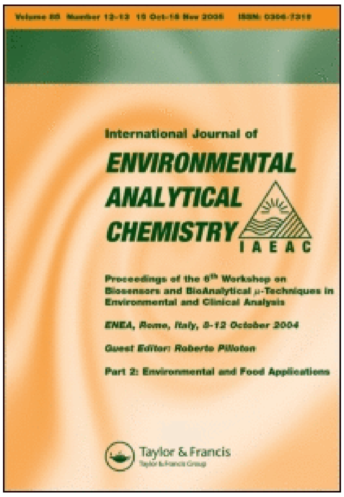

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Gas Chromatographic Analysis of Chlorophenolic, Resin and Fatty Acids in Effluents from Bleaching Processes of Agricultural Residues

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GAS CHROMATOGRAPHIC ANALYSIS OF CHLOROPHENOLIC, RESIN AND FATTY ACIDS IN EFFLUENTS FROM BLEACHING PROCESSES OF AGRICULTURAL RESIDUES

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The laboratory generated spent bleach liquor from the chlorination and caustic extraction stages of bagasse and wheat straw pulps have been analysed both qualitatively and quantitatively for various chlorophenolics, resin and fatty acids using gas chromatography. A number of chlorinated derivatives of phenols, catechols, guaiacols, syringaldehydes, resin acids as well as unchlorinated saturated and unsaturated fatty and resin acids have been identified. The concentrations of various compounds identified have also been compared with the reported $^{96}LC_{50}$ values.

KEY WORDS: Gas chromatography, bleaching effluent, agricultural residue, chlorophenolics, resin and fatty acids.

INTRODUCTION

Wood fibres today account for more than 90% of the world's pulp production, but nonwood fibres are becoming increasingly important, especially in wood deficient countries. Bagasse and straws are among the most important nonwood materials used for pulping representing more than 50% of the total nonwood fibre use.

Paper industry has been a pollution intensive industry. Among the various production processes, bleaching often accounts for the largest toxicity. The compounds responsible for the toxicity of chlorination (C) and caustic extraction (E) effluents are mainly chlorophenolics, resin and fatty acids[1,2]. The chlorophenolics are often formed during the C stage of pulp bleaching and are solublised in the E stage. The nature and concentrations of chlorophenolics formed will depend upon the nature of lignin and bleaching conditions[3,4]. The resin and fatty acids found in bleach plant effluents originate from the raw material. Their amount depend on the fiber species and on the degree of washing of unbleached pulp.

During the last 20 years intense research effort has been devoted to identify various compounds[5-8] in bleach plant effluents and to investigate their possible biological effects[9-13]. These studies have been performed mostly on the softwoods and to some extent on hardwoods. However, very little information is available on the nature and the quantities of various compounds present in bleach plant effluents formed from

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Indian varieties of hardwoods or agroresidues. In the present investigation the results on the identification and determination of various pollutants formed during chlorination and caustic extraction of bleaching of bagasse (B) and wheat straw (W) are reported.

EXPERIMENTAL

All chlorophenols used as reference compounds were obtained from Aldrich, U.S.A. Chlorocatechols, chloroguaiacols, chlorovanillins, chlorosyringaldehydes, chlorosyringols, resin and chloro fatty acids were supplied by Helix, Canada. Fatty acids were acquired from Sigma, U.S.A. Standard solutions of chlorophenols were prepared in water/acetone (90:10) and resin and fatty acids in diethyl ether/methanol (90:10). Solvents viz, normal-hexane, acetone, diethylether and methyl tertiary butyl ether were of HPLC grade. Other reagents used for identification studies were of analytical reagent grade.

The Kappa number (residual lignin) of unbleached washed sulphite pulps (bagasse and wheat straw) taken from a nearby institution were determined (Tappi test method T_{236} cm-85). It was found to be 24 and 26.3, respectively.

The chlorine demand was calculated from the following formula:

$$\%\ \text{chlorine demand} = 0.25 \times \text{Kappa number}$$

Unbleached pulp (equivalent to 35 g oven dried pulp) was bleached in the laboratory to generate effluents. The bleaching conditions are shown in Table 1. The effluents generated in both C and E stages were 1.81 L and 2.02 L respectively. The effluents were characterized by determining the pH, total dissolved solids, BOD_5 (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand) and colour. Dissolved solid (DS), pH, BOD_5 and COD (open reflux method) were determined by standard methods[14]. Colour measurements were performed spectrophotometrically 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[5]. 500 mL of the E stage effluent or 1000 mL of the C stage effluent were adjusted to pH 2 with diluted HCl and extracted, respectively, with 200 mL and 400 mL of diethyl ether/acetone (90:10) for 48 hours with intermittent shaking. A schematic presentation of the analytical method is shown in Figure 1. Extraction of resin and fatty acids from effluents was achieved as suggested by Voss and Rapsomatiotis[8]. 50 mL of the E stage or 100 mL of C stage effluents were

Table 1 Bleaching conditions.

Parameters	*C-stage*	*E-stage*
Cl_2 applied (% demand)	70	—
NaOH applied (%)	—	3
Consistency (%)	3.5	10
pH	1.8–2.0	11–12
Temperature (°C)	25	60
Time (min)	60	75

All chemicals charged as %OD (oven dried) pulp.
Consistency: gram OD pulp per 100 gram pulp suspension.

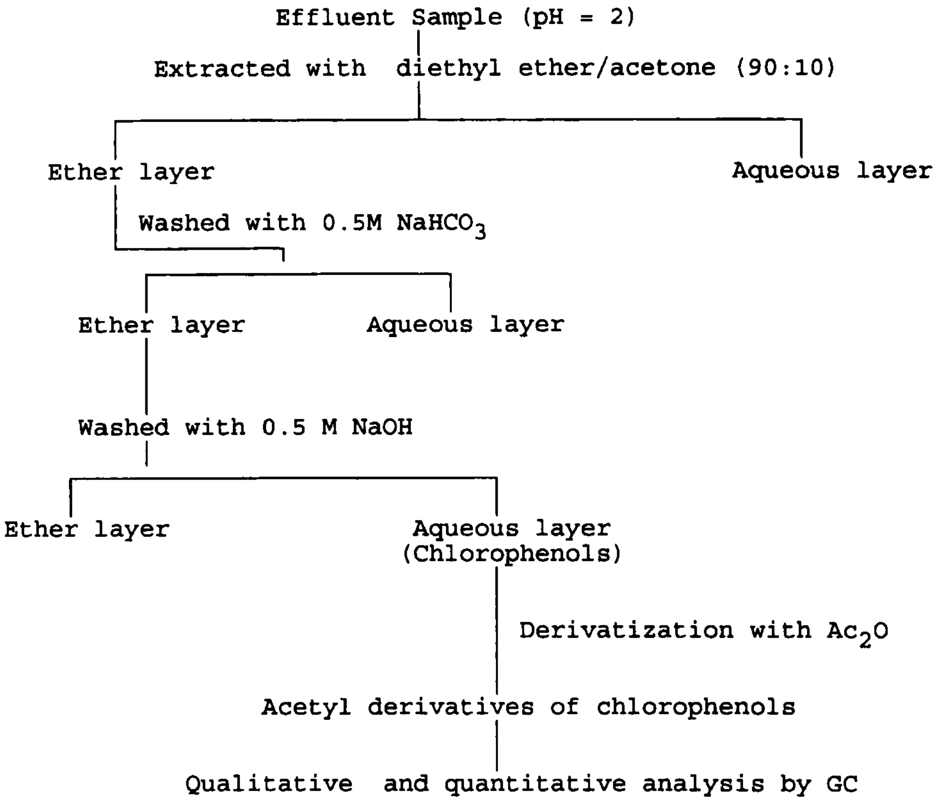

Figure 1 Separation of phenolic compounds from effluents.

adjusted to pH 9 with 0.5 M NaOH and extracted with equal volume of methyl tertiary butyl ether for one hour. A schematic presentation of the rest of the method is shown in Figure 2.

Gas chromatographic (GC) studies were performed on a Shimadzu Gas Chromatograph GC-9A model equipped with a FID detector. The capillary column used for the analysis of chlorophenols as acetyl derivatives[15] and resin and fatty acids as methyl esters[16] were, respectively, a glass Ulbon HR-1 (30 m × 0.32 mm i.d.) from Shimadzu, Japan and fused silica OV-101 (25 m × 0.32 mm i.d.) from Macherey-Nagel, West Germany. The injection was in the splitless mode (2 min) and the carrier gas was nitrogen. The temperature conditions are given in Table 2.

RESULTS

The characteristics of the effluents generated in the laboratory are shown in Table 3. Gas chromatograms of a laboratory prepared mixture of 36 reference chlorophenolic compounds as acetyl derivatives (Table 4) and 28 reference resin and fatty acids as methyl esters (Table 5) are shown in Figures 3 and 4. The corresponding retention time values are given in Tables 4 and 5, respectively.

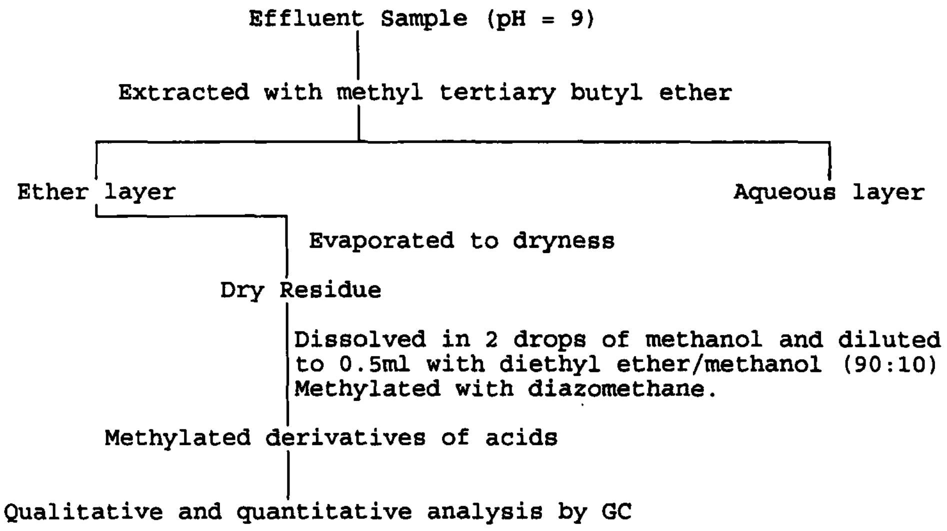

Figure 2 Separation of resin and fatty acids from effluents.

Table 2 GC conditions for the analysis of chlorophenolics and resin and fatty acids.

Parameters	*HR-1*	*OV-101*
Injection and detector temp (°C)	275	300
Column temperature (°C):	80 for 3 min	190 for 4 min
	80–160 at 2°C/min	190–210 at 1°C/min
	160 for 5 min	210–230 at 2°C/min
	160–260 at 10°C/min	230–250 at 3°C/min
	260 for 15 min	250 for 15 min

Table 3 Characteristics of effluents generated in the laboratory.

Parameters	*Bagasse*		*Wheat straw*	
	C	*E*	*C*	*E*
pH	2.3	10.5	2.3	10.6
Dissolved solid (mg/L)	1180	1264	1188	1308
BOD (mg/L)	100	130	104	125
COD (mg/L)	480	600	528	664
Colour (Pt.)	863	3035	1025	3184

The various chlorophenolics, resin and fatty acids were identified by matching the retention time (RT) (± 0.1 min) with those of derivatized standards. However, when the compounds exhibited very close RT values the quantities were determined by taking as if only one compound was present and calculating the average value. For carrying out quantitative analysis, response factors (RF) and extraction efficiencies (EF) of various compounds were determined.

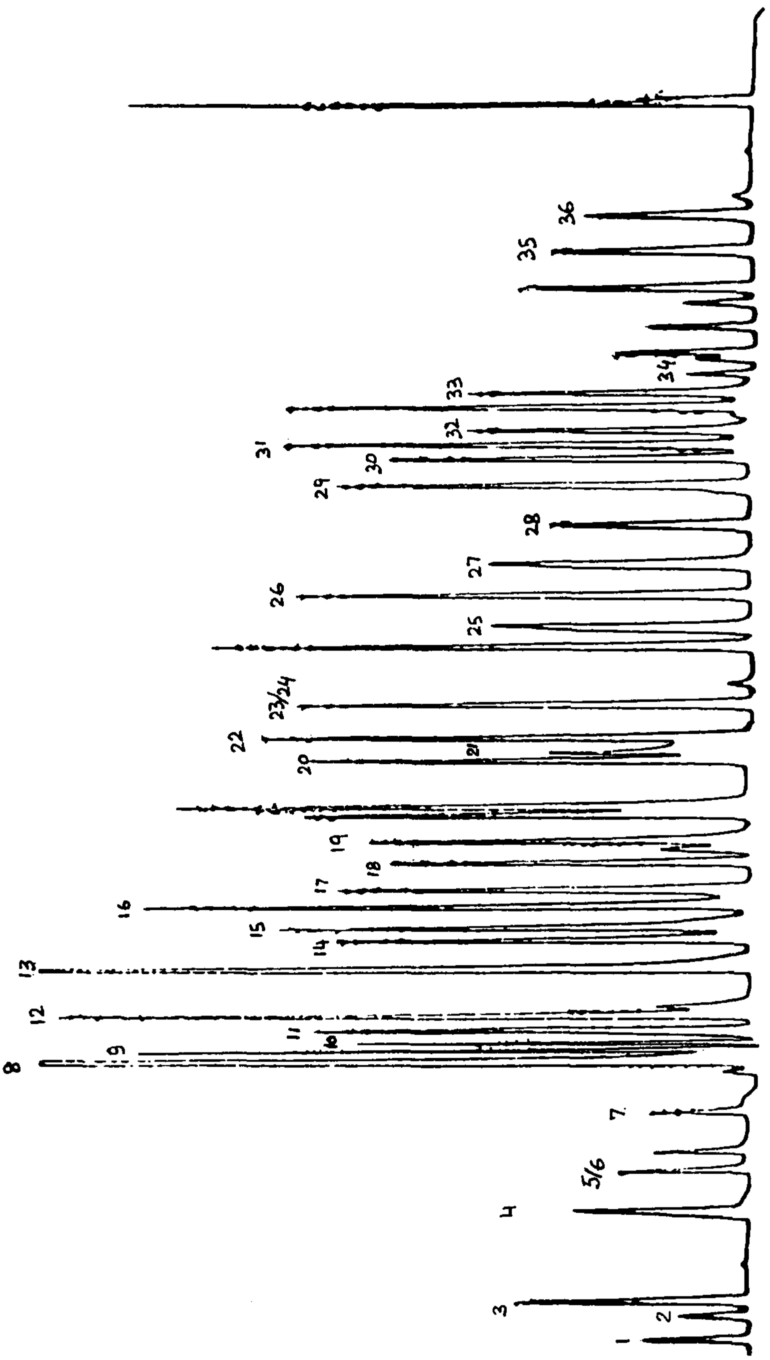

Figure 3 Separation of a mixture of pure standards of chloro phenolic compounds (as given in Table 4).

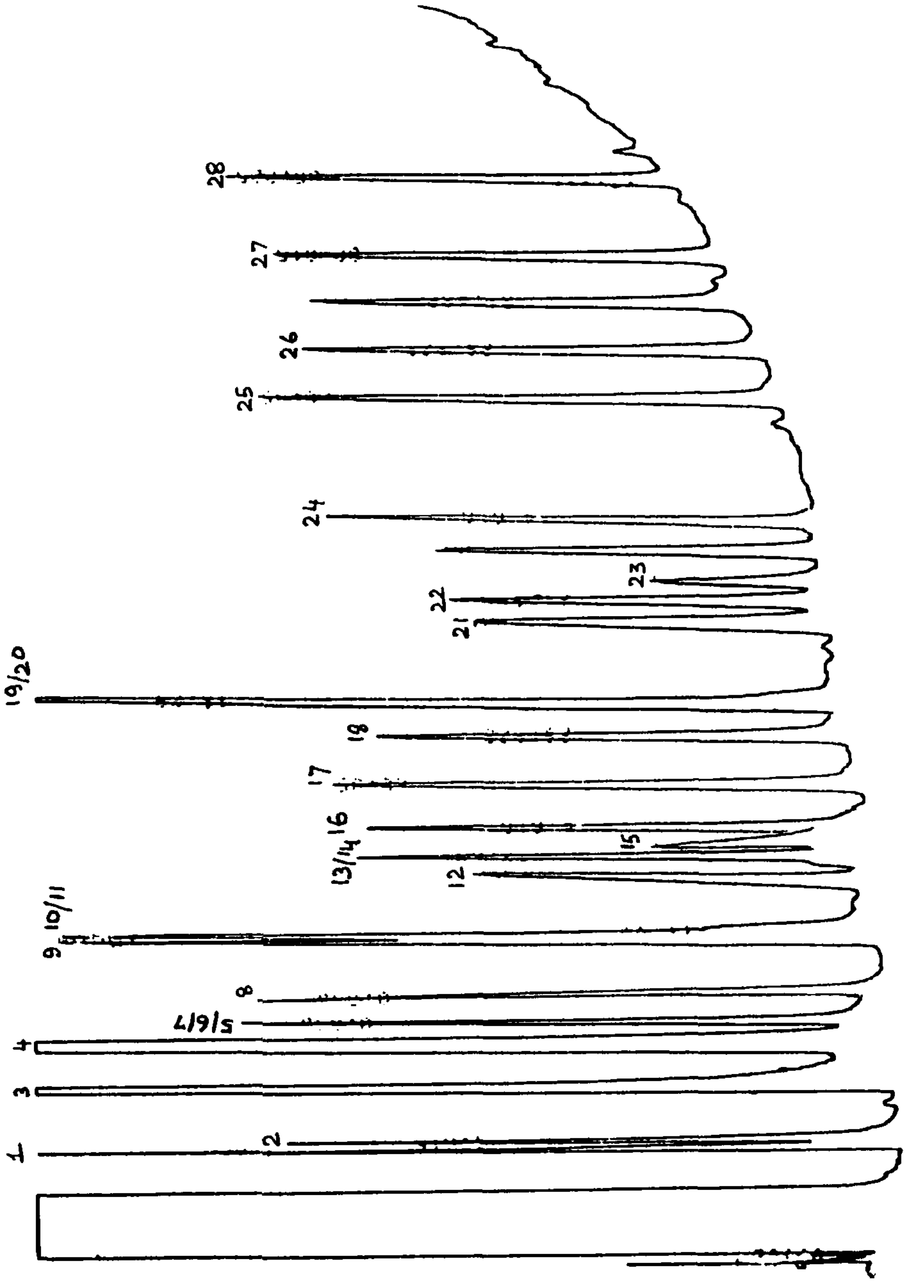

Figure 4 Separation of a mixture of pure standards of resin and fatty acids (as given in Table 5).

Table 4 Retention time (RT) of various chlorophenolic compounds (as acetyl derivatives) in Ulbon HR-1 glass capillary column.

S. No.	*Name of compounds*	*RT (min)*
1	2-Chlorophenol	7.82
2	3-Chlorophenol	8.89
3	4-Chlorophenol	9.03
4	2,6-Dichlorophenol	12.96
5	2,5-Dichlorophenol	13.97
6	2,4-Dichlorophenol	14.05
7	2,3-Dichlorophenol	15.71
8	3,4-Dichlorophenol	17.51
9	6-Chloroguaiacol	17.94
10	4-Chloroguaiacol	18.51
11	5-Chloroguaiacol	18.89
12	2,4,6-Trichlorophenol	19.10
13	2,3,6-Trichlorophenol	21.67
14	2,3,5-Trichlorophenol	22.30
15	2,4,5-Trichlorophenol	22.75
16	4-Chlorocatechol	24.43
17	2,3,4-Trichlorophenol	24.61
18	4,6-Dichloroguaiacol	24.88
19	3,4-Dichloroguaiacol	25.44
20	4,5-Dichloroguaiacol	27.96
21	3,6-Dichlorocatechol	28.51
22	3,5-Dichlorocatechol	29.65
23	3,4,6-Trichloroguaiacol	30.49
24	6-Chlorovanillin	30.58
25	4,5-Dichlorocatechol	33.36
26	3,4,5-Trichloroguaiacol	34.01
27	4,5,6-Trichloroguaiacol	36.04
28	3,4,6-Trichlorocatechol	36.29
29	5,6-Dichlorovanillin	38.07
30	2-Chlorosyringaldehyde	38.75
31	Pentachlorophenol	39.21
32	3,4,5-Trichlorocatechol	39.79
33	Tetrachloroguaiacol	40.58
34	Trichlorosyringol	41.70
35	Tetrachlorocatechol	45.96
36	2,6-Dichlorosyringaldehyde	46.38

The results show that most of the chlorophenolic and resin and fatty acids can be separated in the capillary columns used. The concentrations of various identified chlorophenols and resin and fatty acids in the laboratory generated spent bleach liquor (SBL) are given in Tables 6 and 7, respectively.

DISCUSSION

Chlorophenols

Six categories of chlorophenolic compounds have been found to be present in effluents of the C and E stages of Indian wheat straw and bagasse based bleach plants. These are

Table 5 Retention time (RT) of various resin and fatty acids (as methyl esters) in fused silica OV-101 capillary column.

S. No.	*Name of the acids*	*RT (min)*
1	Palmitoleic (c)	4.48
2	Palmitic (b)	4.92
3	Heptadecanoic (b)	6.55
4	Linoleic (c)	7.74
5	Oleic (c)	8.07
6	Linolenic (c)	8.11
7	Elaidic (c)	8.18
8	Stearic (b)	8.71
9	Pimaric (a)	11.30
10	Nonadecanoic (b)	11.60
11	Sandaracopimaric (a)	11.70
12	Isopimaric (a)	12.90
13	Levopimaric (a)	13.30
14	Palustric (a)	13.30
15	Dihydroisopimaric (a)	13.90
16	Arachidic (b)	15.00
17	Abietic (a)	15.90
18	Neoabietic (a)	17.90
19	Docosahexaenoic (c)	19.20
20	Heneicoceric (b)	19.30
21	Chlorodehydroabietic I (e)	21.60
22	Erucic (c)	22.60
23	Chlorodehydroabietic II (e)	23.00
24	Behenic (b)	24.20
25	Tricosanoic (b)	28.90
26	12,14-Dich. dehydroabietic (e)	30.40
27	Lignoceric (b)	33.30
28	9,10,12,13-Tetrachlorostearic (d)	35.70

(a) Resin acid (RA)
(b) Saturated fatty acid (SFA)
(c) Unsaturated fatty acid (UFA)
(d) Chloro fatty acid (Ch.FA)
(e) Chloro resin acid (Ch.RA)

chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols, chlorosyringaldehydes and chlorovanillins originated from lignin.

Lignin is a polymer formed by an enzyme initiated dehydroabietic polymerization of a mixture of three different para-hydroxy cinnamyl alcohols (para-coumeryl, coniferyl and sinapyl alcohols) . Compared with wood lignin, however, the structure of grass lignin has been less studied. It varies significantly with the source. Some grass lignins are thought to contain mainly para-coumaryl units but others appear to approximate the hardwood lignin[17]. During pulp chlorination, lignin is chlorinated and broken down to simpler chlorophenolic compounds. The solubility of chlorophenolics is low in acidic conditions (C stage) and high in alkaline conditions (E stage). The nature and concentration of different chlorophenolic compounds formed that ultimately end up in SBL depend upon the quantity of lignin i.e. kappa number of pulp, the nature of lignin and bleaching conditions, i.e. chlorine charged, pH, temperature and consistency.

Among the various chlorophenolics in the C stage effluent, 2-chlorosyringaldehyde is the predominant component. Significant contribution comes from dichlorocatechol, 2,6-dichlorosyringaldehyde, 3,4,5-trichlorocatechol, tetrachlorocatechol. Other

Table 6 Concentrations (g/odt) of various chlorophenols in the effluent from wheat straw (W) and bagasse (B) pulps.

S. No.	*Name of the compounds*	*C-stage*		*E-stage*	
		W	*B*	*W*	*B*
1	2-Chlorophenol	0.05	0.02	0.02	—
2	3-Chlorophenol	0.05	—	1.15	—
3	4-Chlorophenol	—	0.10	—	1.20
4	2,6-Dichlorophenol	—	0.15	—	—
5	2,5/2,4-Dichlorophenol	0.46	1.55	8.08	19.00
6	3,4-Dichlorophenol	—	0.05	—	0.11
7	6-Chloroguaiacol	0.05	0.02	0.11	—
8	2,4,6-Trichlorophenol	0.31	1.55	8.08	21.90
9	2,3,5-Trichlorophenol	—	0.15	—	0.11
10	2,4,5-Trichlorophenol	—	0.10	—	—
11	2,3,4-Trichlorophenol	—	0.05	0.57	0.23
12	4,6-Dichloroguaiacol	0.04	—	1.73	1.20
13	3,4-Dichloroguaiacol	0.05	—	0.40	0.40
14	4,5-Dichloroguaiacol	0.26	0.10	8.08	2.90
15	3,6-Dichlorocatechol	—	10.30	—	—
16	3,5-Dichlorocatechol	23.80	9.30	—	27.70
17	3,4,6-Trichloroguaiacol/ 6 Chlorovanillin	0.26	0.52	11.54	11.50
18	3,4,5-Trichloroguaiacol	0.52	0.52	9.80	5.20
19	4,5,6-Trichloroguaiacol	0.05	—	—	0.46
20	3,4,6-Trichlorocatechol	—	0.20	—	—
21	5,6-Dichlorovanillin	0.15	—	—	—
22	2-Chlorosyringaldehyde	44.98	31.00	—	1.70
23	Pentachlorophenol	—	—	16.70	5.77
24	3,4,5-Trichlorocatechol	4.14	14.00	11.54	2.30
25	Tetrachloroguaiacol	0.10	0.52	2.88	1.20
26	Trichlorosyringol	0.31	0.46	4.04	1.80
27	Tetrachlorocatechol	1.03	5.17	1.73	—
28	2,6-Dich. syringaldehyde	10.34	8.30	38.67	30.60

g/odt: gram per oven dried tonne pulp.

chlorophenolics are present in minor quantities. In the E stage effluent maximum share comes from 2,6-dichlorosyringaldehyde. Significant contribution comes from 2,4/2,5-dichlorophenol, 2,4,6-trichlorophenol, 3,4,6-trichloroguaiacol/6-chlorovanillin, pentachlorophenol, 3,4,5-trichloroguaiacol and 4,5-dichloroguaiacol. The quantity of 3,4,5-trichlorocatechol in wheat straw pulp and 3,5-dichlorocatechol in bagasse pulp contributes significantly to the identified chlorophenolic compounds.

The results clearly indicate that in the C stage the quantities of 2-chlorosyringaldehyde, dichlorocatechol and 2,6-dichlorosyringaldehyde are higher in wheat straw than in bagasse, but quantities of 3,4,5-trichlorocatechol and tetrachlorocatechols are higher in bagasse than in wheat straw. However, for E stage the quantities of 2,6-dichlorosyringaldehyde, pentachlorophenol, 3,4,5-trichloroguaiacol, 4,5-dichloroguaiacol and 3,4,5-trichlorocatechol are higher in wheat straw than in bagasse, but quantities of 2,4/2,5-dichlorophenol, 2,4,6-trichlorophenol are higher in bagasse than in wheat straw. 4-Chlorophenol, 2,6/3,4-dichlorophenol and 2,3,5/2,4,5-trichlorophenol are only identified in bagasse but 5,6-dichlorovanillin is identified in wheat straw (Table 6). The results indicate that 65–75% of the identified compounds are di and trichlorophenolic compounds. Among the various categories of reactive groups

Table 7 Concentrations (g/odt) of various resin and fatty acids in the effluent from wheat straw (W) and bagasse (B) pulps.

S. No.	*Name of the acids*	*C-stage*		*E-stage*	
		W	*B*	*W*	*B*
1	Palmitic	36.19	36.19	92.12	67.51
2	Heptadecanoic	0.52	5.17	0.80	9.81
3	Oleic/Linolenic/Elaidic	4.80	11.37	32.88	32.31
4	Stearic	5.68	10.85	16.73	22.50
5	Pimaric	0.41	1.55	—	1.73
6	Nonadecanoic	—	—	—	4.03
7	Sandaracopimaric	0.31	—	—	—
8	Isopimaric	1.29	1.81	—	0.52
9	Levopimaric/Palustric	0.38	0.52	27.69	10.96
10	Dihydroisopimaric	0.26	0.25	12.46	—
11	Arachidic	0.41	0.827	2.07	12.11
12	Neoabietic	—	—	1.73	2.31
13	Docosahexaenoic/ Heneicosanoic	0.77	0.25	12.69	6.63
14	Chlorodehydroabietic I	1.03	0.25	8.07	7.50
15	Erucic	0.72	3.62	—	13.27
16	Chlorodehydroabietic II	1.55	0.52	1.73	4.03
17	Behenic	5.17	3.62	7.50	7.50
18	Tricosanoic	5.17	0.41	2.30	21.92
19	12,14-Dich. dehydroabietic	0.52	0.46	2.88	10.38
20	Lignoceric	1.03	0.052	5.77	10.38
21	9,10,12,13-Tetrachlorostearic	0.31	0.52	2.88	1.15

g/odt: gram per oven dried tonne pulp.

catechols and other chlorophenolic compounds like vanillins, syringaldehydes, syringols etc contribute 69% share for both bagasse and wheat straw pulps. Data (Table 6) showed that the concentration of chlorinated guaiacols were higher in the spent extraction stage liquor than in the spent chlorination liquor. However, chlorinated catechols were predominent in chlorination stage effluents. This is similar to the spent bleaching liquor of wood pulps, and is presumably, due to the low solubility of chlorinated guaiacols and the sorption of these compounds on the fibers at low pH or due to the formation of chloroguaiacols only on the alkaline hydrolysis of chlorinated lignin.

Folke[18] has identified various chlorinated phenolics in combined spent bleaching liquors like, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, dichloroguaiacol, tetrachloroguaiacol, trichlorosyringol and dichlorocatechol during straw pulp bleaching by using DCE/HDD bleaching sequence. These compounds are also identified in Indian variety of wheat straw (Table 6) except 4-chlorophenol. The quantities of these identified compounds are higher in spent bleach liquor of Indian variety of wheat straw than reported by Folke[18] using bleaching sequence DCE/HDD.

Resin and fatty acids

Saturated fatty acids (SFA), unsaturated fatty acids (UFA), resin acids (RA) chlorinated resin acids (Ch.RA) and chlorinated fatty acids (Ch.FA) are identified in the effluents of C and E stages of the bleaching process in the SBL obtained from Indian varieties of wheat straw and bagasse pulps. In general the concentration of individual acids identified is higher in the E than in the C stage effluents. The results indicate that:

- Total identified fatty acid content is much higher than resin acid content.
- Quantities of total saturated fatty acid is much higher than unsaturated fatty acid.
- The quantities of chlorinated resin acid is comparatively much higher than chlorinated fatty acid.

In total, fatty acids palmitic acid has the highest contribution with substantial contributions from stearic and oleic/linolenic/elaidic acids. In case of bagasse, erucic, tricosanoic, arachidic and heptadecanoic acids also contribute substantially while nonadecanoic acid is found in SBL of bagasse. Docosahexaenoic/heneicosanoic, behenic and chlorinated fatty acids are also found in SBL of both bagasse and wheat straw.

Levopimaric/palustric and chloro resin acids contribute maximum share to total resin acids identified. In wheat straw SBL dihydroisopimaric acid has major share while minor quantity of sandaracopimaric acid is identified. The SBL of both wheat straw and bagasse have minor contribution of isopimaric and pimaric acids while dihydroisopimaric acid is present in SBL of bagasse in small quantity.

The identified fatty acids like palmitic, oleic, stearic, arachidic, behenic, lignoceric acid in Indian variety of wheat straw are comparable with those reported by Folke and Palle[19], while the observed concentration of palmitic acid is higher.

Toxicity

The quantities of various chlorophenolic compounds and resin and fatty acids present in C and E stage effluents have been compared with reported $^{96}LC_{50}$ values[4,20,21]. In case of bagasse the quantities of 2,4,6-trichorophenol (0.38 mg/L) and pentachlorophenol (0.1 mg/L) in E stage effluents are observed to be higher than the reported lower limits of $^{96}LC_{50}$ (0.34 and 0.096 mg/L respectively). In case of wheat straw the concentration of pentachlorophenol in E stage effluent (0.29 mg/L) is higher than the reported lower limit of $^{96}LC_{50}$ (0.096 mg/L). The concentration of all other chlorophenolic compounds are lower than or nearly equal to the reported values of $^{96}LC_{50}$.

Further the observed values of concentration of resin and fatty acids (Table 7) in C and E stage effluents of both bagasse and wheat straw are lower than the reported $^{96}LC_{50}$ values. However the concentration of levopimaric/palustric acids in E stage effluents (0.48 mg/L) of wheat straw is found to be of the same order as the reported lower limit of $^{96}LC_{50}$ values (0.5 mg/L).

The $^{96}LC_{50}$ values describe the toxicity of a particular compound when present alone. However, when a number of toxic compounds are present interfering effects may be observed. The threshold concentrations for various sublethal parameter are reported to be approximately between 0.05 and 0.1 of the $^{96}LC_{50}$ value. At concentration of pulp mill effluents in or below this range no sublethal stress have been observed. However, the concentrations of a large number of chlorophenolics, resin and fatty acids identified exceed their threshold concentrations. Hence, the untreated spent bleach liquor of wheat straw and bagasse generated in the laboratory can be considered toxic in nature. Such effluents should not be discharged without treatment.

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