Xylanase Prebleaching of Chemical Pulps

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The various measures taken by the pulp and paper industry to improve the bleach effluents pollution problems are focused on reducing BOD, COD and color. The awareness and the concern about AOX and its control in India has grown in the last few years only. Further "Charter on Corporate Responsibilities for Environmental Protection (CREP)" introduced by Central Pollution Control Board (CPCB) recently has increased the pressure as well as forced the mills to reduce the AOX level in a fixed time frame. Xylanase Pre-bleaching could prove to be one of the promising options to reduce AOX loads in bleach plant effluents.

In the present study the impact of enzyme pretreatment on soda pulps of wheat straw & sarkanda and kraft pulps of bagasse and mixed wood, oxygen delignified wheat straw, sarkanda and mixed wood chemical pulps on bleach chemical consumption, pollution load generation, pulp properties and economic viability is assessed.

The saving in total active chlorine was from 14.6 to 25.9% and NaOH reduction was from 19-20% at the same target brightness. The reduction in AOX levels was 20-30%. The brightness gain was 1.5 to 2.5% ISO at the same level of bleach chemical dose. The enzymatic pretreated pulps showed marginal or no change in strength properties compared to the untreated pulps.

INTRODUCTION

The various measures taken by the pulp and paper industry to improve the bleach effluents pollution problems are focused on reducing BOD, COD and color [1]. The awareness and the concern about AOX and its control in India has grown in the last few years only. Further "Charter on Corporate Responsibilities for Environmental Protection (CREP)" introduced by Central Pollution Control Board (CPCB) recently has increased the pressure as well as forced the mills to reduce the AOX level in a fixed time frame. The current environmental standards of AOX is 2 kg/t which will be progressively reduced to 1.5 kg/t and 1kg/t respectively in the next 5 years as per the recent charter on environment declared by the Govt. of India [2.3]. Achieving the AOX discharge standards as specified in CREP is a great challenge as the level of AOX discharge generally varies between 1.0-2.5 kg/t in large mills and 4.0-6.0 kg/t in small agro based mills due to very high amounts of chlorine usage in their bleaching process [4].

Earlier measure taken by pulp and paper to reduce bleach plant effluents were based on end of pipeline treatment methods. Presently the emphasis of research and development has shifted more towards improving the bleaching processess itself for improving the effluent [5]. Xylanase prebleaching is one such option, which reduces the bleach chemical demand in subsequent bleaching processes, which in turn decreases the organochlorine discharges of bleach effluents.

In 1986 Viikari et al were the first to demonstrate that xylanase prebleaching facilitates the subsequent chemical bleaching of kraft pulps [6]. There after it was confirmed and further developed by extensive laboratory studies with hard wood and softwood pulps [7-9]. The effectiveness of enzyme pretreatment has been shown for non woods [10] and agricultural residue pulps [11-13]. Xylanase aided bleaching has been tested on numerous chlorine based [7,9-12,14,15], ECF[8,16-19] and TCF [8,19-25] bleaching sequences. Reduction in bleach chemicals in the range of 15-35% has been reported for different sequences. At the same level of bleach chemical dose higher final brightness for xylanase pretreated pulps have been reported. Reduction in bleach chemical dose and increase in final brightness of xylanase pretreated pulps have been reported for bagasse pulps in the same study [11]. Xylanase pretreatment has led to reduced concentration of AOX and dioxin in the effluent as less chlorine is needed to achieve a given brightness [11,13,26,27].

Indian medium sized paper mills using agroresidues as raw materials commonly practice the soda pulping and conventional bleaching process for the production of bleached grade pulps and are discharging very high pollution loads in the environment [5]. Aim of the present study was to develop xylanase aided prebleaching process for these mills using wheat straw and sarkanda as raw material and comparing the result with kraft pulps of bagasse and typical Indian mixed wood pulp and provide altering bleaching techniques which reduce chlorine use and means for reduced environment pollution especially with respect to AOX. Another aim of the present study was to see whether pulps with high brightness levels (~87% ISO) could be produced from agroresidues like wheat straw and sarkanda and evaluate if such processes meet the environmental discharge particularly with respect to AOX and are they economically viable.

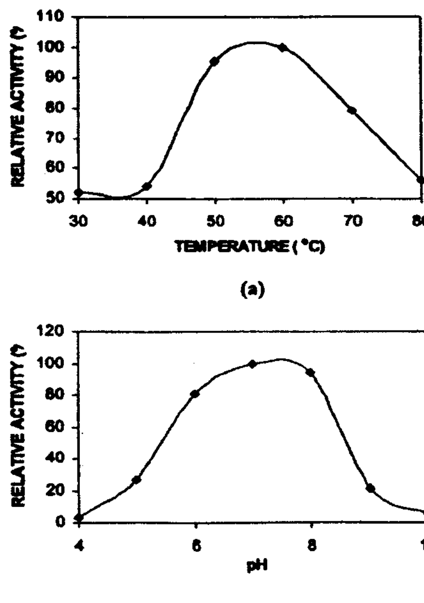

Figure 1 : Activity of Pulpzyme HC (a) at various temperatures (b) at various pH.

MATERIALS AND METHODS

Pulps/Enzyme

Conventinally cooked unbleached wheat straw and sarkanda soda pulps and kraft bagasse and mixed wood pulps were procured from near by paper mills. The pulps were washed and screened in the laboratory. Oxygen pre-bleaching was carried out on wheat straw, sarkanda and mixed wood pulps to reduce their kappa numbers. Both unbleached and oxygen prebleached pulps were characterized by determining the kappa number, pulp viscosity and brightness. The optimized conditions for oxygen prebleaching are given in the Table 1. Commercial Xylanase (Pulpzyme HC) prepared from a cloned Bacillus gene was used for all enzyme experiments. The characteristics of the enzyme are given in the Figs. 1a and 1 b.

Bleaching studies

The non-oxygen pulps were bleached to 80% brightness using bleaching sequences CEH (conventional) and DED (ECF). The oxygen delignified wheat straw, sarkanda and mixed wood pulps were bleached to 87-88% brightness using $D_{50}C_{50}E_pDED$ sequence. 86% ISO brightness was achieved in bagasse pulp without oxygen delignification using $D_{50}C_{50}E_pDD$. All the bleaching experiments were perfomed in triplicate and brightness measured as % ISO. The range of bleach chemical charges studied for various bleach sequences is given in the Table 2.

Characterization of bleaching effluents

Bleach effluents collected after each stage of bleaching were mixed and analyzed for BOD & COD in the laboratory. The AOX was analyzed from CPPRI, Saharanpur.

Strength and Optical Properties

The bleached pulps were beaten in a PFI mill. Hand sheets (60±2 gsm) were made in Swedish hand sheet former. Air-dried sheets were used to determine the various strength (tensile index, tear index, burst index) properties.

Test methods

TAPPI and SCAN standard test methods were used to determine the kappa number, viscosity (CED), tensile

Table 1 : Optimized oxygen prebleaching conditions

Parameter	Wheat straw	Sarkanda	Mixed wood
O_2 charge (kg/cm^2)	6	6	6
Consistency (%)	10	10	10
Retention time (min)	75	75	75
Temperature (°C)	100	110	120
Alkali charge (kg/t)	30	40	40
Magnesium sulfate (kg/t)	2	2	2

Table 2 : Range of bleach chemical charge for bleaching studies for various pulps

Pulp type	Bleaching sequence	Total bleach chemical charge as aCl (kg/t)			
		Wheat straw	Sarkanda	Mixed wood	Bagasse
Non oxygen untreated	CEH	58.4-76.0	62.0-80.8	54.0-63.0	18.0-25.0
	DED	62.8-93.6	67.2-93.2	63.0-76.0	25.0-30.0
	$D_{50}C_{50}E_pDD$	-	-	-	40-48.0
Non oxygen xylanase pretreated	CEH	44.2-76.0	50.4-80.0	24.0-63.0	14.88-25.0
	DED	61.3-93.6	55.5-93.2	48.1-76.0	18.6-30.0
	$D_{50}C_{50}E_pDD$	-	-	-	40-48.0
Oxygen delignified untreated	$D_{50}C_{50}E_pDD$	45.8-55.4	51.8-59.4	45.2-48.16	-
Oxygen delignified xylanase pretreated	$D_{50}C_{50}E_pDD$	33.6-55.4	42.3-59.4	40.64-48.16	-

Table 3 : Standard test methods followed for analysis of pulp and paper

Test No.	Description
Scan - C 18 : 65	Disintegration of chemical pulps for testing
Scan- C 24 : 67	Beating of pulp in a PFI mill
Scan - C 26 : 76	Forming hand sheets for physical testing of pulp
T-227	Determination of CSF, ml
Scan - C 15 : 62	Viscosity of cellulose in cupriethylenediamine
T-236	Kappa number of pulp
T - 403	Bursting strength of paper
T- 404	Tensile breaking length & elongation of paper and paperboard (Using pendulum type tester)
T-414	Internal tearing resistance of paper (Elmendrof type method)
ISO - 2469	Brightness of pulp
BOD (APHA)	Biochemical oxygen demand (5210 B) 5-day BOD test

index, burst index and tear index. Brightness was measured on TECHNIBRITE ERIC 950 from Technibrite Corporation, USA. BOD was estimated by standard test method. COD was estimated by THERMOREACTOR CR 2010 AND PHOTOMETER MPM 2010 manufactured by WTW Germany. The details regarding the standard test methods followed are given in the Table 3.

RESULTS AND DISCUSSION

To cheak the effectiveness of the enzyme various experiments were conducted to determine their optimum reaction conditions for prebleaching. The optimization studies were carried out by determining the reducing sugars released as xylose and are reported else ware [28,29]. The optimum conditions and yields of enzyme pretreatment for non oxygen and oxygen delignified pulps are given in the Tables 4 & 5. The yield data reported is relative to untreated pulp of the same raw material. All bleaching experiments were performed at optimized xylanase dose and constant process conditions (Table 6).

Pulp properties just after xylanase pretreatment

A small reduction in kappa number and increase in brightness is observed in xylanase pretreated pulps (Table 7 & 8). An increase in viscosity was also observed for xylanase pretreated pulps, which may be, attributed to the fact that xylanase degrades/deploymerize low DP xylan. The decrease in kappa number is more for mixed wood pulps than non wood pulps. Kappa number reduction of the similar order is reported for hardwood [9]. mixed wood [11] and bagasse kraft pulp [11]. Increase in viscosity is also reported in xylanase pretreated pulps [11].

Impact of xylanase pretreatment at medium brightness (80% ISO)

Bleach chemical consumption

80% brightness level was achieved in untreated and xylanase pretreated pulps using the sequences CEH and DED

The results show that xylanse pretreated pulps bleached to 80% brightness requires lower bleach chemicals compared to untreated pulps.

At the same pulp brightness, wheat straw pulp bleached to 80% brightness with enzyme pretreatment gave a saving of total active chlorine of 24.2% and 14.6% for CEH and DED sequences. The NaOH savings were 17.1 and 23.2% respectively. Similar results are observed with sarkanda, bagasse and mixed wood pulps (Tables

Table 4 : Optimum enzyme pretreatment conditions and yield for non oxygen pulps

Parameter	Wheatstraw	Sarkanda	Bagasse	Mixed wood
Enzyme dose (IU/g)	14.0	18.2	9.8	14.0
Consistency (%)	10	10	10	10
pH	7.5	7.5	7.5	7.5
Time (min)	120	120	120	120
Temperature (°C)	60	60	60	60
Yield (%)	99.2	99.1	99.2	99.5

Table 5 : Optimum enzyme pretreatment conditions and yields for oxygen delignified pulps

Parameter	Wheatstraw	Sarkanda (%)	Mixed wood (min)
Enzyme dose (IU/g)	9.35	14.0	9.8
Consistency (%)	10	10	10
pH	7.5	7.5	7.5
Time (min)	120	60	120
Temperature (°C)	60	60	60
Yield(%)	99.0	98.9	99.1

9-12). An average reduction of 25-40% in active chlorine consumption in the first bleaching stage has been reported for different pulps in the literature for xylanase pretreated pulps [7-19] using different bleaching sequences.

The increase in brightness at the same bleach chemical dose ranged from 1.5-2.5% ISO for all the four pulps using CEH and DED bleaching sequences (Tables 9-12).

Effluent characteristics

The characteristics of the effluents are shown in Tables 13-16. At a target pulp brightness of 80% due to xylanase pretreatment a reduction in AOX values of combined effluent of xylanase pretreated pulps is observed. The percent reduction in AOX of combined CEH and DED bleach effluent of xylanase pretreated wheat straw pulp is 27.7 and 26.7% respectively. Xylanase pretreated sarkanda, bagasse and mixed wood behaves in a similar way as enzyme pretreated wheat straw pulp. Reduction in AOX concentration in the order of 14-42% is reported in the literature for xylanase pretreated effluents [11-13, 27].

At the same target pulp brightness BOD and COD increase marginally for all pulps with increase in BOD/COD ratio. There is a substantial increase in BOD and COD values at the same bleach chemical dose. The increase in BOD & COD is expected because the enzyme helps in the removal of more lignin & xylans. Such effluents are more amenable to biological degradation due to high BOD/COD ratio [30].

Mechanical properties

Tensile, burst and tear index values as depicted in the Tables 17 and 18 show that the xylanase pretreated bleached pulp show some improvement in these properties at the same pulp brightness but the properties are inferior at the same bleach chemical charge compared to the untreated pulps beaten at the same PFI revolutions. Both enzyme pretreated wheat straw and sarkanda soda pulps for all the three bleaching sequences show similar results.

Results clearly show that both soda (wheat straw, sarkanda) and kraft (bagasse, mixed wood) pulps responds to xylanase pretreatment. The response of enzymatic pre-bleaching is different for different bleaching sequences. At 80% target pulp brightness the order of effectiveness (defined as the decrease in bleach

Table 6 : Pulp bleaching conditions used

Bleaching stage	Bleaching conditions			
	Temperature (°C)	Consistency (%)	Time (min)	End pH
Chlorination	Ambient	3	45	<2
Alkali extraction	70	10	60	> 10.5
Hypochlorite	40	10	180	8.5-9.0
$D_{50}C_{50}$	40	5	60	3.3-4.5
First Dioxide	70	10	90	4.5-5.0
Final Dioxide	70	10	180	5.0-5.5

Table 7 : Enzyme pretreatment results of non-oxygen pulps

Parameter	Wheat straw		Sarkanda		Bagasse		Mixedwood	
	Untreated	Xylanase pretreated	Untreated	Xylanase pretreated	Untreated	Xylanase pretreated	Untreated	Xylanase pretreated
Inlet kappa number	22.0	21.4	26.0	25.3	10.0	9.3	18.0	16.2
Brightness (%)	26.8	27.5	22.1	22.5	47.3	48.4	32.6	34.1
Viscosity(cm^3/g)	629	679	710	730	510	528	740	760

Table 8 : Enzyme pretreatment results of oxygen delignified pulps

Parameter	Wheat straw		Sarkanda		Mixed wood	
	Untreated	Xylanase pretreated	Untreated	Xylanase pretreated	Untreated	Xylanase pretreated
Inlet kappa number	12.0	11.2	15.2	14.3	10.9	9.9
Brightness (%ISO)	39.8	40.9	31.3	32.0	43.9	45.5
Viscosity (cm^3/g)	578	581	624	640	671	679

chemical consumption) of different bleaching sequence is CEH>DED for wheat straw and mixed wood pulps. The bleaching behavior of enzymatic prebleached sarkanda and bagasse pulps is quite different from enzymatic prebleached wheat straw and mixed wood pulps. The order at constant 80% pulp brightness is DED>CEH. The effectiveness of xylanase pretreatment appears to depend on the degree of substitution of elemental chlorine with chlorine dioxide in the chlorination stage. A similar trend has been reported for hardwood and softwood pulps. The hardwood pulps responds better at lower substitution [16] and softwood pulp at higher (100%) substitution [17]. The increase in brightness at the same bleach chemical dose is of the same order for all the four pulps. Moreover the response of the response of enzymatic prebleaching on lower kappa number non wood pulp (bagasse) appears to be less than higher kappa number non wood pulps. The effectivenss of enzymatic pre-bleaching in wheat straw and sarkanda pulps is of the same order as mixed wood pulp. The increase in brightness at the same bleach chemical as observed in the present case is of the similar order as reported for non wood pulps [11]. The optimized dose for both pulps is different. It has been reported that different commercial xylanase show different effectiveness for pulp bleaching and this variation also depends on the type of pulp used.

Xylanase pretreatment yields effluent of lower adsorbable organic halides in the combined effluent of both soda and kraft pulps for all the four raw materials. Bleaching of enzymatic treated pulps yields effluents of higher BOD and COD. The increase in BOD and COD is lower at same target brightness levels than at same bleach chemical dose. Inconsistent results on BOD and COD have been reported in the literature. Some studies indicate in values of BOD and COD of enzymatic treated effluents [6,27] and other report decrease in BOD and COD values [15, 27] in xylanase pretreated effluents but common feature is that BOD/COD ratio increase making them more amenable to biological treatments [30]. The results obtained are in agreement with the above.

Minor or no change in mechanical strength properties due to enzymatic pretreatment is reported [6,11]. The results obtained are in agreement with the above fact.

Impact of xylanase pretreatment at 87% ISO (High brightness)

Higher brightness (86-87% ISO) was achieved in wheat straw, sarkanda and mixed wood pulps after oxygen delignification followed by $D_{50}C_{50}E_pDED$ sequence (O $D_{50}C_{50}E_pDED$). In lower kappa bagasse pulp higher brightness was achieved using the sequence $D_{50}C_{50}E_pDD$. The results of bleaching of xylanase pretreated oxygen delignified wheat straw and sarkanda pulps are similar to xylanase pretreated wheat straw and sarkanda pulps i.e. decrease in bleach chemical consumption (Table 9 and 10), decrease in AOX (Table 13 and 14), minor increase in BOD and COD. increase in biodegradability (Tables 13 and 14) and minor change in mechanical strength properties of the pulp bleached to same target brightness (Table 17 and 18). An increase in final brightness, substantial increase in BOD and COD values, increase in biodegradability and minor change in mechanical strength properties at same bleach chemical consumption (Tables 9,10,13,14,17 and 18). A similar trend is also observed with xylanase

Table 9 : Bleach chemical charge (kg/t) required to obtain 80% and 87% (ISO) brightness of untreated and xylanase pretreated wheat straw soda pulp using different bleaching sequences

		Bleach chemical charge (kg/t) as such								
		CEH			DED			$OD_{50}C_{50}E_pDED$		
Stage	Chemical (kg/t)	Untreated	Xylanase pretreated Constant Charge	Xylanase pretreated 80% brightness	Untreated	Xylanase pretreated Constant charge	Xylanase pretreated 80% brightness	Untreated	Xylanase pretreated Constant charge	Xylanase pretreated 80% brightness
1st	Cl_2	56	56	41.6	-	-	-	16.2	16.2	11.2
	ClO_2	-	-	-	28.0	28.0	22.8	6.16	6.16	4.26
2nd	NaOH	31	31	23.8	40.0	40.0	33.2	19.2	19.2	14.2
3rd	Hypo	20	20	16.0	-	-	-			
	ClO_2	-	-	-	7.60	7.60	7.60	5.70	5.70	5.70
4th	NaOH	-	-	-	-	-	-	10.5	10.5	10.5
5th	ClO_2	-	-	-	-	-	-	3.04	3.04	3.04
Total acl		76.0	76.0	57.6	93.6	93.6	79.9	55.4	55.4	45.4
Final brightness (%ISO)		79.9	82.0	80.1	80.3	81.8	81.8	87.5	88.4	87.5
(σ)		*(0.5)*	*(0.5)*	*(0.7)*	*(0.7)*	*(0.70)*	*(0.7)*	*(0.6)*	*(0.7)*	*(0.7)*

Table 10 : Bleach chemical charge (kg/t) required to obtain 80% and 87% (ISO) brightness of untreated and xylanase pretreated sarkanda soda pulp using different bleaching sequences

		Bleach chemical charge (kg/t) as such								
		CEH			DED			$OD_{50}C_{50}E_pDED$		
Stage	Chemical (kg/t)	Untreated	Xylanase pretreated Constant Charge	Xylanase pretreated 80% brightness	Untreated	Xylanase pretreated Constant charge	Xylanase pretreated 80% brightness	Untreated	Xylanase pretreated Constant charge	Xylanase pretreated 80% brightness
1st	Cl_2	62.8	62.8	50.7	-	-	-	18.2	18.2	13.5
	ClO_2	-	-	-	27.8	27.8	21.9	6.92	6.92	5.13
2nd	NaOH	34.4	34.4	28.3	39.6	39.6	31.8	21.2	21.2	16.5
3rd	Hypo	18.0	18.0	16.0	-	-	-	5.70	5.70	4.56
	ClO_2	-	-	-	7.6	7.6	6.08	10.5	10.5	10.5
4th	NaOH	-	-	-	-	-	-	-	-	-
5th	ClO_2	-	-	-	-	-	-	3.04	3.04	3.04
Total acl		80.8	80.8	66.7	93.2	93.2	73.5	59.4	59.4	47.0
Final brightness (%ISO)		79.8	82.2	80.1	80.3	82.7	80.1	80.1	87.4	88.7
(σ)		*(0.6)*	*(0.8)*	*(0.5)*	*(0.7)*	*(0.5)*	*(0.8)*	*(0.5)*	*(0.6)*	*(0.5)*

Table 11 : Bleach chemical charge (kg/t) required to obtain 80% and 86% (ISO) brightness of untreated and xylanase pretreated bagasse kraft pulp using different bleaching sequences

Stage	Chemical (kg/t)	Bleach chemical charge (kg/t) as such: CEH Untreated	CEH Xylanase pretreated Constant Charge	CEH Xylanase pretreated 80% brightness	DED Untreated	DED Xylanase pretreated Constant charge	DED Xylanase pretreated 80% brightness	$OD_{50}C_{50}E_pDED$ Untreated	$OD_{50}C_{50}E_pDED$ Xylanase pretreated Constant charge	$OD_{50}C_{50}E_pDED$ Xylanase pretreated 80% brightness
1st	Cl_2	17.5	17.5	15	-	-	-	12.5	12.5	10.0
	ClO_2	-	-	-	8.0	8.0	6.46	4.75	4.75	3.8
2nd	NaOH	11.75	11.75	10.5	13.5	13.5	11.5	15.5	15.5	13.0
3rd	Hypo	7.5	7.5	7.5	-	-	-	-	-	-
	ClO_2	-	-	-	3.8	3.8	3.4	5.70	5.70	4.56
4th	NaOH	-	-	-	-	-	-	-	-	-
5th	ClO_2	-	-	-	-	-	-	3.04	3.04	3.04
Total acl		25	25	22.5	30	30	26	48.0	48.0	40.0
Final brightness (%ISO)		80.2	81.9	80.6	79.8	81.6	80.2	85.9	87.1	85.8
(σ)		*(0.7)*	*(0.9)*	*(0.8)*	*(0.9)*	*(0.8)*	*(0.9)*	*(0.7)*	*(0.6)*	*(0.9)*

Table 12 : Bleach chemical charge (kg/t) required to obtain 80% and 86% (ISO) brightness of untreated and xylanase pretreated mixed wood kraft pulp using different bleaching sequences

Stage	Chemical (kg/t)	Bleach chemical charge (kg/t) as such: CEH Untreated	CEH Xylanase pretreated Constant Charge	CEH Xylanase pretreated 80% brightness	DED Untreated	DED Xylanase pretreated Constant charge	DED Xylanase pretreated 80% brightness	$OD_{50}C_{50}E_pDED$ Untreated	$OD_{50}C_{50}E_pDED$ Xylanase pretreated Constant charge	$OD_{50}C_{50}E_pDED$ Xylanase pretreated 80% brightness
1st	Cl_2	44.1	44.1	36.0	-	-	-	12.58	12.58	9.9
	ClO_2	-	-	-	21.3	21.3	17.6	4.78	4.78	3.76
2nd	NaOH	25.0	25.0	21.0	31	31	26.2	15.58	15.58	12.9
3rd	Hypo	18.9	18.9	15	-	-	-	-	-	-
	ClO_2	-	-	-	7.6	7.6	7.6	5.70	5.70	4.56
4th	NaOH	-	-	-	-	-	-	10.5	10.5	10.5
5th	ClO_2	-	-	-	-	-	-	3.04	3.04	3.04
Total acl		63	63	51	76.0	76.0	66.4	48.16	48.16	39.8
Final brightness (%ISO)		80.3	82.6	79.9	80.1	81.9	80.6	86.9	88.1	87.1
(σ)		*(0.5)*	*(0.7)*	*(0.6)*	*(0.7)*	*(0.5)*	*(0.9)*	*(0.8)*	*(0.7)*	*(0.9)*

Table 13 : Characteristics of effluent generated by bleaching of wheat straw pulp

Bleaching sequence	Pulp type	Parameter (kg/t)			
		BOD	COD	BOD/COD	AOX
CEH	Untreated	8.43	38.0	0.221	3.4
	Xylanase pretreated at 80% target brightness	9.84	39.47	0.249	2.5
	Xylanase pretreated at Same chemical dose	12.87	54.84	0.234	-
DED	Untreated	10.32	46.67	0.221	1.4
	Xylanase pretreated at 80% target brightness	11.87	49.73	0.238	1.05
	Xylanase pretreated at Same chemical dose	14.62	62.0	0.235	-
$OD_{50}C_{50}E_{p}DED$	Untreated	6.12	28.0	0.218	1.12
	Xylanase pretreated at 87% target brightness	7.16	30.0	0.238	0.99
	Xylanase pretreated at Same chemical dose	8.92	38.0	0.234	-

Table 14 : Characteristics of effluent generated by bleaching of sarkanda pulp

Bleaching sequence	Pulp type	Parameter (kg/t)			
		BOD	COD	BOD/COD	AOX
CEH	Untreated	9.67	41.18	0.234	4.1
	Xylanase pretreated at 80% target brightness	11.42	42.02	0.271	3.1
	Xylanase pretreated at Same chemical dose	14.1	55.6	0.253	-
DED	Untreated	10.64	50.2	0.211	1.5
	Xylanase pretreated at 80% target brightness	14.88	58.6	0.253	1.1
	Xylanase pretreated at Same chemical dose	16.12	63.6	0.253	-
$OD_{50}C_{50}E_{p}DED$	Untreated	7.36	32.0	0.230	1.5
	Xylanase pretreated at 87% target brightness	8.35	34.0	0.245	1.3
	Xylanase pretreated at Same chemical dose	10.99	40.0	0.274	-

pretreated bagasse and mixed wood pulps (Tables 11,12,15 and 16).

The savings in bleach chemicals of xylanase pretreated pulps at high brightness was lower to that observed at medium brightness. Similarly the increase in final brightness at the same bleach chemical dose for xylanase pretreated pulps is more at 80% brightness than at 87% brightness. The results are in agreement with the literature, which suggests that magnitude of brightness gain becomes smaller at higher pulp brightness, but there remains a potential for chemical savings [16,17].

ECONOMICS OF XYLANASE PRETREATMENT WITH RESPECT TO AOX GENERATION

Economic evaluation of any process modification is essentially made by evaluating the measurable economic impacts in terms of either additional input costs (operating costs) or gain in output cost (value addition).

However, when the variables offer intangible benefits it becomes difficult to assign an economic value or such a benefit. In case of improved environmental performance one can see the viability of a process from it's meeting the set regulatory standards. Non-compliance usually results in closure of an operation. In such situations one can consider the increase input costs for making a system operational as investment cost and the cost of closure for non-compliance as a measurable economic benefit as such an investment. In the present economic analysis of xylanase pretreatment the following costs

Table 15 : Characteristics of effluent generated by bleaching of bagasse pulp

Bleaching sequence	Pulp type	Parameter (kg/t) BOD	COD	BOD/COD	AOX
	Untreated	5.73	23.29	0.246	1.7
CEH	Xylanase pretreated at 80% target brightness	7.53	30.0	0.251	1.6
	Xylanase pretreated at Same chemical dose	8.31	34.91	0.238	-
	Untreated	7.16	30.3	0.236	0.55
DED	Xylanase pretreated at 80% target brightness	8.27	31.68	0.261	0.4
	Xylanase pretreated at Same chemical dose	8.51	32.98	0.258	-
$D_{50}C_{50}E_pDD$	Untreated	8.10	31.64	0.256	1.15
	Xylanase pretreated at 87% target brightness	10.01	36.53	0.274	0.96
	Xylanase pretreated at Same chemical dose	11.2	40.72	0.275	-

Table 16 : Characteristics of effluent generated by bleaching of mixed wood pulp

Bleaching sequence	Pulp type	Parameter (kg/t) BOD	COD	BOD/COD	AOX
	Untreated	8.13	35.3	0.230	2.9
CEH	Xylanase pretreated at 80% target brightness	10.94	42.0	0.260	2.4
	Xylanase pretreated at Same chemical dose	12.27	51.99	0.236	-
	Untreated	10.76	43.77	0.245	1.4
DED	Xylanase pretreated at 80% target brightness	12.77	50.47	0.253	1.3
	Xylanase pretreated at Same chemical dose	13.12	52.90	0.248	-
$OD_{50}C_{50}E_pDD$	Untreated	6.26	27.09	0.231	1.4
	Xylanase pretreated at 87% target brightness	7.44	28.73	0.258	1.0
	Xylanase pretreated at Same chemical dose	8.19	34.32	0.238	-

have been considered towards input :

- Cost of xylanase consumed.
- Change in the input chemical costs for a given pulp brightness level during bleaching compared to such costs for xylanase untreated pulp bleaching.
- The cost of reduction of AOX through end of pipeline treatment technologies (Secondary (biological), tertiary (chemical and adsorption and ion exchange etc. has been taken as an additional cost of operation to meet regulatory standards.
- The intangible benefits of keeping operations sustainable due to environmental compliance with modified bleaching sequence involving xylanase pretreatment, which would otherwise have been closed for non compliance is not included in the current cost estimates.
- The current environmental standards for AOX is 2 kg/t which will be progressively reduced to 1.5 kg/t and 1kg/t respectively in the next 5 years as per the recent charter on environment declared by the Govt. of India [2].
- Other factors such as increased BOD, COD loads and biodegradability of the effluents, improvements in technical pulp properties which may lead to additional advantages/

Table 17 : Mechanical properties of xylanase pretreated wheat straw pulp bleached by various bleaching sequences and beaten with 1500 PFI revolutions.

Bleaching sequence	Pulp type	Tensile Index (Nm/g)	Parameter Burst Index (Kpa m²/g)	Tear Index (mNm²)/g	Freeness CSF,ml
	Untreated	45.42	3.63	6.34	360
CEH	Xylanase pretreated at 80% target brightness	47.93	3.98	6.93	350
	Xylanase pretreated at Same chemical dose	43.69	3.31	6.05	340
	Untreated	46.81	4.24	7.13	380
DED	Xylanase pretreated at 80% target brightness	49.59	4.40	7.86	360
	Xylanase pretreated at Same chemical dose	45.53	3.82	6.65	350
$OD_{50}C_{50}E_pDED$	Untreated	40.85	3.55	5.91	385
	Xylanase pretreated at 87% target brightness	43.59	3.89	5.98	370
	Xylanase pretreated at Same chemical dose	38.74	3.28	5.62	360

Table 18 : Mechanical properties of xylanase pretreated sarkanda pulp bleached by various bleaching sequences and beaten with 2000 PFI revolutions.

Bleaching sequence	Pulp type	Tensile Index (Nm/g)	Parameter Burst Index (Kpa m²/g)	Tear Index (mNm²)/g	Freeness CSF,ml
	Untreated	41.25	2.86	7.2	350
CEH	Xylanase pretreated at 80% target brightness	44.01	3.25	7.59	345
	Xylanase pretreated at Same chemical dose	39.32	2.60	6.59	360
	Untreated	43.70	3.37	7.91	340
DED	Xylanase pretreated at 80% target brightness	46.12	3.65	8.04	370
	Xylanase pretreated at Same chemical dose	41.99	2.93	6.99	380
$OD_{50}C_{50}E_pDED$	Untreated	37.81	2.75	6.59	390
	Xylanase pretreated at 87% target brightness	39.76	2.95	7.16	380
	Xylanase pretreated at Same chemical dose	35.76	2.47	6.17	365

disadvantages are difficult to specify in terms of costs are not considered in the present estimates.

- The capital cost for process modifications have not been considered in the present evaluation.

The consumption of chemicals for bleaching of untreated and xylanase pretreated are given in the Tables 9-12. The estimated bleaching costs are shown in the Tables 19-21. The results indicate that total bleaching costs is higher with xylanase pretreatment for all the raw materials.

Tables 19-21 also indicate that if the cost of AOX reduction is considered (Rs 250 for reduction in AOX of 1 kg/t by biological and chemical methods [4,31]) then the relative cost of enzyme prebleaching decreases.

Table 19 : Bleach chemical cost analysis of wheat straw soda pulp at xylanase cost of Rs 450/kg

Bleaching Sequence	Bleaching cost (Rs/t) of pulp: Xylanase pretreated: Xylanase	Bleach chemical	Total	Untreated	Difference	AOX (kg/t): Untreated	Xylanase pretreated	Reduction Kg/t	Rs./t (@200/kg)	Difference in xylanase Prebleaching cost (Rs/t)
CEH	450	1068	1518	1395	+123	3.42	2.47	0.95	190	-67
DED	450	1935	2385	2280	+105	1.42**	1.05***	0.37	74	+31
$OD_{50}C_{50}E_pDED$	315	1789	2104	1868	+236	1.16**	0.98***	0.18	36	+200

Table 20 : Bleach chemical cost analysis of sarkanda soda pulp at xylanase cost of Rs 450/kg

Bleaching Sequence	Bleaching cost (Rs/t) of pulp: Xylanase pretreated: Xylanase	Bleach chemical	Total	Untreated	Difference	AOX (kg/t): Untreated	Xylanase pretreated	Reduction Kg/t	Rs./t (@200/kg)	Difference in xylanase Prebleaching cost (Rs/t)
CEH	585	1225	1810	1475	+335	4.09	3.12	0.97	194	+141
DED	585	1796	2381	2266	+115	1.49**	1.12**	0.37	74	+41
$OD_{50}C_{50}E_pDED$	450	2324	2774	3101	+327	1.50**	1.29**	0.21	42	+285

* Within the prescribed environmental limits as on March 2003
** Within the prescribed environmental limits as on March 2005
*** Within the prescribed environmental limits as on March 2007

Table 21 : Bleach chemical cost analysis of bagasse kraft pulp at xylanase cost of Rs 450/kg

Bleaching Sequence	Bleaching cost (Rs/t) of pulp: Xylanase pretreated: Xylanase	Bleach chemical	Total	Untreated	Difference	AOX (kg/t): Untreated	Xylanase pretreated	Reduction Kg/t	Rs./t (@200/kg)	Difference in xylanase Prebleaching cost (Rs/t)
CEH	315	351	666	485	+181	1.72	1.56	0.16	32	+149
DED	315	546	861	757	+104	0.55***	0.47***	0.08	16	+88
$OD_{50}C_{50}E_pDED$	315	889	1204	1143	+61	1.00**	0.962	0.03	6	+55

Table 22 : Bleach chemical cost analysis of mixed wood kraft pulp at xylanase cost of Rs 450/kg

Bleaching Sequence	Bleaching cost (Rs/t) of pulp: Xylanase pretreated: Xylanase	Bleach chemical	Total	Untreated	Difference	AOX (kg/t): Untreated	Xylanase pretreated	Reduction Kg/t	Rs./t (@200/kg)	Difference in xylanase Prebleaching cost (Rs/t)
CEH	450	815	1265	1167	+98	2.9	2.45	0.45	90	+8
DED	450	1452	1902	1832	+70	1.42**	1.3**	0.12	24	+46
$OD_{50}C_{50}E_pDED$	315	1347	1662	1812	+150	1.38**	1.0***	0.38	76	+74

* Within the prescribed environmental limits as on March 2003
** Within the prescribed environmental limits as on March 2005
*** Within the prescribed environmental limits as on March 2007

In view of the stringent AOX norms CEH sequence without enzyme pretreatment for all the pulps except low kappa bagasse pulp. CEH sequence with enzyme pretreatment can be adopted for wheat straw, mixed wood and bagasse pulps but not for sarkanda pulp (due to higher kappa number of sarkanda pulp).

Though theoretically achieving the AOX within the prescribed limits may be possible in the laboratory, implementation of tertiary treatment technologies may be very difficult at the mill level presently [3]. It appears that mill may have to consider non conventional bleaching sequences which may require the least end of pipeline treatments. These bleaching technologies (DED in the present case) may be expensive but are discharging AOX within the prescribed limits without treatments. It may probably need a combination of both the approaches (viz. process modification and end of pipe line treatments) to solve the problem of AOX generation.

The response of enzymatic pre-bleaching to oxygen delignified pulps was found to be positive with reduction in bleach chemical demand and associated reduction in AOX loads. However adoption of these options will require addition of costly oxygen delignification step [32].

From the initial studies it appears that xylanase prebleaching is also effective on conventionally cooked soda pulps. The pulps used in the present study were of different kappa numbers and raw materials. To effectively differentiate the impact of xylanase prebleaching on conventionally cooked kraft and soda pulps, the cooking of kraft and soda pulps has to be done of the same raw material at the same targeted kappa number. The response of xylanase prebleaching was lowest on bagasse this may be due to lower kappa number of the pulp or due to the nature of bagasse pulp. It is reported in the literature that impact of xylanase prebleaching is less on bagasse pulp than mixed wood pulp [11].

Today the environmental issues particularly control of AOX are the major challenges before the pulp and paper industry. With the pressure rising to limit the discharge of chlorinated organic compounds due to increased environmental awareness and imposition of stringent discharge norms the Indian pulp and paper industry is likely to face severe problems due to its high level of AOX generation. There is a need of time before alarming situations are reached that Indian pulp and paper mill switch to new bleaching technologies. Xylanase pre-bleaching offers one such option. With likely reduction in enzyme prices xylanase pre-bleaching offers a cost effective and viable bleaching technology for Indian pulp and paper industry.

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