Bleaching of bagasse pulp with enzyme pre-treatment

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Abstract The effluent from pulp bleaching processes containing chlorinated lignin and degraded polyphenolic intermediates remains as a major source of water pollution from the pulp and paper industries. Alternative elemental chlorine free bleaching methods based on the usage of chlorine dioxide, ozone and hydrogen peroxide are potential substitutes. Bio-bleaching methods, which involve pre-treatment of pulp with microbial enzymes such as xylanases, have emerged as viable options. Investigations reported in this paper aim at exploring the suitability of commercial bacterial xylanase enzyme preparations for bio-bleaching of bagasse pulps in conjunction with specific chemical bleach sequences employing hydrogen peroxide (P), alkali extraction (E), ozonation (Z), hypochlorite (H) and chelation (Q) stages. The effluent profiles and pulp qualities obtained for each of the bleach combinations (involving bio-bleaching and chemical bleaching sequences) were monitored. Analysis of the results clearly indicates that the inclusion of enzyme pre-treatment with the TCF (total chlorine free) and ECF (elemental chlorine free) sequences has a significant effect on the effluent (COD, lignin and colour) and pulp quality (kappa number, brightness) parameters. In conclusion, the findings of this investigation indicate the potential promise of enzyme pre-treatment in combination with chemical bleaching to enhance the quality of pulps and combined effluents.

Keywords Bio-bleaching; bagasse-pulp; enzyme; xylanase

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Introduction

The effluent from pulp bleaching processes containing chlorinated lignin and degraded polyphenolic intermediates remains as a major source of water pollution from the pulp and paper industries (Kringstad and Lindstorm, 1984). To meet the regulatory compliance and to prevent toxic effects of chlorinated organics in the receiving waters, the use of chlorine in pulp bleaching has been gradually discontinued in developed countries. Alternative elemental chlorine free (ECF) bleaching methods based on the usage of chlorine dioxide, ozone and hydrogen peroxide have substituted for the conventional ones. However these methods are not economically viable for medium or small capacity mills due to high costs of implementation. Bio-bleaching methods, which involve pre-treatment of pulp with microbial enzymes such as xylanases, have emerged as viable options. Xylanase enzymes apparently cause hydrolytic breakdown of xylan chains (hemicellulose) as well as cleavage of the lignin-carbohydrate bonds, thereby exposing lignin to the action of subsequent chemical bleaching steps (Suurnakki *et al.*, 1994). The advantages of using enzyme pre-bleaching are: reduced energy input, reduced consumption of bleach chemicals in the downstream steps, improved pulp quality (brightness), and minimized discharge of AOX (adsorbable organic halides) and colour in the effluents. However the bio-bleaching technology has been exploited only on softwood and hardwood in North American and Scandinavian countries, while in India bagasse is being increasingly used as the chief agricultural raw material for pulp production with shrinking resources of bamboo and hardwoods. Therefore further studies with regard to applications of enzyme for bagasse pulp bleaching seem to be relevant. Investigations reported in this paper aim at exploring the suitability of commercial bacterial xylanase enzyme preparations, Pulpzyme HC (Nova–Nordisk, Denmark) and B-230 (Esvin Biosystems, Chennai, India) for

bio-bleaching of bagasse pulps in conjunction with specific chemical bleach sequences employing hydrogen peroxide (P), alkali extraction (E), ozonation (Z), hypochlorite (H) and chelation (Q) stages. The objectives of this investigation were to:

- Optimise enzyme activity parameters.
- Assess suitability and effect of enzyme application (X) on subsequent chemical bleaching sequence combinations which may include alkali (E), chelator (Q), ozone (Z), hydrogen peroxide (P) and sodium hypochlorite (H) treatment on pulps with high and low kappa numbers. This was done by examining pulp properties (kappa number and brightness) and combined effluent characteristics (COD, colour, lignin).
- Compare the effect of pre-treatment using two commercially available xylanases.

Materials and methods

Enzyme samples

The commercial xylanase enzyme, Pulpzyme HC, was obtained from Nova-Nordisk, Denmark, and stored in a refrigerator prior to use. Pulpzyme HC isolated from a genetically engineered bacillus is a brown liquid preparation, standardised to 500 EXU/g. One xylanase unit (AXU) is defined as the amount of enzyme which under standard conditions (pH 9, 50°C, 30 minutes of incubation) releases a defined amount of dye from Remazol brilliant blue-xylan complex. Another xylanase enzyme preparation of bacterial origin (B-230), with enzyme action of 2500 EXU/ml, was obtained from Esvin Biosystems Ltd., Chennai, India.

Pulp samples

Samples of unbleached, screened, mechano-chemical bagasse pulp was obtained from Pudumjee Paper Mills Ltd., Chinchwad, Pune, India with initial kappa number of ~50.8. Bagasse chemical (kraft) pulp was obtained from Seshasayee Paper and Boards Ltd., Erode, India with an initial kappa number of ~14.8.

Experimental protocols

Several experimental protocols were selected in an effort to evolve an appropriate bleach sequence incorporating an enzyme prebleach stage as a potential alternative to the CEH (C represents elemental chlorine treatment step) or CEHH sequence, widely adopted by the Indian paper industry. Experiments were conducted to screen specific sequences involving ozonation, peroxidation, hypochlorite treatment, chelation, alkaline extraction, in conjunction with enzyme pre-treatment of unbleached bagasse pulps.

Preliminary trials were carried out on the pulps with the following objectives:

- Enzyme dosage and pH optimisation (using XE sequence).
- Ozone dosage and pulp consistency optimisation (using XZEQP sequence).
- Optimisation of peroxide dosage (using XPP sequence).

Further studies on pulp bleaching were done for the following purposes:

- Evaluation of bleach sequences combinations namely, XE, XEQP, XZEQP, XQPP and XHHQP for the pulp and combined effluent characteristics.
- Effect of multiple xylanase treatment (using XPXP sequence) on the pulp and effluent quality profiles.
- Comparison of the activities of B230 and pulpzyme HC on pulps using XHHP, XHPP and XPHH sequences.

Bleaching trials for enzyme pre-treatment, alkaline extraction, peroxidation, ozonation and hypochlorite treatment were carried out in sets of 250 ml Erlenmeyer flasks maintained at constant temperature using 5 gm of oven dry pulp. Ozonation was done in glass washing bottles, with a working volume of 400 ml at ambient temperature and ozone was generated using a Fischer ozone generator from commercial grade oxygen (IOL), as feed.

Analytical techniques

COD of the effluents were measured by the dichromate closed reflux method (*Standard Methods*, 1992) using a COD reactor (Model 45, 600, Hach Co., Loveland, Colorado, USA). Colour was measured by the cobaltiplatinate method and reported as platinum-cobalt colour units (PCU). One unit equals the absorbance produced by 1 mg/ml of platinum present in the form of cobaltiplatinate ion at 465 nm. Concentration of lignin was determined by measuring the absorbance at 280 nm in methanol medium (3 ml), containing 0.2 ml sample, using an Schimadzu UV-visible absorption spectrophotometer. Kappa number was determined as the volume of 0.1 N $KMNO_4$ consumed by 1 gm of moisture free pulp under prescribed conditions estimated as per Tappi standards (T 236 cm-85). Brightness of pulp was estimated in terms of reflectance relative to magnesium oxide (MgO) standard as percentage ISO using Techni Brite Model TB-1 (Technidyne Corporation Indiana, USA) as per Tappi 525 (ISO 2470). The concentration of reducing sugars present in the effluent samples as solubilized carbohydrates derived from pulp was determined by the dinitro-salicylic acid method, by measuring absorption at 540 nm. Yield of pulp after bleach sequence was determined by air drying pulp sheets for 24 hrs.

Results and discussion

Preliminary trials

Table 1 shows the conditions selected for pulp bleaching stages based on the results obtained from preliminary experiments. Kappa number of the treated pulp and combined effluent quality were used as criteria for arriving at these conditions. An optimal enzyme dosage of 10 Units at pH of 7.5, ozone dosage of 2% and hydrogen peroxide dosage of 4% were selected. The pulp consistency was fixed at 2.5% for the Z stage and 10% for all other bleaching steps.

Bleaching with enzyme pre-treatment

Inclusion of Pulpzyme HC pre-treatment with the TCF and ECF sequences had significant effect on the combined effluent and pulp quality parameters (Table 2). The enzymatic effects on the effluent and pulp qualities are individually listed below:

- Addition of enzyme to any of the bleach sequence combinations increased the COD of the effluent, which may be due to the hydrolytic action of the enzyme and weakening of the carbohydrate bonds in the pulp and its dissolution into the media.
- The lignin concentration of the effluent is also significantly enhanced following enzyme pre-treatment of the bleaching sequence. This may be the consequence of increased exposure of lignin to the action of bleach chemicals.
- The colour of the effluents obtained from the Pulpzyme HC pre-treated bleach sequences is higher than that of the pure chemical bleach sequences. This may be ascribed to the enhanced solubilization of lignin by xylanase pre-treatment.

Table 1 Conditions selected for pulp bleaching stages

Bleaching stage	Pulp consistency (%, w/w)	Temperature (°C)	Dosage	pH	Treatment time (min)
X (Xylanase)	10	50	10 units/g of oven dry pulp	7. 5	120
E (Alkaline extraction)	10	80	2 (% w/w)	11. 5	60
Q (Chelation)	10	55	1. 2	5. 5	30
P (Peroxide)	10	80	4	11. 5	180
Z (Ozonation)	2. 5	28	2	2. 5	14
H (Hypochlorite)	10	45	5	10. 5	60

- Pulpzyme HC pre-treatment in all bleach sequences improved the pulp characteristics as compared to the control. For example there is a significant decrease in kappa number and increase in pulp brightness. Other research groups have made similar observations (Bajpai and Bajpai, 1996; Yang *et al*., 1993). It can be observed from Table 2 that the XHHQP sequence gave the best results. This sequence reduced the pulp kappa number to the lowest value (~ 80% reduction) that is accompanied by enhancement in brightness to an extent of 70%.
- Higher removal of lignin and reducing sugars from enzyme treated pulp resulted in appreciable loss of pulp yield as compared to the chemical bleach sequences.

Studies on multiple xylanase treatment coupled to peroxide treatment

Results of multiple xylanase treatment coupled to peroxidation using XPXP sequences for high kappa number bagasse pulp are shown in Table 3. It can be observed from the table that despite double xylanase treatment (at a dosage of 5 or 10 units) coupled to oxidation with 4% or 2% hydrogen peroxide, dramatic enhancement of pulp quality parameters, namely, kappa number or the brightness, is not achieved compared to the corresponding pure chemical bleach sequence. Results observed by us may imply that multiple enzyme pre-treatment coupled to per-oxidation for pulps with high kappa number (high lignin content) may not be very effective unless effective lignin extraction/delignification steps such as alkaline extraction/oxygen stages are included. In addition it may not be an economical viable alternative. Wong *et al*. (1997) have reported direct brightening by mutiple xylanase treatments during peroxide bleaching of kraft pulps. Prasad *et al*. (1996) observed that two-stage enzyme treatment boosted pulp brightness by 1–3 points.

Comparison of the activities of B230 and Pulpzyme HC on high kappa number and low kappa number pulps

Figures 1 and 2 compare the activities of Pulpzyme HC and B-230 on low and high kappa number pulps based on the pulp kappa numbers. Analysis of the data reveal that the Pulpzyme HC activity was higher by 3–4% compared to B-230 with high kappa number pulp, while with the low kappa number pulp B-230 was found to give slightly lower kappa numbers and better brightness. These results imply that the two commercially available

Table 2 Combined effluent characteristics and pulp qualities of low kappa number bleached pulp after enzyme (Pulpzyme HC) treatment

Sequence	Effluent Parameters			Pulp Parameters		
	COD (mg/ g of oven dried pulp[+])	Lignin (mg/g of oven dried pulp)	Colour (PCU)	Kappa No.	Brightness (% ISO)	Yield loss (%)
E©	10. 5	1. 7	129	14. 6	41	5. 0
XE (T)	37. 5	2.0	188	13. 4	43	5. 0
EQP©	28. 5	4.0	70	8.0	58	4. 0
XEQP (T)	54. 0	4.0	77	7. 0	60	5.6
ZEQP©	36. 0	3. 6	189	8. 4	61	2. 0
XZEQP (T)	69. 4	4.6	325	7. 0	66	6. 0
QPP©	58. 0	4. 0	216	8. 0	64	6. 0
XQPP (T)	136. 4	4. 6	272	5. 4	68	8. 0
HHQP©	61. 6	4. 0	111	5. 0	61	5. 0
XHHQP (T)	175. 5	4. 4	115	3. 0	72	8. 0

[+] Bagasse chemical (kraft) pulp with initial kappa number of 14.8 was obtained from Seshasayee Paper and Boards Ltd., Erode, India; © Represent control experiment where in specified bleach sequence was applied without the enzyme pre-treatment to pulp; (T) represents corresponding chemical bleaching sequence in conjunction with enzyme (Pulpzyme HC) pre-treatment to pulp

Table 3 Combined effluent characteristics and pulp qualities of high kappa number pulp after multiple enzyme treatment coupled to peroxide bleaching

Sequence	Effluent COD (mg/ g of oven dried pulp+)	Parameters Lignin (mg/g of oven dried pulp)	Colour (PCU)	Pulp+ Kappa No.	Parameters Brightness (% ISO)	Yield loss (%)
QPP©	98	18	287	32	34.5	12
XQPP (T) (X = 10 U; Q = 1.2%; P = 4%)	223	22	419	29	39	18
PP©	113	18	630	31	36	12
XPXP (T) (X = 10 U; P = 4%)	248	21	594	28	39	24
PP_1© (P_1 = 2%)	113	18	489	32	35	10
XPX_1P_1 (T) (X_1 = 5 U; P_1 = 2%)	302	21	604	30	37	23

+ Mechano-chemical bagasse pulp with initial kappa number of 50. 8 were obtained from Pudumjee Paper Mills Ltd., Chinchwad, Pune, India. © Represent control experiment where in specified bleach sequence was applied without the enzyme pre-treatment to pulp; (T) represents corresponding chemical bleaching sequence in conjunction with enzyme (Pulpzyme HC) pre-treatment to pulp

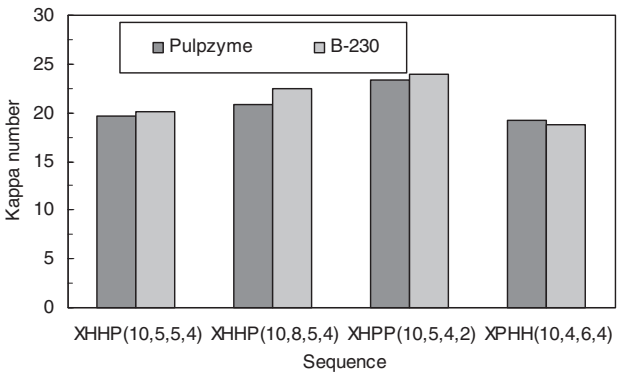

Figure 1 Comparison of B-230 and Pulpzyme HC activity on kappa number of a high kappa number pulp

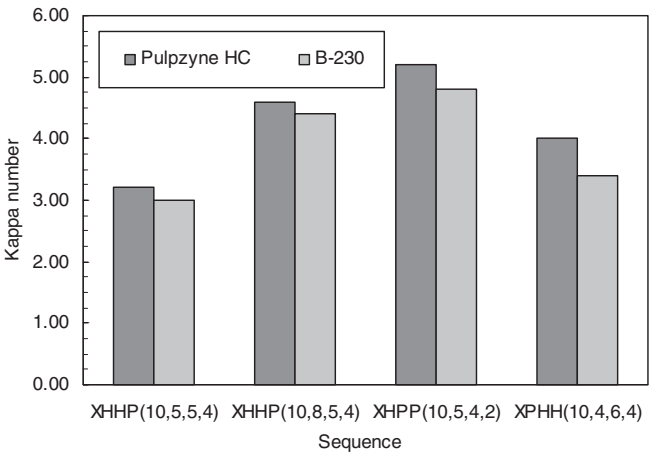

Figure 2 Comparison of B-230 and Pulpzyme HC activity on kappa number of a low kappa number pulp

enzymes perform almost equally well with respect to enhancing the pulp quality parameters.

In conclusion, the findings of this investigation indicate the potential promise of enzyme pre-treatment in combination with chemical bleaching to enhance the quality of pulps. Further trials on a larger scale at a mill site are required for a realistic appraisal of the enzyme pre-treatment concept to achieve ECF grade bleached pulp and reduction in the pollution load of the effluents.

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