Xylanase Prebleaching of Wheat Straw and Sarkanda Soda Pulps

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ABSTRACT

In the present study the impact of enzyme pretreatment on wheat straw and sarkanda soda pulps on bleach chemical consumption pollution load generation and pulp properties for CEH, D50C50ED and DED sequences is assessed. For the same target brightness, in wheat straw pulps the saving in total active chlorine for CEH, D50C50ED and DED sequences was from 16.4 to 24.2%. NaOH reduction was from 15.3 to 23.2% . In sarkanda pulp the saving in total active chlorine for CEH, D50C50ED and DED sequences was from 17.5to 21%. NaOH reduction was from 19.1 to 20.2%. At the same level of bleach chemical dose brightness gain was of the order of 2-3% ISO. The AOX levels reduced by 20-30% in all three sequences. A substantial decrease of colour in combined effluent was observed (20-30%). The strength properties showed marginal increase in the three sequences compared to the control pulps.

INTRODUCTION

The Indian paper industry uses bleaching sequence where chlorine is a predominant bleaching chemical.As a consequence, the bleach plants have become a major source of environmental pollution contributing to chloroorganics release with high BOD, COD, AOX and colour loads. Evironmental and regulatory concerns regarding AOX and other pollution parameters in Indian paper and pulp mills have forced mills to look for altering bleaching techniques which reduce or eliminate the use of elemental chlorine in bleach sequences. Xylanase prebleaching could prove to be one of the promising options since enzymes are readily biodegradable and do not contribute to organochlorine formation.

The main goal in the enzyme aided bleaching of pulps have been directed towards reducing chemicals in bleaching process, thereby reducing the absorbable organic halides (AOX) content of the effluent and making the effluent more amenable to biological treatment.

It has been demonstrated that the main enzyme needed in the enzyme aided bleaching is endo - B-xylanase. Xylanase prebleaching facilitates the subsequent chemical bleaching of kraft pulps (1). The brightness of the pulp was substantially increased by enzymatic treatment and this improved brightness could be exploited for reduction of chlorine chemical consumption or for value addition. Thereafter it was confirmed and further developed by extensive laboratory studies in hard wood and softwood pulps (2-7).

Recently the effectiveness of enzyme pretreatment has been shown for agricultural residue pulps (8-11). Mill trials using xylonite enzymes for bleaching kraft pulp have been carried but successfully since 1989 (12). A significant number of Scandinavian and North American mills are using xylanase in their bleaching process (13). Improved viscosity was reported (14,15)as a result of xylanase treatment after subsequent bleaching. However the viscosity of the pulp was adversely affected when cellulase activity was present. Xylanase pretreatment has led to reduced effluent concentration of AOX and dioxin as less chlorine is needed to achieve a given brightness (16,17). In the same study the effluent BOD almost doubled and there was an increase in effluent COD. The BOD/COD rates also increased indicating that the effluent was more amendable to biological degradation.

It is not clear how xylanase can reduce the amounts

Table 1. Bleaching conditions

Parameter	C	D50C50	D	E	H	D
Consistency (%)	3	5	10	10	10	10
Temperature (°C)	Ambient	40	70	70	70	70
Time (min)	45	60	90	60	180	180
End pH	<2	3-4	3.5-4.5	10-11	9.5-10	3.5-4.5

of chemicals required to bleach pulps to desired brightness levels. A number of hypothesis have been forwarded concerning the nature of the target substrates for xylanase. They include xylan derived chromophores, xylan in lignin carhohydrate complexes, xylan that physically entraps lignin and xylan that influence fibre swelling. An apparent consensus has been that xylanase makes pulp more amenable to chemical bleaching without brightening or delignifying the pulp during the xylanase prebleaching stage.

Though the effectiveness of enzyme has been proved for with soft wood and hard wood pulps, the literature indicates very little information on the use of enzymes for agricultural residue pulps especially straws.

In view of the above facts, experiments were planned to study the impact of enzyme pretreatment on wheat straw and sarkanda soda pulps and compare the impact of enzyme pretreatment on bleach chemical consumption, pollution load generation and pulp properties.

EXPERIMENTAL

Materials

Unbleached wheat straw and sarkanda soda pulps were procured from a paper mill in North India. The pulps were washed and screened in the laboratory. The pulps were neutral (pH between 7 and 7.5). The pulps were characterized for kappa number, viscosity and brightness. Commercial Xylanase (Pulpzyme HC) prepared from a cloned Bacillus gene was used. The characteristics of the enzyme are given in Figs. 1 and 2.

Enzyme pretreatment

Initial tests were conducted to optimize the enzyme pretreatment conditions. Enzyme activity is determined at various pH and temperatures keeping other paratmeters constant. The effectiveness of enzyme was determined on the actual substrate (wheat straw pulp) at varying pH, temperature and dose by determining the CE kappa values. Reducing sugars (as mg/g xylose) were also estimated at the above mentioned parameters. The reducing sugars gave more conclusive results of enzyme optimization . Hence this method was followed for wheat straw and Sarkanda pulps.

Enzyme pretreatment was carried out at optimized conditions. The reference pulps were incubated in the same conditions as enzyme treated pulps with distilled water replacing the enzyme. After the enzyme treatments the pulps were washed before further bleaching. All bleaching experiments were carried out in duplicate.

Bleaching studies

Control and xylanase treated pulps were subjected to conventional (CEH), D50C50ED and DED bleaching sequences at various bleach chemical charges. The impact of enzymatic prebleaching on different bleaching sequences at 80% ISO target brightness levels were compared with regard to bleach chemical consumption, pulp properties and pollution load generation. The bleaching conditions are listed in Table 1. After each bleaching stage the pulps were washed. Apart from the C stage, which was performed at ambient temperature, all other bleaching stages were performed in temperature controlled water baths. All the bleaching experiments were performed in triplicate.

Test methods

The xylanase activity was measured by estimating reducing sugar formed from oat splet xylan (18). Enzyme unit (International units IU) is defined as the amount of enzyme necessary for the production of 1 micromole product/min. Tappi Standard methods were used to calculate the kappa number, viscosity (CED) and brightness of pulps. Hand sheets were prepared to calculate the strength properties. Brightness was measured by Technibrite. BOD and COD were calculated by standard methods.

Colour measurement was performed sprectrophotometrically. A standard solution of 2500

Pt Co units was prepared. This solution was diluted to obtain standard solutions of different colour units. The absorbance of bleaching effluent (adjusted to pH 7.3) was measured at a wavelength 465 nm. The colour of the effluents were calculated from the standard calibration curve between absorbance and colour units.

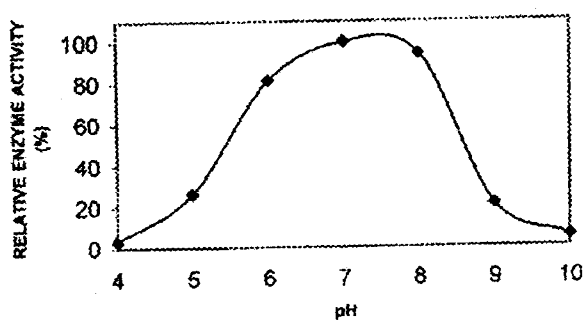

Fig. 1 Relative enzyme activity vs pH

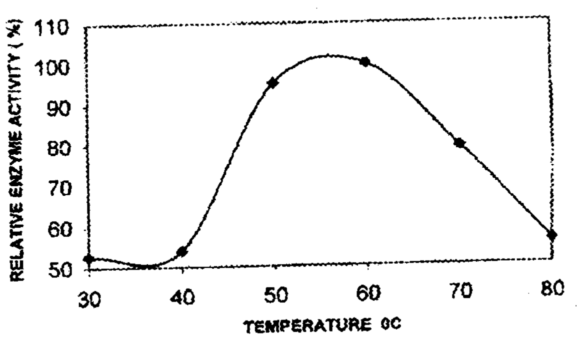

Fig. 2 Relative enzyme activity vs temperature

RESULTS AND DISCUSSION

Optimization of enzyme pretreatment

The enzyme pretreatment optimization is performed by

(a) CE Kappa and final brightness

The enzyme shows the maximum activity between pH and .>-8 at 60°C (Fig. 1, 2). This is in agreement with enzymes of bacterial origin which show highest activity in pH range of 6-9. When the actual substrate (wheat straw soda pulp) was treated with the enzyme, the CE kappa and final brightness values gave the same trend. The CE kappa values were lowest at pH 7.5 and temperature 60°C. The final brightness values obtained did not give conclusive results in some cases. (Tables 2 and 3).

Table 2. CE Kappa and CEH brightness of wheat straw pulp at different pH

pH	CE Kappa	CEH Brightness (% ISO)
6.2	5.5	78.5
6.6	5.2	78.7
7.0	5.1	79.2
7.5	4.7	80.1
8.1	6.0	76.8
8.5	6.1	75.5

Table 3. CE Kappa and CEH brightness of wheat straw pulp at different temperatures

Temperature °C	CE Kappa	CEH brightness (% ISO)
50	4.7	78.9
60	4.5	79.9
70	5.2	80.1

(b) Reducing Sugar equivalents released

Enzyme dose

Varying amounts of enzyme doses were given to the pulp maintained at pH 7.5, temperature 60°C and 10% consistency. The amount of reducing sugars released from the pulp was found to depend on the xylanase dose. Reducing sugars showed a sharp increase from 4.67 to 14.02 IU/g (8.66 - 19.8 mg/g xylose) and then increased slowly to an enzyme dose of 26.3 IU/g (21.7 mg/g xylose). A similar trend seen in Sarkanda pulp though the release of reducing sugars was sharp till 18.7 IU/g and then the increase was very slow (Fig. 3.) The concentration of reducing sugars in sarkanda was less than in wheat straw pulps. The above phenomenon may be due to the restricted assessibility of substrate for xylanase action or saturation of enzyme substrate complex (19). It has been shown that reducing sugar release was maximum at a certain level of enzyme dose and further increase of enzyme dose did not increase solubilization.

pH

The amount of reducing sugars released was maximum at pH 7.5 (neutral) compared to both acidic or alkaline range. Maximum reducing sugars were 19.6 mg/g xylose and 10.6 mg/g xylose for wheat straw and sarkanda respectively. The results show that the enzyme is quite active between pH 7-8 (Fig. 4).

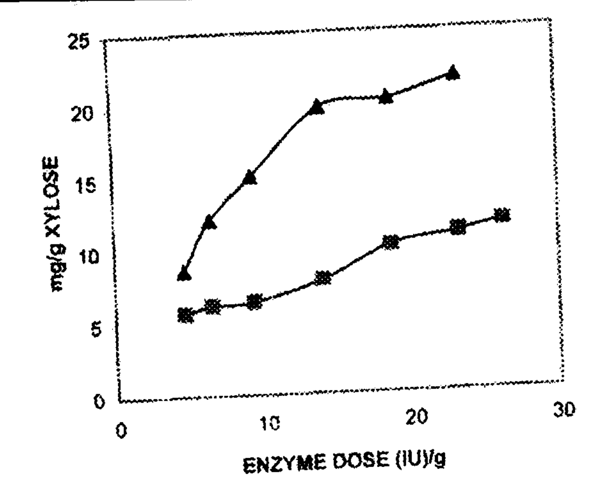

Fig. 3 Reducing sugars vs enzyme dose

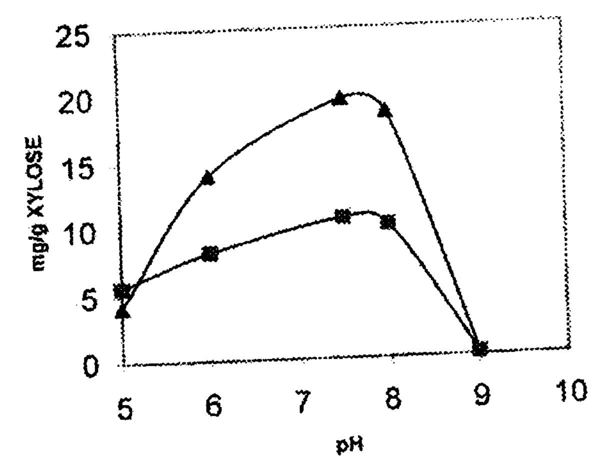

Fig. 4 Reducing sugars vs pH

Temperature

The effect of temperature was studied at optimized dose and pH 7.5 Maximum reducing sugar released at 60°C (Fig. 5). Optimized conditions for enzyme pretreatment are shown in Table 4.

Effect of enzyme pretreatment

Pulp properties

The results of Table 5 confirm the effectiveness of enzyme pretreatments. A reduction of (0.5 - 0.8 points) kappa no. was observed for both pulps. The brightness gain was more for wheat straw pulp compared to

Table 4. Optimum conditions of enzyme pretreatment

Parameter	Wheat straw	Sarkanda
Enzyme dose IU/g	14.02	18.7
Pulp consistency %	10	10
pH	7.5	7.5
Time h	2	2
Temperature °C	60	60

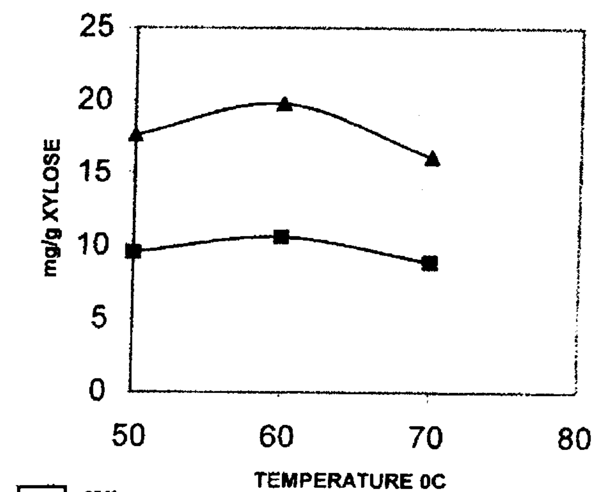

Fig. 5 Reducing sugars vs temperature

sarkanda. There was also an increase in viscosity for enzyme pretreated pulps in both cases. The increase in viscosity may be attributed to the fact that xylanase degrades/depolymerize to low DP xylan. The reduction in kappa number is of the same range as reported in the literature (8, 9). Improved viscosity is also observed in enzyme pretreated pulps. (9, 14, 16).

Effect of xylanase pretreatment on bleach chemical consumption

Bleach chemical consumption for different bleaching sequences were compared between blank and enzyme pretreated pulps for same target brightness. Target brightness of 80% ISO was achieved in CEH and D50C50ED for wheat straw pulp. In the DED sequence even at 30.5 kg/T dioxide charge, only 77% ISO was achieved in wheat straw pulps. In sarkanda pulp 80% brightness was achieved in CEH and D50C50ED bleaching sequences. The target brightness was achieved in DED sequence for sarkanda at a total charge of 35.4 kg/T dioxide.

For the same target brightness, in wheat straw

Table 5. Results of enzyme pretreatment

Parameter	Wheat straw		Sarkanda	
	Control	Enzyme treated	Control	Enzyme Treated
Inlet kappa	22	21.4	26	25.3
CE kappa	5.8	4.5	ND	ND
Brightness (% ISO)	26.8	27.5	22.1	22.5
Viscosity (cm^3/g)	629	679	710	730
Yield (%)	-	99.4	-	99.3

pulps the saving in total active chlorine for CEH, D50C50ED and DED sequences was from 16.4 to 24.2 %, and NaOH reduction was from 15.3% to 23.2%. In sarkanda pulp the saving in total active chlorine for CEH, D50C50ED and DED sequences was from 17.5 to 21% and NaOH reduction was from 19.1 to 20.2% (Table 6 and 7). An average reduction of 25-40% in active chlorine consumption in the first bleaching stage has been reported for hard wood and 15-25% for softwood pulps (20, 21). Brightness of pulps for same bleach chemical charge were compared for blank and enzyme pretreated pulps.

In wheat straw pulp the increase in brightness for CEH, D50C50ED and DED bleaching sequences were 2.2%, 2% and 2.5% ISO respectively. In the sarkanda pulps the brightness increased by 2.4% and 2.2% and 2.5% ISO respectively for CEH, D50C50ED & DED bleaching sequences. A similar brightness gain of 2-3% ISO is reported for bagasse kraft pulps (9). A brightness gain was reported when hypochlorite in the final bleaching stage of CEPH was reduced by 42.2%

Table 6. Bleach chemical consumption (Kg/t) of untreated and enzyme pretreated wheat straw soda pulp

Sequence	Bleach chemical charge (Kg/t) as such								
	CEH			D50C50ED			DED		
	Control	Enzyme pretreated		Control	Enzyme pretreated		Control	Enzyme pretreated	
1st stage									
Cl_2	56	56	41.6	23.6	23.6	18.65	-	-	-
ClO_2	-	-	-	8.97	8.97	7.09	22.9	22.9	19.08
End pH	<2	<2	<2	3.5	3.4	3.4	4.2	4.8	4.3
Reduction Cl_2	-	-	14.4	-	-	5.0	-	-	-
Reduction ClO_2	-	-	-	-	-	1.81	-	-	5.4
2nd stage									
NaOH	31	31	23.8	26.6	26.6	21.6	33.2	33.2	25.9
End pH	10	10.1	9.8	11.0	10.8	10.5	10.0	10.0	10.3
Reduction	-	-	7.2	-	-	5.0	-	-	5.1
3rd stage									
Hypo	20	20	16.0	-	-	-	-	-	-
ClO_2	-	-	4.0	-	-	0.7	-	-	1.54
Reduction	-	-	4.0	-	-	0.7	-	-	1.54
Total act Cl_2 charge	76	76	57.6	64.2	64.2	52.3	80.8	80.8	67.2
Brightness (% ISO)	79.9	82.0	80.1	80.1	82.1	79.8	77.3	79.8	76.9

Table 7. Bleach chemical consumption (Kg/t) of untreated and enzyme pretreated sarkanda soda pulp

Sequence	Bleach chemical charge (Kg/t) as such								
	CEH			D50C50ED			DED		
	Control	Enzyme pretreated		Control	Enzyme pretreated		Control	Enzyme pretreated	
1st stage									
Cl_2	62.8	62.8	50.7	26.2	26.2	20.3	-	-	-
ClO_2	-	-	-	9.96	9.96	7.71	27.8	27.8	21.9
End pH	<2	<2	<2	3.6	4.0	3.7	4.2	4.5	4.5
Reduction Cl_2	-	-	12.1	-	-	5.9	-	-	-
Reduction ClO_2	-	-	-	-	-	2.25	-	-	5.9
2nd stage									
NaOH	34.4	34.4	28.3	29.2	29.2	23.3	39.6	39.6	29.1
End pH	10.3	9.8	10.2	10.5	10.1	10.6	10.5	9.9	11.0
Reduction	-	-	6.1	-	-	5.9	-	-	7.8
3rd stage									
Hypo	18.0	18.0	16.0	-	-	-	-	-	-
ClO_2	-	-	-	6.08	6.08	5.32	7.6	7.6	6.08
Reduction	-	-	2.0	-	-	0.76	-	-	1.52
Total act Cl_2 charge	80.8	80.8	66.6	68.4	68.4	54.6	93.2	93.2	73.6
Brightness (% ISO)	79.8	82.2	80.1	80.1	82.4	80.0	80.2	82.7	80.1

in wheat straw pulp using Sebrile BB xylanase (22).

Effluent chrácteristics

The characteristics of the effluent are shown in Tables 8 and 9. Xylanase pretreatment has led to reduced effluent concentration of adsorbable organic halides, AOX in wheat straw pulp. The percentage reduction of AOX in combined CEH, D50C50ED and DED effluents have been 29.4%, 21.9% and 24% respectively. Reduction in AOX concentration in the order of 14-42% is reported in the literature for the conventional CEH sequences. (8, 11, 13).

At the same target brightness for CEH, D50C50ED, DED sequences BOD and COD increase marginally for both pulps with increase in BOD/COD ratio. The increase in BOD & COD is expected because the enzyme helps in the removal of more lignin &

Table 8. Effect of xylanase pretreatment of effluent characteristics od wheat straw

Parameter	Control			Xylanase treated		
	CEH	D50C50ED	DED	CEH	D50C50ED	DED
Total aCl (kg/t)	76.0	64.2	80.8	57.6	52.3	67.2
BOD (kg/t)	8.43	8.24	9.14	9.84	9.54	11.15
COD (kg/t)	38.05	36.03	39.39	39.47	38.03	42.03
Color (PtCo units)	5190	3225	2370	4113	2564	1966
BOD/COD	0.221	0.228	0.232	0.25	0.250	0.265
AOX (kg/t)	2.44	1.02	1.208	1.722	.796	.918

Table 9. Effect of xylanase pretreatment of effluent characteristics of sarkanda

Parameter	Control			Xylanase treated		
	CEH	D50C50ED	DED	CEH	D50C50ED	DED
Total aCl (kg/t)	80.8	68.4	93.2	66.6	54.6	73.6
BOD (kg/t)	9.67	9.09	10.64	11.42	13.06	14.88
COD (kg/t)	41.18	45.2	50.2	42.02	51.0	58.6
BOD/COD	0.234	0.201	0.211	0.272	0.256	0.253
Color (PtCo units)	7135	5754	3635	4815	4010	2800

Table 10. Strength properties of untreated and enzyme pretreated wheat straw pulp

Parameter	CEH	XCEH	DED	XDED	D50C50ED	XD50C50ED
PFI Revolutions	1500	1500	1500	1500	1500	1500
Freeness CSF, ml	360	375	365	370	355	365
Tear Index $(mNm^2)/g$	6.30	7.34	8.46	8.44	7.44	7.64
Tensile Index (Nm/g)	45.42	48.53	47.19	49.59	46.28	48.91
Burst Index (Kpa m^2/g)	3.63	3.98	4.16	3.67	4.28	4.37

Table 11. Strength properties of untreated and enzyme pretreated sarkanda pulp

Parameter	CEH	XCEH	DED	XDED	D50C50ED	XD50C50ED
PFI Revolutions	2000	2000	2000	2000	2000	2000
Freeness CSF, ml	350	365	340	330	355	375
Tear Index $(mNm^2)/g$	9.0	9.59	8.60	7.26	7.96	6.71
Tensile Index (Nm/g)	41.25	44.01	42.32	43.98	43.72	46.12
Burst Index (Kpa m^2/g)	2.86	3.25	3.02	3.95	3.37	3.65

xylans. Such effluents are more amenable to biological degration due to high BOD/COD ratio. (23).

A substantial decrease of colour in combined effluents is observed in CEH, D50C50ED and DED sequences. The percentage reduction is 20.7, 20.4 and 17 in wheat straw and 32.5, 30.2 and 22.9 in sarkanda pulps respectively.

Strength properties

The enzyme pretreated pulps show marginal increase in strength (tear, tensile and burst indexes) for both pulps (Tables 10 and 11) at same target brightness. It has been shown in the case of wood pulps at the same bleach chemical consumption a decrease of 6-9% in tear and burst indexes (8,9). In bagasse pulps at the same bleach chemical consumption an increase in burst and tensile index are reported for enzyme pretreated pulps (8,11). A similar trend was seen in bamboo pulp (10).

It appears that after bleaching to same brightness level the changes in pulp strength are only indirectly related to the action of xylanase because the lower chemical loadings required, can reduce damage to pulp strength and modifying refining properties. There have been reports that bleach pulps that have been xylanase pretreated are more difficult to refine (10). In contrast, before bleaching less beating of xylanase pretreated pulps seems to be required to reach a given freeness (24).

CONCLUSION

The enzyme prebleaching is possible for both wheat straw and sarkanda pulps. The optimized conditions of enzymes prebleaching are different for both pulps.

A target brightness of 80% ISO is achievable for both wheat straw and sarkanda pulps with and without enzyme prebleaching using CEH and D50C50ED sequences. Sarkanda pulp can be bleached with high chlorine dioxide dose to 80% ISO brightness in DED sequence. There is a significant reduction in bleach chemical consumption in each stage in all the bleaching sequences for enzyme pretreated wheat straw and sarkanda pulps compared to untreated pulps.At the same chemical consumption level the enzyme pretreated pulps show brightness increase between 2-2.5% for both pulps, in each of the bleaching sequences. The combined effluent AOX characteristics of wheat straw enzyme pretreated pulp show a decrease of 21.9-29.4% for different bleaching sequences. The BOD and COD values increase for enzyme pretreated pulps compared to blanks, while enzyme pretreated pulps show a increase in BOD/COD ratio. The enzyme pretreated pulps gave a colour reduction of 17-32.5% in combined effluents for both pulps compared to blank. The enzyme pretreated pulps show marginal increase in tensile, tear and burst index.

REFERENCES

1. Viikari, L., Ranua, M., Kantelinen, A., Linko, M. & Sundquist, J. Bleaching with Enzymes., **Proc. 3rd Interna. Conf. Biotechnol Pulp and Paper Ind. Stockholm** 67 (1986).
2. Yang, J., Lou, G., and Eriksson, L., **Tappi J.** 75 (12) : 95 (1992).
3. Allison. R.W., Clark, T.A. and Wrathall, S.H. **Appita J.**, 46 (5), 349-355 (1993).
4. Allison. R.W., Clark, T.A. and Wrathall, S.H. **Appita J.**, 46 (40), 269-273 (1993).
5. Bajpai, P., Bhardwaj, P.K., **Tappi J.**, 79 (4), 225 (1995).
6. Bajpai, P., Bhardwaj, N.K., Bajpai, P.K. and Jauhari, M.B. **J. Biotechnol.**, 36 (1), 1-6 (1994).
7. Bajpai, P., Bhardwaj, N.K., Maheshwari, S. and Bajpai, P.K. **Appita J.**, 46 (4), 274-276 (1993).
8. Jain et al, **IPPTA J.**, 12, (4) (.4) 77-83 (2000).
9. Jain et al, **IPPTA J., Con. issue,** 52-64 (2001).
10. Bajpai, P and Bajpai P.K. **Tappi J.**, 75 (225-230 (1996).
11. Misra et al **IPPTA Con. issue** 5-14 (2001).
12. Vaheri, M., Mikki, K., Jokela, V., et.al, Proceedings of the Dioxin Conference, **CPPA**, Toronto, 130 (1989).
13. Senior, D.J. and Hamilton, **J., Pulp and Paper** 66 (9) : 111 (1992).
14. Senior, D.J. and Hamilton, J., Bernier, R.L. et.al, **Tappi J.** 75 (11) : 125 (1992).
15. Senior, D.J. and Hamilton, J., **Tappi J.** 76 (8) : 200 (1993).
16. Senior, D.J. and Hamilton, J.J., **Pulp and Paper Sci.**, 18 (5), J 165-168 (1992).
17. Senior, D.J. and Hamilton, J., Bernier, R.L. and DuManoir, J.R. **Tappi J.**, 75 (11), 125-130 (1992).
18. Bailey M.J., Bailey P. And Pantanen, "K. Interlaboratory testing methods for assay of xylanase activity" **J. Biotechnol.** 23:257 (1992).
19. Christov, L.P. and Prior, B.A. **Biotechnol. lett.** 15; 1264-1274 (1993).
20. Vikari, L. Sundguist, J. And Kettunen, J., **Paper and Timber** 73 : 384 (1991).
21. Koponen, R.J., **Pulp and Paper Int.**, 33 (11), 20 (1991).
22. Rathi, C.L. and Udayanchandran, R., **CPPRI, Interaction meet-Biotechnology in Paper Industry-A fresh look,** 41-51 (2001).
23. Oryrko, K.A., **Biotechnol. Adv.** 11: 179 (1993).
24. Bhardwaj, N.K., Bajpai, P., Bajpai, P.K., **J. Biotechnol.** 51:21 (1996).