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REDUCTION OF THE QUANTITY OF CHLORINATED PHENOLICS COMPOUNDS IN BLEACHING EFFLUENT BY PEROXIDE TREATMENT

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ABSTRACT

The spent bleach liquor from the chlorinated stages of Jute Cady and Bamboo pulp has been analyzed both qualitatively and quantitatively for various chlorophenolics compounds using Gas Chromatography in conventional bleaching sequences and after peroxide treatment. A number of chlorinated derivatives of phenols, catechols, guaiacols, syringaldehydes have been identified. The concentrations of various compounds identified have also been compared with the reported $^{96}LC_{50}$. The results show that quantity of the total chlorophenolic compounds formed decreases up to 54% in total chlorophenolic compound in the CEH effluent and the COD and color values are reduced by 35% and 33%, respectively in comparison of conventional bleaching sequences as E stage is changed to E_p stage in Bamboo pulp. And there is a reduction of 52% in total chlorophenolic compound in the CEH effluent when E stage is changed to Ep. and the COD and color values are reduced by 30% and 33% respectively as E stage is changed to E_p stage in Jute Cady pulp.

Key words: Chlorinated phenolics, Bamboo, Jute cady, Peroxide bleaching.

INTRODUCTION

Due to population explosion, rapid industrialization and lack of proper management, the water pollution is continuously increasing with an alarming rate. The industries have increased hap hazardously, having no proper waste water treatment plants. These industries emit pollutants directly in environment without any treatment. Not even a single step of 3R's approach is being followed. The pulp and paper mill industry is a very water intensive and sixth largest polluter. It generates as low as 1.5 m3 of effluent/tone of paper produced. About 500 different chlorinated organic compounds have been identified in paper mill effluent. The high chemical diversity of these pollutants causes a variety of carcinogenic, endocrinic and mutagenic effects on aquatic communities. The brownish color is mainly

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attributed to the complex compounds derived from polymerization between lignin degraded products and tannin during various pulping and bleaching operations. Lignin and its derivatives are difficult to degrade naturally linkages. With this problem one more problem is also in front of the whole society i.e. plantation. The paper industry is totally based on the wood. 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]. Many fast growing annual and perennial plants have been identified, cultivated and studied for their suitability for pulp and paper manufacture[3].

Mainly the studies have been carried out on softwood and some hardwood pulps[4]. A very little data is available on non-wood pulps which are important in India, due to decreasing wood resources[5]. For this work such type of non woods i.e. Jute Cady and Bamboo are 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[6-9]. 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[6,7]. Bamboo, a non wood material, because of long fibers is used by a number of Indian and South East Asian paper mills as it forms a stronger paper and is used as reinforcing fiber in other hard wood/ non wood pulps[8,9]. Jute Cady and Bamboo are being used as raw materials 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[10,11]. The chlorination and first extraction stage account for the largest amount of the toxic chlorinated organic compounds in pulp mill bleachery effluent[12,13]. 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[14]. 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[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]. These bleaching technologies employ as Hydrogen peroxide bleaching[17-19]. As far as Jute Cady and Bamboo concern, only a few studies on the behaviour of effluent during 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.

EXPERIMENTAL

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". Unbleached Bamboo (Bambusa Vulgaris) pulp was procured from from "Cachchar Paper Mill, HNL, Assam". The pulps were washed and screened in the laboratory and air-dried. TAPPI Test method T_{236} 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 g O.D. pulp) was bleached under the conditions shown in Table 1**.** The conditions of peroxide bleaching are given in the Table 1.

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[20] and effluent color was measured on a Shimadzu spectrophotometer model UV[21] 2100/S. Extraction of chlorophenols from the effluents was performed by simple modification of the procedure suggested by Lindstrom and Nordin[22]. 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 2.

Table 1: Bleaching conditions for different sequences

Parameter	Units	Jute Cady				Bamboo			
		C	**E**	**H**	**E_P**	**C**	**E**	**H**	**E_P**
Charge as active Cl	%	8.1	---	5.4	---	3.78	---	3.09	---
Temperature	^oC	30	70	40	70	---	2.19	---	70
Alkali charge as NaOH/H_2O_2	%	---	4.35	---	4.08 1.00	30	70	40	1.61 0.30
Consistency	%	3	10	7	10	3	10	7	10
Retention time	Minute	45	60	230	60	45	60	230	60
End pH	---	≈2.0	10 - 11	10 - 11	10.79	≈2.0	10 - 11	10 -11	11.40

Table 2: GC Conditions

Parameters	OV – 101 Column
Detector	FID
Detector range	10^oC
Carrier gas (N_2) flow rate	20 mL/min
Injection & detector temperature	275^oC
Column temperaturec	80^oC for 3 min.
	80^oC – 160^oC at 2^oC/min
	160^oC for 5 min
	160^oC – 260^oC at 10^oC/min
	260^oC for 15 min
Injection (Split less)	2 min
Sample size	1 μL
Chart speed	2 cm/min

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_2HPO_4 was added. Derivatization and extraction was performed by adding 1 mL of n–hexane and 0.1 mL of acetic anhydride. After shaking the mixture for at least 3 min, 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 and Nordin was used[22]. Some important chlorophenolic compounds, whose concentration were higher or whose toxicity values high i.e. lower $^{96}LC_{50}$ values have also been chosen for analysis.

RESULTS AND DISCUSSION

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)[17-19,23] Figs. 1 and 2. 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[17-19,23].

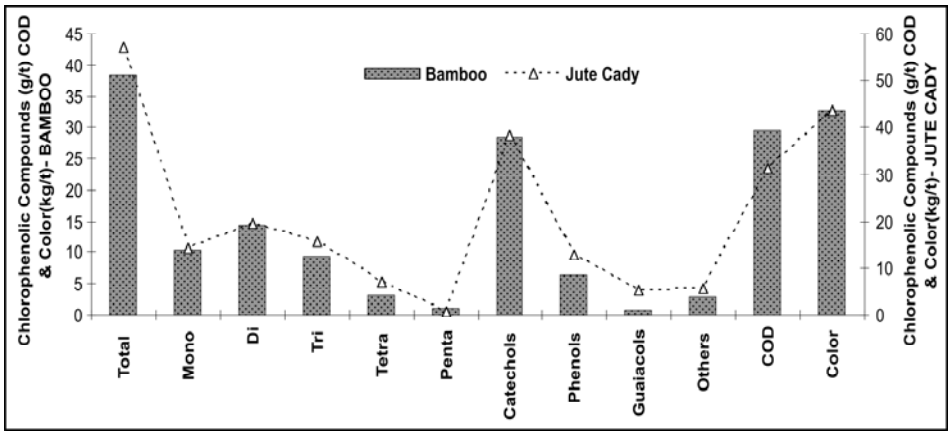

Fig. 1: Comparison on the generation of chlorophenolics, COD and color in C stage effluent of Bamboo & Jute Cady (Normal Bleaching)

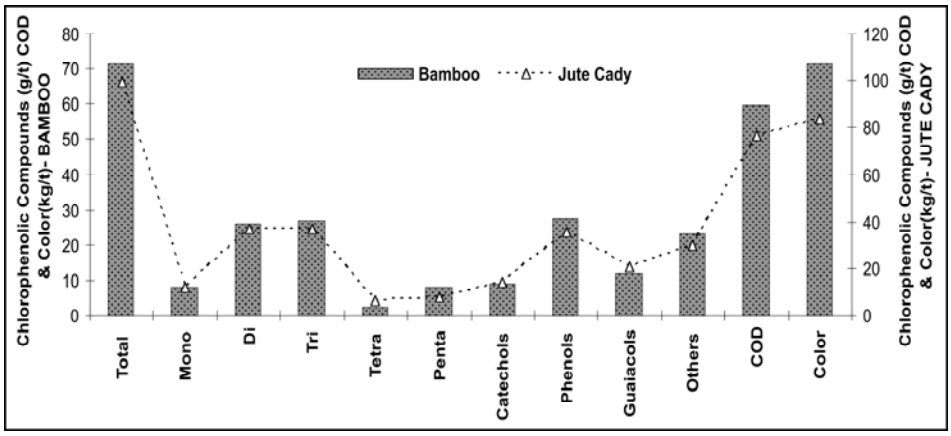

Fig. 2: Comparison on the generation of chlorophenolics, COD and color in E stage effluent of Bamboo & Jute Cady (Normal Bleaching)

In case of Jute Cady pulp, 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 Fig. 3. 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[5,9,12]. 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%.

In the case of, Bamboo 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 (28.59 g/ton) are about 3 times more than present in E stage effluent (8.93 g/ton), chloroguaiacols in E stage effluent (11.92 g/ton) are about 18 times more than in C stage effluent (0.67 g/ton), chlorophenols (27.56 g/ton) in E stage effluent are more than 4 times in C stage effluent (6.28 g/ton); other chlorophenolic compounds present in E stage effluent (23.08 g/ton) are 8 times more than in C stage effluent (2.87 g/ton) Fig. 1 & 2. 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[21]. 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, which also holds true in the present case also[23]. The results show that both chlorocatechols and chlorophenols are ~30%, chloroguaiacols are ~11%, and other chlorinated phenolics compounds around are ~23% of the total chlorophenolic compounds.

There is a reduction of 54% in total chlorophenolic compound in the CEH effluent when E stage is changed to E_p as shown in Fig. 3. A reduction of 81% in E stage effluent in the amount of chlorophenolic compounds is obtained. Mono, di, tri, tetra chlorophenolic compound also decrease by 34%, 51%, 62%, 27%, 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 66%, 19%, 79% and 76%, respectively[17-19]. The COD and color values are reduced by 35% and 33%, respectively as E stage is changed to E_p stage. The pulp brightness is improved by 10.1 point after E stage and 0.9 point after H stage, the pulp viscosity is increased by 9% and the CE kappa number is decreased by 5%.

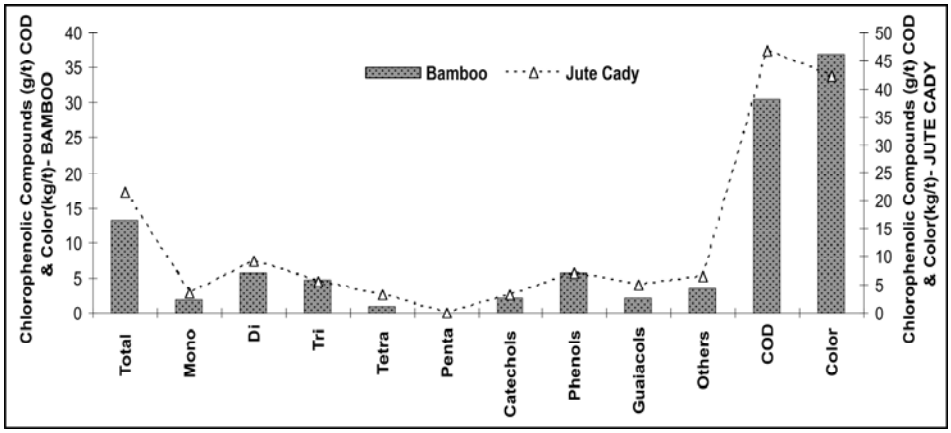

Fig. 3: Comparison on the generation of chlorophenolics, COD and color in E stage effluent of Bamboo & Jute Cady (ClO_2 Bleaching)

Peroxide is an oxidizing and decolouring 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.

CONCLUSION

The results show that quantity of the total chlorophenolic compounds formed during bleaching sequences decrease up to 54% and 52% in the CEH effluent when E stage is changed to E_p in bamboo and jute cady pulp, respectively. 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. One of the important economic considerations in the use of chlorine dioxide in bleaching is the chemical cost. The total chlorophenolics generated with jute cady pulp were higher in comparison with bamboo pulp, due to higher kappa number as well as higher chlorine demand; and it is also due to raw materials composition. 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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