

Gas chromatographic determination of pollutants in the chlorination and caustic extraction stage effluent from the bleaching of a bamboo pulp

C. Sharma, S. Mahanty, S. Kumar *, N.J. Rao

Institute of Paper Technology (U.O.R.), Saharanpur, 247 001 (U.P.), India

Received 28 August 1996; received in revised form 6 March 1997; accepted 12 March 1997

Abstract

The gas chromatographic detection and quantitative determination of various chlorophenolics as well as resin and fatty acids have been carried out in the chlorination and caustic extraction stage effluents generated in the laboratory by bleaching a bamboo pulp. A number of chlorinated phenols, catechols, guaiacols, syringaldehydes and resin acids as well as non-chlorinated saturated and unsaturated fatty acids together with resin acids have been detected. The concentration of various compounds detected have also been compared with the reported $^{96}\text{LC}_{50}$ values. © 1997 Elsevier Science B.V.

Keywords: Bamboo; Bleaching effluent; Chlorophenolics; Gas chromatography; Pollutants; Resin and fatty acids

1. Introduction

The dwindling forest cover and increasing demands of the paper, industry worldwide is increasingly requiring the use of hardwoods and nonwoods (agroresidues and grasses) for making paper. Bamboo (*Bambusa*), a grass, has been one of the most popular raw materials used by the Indian paper industry. It gives a long fibered pulp (comparable to softwoods) that forms a strong paper. With the diminishing forests in India bamboo has also, become scarce but is still used by a large number of paper mills, particularly in east-

ern and southern India.

The paper industry is a high pollution load industry. Among the various sections, bleaching often accounts for the largest fraction of toxicity. The pulp produced by digestion with chemicals is brownish in color and requires bleaching to produce pulps of acceptable brightness. In developing countries the use of chlorine and other chlorinated compounds such as calcium or sodium hypochlorite with an intermediate caustic extraction is common for nonwoody materials.

The compounds responsible for the toxicity of chlorination (C) and caustic extraction (E) stage effluents are chlorophenolics together with resin and fatty acids [1,2]. The chlorophenolics are formed during the C-stage of pulp bleaching and

* Corresponding author. Tel: +91 132 727062; fax: +91 132 727387.

are solublized in the E-stage. The nature and amount of chlorophenolics formed will depend upon the nature of the lignin and the bleaching conditions [3,4]. The resin and fatty acids found in bleach plant effluent originate from the fibrous raw material. Their amount depends on the species and on the degree of washing of the unbleached pulp.

During the last two decades intense research efforts have been devoted to the identification of the various compounds [5–10] in bleach plant effluents and to the investigation of their possible biological effects [11–15]. These studies have been performed mostly on softwoods. Very little information is available on the nature and the quantities of various compounds present in bleach plant effluents formed from Indian varieties of hardwoods or agroresidues. In the present investigation we report the results of the detection and quantitative determination of various pollutants formed during the chlorination and extraction stages of the bleaching of bamboo pulp.

2. Experimental

The chlorophenols and fatty acids used were obtained from the Sigma Chemical Company (St. Louis, USA) and Aldrich Chemical Company (Milwaukee, USA). The chlorocatechols, chloroguaiacols, chlorovanillins, chlorosyringaldehydes, chlorosyringols, resin acids and chloro fatty acids were supplied by Helix Biotech. Corporation (Richmond, B.C. Canada). Solvents comprising *n*-hexane, acetone, diethyl ether and methyl tertiary butyl ether used were HPLC grade. Analytical grade acetic anhydride was used after redistillation. Other reagents used for detection studies were of analytical reagent grade. Standard solutions of chlorophenols were prepared in acetone/water (10:90), resin and fatty acids in methanol/diethyl ether (10:90) solution.

Unbleached washed (bamboo) kraft pulp was provided by Central Pulp and Paper Research Institute (CPPRI), Saharanpur. Tappi Test method T₂₃₆ cm-85 was used to determine the residual lignin content (kappa number = 37.4) of the pulp.

Pulp bleaching was carried out in more than one bleaching stages. A fraction (70%) of the chlorine demand ($0.25 \times$ kappa number) was applied as elemental chlorine in chlorination stage. All chemicals were applied as %O.D. (oven dried) pulp.

Unbleached pulp (35 g O.D. basis) was bleached under the conditions shown in Table 1. The volumes of effluent generated in the C and E stage were 1.81 and 2.02 l, respectively. The effluents were characterized by pH, total dissolved solids, BOD₅ (biochemical oxygen demand), COD (chemical oxygen demand) [16] and color 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 [5]. The E-stage effluent (500 ml) or the C-stage effluent (1000 ml) was adjusted to pH 2 and extracted with 200 and 400 ml of 90:10 diethyl ether/acetone mixture for 48 h, respectively with intermittent shaking. Extraction of resin and fatty acids from effluents has been achieved as suggested by Voss and Rapsomatiotis [8]. The effluent (E-stage 50 ml or C-stage 100 ml) was adjusted to pH 9 and extracted with equal volume of methyl tertiarybutyl ether for 1 h.

Chlorophenols as acetyl derivatives [17], resin and fatty acids as methyl esters [18] were analysed using Shimadzu gas chromatograph (Model GC-9A). The GC conditions are given in Table 2. Retention times (RT) were determined using standard solutions of various chlorophenolic compounds, resin and fatty acids. In each case 1 ml sample was derivatized and 1 μ l of the derivatized extract was injected into the column.

Table 1
Bleaching conditions

Parameters	C-stage	E-stage
Cl ₂ applied (% (demand))	70	—
NaOH applied (% (OD pulp))	—	03
Consistency (%)	3.5	10
pH	1.8–2.0	11–12
Temperature (°C)	25	60
Time (min)	60	75

All chemicals charged as %O.D. (oven dried) pulp.

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

Parameters	HR-1	OV-101
Detector	FID	FID
Detector range	10°	10°
Chart speed (cm min ⁻¹)	5	5
Sample size (μl)	0.5–1	0.5
Injection (min) (split less)	2	2
Column dimensions	30 m × 0.32 mm	25 m × 0.32 mm
Film thickness	0.25 μm	0.27 μm
Injection and detector temp (°C)	275	300
Column temperature (°C)	80 for 3 min	190 for 4 min
	80–160 at 2°C min ⁻¹	190–210 at 1°C min ⁻¹
	160 for 5 min	210–230 at 2°C min ⁻¹
	160–260 at 10°C min ⁻¹	230–250 at 3°C min ⁻¹
	260 for 15 min	250 for 15 min

3. Derivatization procedure

3.1. Chlorophenolics

To 4.5 ml of sample (or diluted sample) taken in teflon lined screw capped glass tube, 0.5 ml of 0.5 M Na₂HPO₄ and 0.05 ml of acetic anhydride were added. After adding 1 ml of *n*-hexane, the mixture was shaken for 3 min and 0.5–1.0 μl of the hexane extract was injected into the HR-1 column.

3.2. Resin and fatty acids

Resin and fatty acids were derivatized with dropwise addition of ethereal solution of diazomethane to 1 ml of the sample till a yellow color persisted for some time. The excess diazomethane was destroyed by dropwise addition of glacial acetic acid. The resulting solution was evaporated to dryness with a current of nitrogen gas. The dried mass was dissolved in methanol/diethylether (10:90) solution and making the total volume 1 ml. A 0.5 μl of this solution was injected into OV-101 column.

3.3. Extraction efficiency determination

3.3.1. Chlorophenolics

The standard solution of 0.1 mg chlorophenolics (1000 ml) was extracted and derivatized. Another solution of 0.1 mg chlorophenolics (1 ml of 100 mg l⁻¹) was derivatized without extraction. The extracted and nonextracted chlorophenolics derivatives were injected into HR-1 column (0.5 μl each) and the peak areas were determined in both the cases. The extraction efficiency (EF) was calculated from the equation:

$$EF(\%) = \frac{\text{Peak area of extracted sample}}{\text{Peak area of nonextracted sample}} \times 100 \quad (1)$$

3.3.2. Resin and fatty acids

The standard solution of resin and fatty acids (50 ml of 0.1 mg l⁻¹) was extracted and derivatized. Another solution (1 ml of 5 mg l⁻¹) containing 5 μg of resin and fatty acid was derivatized without extraction. The extracted and nonextracted resin and fatty acid were injected into OV-101 column (0.5 μl each) and the peak areas were determined in both the cases. The extraction efficiency was calculated using the Eq. (1).

The various chlorophenolics, resin and fatty acids were detected by matching the retention time with those of pure standards within ± 0.1 min. For some compounds the value of RT were nearly the same. In these cases the average quantities were determined. For carrying out quantitative analysis, response factor (RF) and extraction efficiency (EF) of various compounds were determined.

4. Results

The characteristics of effluents generated in laboratory are shown in Table 3. The values of RT and concentration of various detected chlorophenolics, resin and fatty acids are given in Table 4 and Table 5, respectively. The values of RT show that most of the chlorophenolics and resin and fatty acids can be separated on Ulbon HR-1 glass

Table 3
Characteristics of effluents generated in the laboratory

Parameters	Effluent	
	C-stage	E-stage
pH	2.2	10.7
Dissolved solid (mg l ⁻¹)	1088.0	1288.0
BOD (mg l ⁻¹)	120.0	136.0
COD (mg l ⁻¹)	593.0	722.0
Colour (Pt. Co)	1134.0	3875.0

capillary and fused silica OV-101 capillary columns, respectively. The quantities of various categories of chlorophenolics, resin and fatty acids expressed as g per tonne of oven dried pulp

Table 4
Retention time and concentrations of various chlorophenolics in the effluent

Chlorophenolics	RT (min)	C-stage (g odt ⁻¹)	E-stage (g odt ⁻¹)
2-Chlorophenol	7.82	0.21	—
3-Chlorophenol	8.89	—	4.61
4-Chlorophenol	9.03	0.21	1.15
2,6-Dichlorophenol	12.96	0.51	—
2,5-Dichlorophenol ^a	13.97	1.81	9.52
2,4-Dichlorophenol ^a	14.05	1.81	9.52
2,3-Dichlorophenol	15.71	—	0.06
3,4-Dichlorophenol	17.51	0.36	—
6-Chloroguaiacol	17.94	—	0.11
2,4,6-Trichlorophenol	19.10	2.58	25.38
2,3,5-Trichlorophenol	22.30	0.51	0.23
2,4,5-Trichlorophenol	22.75	1.03	—
2,3,4-Trichlorophenol	24.61	0.26	—
4,6-Dichloroguaiacol	24.88	—	1.15
3,4-Dichloroguaiacol	25.44	—	1.15
4,5-Dichloroguaiacol	27.96	—	2.88
3,6-Dichlorocatechol	28.51	7.75	—
3,5-Dichlorocatechol	29.65	23.78	—
3,4,6-Trichloroguaiacol ^a	30.49	0.18	2.88
6-Chlorovanillin ^a	30.58	0.18	2.88
3,4,5-Trichloroguaiacol	34.01	0.36	6.35
3,4,6-Trichlorocatechol	36.29	1.55	—
2-Chlorosyringaldehyde	38.75	20.68	—
Pentachlorophenol	39.21	2.07	46.16
3,4,5-Trichlorocatechol	39.79	35.67	16.15
Tetrachloroguaiacol	40.58	0.51	3.46
Trichlorosyringol	41.70	0.26	2.30
Tetrachlorocatechol	45.96	17.06	6.34
2,6-Dichlorosyringaldehyde	46.38	7.24	46.16

odt, Oven dried tonne pulp.

^a Indicate single unresolved peak.

(g odt⁻¹) are given in Table 6 and Table 7, respectively.

5. Discussion

5.1. Chlorophenols

Six categories of chlorophenolics are present in spent bleach liquor obtained from Indian variety of bamboo pulp. These are chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols, chlorosyringaldehydes and chlorovanillins. The retention times and concentration of various chlorophenolics observed in the bamboo spent bleach liquor are given in Table 4.

Table 5
Retention time and concentrations of various resin and fatty acids in the effluent

Acids	RT (min)	C-stage (g odt ⁻¹)	E-stage (g odt ⁻¹)
Palmitic ^a	4.92	49.11	154.00
Heptadecanoic ^a	6.55	0.36	3.05
Oleic ^{b,f}	8.07	2.58	8.07
Linolenic ^{b,f}	8.11	2.58	8.07
Stearic ^a	8.71	1.03	17.30
Pimaric ^c	11.30	0.31	0.29
Sandaracopimaric ^c	11.70	1.55	5.77
Isopimaric ^c	12.90	2.58	16.15
Dihydroisopimaric ^c	13.90	0.52	—
Arachidic ^a	15.00	0.41	3.46
Neoabietic ^c	17.90	1.55	1.15
Chlorodehydroabietic I ^d	21.60	1.03	8.07
Chlorodehydroabietic II ^d	23.00	3.62	3.46
Tricosanoic ^a	28.90	3.10	1.73
12,14-Dich.dehydroabietic ^d	30.40	1.03	1.15
Lignoceric ^a	33.30	5.17	17.30
9,10,12,13-Tetrach.stearic ^c	35.70	2.06	1.73

odt, Oven dried tonne pulp.

^a Saturated fatty acid.

^b Unsaturated fatty acid.

^c Resin acid.

^d Chloro resin acid.

^e Chloro fatty acid.

^f Indicate single unresolved peak.

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 less studied. It varies significantly with source. Some grass lignins are thought to contain mainly *p*-coumaryl units but other grass lignins appear to approximate the hardwood lignin [19]. 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 they are solubilized in alkaline condition (E-stage). The nature and concentration of different chlorophenolic compounds formed that ultimately end up in SBL depend upon quantity of lignin i.e., kappa number of pulp, nature of lignin, and bleaching conditions, i.e., chlorine charged, pH, temperature and consistency (expressed as g O.D. pulp per 100 g pulp suspension).

Among the various chlorophenolics found in C-stage effluent the maximum contribution came from 3,4,5-trichlorocatechol (35.67 g odt⁻¹). Other significant contribution came from 3,5-dichlorocatechol (23.78 g odt⁻¹), 2-chlorosyringaldehyde (20.68 g odt⁻¹), tetrachlorocatechol (17.06 g odt⁻¹). Small contributions were made by 2,6-dichlorosyringaldehyde (7.24 g odt⁻¹), 3,6-dichlorocatechol (7.75 g odt⁻¹). Minor quantities of 2,4/2,5-dichlorophenol (3.62 g odt⁻¹), 2,4,6-trichlorophenol (2.58 g odt⁻¹), pentachlorophenol (2.07 g odt⁻¹), 3,4,6-trichlorocatechol (1.55 g odt⁻¹), 2,4,5-trichlorophenol (1.03 g odt⁻¹) were also present. Other chlorophenolic compounds detected in the effluent had concentration about 0.5 g odt⁻¹ or less.

In E-stage maximum contribution came from 2,6-dichlorosyringaldehyde (46.16 g odt⁻¹) and pentachlorophenol (46.16 g odt⁻¹). Significant contribution came from 2,4,6-trichlorophenol (25.38 g odt⁻¹), 2,5/2,4-dichlorophenol (19.04 g odt⁻¹), 3,4,5-trichlorocatechol (16.15 g odt⁻¹).

Table 6
Quantity of various categories of chlorophenolics in the bleaching effluent

Chlorophenolics	C-stage (g odt ⁻¹)	E-stage (g odt ⁻¹)	(C + E)	
			(g odt ⁻¹)	%
Chlorine substitution				
Monochlorophenols	21.28	8.75	30.03	9.53
Dichlorophenols	43.26	70.44	113.70	36.09
Trichlorophenols	42.40	53.29	95.69	30.38
Tetrachlorophenols	17.57	9.80	27.37	8.69
Pentachlorophenols	2.07	46.16	48.23	15.31
Reactive group				
Phenols	11.36	96.63	107.99	34.28
Catechols	85.81	22.49	108.30	34.38
Guaiacols	1.05	17.98	19.03	6.04
Other phenols	28.36	51.34	79.70	25.30
Total chlorinated phenolics	126.58	188.44	315.02	100.00

Minor quantities of tetrachlorocatechol (6.34 g odt⁻¹), 3,4,5-trichloroguaiacol (6.35 g odt⁻¹), 3,4,6-dichloroguaiacol/6-chlorovanillin (5.76 g odt⁻¹), 3-chlorophenol (4.61 g odt⁻¹), trichlorosyringol (2.3 g odt⁻¹), tetrachloroguaiacol (3.46 g odt⁻¹), 4,5-dichloroguaiacol (2.88 g odt⁻¹), 4-chlorophenol, 4,6-dichloroguaiacol and 3,4-dichloroguaiacol (1.15 g odt⁻¹ each) were also present. Other chlorophenolic compounds detected in the effluent had concentrations about 0.5 g odt⁻¹ or less.

The chlorophenolics can be categorized on the basis of chlorine substitution. The total quantities of mono, di, tri, tetra and penta chlorophenolic compounds (g odt⁻¹) in C-stage, E-stage and combined spent bleach liquor (C stage + E stage) are given in Table 6. Dichloro and trichloro compounds contribute 66% of the total detected chlorophenolic compounds in the combined SBL. Similarly the components can be categorized based on the reactive groups. Catechols, vanillins, syringaldehydes and syringols contribute 60% of the total chlorophenolics components in the combined SBL. The concentration of chlorinated guaiacols is higher in the E-stage liquor than in the C-stage liquor. The chlorinated catechols predominate in C-stage effluent. This behavior is similar to the behavior observed with effluents of wood pulps. This is presumably, due to the low solubil-

ity of chlorinated guaiacols at low pH and the sorption of these compounds on the fibers. Alternatively these chloroguaiacols may form only upon the alkaline hydrolysis of chlorinated lignin in the E-stage.

5.2. Resin and fatty acids

Table 5 gives various categories of resin and fatty acids detected in the effluent. These are saturated fatty acids, unsaturated fatty acids, resin acids chlorinated resin and fatty acids. The quantities of resin and fatty acids are higher in E-stage effluent than in C-stage effluent. This is due to the higher solubility of resin and fatty acids in alkaline media. The quantities of various chlorinated and non-chlorinated resin and fatty acids in C-stage, E-stage and combined spent bleach liquor (C stage + E stage) are given in Table 7. From the table we can conclude:

1. The quantities of fatty acids are much higher than resin acids.
2. The quantities of total saturated fatty acids are much higher than unsaturated fatty acids.
3. The quantities of chlorinated resin acids are much higher than chlorinated fatty acids.

The palmitic acid was the most significant saturated fatty acid (203 g odt⁻¹) of the detected resin and fatty acids. Other major saturated fatty acids

Table 7
Quantity of various categories of resin and fatty acids in the bleaching effluent

Acids	C-stage (g odt ⁻¹)	E-stage (g odt ⁻¹)	(C+E)	
			(g odt ⁻¹)	%
Non-chlorinated				
Saturated fatty acids	59.18	196.84	256.02	77.74
Unsaturated fatty acids	5.16	16.14	21.30	06.47
Resin acids	6.51	23.36	29.87	09.07
Chlorinated				
Chloro fatty acids	2.06	1.73	3.79	01.15
Chloro resin acids	5.68	12.68	18.36	05.57
Total resin and fatty acids (both chlorinated and non chlorinated)	78.59	250.75	329.34	100.00

were lignoceric (22.5 g odt⁻¹) and stearic acid (18.33 g odt⁻¹). Minor quantities of heptadecanoic, arachidic, tricosanoic acid (3.4–4.8 g odt⁻¹) were also detected. Among the various unsaturated fatty acids oleic/linolenic acids were found in significant amounts (about 21 g odt⁻¹).

Isopimaric was the major resin acid (18.73 g odt⁻¹) detected. Significant amount of sandaracopimaric acid (7.32 g odt⁻¹) was also detected. Minor quantities (0.5–2.7 g odt⁻¹) of pimaric, dihydroisopimaric and neoabietic acid were detected. Both the isomers of monochlorodehydroabietic acid contributed major share (16.18 g odt⁻¹) to the detected chloro resin acids. Minor quantities of 12,14-dichloroabietic acid (2.18 g odt⁻¹) and 9,10,12,13-tetrachlorostearic acid (3.79 g odt⁻¹) were also detected.

6. Toxicity

The toxicity of the effluent was evaluated by comparing the quantities of various chlorophenolics, resin acids and fatty acids detected in the effluent with the values reported in the literature [4,20,21]. ⁹⁶LC₅₀ is the lethal concentration at which 50% of the test organisms will get killed when the test organism is exposed to the toxicant for a period of 96 h under standard test conditions. Reported ⁹⁶LC₅₀ values indicate that chlorophenolics, resin acids, unsaturated fatty

acids and chlorinated resin and fatty acids are toxic. Resin acids are more toxic than unsaturated fatty acids.

The concentrations of 2,4,6-trichlorophenol (0.44 mg l⁻¹) and pentachlorophenol (0.80 mg l⁻¹) in E-stage and dichlorocatechols (0.61 mg l⁻¹) in C stage were found to be higher than the reported respective ⁹⁶LC₅₀ values. The concentrations of all other chlorophenolics, resin and fatty acids were less than the respective ⁹⁶LC₅₀ values.

The ⁹⁶LC₅₀ value indicates the toxic concentration of a particular compound when present alone. However, when a number of toxic compounds are present, interfering effect may be observed. Substantial evidence now exists which indicates that the threshold toxic concentration may be as low as 5–10% of ⁹⁶LC₅₀ values [22].

Apparently concentrations of a large number of chlorophenolics, resin and fatty acids may exceed their respective threshold concentrations. So it can be inferred that the untreated spent bleach liquor of bamboo is of environmental concern.

Acknowledgements

Financial assistance for this work provided by the Council of Scientific and Industrial Research (CSIR), New Delhi, India is gratefully acknowledged.

References

- [1] J.M. Leach, A.N. Thakore, *J. Fish Res. Board Canada* 32 (1975) 1249–1257.
- [2] J.M. Leach, A.N. Thakore, *Prog. Water Technol.* 9 (1977) 787–798.
- [3] R.H. Voss, J.T. Wearing, A. Wong, *Tappi* 64 (3) (1981) 167–170.
- [4] R.H. Voss, J.T. Wearing, R.D. Mortimer, T. Kovacs, A. Wong, *Pap. Puu* 62 (12) (1980) 809–814.
- [5] K. Lindstrom, J. Nordin, *J. Chromatogr.* 128 (1976) 13–26.
- [6] K.P. Kringstad, K. Lindstrom, *Environ. Sci. Technol.* 18 (8) (1984) 236A–248A.
- [7] J. Knuutinen, *J. Chromatogr.* 248 (1982) 289–295.
- [8] R.H. Voss, A. Rapsomatiotis, *J. Chromatogr.* 346 (1985) 205–214.
- [9] B. Holmbom, K.J. Lehtinen, *Pap. Puu* 11 (1980) 673–684.
- [10] T.M. Xie, Z.J. Lu, *Nord. Pulp Pap. Res. J.* 2 (1987) 56–60.
- [11] C.C. Walden, T.E. Howard, *Tappi* 60 (1) (1977) 122–125.
- [12] I.H. Rogers, J.C. Davis, G.M. Kruzynski, H.W. Mahood, J.A. Servizi, R.W. Gordon, *Tappi* 58 (7) (1975) 136–140.
- [13] B. Holmbom, R.H. Voss, R.D. Mortimer, A. Wong, *Environ. Sci. Technol.* 18 (5) (1984) 333–337.
- [14] D.W. Reeve, P.F. Earl, *Pulp Pap. Can.* 90 (4) (1989) 128–132.
- [15] R. Crooks, J. Sikes, *Appita* 43 (1) (1990) 67–76.
- [16] L.S. Clesceri, A.E. Greenberg, R.R. Trussell, *Standard Methods*, 17th ed., Pub. American Public Health Association, 1989, p. 2(74), 4(94), 5(2) and 5(12).
- [17] K. Abrahamsson, T.M. Xie, *J. Chromatogr.* 279 (1983) 199–208.
- [18] A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd ed., Pub. English Language Book Society, London, 1975, p. 292.
- [19] J.M. Harkin, in: G.W. Butler, R.W. Bailey (Eds.), *Chemistry and Biochemistry of Herbage*, Academic Press, New York, 1973, vol. 1, Ch. 7.
- [20] S.A. Heimbürger, D.S. Blevins, J.H. Bostwick, G.P. Donnini, *Tappi* 71 (11) (1988) 69–77.
- [21] H.B. Lee, T.E. Peart, J.M. Carron, *J. Chromatogr.* 498 (1990) 367–379.
- [22] *Environmental Management in the Pulp and Paper Industry*, UNEP-Industry and Environment Manual Series, 1981, vol. 1, pp. 1–59 and 1–64.