



DEGRADATION OF CARCINOGENIC COMPOUNDS BY USING CHLORINE DIOXIDE IN JUTE CADY PULP EFFLUENTS

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ABSTRACT

The chlorinated organic compounds formed during bleaching of pulp have proved to be highly toxic to aquatic organism that affects unfavorably human health as well. These compounds are quite continual in the environment and readily accumulate in organisms. The objective of present investigation is to identify a set of chlorination conditions for Jute Cady pulp in which the production of chlorinated phenolic compounds would be minimal without any adverse impact on pulp quality and mainly focus on the optimize brightness i.e. 80%. The results of our other studies indicate that the changes in various C stage bleaching conditions and changes in bleaching sequence can give effluent of lower chlorophenolic compounds but the final brightness is different. In this study, a target pulp brightness of 80% ISO was chosen and to get the target brightness the bleach chemical demand has been changed. In sequential bleaching (i.e. CEH), the bleach chemical demand is 13.5%, but when the sequence changed to D₅₀C₅₀EH, the bleach chemical demand drops to 10.25% and the toxicity reduces by 44%, In continuation of chlorophenolics compounds, COD and color reduce by 42% and 54%. The beneficial point is that pulp viscosity is increased and target brightness is achieved.

Key words: Chlorine dioxide, Jute, Pulp, Effluent, Carcinogenic, Degradation.

INTRODUCTION

The conventional bleaching sequence does not achieve the target brightness i.e. 80% without the side effect on the mechanical quality of pulp. It is achievable by chlorine dioxide in first chlorination stage. The studies highlight the multiple advantages of hydrogen peroxide to bleaching of pulp.

The requirement of paper and paperboard is growing by 2.1% annually in the long term, reaching an estimated 490 million tones (MT) by 2020¹. India's annual per capita

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paper consumption is only 8 kg against world per capita paper consumption 50 Kg². Total fiber consumption for production of paper and paper board in India will nearly be doubled between 2010 and 2020. India's total wood fiber deficit is increased at an 11.3% annual growth rate upto 2016³. So it is a requirement of time to search new alternative and renewable sources of fibers⁴, because 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 ha.. Many fast growing annual and perennial plants have been identified, cultivated and studied for their suitability for pulp and paper manufacture.

Jute (*Corchorus capsularis*) is one of them. Jute is a herbaceous annual plant from the Tiliaceae family, mostly grown in Southeast Asian countries. Jute fiber is collected from the bast or outer region of the stem after retting of the whole plant and is a good source of different grades of pulp⁵. With the increasing concern over forest destruction and the increasing demand of paper pulp, the importance of jute for this purpose may increase. There have been previous published studies describing the characteristics of jute fibers, including the content of their main organic fractions, particularly lignin and carbohydrates, and its behavior during pulping⁶. Moreover, 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^{7,8}. 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 COD⁹.

However, as per our knowledge, no comprehensive research deals with generation of chlorophenolic compounds and their environmental impacts on specially Jute Cady^{10,11}. In previous publications, the identification of chlorophenolics compounds after using chlorine dioxide have been reported, but there was no concern about the target brightness¹²⁻¹⁴. The brightness vary by sequences to sequences. But in present work, the amount of toxic compounds is being reduced keeping an eye on the target brightness i.e. 80%. This paper focuses to study the formation of different chlorophenolic compounds formed during the bleaching of Jute Cady pulp and to identify and estimate the different chlorophenolic compounds formed and present in different bleaching effluents viz. C, E, H, D etc. Particularly the impact of bleaching conditions on the formation of chlorinated phenolics while chlorination stage bleaching.

EXPERIMENTAL

Pulp sample

Unbleached Jute Cady (*Cassia Acetifolia*) pulps were taken from Shreyans Paper Mill, Ahmedgarh, Punjab, India. The pulps were washed and screened in the laboratory and air-dried. Oxygen pretreatment conditions were optimized afterwards. Thick pulp pads were prepared (T218 sp-02) and evaluated for their kappa number (TAPPI 1992), brightness % (ISO) (T 452 om-02), and CED viscosity (T230 om-04) per standard TAPPI methods (TAPPI 2000-2001). The kappa number (residual lignin) of the pulps was determined by the standard TAPPI method (TAPPI 1992).

The chlorine demand was calculated using the following formula:

$$\text{Chlorine demand (\%)} = 0.25 * \text{Kappa number} \quad \dots(1)$$

Bleaching sequences

All of the bleaching steps were performed in polythene bags and in a temperature controlled water bath except chlorination, which was performed in a plastic bottle at ambient temperature. The pulp and the chemicals were kneaded to achieve the desired pulp consistency by hand mixing or shaking the bottle from time to time during bleaching. The unbleached pulp equivalent of 25 g OD (oven dry) was taken and all the bleaching experiments were conducted in duplicates. Of the total bleach chemical dose, 70% was charged in the C stage and the remaining 30% was charged in the H stage. The alkali was charged according to the following formula:

$$\text{Alkali charge (\%)} = \frac{1}{2} \text{C stage charge (\%)} + 0.3 \quad \dots(2)$$

The chlorination (C) stage bleaching was performed by partially substituting chlorine by chlorine dioxide as active chlorine. The substitution was 50%. The addition of chlorine in advance of chlorine dioxide in a sequential chlorination decreases the chlorinated phenolic compounds and the toxicity. Adding the chlorine before the chlorine dioxide in the C stage is less effective in delignifying the pulp than the reverse mode of adding the ClO₂ first. D/C mode of addition in C stage was followed. The bleaching conditions for each stage are reported in Table 1. The bleached pulp after each stage was washed with 2 L of water and the volume of the effluent collected in each stage was kept constant. The collected effluents from the different stages was used for the analysis of the chlorophenolic compounds. COD and color were analyzed using standard methods¹⁵.

Alkaline extraction (E)

The required amount of alkali (NaOH) and water were mixed with the pulp suspension in order to achieve a pulp consistency of 10% in a polythene bag. The bag was placed in a water bath maintained at 70°C. The pulp was kneaded from time to time for proper mixing. The final pH was recorded. After the alkali extraction, the pulp was washed and the effluent was collected for further analysis.

Hypochlorite (H) stage bleaching

The washed alkali extracted pulp was mixed with a requisite amount of bleach liquor and water in order to achieve a 10% pulp consistency. The initial pH was adjusted between 10 and 11. At 30 min intervals, the pH of the pulp was checked and adjusted to a pH of 10 by dilute NaOH in order to achieve a final pH between 10 and 10.5. The contents were transferred to a plastic bag that was placed in a water bath at 40°C. The bag was removed after 3.5 hr and the pulp was washed and then the effluent was collected for further analysis.

Analysis of various chlorophenols

In order to separate the chlorophenolic compounds from the effluents, a procedure suggested by Lingston and Nordin¹⁶ was used. The pH of the combined effluent was adjusted to 2. Then, the chlorophenolic compounds were extracted from the effluent for 48 hr with 400 mL of a mixture of 90% ethyl ether and 10% acetone per liter of effluent. For derivatization, a 4.5 mL sample of the standard chlorophenolic compounds was placed in a PTFE lined, screw capped, glass tube and 0.5 mL of a buffer solution of 0.5 M Na₂HPO₄ was added. One mL of n-hexane and 0.05 mL of acetic anhydride were added in order to derivatize and extract the chlorophenolic compounds. The mixture was shaken for 3 min and 1 µL of the acetyl derivative taken from the hexane layer with a syringe was injected into the GC column. Gas chromatographic studies were carried out with a Shimadzu gas chromatograph, Model GC-9A. Chlorophenols as acetyl derivatives were analyzed in an Ulbon (Shimadzu) HR1 glass capillary column. The constituents were identified by matching the retention time (+0.1) of a particular peak with that of a pure reference standard. A quantitative analysis of various chlorophenols was completed using peak area, response factor, and extraction efficiency values.

Quantitative analysis of various chlorophenols

The response factor and extraction efficiency of various chlorophenols were determined for quantitative analysis of the chlorophenolic compounds.

Response factor

One milliliter of standard solution of chlorophenol was derivatized per the procedure described above. One micro-liter of the n-hexane layer was injected into the column. The area of the peak was recorded and the response factor (RF) was calculated as follows:

$$\text{RF} = \text{Area of the peak} / \text{Wt. of the sample injected} \quad \dots(3)$$

Extraction efficiency

For the extraction of various standard chlorophenolic compounds, 1 mL standard solution of various chlorophenols was diluted to 1 L with distilled water. The pH of the solution was adjusted to 2. The chlorophenolic compounds were then extracted from the solution with a 400 mL mixture of 90% ethyl ether and 10% acetone for 48 hr and derivatized as an acetyl derivative as described above. One microliter of the derivatized sample was injected into the column and the peak area was recorded. From the peak area, the amount of chlorophenolic compounds present in the extracted sample was determined. The percentage extraction efficiency was calculated as follows:

$$\text{Extraction efficiency (\%)} = \left(\frac{\text{Quantity in the extracted sample}}{\text{Quantity in the sample before extraction}} \right) \times 100 \quad \dots(4)$$

The retention times, response factors, and extraction efficiency values of various chlorophenolic compounds were determined. These values were the average of at least three values. The retention time indicated that most of the chlorophenolic compounds studied could be resolved on the capillary column of HR-1. The various chlorophenols in the effluents of the bleaching sequences were identified by matching the retention time (± 0.1 min) of a component with that of a pure standard.

RESULTS AND DISCUSSION

To get the target brightness i. e. 80% the bleach chemical demand has been changed. In sequential bleaching (i.e. CEH), the bleach chemical demand is 13.5%, but when the sequence changed to D₅₀C₅₀EH, the bleach chemical demand drops to 10.25%. All the other parameters remain same. The results show that there is a substantial decrease in the amount of total chlorophenolic compounds i.e. by 44%. The contribution of mono, di, tri, tetra, & penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 1. In C, E and H stage effluent, there is reduction of total

chlorophenolic compounds by 35%, 48% and 62%, respectively (Fig. 1). In mono, di, tri, tetra and penta chlorophenolic compounds, there is a reduction of 44%, 35%, 44%, 64%, 65%, respectively (Figs. 1).

Table 1: Conditions of chlorine dioxide substituted CEH bleaching sequences with Jute Cady pulp

Parameter	Units	C	D ₅₀ C ₅₀	D	E	H
Charge as active Cl	%	8.1	8.1	8.1	---	5.4
Alkali charge as NaOH	%		---	---	4.35	---
Residual chlorine (of total)	%	0.93	0.93	0.64	---	0.49
Temperature	°C	45	50	70	70	40
Consistency	%	3	6	10	10	7
Retention time	Minute	45	60	90	60	230
End pH	---	2.09	3.72	4.05	11.87	11.43

Table 2: GC conditions for the separation of chlorophenolics

Parameters	
Detector	FID
Detector range	10°
Carrier gas (N ₂) flow rate	20 mL/min
Injection & detector temperature	275°C
Column temperature	80°C for 3 min 80°C - 160°C at 2°C/min 160°C for 5 min 160°C - 260°C at 10°C/min 260°C for 15 min
Injection (Splitless)	2 min
Sample size	1 µL
Chart speed	2 cm/min

A similar trend of reduction has shown by catechols (49%), phenols (32%), guaiacols (46%) and others chlorophenolic compounds (51%) whose concentration are decreased, as bleach chemical demand decrease from 13.5 to 10.25% (Fig. 1) except some chlorophenolic compounds in C stage effluent.

The results indicate that all individual chlorophenolic compounds decreases, and there is large reduction in the quantity of 2,5 dichlorophenol, 4 chlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorocatechol, 3,4,6 trichloroguaiacol, pentachlorophenol, tetrachlorocatechol and 5,6 dichlorovanillin. The effluent COD and color reduce by 42% and 54%, respectively. The brightness is increased to 80.6%. There is also a gain of 28% in viscosity¹⁷. The CE kappa number remains nearly unchanged.

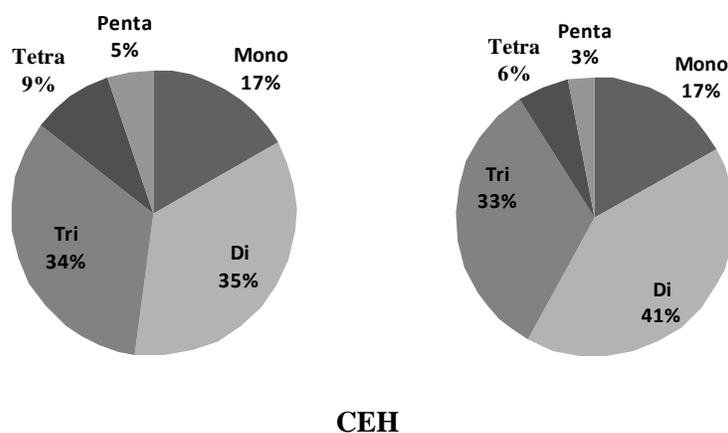


Fig. 1: The contribution of different chlorophenolic compounds in different sequences, when target brightness achieved

CONCLUSION

No doubt the above changes give reduction in the formation of chlororganics but give a pulp of different brightness than obtained from CEH sequence. In order make comparisons pulp properties must be similar. The pulp of 80% ISO brightness has been chosen for the study. The results of the study are summarized as by changing C stage to D₅₀C₅₀ stage gives reduction in chlorophenolics by 52-56%, in color by 42-48% and in COD by 54-67% with improvement in pulp viscosity by 24-28% i. e. stronger pulp. It requires major capital investment in the form of chlorine dioxide plant. The cost of bleaching will also increase as chlorine dioxide is much more expensive than chlorine. But we achieve the target brightness and as well as the quantity of carcinogenic compound are sharply reduced.

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