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IMPACT OF SPLITTING OF CHEMICAL DOSES IN C STAGE ON TOXICITY DURING PAPER PRODUCTION

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Abstract: The laboratory generated spent bleach liquor from the chlorination stages of Bamboo pulp has been analysed both qualitatively and quantitatively (without washing and with washing) for various chlorophenolics acids using gas chromatography. 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 $^{96}LC_{50}$ values. The results indicates that splitting of chlorine dose gives 47% lower formation of chlorinated phenolic compounds in without washing in splitting of chemical dose in C stage and the total chlorophenolic compounds decrease by 54% which is 7% more in comparison to chlorination stage (Dosage being splitted into two equal parts and no in between washing has taken place).

Keywords: Bamboo; Bleaching effluent; Chlorophenolics; Gas Chromatography; Splitting of chemical dose.

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INTRODUCTION

Due to population explosion, rapid industrialization and lack of proper planning, water pollution is increasing at an alarming rate (Richardson, 2007). Industries have increased hap hazardously, having no proper waste water treatment plants. They emit pollutants directly in environment without treatment (Qadir *et al.*, 2008). Not even a single step of 3R's (Reduce, Reuse and Recycle) is being followed. The pulp and paper mill industry is a very water intensive and sixth largest polluter (Anonymous, 1998). It generates as low as 1.5m^3 of effluent/tone of paper produced (Szolosi, 2003). About 500 different chlorinated organic compounds have been identified in paper mill effluent (Savant et.al, 2006). The high chemical diversity of these pollutants causes a variety of carcinogenic, endocrinic and mutagenic effects on aquatic communities (Ali, 2001). The brownish color is mainly 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 because of the strong linkages within their molecular structure, especially biphenyl-type carbon to carbon linkages (Karrasch *et al*., 2006). 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 ha (Pekka *et al.*, 2002; *Prakash et al.*, 2013c). Many fast growing annual and perennial plants have been identified, cultivated and studied for their suitability for pulp and paper manufacture (Prakash, 2012a; Malhotra *et al.*, 2013). 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 (Prakash *et al*., 2013c; Thompson *et al*., 1996; Low *et al*. 2006). It 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 (Panwar *et al*., 2002; Prakash, 2012b). The chlorination and first extraction stage account for the largest amount of the toxic chlorinated organic compounds in pulp mill bleachery effluent (Bajpai *et al*., 1996; Heirmburger, 1988; Lindstom, *et.al*, 1976; Tsai, *et.al*, 1994; Voss *et al*., 1980). 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 (Kringstad *et al*., 1988, Osterberg *et al*., 1985).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 is reported to cause acute toxicity and mutagenicity due to their ability to penetrate living cell membrane (Berry *et al*., 1985; Wong e*t al*., 1978). Therefore the chlorinated organic compounds generated in bleach plant effluent are of great environmental concern in conventional CEH or CEHH bleaching sequences. The process of chlorination (C) stage bleaching was modified by splitting the chlorine dose (with or without in between washing) and the results indicates the reduction of toxic chlorinated organic compounds (Hise, 1989; Hise *et al*., 1992).

The mainly studies have been carried out on softwood and some hardwood pulps (Kachi *et al*., 1980; Ibarra e*t al*., 2005). A very little data is available on non-wood pulps which are important in India, due to decreasing wood resources (Sharma, 1999; Prakash *et. al*., 2013a). In the present investigation we report the results of the detection and quantitative determination of various pollutants formed during the above discussed stages by using GC chromatography.

EXPERIMENTAL

The Various isomers of chlorophenols (Aldrich USA), chloroguaiacols, chlorocatechlols, chlorovanillins, chlorosyringaldehydes (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 bamboo pulp was procured from a paper mill located in eastern India. The pulp was washed and screened in the laboratory and air dried. TAPPI (T-236) test method was followed to determine the kappa number of pulp. Pulp bleaching was carried out in more than one bleaching stages. Efforts were made to achieve the target brightness for bamboo pulp, however due to differences in morphological structure resisting the easy diffusion of chemicals and the presence of condensed lignin in the inaccessible regions of the fibers, the bleach liquor demand increased. Unbleached pulp (40 g O.D. pulp) was bleached under the conditions shown in Table 1. The process of chlorination (C) stage bleaching was modified by splitting the chlorine dose (with or without in between washing). Half of the required amount of bleach liquor was added to the pulp suspension. The bleaching under C stage conditions was continued for 20 minutes, where after the remaining quantity of bleach liquor was added to the pulp suspension. Further bleaching was continued for the rest of the time. In one case after first chlorination stage the pulp was washed on a buchner funnel. Remaining bleach liquor was added to washed pulp and after completion of C_2 stage the pulp was again

washed. Both effluents were collected, mixed and used for effluent quality and estimation of chlororganics. In other case, the washing after C_1 stage was not performed. The washing was done after C_2 stage. The effluent after C_2 stage was collected and used for effluent quality and chlororganics estimation. 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 by standard method. (508 B) closed reflex titrametric method and effluent color was measured on a Shimadzu spectrophotometer model UV 2100/S. Extraction of chlorophenols from the effluents was performed by simple modification of the procedure suggested by Lindstrom and Nordin (Lindstrom *et al*., 1976). The effluents were adjusted to pH 2 and extracted with 400 ml/L of 90:10 diethyl ether and acetone mixture for 48 h. Chlorophenols as acetyl derivatives were analyzed using Shimadzu Gas Chromatograph (Model GC- 9A). The experimental conditions are given in Table 2.

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 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 (Lindstrom *et al*., 1976). Some important chlorophenolic compounds, whose concentration are higher or whose toxicity values are high i.e. lower $^{96}LC_{50}$ values have also been chosen for analysis.

RESULTS AND DISCUSSION

The six categories of chlorophenolics are present in spent bleach liquor obtained from Indian variety of bamboo pulp. These are chlorophenols, chloroguaiacols, chlorocatechols, chlorosyringols, chlorosyringaldehydes and chlorovanillins. Chlorosyringols, chlorosyringaldehydes and chlorovanillins are listed and discussed under other chlorophenolics. The structure of lignin is very complex. It is a polymer formed by an enzyme initiated dehydroabietic polymerization of a mixture of three different p-hydroxy cinnamyl alcohols (p-coumeryl, coniferyl and sinapyl alcohols). Compared with wood lignin, the structure of grass lignin has been studied less. It varies significantly with source. Some grass lignins are thought to contain mainly p-coumaryl units but other grass lignins appear to approach the hardwood lignins. During pulp chlorination, lignin is chlorinated and breaks down to simpler chlorophenolic compounds. The solubility of chlorophenolics is low in acidic condition (C stage) and these are solubilized in alkaline condition (E stage).

Without pulp washing: The chlorine dose in C stage has been divided into two equal parts. Firstly chlorination has been performed with half the dose and then chlorination with the next half dose is performed. No washing of pulp has been done between two chlorine stages. The extraction and hypochlorite stages are performed under same conditions as performed without chlorine splitting. The results are given in Table 3. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figures 1-2. The results shown in Figures 1-2 indicates that quantity of mono, di, tri, tetra, penta chlorophenolic compounds, phenols, catechols, guaiacols and other chlorinated compound in C, E, H stage effluents, all decrease with the use of split chlorine dose in C stage. Lieber Gott has also reported a decrease in the formation of chlorinated compounds when chlorine dose was split into two portions (Hise, 1989, Hise e*t.al* 1992). The results shown in Figures 1-2 indicates that splitting of chlorine dose gives 47% lower formation of chlorinated phenolic compounds in CEH stage effluent (Hise, 1989; Hise *et.al.* ,1992) 50% reduction in chlorinated phenolic compounds in C stage effluent, 44% reduction in E stage effluent and 51% reduction in H stage effluent. The reduction of 41%, 46%, 45%, 36% and 67% of mono, di, tri, tetra and pentachlorophenolic compounds respectively is observed (Table 3, Figures 1-2). Similarly the

formation of phenol, catechol, guaiacol and other chlorinated compounds is reduced by 51%, 45%, 33%, and 48% respectively (Table 3, Figures 1-2)

A very large decrease in 2,4 dichlorophenol, 2,5 dichlorophenol, 2,4,6 trichlorophenol, 3,4 dichlorocatechol, 5 chlorovanillin, 4 chlorocatechol, 3,5 dichlorocatechol, 2,3,4,6 tetrachlorocatechol is observed when chlorine dose in C stage is splitted into two equal doses and no washing between chlorination stages has been done. A reduction of 13% in effluent COD (Figures 1-2) and 19% in effluent color was also observed (Figures 1-2). The pulp brightness is improved by 0.5 point after E stage and 0.4 point after H stage and appreciable increase in pulp viscosity (23%) (Figures 1-2) is observed. So splitting of chlorine dose reduces the pollution load and gives a stronger and brighter pulp. The splitting of chlorine dose means applying lower concentration of chlorine over longer period making mild attack on cellulose and hemicellulose giving lower dissolution of carbohydrate fraction giving lower effluent COD and color. Mild attack on cellulose gives lower pulp degradation and will yield stronger pulp of higher viscosity.

With pulp washing: As the chlorine dose in C stage has been divided into two equal parts, pulp washing has been done after applying first chlorine dose. The rest half dose is applied on the pulp after first chlorination stage and after completion of second chlorination stage again pulp washing has been done. Both C1 and C2 effluents are collected, mixed and used for further analysis. The results are given in Table 3. The results show that the amount of chlorophenolic compounds decrease more when pulp is washed after the first split chlorination stage.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figures. 1-2.The total chlorophenolic compounds decrease by 54% which is 7% more in comparison to chlorination stage (Dosage being splitted into two equal parts and no in between washing has taken place). A reduction of 54% in C stage, 48% in E stage and 54% in H stage effluent in total chlorophenolic compounds is observed (Table 3, Figures 1-2).The reduction of 44%, 50%, 51%, 46%, and 68% in mono, di, tri, tetra, and penta chlorophenolic compounds respectively is also observed (Table 3, Figures 1-2) (Hise, 1989; Hise *et.al,* 1992). A similar trend has also been shown by phenols, catechols, guaiacols and other chlorophenolic compounds, the respective reductions being 55%, 50%, 37%, and 50% (Table 3, Figures 1-2). This is in agreement with the results reported by various authors that in general chlorocatechols are predominantly present in C stage effluent and chloroguaiacols in E stage effluent. The presence of different categories of chlorophenolic compounds in bleaching effluents have been reported by Chhaya, Abrahamson and Malhotra, the order being: C > E >> H (Abrahamson *et al*., 1983; Sharma, 1999; Malhotra, 2013

Table 1. Bleaching conditions of splitting of chlorine dose in C stage

Parameters	Units	Bamboo					
		$C_{w.w.}$ EH			$C_{w.o.}$ EH		
		C	E	H	C	E	H
Charge as active Cl	%	3.78	---	3.09	3.78	---	3.09
Alkali charge as NaOH	%	---	2.19	---	---	2.19	---
Residual chlorine (of total)	%	0.93	---	1.88	1.13	---	1.92
Temperature	^oC	30	70	40	30	70	40
Consistency	%	3	10	7	3	10	7
Retention time	Minute	45	60	230	45	60	230
End pH	---	1.79	12.57	11.46	1.82	12.40	11.34

The effluent COD is reduced by 16% and color is reduced by 22% (Figures 1-2). There is an increase in brightness of 0.6 point after E stage and 0.5 point after H stage, viscosity is improved by 24% and CE kappa number is reduced by 4% (Figure 1-2) Washing of pulp after first chlorination stage removes the water soluble fraction of the lignin and other color constituents

which consumes a portion of chlorine when fresh chlorine is charged in second split chlorination stage. The lignin and other colored constituents are attacked better, forming a lower CE kappa number and gives some improvement in pulp brightness after E and H stages.

Table 2. GC Conditions

Parameters	
Detector	FID
Detector range	10⁰
Carrier gas (N_2) flow rate	20ml/min.
Injection and Detector temperature	275ºC
Column temperature	80ºC for 3 min.,
	80ºC-160º at 2ºC/min.
	160ºC for 5 min.
	160ºC - 260ºC at 10ºC/min.
	260ºC for 15 min.
Injection (split less)	2 min.
Sample size	0.5 µl
Chart speed	2 cm/min

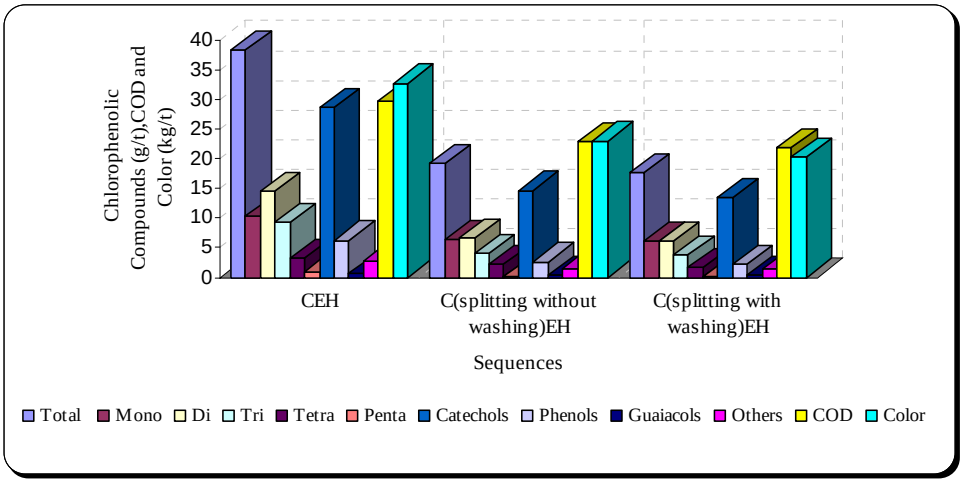

Figure 1. Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in C stage effluent

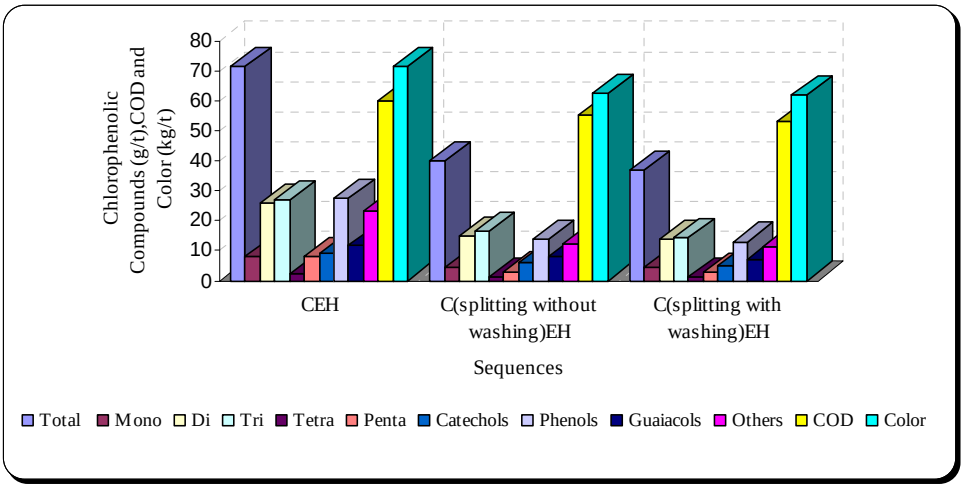

Figure 2. Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in E stage effluent

Table 3. Effect of splitting of chlorine dose in C stage (with and without washing) on formation of chlorophenolic compounds in various effluents

	Normal CEH			C (splitting) EH					
				Without pulp washing			With pulp washing		
	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	0.80	0.39	0.14	0.24	0.21	0.09	0.23	0.21	0.09
2,5 Dichlorophenol	1.43	2.89	0.21	0.33	1.43	0.15	0.31	1.41	0.15
2,3 2,4 Dichlorophenol	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol	-	0.25	-	-	0.13	-	-	0.12	-
2,6 2,4 Dichlorophenol	0.11	2.56	-	0.04	1.87	-	0.03	1.87	-
4-Chlorophenol	0.23	-	-	0.23	-	-	0.20	-	-
3-Chlorophenol	0.49	1.94	-	0.31	0.97	-	0.29	0.89	-
4-Chloroguaiacol	0.02	-	-	0.02	-		0.01	-	-
5-Chloroguaiacol	-	1.46	0.06	-	0.89	0.04	-	0.85	0.04
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.11	-	-	0.09	-	-	0.09	-	-
2,3,5-Trichlorophenol	0.16	3.12	0.33	0.11	1.86	0.21	0.09	1.58	0.19
2,4,6-Trichlorophenol	0.22	2.01	-	0.03	1.39	-	0.02	1.36	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.80	5.88	0.34	0.65	2.97	-	0.55	2.51	-
3,6 Dichloroguaiacol	0.10	-	-	0.05	-	-	0.03	-	-
3,4 Dichloroguaiacol	0.18	4.93	-	0.15	2.65	-	0.12	2.33	-
3,4-Dichlorocatechol	3.78	1.06	-	2.12	0.71	-	1.96	0.68	-
3,4-Dicholorophenol	0.65	-	0.65	0.30	-	0.39	0.26	-	0.38
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.06	-	-	0.05	-	-	0.05	-
5-Chlorovanillin	1.95	2.69	0.15	1.06	1.36	0.13	1.01	1.34	0.11
5,6 Dichloroguaiacol	-	2.39	-	-	1.78	-	-	1.72	-
4-Chlorocatechol	2.65	-	-	1.23	-	-	1.16	-	-
3,5-Dichlorocatechol	5.85	-	-	2.44	-	-	2.28	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.28	0.51	-	0.14	0.28	-	0.12	0.25	-
3,5,6-Trichloroguaiacol	-	0.21	-	-	0.09	-	-	0.09	-
3,4,6-Trichloroguaiacol	-	2.11	-	-	1.96	-	-	1.76	-
3,5-Dichlorosyringol	-	1.32	0.11	-	0.88	0.05	-	0.79	0.04
3,4,5-Trichloroguaiacol	0.01	-	-	-	-	-	-	-	-
3-Chlorocatechol	4.54	-	-	3.18	-	-	3.11	-	-
6-Chlorovanillin	0.02	1.75	-	0.02	1.17	-	0.02	1.08	-
3,6-Dichlorocatechol	0.79	0.38	-	0.57	0.24	-	0.43	0.22	-
4,5,6-Trichloroguaiacol	0.35	0.40	-	0.22	0.36	-	0.22	0.33	-
2-Chlorosyringaldehyde	0.26	-	-	0.18	-	-	0.16	-	-
4,5-Dichlorocatechol	0.65	-	-	0.43	-	-	0.40	-	-
Pentachlorophenol	1.00	8.26	0.34	0.12	3.05	-	0.09	2.99	-
3,4,5-Trichlorocatechol	6.78	5.92	-	2.34	3.95	-	2.34	3.15	-
Tetrachloroguaiacol	0.01	0.11	-	0.01	0.10	-	0.01	0.08	-
Trichlorosyringol	0.47	7.44	0.67	0.25	3.72	0.45	0.21	3.56	0.40
3,4,6-Trichlorocatechol	0.55	-	-	0.36	-	-	0.32	-	-
2,6-Dichlorosyringaldehyde	0.17	6.72	-	0.02	3.36	-	0.02	3.07	-
5,6-Dichlorovanillin	-	3.16	-	-	1.67	-	-	1.58	-
Tetrachlorocatechol	3.00	1.57	0.32	1.98	1.05	0.13	1.53	1.03	0.13
Total	38.41	71.49	3.32	19.22	40.15	1.64	17.62	36.9	1.53

C stage bleaching conditions: $C_{end\ pH} \geq 2$, Temperature 30°C and Consistency 3%

CONCLUSION

Splitting of chlorine dose in C stage in two equal portions also reduce the generation of chlorophenolics by 52-57%. The reduction in effluent color is 23-28% and COD is 34-35% with 20-21% improvement in pulp viscosity. This change requires small capital investment in the form an additional C stage tower, pump and chlorine mixer. Reduced concentration of chlorophenolics in the bleach plant effluents is desirable to check the harmful effect of such hazardous chemicals which have been found to be resistant to biodegradation and accumulate in body and likely to cause danger diseases.

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