0.5
Time (min) at O ₂ Pressure, 5.0/2.5 Kg/cm ²	30/90	30/90	30/90	30/90
Temperature (°C)	70±2	70±2	70±2	70±2
Permanganate Number	2.0	1.6	1.8	2.2
Brightness (ISO %)	57.4	59.0	58.7	57.2
COD (mg/l)	2825	2450	2520	2550
BOD (mg/l)	810	603	625	705
Colour (Pt. Co. Unit)	2685	2325	2420	2385
D₁ stage				
ClO ₂ (%)	0.9	0.6	0.7	1.0
Time (min)	180	180	180	180
Temp (°C)	70±2	70±2	70±2	70±2
Residual ClO ₂ (%)	0.06	0.04	0.05	0.03
Brightness (ISO %)	87.2	87.7	87.3	87.2
COD (mg/l)	650	280	410	665
BOD (mg/l)	152	75	110	145
Colour	780	510	600	750
D₂ Stage				
ClO ₂ (Kg/T)	0.2	0.2	0.2	0.2
Time (min)	180	180	180	180
Temp (°C)	70±2	70±2	70±2	70±2
Residual ClO ₂ (%)	0.01	0.01	0.01	0.01
Brightness (ISO %)	89.0	89.5	88.8	89.0
Effluent				
AOX in mixed Effluent (C _D :E _{OP} :D ₁ :D ₂ ::3.6: 1:1:1) (mg/l)	58	51	54.6	59.8

a – Active alkali dose (%)

After extensive washing of pulp with distilled water, bleached pulp was refined to 32–33 °SR (degrees of Schopper Riegler) for strength properties determination (Table 5).

Table 5. Strength Properties of Final Bleached Biokraft Pulp

Parameter	Control	Pretreated		
	16% AA ^a	16% AA ^a	14% AA ^a	12% AA ^a
No of Revolution (PFI)	1800	1100	1300	1400
Freeness (°SR)	32	33	32	33
Bulk (cc/g)	1.45	1.68	1.51	1.48
Breaking length (m)	5010	5620	5414	5362
Burst Index (kN/g)	3.4	3.9	3.7	3.5
Tear Index (mN/m ² /g)	5.91	6.20	5.87	5.94
Double Fold (No.)	39	48	56	64

a – Active alkali dose

Analytical Methods

Cellulose, hemicellulose, and holocellulose contents were determined according to the standard methods (Parsons 1963; Updegraff 1969; Deschatelets et al. 1986). Lignin and pitch were determined according to TAPPI Test Methods T 222 om–98, and T 204 om–88, respectively. Permanganate number, a measure of lignin content, was determined by reaction of pulp samples with acidified potassium permanganate solution according to TAPPI Test Method T 214 (TAPPI 1996). Viscosity, an indicator of cellulose chain length, was determined by dissolving the pulp in cupriethylene diamine (CED) solution and measuring the viscosity of a 0.5% solution with an Ostwald Viscometer (TAPPI Method T 230). Brightness of the paper sheets was determined with a Technibrite instrument (Model TB1c). Strength properties of handsheets were tested according to TAPPI test methods. The effect of fungal pretreatment on the properties of effluent was also investigated. COD (chemical oxygen demand), BOD (Biochemical oxygen demand), and AOX (absorbable organic halogens) were determined according to the standard methods. The experiments were performed in duplicate, and results are the mean of two readings. Scanning Electron Micrograph (SEM) studies were performed for unbleached control and pretreated fiber to study the after-effects of fungal pretreatment.

RESULTS AND DISCUSSION

White-rot fungi can degrade all the major components of wood, *i.e.* cellulose, hemicellulose, and lignin, since they can secrete lignin-degrading enzymes, cellulase, and hemicellulase at the same time (Eriksson 1990). However, different fungal strains may secrete these enzymes in different proportions. The lignin-degrading fungal strains of *Ceriporiopsis subvermispota* L-14807 SS-3 cultures grew well on mixed wood chips,

and maximal growth was obtained after 3 weeks. Fungal-treated chips were brighter than control chips, and about 1–2% weight loss was recorded due to pretreatment.

Pretreatment with Fungus

Fungal pretreatment was applied to the hardwood chips in order to study the effect of pretreatment on cellulosic and hemicellulosic contents. Pretreatment with the fungal strain *C. subvermispora* 1-14807-SS-3 was carried out for 3 weeks [Inoculum level; 6 g/ T wood (dry weight basis)], resulting in an increase in cellulosic and hemicellulosic contents compared to the control (Table 1). On the other hand, lignin contents were reduced due to the action of lignin-degrading enzymes secreted by the fungi. Similar weight loss results were observed by Bajpai et al. (2001) with eucalyptus pulp, where 3.57% reduction in lignin content was observed due to pretreatment with fungus. Nearly 2% yield loss was observed with *P. chrysosporium* (Myers et al. 1998). However in the case of *Punctularia artropurpurascens*, 5 months time was required to observe a weight loss of 1.2% in the case of eucalyptus hardwood (Ferraz et al. 2000). A similar type of result was observed with *Trametes versicolor*, but after 4 weeks (van Beek et al. 2007).

Biokraft Pulping

After pretreatment with a fungal strain, cooking was performed. Cooking of reference chips was conducted at 16% AA (Active Alkali) charge. Other cooking conditions included 21.5% sulphidity; 3:1 liquor/ wood ratio, and 160 °C cooking temperature (Fig. 1). Cooking was carried out with the same AA dose for control and fungal treated chips. A reduced dose of AA was also used for fungal-treated wood chips. The final yield of the pretreated pulp was marginally lower by 0.3% with the same AA dose, and a reduction of 14.3% was observed in the permanganate number. The yield decrease was due both to the dissolution of lignin as well as the concurrent attack on the carbohydrates (Scott and Akhtar 1995). However reduced yield of pretreated pulp without any reduction in permanganate number was reported by Bajpai et al. (2001). Similarly 0.5% reduction in pulp yield after fungal pretreatment was also reported by Christov et al. (1998). With equal AA charge and the same cooking conditions, cooking time for the pretreated chips was 11.7% less, compared to control chips. Therefore, pretreatment led to a reduction in the energy requirement during the cooking process. A similar type of result was observed in case of pretreatment with *Ceriporiopsis subvermispora* CZ-3, where extended cooking for 30 min was required for a control sample to obtain the same results as was obtained with a fungal pretreated sample (Scott and Akhtar 1995). Similarly, a reduction of 0.2% and 0.1% for unbleached screened yield was observed with 14% and 12% AA dose, respectively (Table 2). This may be due to the fact that lignin contents were reduced in pretreated wood chips compared to the untreated chips. Also a reduction in the kappa number was observed after cooking with the same and reduced dose of AA compared to the control. A reduction of 14.3% and 4.3% in kappa number was observed with 16% and 14% AA dose, respectively.

Strength properties and whiteness of the unbleached, pretreated pulp were higher, compared to the control. A maximum gain of 6.7% in brightness was observed for pretreated chips when the same dose of AA was used. However, reduced brightness was

observed with the reduced AA dose for pretreated wood chips (Fig. 2). Similarly, gains of 2 points and 10% in brightness of unbleached pulp were also reported by Bajpai et al. (2001) and Atik et al. (2006), respectively.

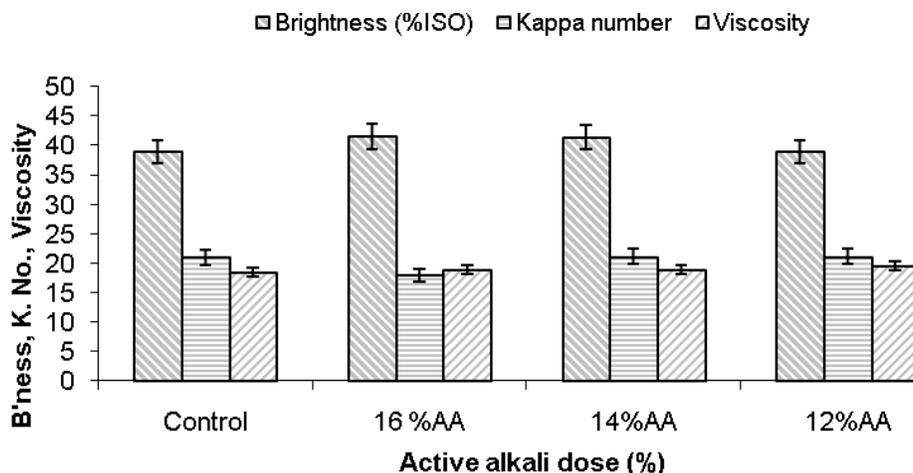


Fig. 1. Effect of fungal treatment with *C. subvermispora* on brightness, kappa no. and viscosity after kraft pulping

An increase of 6.4% with 14% AA dose and a marginal increase of 0.3% with 12% AA dose were observed in comparison to control untreated chips (Table 2). Similarly, an increase of 22.1% and 25.8% in tensile strength was observed with 14% and 12% AA dose respectively (Table 3). Reduction of 21.6% on the same AA dose was also observed in beating time of the unbleached pulp as compared to the control. This change would make the pretreatment process more economical in term of energy consumption. Similarly, energy savings results were also reported by other workers (Scott and Akhtar, 1998; Myers et al. 1998; Bajpai et al. 2001). Burst index and tear index increased by 68.2% and 24.3%, respectively, for unbleached pretreated pulp with 12% AA dose (Table 3).

Bleaching of Biokraft Pulp

A conventional bleaching sequence (C_D , E_{OP} , D_1 , D_2) was followed for the control and pretreated pulp. Most of the available reports on biopulping followed either a two step ($Na_2S_2O_4 + H_2O_2$) bleaching sequence (Yang et al. 2007) or a C, H, E, D sequence (Bajpai et al. 2001). Bleaching of pretreated pulp with reduced AA dose (14%) gave comparable results, as was obtained with the control with higher (16%) AA dose (Table 4). Fungal pretreatment resulted in 4.8% less consumption of Cl_2 for obtaining the same brightness as was obtained with untreated wood chip pulp. The same amount of Cl_2 reduction was also observed with a different bleaching sequence by Gutiérrez et al. (2000). Similarly, a 10% reduction in permanganate number was also observed in case of pretreated pulp after the E_{OP} stage. A maximum gain in brightness was observed after the D_1 stage, where an increase of 48.7% was observed in the case of pretreated pulp with 14% A.A dose. With the same alkali dose, 27.3% less consumption of ClO_2 was also reported during bleaching (Table 4). A marginal increase of 0.6% was observed in the

final brightness of the pretreated pulp with the same AA dose as was used for the control pulp.

Physical properties of the pretreated bleached kraft pulp also increased significantly compared to untreated pulp. Increases of 12%, 4.9%, and 23% were observed for breaking length, tear index, and double folds, respectively, in case of pretreated bleached pulp, compared to control with same AA dose (Table 5). A similar type of observation was also recorded for pretreated bleached kraft pulp by Myers et al. (1998).

Other strains *viz.* *Trametes versicolor* and *P. brevispora* were also found to be suitable for bio-kraft pulping of mixed wood chips. The active alkali charge was reduced by 30 kg/T and 10 Kg/ T by pretreatment with *T. versicolor* and *P. brevispora*, respectively, compared to control chips. The beating response and the quality of the biopulp in terms of brightness and strength were better than those of the control. These results clearly show that fungal pretreatment of mixed wood offers benefits for kraft pulping. Fungal pretreatment on kraft pulp has been studied to a lesser extent, and the potential benefits are not as clear (Akhtar et al. 1997, 1998; Wolfaardt 1993). About 18% reduction in kappa number of pine wood was observed when treated with lignin-degrading fungi (Oriaran 1990b).

Pretreatment of wood chips with a fungal strain will also lead to a reduction in pollution load. Less consumption of active alkali also leads to a reduction in COD and BOD values of the final effluent. It was observed that COD contents were reduced by 52.1% and 81.2% for C_D and E_{OP} stage effluent, respectively at 14% AA dose. A reduction of 32.6%, 41.5%, and 33.2% was observed for COD, BOD, and colour values at C_D stage effluent, respectively, with the same AA dose as was used for the control (Table 6). In the E_{OP} stage COD, BOD, and colour values were reduced by 13.3%, 25.6%, and 13.4%, respectively (Table 6).

Table 6. Percent Reduction of COD, BOD and Colour in Each Stage of Bleaching

Stage	Parameters	Pretreated	
		16% AA ^g	14% AA ^g
CD ^a	COD ^d	32.6	17.0
	BOD ^e	41.5	21.5
	Color ^f	33.2	19.1
EOP ^b	COD ^d	13.3	10.8
	BOD ^e	25.6	22.8
	Color ^f	13.4	9.9
D1 ^c	COD ^d	56.9	36.9
	BOD ^e	50.7	27.6
	Color ^f	34.6	23.1

a – Addition of Cl₂ stage; b – Extraction stage of bleaching; c – Addition of ClO₂ stage; d – Chemical Oxygen Demand; e – Biochemical Oxygen Demand; f – colour removal (Pt: Co unit); g – Active alkali dose

Most earlier reports did not deal with the study in the reduction of COD, BOD values. The ratio of reduction in AOX contents for mixed effluent of C_D, E_{OP}, D₁, D₂ stage in 14 and 16% AA charged experiments was 5.9 and 12.1%, respectively (Fig. 2), compared to control values. No previous report is available where a fungal pretreatment study was carried out for AOX level determination.

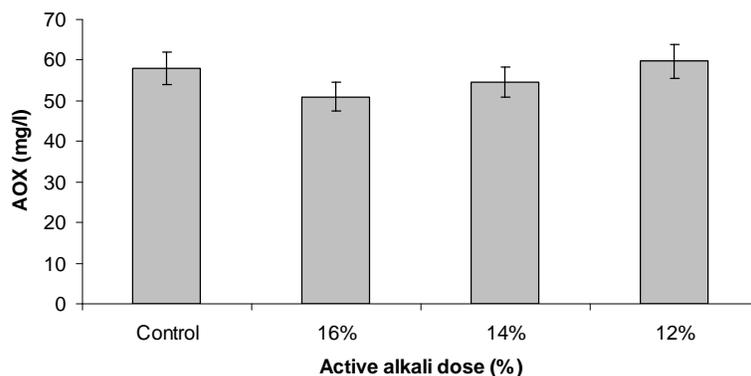


Fig. 2. Variation in AOX contents with different alkali doses

Results of pretreatment were also confirmed through Scanning Electron Micrographs (SEM) (Figs. 3-4). Electron microscopy clearly showed that pretreatment of chips with fungal strains led to the swelling and softening of the cell wall, which led to an increase in the porosity of the wood chips (Fig. 4). Similarly, after pretreatment with different white-rot fungi, an increase in external fibrillation was also observed (Yang et al. 2007). Increased porosity and disrupted cell wall required less amount of pulping and bleaching chemicals, and hence made the process more eco-friendly (Scott et al. 1996)

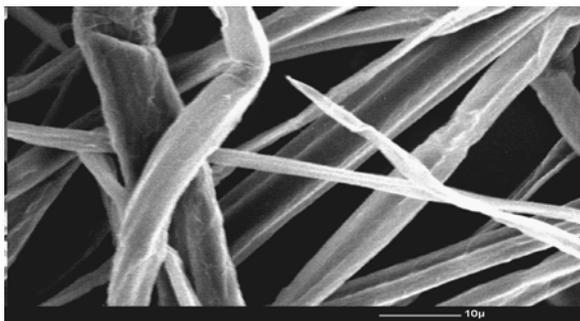


Fig. 3. Scanning Electron Micrograph (SEM) of untreated (control) wood fiber at 1500x

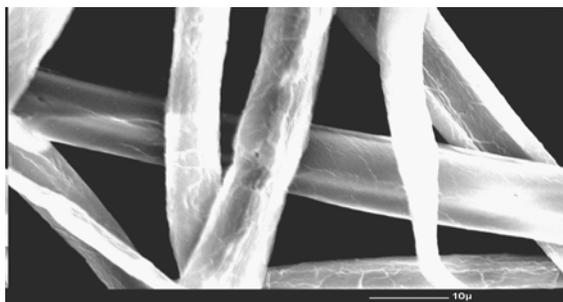


Fig. 4. SEM showing effect of fungal pretreatment on hardwood fiber at 1500x

CONCLUSIONS

1. Fungal pretreatment was effective in improving chemical pulping and bleaching efficiency of kraft pulp. It follows that paper mills that have bottlenecks in their recovery operations could benefit from decreased active alkali as a result of using fungal pretreatment.
2. With the same active alkali charge and under the same cooking conditions, treated chips cooking time was less, and a reduction in beating time of unbleached pulp was also observed. Hence, pretreatment will help to reduce the energy in the cooking and beating process.
3. Fungal pretreatment was responsible for reduced consumption of pulping chemicals and led to significant reductions in effluent pollution load and emissions of hazardous gasses. This is the first report on biopulping with the C_D, E_{OP}, D₁, D₂ bleaching sequence.
4. Pretreatment was responsible for significant improvement in physical properties compared to the control sample, even with reduced dose of AA.
5. From an environmental aspect, extensive research for different pulping and bleaching stages were carried out, and stepwise evaluation in the reduction of BOD, COD, AOX, and colour value was performed.

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