

Enzymatic Approach for Effective Environmental Management

Arvind Kumar Sharma *, Anurag Sharma, Satish Sharma and Yogesh Patil

*Anmol Polymers Pvt. Ltd., 1003, GD-ITL Tower, Netaji Subhash Place, Ring Road, Pitampura New Delhi- 110 034.,

Biocon India Ltd., 20th K.M., Hosur Road Electronics City, P.O. Bangalore-560 100

Abstract

In the context of environmental management, there is an increasing concern for Pulp and Paper Industry to bring down BOD, COD and AOX level in the final discharge from the mills, In India, enzymes are the latest introduction in pulp bleaching sequence. Few mills in the country are already using enzymes in pre-bleaching stage and have successfully reduced the chlorine consumption by 15-25%. This has reduced the bleach plant effluent load going to the ETP for treatment. Use of enzymes in pre-bleaching is an established technology and many other mills are trying to use the same for different purposes. Enzymes are also used for deinking, improved refining operations and for effluent decolourisation. Case studies for the above mentioned uses in actual mill conditions are presented to demonstrate the practicability of the use of enzymes in the conditions prevailing in the Indian Pulp and Paper Industry.

INTRODUCTION

The quality of life existing on earth is indirectly linked to the overall quality of environment. In recent years, tremendous pressure has been felt to preserve environment and globally so many measures have been adopted to save greenery, fresh air, water and land resources. Biotechnology is one of the major tools towards maintaining the clean and green environment.

In present circumstances due to more awareness in society and mounting pressure from all sections, Paper Industry has to adopt cleaner production technologies by reducing the use of chlorine and its compounds in bleaching sequence resulting in reduced generation of Adsorbable Organic Halides i.e. AOX.

Most of the Paper Mills have either obtained ISO Certifications or undergoing process to achieve the

same to join march towards joining hands with market leaders to manage and preserve environment. The main focus in this direction is waste minimization, conservation of natural resources, energy and modification of present manufacturing set up by cleaner technologies.

The Biotechnological approach by application of enzymes in various fields like Bleaching, Biodeinking and refining has been successfully employed in various Paper Mills in India to reduce bleaching chemicals, energy and deinking chemicals like Caustic Soda, Silicate etc.

Enzymatic Pre-bleaching

During the bleaching sequence, a significant amount of organic material is dissolved in chlorination and extraction stage. Where chlorine is extensively used for bleaching, an appreciable quantity of organically bound chlorine finds its way in the effluent which is reported as Adsorbable Organic Halides (AOX). Biopulp is a liquid thermostable alkaline

hemicelluloses (xylanase) enzyme for use as a bleach-boosting agent in the pulp and paper industry. It is used to improve bleachability of Softwood/Hardwood/Agro pulps at higher temperatures. Enzyme selectively removes Xylan from the surface and pores of the fibres, which facilitates the subsequent bleaching, reducing the bleaching chemicals required to reach the same degree of delignification.

Enzyme pre-bleaching using xylanase enzyme i.e. Bio-pulp offers a solution by improving the effectiveness of conventional bleaching chemicals in removing lignin. It is used to improve the bleachability of softwood/hardwood/Agro pulps at high temperatures. The enzyme is produced by a selected microorganism. When pulp is treated prior to bleaching with BIOPULP, a substantial reduction is observed in the amount of bleaching agent consumed to achieve a given level of brightness. The efficiency of BIOPULP varies with temperature and pH. The most optimal conditions for use are

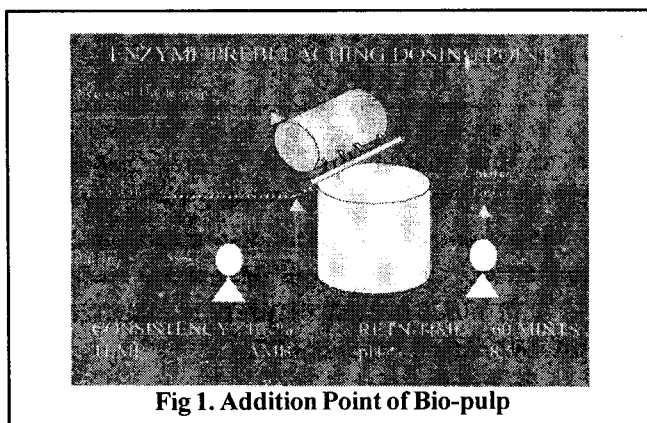


Fig 1. Addition Point of Bio-pulp

: pH 7.5 - 8.5 and temperature of 40-50°C. A treatment time of about 1-4 hours is suitable.

RESULTS AND DISCUSSION

Mill Applications

Bleach Boosting Enzyme is successfully being used by various mills on commercial scale. In some cases, the target was to reduce chlorine consumption for getting the same brightness but other mills wanted to increase the final brightness

at same chemical dosage without any side effect on pulp strength properties and environment.

Case Study -1

This mill is producing around 350 TPD bleached paper and approximately 100 TPD rayon grade or paper grade pulp. The raw material is hardwood and bagasse. The details of bleaching conditions, chemical dosage and strength properties of pulp are given in Table 1 and 2.

Sample of effluent discharge from the bleach plant as well as the discharge from the mills are analyzed. Appreciable reduction in AOX is indicated. The findings of blank vis-a-vis enzyme treated pulp with respect to AOX levels are given in Table-3.

For bagasse pulp, attempts were made to achieve the required brightness by totally eliminating elemental chlorine and using hydrogen peroxide in alkali extraction stage.

Case Study-2

This mill is producing 215 TPD paper and raw mainly hardwood/bamboo mix. In this mill, the

objective was to reduce 15% chlorine at the same brightness level of the final pulp.

Observations:-

- (1) After 2 days trial run, it was observed that after reducing 15% chlorine the brightness range was almost the same @ 295 gms Biopulp per tonne of pulp.
- (2) In normal bleaching, there was variation of 3-4 points in final brightness i.e. 82-86, but with Biopulp trial, this variation was limited to 20° only and the brightness remained between 83.5-85.5. In view of the performance of enzyme, it has been decided to take a longer plant run for one month to see the effects of enzyme after prolonged use.

Case Study -3

This mill is producing 100 TPD bleached varieties of paper using agriculture residue pulp like straw/Bagasse etc. Followings are the objectives:-

- To achieve higher final brightness or reduction in chemical consumption.

Table-1 Details of Enzyme Pre-Bleaching in Wood based Pulp

Particular		Without Enzyme	With Enzyme	
Enzyme Treatment			I	II
Enzyme	gm/T	0	300	300
Temperature	°C	50	50	50
Retention Time	min.	60	60	60
pH		8.0-9.0	8.0-9.0	8.0-9.0
Kappa No.		19.1-22.5	17.0-18.8	16.6-19.3
Chlorine/Chlorine dioxide stage				
Cl ₂	%	2.5	2.5	2.5
ClO ₂	%	0.34	0.34	0.34
pH		2.0-3.0	2.0-3.0	2.0-3.0
Kappa No.		9.8-11.9	6.8-7.3	6.7-7.6
Alkali Extraction/Peroxide Stage				
NaOH	%	1.1	1.1	1.1
H ₂ O ₂	%	0.5	0.5	0.5
pH		9.5-10.5	9.5-10.5	9.5-10.5
Kappa No.		8.0-9.3	4.9-5.3	4.7-5.6
Hypo I Stage				
Hypo(as Cl ₂)	%	2.3	2.3	1.88
pH		8.0-9.0	8.0-9.0	8.0-9.0
Hypo II Stage				
Hypo (as Cl ₂)	%	1.75	1.75	0.66
pH		7.5-8.0	83.0-84.5	83.1-84.3
Brightness	%	82.3-83.4	7.5-8.0	7.5-8.0
Chlorine Dioxide Stage				
ClO ₂	%	0.2	0.2	0.2
pH		3.0-5.0	3.0-5.0	3.0-5.0
Brightness	%	84.5-85.3	87.0-87.8	87.0-87.5
Viscosity(0.5 CED)cp		4.0-4.4	4.9-5.1	5.05-5.15
PC No.		1.0-1.1	0.5-0.69	0.4-0.62
Yellowness	%	5.17-6.39	2.9-4.0	2.6-3.9
Strength Properties at 35° SR				
Burst Index	Kpa.m ² /g	3.04	2.94	2.94
Tear Strength	mN	294	282	318
Breaking Length(meter)		4890	5070	5120
Double fold (No)		18	15	17

Table-2 Details of Enzyme Pre-Bleaching in Bagasse Based Pulp

Particular		Without Enzyme	With Enzyme		
Enzyme Treatment			I	II	III
				ECF	ECF
Enzyme	gm/T	0	300	300	300
Temperature	°C	50	50	50	50
Retention	min.	60	60	60	60
pH		8.0-9.0	8.0-9.0	8.0-9.0	8.0-9.0
Kappa No.		11.4-13.6	9.84-11.14	9.04-10.56	9.12-10.8
Chlorine/Chlorine dioxide stage					
Cl ₂	%	2.2	1.5-1.6	0	0
ClO ₂	%	0.14	0.12-0.14	0.46	0.46
pH		1.0-1.8	1.5-2.0	1.5-2.0	1.5-2.0
Kappa No.		4.0-4.73	3.2-4.98	3.2-5.28	2.56-4.48
Brightness	%	56-61	58-62	59-64	58-66
Alkali Extraction/Peroxide Stage					
NaOH	%	1.5	1.48	1.0-1.27	1.2
O ₂	%	0.4	0.4	0.4-0.5	0.4
H ₂ O ₂	%	0	0	0	0.27
pH		9.5-10.5	9.5-10.5	9.5-10.5	9.5-10.0
Kappa No.		1.19-1.68	1.2-1.84	0.96-1.42	0.72-1.60
Brightness	%	68-72	67-72	74-78	75-85
Chlorine Dioxide Stage					
ClO ₂	%	0.46	0.46	0.45-0.48	0.49
pH		3.0-4.0	3.0-4.0	3.0-4.0	3.0-4.0
Brightness	%	86.6-89.0	86.4-88.0	87.5-89.5	88.2-90.2
Viscosity(0.5 CED)cp		11.8-12.7	13.7-17.7	17.7-18.0	16.9-18.9
PC No.		0.24-0.42	0.16-0.30	0.12-0.30	0.12-0.30
Yellowness	%	1.52-2.0	1.03-1.8	1.0-1.76	0.45-0.76
Strength Properties at 35° SR					
Burst Index	Kpa.m ² /g	3.04	3.04	3.14	3.14
Tear Factor	mN	312	312	294	288
Breaking Length(meter)		4980	4880	5050	5230
Double fold (No)		14	19	18	15

Table-3 AOX Levels (Kg/T) in Effluent

Particular	Normals	Enzyme Treated	% Reduction
Bleach Effluent (Writing ptg paper wood based)	2.39	1.37	42.6
Bleach Effluent (Writing ptg paper bagasse based)	1.28	1.07	16.4
Final Discharge	0.96	0.84	12.5

- To reduce organic chlorine level(AOX) in effluent.
- To reduce colour reversion and yellowness. After taking trial, the enzyme is now being continuously used and the following benefits have been achieved:-
- A reduction of 1 kappa no. after treatment in unbleached pulp.
- A reduction of 1.8-1.9 kappa no. after alkali extraction in case of enzyme treated pulp compared to control.
- No significant difference in brightness was found in control, enzyme treated pulp and those made with 2% less chlorine during bleaching.

Beside the above mills, few other mills based on

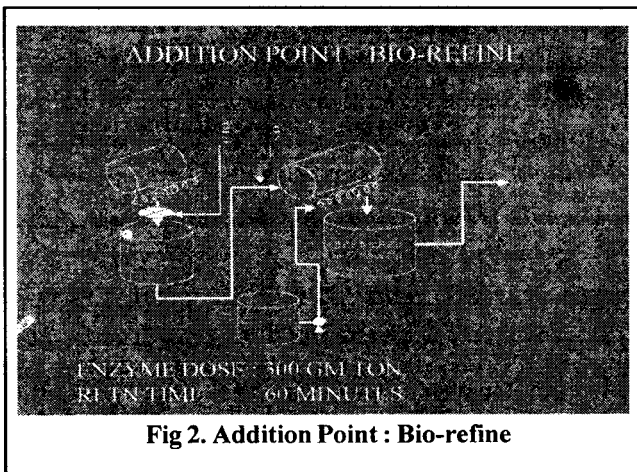
hardwood, bagasse, straw etc. are using Bio-pulp and are fully satisfied with the performance which includes better brightness, less yellowness, less colour reversion in paper and above all reduce AOX level in effluent.

Biorefining

Refining of pulp is an essential feature in order to hydrolyse the fibres for requisite paper properties. This is normally done by processing pulp through disc refiners, which fibrillates and swells the fibres. Addition of an enzymatic product Bio-refine L@300 grams per tonne of pulp has been put to use which enhances freeness(degree SR)by 6 units at the same level of refiner loadings. Details on the finding of enzyme treated vis-a-vis blank for wood based pulp is given in Table-4

Table-4 :- Evaluation of Refining Aid (Biorefine-L) in Wood pulp

Particulars	Blank	
	Set I	Set II
Pulp pH	7.1	7.1
Slushing Time (minute)	5.0	5.0
Stock consistency (%)	1.78	1.78
Initial Freeness (°SR)	17	17
Biorefine - L (gm/tonne)	X	300
Retention Time (minute)	X	30
Beating Time (minute)(with constant)	45	45
Final freeness (°SR)	34	40
Strength Properties		
Burst Index (Kpa. m ² /g)	3.13	3.43
Tearing Strength (mN)	359	347
Breaking Length (meter)	5065	5965
Double Fold (No)	11	13



Process Condition (In Valley Beater)

O.D. Pulp : 300 gm
Water : 15 Litre

BIOREFINE L is a unique formulation containing cellulose and hemicellulases as main enzymes activated together with low level of xylanase and mannose. BIOREFINE L is produced using a submerged fermentation of a selected strain of *Trichoderma reesei*. BIOREFINE L mainly acts on the surface of the fibre in the acidic to neutral pH range (pH6.5-7.5) and between temperature of 45-65°C. The fibre modification by BIOREFINE L results in the enhancement of water removal from paper pulp processing and also pulp refining energy reduces to about 10-25%. If refining follows the enzyme treatment, increased fibrillation can be observed due to enhanced beatability/refining of the fibres. The enzyme dosage is about 300 gm/tonne of pulp and a retention time of about 60 minutes at final washer out let as shown in Fig.-2 with the use of Bio-refine L, refining of pulp becomes effective in reducing energy consumption in wood based pulp thereby saving 100 kWh/tonne of refining energy resulting in substantial economical advantages.

Deinking

Waste paper recycling in India has bright future. More and more Paper mills are either fully or partially depending upon waste paper recycling. In normal deinking system so many chemicals like caustic soda, sodium silicate hypo etc are used,

but in bio-deinking system only Biodeink-D enzyme is used in pulper while in flotation cell, surfactant is required. Refining energy requirement is also reported low in system where biodeinking is in use, since some ingredients help to increase the freeness. Costwise also biodeinking has proved to be economical in comparison to conventional system. The effluent B.O.D and C.O.D load is less in comparison to normal system. Deinking is another area in which enzymes have found application.

Enzymatic Deinking Process

In the pulper the fibres are separated by mechanical action rupturing the fibre surface. Fibres get a shearing action and microfibrils get developed over the fibre surface. Cellulase attacks the fibre surface. The microfibrils on the surface are decomposed by cellulase, thereby ink particles on the surface gets released. The fibres get uniform shaped, thus it can increase the drainage rate of water on the paper machine and ultimately there can be savings in power consumption.

BIO-DEINK-D is used in high density pulping in the pulper (old newsprint etc) of around 10% OD consistency along with a non-ionic surfactant. BIO-DEINK-D helps in easy release of ink particles which are further separated in froth floatation process. BIO-DEINK-D also improves the brightness of the paper, BIO-DEINK-D can be used over a pH range of 6.5-7.5 and a temperature of 45-55°C.

The dose of BIO-DEINK-D is dependent upon the type of pulp and can be optimized between 0.03 to 0.05% based on the effect desired and the process economics. The treatment time/retention time is related to the dose rate but on an average, it can be around 20 to 45 minutes.

Case Study -1

- Pulp became more clean, no. of ink particles were reduced, though there was not much improvement in the brightness of the pulp.
- Yellowness of the pulp was reduced and improvement in the whiteness was also there.
- Caustic and sodium silicate was not added so there was no colour reversion.

- There was no adverse effects on the runnability of the machine.
- Biodeink-D is an eco-friendly product, so AOX level in effluent will be reduced.

Case Study -2

Trial Description

- Trial of Biodeink-D and Anmopulp was started.
- Dosing was kept @300 grm/tonne of raw material (Bio-deink-D) and 1.2 kg/ton of raw material (Anmopulp)
- Initially furnish was taken of good quality for special quality paper.
- Furnish was changed on to see the impact on pulp brightness

Observations

- 1) Sufficient foaming observed in both cells
- 2) The brightness gain was 7.5-8.0 from pulper to Chest No. 5 in comparison to normal deinking system.
- 3) The visual cleanliness of paper is slightly better than the conventional deinked pulp.

It is decided to take a 10 days trial to establish the results and work out the costing. In initial trial, the cost of deinking chemicals seems to be lower than the conventional deinking chemical cost.

Enzymes in Pipeline

Few other enzymes have promising future for pulp and paper industry namely in colour removal of effluent, stickies control and conversion of bagasse pith to pultry feed. For colour removal, initial trials have shown encouraging trends. In laboratory scale study, there is substantial reduction (upto80%) in colour of untreated effluent.

CONCLUSION

Biotechnology offers excellent opportunities towards sustainable development and resource conservation. The pre bleaching has already been established as a useful technology for pulp and paper industry towards reduction of AOX levels. The benefits can be achieved depending upon the focus of the mill, but it is a significant step towards reducing AOX load. Biorefining offers great potential in

conservation of electrical energy. Biodeinking replaces the other chemicals used in deinking which ultimately helps to reduce BOD and COD levels. Since enzymes are very selective in their actions, one has to use them judiciously under carefully controlled conditions to exploit their full potential. It is very important for the suppliers of enzymes and mill personal to work together in establishing the optimum conditions of application of enzymes which may differ from one mill to another.

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