A New Biobleaching Process Offers A Cost Effective Route For Achieving Elemental Chlorine Free (ECF) Bleaching

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ABSTRACT: An innovative technology, namely, ***ET- Biobleaching Process****, developed indigenously by us for achieving Elemental Chlorine Free (ECF) bleaching of bagasse pulps has been described here. In this process, the unbleached of bagasse pulp is treated with a microbial enzyme, which increases the brightness of the pulp, thereby, significantly reducing the consumption of bleach chemicals. With the use of the microbial enzyme, the consumption of chlorine is reduced by 20% and peroxide by 35-50%. By adopting this new and innovative technology, the consumption of elemental chlorine can be reduced or even completely eliminated. Further, the colour of the bleach plant effluents is significantly decreased, due to partial or complete elimination of chlorination and alkali extraction stages. Therefore, this biobleaching process in combination with simpler bleaching systems, such as, peroxide and hypo (as against expensive oxygen and ozone systems) seems to offer an affordable route even for the small/medium scale paper mills to adopt ECF bleaching.*

INTRODUCTION

Paper mills manufacturing bleached chemical pulp consume large quantities of chlorine and ultimately release huge amounts of chlorinated organic matter into the receiving waters (1). Most of the chlorinated organic compounds, formed when chlorine and chlorine compounds are used, have been identified as toxic (2), mutagenic (3), persistent and/or bioaccumulative (4). The large scale pollution due to the excessive use of elemental chlorine in bleaching process and the growing concern over the release of these undesirable materials into the environment forced researchers to seek an effective alternative for chlorine [Total Chlorine Free (TCF) Bleaching] or at least to reduce the use of chlorine [Elemental Chlorine Free (ECF) Bleaching] in bleaching (5).

Chlorine dioxide, ozone and oxygen delignification have been adopted as alternatives or partial substitutes for chlorine; however, these are not used in most of the paper mills, due to their high capital cost which is not viable for pulp mills of capacity less than 100 tpd. To address this problem, research

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is recently focused on the use of microbial enzymes in the bleaching process to reduce consumption of chlorine based chemicals and this innovative approach of using microbial enzymes as pretreatment is termed as **Biobleachig**. Pretreatment of pulp with microorganisms or enzymes, therefore, has generated a great deal of interest, because it seems to offer a more cost effective solution in this direction (6,7). Biobleaching followed by peroxide bleaching step not only offers a more affordable ECF bleaching system for medium and small mills, but also reduces bleaching cost for mechanical grade pulp which has to use only peroxide as the brightening agent.

Biobleaching

In Biobleaching process, the unbleached pulp is treated with the microbial enzymes prior to the conventional bleaching process. The pretreatment with enzymes substantially reduces the consumption of bleaching chemicals. Due to the reduced application of chemicals, pollution load arising out of these chemicals is considerably reduced (8). Moreover, the pretreatment does not affect the properties of the paper and is expected to be cost effective. Earlier attempts to use microorganisms as such, in biobleaching were, though successful, created problems in the separation of the microorganisms from the bleached pulp and, therefore, microbial enzymes were used in later trials (9-14).

The expected short term impact of biological treatment will be, the elimination of elemental chlorine from the bleach plant without sacrificing on the pulp quality or any increase in chemical costs. In longer terms, this new approach will be important in the pulp bleaching processes since it would admit no chlorine containing effluents, that are substantially improved in terms of acute and chronic toxicological effects and that are fully recyclable as process waters.

Biobleaching Enzymes

A few biobleaching enzymes have been identified from some fungi belonging to the group, Basidiomycetes and most of them are xylanase based enzymes. The concept of biological bleaching with xylanases emerged from efforts to selectively remove hemicellulose from chemical pulps and prepare dissolving grade pulp, suitable for derivatisation to cellulose acetate, rayon etc (15). It was later found that xylanase pretreatment of pulp caused reduction in lignin content and that savings in chemicals can be obtained (16). When cellulase free xylanases have been applied to pulps, reduction in bleach chemical requirements have been concomitant with improvements in viscosity and paper properties, such as beatability, tear strength and brightness. Reduction in chlorine usage in part, due to xylanase treatment of pulp has also shown to substantially lower levels of adsorbable organic halides (AOXs) and dioxins in mill effluents (17).

Xylan is the predominant hemicellulose in hardwood kraft pulp (90%) and is a significant component of softwood kraft pulp hemicellulose (50%) (19). In hardwoods, the bonding between lignin and hemicellulose is primarily between lignin and xylan, possibly through arabinose side chains (20), which can be removed by xylanase. Xylanase is the most studied hemicellulase for this reason (21,22).

Despite the predominance of xylan in kraft pulps, only about 20-25% of the xylan can be hydrolysed by xylanase (23). Diffusional limitations due to the relatively large molecule of the xylanase may be a factor (24), as typical pore sizes in kraft and sulphite pulps are only 5-6 nm (25). It has also been suggested that uneven distribution on hemicellulose may limit accessibility of the enzyme to the xylan (21). Nevertheless, xylanases are widely used as a pretreatment for achieving ECF bleached pulp.

In addition to xylanases, the other important lignin degrading enzymes are lignin peroxidases (LiP), manganese peroxidases (MnP) and laccases (18). Activity of both LiP and MnP may take place only in the presence of the cosubstrate, hydrogen peroxide. Further, MnPs require Mn^{2+}, which is oxidised to Mn^{3+}. Mn^{3+} is the real oxidising agent that attacks the lignin molecule. Laccase utilises molecular oxygen as a cosubstrate. Very recently, a mediator system for the laccase enzyme has been reported (18). Laccase isolated from the fungus, Coriolus versicolor, acts very effeciently in the presence of a mediator system, which is a rather conventional low molecular and environmentally safe chemical. TCF bleaching may also be possible with the application of laccase/ mediator system.

Biobleaching Trials carried out by others

Biobleaching trials with microbial enzyme on unbleached kraft wood pulps reduced the lignin content, but did not improve the brightness. In the biobleaching processes, the unbleached pulp is pretreated with acid (concentrated Sulphuric acid is used in most cases) to bring down the pH, since, the enzymes are active at acidic range. Further, the biobleaching process is carried out at elevated temperatures (40-70° C). In addition to pH and temperature, the pulp is treated with the enzymes for more than one hour.

Recently, xylanase pretrement has attained the commercial status (22) and several mill scale trials have been carried out. At the Enso-Gutzeit Oy mill in Finland, a 1000 tonne run with enzymatic bleaching economically reduced chlorine consumption by 25-30% (26). Another mill scale trial during a 800 tonne run resulted in a 12% reduction in chemical requirement in a softwood kraft mill (17). Crestbrook Forest Industries, British Columbia is using xylanase pretreatment at full scale and has reduced chlorine comsumption by 11% (27). Recently, the Aanekoski mill in Finland used an enzyme with oxygen delignification and hydrogen peroxide bleaching to produce over 50,000 tonnes of totally chlorine free pulp (27). Earlier, Voest-Alpine Industries, Austria, have successfully carried out mill scale trials with hardwood kraft pulps and achieved savings of more than 30% in chlorine consumption (28). The biobleaching process with xylanase based enzymes has also been commercialised in Japan, Czeckoslovakia and Denmark. A few mill scale trials have been successfully carried out in a mill in Japan and recently, the technology has been adopted in Canada (29). A total of only 10 mills were known to use xylanase pretreatment on a commercial scale and more than 80 mill scale trials have been carried out (30). Of late, the technology is gaining wider acceptance in Canada and Europe.

R & D WORK CARRIED OUT AT ESVIN TECH

Since most of the enzymes are active at acidic pH and elevated temperatures, it was preferred to identify microorganisms / enzyme systems that would act efficiently at neutral/ alkaline pH (the pH of the unbleached pulp is neutral/ alkaline) and at a wide range of temperatures. We have isolated and identified several microorganisms with specific lignin degrading ability and after a detailed and thorough investigation, we have evolved the **ET - Biobleaching Process** in which the microbial enzyme system is active at ambient temperature and neutral/ alkaline pH range. Further, the reaction time is very short, just 30-60 minutes.

The major objectives of this study were:

1. To carry out biobleaching trials with bagasse pulps,
2. To incorporate ET - Biobleaching process as a pretreatment to conventional bleaching sequences to reduce the consumption of bleach chemicals (elemental chlorine or peroxide) and to increase the final brightness to expected levels without compromising on the properties of the bleached pulp; and
3. To recommend a suitable elemental chlorine free (ECF) bleaching system by adopting the ET-Biobleaching Process, for Mechanochemical, Chemical Bagasse and Dissolving grade pulps.

Preliminary trials were carried out with microbial enzymes to assess their bleaching efficiency of unbleached bagasse pulps. The culture conditions, such as pH, temperature and treatment time were optimised to extract maximal amounts of lignin degrading/modifying enzymes. The enzyme which bleached the pulp to maximal brightness, without affecting the strength properties was taken for further trials. Several bleaching trials were conducted in laboratory scale to ascertain the efficiency of Esvin Tech (ET) Biobleaching Process and the results are presented here.

RESULTS

Effect of Biobleaching on the Consumption of Bleach Chemicals

Biobleaching trials were carried out to evaluate the reduction in the consumption of elemental chlorine in case of Chemical Bagasse Pulp (CBP), Mechanochemical Pulp (MCP) and Dissolving Grade Pulp (DGP) and Hydrogen Peroxide, in case of Mechanical Bagasse Pulp (MBP).

Reduction in Elemental Chlorine consumption in case of Chemical Pulps

When the unbleached pulp was pretreated with the microbial enzyme (prior to the conventional C-E-H bleaching process), the consumption of elemental chlorine was reduced by 20% in case of CBP, 13.76% in MCP and about 15% with DGP (Table-1). There was slight reduction in the consumption of Hypo during the CEH bleaching of CBP, while with MCP, the consumption was slightly more than the control. Howere, in DGP, there was hardly any change in Hypo consumption. Due to biobleaching and reduction in the consumption of chlorine, the strength properties of the treated pulp samples were not altered (Table-1; Fig.1).

Reduction in Peroxide consumption in case of Mechanical Pulps

The unbleached MBP was treated with the microbial enzyme (crude enzyme) prior to peroxide bleaching. Peroxide at 1.0% was applied over enzyme treated pulp, while 1.5% was applied to untreated unbleached

TABLE-1.

EFFECT OF BIOBLEACHING ON THE CONSUMPTION OF BLEACH CHEMICALS

Particulars		Dissolving Grade Pulp		Chemical Bagasse Pulp		Mechanochemical Pulp		Mechanical Bagasse Pulp	
		Control (CEH)	Treated (BCEH)	Control (CEH)	Treated (BCEH)	Control (CEH)	Treated (BCEH)	Control (P)	Treated (BP)
Total Chlorine Applied	**Kg/t**	30.00	25.00	37.00	31.00	135.00	115.00		
Chlorine as Gas		20.00	15.00	28.00	23.00	100.00	80.00		
Chlorine as Hypo		10.00	10.00	9.00	8.00	35.00	35.00		
Total Chlorine Consumed	**Kg/t**	27.80	23.60	37.00	30.20	133.00	114.70		
Chlorine as Gas		19.10	14.90	28.00	22.20	100.00	80.00		
Chlorine as Hypo		8.70	8.70	9.00	8.00	33.00	34.70		
Redn in Elemental Chlorine consumption	**%**		**22.00**		**20.71**		**20.00**		
Redn in Total Chlorine consumption	**%**		**15.11**		**18.38**		**13.76**		
Total Peroxide Applied	**Kg/t**							**15.00**	**10.00**
Redn in Peroxide Applied	**%**								**33.33**
Brightness	**%**								
Initial		53.20	57.30	44.20	47.70	25.40	31.90	28.50	38.70
Final		90.00	89.40	81.00	81.00	74.50	74.40	43.40	45.70
Strength Properties									
Freeness	mL CSF	305.00	305.00	300.00	300.00	245.00	235.00	120.00	140.00
Breaking Length	M	3600.00	3400.00	6200.00	6200.00	5900.00	5800.00	3850.00	3660.00
Tear Factor		48.00	48.00	50.00	50.00	49.00	49.00	49.50	48.00
Burst Factor		22.00	22.00	39.00	38.00	34.00	32.80	16.80	16.10

B: Biobleaching; C: Chlorination; E: Extraction; P: Peroxide; H: Hypo

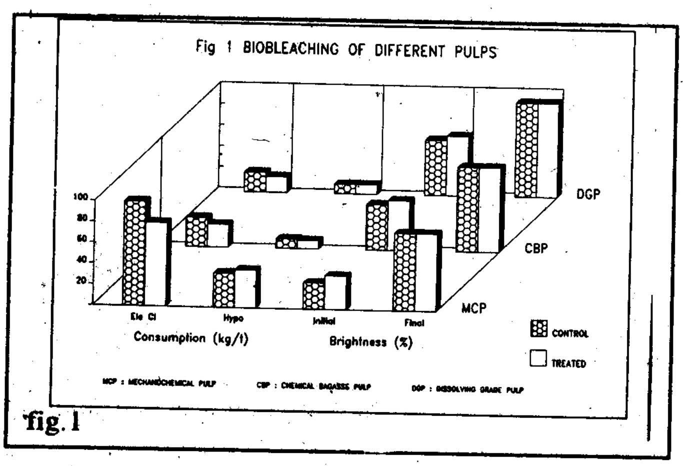

fig.1

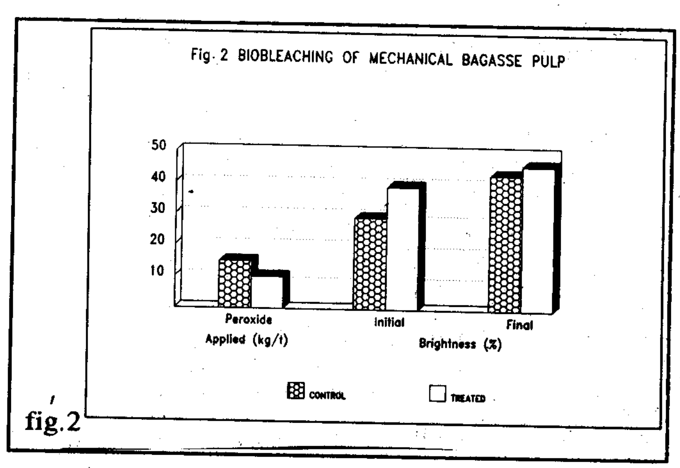

fig.2

MBP. In addition to the reduction (about 35%) in peroxide consumption, brightness of the enzyme treated pulp increased by 2.1% (Fig.2). The Strength properties of the biobleached pulp were comparable with that of untreated pulp (Table-1).

Effect of Biobleaching on Elemental Chlorine Free (ECF) Bleaching of Pulps

In order to achieve ECF bleaching, elemental chlorine was completely eliminated in the bleaching process and Hydrogen Peroxide was used as the alternative bleach chemical. When the pulps were pretreated with the microbial enzyme (prior to bleaching with peroxide and hypo), there was significant reduction in the consumption of Peroxide.

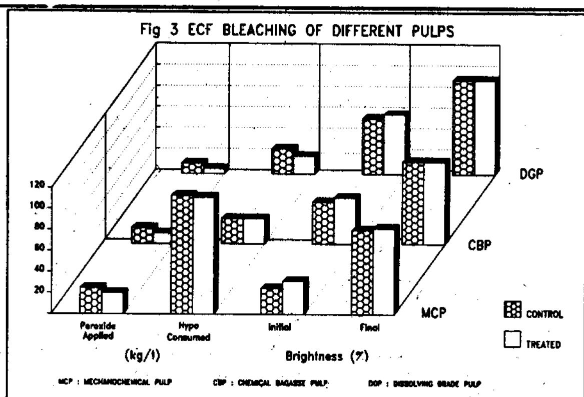

fig.3

ECF Bleaching trials with Mechanochemical Pulp

In order to avoid elemental chlorine, bleaching trials were carried out with Peroxide and Hypo on Mechanochemical pulp (MCP) (C-E-H bleach sequence is followed at present for MCP). Further, to reduce peroxide consumption and to increase the brightness (>80%) the unbleached pulp was pretreated with the microbial enzyme. In addition to the reduction in peroxide consumption (20%), the target brightness was achieved in the enzyme treated pulp sample (Fig.3). The strength properties of the treated pulp were almost similar to control (Table-2).

ECF Bleaching trials with Chemical Bagasse Pulp

Biobleaching trials carried with CBP indicated that ECF bleaching may be achieved with the use of Peroxide and Hypo. When unbleached CBP was pretreated with the microbial enzyme, there was a reduction of about 33% in the consumption of Peroxide (Table-2). The final brightness obtained was 80% (Fig.3). The strength properties were similar to conventionally bleached pulp.

TABLE-2.

EFFECT OF BIOBLEACHING ON ELEMENTAL CHLORINE FREE BLEACHING OF PULPS

Particulars		Mechanochemical pulp		Chemical Bagasse Pulp		Dissolving Grade Pulp	
		Control (PHPH)	Treated (BPHPH)	Control (PHPH)	Treated (BPHPH)	Control (PHH)	Treated (BPHH)
Total Peroxide Applied	Kg/t	25.00	20.00	15.00	10.00	10.00	5.00
Total Peroxide Consumed	Kg/t	13.20	8.60	5.60	4.40	4.40	2.70
Redn in Peroxide Applied	%		**20.00**		**33.33**		**50.00**
Total Hypo Applied	Kg/t	120.0	120.0	30.00	30.00	40.00	40.00
Total Hypo Consumed	Kg/t	113.0	111.3	23.50	23.50	24.30	16.60
Redn in Hypo Consumed	%		**1.50**				**31.69**
Brightness	%						
Initial		25.40	31.90	40.40	43.50	53.20	57.30
Final		80.00	82.00	79.00	79.70	89.50	90.00
Strength Properties							
Freeness	mL CSF	210.00	210.00	300.00	300.00	314.00	345.00
Breaking Length	m	7060.00	6810.00	4500.00	3900.00	3000.00	3000.00
Tear Factor		35.80	33.20	55.00	55.00	49.00	51.00
Burst Factor		32.00	31.80	27.00	28.00	18.00	18.00

B: Biobleaching; P: Peroxide; H: Hypo

ECF Bleaching trials with Dissolving Grade Pulp

Biobleaching trials conducted with dissolving grade pulp indicated that by adopting ET-Biobleaching Process, it is possible to achieve ECF bleaching. It is clear from the results that with the biobleaching followed by peroxide and hypo bleaching, the target brightness (90%) is easily achieved without any change in other properties. Further, by using the enzyme, the consumption of peroxide is significantly reduced by about 50% (Table-2; Fig.3).

Comparison between ET-Biobleaching and Imported Enzyme Processes

In order to assess the efficiency of our Biobleaching Enzyme/Process, trials were carried out with an 'imported' commercial preparations of a xylanase based enzyme (hereafter referred to as CE 1 and CE 2), using Dissolving Grade Pulp (DGP) and Chemical Bagasse Pulp (CBP).

Under the conditions prescribed for the imported enzyme, when CE 1 was applied as a pretreatment to DGP and bleaching carried out with 50 % less of peroxide, the final brightness obtained was 89.3% (brightness in control sample was 90.0%). With CE 2, 'an enzyme concentrate', the final brightness was 88.9%, compared to 91.0% brightness obtained with our ET-Enzyme (Table-3).

When trials were conducted with CBP, under conditions prescribed for imported enzyme, the final brightness of CE 1 treated pulp was 79.8% (brightness of control sample was 80.0%), when the enzyme was applied as a pretreatment and bleaching done with 33.3% less of peroxide. When CE 2 was used, the final brightness was 79.6%, compared to 81.0% obtained with our ET-Enzyme (Table-3).

The results clearly indicate that ET-Enzyme is as efficient as the imported xylanase based enzyme. However, our ET-Biobleaching Process does not require acid and steam (to reduce the pH of the pulp and to increase the temperature) and therefore, our process is more cost effective.

TABLE-3.

COMPARISON BETWEEN ET-BIOBLEACHING AND 'IMPORTED ENZYME' PROCESSES

Trials with Dissolving Grade Pulp

Particulars		Control (PHH)	CE 1 (BPHH)	CE 2 (BPHH)	ET-Enzyme (BPHH)
Total Peroxide Applied	Kg/t	10.00	5.00	5.00	5.00
Redn in Peroxide	%		**50.00**	**50.0**	**50.0**
Total Hypo Applied	Kg/t	12.00	12.00	12.00	12.00
Total Hypo Consumed	Kg/t	8.90	9.40	9.10	9.60
Brightness	%				
Initial		57.0	59.8	59.6	61.0
Final		90.0	89.3	88.9	91.0

Trials with Chemical Bagasse Pulp

Particulars		**Control (PHPH)**	**CE 1 (BPHPH)**	**CE 2 (BPHPH)**	**ET-Enzyme (BPHPH)**
Total Peroxide Applied	**Kg/t**	15.0	10.0	10.0	10.0
Redn in Peroxide	%		**33.3**	**33.3**	**33.3**
Total Hypo Applied	Kg/t	26.00	26.00	26.00	26.00
Total Hypo Consumed	Kg/t	14.00	18.70	18.20	17.50
Brightness	%				
Initial		45.0	48.8	48.5	49.0
Final		80.0	79.8	79.6	81.0

Imported Commercial Enzyme referred as CE 1 & CE 2

CONCLUSION

It is concluded from the results that-

1. The brightness of the unbleached pulp increases by 5-10 units when pre-treated with the microbial enzyme.
2. The consumption of elemental chlorine can be reduced by about 15-20% with the use of microbial enzyme during CEH bleaching of the pulps. The target brightness is easily achieved, even though the consumption of bleach chemical is reduced.
3. Cost effective ECF bleaching may easily be achieved with the use of Peroxide as the alternative bleach chemical, instead of elemental chlorine, in case of Chemical Bagasse Pulp, Mechanochemical Pulp and Dissolving Grade Pulp.
4. When the unbleached pulps were pretreated with the microbial enzyme prior to bleching with peroxide, consumption of peroxide is reduced significantly.
5. Due to ECF bleaching along with enzyme pretreatment (though less bleach chemicals are used), higher brightness of pulp is achieved without any change in the strength properties.
6. The brightness results obtained with ET-Biobleaching Process are comparable to that of commercial preparations of an 'imported' xylanase based enzyme. Our ET-Enzyme is, therefore, as efficient as the imported enzyme. Our biobleaching process is also advantageous, since this does not require acid and steam (to make the pulp acidic and to raise the temperature, like other processes).
7. The colour of the bleach plant effluent is significantly reduced by adopting the ET-Biobleaching Process, because of the elimination of chlorination and alkali extraction stages.

ADVANTAGES OF ET-BIOBLEACHING PROCESS

The uniqueness of Esvin Tech (ET) Biobleaching Process is that the process is adoptable on non-wood material, viz, **Bagasse Pulp**, which has not been attempted elsewhere.

The most important advantages of the ET-Biobleaching Process are as follows:

1. The enzyme is active at neutral/ alkaline pH, unlike other biobleaching enzymes which are active only at acidic pH ranges.
2. The enzyme is very efficient at ambient temperature, while most of the enzymes used in other processes are active only at higher temperatures (40 to 70° C). However, the enzyme identified by Esvin Tech is also active over a wide range of temperatures, viz, 25-70° C.
3. In addition to the savings due to the reduction in chlorine/ peroxide consumption, further savings could be achieved by avoiding the use of acid (to bring down the pH) and steam to raise the temperature.
4. The unbleached pulp is treated with the enzyme for 30 to 60 min as against 1 to 3 h treatment time for other enzyme systems and even several days, in case of microbes which are used as such.
5. Cost effective ECF bleaching is easily achieved with the incorporation of ET-Biobleaching Process.
6. The colour of the bleach plant is reduced to significant levels, since the chlorination and alkali extraction stages are eliminated with the adoption of ET-Biobleaching Process.

FUTURE PROSPECTS

The use of xylanase as a bleaching aid is currently the only biological bleaching technology to be applied at commercial scale (22). Many mills are doing test runs and a few are using xylanases at mill scale levels. What makes this option attractive is that xylanase can be used economically in a short time period with existing equipment. Although there are no data available on the effectiveness of xylanase with chlorine free bleaching, a patent application for an enzyme + ozone + hydrogen peroxide process has been filed and a mill has produced totally chlorine free pulp using an enzyme treatment combined with oxygen delignification together with hydrogen peroxide bleaching (27).

Public perceptions of chlorine and industrial processes involving chlorine have fuelled a change in the bleaching practices of many a mills. This presents a challange and opportunity for biotechnology. The success of biological bleaching will depend upon the resolution of certain technical problems and upon the cost effectiveness of the technology relative to other chlorine free bleaching strategies.

ECONOMICS

It is evident from the results obtained in this study that the biobleaching process may successfully be adopted on a variety of pulps. In case of C-E-H bleach sequence adopted in bleaching of chemical and semi-chemical pulps, biobleaching can significantly reduce chlorine consumption, whereas, in case of dissolving grade pulp. the bleaching sequence can be peroxide and hypo, provided the expensive peroxide consumption can be reduced. Biobleaching is also able to reduce the consumption of peroxide in the bleaching of mechanical bagasse pulps, rendering the manufacture of newsprint econimical Is is estimated from the bench scale studies completed thus far, that for a mill of 100 tpd, the pay back period would be 4-5 years, in case the biobleaching process is adopted at mill scale.

Therefore, it may be appreciated that biobleaching process is an economical route for achieving ECF bleaching and hence may be suitably adopted by both small and medium mills, who cannot otherwise afford ECF bleaching.

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