

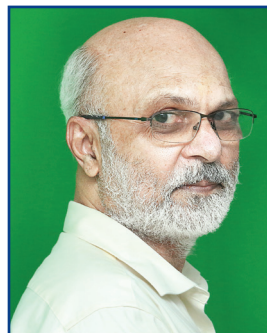
GREEN, BIOBASED SOLUTIONS FOR PAPER INDUSTRY



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Abstract:

Over the last decade, the paper industry in India is growing rapidly with consistent growth in demand. As a result, production of paper in all sectors of the industry has been growing. The process to convert natural raw materials into the final paper is multistage & complex. The industry currently faces many challenges regarding process efficiency & chemical consumptions at every stage of processing. It has direct impact on the energy & water consumption, cost of manufacturing and environment concerns. This demands improvements in the existing processes and new add-on technologies which are preferably, green & natural. At the same time, due to competition from many international producers, the industry is in search of cost effective and energy efficient solutions.

The present article is primarily focused on addressing these challenges by offering a technology for -

1. Improving cooking efficiency
2. Reducing sulphurous gas emissions
3. Reducing bleaching chemicals
4. Reducing microbial growth, slime & odor

The novel technologies proposed in this paper will help paper industry to reduce or in some cases eliminate the utilization of toxic chemicals while making the process eco-friendly. The biobased & green approach will not only improve the final paper quality but will also help in building a good & healthy working condition in the mill.

Keywords: Probiotics, Bleaching, Environmental issue, Microbial slime, VFA

Introduction:

Probiotics & biobased technologies are safe, cost effective and environment friendly solutions for the paper industry. The current research article presents a unique technology platform based on the use of metabolites produced through a novel fermentation process using a consortium of probiotic microbes & biobased ingredients. All the technologies developed on this platform are unique in terms of its composition & application. The different bio-based technologies presented include:

1. Cooking enhancement & odor control for hardwood & agro-based mills
2. De-lignification & bleaching enhancement with reduced chemicals
3. Microbial growth, slime & odor control in paper making process & product

These technologies will effectively replace/ reduce the overall conventional chemical consumption at multiple levels of paper manufacturing and will help in reducing the environmental impact considerably.

Materials & Methods

The different biobased technologies presented in this paper is process specific and optimized in lab trials using standard methods. The required raw materials are collected from mills or purchased from authorized sources.

Materials

1. Hardwood chip samples - eucalyptus, casurina, Subabul & mixed species
2. Pulp from various bleaching stages (ODL, Do, E_{OP} D1)
3. Stickies & pitch from different processes

Methods

Cooking & bleaching studies are conducted as per the established process standards. The process output parameters including kappa, brightness, DCM extractives, viscosity, black liquor analysis & rejects are tested using TAPPI standards. The microbial test such as zone of inhibition & MIC (Minimal Inhibitory Concentration) are conducted using the standard procedures of 'American society for microbiology'.

Results & Discussion

The various technologies presented are studied under the standard lab conditions. The results obtained are validated by performing a field trial in actual mill process conditions. The different technology mechanisms involved in the product applications are discussed below.

- Competitive inhibition-** A group of beneficial microbes are placed in a novel consortium. It works with a competitive inhibition mechanism and play an important role in odor reduction¹, metal sequestration² & Sulphur compounds removal³. These microbes competitively suppress the growth of contaminant microbes responsible for biofilm & slime formation. This helps in effective reduction of odor causing compounds including volatile fatty acids, mercaptans & sulphides.
- Sulphur sequestration-** A class of sulphur metabolizing microbes³ are present in the consortium. These specific bacteria play an important role in oxidation of reduced sulphur compounds³. This part of technology helps in effective reduction of volatile sulphur emissions.
- Bio-dispersion-** A biobased dispersion chemistry is used. The various phenomenon includes surface tension reduction, enhanced impregnation, dispersion of hydrophobic contaminants⁴. These chemistries are defined based on the HLB (Hydrophobic Lipophilic Balance) value, emulsification index, CMC (Critical Micellar Concentration) & surface tension properties. The selection of required bio-dispersant is done based on the application such as slime & biofilm disruption, pitch/stickies dispersion & dissolution and wood impregnation.
- Microbial growth retardation-** A novel technology is used with selective growth control mechanism for gram (-) bacteria over gram (+) bacteria. The biobased ingredients work by retarding the cell multiplication rate through various degrading mechanisms⁵. The technology

efficiently works on the reduction of microbial growth rate of contaminant microbes.

- Biosorption-** A biobased process with effective metal sequestration chemistry⁶. The beneficial microbial biomass works as the source of biosorbent. It works with different mechanisms including ion exchange, adsorption, complexation, transport & chelation⁷.
- Delignification-** A biobased oxidation mechanism. It enhances the delignification process by generating insitu peracids from the specific organic acids present in the product⁸. The technology utilizes sequestering & pH buffering mechanism for enhanced delignification and bleaching process.

Each biobased mechanism in combination with the others, offers a unique solution for different process applications in paper making. The results obtained from lab studies for different process applications are presented & discussed below.

1. A cooking enhancement & odor control

A bio-dispersion & sulphur sequestration chemistry is used in the process of the cooking enhancement program. Different experiments are carried out in the lab to evaluate & establish the performance for-

- a. Reduction of percentage of active alkali (1 point)
- b. Reduction in sulphureous gases & odor (60-70%)
- c. Reduction in H-Factor

The studies are conducted in a lab digester under the standard cooking conditions using mixed hardwood chips. The blank is processed without the biobased cooking enhancer technology keeping all the cooking parameters constant. The test has used the biobased product at 800 g/mt of bleached pulp with 18% of active alkali. The AA% used in case of blank is 19%. The lab results from this study are given in Table 1.

Parameters	Blank	Biobased Trial
Cooked pulp analysis		
AA Charged (%)	19	18
Un-screen yield (%)	50.4	50.2
Screened rejects (%)	2.8	2.2
Screen yield (%)	47.6	48.2
Kappa No.	26.7	25.0
Iso brightness (%)	24.8	25.2
Black liquor properties		
pH	13.2	13.0
Total solids (%)	20.1	19.7
TTA as Na ₂ O gpl at 200 gpl total solids	42.6	40.9
RAA as Na ₂ O gpl at 200 gpl total solids	12.3	10.2
H ₂ S (ppm)	598	184

Table 1: Lab digester analysis of cooked pulp

The results have shown better cooking at reduced active alkali concentration. The screen yield was found to be increased with lower rejects and a gain in brightness. The H_2S concentration was found to be reduced by 70% and correlated with a significant reduction in the perception of odor.

The technology is further validated by a plant scale run to establish the lab results. The data obtained are presented in Figs. 1 & 2.

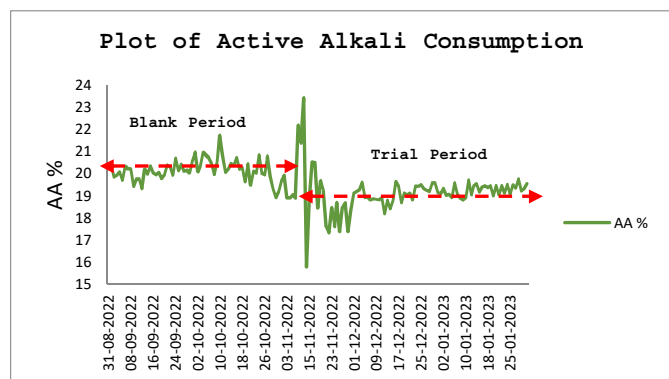


Fig. 1: Active alkali consumption (Blank period: 31/08 to 26/10/22; Trial period: 27/10/22 to 25/01/23)

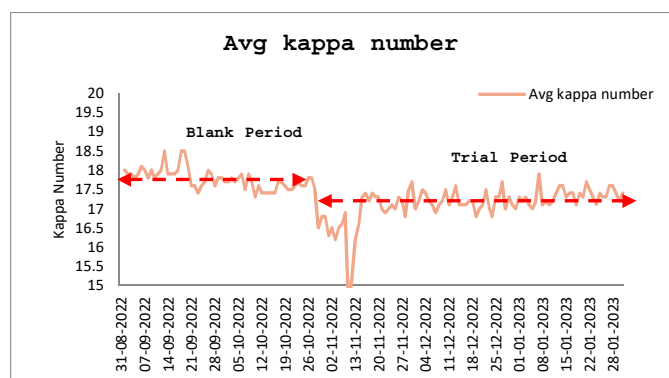


Fig. 2: Avg. Kapp No. (Blank period: 31/08 to 26/10/22; Trial period: 27/10/22 to 25/01/23)

The trial period has shown a reduction in average active alkali consumption from 20.5 to 19.0% and kappa number from 17.8 to 17.3. The H factor is reduced from 700 to 550. The results are in line with the lab trials and have shown an improvement in the cooking process.

2. Efficient delignification & bleaching

A biosorption & delignification technology is used to make the bleaching process more efficient. The technology is evaluated in the lab by conducting the study at various stages of bleaching. Dosage & dosing point optimization has been done to achieve the optimum brightness. Dosages of the novel biobased bleach enhancer formulation ranging from 150-300 g/MT of bleached pulp at various dosage points D_0 , E_{op} & $D1$ was studied. The optimized data is summarized in the Table 2

Parameters	UOM	D ₀		E _p		D1	
		Blank	Trial	Blank	Trial	Blank	Trial
Biobased bleach enhancer	g/MT	0	200	0	150	0	0
Process parameters							
Pulp OD weight	g	30		25		20	
Consistency	%	10		10		10	
Temperature	°o.	60		75		80	
Time	Min	45		90		180	
pH		2.5-3.5		11-12		5-5.5	
Chemicals							
ClO ₂	kg/MT	4.74		0	0	3.16	
NaOH	kg/MT	0		2.0		0	
H ₂ O ₂	kg/MT	0		1.5		0	
Pulp properties (post bleaching)							
pH		3.3	3.2	12.2	12.4	5.2	5.2
ClO ₂ Consumed	%	4.74	4.74	NA	NA	2.85	2.78
NaOH Consumed	%	NA	NA	1.18	0.82	NA	NA
H ₂ O ₂ Consumed	%	NA	NA	1.45	1.46	NA	NA
Brightness (Initial pulp)	% ISO	54.8					
Brightness (Final pulp)	% ISO	71.5	72.9	84.4	85.0	88.0	88.7

Table 2: Lab scale bleaching data with biobased enhancer

The data presented in the table is average of triplicate trials. Each bleaching stage has shown a gain in the brightness in the range of 0.6-1.5 ISO%. The residual chlorine & alkali in the both $D1$ & E_p stage has indicated a further scope of chemical reduction in both the stages.

The technology is further validated by conducting trials on a mill scale. A consolidated data for 90 days for D_0 , E_{op} & $D1$ stage is summarized in the Fig. 3.

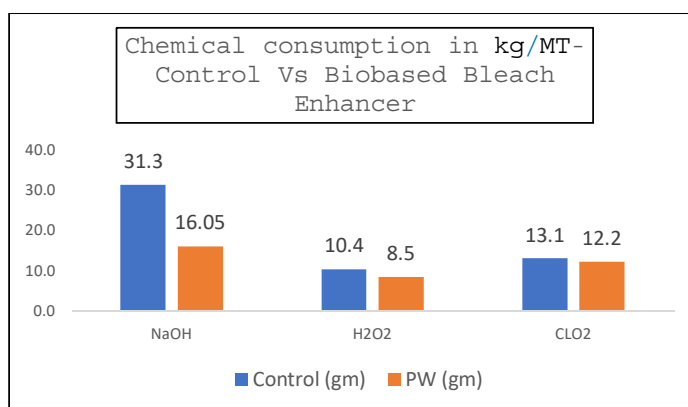


Fig. 3: Average chemical consumption of different bleaching chemicals

It can be seen from the graph that the overall sodium hydroxide consumption has reduced by 48.7%, peroxide by 18.7% & chlorine dioxide by 7% when the technology was used at a dosage of 270 g/MT of the pulp.

Both the lab & process scale study has indicated the scope of chemical reduction for the bleaching process of the pulp and also reduced TDS and effluent load.

3. Microbial growth, slime & odor control

Microbial fouling and related issues are the most complex problems to tackle in pulp & paper industry. Considering the complexity, a combination technology approach has been used to solve the problem. The novel approach includes the use of a combination of beneficial microbes, a selective growth retarder & a bio-dispersant. The initial lab experiments were conducted under controlled microbiology conditions with *E. coli* & *A. niger* as the common contaminants. Zone of inhibition & MIC studies were conducted. Different dosages & dilutions are used to establish the efficacy of the technology. The bacterial study was carried out for 24 h of incubation period & the fungal study at 72 h. The results obtained for zone of inhibition study are documented in Figs. 4 & 5.



Fig. 4: Zone of inhibition study with *E. coli* at different concentrations

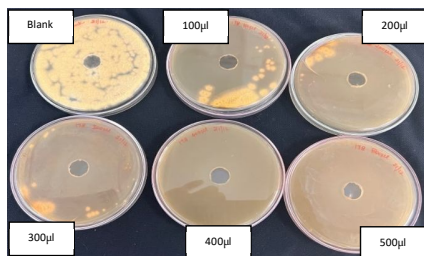


Fig. 5: Zone of inhibition study with *A. niger* at different concentrations

The complete inhibitory effect of biobased growth retarder technology was found to be at 70 µl for *E. coli* & 400 µl for *A. niger*. The data obtained is further validated with MIC studies with 18 h of incubation in case of both the cultures. Product concentrations are studied in increasing concentration from tube No. 1 upto 10. The results obtained are documented Figs. 6 & 7.

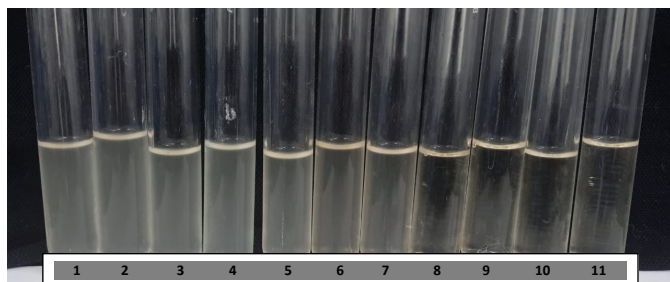


Fig. 6: Zone of inhibition study with *E. coli*

The results obtained showed that the MIC for the product on 50% reduction scale is 160 ppm whereas at 90% reduction is 2500 ppm.

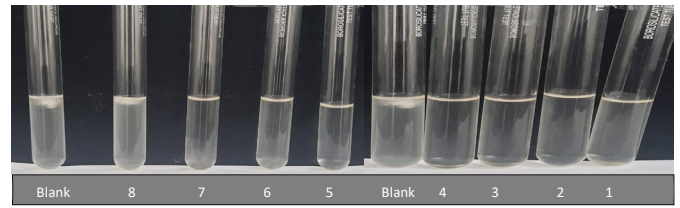


Fig. 7: Zone of inhibition study with *A. niger*

The obtained results showed that a nil growth is observed beyond tube no. 4 with concentration of 500 ppm.

Further trials were conducted under the mill conditions to monitor the output in terms of ORP (Oxidation Reduction Potential) values in process back water & VFA (Volatile Fatty Acids) reduction in paper. The data monitoring was done over a period of 6 months. The results obtained for improvement in the ORP of the water & VFA of the final paper is documented in Figs. 8 & 9

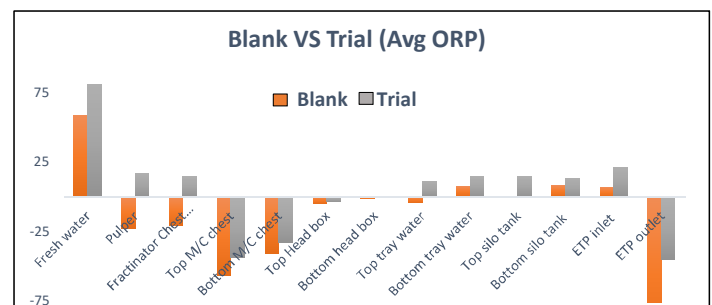


Fig. 8: ORP trend from complete water system

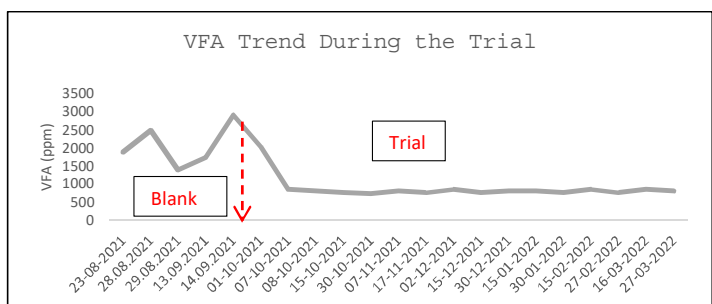


Fig. 9: Average paper VFA during 6 months of the trial

The average data obtained for 6 months of trial has shown 30-40% improvement in ORP values as compared to the blank conditions. The same has been reflected in the VFA of the paper. The average blank VFA of 2000-3000 ppm has been reduced to 700-800 ppm.

Fig. 10 shows the actual images of slime formation in the machine parts before & after running the technology trial.



Fig. 10: Slime formation on the machine parts (Left- Before trial, Right- After trial)

The application of biobased technology has shown substantial reduction in the slime formation with improved water & paper conditions.

Conclusions

The bio-based technologies presented in this paper present a green gateway for paper industry. These technologies can contribute to reduction of H-factor, active alkali, bleaching chemicals, malodorous gas emissions when used at various stages of processing and also help in making the processes more energy efficient & environmentally friendly. In addition to these benefits these technologies have delivered significant cost savings. The novel beneficial microbes make the water quality better in an eco-friendly way and help in water conservation. The technologies presented in this paper provide a green option to improve the environment footprint in a sustainable way. Adoption of these technologies can lead the paper industry towards cleaner & greener processes and reduce the climate change impact & carbon footprint of the industry. Water is a critical resource on the earth and any attempt towards making it more recyclable will be an effort towards making the mother earth greener & cleaner. The green technologies presented here are a promising solution for pulp and paper industry to solve many challenges faced by the industry today.

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