

# Comparative Studies of ClO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> Bleaching Stages on the Formation of Chlorophenolic Compounds in Jute Cady Pulp

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**Abstract** –Elemental chlorine and chlorine compounds are commonly used in the developing countries for bleaching of pulp. The study deals with the bleaching of Jute Cady pulp with chlorine, chlorine dioxide, peroxide and O<sub>2</sub> treatment and identification of various chlorophenolics compounds. The results show that quantity of the total chlorophenolic compounds formed decreases up to 77% at 100% replacement of chlorine by chlorine dioxide in C stage. A 40% and 79% reduction in COD and color value respectively indicate a significant drop in pollution load. There is a reduction of 52% in total chlorophenolic compound when E stage is changed to E<sub>p</sub>. The COD and color values are reduced by 30% and 33% respectively as E stage is changed to E<sub>p</sub> stage. Oxygen delignification stage reduced the formation of chlorophenolic compounds by 73%. The effluent COD and the color value is reduced by 45% and 28% respectively during this stage.

**Keywords** – O<sub>2</sub> bleaching; chlorinated phenolics; jute cady; peroxide bleaching; chlorine dioxide bleaching

## 1. Introduction

The world wide demand for paper and paperboard is continuously increasing with an average growth rate of 2.8% per annum [1]. In India, the annual current production gap is 0.7 million tonnes and is expected to become 1.5 times more by 2015. In India, forest and woodlands occupy around 20%, agricultural land 50% and uncultivated, non-agricultural and barren land 30% respectively of a total land area of 328.8 million hectare [2]-[3]. Many fast growing annual and perennial plants have been identified, cultivated and studied for their suitability for pulp and paper manufacture [4].

Mainly the studies have been carried out on softwood and some hardwood pulps [5]. A very little data is available on non-wood pulps which are important in India, due to decreasing wood resources [6]. For this work such type of non wood i.e. Jute Cady is taken. Jute is one of the promising non wood raw materials which can give international quality pulp and can compete and replace the imported softwood pulp [7]-[8]. Jute is annual plant widely cultivated in eastern and central part of India. It is seasonal agricultural produce of tropical countries. India, Bangladesh, Malaysia, Thailand etc which are the principle jute producer countries. India is the world's largest producer of jute and it contributes about 2/5 of the world jute production. Jute Cady is being used as a raw material by small and medium sized paper mills in India, where conventional CEH or CEHH bleaching sequences are still being followed. Since most of these mills are not having chemical recovery, they produce pulp of higher kappa number and subsequently use higher chlorine dosage in bleaching stage to achieve desired brightness levels. Moreover, due to inherent poor drainage properties coupled with poor washing efficiency

of the washers, a large amount of dissolved organics are also carried over along with pulp to bleaching process. The low bleaching response of the pulp gives higher consumption of chlorine. This results in generation of high level of color and COD [9]-[11]. The chlorination and first extraction stage account for the largest amount of the toxic chlorinated organic compounds in pulp mill bleachery effluent [11]-[12]. Approximately 75 to 80% of the organically bound chlorine in bleach plant effluent is in high molecular weight material, which is not easily identified or even characterized [13]. These high molecular weight chlorinated organic compounds constitute the major contributor to the color and TOCl of the effluent. They accumulate in the receiving streams and over a period of time break down into low molecular mass compounds with detrimental biological effects. Low molecular weight chlorinated organic compounds formed during bleaching of pulp using elemental chlorine are reported to cause acute toxicity and mutagenicity due to their ability to penetrate living cell membrane [14]-[15]. Therefore the chlorinated organic compounds generated in bleach plant effluent are of great environmental concern in conventional CEH or CEHH bleaching sequences.

Totally chlorine free bleaching processes have been introduced, largely in response to environmental restrictions and market demands [16]-[17]. These bleaching technologies employ oxygen based bleaching agents such as Oxygen delignification [18]-[24] Chlorine dioxide [25]-[28] and Hydrogen peroxide [29]-[31]. As far as Jute Cady is concern, only a few studies on the behaviour of effluent during O<sub>2</sub>, ClO<sub>2</sub> and peroxide bleaching sequences have been published. In the present investigations, the results of the detection and quantitative determination of various pollutants formed

during the above discussed stages using GC chromatography are reported to help in optimization of the process.

## 2. Experimental Setup

Various isomers of chlorophenols (Aldrich, USA) Chloroguaiacols, chlorocatechols, chlorovanillins, chlorosyringaldehydes, and chlorosyringols (all from Helix, Canada) were used as authentic reference compounds. n-hexane and acetone used were of HPLC grade and diethyl ether of LR grade. Analytical grade acetic anhydride was used after redistillation. Other reagents used for identification studies were of analytical reagent grade. Standard solutions of chlorophenols were prepared in 10% acetone water. Unbleached Jute Cady (Cassia Acetifolia) pulp was procured from "Shreyans Paper Mill, Ahmedgarh, Punjab". The pulp was washed and screened in the laboratory and air-dried. TAPPI Test method T<sub>236</sub> cm- 85 was used to determine the residual lignin content of the pulp. Pulp bleaching was carried out in more than one bleaching stages. Efforts were made to achieve the target brightness for pulp. Unbleached pulp (40 gm O.D. pulp) was bleached under the conditions shown in Table 1. The conditions of peroxide and chlorine dioxide bleaching are given in the Table1. For the O<sub>2</sub> delignification the pulp was bleached with oxygen in the electrically heated, rotary digester of capacity 15 liter.

**Table 1.** Bleaching conditions for different sequences

Parameter	Units	C	E	H	D	E <sub>p</sub>
Charge as active Cl	%	8.1	---	5.4	8.1	---
Alkali charge as NaOH / H <sub>2</sub> O <sub>2</sub>	%	---	4.35	---	---	4.08
Temperature	°C	30	70	40	70	70
Consistency	%	3	10	7	10	10
Retention Time	Minute	45	60	230	90	60
End pH	---	≈	10	-	10	-
		2.0	11	11		

The oxygen prebleaching conditions and pulp characteristics of oxygen delignified pulp are shown in Table2. The oxygen bleaching was targeted at a kappa number drop of 50 – 55% without much sacrificing on viscosity. The bleach effluents generated during each stage of bleaching were collected, diluted to 2 liter and 100 ml of this effluent was used for COD and color determination. The COD was determined [33] and effluent color was measured on a Shimadzu spectrophotometer model UV 2100/S [34]. Extraction of chlorophenols from the effluents was performed by simple modification of the procedure suggested by Lindstrom and Nordin<sup>31</sup>. The effluents were adjusted to pH 2 and extracted with 400 ml/L of 90:10 diethyl ether and acetone mixture for 48 hrs. Chlorophenols as acetyl derivatives were analyzed using Shimadzu Gas Chromatograph (Model GC- 9A). The experimental conditions are given in Table 3.

## 3. Derivatization Procedure

To 4.5 ml of sample taken in a PTFE lined screw capped glass tube, 0.5 ml of buffer solution of 0.5 Na<sub>2</sub>HPO<sub>4</sub> was added. Derivatization and extraction was performed by adding 1ml of n-hexane and 0.1 ml of acetic anhydride. After shaking the mixture for at least 3 minutes, 1 µl of the acetyl derivative was taken from the hexane layer by a syringe and it was injected into the capillary column of GC for analysis.

### • Determination of Extraction Efficiency

The procedure suggested by Lindstrom K et.al was used [35]. Some important chlorophenolic compounds, whose concentration were higher or whose toxicity values high i.e. lower <sup>96</sup>LC<sub>50</sub> values have also been chosen for analysis.

**Table 2.** O<sub>2</sub> prebleaching conditions and characteristics of O<sub>2</sub> delignified pulp

Parameter	Units	Jute Cady
O <sub>2</sub> charge	kg / cm <sup>2</sup>	6
Consistency	%	10
Time	minute	75
Temperature	°C	110
Alkali charge	kg / t	35
Magnesium sulphate	kg / t	2
Kappa No.	Non O <sub>2</sub>	---
	O <sub>2</sub> delignified	27.0
Viscosity	Non O <sub>2</sub>	15.93
	O <sub>2</sub> delignified	29.0
Brightness	Non O <sub>2</sub>	cp
	O <sub>2</sub> delignified	22.74
Brightness	Non O <sub>2</sub>	%ISO
	O <sub>2</sub> delignified	12.50
		25.92

**Table 3.** GC Conditions

Parameters	
Detector	FID
Detector Range	10° C
Carrier gas (N <sub>2</sub> ) flow rate	20 ml/min.
Injection & Detector temperature	275°C
	80°C for 3 min.
	80°C – 160°C at 2°C/min.
Column Temperature	160°C for 5 min.
	160°C – 260°C at 10°C/min
	260°C for 15 min.
Injection (Split less)	2 min.
Sample Size	1µl
Chart speed	2 cm/min.

## 4. Results and Discussions

The Jute Cady pulp was bleached to 80% ISO brightness by CEH sequence under normal bleaching conditions and the effluent analyzed for different chlorophenolic compounds. Results show that chlorocatechols, generated in C stage effluent (33.62 g / ton) are about 3 times more than present in E stage effluent (13.86 g / ton), chloroguaiacol in E stage effluent (20.44 g / ton) are about 4 times more than in C stage effluent (5.28 g / ton) chlorophenols (35.28 g / ton) in E stage effluent are more than 3 times in C stage effluent (12.73 g/ton ) other compounds, present in E stage effluent (29.98 g/ton) are 6 times more than in C stage effluent (5.51 g / ton). It has also been reported by various authors that in general chlorocatechols are predominantly

present in C stage effluent and chloroguaiacol in E stage effluent [36]. Microgram levels of pentachlorophenol have also been detected by Guerre et.al for both C and E stage effluent. The quantity of different chlorophenolic compounds is much less in H stage effluent as compared to C stage effluent. This is due to the fact that 75 – 80% of the lignin gets removed during C and E stages of pulp bleaching. The quantity of chlorophenolic compounds present in E stage effluent is much higher than in C stage effluent. The results show that chlorocatechols and chlorophenols are predominant phenols contributing about 30% each. Similarly di and tri chlorophenolics also contribute about 35% share each, mono, tetra, pentachlorophenolic compounds are ~17%, 9% and 5% respectively of the total chlorophenolic compounds.

The study has been performed by substituting chlorine by chlorine dioxide in C stage. The results show that quantity of the total chlorophenolic compounds formed decreases up to 77% as shown in Figures 1-2. A decrease of 83% in C stage effluent, 74% in E stage effluent and 87% in H stage effluent is observed when chlorine in C stage is completely replaced by  $\text{ClO}_2$ . The formation of mono, di, tri, tetra, and penta chlorophenolic compounds decrease up to 81%, 73%, 76%, 82%, and 100% at 100% chlorine substitution by chlorine dioxide. Likewise the formation of catechols, phenols, guaiacols and other chlorophenolic compounds decrease up to 83%, 76%, 76% and 75% respectively at substitution of chlorine by  $\text{ClO}_2$  in C stage. A 38% reduction in effluent COD and 62% reduction in color value of CEH effluent indicate a significant drop in pollution load. Under same conditions the viscosity of pulp is improved by 24% and brightness of pulp is improved by 14.4 point after E stage and 8.7 point after H stage and CE kappa number is reduced by 6%. Chlorine dioxide is a highly selective bleaching agent as it attacks only lignin. It is also a strong decolorization agent. Increased substitution of chlorine by chlorine dioxide reduces the attack on cellulose that reduces the drop in pulp viscosity very significantly i.e. higher pulp viscosity and lower dissolution of cellulose fragments giving much lower effluent COD and color. The chlorine dioxide can give a pulp of higher brightness and cleanliness without impairing its strength.

Reinforced extraction stage with peroxide has been performed i.e.  $E_p$ . The total chlorophenolic compounds decrease appreciably when E stage changes to  $E_p$  stage; there is no change in the conditions of chlorination and hypochlorite stage<sup>26</sup>. There is a reduction of 52% in total chlorophenolic compound in the CEH effluent when E stage is changed to  $E_p$  as shown in Figures 1-2. A reduction of 78% in E stage effluent in the amount of chlorophenolic compounds is obtained. Mono, di, tri, tetra chlorophenolic compound also decrease by 34%, 50%, 61%, 31% respectively, pentachlorophenolic compound was not detected in E and H stage effluents. A similar trend is shown by phenols, catechols, guaiacols and other chlorophenolic compounds as reduced by 60%, 25%, 63% and 67% respectively. The COD and color values are reduced by 30% and 33% respectively as E stage is changed to  $E_p$  stage. The pulp brightness is improved by 7.8 point after E stage and 1.2 point after H stage, the pulp viscosity is increased by 5% and the CE kappa number is

decreased by 13%. Peroxide is an oxidizing and decoloring agent. The chlorophenolic compounds are oxidized and thus reducing the quantity of chlorophenolics in  $E_p$  stage effluent. The oxidation reaction results in increased dissolution of lignin fragments giving a lower effluent COD and small reduction in CE kappa number of pulp. The bleaching action of peroxide also slightly improves the brightness of the pulp.

Oxygen delignified pulp was bleached by CEH sequence. Oxygen delignification stage (prebleaching stage) reduced the formation of the chlorophenolic compounds by 73% as shown in Figures 1-2. A reduction of total chlorophenolic compounds by 75% in C stage and 72% in E stage effluent by oxygen delignification. In case of mono, di, tri, tetra and penta chlorophenolic compounds, a reduction of 71 - 77% is being observed. The similar trend is shown by phenols, catechols, guaiacols and others chlorophenolic compounds. These are also reduced by 70 - 74%. The effluent COD is reduced by 45% and the color value is reduced by 28%. There is major improvement in brightness by 7.2 points after H stage but viscosity drop by 5% and the CE kappa number is reduced by 20%. The process of oxygen delignification is another way to reduce the amount of chlorophenolic compounds. This procedure is used to reduce the pulp kappa number by 40 – 50% which in turn reduces the bleach chemical demand in the following C, E, and H stages to nearly the same extent which reduces the environmental loads – chlorophenolic compounds, COD and color very significantly.

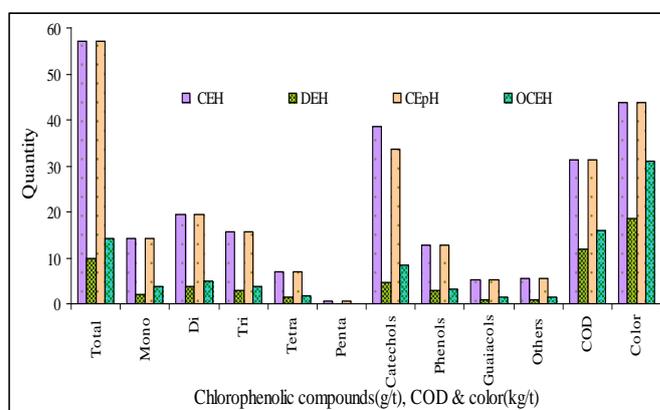


Figure 1. Effect of changed sequence on the generation of chlorophenolics, COD and color in C stage effluent.

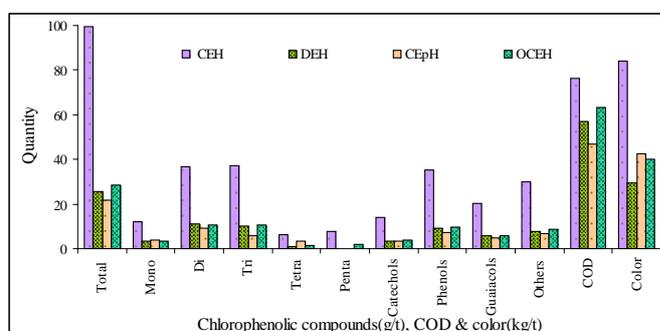


Figure 1. Effect of changed sequence on the generation of chlorophenolics, COD and color in E stage effluent.

## 8. Conclusions

The results show that quantity of the total chlorophenolic compounds formed during bleaching sequences decrease up to 77% at 100% replacement of chlorine by chlorine dioxide in C stage. It indicates a significant drop in pollution load. One of the important economic considerations in the use of chlorine dioxide in bleaching is the chemical cost. There is a reduction of 52% in total chlorophenolic compound in the CEH effluent when E stage is changed to E<sub>p</sub>. This modification may not require additional capital investment and can be easily implemented in existing set up of the mill. There will be a small increase in the cost of bleaching which can be easily absorbed due to improvement in the quality of the end product. Oxygen delignification stage (prebleaching stage) reduced the formation of chlorophenolic compounds by 73%. It is however an excellent approach to reduce the pollution load yet requires major capital expenditure in the form of oxygen reactor, oxygen manufacturing and storage facilities, medium consistency reactor, additional washer and pumps. Reduced concentration of chlorophenolics in the bleach plant effluents is desirable to check the harmful effects of such hazardous chemicals which have been found to be resistant to biodegradation and accumulate in the body and likely to cause dangerous diseases. The studies indicate that these bleaching stages can reduce the chlorophenolics compounds substantially.

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