

## Characterization of chlorinated organic material in Eucalyptus pulp bleaching effluents

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Elemental chlorine and chlorine compounds are commonly used in the developing countries for bleaching of pulp. The study deals with the bleaching of eucalyptus pulp with chlorine, hypochlorite, and chlorine dioxide and identification of various organochlorine compounds generated in the bleach effluents at different stages. Molecular weight distribution of macromolecules present in bleach effluents at different stages have also been studied

**Keywords:** Eucalyptus pulp, Bleaching, Organochlorine compounds, Toxic effluent

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### Introduction

The pulp produced by chemical pulping requires bleaching to produce bright pulps. Elemental chlorine and chlorine compounds are commonly used, particularly in the developing countries for bleaching of pulp. Various kinds of chlorinated phenols, phenolic carboxylic acids, dicarboxylic acids, resin acids and hydrocarbons originating from lignin and/or extractions of wood are found to be present in the bleach effluent<sup>1-12</sup>. Studies<sup>13-15</sup> indicate that some of the chlorinated organic compounds present in the wastewater of bleached pulp mills are toxic, mutagenic, and resistant to biodegradation. Some of the compounds known to impart toxicity are; 2,4,5-trichlorophenol, tetra- and penta-chlorophenols, tetra-chlorocatechol, 3,4,5-trichloroguaiacol tetra-chloroguaiacol, polychlorinated dibenzo-p-dioxins (PCDD), and furans (PCDF). The components of particular concern are tetra-chlorodioxin (TCDD) and tetra-chloro difuran (TCDF)<sup>16,17</sup>. The detection<sup>1</sup> of TCDDs and TCDFs in pulp and paper mill effluents prompted many researchers to study the release and control of toxic pollutants in the pulp bleaching process with chlorine or chlorine derivatives.

Softwoods, which are used in large proportion by European and North American countries for pulping processes, are reported to release high amount of chlorinated organics on chlorine bleaching.<sup>13,18,19</sup> Not much information is available on the nature and quantities of various organochlorine compounds present in bleach plant effluents formed from Indian varieties of hard woods or agro-residues. In our earlier work<sup>20</sup>, we have studied the effect of different pulping and bleaching conditions on the generation of pollutants, e.g., colour, COD, AOX, EOX and POX, using Eucalyptus as raw material. In the present study, we report the results of the detection and quantitative determination of various pollutants formed during different bleaching (chlorine and chlorine compounds) sequences, using Eucalyptus (*Eucalyptus teretecornis*), which is one of the important pulping raw materials in Indian subcontinent and several other countries, including Australia, Brazil and European community. All the organochlorine compounds may not be toxic. For example, many chlorophenols and chloroacetones, in addition to other chloroorganics, are toxic. It is therefore, necessary to identify these compounds at different stages of bleaching to assess the extent of toxicity in bleaching effluents. This study will help in deciding about the bleaching stages to be followed in the pulp & paper industry.

### Experimental Procedure

### A. Materials

Eucalyptus pulps of kappa number 18.7, 19.7, 22.5 and 20.2 were used for bleaching in  $C_D E_0 H_1 H_2$ ,  $C E_P H_1 H_2$ ,  $C H_1 H_2$  and  $C_D E_0 D_1 D_2$  sequences, respectively. The chemicals used in bleaching were laboratory grade procured from SD Fine Chemicals Ltd, Bombay and chlorine water was prepared from a commercial grade chlorine cylinder. Chlorine dioxide was produced *in situ* from sodium chlorite. Various chemicals used in extraction chloroorganics were AR also procured from S D Fine Chemicals Ltd, Bombay.

### B. Bleaching

Prior to bleaching, disintegration of the unbleached pulp was carried out at 3 per cent consistency for 4-5 min, using a pulp disintegrator. The dispersed pulp was then filtered, washed, and collected for subsequent bleaching studies. For chlorination (C stage) of pulp, adequate quantity of chlorine water and tap water were added to the pulp slurry in a plastic container and the mixture was shaken intermittently (at an interval of 10 min) for 45 min. After the reaction was over, pulp slurry was filtered and the filtrate was collected in a cooled flask. The pulp was washed with 500 mL of water in two stages and the filtrate in each stage was passed through the pulp mat so that residual fines get entrapped in pulp mat. The bleaching conditions for different sequences are given elsewhere<sup>20</sup>. The filtrate and washings were collected, mixed and stored in a refrigerator for characterization.

For  $ClO_2$  (D stage) bleaching the pulp slurry was taken in a polythene bag,  $ClO_2$  water was added which was prepared by adding HCl to  $NaClO_2$  and the strength of  $ClO_2$  was determined as per Tappi method (T611 om - 84) and was shaken intermittently at 70°C for 3 h.

In oxidative extraction ( $E_0$ ) stage the pulp was taken in a polythene beaker, adequate quantity of water and sodium hydroxide solution were added. The pulp slurry was mixed manually with a spatula. It was then transferred to the bombs of Autoclave digester. The pulp slurry was kept under oxygen pressure and at 60°C. After 2 h, oxygen pressure was released and the pulp was filtered under vacuum. It was subsequently washed with water twice. The filtrate and the washings (in each stage) were once more recirculated. Finally the entire filtrate and washings were collected, mixed, and stored for characterization.

For hypo-stages ( $H_1$  and  $H_2$ ) the pulp was taken in a polythene bag, pH was maintained at ~ 10 by NaOH, 0.1 per cent sulphamic acid was added, followed by calcium hypochlorite. The doses were decided depending upon the kappa no. of the pulp obtained from the previous bleaching step. It was shaken intermittently at 40°C for 3 h.

The pulp consistency was 3 per cent in chlorination stage, 4 per cent in chlorine dioxide substituted chlorination ( $C_D$ ) stage, and 10 per cent in all other stages. The treatment temperature was 30°C for C stage, 40-45°C for  $C_D$  stages, 65°C for  $E_0$  and hydrogen peroxide reinforced extraction ( $E_P$ ) stages, 40°C for  $H_1$ , 35°C for  $H_2$ , and 75°C for  $D_1$  and  $D_2$  stages. The treatment time was 45 min for C and  $C_D$  stages, 120 min for  $E_0$  and  $E_P$  stages, 180 min for  $H_1$ , 120 min for  $H_2$  and 180 min for D stages. All the bleaching experiments were conducted with 100-134 g pulp and repeated at least four-times.

The filtrate and subsequent washings in each stage of bleaching of the pulp were immediately collected and measured. The combined filtrate and washings for analysis were filled to the brim in a 250 mL polythene bottle and kept below 4°C.

### C. Analysis

**Kappa number** — Kappa no., a measure of residual lignin in the pulp of was determined as per Tappi Test Method no. T 236 om -99.

**Chlorophenolics** — Forty-two chlorophenolic standards, used for the analysis were procured from different sources. 2-chlorophenol and 4-chlorophenol from SD Fine Chemicals Ltd, Bombay; 2,4-dichloro phenol from Fluka Chemie AG, Buchs; 2,3,4,6-tetrachlorophenol from Lancaster, England; 2,6 di-chlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and penta-chlorophenol from Aldrich Chemical Company, Inc., Milwaukee, USA and rest of the compounds were procured from Helix Biotech Corporation, British Columbia, Canada. Extraction of the chlorophenolics was performed by converting acetyl derivatives as follows<sup>21</sup>. Effluent sample was concentrated by 10-times. 75 mL concentrated sample was taken in a conical flask, 25 mL acetone was added and pH was adjusted to  $7.0 \pm 0.1$  by NaOH/ $H_2SO_4$  solution. 1.6 mL of 60 per cent w/v  $K_2CO_3$  solution was

added and pH was adjusted to  $11.6 \pm 0.1$  by NaOH solution. The solution was transferred in a round bottom flask and 5 mL redistilled acetic anhydride was added. The flask was kept in a water bath at  $50^\circ\text{C}$  for half-an-hour, 20 ml of 5 per cent w/v  $\text{K}_2\text{CO}_3$  solution was added and stirred for 15-20 min with a magnetic stirrer. The resulting solution was extracted with *n*-hexane three-times ( $3 \times 15$  mL) using a separating funnel. 15-20 mL of 5 per cent w/v  $\text{K}_2\text{CO}_3$  solution was added in the combined solvent extract in the separating funnel and shaken. The solvent layer was taken out carefully, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Extract was filtered through cotton and the filtrate volume was reduced to 5-7 mL by distillation. Acetyl derivative of standard chlorophenolics was prepared by the similar procedure, using 10-25 mg of the compound. Analysis of the chlorophenolics was done with the help of Gas Liquid Chromatograph (Nucon make, model 5765) by injecting 1  $\mu\text{L}$  of the *n*-hexane extract in wide bore capillary column BPX5 (30 m length) under splitless condition using electron capture detector (ECD).  $\text{N}_2$  was used as carrier gas at a flow rate of 20 mL/min. Oven temperature was programmed from 130 to  $220^\circ\text{C}$  with an increment of  $3^\circ\text{C}/\text{min}$ . Injector and detector temperatures were 240 and  $280^\circ\text{C}$ , respectively.

**Chloroacetones**—Three standard chloroacetone compounds were used for the calibration. 1,1,1-trichloroacetone was procured from Aldrich Chemical Company, Inc., USA, and 1,1,3-trichloroacetone and hexa-chloroacetone were procured from Fluka Chemie, AG, Buchs. Chloroacetone was determined as follows:

Effluent sample was concentrated 10-times. 25 mL of concentrated effluent sample was treated with NaCl (8-10 g) and extracted thrice with diethyl ether ( $3 \times 25$  mL). The combined ether extract was washed with 50 mL saturated NaCl solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The extract was filtered, using cotton. After filtration the ether was distilled out to reduce the volume to 5-7 mL. Analysis of the chloroacetone extract was done with the help of Gas Liquid Chromatograph (Nucon make, model 5765). Wide bore capillary column BPX5, ECD and splitless condition were used.  $\text{N}_2$  was used as carrier gas at a flow rate of 20 mL/min. 1  $\mu\text{L}$  of the sample was injected. The oven temperature was programmed from 80 to  $180^\circ\text{C}$  with an increment of  $3^\circ\text{C}/\text{min}$ . The injector and detector temperatures were kept at 240 and  $280^\circ\text{C}$ , respectively.

**Molecular Weight Distribution** — Molecular weight distribution of dissolved polymeric components in effluent samples was determined by HPLC/GPC system of Waters Associates Boston, USA as per manual of manufacturer (Ultrahydregel 500, 250, and 250 columns at ambient temperature, U6K injector, deionised water purified with Millipore system as mobile phase at a flow rate of 0.8 mL/min, pump model 510, detection by differential refractometer (R 01) and recorder (Data Module 7301).

## Results and Discussion

In  $\text{C}_\text{D}\text{E}_\text{O}\text{H}_1\text{H}_2$  bleaching sequence in majority (89 per cent) of the chloroacetones were generated in  $\text{C}_\text{D}$  stage alone, whereas  $\text{E}_\text{O}$  contributed the least amount of the same (Table 1). Insignificant amount of hexa-chloroacetone, which is the most toxic in the group was generated during the bleaching of eucalyptus pulp under the specific bleaching conditions. Unlike bamboo the generation of chlorophenolics in eucalyptus pulp bleaching (Table 1) is comparatively low. The chlorophenolics generated, in order of decreasing magnitude, were mono-, tri-, di-, tetra- and penta-chlorophenolics. The highest amount of mono-chlorophenolics was generated in  $\text{E}_\text{O}$  stage. The generation of di- and tri-chlorophenolics was relatively higher in  $\text{E}_\text{O}$  stage. Penta-chlorophenol, which is the most toxic in the group of chlorophenolics, was generated by a small amount in  $\text{E}_\text{O}$  stage.

HPLC/GPC chromatograph of  $\text{C}_\text{D}$ ,  $\text{E}_\text{O}$   $\text{H}_1$  and  $\text{H}_2$  stage effluent indicates that the macromolecules present in the effluent are having molecular weight well below 1000 Da. In  $\text{CE}_\text{p}\text{H}_1\text{H}_2$  bleaching sequence, 87.3 per cent chloroacetones were generated in the chlorination stage (Table 2). 111-trichloroacetone and 113-trichloroacetone were generated in equal amounts in chlorination stage. Generation of hexa-chloroacetone was insignificant. All the four bleaching stages generated large amounts of chlorophenolics (Table 2). The chlorophenolics generated in order of decreasing magnitude, were tri-, mono-, tetra-, di- and penta-chlorophenolics.  $\text{C}$  stage generated the largest amount of mono- and tetra- chlorophenolics, whereas  $\text{E}_\text{p}$  stage was responsible for generation of the largest amount of di- and tri-chlorophenolics.  $\text{H}_1$  stage generated appreciable amount of penta-chlorophenol, the most toxic compound in the group.

Molecular weight distribution studies indicate that there are no molecules having molecular weights above

6000 Da in C, E<sub>p</sub>, H<sub>1</sub>, and H<sub>2</sub> stage bleaching effluents. Most of the molecules are having molecular weights below 1000 Da.

In CH<sub>1</sub>H<sub>2</sub> bleaching sequence majority (98.1 per cent) of the chloroacetones were generated in C stage alone (Table 3). Generation of hexa-chloroacetone, most toxic in the group, was quite insignificant. Chlo-

Table 1 — Generation of chloroacetones and chlorophenolics in eucalyptus pulp bleaching with C<sub>D</sub>E<sub>O</sub>H<sub>1</sub>H<sub>2</sub> sequence

Sl No.	Compound	C <sub>D</sub> (µg/L)	E <sub>O</sub> (µg/L)	H <sub>1</sub> (µg/L)	H <sub>2</sub> (µg/L)
<i>Chloroacetones</i>					
1	111-trichloro acetone	565.0	36.0	90.7	32.0
2	113-trichloro acetone	1950.0	6.4	21.8	22.0
3	Hexachloroacetone	48.8	ND	16.0	8.1
<i>Chlorophenolics</i>					
1	2CP	ND	504	ND	95
2	4CP	ND	ND	3	5
3	24DCP	ND	4	ND	ND
4	26DCP	3	2	8	2
5	246TCP	12	22	1	1
6	245TCP	ND	ND	0.1	ND
7	TECP	ND	1	0.2	Traces
8	PCP	ND	5	ND	ND
9	3CC	8.8	ND	1	1.5
10	4CC	14	15	7.5	3.5
11	34DCC/36DCC*	85.5	2.2	2.2	2.0
12	35DCC	3.5	ND	0.5	ND
13	45DCC	18	1.5	0.3	0.8
14	346TCC	33	14	0.2	0.35
15	345TCC	68	0.75	1.8	1.7
16	TECC	166	1.9	4.3	2.0
17	4CG/5CG*	0.7	ND	294	ND
18	6CG	ND	ND	ND	3.4
19	35DCG	ND	ND	ND	ND
20	46DCG	ND	1.4	0.05	ND
21	34DCG	0.5	4.5	0.15	0.2
22	56DCG/45DCG*	ND	12.5	ND	ND
23	36DCG	ND	ND	ND	ND
24	346TCG/356TCG*	0.4	11.0	0.25	0.1
25	345TCG	12	182.0	4.5	3.3
26	456TCG	8	ND	0.5	ND
27	TECG	2.3	51.6	1.2	0.05
28	3CS	17.2	ND	107.0	15.0
29	35DCS	ND	ND	ND	ND
30	TCS	13.3	164.0	3.1	1.6
31	345TCVE	ND	ND	ND	ND
32	346TCVE	ND	ND	0.35	0.02
33	TECVE	ND	ND	ND	ND
34	6CVA/5CVA*	ND	169.0	3.9	ND
35	56DCVA	6.8	25.0	1.05	0.3
36	2CSA	ND	ND	ND	ND
37	26DCSA	3.4	150.0	2.4	1.4
Monochlorophenolics		40.7	688.0	416.4	123.4
Dichlorophenolics		120.7	197.1	14.7	6.7
Trichlorophenolics		146.7	393.8	11.8	9.07

Tetrachlorophenolics	168.3	54.5	5.7	2.05
Pentachlorophenolics	ND	5.0	ND	ND

Note: The individual compounds in the group with (\*) mark could not be identified

ND: Non-detectable, NA: Not applicable

Table 2 — Generation of chloroacetones and chlorophenolics in eucalyptus pulp bleaching with CE<sub>p</sub>H<sub>1</sub>H<sub>2</sub> sequence

Sl No.	Compound	C (µg/L)	E <sub>p</sub> (µg/L)	H <sub>1</sub> (µg/L)	H <sub>2</sub> (µg/L)
<i>Chloroacetones</i>					
1	111-trichloroacetone	361.0	146.0	23.0	10.0
2	113-trichloroacetone	395.0	68.0	10.7	15.7
3	Hexachloroacetone	32.9	ND	0.7	19.3
<i>Chlorophenolics</i>					
1	2CP	ND	ND	ND	ND
2	4CP	ND	ND	ND	9.0
3	24DCP	ND	13	ND	ND
4	26DCP	ND	ND	ND	5.0
5	246TCP	15.0	86.0	3.0	1
6	245TCP	ND	ND	ND	ND
7	TECP	ND	28	0.04	ND
8	PCP	ND	1.0	188.0	0.1
9	3CC	ND	ND	ND	ND
10	4CC	20.0	1.0	24.0	13.0
11	34DCC/36DCC*	506.0	73.0	0.03	ND
12	35DCC	2.5	ND	0.3	ND
13	45DCC	ND	ND	0.2	0.3
14	346TCC	1135.0	1645.0	0.05	0.1
15	345TCC	48.0	ND	0.1	ND
16	TECC	1512.0	93.0	0.01	1.2
17	4CG/5CG*	3268.0	ND	ND	464.0
18	6CG	ND	752.0	ND	ND
19	35DCG	ND	ND	ND	ND
20	46DCG	ND	6.5	0.15	ND
21	34DCG	8.7	70.0	0.05	0.02
22	56DCG/45DCG*	78.0	866.0	0.3	ND
23	36DCG	ND	ND	ND	ND
24	346TCG/356TCG*	ND	ND	0.05	0.04
25	345TCG	271.0	3030.0	3.0	548.0
26	456TCG	9.5	37.0	0.15	ND
27	TECG	312.0	1279	0.5	0.3
28	3CS	ND	ND	15.0	ND
29	35DCS	2.0	77.0	0.5	ND
30	TCS	182	1885	3.0	1.1
31	345TCVE	ND	ND	ND	ND
32	346TCVE	55.0	ND	0.02	ND
33	TECVE	ND	ND	ND	ND
34	6CVA/5CVA*	ND	ND	1.0	1.5
35	56DCVA	128.0	507.0	0.1	0.2
36	2CSA	ND	ND	ND	0.2
37	26DCSA	19.0	503.0	0.3	1.3
Monochlorophenolics		3288.0	753.0	40.0	489.0
Dichlorophenolics		744.0	2116.0	1.93	7.0
Trichlorophenolics		1719.0	6683.0	9.4	550.0

Tetrachlorophenolics	1824.0	1396.0	0.91	1.5
Pentachlorophenolics	ND	13.0	188	0.1

Note: The individual compounds in the group with (\*) mark could not be identified

ND: Non-detectable, NA: Not applicable

Table 3 — Generation of chlorophenolics in eucalyptus pulp bleaching with CH<sub>1</sub>H<sub>2</sub> sequence

Sl No.	Compound	C (µg/L)	H <sub>1</sub> (µg/L)	H <sub>2</sub> (µg/L)
<i>Chloroacetones</i>				
1	111-trichloroacetone	437.2	1.4	2.9
2	113-trichloroacetone	391.2	7.1	14.3
3	Hexachloroacetone	2.6	16.4	ND
<i>Chlorophenolics</i>				
1	2CP	3428.0	1550.0	ND
2	4CP	ND	ND	171.0
3	24DCP	7.0	29	28.0
4	26DCP	2.0	ND	73.0
5	246TCP	31.0	28.0	12.0
6	245TCP	ND	ND	Traces
7	TECP	ND	Traces	0.1
8	PCP	ND	ND	ND
9	3CC	ND	ND	ND
10	4CC	55.0	ND	30.0
11	34DCC/36DCC*	83.0	5.0	5.0
12	35DCC	23.0	ND	2.0
13	45DCC	13.0	ND	ND
14	346TCC	23.0	ND	Traces
15	345TCC	34.0	0.3	1.0
16	TECC	96.0	1.0	3.0
17	4CG/5CG*	ND	472.0	ND
18	6CG	ND	1616.0	61.0
19	35DCG	ND	ND	ND
20	46DCG	ND	ND	0.3
21	34DCG	4.0	7.0	6.0
22	56DCG/45DCG*	ND	7.0	3.0
23	36DCG	82.0	283.0	0.4
24	346TCG/356TCG*	3.0	9.0	ND
25	345TCG	2.0	78.0	1.0
26	456TCG	ND	11.0	0.8
27	TECG	ND	29.0	1.0
28	3CS	ND	445.0	84.0
29	35DCS	7.0	ND	ND
30	TCS	10.0	78.0	1.0
31	345TCVE	ND	ND	ND
32	346TCVE	ND	ND	1.0
33	TECVE	ND	ND	ND
34	6CVA/5CVA*	ND	ND	ND
35	56DCVA	48.0	10.0	6.0
36	2CSA	188.0	30.0	ND
37	26DCSA	20.0	103.0	3.0
Monochlorophenolics		3671.0	4083.0	346.0
Dichlorophenolics		289.0	444.0	126.7
Trichlorophenolics		103.0	204.0	15.8

Tetrachlorophenolics	96.0	30.0	4.1
Pentachlorophenolics	ND	ND	ND

Note: The individual compounds in the group with (\*) mark could not be identified

ND: Non-detectable, NA: Not applicable

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Table 4 — Generation of chloroacetones and chlorophenolics in eucalyptus pulp bleaching with C<sub>D</sub>EoD<sub>1</sub>D<sub>2</sub> sequence

SI No.	Compound	C <sub>D</sub> (µg/L)	E <sub>0</sub> (µg/L)	D <sub>1</sub> (µg/L)	D <sub>2</sub> (µg/L)
<i>Chloroacetones</i>					
1	111-trichloroacetone	260.0	10.8	33.0	4.9
2	113-trichloroacetone	190.0	ND	12.0	2.8
3	Hexachloroacetone	5.7	ND	0.7	ND
<i>Chlorophenolics</i>					
1	2CP	11	1	3.0	0.5
2	4CP	133	0.1	10.0	1.0
3	24DCP	5	0.1	0.1	Traces
4	26DCP	0.1	0.1	0.2	ND
5	246TCP	2	10	1	ND
6	245TCP	ND	ND	ND	ND
7	TECP	ND	ND	Traces	Traces
8	PCP	0.1	ND	ND	ND
9	3CC	ND	42	83	ND
10	4CC	133	59	63	3.1
11	34DCC/36DCC*	91	2	4	0.7
12	35DCC	6	7	ND	ND
13	45DCC	598	ND	ND	ND
14	346TCC	27	26	0.7	ND
15	345TCC	ND	ND	ND	ND
16	TECC	80	ND	0.02	0.8
17	4CG/5CG*	ND	2064	ND	73
18	6CG	1039	ND	ND	ND
19	35DCG	ND	ND	ND	ND
20	46DCG	2	8	1	0.2
21	34DCG	ND	ND	ND	0.1
22	56DCG/45DCG*	3	28	0.05	0.2
23	36DCG	ND	ND	ND	ND
24	346TCG/356TCG*	2	5	ND	Traces
25	345TCG	35	567	16	6.9
26	456TCG	2	ND	ND	ND
27	TECG	ND	412	0.1	0.05
28	3CS	ND	ND	ND	ND
29	35DCS	ND	ND	ND	ND
30	TCS	18	234	6	ND
31	345TCVE	ND	ND	Traces	0.03
32	346TCVE	ND	ND	ND	ND
33	TECVE	ND	ND	ND	ND
34	6CVA/5CVA*	ND	330	6	3
35	56DCVA	ND	11	ND	ND
36	2CSA	ND	100	3.5	1.3
37	26DCSA	0.6	98	0.6	Traces
Monochlorophenolics		1316	2596	168.5	81.9
Dichlorophenolics		706	154.2	6.0	1.2
Trichlorophenolics		86	842	23.7	6.9
Tetrachlorophenolics		80	412	0.3	0.9
Pentachlorophenolics		0.1	ND	ND	ND

Note: The individual compounds in the group with (\*) mark could not be identified

ND: Non-detectable, NA: Not applicable



rophenolic compounds were generated in all the stages of bleaching (Table 3). The chlorophenolics generated, in order of decreasing magnitude, were mono-, di-, tri-, and tetra-chlorophenolics. Penta-chlorophenol was not generated in the bleaching process. C stage is the largest source of generation of mono-, di-, tri-, and tetra-chlorophenolics, followed by H<sub>1</sub> stage which generated more chlorophenolics than H<sub>2</sub> stage, as a result of which the effluent might not be so toxic.

All macromolecules present in the effluent of C, H<sub>1</sub> and H<sub>2</sub> stage are having molecular weights below 1000 Da, as reflected in GPC chromatogram.

In C<sub>D</sub>E<sub>0</sub>D<sub>1</sub>D<sub>2</sub> bleaching sequence the generation of chloroacetones was quite low (Table 4). Out of the total 7.3 g of chloroacetones per tonne of unbleached pulp, 87.7 per cent were formed in C<sub>D</sub> stage alone. Generation of hexa-chloroacetone the most toxic in the group, was quite insignificant. The chlorophenolics generated, in order of decreasing magnitude, were mono-, tri-, di-, and tetra-chlorophenolics. Generation of penta-chlorophenol was virtually absent in this bleaching process. E<sub>0</sub> stage was the highest producer of mono-, tri-, and tetra-chlorophenolics, whereas C<sub>D</sub> stage was responsible for generation of the largest amount of di-chlorophenolics (Table 4).

Molecular weight distribution of macromolecules present in effluents of C<sub>D</sub>, E<sub>0</sub>, D<sub>1</sub> and D<sub>2</sub> stage determined with HPLC/GPC clearly shows that the molecules higher than 1000 Da are totally absent in all the effluents.

## Conclusions

The study indicates that bleaching conditions have a great effect on generation of various organochlorine compounds in the bleaching effluent. Most of the chloroacetones are generated in C and C<sub>D</sub> stage. Hexa-chloroacetone the most toxic in the group, is very low in all cases. Chlorophenolic compounds are generated in all stages of the bleaching process. Mono-chlorophenolics are formed by the largest amount in both chlorination and hypochlorite stage followed by tri-, di-, and tetra-chlorophenolics.

## References

- 1 Murtedza M M, Matayun M & Lim T S, Chlorinated organics in tropical hardwood kraft pulp and paper mill effluents and their elimination in an activated sludge treatment system, *Pertanika*, **12**(3) (1989) 387.
- 2 Rajan P S, Chen C L & Gratze J S, Formation of chloro-organics during chlorine bleaching of softwood kraft pulp, Part 2, Chlorination of pine kraft lignin fractions, *Holzforschung*, **50**(2) (1996)165.
- 3 Bajpai P & Bajpai P K, *Organochlorine compounds in bleach plant effluents — genesis and control* (Pira International, UK) 1996.
- 4 Earl P F & Reeve D W, Chlorinated organic matter in bleached chemical pulp production. The effect of chlorination – stage variables on chlorinated organic matter in effluent, *Tappi J*, **72**(10) (1989)183.
- 5 Salthammer T, Klipp H, Peek R D & Marutzky R, Formation of polychlorinated dibenzo *p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) during the combustion of impregnated wood, *Chemosphere*, **30**(11) (1995) 2051.
- 6 Torngren A & Gellerstedt G, Why do E C F bleached kraft pulps contain organic bound chlorine?, Presented at the *Int Pulp Bleach Conf*, Helsinki, Finland, (1998).
- 7 Reeve D, Bleaching technology in the 21<sup>st</sup> century, 1997, a briefing on recent developments, *Japan Tappi J*, **51**(10) (1997)1552.
- 8 Torngren A & Gellerstedt G, The nature of organic bound chlorine from ECF- bleaching found in kraft pulp, Presented at the *Intl Sym Wood Pulp Chem*, Montreal, Canada, (1997).
- 9 Barroca M J M C, Seco I M, Fernandes P M M, Ferreira L M G A & Castro J A A M, Reduction of AOX in the bleach plant of a pulp mill, *Environ Sci Technol*, **35**(21) (2001) 4390.
- 10 Gune N V, Total water management in pulp and paper industry with focus on achieving zero effluent discharge status, *IPPTA*, **12**(4) (2000) 137.
- 11 Herve S, Paasivirta J & Heinonen P, Trends of organochlorine compounds in Finnish inland waters, *Environ Sci Pollut Res*, **8**(1) (2001) 19-26.
- 12 Kostamo A, Medvedev N, Pellinen J, Hyvarinen H & Kukkonen J V K, Analysis of organochlorine compounds and extractable organic halogen in three subspecies of ringed seal from Northeast Europe, *Environ Toxicol Chem*, **19**(4) (2000) 848.
- 13 Kringstand K P & Lindstrom K, Spent liquors from pulp bleaching, *Environ Sci Technol*, **18** (1984) 236A-248A.

- 14 Leach J M, Mueller J C & Walder C C, Biological detoxification of pulp mill effluent, *Process Biochem*, **13** (1978) 18-21.
- 15 Mueller J C Leach, J M & Walden C C, Detoxification of bleached kraft mill effluents a manageable problem, *Tappi J*, **60** (1977) 135-137.
- 16 Rosenburg C, Kontasas H, Tornaes J, Mutanen P, Jappinen P, Vainio H., Patterson D G & Needham L L, PCDD/PCDF levels in the blood of workers at a pulp and paper mill, *Chemosphere*, **31**(8) (1995) 3933.
- 17 Troyanskaya A F, Rubtsova N A & Moseeva D P, The effect of the pulp and paper and forest industries on the environmental pollution with persistent organochlorine compounds, Presented at the *Sixth IAWQ Symp Forest Ind Wastewat, Tampere, Finland* (1999).
- 18 Holmbom B & Lehtinen K L, A procedure for the analysis of toxic compounds in pulp mill wastewater, *Pap Puu*, **62** (1980) 523-526.
- 19 Xie T M & Lu Z J, A preliminary study of chlorophenolics in nonwood pulp bleaching effluents, *Nord Pulp Pap Res J*, **2** (1987) 56-60.
- 20 Roy M, Chakrabarti S K, Bharadwaj N K, Chandra S, Kumar S, Singh S, Bajpai P K & Jauhari M B, Generation of chlorinated organic material in eucalyptus pulp bleaching using different bleaching sequences, *J Sci Ind Res*, **62** (2003) 707-713.
- 21 Louch J R, LaFleur E L, Wilson G, Bautz D, Woodrow D, Teitzel H, Jones J & Mark M, Development and validation of analytical methods for the determination of phenolic compounds in pulp and waste water treatment plant sludges, *Tappi J*, **76**(3) (1993) 71.

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