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RESEARCH ARTICLE

Studies of O_2 Pretreatment on the Formation of Chlorinated Phenolics in Nonwood Pulps

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ABSTRACT

Chlorine and its compounds are commonly used in the developing countries in bleaching process of pulp. The bleaching of Bamboo pulp with chlorine, O_2 treatment and identification of various chlorophenolic compounds is studied. Chlorophenolic compounds formation is reduced by 74% during oxygen delignification stage (prebleaching stage). The COD of effluent is reduced by 30% and the value of color is reduced by 46% during this stage. In case of Jute Cady pulp, the chlorophenolic compounds formation is reduced by 73%. The COD of effluent is reduced by 45% and the value of color is reduced by 28% during this stage.

Key words: *O_2 bleaching, chlorinated phenolics, bamboo, jute cady, toxicity*

INTRODUCTION

Demand of paper and paperboard in the whole world is consecutively increasing by the rate of 2.8% per annum. In India, the annual current production gap is 0.7 million tones and it is likely to happen 1.5 times more by 2020. In India, forest and woodlands cover about 20% land, agricultural area cover about 50% land and uncultivated, non-agricultural and barren area cover about 30% land respectively of the total land area of 328.8 million hectare[Pekka, *et al*., 2002]. For suitability of pulp and paper manufacturing many annual and perennial plants have been identified, cultivated and studied.

Mainly the Softwood and some hardwood pulps are studied [Hou, *et al.,* 2011]. Only a little data is available on non-wood pulps which are important in India, owing to decreasing wood resources [David, *et al.,* 2005]. In this experiment we work on non-woods such as Jute Cady and Bamboo. Jute is one of the promising non wood raw materials which can help in manufacturing the international quality pulp and can compete or replace the softwood pulp. Jute is annual plant which is widely cultivated in eastern and central part of India. It is seasonal agricultural plant of tropical countries such as India, Bangladesh, Malaysia, Thailand etc. These countries are the principle jute producers. India is the world's largest producer of jute and it contributes about 2/5 of the world jute production. Bamboo is a non-wood material, because of its long fibers it is used in number of Indian and South East Asian paper mills and helps to forms a stronger paper and also used as reinforcing fiber in other hard wood/ non wood pulps [Low, *et al.,* 2006, Prakash, *et al.,* 2013]. In India's small and medium sized paper mills jute cady and bamboo are being used in the form of raw material where conventional CEH or CEHH bleaching methods are still being followed. Most of these mills are not using chemical recovery process, due to which higher kappa number pulp is manufacture and subsequently these mills use higher chlorine dosage in bleaching stage to achieve desired brightness levels [Qadir, *et al.,* 2008]. Moreover, because of poor drainage systems with poor washing efficiency of the washers, a large amount of dissolved organics are also carried over along with pulp to bleaching process [Savant, *et al.,* 2006, Ali, *et al.,* 2001]. Higher amount of chlorine is consumed because of the low bleaching response of the pulp, which results the high level of COD and color [Panwar, *et al.,* 2002]. In the chlorination and first extraction stage, largest amount of the toxic chlorinated organic compounds in pulp mill bleachery effluent are found [Szolosi, *et al.,* 2003].

Approximately 75 to 80% of the organically bound chlorine is in high molecular weight material in bleach plant effluent, which is not easily identified or characterized [Karrasch, *et al.,* 2006]. 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. During bleaching of pulp Low molecular weight chlorinated organic compounds formed by using elemental chlorine which is reported to cause acute toxicity and mutagenicity due to their capability to penetrate the cell membrane of the living [Richardson, *et al.,* 2007]. So the bleach plant effluents like chlorinated organic compounds require the great environmental concern in conventional CEH or CEHH bleaching sequences [Requejo, *et al.,* 2012]. Now days, totally chlorine free bleaching processes have been introduced, in response to market demands and environmental restrictions [Takagi, *et al.,* 2009]. Oxygen based bleaching agents such as Oxygen delignification is employ in these bleaching technology [Dongcheng, *et al.,* 2007, Khristova, *et al.,* 2003, Leh, *et al.,* 2008, Patel, *et al.,* 2008, Salmela, e*t al.,* 2008, Thi Hong Man Vu, *et al.,* 2004, Malhotra, *et al.,* 2013, Prakash, *et al.,* 2012]. In concern of Jute Cady and Bamboo, only a few studies on the behavior of effluent during O_2 pre bleaching sequences have been published. In the present investigations, the results of the detection and quantitative determination of various pollutants generate during the above discussed stages using GC chromatography are reported to help in optimization of the process.

EXPERIMENTAL SETUP

Numerous isomers of chlorophenols (Aldrich, USA) such as- Chloroguaiacols, chlorocatechols, chlorovanillins, chlorosyringaldehydes, and chlorosyringols (all from Helix, Canada) were used as authentic reference compounds. HPLC grade n-hexane and acetone and LR grade diethyl ether were used in this experiment. After redistillation analytical grade acetic anhydride was used. Other reagents were of analytical grade which were used for identification studies. In 10% acetone water standard solutions of chlorophenols were prepared. 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. To determine the residual lignin content of the pulp TAPPI Test method T_{236} cm- 85 was used. Pulp bleaching was carried out in multi bleaching stages, to achieve the target brightness for pulp. Unbleached pulp (40 gm O.D. pulp) was bleached under the conditions which is shown in Table 1**.** For the O_2 delignification the pulp was bleached with oxygen in the electrically heated, rotary digester of capacity 15 liter.

The oxygen prebleaching conditions and pulp characteristics of oxygen delignified pulp are shown in Table 2. We tried the pulp by O_2 pretreatment and its kappa number drop by 50–55% without affecting the viscosity. After every stage generated effluents were collected and we made its volume of 2 liter and we took 100 ml of this effluent for COD and color determination experiment. The COD was calculated [Training Manual on COD analysis, E. Merck (I) LTD., Mumbai] and color of effluent was determined by spectrophotometer model UV 2100/S [WTW instructional manual]. All the extraction procedure was done by the method Lindstrom and Nordin [Lindstom, *et al.,* 1976]. In this determination we used Shimadzu Gas Chromatograph (Model GC- 9A). All the experimental conditions are summarized in Table-3.

Table 1: Bleaching conditions for different sequences

Parameter	Units	Jute Cady			Bamboo		
		C	E	H	C	E	H
Charge as active Cl	%	8.1	---	5.4	3.78	---	3.09
Alkali charge as NaOH / H_2O_2	%	---	4.35	---	---	2.19	---
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	---	≈ 2.0	10 - 11	10 - 11	≈2.0	10-11	10-11

Table 2: O_2 Prebleaching Conditions and characteristics of O_2 Delignified pulp

Parameter		Units	Jute cady	Bamboo
O_2 charge		kg / cm^2	6	6
Consistency		%	10	10
Time		minute	75	75
Temperature		°C	110	110
Alkali charge		kg / t	35	25
Magnesium sulphate		kg / t	2	2
Kappa No.	Non O_2	---	27.0	12.5
	O_2 delignified	---	15.93	6.38
Viscosity	Non O_2	cp	29.0	16
	O2 delignified	cp	22.74	10.92
Brightness	Non O_2	%ISO	12.50	23.18
	O_2 delignified	%ISO	25.92	32.39

Table 3: GC Conditions

Parameters	
Detector	FID
Detector Range	10°
Carrier Gas (N) Flow Rate	20 ml/min.
Injection and 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 (Split less)	2 min.
Sample Size	1µl
Chart Speed	2 cm/min.

DERIVATIZATION PROCEDURE

A sample of 4.5 ml is taken in a PTFE screw capped glass tube and mixed with 0.5 ml buffer solution of 0.5 Na_2HPO_4. By adding 1ml of n–hexane and 0.1 ml of acetic anhydride in the sample, derivatization and extraction were done. Then shake the above mixture and from the hexane layer 1ul of derivative was used for GC analysis.

DETERMINATION OF EXTACTION EFFICIENCY:

The Lindstrom, *et al.* (1976) procedure was used for determination of extraction efficiency.

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). 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. 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. 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.

Oxygen delignified pulp was bleached by CEH sequence. Oxygen delignification stage (prebleaching stage) reduced the formation of the chlorophenolic compounds by 73%. 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.

In 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). 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. 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. 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 Oxygen delignified pulp was bleached by CEH sequence. Oxygen delignification stage (prebleaching stage) reduced the formation of the chlorophenolic compounds by 74%. A reduction of total chlorophenolic compounds by 75%in C stage and 73% in E stage effluent by oxygen delignification. In case of mono, di, tri, tetra and penta chlorophenolic compounds, a reduction of 65-89% is being observed. The similar trend is shown by phenols, catechols, guaiacols and others chlorophenolic compounds. These are also reduced by 68-79%. The effluent COD is reduced by 30% and the color value is reduced by 46%. There is major improvement in brightness by 6.6 points after H stage but viscosity drop by 8% and the CE kappa number is reduced by 12%. 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.

CONCLUSION

The results show that quantity of the total chlorophenolic compounds formed during oxygen delignification stage (prebleaching stage) reduced by 74% & 73% in case of Bamboo & jute cady respectively. It indicates a significant drop in pollution load. 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. 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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