

Enzymatic Prebleaching of Pulps- Challenges & Opportunities in Indian Paper Industry

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ABSTRACT

Strict legislation and the environmental concerns regarding imposition of the effluent discharge norms in respect of Absorbable Organic Halides (AOX) in Indian paper industry is forcing the mills to look for alternate techniques to reduce or eliminate the use of elemental chlorine in bleach sequence. Among various technological options available, xylanase enzyme prebleaching could prove to be one of the promising options before the mills to reduce the generation of chlorinated organic compounds while improving the final brightness of bleached pulps. Although the technology has commercially been adopted in number of paper mills world-wide, but as far Indian paper industry is concerned, it is still in the developing stage.

Central Pulp & Paper Research Institute carried out extensive studies in the area of xylanase prebleaching of pulps procured from wood and non-wood based mills. The present paper discusses the response of five identified xylanase enzyme preparations on the pulps procured from wood based (eucalyptus +bamboo) and bagasse based mills. Out of five enzyme preparations, four are available globally and one produced from an indigenous microbial strain. The response of three xylanase enzymes was found to be encouraging. The savings in terms of elemental chlorine is found to be to the tune of 15-20% during conventional CEH bleach sequence with simultaneous reduction of AOX level to 20-30% in both Kraft wood and Kraft bagasse pulps. Brightness gain to a level of 2.5-3.5% ISO could be attained, while maintaining similar or slightly improved strength properties. Based on these findings, efforts are continued to commercialise the process in Indian paper mills employing identified xylanase enzymes.

INTRODUCTION

In the rapidly changing field of pulp bleaching, efforts have been made to adjust the process to meet the current challenges, which are driven by the environmental and economic forces. The environmental concern regarding imposition of the effluent discharges norms for AOX is forcing the industry to reduce or eliminate the use of chlorine or

chlorine based chemicals in bleach sequence. Many of the alternate technologies have not yet proved feasible especially because of higher investment and operating cost and also the negative effect on the pulp quality.

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Under the prevalent conditions enzymatic prebleaching of pulps employing xylanases enzymes could prove to be a promising option as an environmental friendly technology & is early adaptable by the pulp and paper industry.

The primary goal of chemical pulp bleaching is to reduce the residual lignin of pulp without effecting the carbohydrate and/ or the physical properties of the pulps. Two different enzyme approaches have been generally in use for achieving the goal, which include.

1. Use of hemicellulases (specifically xylanases) enzymes as prebleaching agents (bleach booster) for enhancing the chemical removal of lignin in multistage bleaching sequence.

2. Another alternative approach is direct delignification of the unbleached pulps using enzymes called ligninases or laccases, which acts directly on the residual lignin in the pulp (2).

The first approach, which is the use of xylanase enzyme as prebleaching agents for chemical pulps has been successfully, applied in pulp and paper mills worldwide using various xylanases preparations of different origins. But the technology still is in nascent stage as far as Indian Paper Industry is concerned.

Xylanase enzymes used in bleaching of chemical pulps are being developed by Companies which claim their products suitable as prebleaching agents for the pulps produced in the paper industries. However, these enzymes, which are marketed by several suppliers are found to be highly sensitive to the conditions like temperature , pH & doses of the enzymes (3,4). Therefore it becomes difficult for the pulp and paper mills to decide which particular enzyme should suit to the specific requirement of their industry in order to achieve desired effect.

In view of the above, Central Pulp & Paper Research Institute (CPPRI) has been engaged for the last many years in conducting studies on evaluation of various xylanase enzyme preparations which are available globally and also being developed indigenously by several reputed biotechnological laboratories to study their response on the type of pulps produced in Indian paper mills (5).

The present paper highlights the studies carried out at the Institute in which several xylanase enzymes have been evaluated for their bleach response on Kraft wood and Kraft bagasse pulps, in order to explore potential for commercial application of the enzyme prebleaching technology in Indian paper industry.

MATERIALS & METHODS

Sources of Xylanase enzymes:

Several xylanase enzyme preparations used in the present investigation were procured from National & International enzyme manufacturing companies / laboratories which are denoted as AB,C,D, & E The details about the xylanase preparation is given in Table -1.

Pulp Samples:

Wood Kraft Pulp samples were procured from a nearby large integrated Pulp & Paper Mill employing Eucalyptus as major raw material where as Kraft bagasse Pulp was obtained from an agrobased mill in Maharashtra equipped with chemical recovery system.

Enzyme assay Techniques:

All the enzymes were tested for filter paper activity for cellulase contamination by the method of Mandals & Weber and xylanase activity was measured

TABLE-1	
SOURCES OF XYLANASE ENZYMES	
Xylanase enzyme	Source
A	Produced indigenously from an indigenous microbial strain
B	Indigenously manufactured
C	Imported
D	Imported
E	Indigenously manufactured

TABLE-2					
ENZYME PRETREATMENT CONDITIONS					
	Pulp treated with Enzymes				
Parameters	A	B	C	D	E
Dose of enzyme, IU/g	7.0	10	5.0	5.0	10
Consistency of pulp, %	10	10	10	10	10
Retention time, min	120	120	120	120	120
pH at 25°C	6.2	8.2	8.5	8.5	8.5
Temperature, °C	45-50	45-50	45-50	45-50	45-50

TABLE-3			
PROCESS CONDITIONS USED DURING BLEACHING OF PULPS			
Particulars	Chlorination Stage	Alkali Extraction Stage	Hypo Stage
Temperature, °C	Ambient	60	40
Pulp Consistency, %	3.0	8.0	8.0
Retention Time, min	30	60	120
Final pH	1.8-2.0	>10.5	>9.0

by the method of Bailey et. al (1).

Xylanase Pretreatment of Pulps:

Enzymatic Pretreatment of the pulps was carried out under the optimised conditions as mentioned in Table -2.

Process conditions used during bleaching of Pulps:

Process conditions employed for bleaching of Pulps both with & with out enzyme preparation is shown in Table - 3.

RESULTS AND DISCUSSION

While optimising the dosages of enzymes during enzyme treatment of wood Kraft and bagasse Kraft pulps, it was observed that excess dosages of xylanase enzymes for a longer time has resulted in decreased pulp yield and strength properties of the pulps. This could probably be due to loss of hemicelluloses by the action of enzyme. However under optimised dosages of

enzymes i.e. 5-7 IU/gm of pulps and optimised treatment condition (Table-2), no significant loss in pulp yield could be observed except with enzyme preparation E wherein even the treatment of the pulp at optimised conditions of time and temperature could result in 1.5% pulp yield loss along with drop in viscosity which was reduced from 560 to 510 cm³/g of the pulp leading to loss in strength properties (Table-4). Reasons for the same could be attributed to contamination of xylanase with cellulase activity, which could be ascertained by determination of the cellulase activity in xylanase enzyme by filter paper activity. Therefore this enzyme named as E was found to be unsuitable for its application in bleaching of pulps.

Effect of xylanase treatment on bleach chemical requirement

Bleaching of the xylanase enzyme treated Kraft pulps, both wood and bagasse have been found to respond in a different manner than untreated pulps while bleaching with conventional CEH bleach sequence. Based on optimisation studies of the chlorine

TABLE-4
CHARACTERIZATION OF UNBLEACHED PULP FOR YIELD & OTHER PARAMETERS OF WOOD KRAFT PULP BEFORE & AFTER ENZYME TREATMENT

Parameters	Control	Pulp treated with enzymes				
		A	B	C	D	E
Pulp yield, %	99.89	99.82	99.62	99.80	99.74	98.10
Kappa number of Pulp,	18.0	16.5	16.7	16.6	17.0	16.0
Brightness, % ISO	27.5	28.5	29.0	28.4	28.0	29.0
CED Viscosity, cm ³ /g	560	620	590	557	604	510

TABLE-5
EFFECT OF ENZYME PRETREATMENT ON BLEACH CHEMICAL REQUIREMENT USING VARIOUS XYLANASE PREPARATIONS ON KRAFT WOOD PULP

Parameters	Control	Pulp treated with enzymes									
		A		B		C		D		E	
		ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2
Savings in elemental Chlorine	--	--	15	--	15	--	14	--	9.3	--	
% Reduction in Kappa No. after X Stage	--	8.0		7.2		7.3		5.5		11.1	
% Reduction in Kappa No. XCE Stage	--	28.0	--	25.9	14.5	26.0	16.0	27.0	23.0	--	--
Final brightness of the pulp, % ISO	80.0	82.5	80.0	82.5	81.3	83.0	80.2	82.0	80.0	83.0	80.0
X - Enzyme treatment XCE - Enzyme, Chlorination & Extraction ET1 - Enzyme treated Pulp treated with similar chlorine dose ET2 - Enzyme treated Pulp treated with optimised less chlorine dose											

dosages during chlorination stage, it was observed that significantly less chlorine is required to bleach Kraft wood and Kraft bagasse pulps while bleaching to similar targeted brightness level.

Table -5 shows the effect of various xylanase preparations on the bleach chemical requirement during conventional CEH bleach sequence of wood Kraft pulps with a targeted brightness level of 80% ISO. From the results shown it is clearly seen that there is a reduction of nearly 14-15% of chlorine demand with all the enzymes preparations in case of wood Kraft

pulps except enzyme preparation D, where chlorine saving of only 9.3% could be noticed. Further the enzyme treated pulps could be bleached to higher brightness with a gain in brightness level of 2-3% ISO in all the cases while using similar chlorine dosages as in case of control pulp sample

Reduction in chlorine requirement or improved pulp brightness in case of enzyme treated pulps was reflected from the reduction in Kappa number of the unbleached pulps after enzyme treatment and further after the alkali extraction stage. The reduction in

TABLE-6			
ENZYMATIC PREBLEACHING OF KRAFT WOOD PULP USING XYLANASE			
Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment			
Particulars	Control	Enzyme B	Enzyme D
Chlorination			
% Chlorine Applied	3.9	3.3	3.54
%, Chlorine Consumed	94	99	96
%, Chlorine savings	--	15	9.23
Alkali Extraction			
% NaOH Applied	1.30	1.30	1.5
% NaOH Consumed	61.1	63.2	58.3
Final pH	10.88	10.76	11.21
Kappa no.	3.51	2.99	3.2
Hypo Stage			
% Hypo Applied	1.8	1.8	1.8
% Hypo Consumed	71.0	75.0	68
Brightness, % ISO	80.0	82.5	82.0
Brightness Gain, %	--	2.5	2.0
Strength and Optical properties of the wood kraft pulps before & after enzyme treatment using two identified xylanase enzymes B & D			
Parameters	Control	Enzyme B	Enzyme D
Revolution PFI	4000	4000	4000
Freeness, CSF	220	250	250
Apparent density, g/m ³	0.79	0.76	0.75
Burst index, kPa.m ² /g	4.43	4.49	4.51
Tensile Index, kPa.m ² /g	64.4	64.3	64.4
Tear Index, Mn m ² /g	5.3	6.0	5.3
Optical Properties			
Opacity, %	92.2	91.2	91.0
Yellowness, %	14.94	9.79	10.65

kappa number by 7-8% after enzyme treatment and further reduction of kappa number by more than 25% after alkali extraction was achieved in enzyme treated pulps.

Similar observation were made in case of Kraft bagasse pulps where nearly 18% reduction in chlorine demand could be observed in enzyme treated pulps with targeted brightness level of 83.0% wherein brightness gain of 2.0% ISO could be achieved when

TABLE-7

YIELD & OTHER CHARACTERISTICS OF UNBLEACHED KRAFT BAGASSE PULP BEFORE & AFTER ENZYME TREATMENT USING IDENTIFIED XYLANASE (B) ENZYME

Parameters	Pulp treated with Enzyme	
	Control	Enzyme treated
Pulp yield, %	99.20	99.02
Kappa number of unbleached Pulp	26.2	25.5
Kappa No. of CE Stage	5.07	4.04
Brightness, % ISO	30.3	30.8
CED Viscosity	535	520

the enzyme treated pulp was bleached with similar chlorine dose of 5.1% as in case of control pulp. Results are shown in Table -8. This reduction in chlorine demand and gain in pulp brightness is also reflected from reduction in kappa number of the enzyme treated pulp where 20% reduction in kappa number after alkali extraction stage could be noticed.

Effect of enzyme treatment on unbleached pulp yield and physical properties of wood Kraft and bagasse Kraft pulps.

Table-6 shows the bleach chemical demand strength & optical properties of Kraft wood pulp treated with identified xylanase enzyme preparations B&D against control. From the results shown in Table-6 it is clearly evident that with a savings of nearly 15% chlorine demand employing enzyme preparation B, no loss in strength properties like burst, tensile & tear could be noticed, however the tear index was improved significantly from 5.3 Mn m²/g to 6.0 Mn m²/g whereas in case of enzyme D treated pulps, the strength properties, though were at par with control pulp but the chlorine savings were lower i.e. 9.3% only. With regards to the optical properties of the enzyme treated pulps, there is an improvement in the yellowness of the pulp both with enzyme preparations B & D, Since the yellowness of the enzyme treated pulps were decreased from 14.94 % to 9.79% & 10.65% respectively.

Similar observations could be made in case of Kraft bagasse pulps. Treatment of the Kraft bagasse pulp with xylanase enzyme B preparation showed no loss in pulp yield or pulp viscosity (Table -7). Bleach chemical demand of both enzyme treated and untreated

pulps & the results of strength properties were shown in Table-8. From the results it is clearly evident that strength properties of the enzyme treated pulps like Burst, Tear and Tensile could be maintained at par with control pulps with improvement in optical properties particularly in respect of yellowness which was dropped from 13.5 to 9.2-9.6% (Table-8).

Impact of enzyme treatment on environment

Characterisation of the resultant bleach effluent from wood Kraft pulps and Kraft bagasse pulps before the after enzyme treatment indicated that effluent properties namely AOX (Adsorbable Organic Halides) & COD are improved indirectly through the use of xylanase treatment which helps in release of lignin and other chromophore bearing compounds and allowing the use of lesser quantities of elemental chlorine or other chlorine based compounds in subsequent bleach sequence. Results of characterisation of enzyme treated wood Kraft pulp and Kraft bagasse pulps against control pulps are shown in Table -9. From the table it is clearly indicated that AOX level was reduced to 0.69kg/tp in case of hard wood Kraft & 1.0kg/tp in Kraft bagasse pulps compared with control pulps where AOX was reduced from 2.29kg/tp to 1.6 kg/tp and from 4.13 kg/tp to 3.13 kg/tp respectively. Further decreased ratio of COD to BOD from 7.7 to 3.9 and from 4.12 to 3.33 in bleach effluent from Kraft wood and Kraft bagasse after enzyme treatment is an indication of improved biological treatability of the bleach effluent.

CONCLUSION

1. Enzymatic prebleaching of chemical pulps using

TABLE-8
XYLANASE PRETREATMENT OF KRAFT BAGASSE PULPS & STRENGTH & OPTICAL PROPERTIES

Parameters	Control	ET1	ET2
Chlorination			
% Chlorine Applied	5.1	5.1	4.2
%, Chlorine Consumed			
%, Chlorine savings	--	--	17.6
Alkali Extraction			
% NaOH Applied	2.0	2.0	2.0
% NaOH Consumed	74.2	61.2	73.8
Final pH	10.24	11.55	10.25
Kappa no. of Pulp	5.07	4.04	4.30
Hypo Stage			
% Hypot Applied	2.0	2.0	2.0
% Hypo Consumed	80.0	80.0	74.0
Final brightness of the pulp % ISO	83.0	85.0	84.0
Strength and Optical Properties			
Parameters	Control	ET1	ET2
Revolution PFI	500	500	500
Freeness, CSF	335	350	355
Apparent density, g/m ³	0.66	0.74	0.72
Burst index, kPa.m ² /g	2.60	3.05	2.55
Tensile Index, kPa.m ² /g	45.5	56.0	45.0
Tear Index, Mn m ² /g	4.05	4.40	4.20
Optical Properties			
Brightness of pulps, % ISO	83.0	85.0	84.0
Yellowness	13.5	9.2	9.6
<ul style="list-style-type: none"> ● ET1 -- Pulp treated with similar chlorine dose ● ET2 -- Pulp treated with less optimised Chlorine dose 			

xylanase enzyme could prove to be an effective technology in reducing the chlorine demand to the tune of 15% & 18% with gain in bleached pulp brightness of 2-3% ISO while reducing the

AOX level in bleach effluent to more than 25% in case of wood Kraft and Kraft bagasse pulps.

2. Xylanase enzyme respond better on wood Kraft

TABLE-9
CHARACTERISTICS OF BLEACH EFFLUENTS OF KRAFT WOOD & KRAFT BAGASSE PULPS BEFORE & AFTER ENZYME TREATMENT USING XYLANASE ENZYME B

Parameters	Wood Kraft Pulp		Bagasse Kraft Pulp	
	Control	Enzyme treated	Control	Enzyme treated
AOX, kg/tp	2.29	1.60	4.13	3.13
COD, kg/tp	23.3	28.5	34.6	50.7
BOD, kg/tp	3.02	7.31	8.5	15.0
COD : BOD ratio	7.7:1	3.9:1	4.1:1	3.3:1

pulps than non woody raw materials due to the nature of the hemicelluloses wherein it has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in Pulps from Kraft bagasse mills due to the nature of the hemicelluloses. It has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in pulps from agro residue raw materials.

3. Studies indicated that before selection of a particular xylanase enzyme preparation it is important to evaluate the enzymes for their activity and cellulase contamination, since excess dose of xylanase enzyme and cellulase contamination results in loss of pulp yield and strength properties of the pulp as in case of enzyme preparation E.
4. Before introducing enzyme- prebleaching technology in any mill it is important to evaluate particular enzyme preparation for its response towards pulp being produced in the mill for various parameters as discussed in the paper.
5. Enzyme being sensitive and specific in nature, it is very important to optimise the temperature, pH, dosages and proper dispersion or mixing of the enzyme with the pulp in order to achieve the targeted response.
6. The technology is relatively new as far as Indian paper industry is concerned. Efforts are required by researches, technologists and enzyme manufacturers to isolate new xylanase enzymes suitable for pulps being produced in Indian paper industry from wood and non wood based

raw materials and also to investigate the effect of other hemicellulases and lignolytic enzymes like laccase and lignin peroxidases on pulp bleaching to further reduce requirement of chlorine based chemicals.

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