Making The Traditional CEH/CEHH Bleaching More Friendly Towards The Environment

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ABSTRACT:-- Modifications in the conventional CEH CEHH bleaching, the most common sequences followed in the Indian pulp and paper industry, led to remarkable pollution reduction making them more friendly towards the environment. Changes in the method of chlorination and introduction of oxygen pre-bleaching and pre-treatment with hemicellulolytic enzymes yielded considerable reduction in the COD and other parameters. The experiments did not necessitate the introduction of modern extended pulping methods to reduce the pollution loads.

KEY WORDS:-- Bleaching, COD, BOD, Colour, AOX, Oxygen delignification, Chlorine di oxide, Enzyme

INTRODUCTION

As the global awareness of water and air pollution is increasing, the emphasis on pollution prevention has tremendously increased in the past few decades and as the result the environmental state regulations have become more strict. Pulp and paper industry is no exception. In view of the recent promulgation of more stringent environmental regulations the pulp and paper industry is forced to look for options that reduce the classical pollution parameters like Colour, COD, BOD, and AOX etc., emanating from the bleach plant, which is one of the major sources of pollution. Though various measures are being taken to mitigate the impact on the environment, there are certain areas which need immediate attention.

With regard to the pulp and paper industry, the major pollutants in the effluent are BOD, COD, Colour and Total Organic Chlorine. The bleach plant effluents have been put on the priority list for environmental regulations.

THE NEED FOR MODIFICATIONS IN THE BLEACHING OF PULP

Pulping bleaching and papermaking are the three major wastewater sources for the industry. Internal measures are taken to reduce the pulpmill effluents by methods like recovery, spillage minimisation and good housekeeping. Likewise, the papermaking effluent can also be reduced by resorting to white water recycling and use of save alls. But very limited scope exists for the reduction of the bleach plant efluent. Recycling of the bleach plant effluent invites reluctance and resistance, owing to its corrosive nature and scale forming tendency.

The chlorinated organics generated during the bleaching process, not only exert oxygen demand, but also contributes effluent colour and toxicity. These are responsible for the mutagenicity and carcinogenicity of the effluent.(!)

Though steps are being taken by many countries to implement environmentally friendly techniques like Elemental chlorine free (ECF) and Total Chlorine free (TCF) bleaching sequences,

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immediate implementation of such technologies in the Indian context, requires major modifications.

Hence options for minimising the pollution load emanating from the conventional bleaching sequences with reference to color COD, BOD and AOX have been thought of, that need no major modifications, but a little amount of retrofitting. The modifications suggested in the conventional bleaching sequences of hardwood and bagasse chemical pulps will certainly reduce the pollution levels considerably. The need of the hour being minimising pollution levels, the options discussed will help in reducing the COD, BOD, Colour and chlorinated organics. The paper discusses the options available for pollution reduction, in the conventional bleaching sequences, without affecting the final brightness or quality of the pulp.

EXPERIMENTAL

Pulp

Unbleached kraft screened pulp of eucalyptus hybrid hardwood and bagasse were collected from the pulpmill. The pulps were washed over 250 mesh, thickened in the laboratory hydro extractor and stored in polythene bags. The characteristics of unbleached pulps are given in Table 1.

Table-1

Unbleached Pulp Characteristics

HARDWOOD KRAFT PULP		
KAPPA NUMBER	18	
BRIGHTNESS	24	% ISO
VISCOSITY	14	CPS
HARDWOOD KRAFT PULP		
KAPPA NUMBER	8.4	
BRIGHTNESS	52	% ISO
VISCOSITY	21	CPS

Bleaching Experiments

Laboratory scale bleaching experiments were carried out in polythene bags, except chlorination which was performed in polythene bottles with air tight lid. Exploratory tests were carried out with 20 g. (o.d) pulp while large scale bleaching was performed on 100 g. (o.d) pulp. The pulps, except the cholrinated pulp, after the prescribed bleaching period, was brought down to 5% consistency and then dewatered with backwater recirculation of the fines. The pulps were then washed with water equivalent to twenty times of the o.d. pulp taken. In case of chlorination which was performed at 3% consistency, the pulp was dewatered after the bleaching period and then washed as mentioned above. The effluent generated from each stage was finally mixed and the combined pollution load from a particular sequence was determined.

The conditions maintained at the various stages of bleaching are given in Table 2. In stepwise chlorination, the total chlorine to be charged was dosed in three parts with 10 minutes gap between subsequent doses. High consistency chlorination was performed in polythene bags with hand mixing. The required amount of chlorine was charged in the form of chlorine water. In all the experiments, the chemicals added in the extraction and hypochlorite stages were kept constant (Tables 3, 6). Modifications were carried out only in the chlorination stage.

Oxygen delignification was performed in electrically operated programmable rotating digester. Molecular oxygen was injected through specially made adaptor to the desired experimental pressure. The pulp was mixed with Magnesium sulphate and sodium hydroxide manually prior to oxgen delignification condition given in Table 2, were arrived at using the plackett and Burman design of experiments, to kappa number reduction of 50% of the initial.

Table-2

Bleaching Conditions

PARAMETER	Chlorination	Extraction			Hypo	Oxygen	Enxyme
	C	E	E(O)	E(P)	H	O	X
Consistency, %	3	8	8	8	8	8	10
Temperature, C	Ambient	60	90	60	40	120	50
Reaction Time, mts	30	60	60	60	120	60	120
Exit pH	2.0	10.5	10.5	10.5	8.5-9 5	--	5
Oxygen pressure, MPa	--	--	0.2	--	--	0.5	--

Oxidative extraction using oxygen was performed similarly under specified condition.

Oxidative extraction with peroxide was performed by adding the peroxide after the alkali addition.

For enzyme pretreatment, pure xylanase was used. A constant dosage of 8XU/g was administered and the pH was maintained at 4.5 throughout the treatment period of 120 minutes. The temperature was maintained at 50^0 C.

Analysis

Pulp kappa number, brightness, viscosity and strength properties were determined according to Tappi standards. The effluent characterisation with respect to colour, BOD and COD were performed as per BIS. The optical properties were measured using the Elrepho 2000 brightness tester.

AOX

AOX was calculated using the empirical formula (10)

AOX kg/t =0.1[C + 0.2D + 0.6H]

C, D and H expressed as Cl_2 in kg/t.

RESULTS AND DISCUSSION

Back Ground for our Studies

The conventional bleaching of chemical pulps involves chlorine and chlorine containing compounds like calcium/sodium hypochlorite and chlorine di oxide. The sequences chosen depend on the target brightness and the most common sequences adopted for the bleaching of kraft pulps are CEH, CEHH, CEHEH, CEHD, CEHED and CEDED (2). The pulps are bleached in a number of stages, in order to preserve the pulp from degradation. To facilitate effective chemical reaction, the pulps have to be necessarily washed with water, after each stage. This ultimately results in an effluent with the coloured dissolved material along with a little amount of suspended matter thus accounting for the Biochemical Oxygen demand (BOD), Chemical Oxygen demand (COD) and Adsorbable Organic Halides (AOX).

Chlorine and chlorine containing compounds have proved to be the most versatile and most economic bleaching agents. In the Indian context, where most of the mills adopt only these agents in the majority of the bleaching sequences, immediate switch over to the environmentally benign bleaching technologies like Total Chlorine Free (TCF) bleaching and Elemental Chlorine Free (ECF) bleaching is practically difficult in the foreseeable future.

Hence our studies were primarily oriented towards modifying the existing conventional bleaching sequences, resulting in the same ultimate brightness but with lesser pollution load. So the approach has been a simple one aiming at reduced Colour, BOD, COD and AOX, with modified chlorination or reduced chlorination.

Modified Chlorination

Modifications in the chlorination have been proved to be effective in reducing the pollutants without affecting the pulp properties. For the same chlorine charge, changes in chlorination can considerably reduce the AOX formation, significantly in addition to COD (2). The options available for modification of the chlorination stage include

- **Stepwise chlorination, CCC**
- **Multistage chlorination, C-E-C-E**
- **Low kappa factor chlorination, Low C**
- **Chlorine di oxide substitution, D/C**
- **High consistency chlorination, High Cy C**

Stepwise chlorination : CCC stage

In the stepwise chlorination, the total chlorine to be applied (K x 0.18) was charged in steps. Tables 3, 6 show that in the CCC stage, the total chlorine was divided into three portions and was

Table-3

Modified Sequences for Hardwood Kraft Pulp

Bleaching Sequence	Chemicals applied %						
	C	D	E	P	H I	H II	X
C-E-H-H	3.25	--	2.0	--	1.8	0.5	--
CCC-E-H-H	1.08x3	--	2.0	--	1.8	0.5	--
C-E-C-E-H-H	1.63x2	--	2.0+2.0	--	1.8	0.5	--
D/C-E-H-H	1.95	1.3	2.0	--	1.8	0.5	--
High cy C-E-H-H	3.25	--	2.0	--	1.8	0.5	--
Low C-E-(O)-H-H	2.18	--	2.0	--	1.8	0.5	--
Low C-E(P)-H-H	2.18	--	2.0	0.5	1.8	0.5	--
X-Low C-E(P)-H-H	1.66	--	2.0	0.5	1.8	0.5	8XU/G
O-C-E-H	1.60	--	2.0	--	1.8	--	--
O-C-E(P)-H	1.12	--	2.0	0.5	1.8	--	--

XU stands for Xylanase Units

Table-4

Bleached Hardwood Pulp Characteristics

Bleaching sequence	Brightness %ISO	Viscosity CPS	Shrinkage %
C-E-H-H	83.0	4.4	4.5
CCC-E-H-H	82.7	4.6	4.3
C-E-C-E-H-H	85.0	3.8	5.3
D/C-E-H-H	84.9	4.4	4.1
High cy C-E-H-H	81.1	5.2	3.9
Low C-E(O)-H-H	81.8	5.4	4.7
Low C-E(P)-H-H	81.2	4.6	4.0
X-Low C-E(P)-H-H	82.5	5.3	5.3
O-C-E-H	84.2	3.2	3.9
O-C-E(P)-H	81.7	3.3	4.0

Table-5

Hardwood Bleach Effluent Characteristics

Bleaching sequence	Colour KG/T	COD KG/T	BOD KG/T
C-E-H-H	72.8	58.3	4.3
CCC-E-H-H	67.7	55.9	4.0
C-E-C-E-H-H	65.2	48.7	6.9
D/C-E-H-H	59.3	47.4	5.0
High cy C-E-H-H	44.1	49.3	4.4
Low C-E(O)-H-H	42.3	42.2	3.0
Low C-E(P)-H-H	56.7	50.1	2.7
X-Low C-E(P)-H-H	50.8	37.3	3.3
O-C-E-H	11.5	35.5	7.1
O-C-E(P)-H	7.8	29.2	7.7

Table-6

Modified Sequences for Bagasse Kraft Pulp

Bleaching sequence	Chemicals applied % C	D	E	H	P
C-E-H	1.47	--	1.0	0.5	--
CCC-E-H	0.49x3	--	1.0	0.5	--
C-E-C-E-H	0.74x2	--	1.0+1.0	0.5	--
D/C-E-H	0.88	0.59	1.0	0.5	--
High cy C-E-H	1.47	--	1.0	0.5	--
Low C-E(O)-H	0.94	--	1.0	0.5	--
Low C-E(P)-H	0.94	--	1.0	0.5	0.5
O-H	--	--	--	0.5	--

charged sequentially, with a gap of 10 minutes between subsequent dosage. Literature survey shows that among the substitution and addition reactions taking place during chlorination, it is the substitution reaction that is responsible for AOX formation (3). Hence the stepwise charging of the chlorine prevents the formation of the AOX by retarding the substitution reactions to some extent (3). It may be seen from the Tables 5, 8 that, by resorting to stepwise chlorination, there is also a reduciton in the colour and COD. The final brightness achievement after the complete bleaching sequence remained unaltered (Tables 4, 7).

Multistage chlorination : C-E-C-E stage

In the multistage chlorination the total chlorine addition was split into two stages with an extraction stage in between. This approach was also a similar

Table-7

Bleached Bagasse Pulp Characteristics

Bleaching sequence	Brightness % ISO	Viscosity cps	Shrinkage %
C-E-H	84.6	19.3	4.0
CCC-E-H	84.0	20.4	1.9
C-E-C-E-H	85.6	17.0	3.9
D/C-E-H	85.6	18.1	1.9
High cy C-E-H	83.2	20.1	2.3
Low C-E(O)-H	81.9	21.1	2.3
Low C-E(P)-H	82.1	13.6	3.3
O-H	85.1	17.6	--

Table-8

Bagasse Bleach Effluent Characteristics

Bleaching sequence	Colour KG/T	COD KG/T	BOD KG/T
C-E-H	35.6	29.9	2.2
CCC-E-H	25.4	23.5	1.7
C-E-C-E-H	25.9	29.9	3.7
D/C-E-H	21.8	25.9	2.6
High cy C-E-H	18.3	23.2	1.8
Low C-E(O)-H	14.5	24.4	2.1
Low C-E(P)-H	16.3	24.1	3.9
O-H	--	8.0	1.4

one to the stepwise chlorination. After the first stage chlorination the pulp was subjected to an extraction stage followed by second stage chlorination and extraction. This sequence (C-E-C-E) significantly improved the bleaching response. Also, longer the sequences better the bleachability, owing to the better availability of chemicals for bleaching (3). The ultimate brightness after the complete sequence was higher in comparison to the normal sequence for both hardwood and bagasse pulps (Tables 4, 7).

Low Kappa factor chlorination : Low C

The chlorine quantity required for proper chlorination of the pulp is determined on the basis of the kappa factor or active chlorine multiple, expressed as a percentage on oven dry pulp divided by the kappa number of the pulp entering the chlorination stage. The selection of the kappa factor in addition to the unbleached pulp kappa number, also depends on the black liquor carry over from the brown stock washer (4). But more than the Kappa number of the unbleached pulp, it is the actual amount of elemental chlorine charged, that decides the formation of AOX. The lignin content of the pulp does not significantly influence the amount of AOX formed during bleaching (5). There is marked increase in dioxin formation with increasing chlorine multiple. Below a particular kappa factor, the formation of dioxins are significantly reduced (6).

Therefore, chlorination experiments were carried out with low chlorine charge, by resorting to low kappa factors. The optimum kappa factor of 0.18 was reduced to 0.12 in case of hardwood and in case of bagasse pulp, it was reduced to 0.11 from 0.17. The reduced chlorine charge was compensated by incorporating the oxidative extraction with peroxide or oxygen, in place of regular extraction. Hence in our experiments, the low chlorine charge was followed by an E (O) stage or an E (P) stage (Tables 4, 7). A substantial reduction in colour of the effluent was be observed along with a reduction in COD. The AOX reduction was proportional to reduction in the chlorine charge.

Chlorine di oxide substitution: D/C

Substitution of the elemental chlorine with Chlorine di oxide is an established method to reduce the AOX formation and low COD effluent (7). As the elemental chlorine is the sole precursor for the formation of chlorinated organics, any attempt to reduce the chlorine will reduce the AOX formation. Substitution of the elemental chlorine with chlorine di oxide has several advantages.

The colour of the effluent is reduced and the viscosity of the pulp is preserved. Above all the formation of AOX is considerably reduced. The chlorine di oxide substitution is being practised in several mills with encouraging results. The reduction in COD and BOD is not significant (8). The present studies produced similar results as shown in Tables 5, 8 and substantiate the fore going.

High consistency chlorination : High Cy C

The consistency during chlorination is maintained at 3% to have efficient mixing of chlorine gas with the pulp. If chlorination is performed at higher consistencies, significant reduction in fresh water input can be envisaged, resulting in reduced effluent. In our experiments, chlorination of the pulps was performed at 10% consistency in polythene bags, and the chlorine to be charged was dosed as chlorine water and then mixed manually. Subsequent bleaching with extraction and hypochlorite resulted in lower effluent quantity and lower colour, COD and BOD. The final brightness was slightly lower (Tables 4, 7).

Efforts towards reduction in the Total Chlorine Requirement

The amount of chlorine usage is a direct function of the unbleached pulp kappa number. Hence any effort towards kappa number reduction will ultimately result in the reduction of chlorinre usage. The increased motivation to decrease the total effluent load and the usage of chlorine and chlorine containing compounds has yielded a number of modern concepts such as the following:

- **Extended delignification**
- **Oxygen delignification**
- **Enzyme pre-treatment**

Thus, reducing the incoming Kappa number of the unbleaced pulp to the bleach plant has been the most promising method that significantly reduces the colour, COD, BOD and AOX of the effluent. Among the methods suggested above, the extended delignification using methods like RDH, MCC, EMCC require major modifications. In the Indian context, when small paper mills opt non-woody raw materials like sugar cane bagasse very low kappa numbers can be attained by both the kraft process and soda process aided by addition of suitable additives like Anthra Quinone. This strategy removes the requirement of the above mentioned extended delignification methods.

Oxygen delignification: O

In the context of pollution reduction, Oxygen is the best available option for reducing the initial kappa number of the unbleached pulp. The Oxygen delignification to 50% of the initial kappa number was performed for both hardwood and bagasse pulps. The Oxygen delignified pulps were subjected to conventional bleaching using the CEH/ CEHH sequence. The results given in Table 5, 8 show an excellent reduction in the pollutants level. Of all the approaches, the oxygen pretreatment to lower the initial kappa of the pulps seems to be the best option. In the case of bagasse pulp, where the initial kappa number is low, oxygen delignified pulp requires only a single stage hypochlorite bleaching that too with 1.0 hypo charge, to reach 85% ISO brightness target, with substantial reduction in the Colour, COD. The oxygen delignified pulps showed good response to bleaching to target level with reduced chemicals (Table 4, 7).

Enzyme pre-treatment : X

Yet another pretreatment step that is emerging as an easy and promising method, to reduce the bleach chemicals, is the enzyme pretreatment. The Xylanase enzymes belonging to the family of hemicellulases have been found to be effective in reducing the bleach chemical requirements (9). They are sometimes even referred as the bleach boosters because, they have been found to be able to improve the brightness ceiling considerably.

The hardwood pulp was subjected to enzyme pretreatment under the specified condition (Table 3). Though the enzyme treatment does not reduce the kappa number of the pulp, it cleaves the bond between the lignin and the redeposited hemicellulose, thereby enhancing easy removal of the lignin during the subsequent bleaching stages, even with reduced chemicals. The results shown in the Table-4 indicate that even with 8XU/G enzyme charge, the brightness target of 82-83% ISO was easily achieved with low chlorine charge of 1.66% as against 3.25% in the conventional sequence. This lead to a considerable reduction of the AOX in the effluent owing to low chlorine charge.

AOX Generation

Since AOX formation is direct function of the chlorine charge, and not the kappa number, the sequences involving lower chlorine dosage than the optimised chlorine, will no doubt generate lower amount AOX. Hence the options suggested have been aimed at reducing the AOX generation without affecting pulp properties. Likewise, the modifications in the chlorination are oriented only towards the same objective of reducing the AOX. The results shown in figure 1 indicate the reduction in AOX formation achieved by modified bleaching sequences.

PULP QUALITY

The modifications suggested in the conventional bleaching sequences with special reference to pollution reduction, did not have any pronounced effect

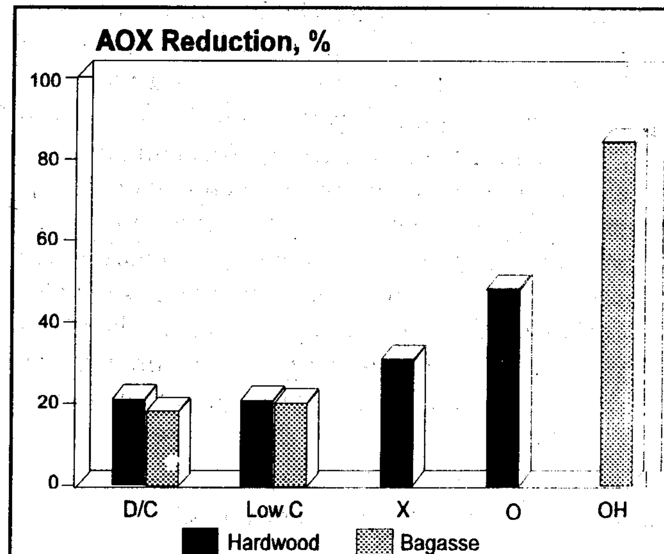

Fig.-1: AOX Reduction by Replacement of C in CEHH/CEH on the strength properties of the bleached pulps. The results shown in Tables 9, 10 show that the sequences with oxygen delignification in case of hardwood have suffered a reduction in tear while other sequences did not pose any problem on the pulp quality. Similarly the effect of the modified sequences on the strength properties of bleached bagasse pulp is also not that much pronounced.

Table-9

Strength Properties of Bleached Hardwood Pulp at 300 ml CSF

Bleaching sequence	Tensile Index NM/G	Tear Index mN.M²/G	Burst Index kPa.M²/G
C-E-H-H	73.8	6.49	5.54
CCC-E-H-H	72.4	6.63	5.00
C-E-C-E-H-H	73.0	5.38	4.87
D/C-E-H-H	75.0	6.25	5.25
High cy C-E-H-H	71.6	6.41	4.91
Low C-E(O)-H-H	65.6	6.67	4.77
Low C-E(P)-H-H	71.6	6.33	4.97
X-Low C-E(P)-H-H	63.8	6.42	4.19
O-C-E-H	60.2	5.15	4.14
O-C-E(P)-H	63.5	4.88	4.03

Table-10

Strength Properties of Bleached Bagasse Pulp at 300 ml CSF

Bleaching sequence	Tensile Index NM/G	Tear Index mN.M²/G	Burst Index kPa.M²/G
C-E-H	61.6	6.12	4.03
CCC-E-H	61.8	6.42	4.50
C-E-C-E-H	59.8	5.98	4.01
D/C-E-H	62.4	6.40	4.13
High cy C-E-H	63.0	6.17	4.14
Low C-E(O)-H	58.9	6.41	4.35
Low C-E(P)-H	60.3	5.75	4.02
O-H	58.4	6.54	4.02

CONCLUSIONS

* Modifications in the chlorination reduced the pollution load of the bleach plant effluents with the conventional CEH and CEHH sequences.
* Reducing the chlorine charge seems to be a promising option for reducing the colour, COD and AOX generation.
* Reduction in BOD by the modified approaches is not significant.
* Oxygen delignification and Enzyme pretreatment are very encouraging pretreatments to reduce pollution load.
* The approaches suggested require only a little amount of retrofitting and no major modifications, except oxygen delignification, which requires very high capital investment.
* The sequences suggested do not have any impact on the pulp quality while they reduce the pollution load.

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REFERENCES

1. Yin, C.F., Joyce, T.W., Chang, H.M.. in International symposium on wood and Pulping chemistry, 1989 P 103.
2. Allan M Springer, Liebergott, N., Van Leirop, B., Fleming, B.I., Textbook on Industrial Environmental control-Pulp and Paper Industry, 1993 P 282.
3. Hans U Suss, Wilfried L Eul., Norbert Nimmerfroh, Jurgen Meier, Tappi Pulping conference, 1989, P 219.
4. Hise, R., Hintz, H., Environmental issues - An Anthology of 1989 P 123.

5. Axegard, P., Bleach Plant operations seminar, 1989 P 133.

6. Dillner, B., Larsson, L., Tibbling, P., Environmental issues- An Anthology of 1989, P 153.

7. Basta, J., Holtinger, L., Hook, J., Lundgren, P., Pulping conference 1989, P 139.

8. Grundelius, R., Mitchell, K., Rankin, J., Pulping conference 1989 P 171.

9. Tolan, J.S., in Non Chlorine Bleaching conference, 1993, South Carolina, USA, P 40.

10. Lewko, L., Van Donkelar, A., in Paper Vol 19:11 (91) P 31.