Enzymatic Pretreatment of Pulp For Reduction In Consumption of Bleach Chemicals

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ABSTRACT

An Australian based microbial enzyme, is found to be very effective in biobleaching of bagasse and wood based pulps, ranging from low kappa dissolving grade pulps to high kappa mechanical pulps. The enzyme on treatment with unbleached pulp, while increasing the brightness of the pulp also reduces the consumption of bleach chemicals significantly. Further, the colour of the effluents is decreased markedly as a result of partial or complete elimination of chlorination and alkali extraction stages.

The uniqueness of this biobleaching enzyme is that, it is active on a wide range of pH, unlike most of the biobleaching enzymes, which are efficient only in acidic pH ranges. More particularly, the enzyme is effective even at ambient temperatures and requires a reaction time of only 30-60 min compared to most of the enzymes used in other biobleaching processes, which are active only at elevated temperatures, say, 50-70 C and that too requiring 1-3h for reaction.

Detailed laboratory scale biobleaching trials have been carried out on disparate grades of pulp, such as, dissolving grade pulps of low pH and low lignin content through chemical pulps of high pH and mechanical pulps of high lignin content. The pretreatment of unbleached pulp with the enzyme reduced the consumption of elemental chlorine by about 25% in bleaching of chemical grade (bagasse) pulps (C-E/H-H bleaching sequence). Likewise, in case of mechanical grade of pulps, the enzyme treatment resulted in significant reduction in consumption of hydrogen peroxide in bleaching, whether the pulp treated was bagasse based CMP or wood based CTMP/CSRMP. There was no perceptible change in strength and optical properties.

When the microbial enzyme was used as pretreatment followed by peroxide and/or hypo stages with an objective to achieve ECF bleaching, the enzyme could reduce the consumption of peroxide by 50% in case of chemical pulps (bagasse) and dissolving grade pulps (hard wood). The target brightness is easily achieved and the biobleached pulp exhibited similar/better strength properties. The results clearly confirm that this microbial enzyme is quite versatile, both in terms of its ability to perform

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under different operating conditions and also on a wide range of pulps, compared to all other biobleaching enzyme currently available in the market. This paper presents laboratory/pilot scale results of biobleaching of a variety of pulps together with cost-benefit analysis for a few cases.

INTRODUCTION

The large scale pollution due to the excessive use of elemental chlorine in bleaching process and the growing concern over the release of these undesirable materials into the environment forced researchers to seek an effective alternative for chlorine. Chlorine dioxide, ozone and oxygen delignification have been adopted as alternatives or partial substitutes for chlorine, however, these alternatives due to their high capital cost, seem to have best economics at capacities 450 tpd and above.

To address this problem, research is recently focused on the use of microbial enzymes in the bleaching process to reduce consumption of chlorine based chemicals and this innovative approach of using microbial enzymes as pretreatment is termed as **Biobleaching.** Pretreatment of pulp with enzymes, therefore, has generated a great deal of interest, because it seems to offer a more cost effective solution in this direction (1,2). Biobleaching followed by peroxide bleaching step not only offers a more affordable ECF bleaching system for medium and small mills, but also reduces bleaching cost for mechanical grade pulp which has to use only peroxide as the brightening agent. Due to the reduced application of chemicals, pollution load arising out of these chemicals is considerably reduced (3). Moreover, the pretreatment does not affect the strength properties of the pulp and is expected to be cost effective.

Since most of the enzyme based processes are active at acidic pH and elevated temperatures, it was preferred to identify enzymes that would act efficiently at neutral/alkaline pH (the typical pH of the unbleached pulp is neutral/alkaline) and at a wide range of temperatures. Detailed laboratory scale biobleaching trials have, therefore, been carried out with several internationally available microbial enzymes on disparate grades of pulp, such as, dissolving grade pulps of low pH and low lignin content through chemical pulps of high pH and mechanical pulps of high lignin content, in order to identify the most suitable enzyme. Amongst the several enzymes tried, **B230** developed by biotech International Limited (BIL), Australia, was found to be the most ideal microbial enzyme for application on a wide variety of pulps. The results of the laboratory/ pilot scale trials conducted with B230 are presented here.

THEORY AND MECHANISM

The use of xylan attacking enzymes, xylanases, for pulp bleaching is getting considerable importance and achieved interesting results in recent years. The distribution and composition of xylan in lignocellulosic raw materials play important role in biobleaching process. **Table-1** shows the composition of polysaccharides in various raw materials. It is observed that in bagasse, hardwood and straw, the xylan proportion is considerably more and hence pretreatment of such pulps with xylanases could be gainfully employed (4).

Table-1

Composition of Polysaccharides in various Lignocellulosic Raw Materials

No.	Raw Material	Glucan (%)	Xylan (%)	Mannan (%)	Arabinose (%)
1	Pine	42.37	05.94	11.02	01.28
2	Bagasse	38.84	21.43	00.20	01.40
3	Spruce wood	41.90	06.10	14.30	01.20
4	Beech wood	50.40	23.10	-	-
5	Birch wood	21.40	12.20	-	-
6	Wheat Straw	24.90	18.90	-	15.10
7	Palm Stalk	25.30	11.70	-	01.20
8	Reed Grass	42.20	21.50	02.70	-
9	Kenaf				
	Core	NA	28.25	-	-
	Bast	NA	17.48	-	-

Table-2			
Test Conditions			
Parameters	**Enzyme Treatment**	**Peroxide Bleaching**	**Hypo Bleaching**
Lab/Pilot Scale Trials			
Pulp Consistency (%)	7-8	7-8	7-8
Dosage	1L/t	1.5-5.0*	1.0-1.8*
pH	No adjustment	11	10.5
Temperature (C)	Ambient	70	45
Treatment Time (Min)	30-60	90	60
Mill Scale Trials			
Pulp Consistency (%)	7-8	18-20	
Dosage	1 L/t	4.5%	
pH	8.0-8.6	11	
Temperature (C)	45-50	80-85	
Treatment Time (Min)	60	120	
* Varies from dissolving grade to mechanical pulps			

The success of biological bleaching will depend upon the type of raw materials, such as, hardwood, softwood etc and also enzymes such as xylanases or mannanase.

A number of theories have been proposed to explain the improved delignification with hemicellulase enzymes.

1. The simplest theory is that the enzyme treatment causes a physical loosening of the fibre wall due to partial depolymerisation of hemicellulose chains which facilitates extraction of residual lignin during bleaching (5,6).

2. The other possible explanation for xylanase action in bleaching is that the disruption of xylan chain by xylanases interrupts lignin-carbohydrate bonds, improves the accessibility of bleaching chemicals to the fibre and facilitates the removal of solubilised lignin in bleaching (6).

3. Another explanation involves the role of redeposited xylans (5). It is well known that parts of xylan that were initially dissolved in kraft pulping can be readsorbed or redeposited on within the pulp fibres. The redeposited xylan may physically shield the residual lignin from bleaching chemicals. Xylanase hydrolyse part of redeposited lignin, allowing better access of bleach chemicals to the residual lignin and easier extraction of lignin from pulp fibres.

In addition to xylanases, the other important lignin degrading enzymes, such as, Lignin Peroxidases, Manganese Peroxidases and Laccases, are considered to have direct brightening effect. Further detailed studies are under progress on this **Biobrightening** technology.

EXPERIMENTAL

Unbleached pulp samples collected from different paper mills were brought for our Biotech Lab at Erode and laboatory and pilot scale trials were carried out. Pilot scale trials were carried out following the same conditions in a bioreactor, designed and fabricated at our associate company, Seshasayee Paper and Boards Limited (SPB), Erode. The test conditions are mentioned in **Table-2.**

RESULTS

Laboratory Scale

1. When the unbleached pulp as pretreated with the microbial enzyme, prior to the conventional C-E/H-H bleaching process, the consumption of elemental chlorine was reduced by 25% in case of Chemical Bagasse Pulps (CBP) and a final brightness of 82.50% was achieved against the target brightness of 80%. The strength properties of the biobleached pulp were comparable with that of untreated pulp.

2. For ECF bleaching, peroxide was applied to CBP instead of elemental chlorine. Due to the enzyme pretreatment, a reduction of 50% was achieved in the consumption of peroxide with a final brightness of 83.20%.

3. In case of Dissolving Grade Pulp (DGP), to achieve ECF bleaching, peroxide was tried. When the unbleached DGP was treated with B230 prior to peroxide bleaching, the consumption of peroxide reduced by 50% and the target brightness of 90% was obtained.

4. When the unbleached hardwood CMP was treated with the microbial enzyme prior to peroxide bleaching, a reduction of about 25% in peroxide consumption was achieved.

The results are presented in **Table-3.**

Pilot Scale

1. Unbleached CBP was treated with the enzyme in the bioreactor and peroxide bleaching was carried out as mentioned earlier. A saving of 50% in peroxide was achieved in the enzyme treated pulp. However, the final brightness was only 78-79%. Further trials are in progress to achieve a final brightness of +80%.

The results are presented in Table-3.

Mill Scale

1. About 55t of CMP was treated with B230 in a recently conducted mill scale trials at a newsprint manufacturing mill. The dosage of peroxide was 4.5% (similar dosage was applied for untreated pulp). The results obtained in the mill trials are tabulated in **Table-4.** Final bleached pulp brightness was 72-74% as against the target brightness of 68-71%. The tear factor of the enzyme treated pulp improved appreciably. There was hardly any improvement in brightness when the dosage of enzyme was doubled. Newsprint manufactured from the enzyme treated pulp showed improvement in brightness, tear factor and breaking length.

Comparison with other Biobleaching Enzymes

The results obtained with B230 was satisfactory and better than that of the other commercial preparations of xylanase based enzymes **(Table-5).** Our biobleaching process is also advantageous, since this does not require steam (to raise the temperature, like other processes).

CONCLUSION

It is concluded from the results that-

1. The brightness of the unbleached pulp increase appreciably when pre-treated with the microbial enzyme.

2. The consumption of elemental chlorine can be reduced by 25% with the use of microbial enzyme during CEH bleaching of the pulps. The target brightness is easily achieved, even though the consumption of bleach chemical is reduced.

3. Cost effective ECF bleaching may easily be achieved with the use of Peroxide as the alternative bleach chemical, instead of elemental chlorine, in case of Chemical Bagasse Pulp and Dissolving Grade Pulp.

4. Due to ECF bleaching along with enzyme pretreatment (though less bleach chemicals are used), higher brightness of pulp is achieved without any change in the strength properties.

5. The colour of the bleach plant effluent is significantly reduced by adopting this Biobleaching Process, because of the elimination of chlorination and alkali extraction stages.

6. When the unbleached pulps were pretreated with the microbial enzyme prior to bleaching with peroxide, consumption of peroxide is reduced very significantly.

7. The uniqueness of this biobleaching technology is that the process is adoptable on nonwood material, viz., Bagasse Pulp, which has not been attempted elsewhere.

Table-3

Biobleaching Trials with B230

Mill No.	Raw Material	Pulp Type	Present Bleach Sequence	Proposed Bleach Sequence	Target Brightness (ISO)	Lab Scale Status	Lab Scale Brightness Achieved (%)	Lab Scale Reduction in Peroxide (%)	Pilot Scale Status	Pilot Scale Brightness Achieved (%)	Pilot Scale Reduction in Peroxide (%)
1	Bagasse	Chemical Pulp	C-E/H-H	X-P-H-H	+80	Completed	83.2	50	In progress	78-79	50
2	Wood	Dissolving Grade	C-E-H	X-P-H-H	+90	Completed	91-92	50			
3	Wood	CMP	P	X-P	68-70 (PV)	Completed	70(PV)	25	In Progress		
4	Wood	CSRMP	P	X-P	60	In Progress	58	28	In Progress		
5	Wood	Dissolving Grade	C-Eo-H-D	X-P-H-D	+90	In Progress	90	20	In Progress		
6	Bagasse	Mechanical Pulp	P	X-P	50	In Progress	50	30	In Progress		

Table-4 Mill Scale Biobleaching Trials CMP (Wood)			
Description		Regular Process (P)	Enzyme Treated (X-P)
Quantity of Pulp Treated	(T)		55.0
Dosage of B230 Enzyme	(L/T)		1.0
Dosage of Peroxide	(%)	4.5	4.5
Brightness	(PV)		
Initial		52.0-52.5	55.0
Final		68.0-70.0	73.8-74.2
Tear Factor		25.0-28.0	30.0-31.0
Newsprint Properties			
Brightness	(PV)	62.0-63.0	63.5-64.6
Tear Factor		48.0-50.0	50.0-54.0
Breaking Length	m	3000-3100	3100-3200

8. The B230 enzyme is active at neutral/alkaline pH, unlike other biobleaching enzymes which are active only at acidic pH ranges. The enzyme is very efficient at ambient temperature, while most of the enzymes used in other processes are active only at higher temperatures (40 to 70 C). The unbleached pulp is treated with the enzyme for 30 to 60 min as against 1 to 3 h treatment time for other enzyme systems and even several days, in some cases.

9. Detailed laboratory/pilot scale trials are in progress with mechanical bagasse pulp, CSRMP and dissolving grade pulps.

ECONOMICS

Biobleaching is able to significantly reduce the consumption of peroxide in the bleaching of mechanical pulps, rendering the manufacture of newsprint economical. Further, it is evident from the results obtained in this study that the biobleaching process may successfully be adopted on a variety of pulps. In case of C-E-H bleach sequence adopted in bleaching of chemical pulps, biobleaching can significantly reduce chlorine consumption, whereas, in case of dissolving grade pulp, it can totally eliminate elemental chlorine and the bleach sequence can be peroxide and hypo combinations. The expected savings in the cost of peroxide due to enzymatic pretreatment is depicted in **Table-6.**

Therefore, it may be appreciated that the biobleaching process is an economical route not only for bleaching of mechanical pulp which uses peroxide, but also for achieving ECF bleaching and hence may be suitably adopted by both small and medium mills, who cannot otherwise afford ECF bleaching.

COMMERCIAL PROSPECTS

Recently, xylanase pretreatment has attained the commercial status and several mill scale trials have been carried out. At the Enso-Gutzeit Oy mill in Finland, a 1000 tonne run with enzymatic bleaching economically reduced chlorine consumption by 25-30% (7). Recently, the Aanekoski mill in Finland used an enzyme with oxygen delignification and hydrogen peroxide bleaching to produce over 50,000 tonnes of totally chlorine free pulp (8). Earlier, Voest-Alpine Industries, Austria, have successfully carried out mill scale trials with hardwood kraft pulps and achieved savings of more than 30% in chlorine consumption (9). The biobleaching process with xylanase based enzymes has also been commercialised in Japan, Czeckoslovakia and Denmark. A few mill scale trials have been successfully carried out in a mill in Japan and recently, the technology has been adopted in Canada (10). A total of only 10 mills were known to use xylanase pretreatment on a commercial scale and more than 80 mill scale trials have been carried out (11). Of late, the technology is gaining wider acceptance in Canada and Europe.

Table-5				
Comparison of Competing Biobleaching Enzymes				
Company	**CIBA-GEIGY**	**NOVO NORDISK**	**BIOCON**	**BIL**
Source Country	Switzerland*	Denmark	India	Australia
Trade Name	IRGAZYME	PULPZYME	BLEACHZYME	B230
Culture	NA	Bacteria	NA	Bacteria
Enzyme	Xylanase	Xylanase	Xylanase	Xylanase
Enzyme Activity	15000 IU/mL	500 exu/mL	30000 IU/mL	2500 xu/mL
Purified/Conc Enzyme	yes	yes	yes	yes
Dosage on Pulp	0.5 L/t	0.5-1.0 L/t	0.2-0.5 L/t	1.0 L/t
Commercialisation Status	Commercialised	Commercialised	Not Ready	Ready
Treat. Conditions:				
Pulps Used	Chemical Bagasse Pulp Dissolving Grade Pulp	Chemical Bagasse Pulp	Chemical Bagasse Pulp Dissolving Grade Pulp Chemi Thermo Mech Pulp	Chemical Bagasse Pulp Dissolving Grade Pulp CMP CSRMP
Pulp Consistency	10%	10%	3%	8%
Temperature	50-60 C	60 C	45-50 C	60
pH	7.0-8.0	6.0-9.5	6.0-6.5	7.0-8.5
Time	180 Min	60 Min	180 Min	30 Min
Lab Trials at EBL	Target Results Not Achieved	Targets Results Not Achieved	Targets Results Not Achieved	Results Satisfactory

SANDOZ : **CARTAZYME** Conc Enzyme, 65000 IU/g, pH 4-5, Temp 40-55 C, 0.2 L/t, Commercialised

ALKO : **ECOPULP,** Conc Enzyme, 20000 IU/g, pH 5-6, Temp 50-55 C, 0.5 L/t, Commercialised

* : Not in Production

NA : Not Available

Table-6

Biobleaching Process-Saving in Peroxide-Cost Benefit to the Mill

Mill #	Raw Material	Pulp Type	Capacity	Present	Proposed	Peroxide Dosage %		Saving in Peroxide		Savings Rs. per tonne of pulp
			tpd	Bleach Sequence	Bleach Sequence	Actual	After Enzyme Treatment	TPD	Kgs/tonne of Pulp	
1	Bagasse	CMP	150	P	X-P	3.00	1.95	1.58	10.50	204.00
2	Wood	CTMP	60	P	X-P	4.50	3.37	0.68	11.30	226.00
3	Wood	CSRMP	200	P-H	X-P-H	3.50	2.45	2.10	10.50	210.00
4	Wood	Dissolving Grade	200	C-Eo-H-E-D	X-P-H-D	4.00	3.00	2.00	10.00	200.00
5	Bagasse	Semi Chemical	50	C-E-H	X-P-H-H	2.50	1.25	0.63	12.60	250.00
6	Wood	CMP	200	P	X-P	5.00	3.50	3.00	15.00	300.00

- Commercially available Peroxide at 50% Conc. Cost - Rs. 20,000/- per ton

Developed countries are pursuing pretreatment with microbial enzyme as an alternative/supplementary strategy to adopt ECF bleaching, since Oxygen/Chlorine Dioxide/Ozone bleaching processes are found to be capital intensive. Whereas, in case of developing countries, this enzyme pretreatment would be more relevant and economically attractive to reduce the consumption of peroxide in the bleaching of mechanical grade pulp, which is a major component of newsprint furnish. The Indian Newsprint, because of the low brightness of the raw materials used, has a higher bleaching cost, which is one of the factors, besides power cost, preventing it being globally competitive. Therefore, this enzyme pretreatment is very advantageous to newsprint Mills. However, if environmental compulsions require ECF bleaching to be adopted even in developing countries, it would seem logical to introduce such ECF bleaching first in dissolving grade pulps due to the very low lignin content and high target brightness to be achieved (+90) for such pulps. Further, biobleaching followed by Peroxide and Hypo stages, due to the very low capital cost (no need for on-site generation of peroxide), have great competitive edge over capital intensive Chlorine dioxide and Ozone based routes, especially in developing countries where financial resource is a serious constraint.

ACKNOWLEDGEMENT

We thank **Biotech International Limited (BIL),** Perth, Australia, for supplying us the B230 enzyme and deputing their Research Scientist, Mr Alex Roullo, for us to carry out our first mill scale trials. We thank the Management of **Sun Paper Mill Limited (SPM)** for extending their mill facilities for carrying out mill trials. We would like to express our profound thanks to the management of **Seshasayee Paper and Boards Limited (SPB)** for extending infrastructure facilities.

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