Effect of Persulphate Pretreatment on the Formation of Chlorinated Phenolic Compounds

Divya Prakash
Indian Institute of Technology
Roorkee, India
divya1sharma1@gmail.com

Rachna Malhotra
Indian Institute of Technology
Roorkee, India

Satish Kumar
Indian Institute of Technology
Roorkee, India

Abstract—**Estimation of different chlorophenolic compounds formed during CEH bleaching of oxygen and persulphate-peroxide pretreated wheat straw soda pulp has been carried out. The results have been compared with CEH bleaching without any pretreatment. The results show that CEH effluent is toxic in nature as it contains many chlorophenolic compounds with concentration exceeding the 96LC50 values. Results indicate that chlorocatechols are predominant in CEH, cholorosyringaldehydes in (PxP)CEH and chlorophenols in OCEH bleaching effluents. The results further indicate that persulphate-peroxide pretreatment reduces the amount of chlorinated phenolics formed by 36% to 109.9g/t and the number of identified chlorophenolics to 24 from 26 in CEH. Oxygen pretreatment reduces the amount of chlorinated phenolics by 86% to 22.8 g/t and the number of chlorophenolics to 14 thereby reducing the toxicity of the effluent.**

Keywords- ***Chlorophenolics, persulphate, prebleaching, wheat straw, bleaching effluent***

I. INTRODUCTION

Chlorophenolic compounds such as chlorophenols, guaiacols and catechols are produced as degradation products of lignin during pulp bleaching using chlorination processes [1, 2].The compounds responsible for the toxicity of C stage effluent are mainly chlorophenols, which contributes 80% of the toxicity at a charge equivalent to 50% of chlorine demand [3]. This effluent is partly responsible for contributing effluent color, acute/chronic toxicity, mutagenicity and carcinogenicity [4,5,6]. The E stage effluent contributes to 90% of acute toxicity, with major species being 3,4,5-trichloroguaiacol, tetrachloroguaiacol [4] and several fatty acids (e.g. mono & di chlorodehydroabietic acid and epoxystearic acid) [1]. The hypochlorite bleaching is the major contributor of chloroform and carbon tetrachloride which are classified as carcinogen [4,5,6].

Nature and quantities of various chlorophenolic compounds present in bleach plant effluents formed from wood and non wood based pulps is reported [7,8,9,10] but no information is available on the effect of sodium persulphate pretreatment stage on the formation of organochlorine compounds. The reduction of residual lignin before bleaching process reduces the emission of chlorophenolic compounds, thus persulphate pretreatment effect on chlorophenolic generation had to be established. In the present communication we report the results on the generation of different chlorophenolics formed during the CEH bleaching of wheat straw soda pulp using persulphate-peroxide (PxP) pretreatment. The results are compared with oxygen pretreatment.

II. EXPERIMENTAL

All chlorophenols used were obtained from Aldrich (Milwaukee, WI, USA). Chlorocatechols, chloroguaiacols, chlorovanillins, chlorosyringaldehydes and chlorosyringols were supplied by Helix Biotech (Richmond BC, Canada). Standard solutions of chlorophenols were prepared in 10:90 acetone-water. Solvents viz. n-hexane and acetone used was of HPLC grade. Analytical grade acetic anhydride was used after redistillation. Other reagents used for detection were of analytical reagent grade.

Unbleached washed wheat straw soda pulp was taken from a nearby mill. The kappa number (residual lignin) of the pulp was determined (Tappi Test Method T_{236} cm-85) and was found to be 23.7.

- Oxygen pre-bleaching

Oxygen prebleaching was performed in autoclaves by adding calculated amount of NaOH (40gpl) and $MgSO_4$ in the disintegrated pulp and10% pulp consistency was maintained. After expelling air, autoclaves were filled with oxygen gas to a pressure of 6kg/cm^2 and were placed in a glycol bath preheated

to 100^{0}C for a period of 75 minutes. The autoclaves were taken out, cooled in water to room temperature. Pulp was taken out and washed.

- Persulphate / Persulphate peroxide pre-bleaching

Optimized quantity of sodium persulphate was charged in to disintegrated pulp sample along with NaOH and EDTA. 10% pulp consistency was maintained. Plastic bags were placed in water bath at 40^{0}C and pulp was mixed several times. After completion of 4h, plastic bags were removed, pulp was washed and effluent was collected for environmental parameters. In persulphate-peroxide prebleaching, peroxide and $MgSO_4$ were also added along with other chemicals.

The chlorine demand was calculated from the formula:

Chlorine demand (%) = 0.25 X Kappa number

Pulp bleaching is carried out in more than one bleaching stage. Seventy percent of chlorine demand has been applied as elemental chlorine in the chlorination stage. All chemicals are applied as percentage oven dried (%OD) pulp. Unbleached pulp, oxygen pretreated and (PxP) pretreated pulps (equivalent to 25g OD) were bleached in the laboratory to generate effluents. The bleaching conditions are shown in Table 1. Bleached pulp after each stage of CEH bleaching was washed on a Buchner funnel and the effluent collected was transferred to 2L volumetric flask and the volume was made up to the mark by adding distilled water. The collected effluents were combined and this effluent was used for analysis of chlorophenolics.

TABLE I. BLEACHING CONDITIONS OF WHEAT STRAW PULP

Condition	Bleaching sequence										
	CEH			*OCEH*				*(PxP)CEH*			
	C	*E*	*H*	*O*	*C*	*E*	*H*	*(PxP)*	*C*	*E*	*H*
aCl (%)	4.15	-	1.78		1.75	-	0.75	-	1.75	-	0.75
NaOH (%)	-	2.38	-		-	1.18	-	2.0	-	1.18	-
H_2O_2 (%)	-	-	-	-	-	-	-	0.5	-	-	-
$Na_2S_2O_8$ (%)	-	-	-	-	-	-	-	2.5	-	-	-
O_2 pressure	-	-	-	6	-	-	-	-	-	-	-
$MgSO_4$ (%)	-	-	-	0.2	-	-	-	0.2	-	-	-
EDTA (%)	-	-	-		-	-	-	0.5	-	-	-
Temp. (ºC)	Amb.	70	40	100	Amb.	70	40	40	Amb.	70	40
Cy (%)	3.0	10.0	7.0	10	3.0	10.0	7.0	10	3.0	10.0	7.0
RT (min.)	45	60	210	75	45	60	210	240	45	60	210
Brightness(%)	-	-	80.2		-	-	80.6		-	-	80.5
Viscosity (cP)	-	-	18.6		-	-	19.5		-	-	18.9

- Separation of Chlorophenolics from the effluent:

The procedure suggested by Lindstrom *et.al.* [11] was followed to achieve the separation of chlorophenolics from the effluents. A schematic presentation of the method followed is depicted in the flow chart (Figure 1). The pH of the combined effluent was adjusted to 2. Then the effluent was extracted for 48h with 400ml of 90% ethyl ether and 10% acetone mixture per liter of effluent.

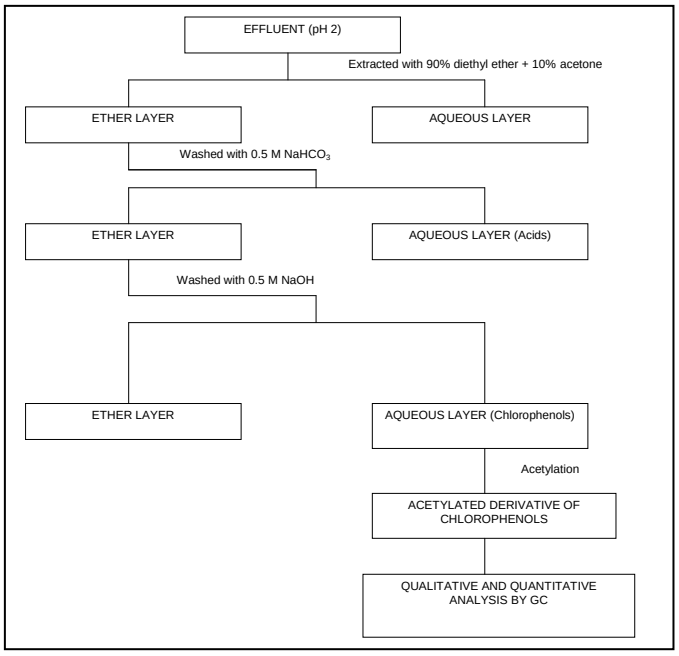

Figure 1. Separation of chlorophenolic compounds from effluents

III. DERIVATIZATION PROCEDURE

4.5ml of the sample of standard chlorophenolics was taken in a PTFE lined screw capped glass tube and 0.5ml of buffer solution of 0.5M Na_2HPO_4 was added. 1ml of n-hexane and 0.05ml of acetic anhydride were added to derivatize and extract the chlorophenolics. The mixture was shaken for 3 minutes and 1μl of acetyl derivative taken from the hexane layer through a syringe, was injected into the GC column [11].

Gas chromatographic studies were carried out on a Shimadzu gas chromatograph Model GC-9A. The analysis of chlorophenols as acetyl derivatives were performed on Ulbon (Shimadzu) HR-1 glass capillary column. The GC conditions maintained are given in Table 2. The identification of the constituent was done by matching the retention time ($\pm$0.1) of a particular peak with that of pure reference standard. The quantitative analysis has been done using peak area, response factor and extraction efficiency values.

IV. RESULTS AND DISCUSSION

The concentration of various detected chlorophenolics in the combined effluent has been measured as mg/l and converted it in to g/t OD pulp. These values are given in Table 3. The quantities of various categories of chlorophenolics in the combined effluent are shown in Figures 2-4. The effect of oxygen and (PxP) pretreatment on the reduction pattern of chlorophenolics is shown in Figure 5.

- CEH effluent

A total of 26 compounds are detected In combined CEH effluent with 5 compounds viz. 2,3,4,6-tetrachlorophenol, 5-chloroguaiacol, 5-chlorovanillin, tetrachlorocatechol and trichlorosyringol contributing a major share. The category wise formation of chlorophenolics follows the order:

Chlorocatechols » Chlorosyringols > Chlorophenols ≥ Chlorovanillins > Chloroguaiacols » Chlorosyringaldehydes.

Results are similar to that reported by different authors [7, 8] that chlorocatechols, guaiacols and syringols are byproducts of pulp bleaching with chlorine. Total quantity of chlorophenolics formed in CEH effluent is 171.9g/t of pulp, about 52% share is of chlorocatechols with tetachlorocatechol (60.9g/t) and 3,5 dichlorocatechol (17.8g/t) contributing major share. Chlorosyringols contribute 13% share to the total chlorophenolic formation, the contribution coming from only one compound trichlorosyringol (21.6g/t). Of the di, tri, tetra and pentachlorophenol, 2,3,4,6-tetrachlorophenol is found to have highest value 9.9g/t. 5-chlorovanillin contributes 78% share to total chlorovanillin formation value being 15g/t. Chloroguaiacols form 10% of total chlorophenols with 5-chloroguaiacol followed by 3,4 dichloroguaicol while chlorosyringaldehydes are lowest in quantity forming 3% of total chlorophenolic compounds with major contributor being 2,6 dichlorosyringaldehyde (3.2g/t).

Effluent toxicity depends upon concentration of individual compounds. The 96LC50 values indicate that pentachlorophenol, catechols, tri and tetrachloroguaiacol and 2,4,6-trichlorophenol are relatively more toxic than 2,4dichlorophenol and dichloroguaiacol. The concentration of pentachlorophenol (0.2mg/l), tetrachlorocatechol (5.1mg/l), dichlorocatechol (1.7mg/l) exceeds the upper limits of 96LC50. The concentration of 3,4,5-trichlorocatechol (0.02mg/l), dichloroguaiacol (0.4mg/l) and tetrachloroguaiacol (0.09mg/l) are lower than the lower limits of 96LC50 values. Quantity of trichloroguaiacol (0.13mg/l) is much lower than the lower limits of 96LC50 value. The 96LC50 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 concentration for various sub lethal parameters is reported to be approximately between 0.05 and 0.1 of the 96LC50 value. At the concentration of pulp mill effluents in or below this range no sub lethal stress has been observed. However, the concentration of some of the chlorophenolics identified exceeds their threshold concentrations. Hence, the untreated effluent generated from CEH bleaching sequence of wheat straw pulp can be considered toxic in nature.

- (PxP)CEH effluent

24 chlorophenolic compounds are detected In combined CEH effluent of (PxP)CEH sequence with total quantity being 109.9g/t. Results are given in Table 3. Although there is overall reduction in the total chlorophenolics generation yet quantities of some of the compounds is found to increase as shown in the Figure 5. The category wise formation of chlorophenolics follows the order: Chlorosyringaldehydes > Chloroguaiacols > Chlorosyringols ≥ Chlorophenols > Chlorocatechols > Chlorovanillins. The quantity of the total chlorophenolics is found to be higher in CEH effluent than (PxP)CEH effluent (Table 3). In CEH effluent chlorosyringaldehydes are found to be lowest but in (PxP)CEH sequence chlorosyringaldehydes (25% of the total) form a major proportion as shown in Figures 2 and 3.

In (PxP)CEH the overall quantity of chlorophenols (Di, tri, tetra and pentachlorophenol) is reduced from 19.4g/t to 17.9g/t but the quantity of pentachlorophenol has increased from 2.5g/t in CEH to 4.5g/t in (PxP)CEH. 2,3,4,6-tetrachlorophenol remains unchanged and 2,3-dichlorophenol is reduced from 0.6g/t to 0.3g/t. The quantity of chloroguaiacols is found to increase from 17.3g/t in CEH effluent to 23.9g/t in (PxP)CEH effluent. 3,6-dichloroguaiacol, 4,6-dichloroguaiacol, 3,4,6-trichloroguaiacol, 3,4,5-trichloroguaiacol are present in (PxP)CEH effluent but not in CEH effluent. The quantity of 3-chloroguaiacol, 6-chloroguaiacol, 4,5,6-trichloroguaiacol and tetrachloroguaiacol is increased and values are 2.8g/t, 7.4g/t, 4.1g/t and 1.4g/t respectively but the quantities of 4-chloroguaiacol and 5-chloroguaiacol are reduced to 0.1g/t and 0.2g/t respectively. Chlorovanillins are reduced from 19.3g/t in CEH to 8.9g/t in (PxP)CEH with 5-chlorovanillin quantity being reduced from 15g/t to 4.7g/t but 6-chlorovanillin is increased to 4.2g/t. Chlorocatechols are reduced substantially by (PxP) pretreatment to 14.7g/t in comparison to CEH where it is 89.7g/t (Figure 5). Major component of chlorocatechols in CEH were tetrachlorocatechol and 3,5-dichlorocatechol which are not formed in (PxP)CEH sequence. The quantities of three other chlorocatechols, 3-chlorocatechol, 4,5-dichlorocatechol and 3,4,5-trichlorocatechol are increased to 7.9g/t, 5.3g/t and 0.3g/t respectively. Trichlorosyringol is reduced in (PxP)CEH sequence from 21.6g/t to 18.1g/t. The concentration of pentachlorophenol (0.4mg/l) exceeds the higher limits of 96LC50 values (Table 4) while tetrachlorocatechol (5.08mg/l) formed in large quantities in CEH bleaching effluent is not detected in (PxP)CEH effluent. The concentration of dichlorocatechol (0.53mg/l) is near to lower limits of 96LC50 value. The concentration of 3,4,5-trichlorocatechol (0.03mg/l), trichloroguaiacol (0.45mg/l), dichloroguaiacol (0.56) and tetrachloroguaiacol (0.1mg/l) is found to be quite lower than the lower limits of 96LC50 value. Hence (PxP) pretreatment reduces the toxicity of the CEH effluent from (PxP)CEH sequence.

- OCEH Bleaching Sequence

The chlorophenolics formation is drastically reduced In the combined CEH effluent of OCEH bleaching sequence in comparison to CEH and (PxP)CEH sequence, the total quantity being 22.8g/t. The results are given in Table 3. The category wise formation of chlorophenolics follows the order:

Chlorocatechols > Chlorophenols > Chlorovanillins > Chloroguaiacols > Chlorosyringols.

Chlorophenols (Di, tri and tetrachlorophenols) have been reduced substantially in OCEH combined effluent in comparison to CEH effluent (Figure 4**)** while quantity of only 2,3-dichlorophenol is increased (0.8g/t) (Table 3). Also, 2,4-dichlorophenol is formed only in OCEH effluent, the value being

0.4g/t. In OCEH sequence, chloroguaiacols are reduced substantially, from 17.3g/t in CEH to 2.4g/t. Chlorovanillins are reduced from 19.3g/t to 5.2g/t and chlorosyringols from 21.6g/t to 1.7g/t. Results of the present study are similar to that reported by Voss et.al. that the generation of chlorovanillins and chloroguaiacols in bleaching are directly related to chlorine dosages but the reduction is much more than the reduction the reduction in chlorine dose.

In combined CEH effluent of OCEH sequence, 14 chlorophenolic compounds are detected while in CEH effluent of (PxP)CEH sequence 24 chlorophenolic compounds are detected (Table 3). By (PxP) pretreatment quantity of chlorophenols (di, tri, tetra and pentachlorophenol) in CEH effluent is reduced from 17.9g/t to 6.6g/t in oxygen pretreatment as given in Table 3. No formation of pentachlorophenol occurs by oxygen pretreatment. Chloroguaiacols are formed in much lower quantities by oxygen pretreatment than (PxP) pretreatment, the values being is 23.9g/t in (PxP) to 2.4g/t in oxygen. Chlorovanillins, chlorocatechols and chlorosyringols formation is also reduced substantially by oxygen pretreatment than (PxP) pretreatment as shown in Figure 5. But the quantity of 4-chloroguaiacol and 5-chloroguaiacol is higher in oxygen than (PxP).

The formation of chlorophenolics in the bleaching effluents depends upon chlorine charge. The lower amount of chlorine is used in the (PxP)CEH and OCEH sequences over CEH sequence, thereby forming lesser quantity of the total chlorophenolics in the present study which is in agreement with the results of many authors (3, 5, 9). However same quantity of chlorine is charged in (PxP)CEH and OCEH but the quantity of chlorophenolics generated in OCEH is lower than (PxP)CEH. The quantity of chlorine is also a function of pulp kappa number before CEH sequence. Oxygen pretreatment gives a pulp of lower kappa number (12.3) than (PxP) pretreated pulp (16.6). The chlorophenolic content is reduced substantially by oxygen delignification stage and highly toxic compounds like pentachlorophenol, tetrachlorocatechol, 3,4,5-trichloroguaiacol and tetrachloroguaiacol are not detected in OCEH effluent, thus the effluent toxicity decreases. The concentration of dichlorocatechol (0.44mg/l) and dichloroguaiacol is lower than the lower limits of reported 96LC50 values. 2,4-dichlorophenol is not detected in CEH or (PxP)CEH bleaching effluent but occurs in OCEH effluent, though its quantity (0.03mg/l) is much lower than the reported 96LC50 value.

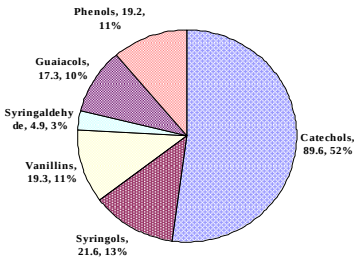

Figure 2. Proportions of various categories of chlorophenolics in CEH combined effluent

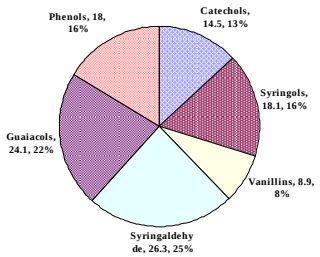

Figure 3. Proportions of various categories of chlorophenolics in (PxP)CEH combined effluent

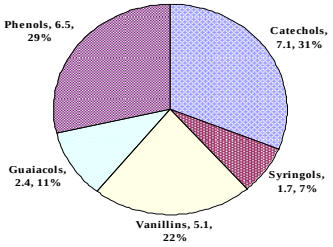

Figure 4. Proportions of various categories of chlorophenolics in OCEH combined effluent

V. CONCLUSION

- Predominant chlorophenolics in effluent are: CEH - Chlorocatechols, (PxP)CEH - Chlorosyringaldehydes and OCEH – Chlorophenols
- The untreated effluent from CEH sequence can be considered toxic in nature as the concentration of a large number of chlorophenolics identified exceeds their threshold concentrations.

(PxP) and oxygen prebleaching stages reduce the generation of chlorophenolics by 36% in (PxP)CEH and by 86% in OCEH.

REFERENCES

[1] Leech, J.M. & Thakore, A.N., (**1975**). Isolation and identification of constituents toxic to juvenile rainbow trout (Salmo gairdneri) in caustic extraction effluent from kraft pulp mill bleach plants. J. Fish Res. Board, Canada, **32**, 1249.

[2] Xie, Tian-Min & Lu, Zi-Jian., **(1987)**. A preliminary study of chlorophenolics in non-wood pulp bleaching effluents. Nor. Pulp & Pap. Res. J., **2**, 56-60.

[3] Voss, R.H., Wong, A. & Wearing, J.T., **(1981)**. Effect of softwood chlorination on the formation of toxic chlorinated compounds. Pulp & Pap. Can. J., 82, **2**, 97-105.

[4] Panwar, S., Mishra, S., Endlay, N., Mathur, R.M. & Kulkarni, A.G., **(2004)**. Toxicity reduction of bleach plant effluent by using chemical additives. IPPTA J., **6**, 3, 45–52.

[5] Szolosi, O. (**2003**). Water cycle with zero discharge at Visy Pulp and Paper, Tumut, NSW. *Water*, (Australia) **30**, 34-36.

[6] Savant, D.V.R. Abdul-Rahman and D.R. Ranade. **(2006)**. Anaerobic degradation of absorbable organic halides (AOX) from pulp and paper industry wastewater. *Biores. Technol*., **97,** 1092-1104.

[7] Sharma, C., Mohanty, S., Kumar, S. & Rao. N.J., **(1996)**. Gas chromatographic analysis of chlorophenolic, resin and fatty acids in effluents from bleaching processes of agricultural residues. Intern. J. Environ. Anal. Chem., **64**, 289-300.

[8] Prakash D., Kumar S., **(2013)** "Gas chromatographic studies of chlorophenols on the substitution of chlorine dioxide in Bamboo", Innovative Research in Chemistry, **1**: Issue 1, 14-21.

[9] Mc Kague, A.B. & Carlberg, G. Effluent characteristics & composition. Pulp Bleaching - Principles & Practices edited by Dence & Reeve.

[10] Axegård, P. & Renberg, L., (**1998)**. The minimal impact of bleached kraft mill effluent. Pulp & Pap. Can. J., **99**, 4, 85 -90.

[11] Lindstrom, K. & Nordin, J., **(1976)**. Gas chromatography mass spectrometry of chlorophenols in spent bleach liquors. J. Chromat., **128**, 13-26

TABLE II. GC CONDITIONS

Parameters	
Detector	FID
Detector range	10^{o}
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

TABLE III. CONCENETRATION CONCENTRATION (G/T OD PULP) OF CHLOROPHENOLICS DETECTED IN CEH EFFLUENT OF DIFFERENT BLEACHING AGENTS.

S.No	**Chlorophenolic compounds**	**Sequence**		
		CEH	*(PxP)CEH*	*OCEH*
1	2,5-Dichlorophenol	0.3	-	0.3
2	2,3-Dichlorophenol	0.6	0.3	0.8
3	2,4-Dichlorophenol	-	-	0.4
4	3-Chloroguaiacol	0.1	2.8	-
5	2,6-Dichlorophenol	5.8	-	0.4
6	4-Chloroguaiacol	0.1	0.1	0.1
7	5-Chloroguaiacol	7.1	0.2	1.6
8	6-Chloroguaiacol	2.3	7.4	-
9	2,3,6-Trichlorophenol	0.1	-	0.1
10	2,3,5-Trichlorophenol	-	2.8	-
11	3,4-Dichloroguaiacol	5.1	-	0.7
12	3,6-Dichloroguaiacol	-	5.8	-
13	4,6-Dichloroguaiacol	-	0.9	-
14	5-Chlorovanillin	15.0	4.7	3.9
15	4-Chlorocatechol	2.1	-	-
16	3,4-Dichlorocatechol	-	1.0	-
17	3,5-Dichlorocatechol	17.8	-	-
18	3,6-Dichlorocatechol	-	-	5.3
19	3,4-Dichlorophenol	-	0.8	-
20	2,3,4,6-Tetrachlorophenol	9.9	9.6	4.5
21	3-Chlorocatechol	4.2	7.9	1.8
22	6-Chlorovanillin	3.2	4.2	1.2
23	3,4,5-Trichloroguaiacol	-	0.6	-
24	3,4,6-Trichloroguaiacol	-	0.8	-
25	4,5,6-Trichloroguaiacol	1.5	4.1	-
26	2-Chlorosyringaldehyde	1.7	7.9	-
27	4,5-Dichlorocatechol	2.0	5.3	-
28	Pentachlorophenol	2.5	4.5	-
29	3,4,5-Trichlorocatechol	0.2	0.3	-
30	Tetrachloroguaiacol	1.1	1.4	-
31	Trichlorosyringol	21.6	18.1	1.7
32	3,4,6-Trichlorocatechol	2.4	-	-
33	2,6-Dichlorosyringaldehyde	3.2	18.4	-
34	5,6-Dichlorovanillin	1.1	-	-
35	Tetrachlorocatechol	60.9	-	-
Total		171.9	109.9	22.8