Effect of Enzyme Treatment in Pre-Bleaching Stage on Bleached Kraft Mill Pulp & Quality of Bleach Effluents Generated.

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Unbleached pulp having kappa 26.0 and pH 10.2 was treated with a specific Endo-Xylanase (enzyme) at various temperatures for 60 minutes which resulted in lowering of the pulp kappa by one degree. Subsequently bleaching was carried out under C-Ep-H-D sequence for attaining 87-88% P. V. brightness of enzymes treated pulp & comparison made with similar pulp obtained without enzyme pre-treatment. It is observed that Endo-xylanese dosage of 2.0 kg/ton of pulp reduced 15.0% chlorine requirement and the brightness gain is 0.5% P.V. against blank experiment. Enzyme treated pulp at temperature 40°, 45° and 50°C is observed to have shrinkage in increasing order for the same final bleached pulp brightness of 87-88% P. V. but less than blank experiment. But reverse trend was observed in case of bleached pulp viscosity. Fines in enzyme treated bleached pulp are lower than non-enzyme bleached pulp while physical strength properties of pre enzyme treated bleached pulps are higher than blank experiment. It is also observed that pollution load in terms of COD, and dissolved solids contents in enzyme treated bleached pulps under C-Ep-H-D sequence increased with increase in temperature at pre-enzyme treatment stage.

INTRODUCTION

Mounting environmental pressure and awareness has led the paper industry to look for cleaner production options in terms of reduced consumption of chlorine and its compounds during bleaching operations to minimize the discharge of chlorinated organics in the effluent since Chlorinated phenolic compounds are toxic and resistant of bio-degradation[1-4]. In this context process such as biobleaching is emerging as a major substitute to conventional bleaching process utilizing elemental chlorine to minimize environmental degradation. One such promising technology is with xylanase enzyme delignification prior to bleaching as it has produced encouraging results[5,6]. Xylan creates a physical barrier to chlorine and sodium hydroxide accessibility to lignin. In addition there is evidence that xylan and lignin are chemically bound[7]. Partial and selective hydrolysis of hemicellulose by xylanase enzyme reduces the bonding between lignin and cellulose[8,9]. Xylanase effects the removal of specific lignin structure leaving a residual lignin in pulp that may be more responsive to bleach chemical oxidation than the residual lignin in the conventional pulps[10,11].

One such enzyme selected for pre bleaching was an aqueous solution of bacterial Endo-Xylanase and was tried with the mill unbleached pulp under C-Ep-H-D bleaching sequence.

RESULTS & DISCUSSIONS

Bleaching of pre-enzyme treated and untreated mill unbleached pulp under C-Ep-H-D sequence.

Decker unbleached pulp throughout the above bleaching experiments has mixed bamboo and mixed hard woods in 65:35 proportion with kappa 26.0 and pH of 10.2.

To get the real benefit of bio-bleaching mill pulp was treated with Endo-Xylanase 2.0 kg/ton of pulp at 40°, 45° and 50°C for 60 minutes which resulted in reduction of intial pulp kappa 26.0 by one degree after enzyme treatment. The enzyme treated pulps were further bleached under C-Ep-H-D sequence by reducing around 15% of total chlorine in chlorination and hypochlorite stages. Process data with respect to the bleaching conditions, results of blank experiment and enzyme treated pulps bleached under C-Ep-H-D sequence are tabulated in Table 1. It is observed that brightness in blank as well as xylanase/C-Ep-H-D sequence bleached pulps was nearly

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Table 1: Bleaching of mill pulp (with and without pre enzyme treatment) under C-Ep-H-D sequence.

Particular	Blank Pulp Kappa No. 26.0	Enzyme addition at 40°C followed by bleaching under C-Ep-H-D Sequence	Enzyme addition at 45°C followed by bleaching under C-Ep-H-D Sequence	Enzyme addition at 50°C followed by bleaching under C-Ep-H-D Sequence
	Expt. No.1	Expt. No. 2	Expt. No.3	Expt. No.4
Chlorination Stage				
i) Chlorine applied, %	6.0	5.1	5.1	5.1
ii) Chlorine consumed, %	5.88	5.05	5.05	5.05
iii) End pH,	1.8	1.8	1.8	1.8
iv) Consistency, %	3.0	3.0	3.0	3.0
v) Temp. °C	Room	Room	Room	Room
vi) Time, mnts	60	60	60	60
Alkali Extraction Stage				
i) Caustic applied, %	1.8	1.6	1.6	1.6
ii) H_2O_2 applied, %	0.4	0.4	0.4	0.4
iii) End pH,	10.4	10.3	10.2	10.1
iv) Consistency, %	10.0	10.0	10.0	10.0
v) Temp. °C	65±1	65±1	65±1	65±1
vi) Time, mnts	60	60	60	60
Calcium Hypochlorite Stage				
i) Hypochlorite applied, %	3.9	3.4	3.4	3.4
ii) Hypochlorite consumed, %	3.63	2.86	2.85	2.80
iii) Sulphamic Acid,%	0.1	0.1	0.1	0.1
iv) Buffer added, %	1.2	0.9	0.9	0.9
v) End pH	8.5	8.1	8.5	8.7
vi) Consistency, %	10.0	10.0	10.0	10.0
vii) Temp. °C	40±1	40±1	40±1	40±1
viii) Time, mts	120	120	120	120
Chlorine dioxide Stage				
i) Chlorine dioxide applied, %	0.6	0.6	0.6	0.6
ii) Chlorine dioxide consumed, %	0.56	0.54	0.50	0.48
iii) End pH	5.5	5.4	5.2	5.1
iv) Consistency, %	10.0	10.0	10.0	10.0
v) Temp. °C	70±1	70±1	70±1	70±1
vi) Time, mnts	120	120	120	120
Final Results				
i) Total chlorine applied, %	9.9	8.5	8.5	8.5
ii) Total chlorine consumed, %	9.51	7.91	7.90	7.85
iii) Pulp Brightness, % P. V.	87.0	87.0	87.5	87.5
iv) Pulp shrinkage, % (on O.D. pulps)	13.0	12.2	12.1	12.7
v) Pulp Viscosity (0.5% C.E.D.), Cps i)	7.0	7.8	7.7	7.3

Table 2: Fiber classification of mill pulp (with and without pre enzyme treatment) bleached under C-Ep-H-D Sequence

Mesh size, mm.	Expt. No. 1	Expt. No. 2	Expt. No. 3	Expt. No. 4
	Fibre retention, %			
+ 40	48.12	47.12	46.88	46.40
- 40 + 70	21.65	21.53	21.43	22.10
- 70 + 100	13.53	14.89	15.39	15.13
- 100 + 140	2.60	3.58	3.76	3.90
-140	14.10	12.88	12.54	12.47
Total	100.0	100.0	100.0	100.0

same but the pulp viscosity was higher at 40ºC followed by 45ºC and 50ºC enzyme treated pulps. Similar trend was observed with bleached pulp shrinkage.

Comparison of pulp viscosity of enzyme treated and untreated bleached pulps are shown in Fig. 1. There was 0.5% P. V. pulp brightness gain at 45º and 50ºC enzyme treated pulps that were finally bleached under C-Ep-H-D bleaching sequence compared to blank experiment.

Fibre classification of enzyme pre treated and untreated bleached pulps

Unbleached mill pulp (with and without enzyme treatment) which was bleached under C-Ep-H-D sequence was analyzed for fibre classification. As may be seen from Table 2. fines fraction passing through 140 mesh were on lower side compared to blank experiment and similar trend was observed with fibre retention on 40 mesh (Fig.2).

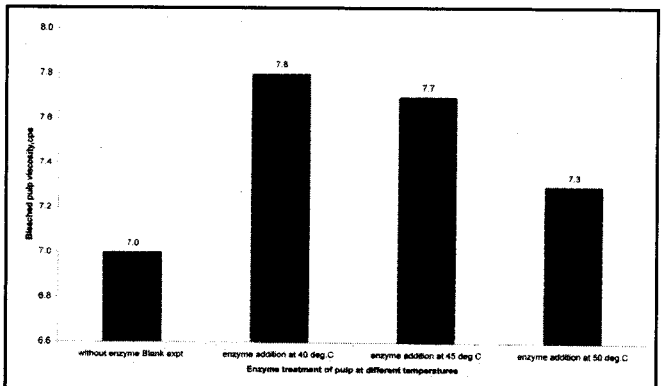

Fig. 1 Effect of enzyme addition at different temperature followed by C-Ep-H-D bleaching sequence on pulp viscosity

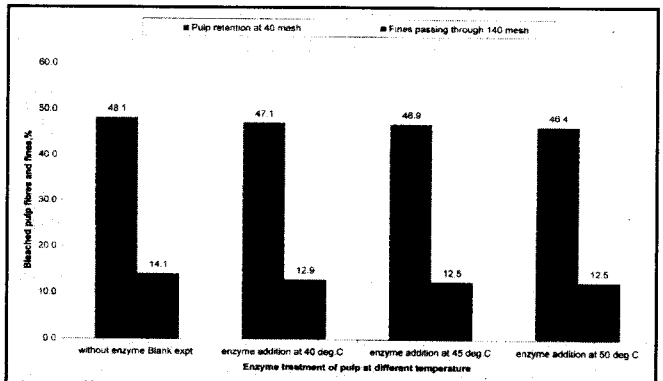

Fig. 2 Effect of enzyme addition at different temperature followed by C-Ep-H-D bleaching sequence on bleached pulp fibres

Comparison of physical strength properties of pre-enzyme treated and blank bleached Pulps

Enzyme untreated and treated

Table 3: Physical Strength Properties of mill pulp (with and without pre enzyme treatment) bleached under C-Ep-H-D sequence.

Particulars	Expt. No. 1	Expt. No. 2	Expt. No. 3	Expt. No. 4
Number of beating revolution in P. F. I. Mill rpm	4800	5000	5000	5000
Final Freeness ºSR of pulp	30	30	30	30
Bulk c. c. / gram	1.43	1.43	1.43	1.43
Tensile Index, N. m/g	62.1	65.4	68.2	63.1
Burst Index, K. Pa. m^2/g	4.24	4.50	4.57	4.23
Tear Index, m N. m^2/g	6.20	6.86	6.86	6.30
Double fold	64	103	137	102

bleached pulps were subsequently evaluated for physical strength properties & the results are shown in Table 3. It may be seen from the above Table 3. that tensile Index, burst index and tear index of enzyme treated bleached pulps are higher than non enzyme treated bleached pulps. Reduction by 15% of total chlorine after enzyme

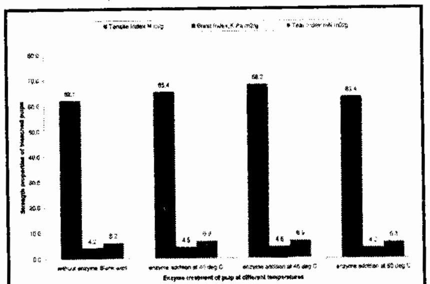

Fig. 3 Effect of enzyme addition at different temperature followed by C. Ep-H-D bleaching sequence on strength properties of bleached pulps

treatment minimised degradation of pulp to some extent which has resulted in improvement in physical strength properties under C-Ep-H-D sequence. This is because Xylanase treatment of unbleached pulp at higher temperature degrades the hemi cellulose therefore the physical strength properties were found comparatively inferior to enzyme treated pulp at lower temperature followed by C-Ep-H-D bleaching sequence. (Fig.3.)

Comparison of pollution load generated by bleaching with & without enzyme treated unbleached pulps at different temperatures under C-Ep-H-D sequence

Effluent characteristics at each stage of bleaching (with and without pre treatment of enzyme) under C-Ep-H-D sequence are observed as follows:

Chlorination stage effluent

Total chlorine was reduced by 15.0% in chlorination and hypochlorite stage after enzyme

Table 4: Effluent analysis at each stage of bleaching of mill pulp (with and without pre enzyme treatment) under C-Ep-H-D sequence.

Sampling points	Chlorination Stage				Caustic extraction Stage				Hypochlorite Stage				Chlorine dioxide Stage			
	Expt. No.1	Expt. No.2	Expt. No.3	Expt. No.4	Expt. No.1	Expt. No.2	Expt. No.3	Expt. No.4	Expt. No.1	Expt. No.2	Expt. No.3	Expt. No.4	Expt. No.1	Expt. No.2	Expt. No.3	Expt. No.4
pH	1.8	1.8	1.8	1.8	10.4	10.3	10.2	10.1	8.5	8.5	8.5	8.4	5.5	5.4	5.2	5.1
C. O. D. mg/l	690	700	720	750	2052	1687	1839	2029	1504	1277	1401	1450	555	448	477	492
Chloride, mg/l	2250	1900	1860	1860	620	520	510	525	5700	4900	4850	4850	360	340	350	350
S. Solid, mg/l	232	194	205	218	394	345	380	452	952	860	876	922	188	158	150	144
Dissolved Solids, mg/l	3300	3294	3366	3496	3758	3614	3454	3558	14710	12346	12618	12884	2208	2146	2172	2180
Colour, Pt. co. Unit	225	225	237	245	7500	7000	7700	7790	-	-	-	-	-	-	-	-

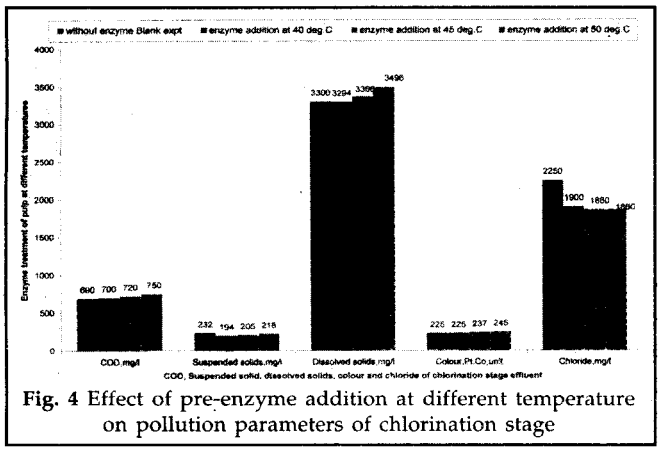

Fig. 4 Effect of pre-enzyme addition at different temperature on pollution parameters of chlorination stage

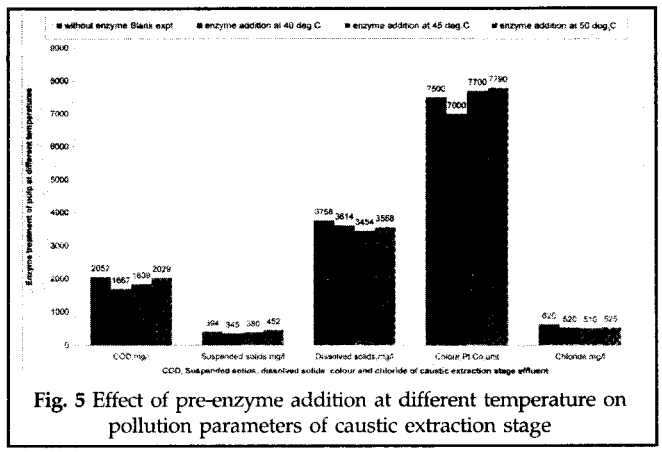

Fig. 5 Effect of pre-enzyme addition at different temperature on pollution parameters of caustic extraction stage

treatment and the effluent characteristics in chlorination stage were examined for different parameters (Table.4). It was observed that,

i) COD is higher than blank but in increasing order with increase in temperature of enzyme addition.

ii) Suspended solids are less than blank but in increasing order with increase in temperature of enzyme addition.

iii) Dissolved solids are nearly some at 40ºC but higher at 45º & 50ºC compared to blank.

iv) Chloride are less at 40º, 45º & 50ºC than blank.

Comparison of chlorination stage effluent parameters for enzyme pretreated pulp and blank experiment are shown in Fig.4.

Caustic extraction stage effluent

Alkali was reduced by 0.2% as per chlorine demand compared to blank experiment in the caustic extraction stage to remove chlorolignins. It was observed that

i) COD is less than blank but was in increasing order of temperature 40º, 45º & 50ºC.

ii) Suspended solids are less at 40º, 45ºC but higher at 50ºC than blank.

iii) Dissolved solids and chloride are less at 40º, 45º & 50ºC than blank.

iv) Colour of effluent is less than blank at 40ºC but was higher at 45º & 50ºC than blank.

Comparison of caustic extraction stage effluent parameter for enzyme pretreated pulp and blank experiment are shown in Fig.5.

Calcium hypochlorite stage effluent

In the Hypochlorite stage chlorine was reduced by 0.5% compared to blank experiment. Reduction in effluent parameter like COD, suspended solids, dissolved solids and chloride were observed.

i) COD, suspended solids and dissolved solids were in increasing order of temperature at 40º, 45º & 50ºC but less than blank experiment.

ii) Chloride was also lower at various reaction temperatures as expected than blank experiment.

Hypochlorite stage effluent parameters for pre enzyme treated bleached pulps are compared with blank experiment in Fig.6.

Chlorine dioxide stage effluent

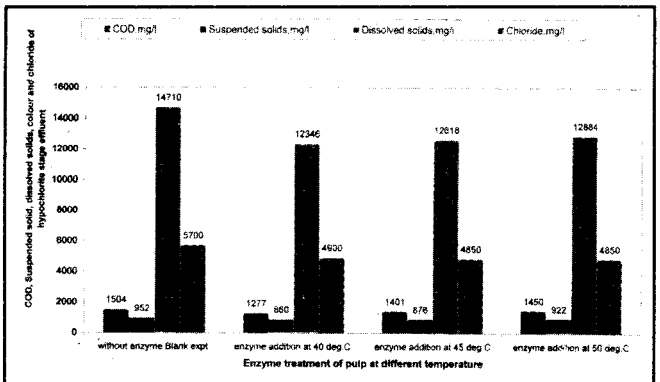

Fig. 6 Effect of pre-enzyme addition at different temperature on pollution parameters of hypochloride stage effluent

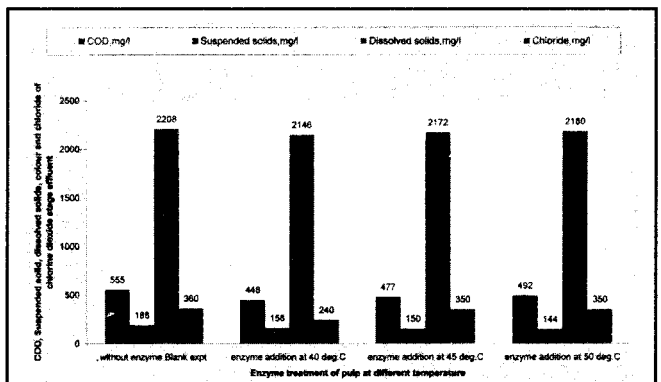

Fig. 7 Effect of pre-enzyme addition at different temperature on pollution parameters of chlorine dioxide stage

Untreated and treated enzyme pulps bleached under C-E-H bleaching sequence were further treated with 0.6% chlorine dioxide in the final stage of bleaching to achieve the target brightness 87-88% P. V. It was observed that:

i) COD and dissolved solids were increasing order of temperature 40º, 45º and 50ºC but less than blank experiment.

ii) Suspended solids were also lower than blank experiment but showed a decreasing trend with increase in enzyme treatment temperature.

A graphical presentation of pre enzyme treated and untreated pulp effluent parameters after final stage of bleaching are depicted in Fig.7. In all the pre enzyme treated pulps at 40ºC, 45º C, 50ºC followed by C-Ep-H bleaching sequence showed that pollution load in each stage of bleaching was lower than blank experiment which is explained by the fact that Xylanase effects the removal of specific lignin structure leaving a residual lignin in the pulp that may be more responsive to bleach chemical oxidation than residual lignin in conventional pulps[9,10]. The lower pollution load generated in enzymatic treatment followed by C-Ep-H-D bleaching is also confirmed by lower amount of total pulp shrinkage compared to blank experiment.

CONCLUSION

Endo-Xylanase (enzyme) treatment of mill unbleached pulp (kappa 26.0) resulted in decrease by 15% of chlorine requirement under C-Ep-H-D bleaching sequence to achieve 87-88% P. V. brightness while resulting in 0.5% gain in pulp brightness at the final stage of bleaching compared to blank experiment. It is also observed that physical strength properties of pre enzyme treated bleached pulps were higher than blank experiment while the pollution load in terms of COD was little on higher side in pre enzyme treated pulps at 50ºC in chlorination stage compared to blank experiment. It is further observed that pre-enzyme treatment at 50ºC increased pulp shrinkage and reduced physical strength properties of the bleached pulp but was still lower than blank experiment.

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