Monitoring of Chloro-Organic Compounds From Indian Paper Mills Wastewater

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ABSTRACT

Untreated and treated wastewater samples were collected from eight paper mills from different parts of India for the monitoring studies. Six categories of chlorophenolic compounds (chlorophenols (CP), chlorocatechols (CC), chloroguaiacols (CG), chlorosyringol (CS), chlorosyringaldehyde (CSA), and chlorovanillin (CV)) and four cRFA compounds, i.e. chlorodehydroabietic acid (CDAA), 12,14-dichlorodehydroabietic acid (DCDAA), 12,13-dichlorostearic acid (DCSA), and 9,10,12,13-tetrachlorostearic acid (TCSA) were detected in the paper mills wastewater. 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) was also detected in the wastewater samples of two mills. The concentration range of chlorophenolics, cRFA, and 2,3,7,8-TCDD detected in untreated wastewater of pulp and paper mills was 12-239 µg L^{-1}, 37-157 µg L^{-1}, and 0-5.4 ng L^{-1}, respectively. Among CP, 2,4-dichlorophenol, 2,5-dichlorophenol, and 2,4,5-trichlorophenols are the dominating compounds detected in paper mill wastewaters. It was observed that the removal of chloro-organics was low by activated sludge process (ASP) and the treated wastewater discharges from the paper mills still contained significant amounts of toxic compounds which are harmful for the receiving aquatic bodies.

Keywords: *AOX, chlorophenolics, chloro resin & fatty acids (cRFA), GC-MS, paper mill wastewater, 2,3,7,8-TCDD*

Introduction

India has more than 600 paper mills varying in size of production, type of product, and scattered all over the country. The country's paper is mainly manufactured from hardwood and bamboo fiber (40%) followed by agro waste (30%) and recycled fiber (30%) [1]. Every year this industry discharges millions of liters of highly polluted wastewater into the aquatic water receiving bodies [2, 3]. This industry consumes large volume of fresh water, next to agriculture sector and is also country's sixth largest consumer of energy [4].

Kraft pulping is the most commonly employed pulping process in Indian paper mills, which utilizes sodium hydroxide and sodium sulfide for dissolving the lignin component of wood to separate the fibers for papermaking [5, 6]. A large number of organic compounds are generated during the manufacture of paper. Many of these are simple aliphatic and aromatic compounds formed from degradation of lignin during pulping process. No two paper mills discharge identical wastewaters. Due to the diversity in the usage of raw materials, scale of production and wastewater treatment strategies, there is a wide variation in the discharges [7]. The larger mills have equipped with chemical recovery plant for recovery of chemicals from the spent liquor. This process is not economically viable for the smaller mills to operate [4]. As a result, the small scale paper mills and several medium sized mills are considered to be more polluting since they discharge their wastewater generated from pulping and bleaching sections, directly into the receiving water bodies [8].

Chlorinated organic compounds both aliphatic and aromatic are generated during bleaching process. The bleaching agent conventionally used is elemental chlorine, which is cost-effective but it generates group of toxic compounds in wastewaters. Among these compounds, chlorinated phenolics, cRFA, chlorinated dioxins and furans are primarily generated from chlorination and alkali extraction stages. As the application of elemental chlorine leads to the generation of more toxic compounds, some Indian paper mills have also started using alternative bleaching agents such as chlorine dioxide, hydrogen peroxide, elemental oxygen and ozone. The discharge limit for AOX in case of large paper mills wastewater has been notified as 1.0 kg per ton of paper production [9, 10].

Simple aliphatic and aromatic compounds are degraded in the biological treatment practiced by the Indian paper industries. To some extent some lower substituted chlorinated phenolics are also degraded. But tri, tetra, penta chlorophenolics, cRFA, chlorinated dioxins and furans, are not effectively degraded and persist in treated wastewaters. Thus the wastewater is expected to contain many of such compounds in varying proportions depending upon the raw material used (soft wood, hard wood, agricultural residues, grasses etc), dose and nature of bleaching chemicals used, wastewater treatment process adopted by the paper industry.

More than 500 different chlorinated and non chlorinated organic compounds have been identified in the wastewaters of paper industry. This information is based largely on soft woods or some hard woods species from developed countries. India is using agricultural residues, grasses and local varieties of hard woods for paper making. Thus the nature and concentration of the different organic compounds, both chlorinated and non-chlorinated are expected to be different.

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The aim of the present investigation was to monitor the Indian paper mill wastewaters for chlorinated toxic compounds (AOX, chlorophenolics, cRFA, and 2,3,7,8-TCDD) with a view to know which compounds are present and at what levels and whether these get removed by the wastewater treatment processes adopted by the Indian paper industry

Material and Methods

The chlorophenols, chloro resin and fatty acids (cRFA) used were obtained from the Aldrich (Milwaukee, USA) and Sigma (St. Louis, USA). The chlorocatechols, chloroguaiacols, chlorovanillins, chlorosyringaldehydes, and chlorosyringols, were supplied by Helix Biotech. Corporation (Richmand, B.C. Canada). Standard solution of 2,3,7,8-TCDD (50 µg/ml) was supplied by Cambridge Isotope Laboratory (Massachuttes, USA). Solvents i.e. acetone, benzene, ethyl acetate, toluene, *n*-hexane, cyclohexane, methanol, tertiary butyl methyl ether, methylene chloride, used were HPLC grade and other solvents i.e. ethanol, diethyl ether, and n-nonane used were Laboratory grade. The wastewater samples (before biological treatment and after biological treatment) were collected from 8 different paper mills, hereafter designated as Mill A, B, C, D, E, F, G and H, from different parts of India. Wastewater samples were analyzed immediately in the laboratory for pH, COD, BOD, color, AOX, chlorophenolics, and cRFA. pH was measured on a Toshniwal pH meter. Color measurement was performed spectrometrically on Analytic Jena spectrophotometer (Model Spekol 2000). COD and BOD estimation was done by the standard methods [11]. AOX was determined by Dextar AOX analyzer (Thermo Electron Corporation).

Gas chromatography-Mass spectrometry (GC-MS) was used for the qualitative and quantitative analysis of chlorophenolics in the wastewater. The extraction of various chlorophenolics was done as per the procedure suggested by Lindstrom & Nordin [12] using diethyl ether:acetone (90:10) solution. The chlorophenolics were converted to readily volatile acetyl derivatives prior to GC-MS analysis. The acetylation was done with acetic anhydride based on procedure suggested by Abrahamsson and Xie [13]. The analysis of various chlorophenolics as acetyl derivatives was performed on Gas Chromatograph (GC) coupled with Mass Spectrometer (MS) (Trace GC Ultra-DSQ, Thermo Electron Corporation). The derivatized sample was injected into the TR-5 fused silica capillary column (containing 5% phenyl methyl polysiloxane) using an auto sampler (AI 3000, Thermo Electron Corporation). The detailed GC-MS conditions for the analysis chlorophenolics are given in other publication [14]. The various chlorophenolics were first identified by matching their mass spectrum with that obtained from the NIST library. Once main peaks were identified, pure standard solutions of target compounds (as acetyl derivatives) were injected into the GC-MS for determining the retention times (RT) of respective chlorophenolics.

Gas chromatography (GC) was used for the qualitative and quantitative analysis of cRFA. The extraction of cRFA from wastewater was achieved as suggested by Voss and Rapsomatiotis using tertiary butyl methyl ether as solvent [15]. The cRFA were converted to their readily volatile methyl esters prior to GC analysis. Methylation was done with diazomethane according to the procedure suggested by Vogel [16]. After extraction, all samples of cRFA as methyl esters, were injected into the Optima-1-MS fused silica capillary column (30m x 0.25mm i.d. with 0.25µm film thickness) containing 100% dimethyl polysiloxane and were analyzed using Gas Chromatograph (Trace GC Ultra, Thermo Electron Corporation). The GC conditions for the analysis of cRFA are given in other publication [17]. GC was used for the qualitative and quantitative analysis of 2,3,7,8-TCDD present in the wastewater samples. The extraction and analysis of 2,3,7,8-TCDD was carried out according to the procedure of NCASI [18]. Target compounds were identified by comparing RT with those of derivatized standards and quantified with the help of response factor of the specific compound.

Results and Discussion

For the monitoring studies, wastewater samples (combined) were collected from eight paper mills (designated as Mill A, B, C, D, E, F, G, and H) from the different parts of India.

Table 1 summarizes the raw material, pulping process, bleaching process, and type of biological treatment system for each mill. A variety of raw materials are used by different paper mills i.e. hard wood (Mills A, E, and G), bamboo (Mill E), wheat straw (Mill B, C, D, F, and H), bagasse (Mill C, D, and G), and sarkanda (Mill D). The pulping processes employed by selected mills are kraft, alkaline sulphite, and soda process. The bleaching sequence employed by mills include CEH, CEHH, OCEHH, OCE_PHH, $(D/C)E_{OP}D_1D_2$, $DE_{OP}D$, and $O(D/C)E_PD$. Among eight mills, six mills (Mill A, C, E, F, G, and H) are using chemical recovery process. All the mills are using

Table 1 : Details of Paper mills from which wastewater samples were collected

S. No.	Mill	Raw Material	Pulping Process	Bleaching Sequence	Chemical Recovery Process	Treatment Process
1.	A	Mixed hard wood	Kraft	OCE_PHH	Yes	ASP
2.	B	Wheat straw	Soda	CEHH	No	ASP
3.	C	Bagasse, wheat straw	Soda	OCEHH	Yes	ASP
4.	D	Sarkanda, bagasse, wheat straw	Alkaline sulphite	CEH	No	ASP
5.	E	Hard wood, bamboo	Kraft	$(D/C)E_{OP}D_1D_2$	Yes	ASP
6.	F	Wheat straw	Soda	$DE_{OP}D$	Yes	ASP
7.	G	Bagasse, hard wood	Kraft	$O(D/C)E_PD$	Yes	UASB/ASP
8.	H	Wheat straw	Soda	CEHH	Yes	ASP

ASP- Activated sludge process, UASB- Upflow anaerobic sludge blanket reactor, C- chlorination stage, D- chlorine dioxide stage, E- extraction stage, E_P- H_2O_2 reinforced extraction stages, E_{OP}- H_2O_2 and O_2 reinforced extraction stages, H- Hypochlorite stage, O- oxygen delignification stage

activated sludge process (ASP) for the treatment of wastewaters except Mill G which is using upflow anaerobic sludge blanket reactor (UASB) and ASP for wastewater treatment.

The collected wastewaters were analyzed for pH, BOD, COD, color, and chloro-organics i.e. AOX, chlorophenolics, cRFA, and 2,3,7,8-TCDD. Six categories of chlorophenolic compounds (chlorophenols (CP), chlorocatechols (CC), chloroguaiacols (CG), chlorosyringol (CS), chlorosyringaldehyde (CSA), and chlorovanillin (CV)) and four cRFA compounds, i.e. chlorodehydroabietic acid (CDAA), 12,14-dichlorodehydroabietic acid (DCDAA), 12,13-dichlorostearic acid (DCSA), and 9,10,12,13-tetrachlorostearic acid (TCSA) were detected in the paper mills wastewater. The corresponding GC chromatograms for laboratory prepared mixture of 26 standard chlorophenolic compounds, 4 standard cRFA, and 2,3,7,8-TCDD standard are shown in Figs. 1, 2, and 3, respectively.

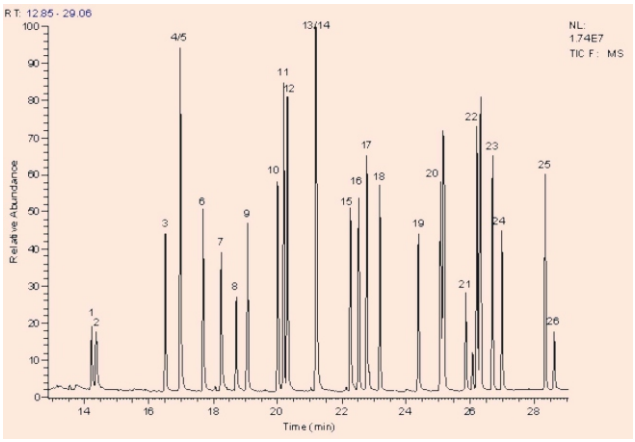

Fig. 1: Chromatogram of a mixture of pure standards of chlorophenolic compounds

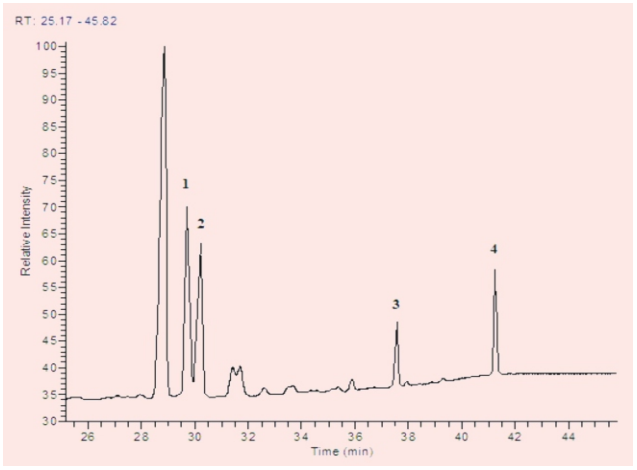

Fig. 2: Chromatogram of a mixture of pure standards of cRFA

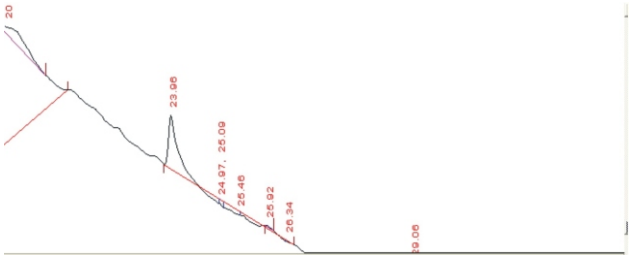

Fig. 3: Chromatogram of 2,3,7,8-TCDD standard

pulp and paper mills varied from 4.7 to 7.3, thus indicating a wide pH variation in the untreated wastewaters from different mills (Table 2). The wastewater pH for several mills was nearly neutral and color varied from 959 to 3035 Pt-Co mg L^{-1}). Mill E and G had low color values 959 and 980 Pt-Co mg L^{-1}, respectively, whereas Mill D had highest color value of 3035 Pt-Co mg L^{-1}. All the eight mills had

Table 2 : Characteristics of Paper Mill Wastewater before biological treatment

Parameter	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
PH	7.2	6.4	5.9	4.7	7.3	6.2	7.2	7.0
Color (Pt-Co. mg L^{-1})	2401	1477	2101	3035	959	1659	980	2867
COD (mg L^{-1})	1071	1732	933	2035	549	1451	399	1185
BOD (mg L^{-1})	308	535	272	582	185	460	110	370
BOD/COD ratio	0.288	0.309	0.292	0.286	0.337	0.317	0.276	0.312
AOX (mg L^{-1})	12.0	29.5	18	37.5	25.5	19.7	7.41	23.9
Chlorophenolics (µg L^{-1})	140.8	57.4	78.7	238.9	54.4	57.6	11.5	203.1
cRFA (µg L^{-1})	57.7	108.8	47.9	157.1	52.5	70.4	36.5	106.3
2,3,7,8-TCDD (ng L^{-1})	ND	3.76	ND	5.38	ND	–	ND	–

ND= not detected

Wastewater characteristics before biological treatment

The characteristics of combined wastewater collected (before biological treatment) from different paper mills are shown in Table 2.

General parameters

Results show that the pH of the untreated wastewaters for different

significant difference in the color values, which may be due to differences in raw materials and bleaching sequences used, by different mills.

The COD and BOD for different pulp and paper mills ranged from 399-2035 mg L^{-1} and 110-582 mg L^{-1}, respectively (Table 2). The COD and BOD levels of Mill D wastewater sample were almost double than those of Mill A and C. Lowest COD and BOD levels were observed in Mill G sample. This is due to the presence of

upflow anaerobic sludge blanket reactor (UASB) prior to the activated sludge process (ASP) which reduces the organic load for further treatment. The BOD/COD ratio varied from 0.276 to 0.337 which is quite low (<0.5). It means that the wastewater samples of different pulp and paper mills contain higher quantities of recalcitrant compounds than those of biodegradable compounds.

Highest pollution load was observed in the wastewater of Mill B and D. This is due to the use of agricultural residue as raw materials, conventional bleaching sequence (CEHH and CEH), and the absence of chemical recovery process. Tiku et al. surveyed four paper mills in India and reported pH, COD and BOD values for combined pulp mill effluent which were 6.92-7.45, 985-1216 mg L^{-1}, and 466-622 mg L^{-1}, respectively [19]. In the present study the range for these parameters is wider due to the variety of process variables for the selected pulp and paper mills.

Chloro-organics

The AOX value for different mills varied from 7.4 - 37.5 mg L^{-1} (Table 2). Highest value of AOX was observed for Mill D followed by Mill B as both the mills are using conventional bleaching sequences CEH and CEHH, respectively. AOX concentration was comparatively lower for the mills which are using prebleaching oxygen delignification (O) stage or chlorine dioxide (D) stage instead of chlorination (C) and hypochlorite (H) stage.

Table 3 : Chlorophenolic compounds in paper mill wastewater before biological treatment

S.No.	Name of compound	Concentration (µg L^{-1})							
		Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
1.	3-CP	0.78	0.54	0.52	10.27	0.87	ND	0.47	1.67
2.	4-CP	0.31	0.21	0.19	4.06	0.33	0.45	0.19	0.67
3.	2,6,-DCP	1.29	0.31	1.16	0.83	0.68	0.11	0.20	8.69
4.	2,5,-DCP	1.66	10.07	11.07	20.41	5.05	14.67	0.93	27.38
5.	2.4.-DCP	0.66	4.24	4.64	86.33	2.10	6.18	0.31	11.52
6.	2,3,-DCP	ND	0.03	0.05	0.30	ND	ND	ND	0.04
7.	3,4-DCP	ND	ND	0.17	ND	0.13	ND	ND	0.25
8.	4-CG	2.03	0.77	0.49	0.20	0.58	0.56	0.47	13.25
9.	2,4,5-TCP	5.12	4.87	21.71	71.21	7.49	5.33	0.35	51.80
10.	2,3,6-TCP	ND	ND	0.05	ND	0.07	ND	ND	0.37
11.	2,3,5-TCP	ND	0.18	ND	0.33	0.17	0.37	ND	0.86
12.	2,4,6-TCP	0.15	0.22	0.11	1.35	0.05	0.15	ND	ND
13.	4,5-DCG	2.08	0.66	2.77	0.82	0.94	1.08	0.12	29.67
14.	2,3,4-TCP	0.11	0.08	0.13	0.75	0.08	0.10	0.07	1.00
15.	4,6-DCG	0.23	1.60	0.96	0.98	5.98	2.93	0.14	6.45
16.	3,6-DCC	ND	5.33	4.83	4.83	10.30	10.29	4.37	16.27
17.	3,5-DCC	ND	ND	2.28	ND	1.88	2.33	3.02	2.04
18.	3,4,6-TCG	ND	8.52	2.81	0.48	0.69	0.69	ND	0.54
19.	3,4,5-TCG	0.04	0.90	0.57	19.71	1.89	1.38	ND	1.43
20.	4,5,6-TCG	0.08	0.42	0.56	0.27	0.63	0.49	ND	4.19
21.	5,6-DCV	ND	ND	0.57	ND	0.20	0.48	ND	0.35
22.	PCP	ND	ND	0.18	0.38	ND	ND	ND	ND
23.	TeCG	0.25	1.28	1.55	2.04	2.71	1.87	ND	1.22
24.	TCS	ND	2.80	2.56	4.05	6.40	ND	ND	2.50
25.	TeCC	ND	4.06	4.82	2.21	1.50	1.92	0.25	3.68
26.	2,6-DCSA	ND	10.33	13.93	7.08	3.69	6.23	0.59	17.28
	Total	**14.8**	**57.4**	**78.7**	**238.9**	**54.4**	**57.6**	**11.5**	**203.1**

D-di; T-tri; Te-tetra; P- penta; CP- chlorophenol; CG-chloroguaiacol; CC-chlorocatechol; CV-chlorovanilin; CSA-chlorosyringaldehyde

The concentration of chlorophenolics varied from 11.5-238.9 µg L^{-1}, for different mills (Table 2). The results indicate that six categories of 26 chlorophenolic compounds (CP, CC, CG, CS, CSA, and CV) were detected in the pulp and paper mills wastewater. The concentrations of each chlorophenolic compound ranged from less than the detection limit to the highest value as given in Table 3. Very high concentration of chlorophenolics was observed in Mills D and H wastewater samples. This is due to the adoption of conventional bleaching sequences i.e. CEH and CEHH by the Mill D and H, respectively. The lowest concentration of chlorophenolics was observed for Mill G which is using O(D/C)E_PD bleaching sequence. 4-CP, 2,6-DCP, 2,5-DCP, 2,4-DCP, 4-CG, 2,4,5-TCP, 4,5-DCG, 2,3,4-TCP, 4,6-DCG, were detected in all the wastewater samples. The highest concentration of 2,4,5-TCP, 2,6-DCSA, 2,4,5-TCP, 2,4-DCP, 3,6-DCC, 2,5-DCP, 3,6-DCC, and 2,4,5-TCP, was observed in the wastewater of Mill A, B, C, D, E, F, and G, respectively. The highest share of 3,6-DCC was observed in the wastewater of Mill E and G. Both the mills are using D/C bleaching stage for unbleached pulps. It means that the highest formation of 3,6-DCC in these mills may be due to D/C stage.

The concentration of chlorophenolics is highest in the Mill D which is using CEH sequence. Mill H has about 80% chlorophenolics and is using CEHH sequence. Another Mill B is also using CEHH with wheat straw like Mill H but chlorophenolics formation is much less i.e. nearly one-fourth of Mill H. Mill B is using continuous digester and cooking pulp to much lower kappa number in comparison to Mill H which is using batch digester and their pulp kappa number is much higher. Mill C which is using oxygen before CEH is showing next lower concentration. Mills E and F are using chlorine dioxide based bleaching sequence i.e. D/C$E_{OP}D_1D_2$ and D$E_{OP}D_1D_2$. The formation of chlorophenolics in chlorine dioxide is much lower in comparison to C or H stage and thus gives lower chlorophenolics. Lowest concentration of chlorophenolics is obtained with Mills A and G which are using oxygen delignification stage and using hard woods as raw materials. Based on total chlorophenolics concentration, the mills follow the order:

D > H > C > B .F > E > A > G.

Table 4 shows the concentration of chlorophenolics (according to category) in paper mill wastewater before biological treatment. Examination of data reveals that CPs contributed the highest share among all the categories except Mill G and their concentration varied from 10.1 to 195.8 µg L^{-1} for different mills. The concentration of CC, CS, CSA, and CV ranged from less than the detection limit to the maximum value listed in Tables 3 and 4. CP and CG were detected in all the mill samples. On percent basis, the share of CP varied from 22 to 82% of the total chlorophenolics content. The share of CG, CC, CSA, CS, and CV was from 6.4-31.8%, 3.1-66.5%, 3-18%, 1.2-11.8%, and 0.2-0.8%, respectively, of the total chlorophenolics content. Based on the data, the order of chlorophenolics detected in untreated paper mill samples was:

CP > CG > CC > CSA > CS > CV

Table 5 shows the concentration of chlorophenolics (based on Cl atom substitution) in paper mill wastewater before biological treatment. Data shows that monochlorophenolics (MCP), dichlorophenolics (DCP), trichlorophenolics (TCP) and tetrachlorophenolics (TeCP) were detected in all mills samples. Pentachlorophenolics (PCP) was detected only in Mill C and Mill D

Table 4 : Chlorophenolics (category wise) in paper mill wastewater before biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Chlorophenols (CP)	10.09	20.75	39.97	195.83	17.02	27.34	2.52	104.26
Chloroguaiacols (CG)	4.71	14.15	9.70	24.50	13.42	8.99	0.73	56.76
Chlorocatecols (CC)	ND	9.39	11.93	7.42	13.68	14.53	7.64	21.99
Chlorosyringols (CS)	ND	2.80	2.56	4.04	6.40	ND	ND	2.50
Chlorosyringaldehyde (CSA)	ND	10.33	13.93	7.08	3.69	6.23	0.59	17.28
Chlorovanilline (CV)	ND	ND	0.57	ND	0.20	0.48	ND	0.35
Total	**14.80**	**57.42**	**78.66**	**238.87**	**54.41**	**57.57**	**11.48**	**203.14**

Table 5 : Chlorophenolics (based on Cl atom) in paper mill wastewater before biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Monochlorophenolics (MCP)	3.12	1.52	1.21	14.52	1.78	1.01	1.12	15.60
Dichlorophenolics (DCP)	5.92	32.58	42.42	121.59	30.95	44.29	9.69	119.93
Trichlorophenolics (TCP)	5.51	17.99	28.49	98.13	17.47	8.49	0.42	62.70
Tetrachlorophenolics (TeCP)	0.25	5.34	6.37	4.25	4.21	3.78	0.25	4.90
Pentachlorophenolics (PCP)	ND	ND	0.17	0.38	ND	ND	ND	ND
Total	**14.80**	**57.42**	**78.66**	**238.87**	**54.41**	**57.57**	**11.48**	**203.14**

wastewater samples. DCP contributed the highest share of the total chlorophenolics content and their concentration varied from 5.9 to 121.6 µg L^{-1} for different mills. The concentration of MCP, TCP, TeCP, and PCP was from 1.0-15.6, 0.4-98.1, 0.3-6.4, 0.2-0.4 µg/L. On percent bases, DCP contributed the highest share (40-84.4%) followed by TCP (3.6-41.1%), MCP (1.5-21.1%), TeCP (1.7-9.3%), and PCP (0.16-0.22%) in untreated paper mill wastewater. Based on the data, chlorophenolics detected in untreated paper mill samples followed the order:

DCP > TCP > MCP > TeCP > PCP

Four cRFA compounds, i.e. CDAA, DCDAA, DCSA, and TCSA were detected in the paper mill samples. The quantity of cRFA detected in paper mill samples is shown in Table 6. The total concentration of cRFA was from 36.5-157.1 µg L^{-1} (Table 6). Higher concentration of cRFA was observed in Mills B, D and H wastewater samples and lowest concentration of cRFA was observed for Mill G. The concentration of DCSA, CDAA DCDAA, and TCSA was from 7.26-65.71, 0.98-61.82, 6.27-22.86, and 6.68-49.15 µg L^{-1}, respectively, for different mills. CDAA was not detected in Mill C sample. Among cRFA, highest concentration of TCSA was observed in the untreated wastewater of Mill A, B, C, E and H.

Table 7 shows the concentration of chloro resin acids (cRA) and chloro fatty acids (cFA) in paper mill wastewater before biological treatment. The concentration of cFA and cRA was from 18.40-76.14 and 7.25-84.68 µg L^{-1}, respectively. The concentration of cFA was higher in samples of Mill A, B, C, E, G, and H while concentration of cRA was higher in samples of Mill D and F. The share of cFA and cRA was from 40.2-87.4 and 12.6-59.8%, respectively.

The estimation of 2,3,7,8-TCDD was not performed on samples of Mills F and H as the sample supplied was insufficient. The wastewater of six paper mills was analyzed for 2,3,7,8-TCDD and it was only detected in the samples of Mills B and D (Table 2). Both the mills are using conventional bleaching sequences i.e. CEHH and CEH. The concentration of 2,3,7,8-TCDD for mills B and D was 3.76 and 5.38 ng L^{-1} respectively. 2,3,7,8-TCDD was not detected in the paper mills samples which are using bleaching sequences other than conventional i.e. OCE_PHH, OCEHH, $D/CE_{OP}D_1D_2$ and OD/CE_PD.

Table 6: cRFA in paper mill wastewater before biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
DCSA[a]	19.75	26.99	12.75	65.71	11.43	9.35	7.26	41.2
CDAA[b]	0.98	14.09	ND	61.82	3.88	28.94	5.93	15.94
DCDAA[b]	6.27	18.52	10.52	22.86	12.15	13.15	12.15	14.63
TCSA[a]	30.70	49.15	24.61	6.68	25.07	18.93	11.14	34.5
Total	**57.7**	**108.8**	**47.9**	**157.1**	**52.5**	**70.4**	**36.5**	**106.3**

a-chloro fatty acid; b-chloro resin acid

Table 7: cRA and cFA in paper mill wastewater before biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
cFA	50.45	76.14	37.36	72.39	36.50	28.27	18.40	75.70
cRA	7.25	32.61	10.52	84.68	16.03	42.09	18.08	30.57

Table 8 : Characteristics of pulp and paper mill wastewater after biological treatment

Parameter	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
PH	7.7	7.0	6.8	6.4	7.1	7.4	7.7	7.7
Color (Pt-Co. mg L^{-1})	988	838	787	1250	296	723	268	998
COD (mg L^{-1})	288	826	320	691	152	368	133	312
BOD (mg L^{-1})	28	135	32	74	18	38	16	38
BOD/COD ratio	0.097	0.163	0.100	0.107	0.118	0.103	0.120	0.121
AOX (mg L^{-1})	7	18.5	12.5	17.5	17	11.9	4.1	13.8
Chlorophenolics (µg L^{-1})	10	35.9	47.9	167.7	22.6	37.4	3.6	117.6
cRFA (µg L^{-1})	44.5	35.7	27.1	110.7	26.3	47.6	19.2	68.1
2,3,7,8-TCDD (ng L^{-1})	ND	2.26	ND	4.22	ND	–	ND	–

ND= not detected

Wastewater characteristics after biological treatment

The characteristics of combined wastewater collected (after biological treatment) from different paper mills is shown in Table 8.

General parameters

Results show that the pH of the wastewaters for different paper mills was from 6.4 to 7.7 (Table 8). The wastewater pH of Mills B, C, E, and F was near about neutral. For color, it varied from 268 to 1250 Pt-Co mg L^{-1}. Mills E and G had low color with value of 296 and 268 Pt-Co units, respectively, whereas Mill D had highest color value of 1250 Pt-Co mg L^{-1}. All the eight mills had significant difference in the color values, which may be due to difference in process parameters and initial load of color feed to ASP.

The COD and BOD for different paper mills were from 133-826 mg L^{-1} and 16-135 mg L^{-1}, respectively (Table 8). The COD and BOD levels of Mill C wastewater sample were higher than other mills. Lowest COD and BOD levels were observed in Mill G sample. This is due to the presence of UASB prior to the ASP which reduces the initial organic load for ASP. The BOD/COD ratio varied from 0.097 to 0.163 which is very low (<0.5). It means that the wastewater samples discharged by different paper mills contained high quantities of non-biodegradable compounds.

Highest pollution load was observed in the wastewater of Mill B and D. The use of CEHH and CEH bleaching sequences in Mills B & D, respectively and the absence of chemical recovery process are the main reasons of high pollution load generation. Tiku et al. surveyed four paper mills in India and reported pH, color, COD and BOD values for combined pulp mill effluent which were 6.28-7.53, 764-900 Pt-Co mg L^{-1}, 275-535 mg L^{-1}, and 60-83 mg L^{-1}, respectively, for effluent treatment plant (ETP) outlet [19].

Table 9 : Chlorophenolic in paper mill wastewater after biological treatment

S.No.	Name of compound	Concentration (µg L^{-1})							
		Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
1.	3-CP	0.09	0.14	0.09	8.62	ND	ND	ND	0.73
2.	4-CP	0.02	0.05	0.01	3.69	0.01	0.22	ND	0.24
3.	2,6,-DCP	1.20	0.73	0.05	2.36	0.09	2.09	ND	5.80
4.	2,5,-DCP	1.61	9.75	1.08	16.93	1.27	9.46	0.47	19.19
5.	2.4.-DCP	0.66	4.12	0.41	71.43	0.48	3.93	0.14	6.47
6.	2,3,-DCP	ND	0.02	ND	0.31	ND	ND	ND	0.01
7.	3,4-DCP	ND	ND	0.16	ND	ND	ND	ND	0.09
8.	4-CG	0.11	0.32	ND	0.18	ND	0.23	0.27	6.62
9.	2,4,5-TCP	5.06	3.95	1.23	47.56	2.88	4.42	0.10	27.40
10.	2,3,6-TCP	ND	ND	ND	ND	ND	ND	0.05	0.24
11.	2,3,5-TCP	ND	0.11	0.12	0.21	0.13	0.22	0.11	0.57
12.	2,4,6-TCP	ND	ND	0.028	0.77	0.03	0.08	ND	ND
13.	4,5-DCG	0.79	0.31	ND	0.41	0.37	0.47	ND	018.44
14.	2,3,4-TCP	0.03	0.42	0.10	0.65	ND	0.08	ND	0.72
15.	4,6-DCG	0.14	1.31	0.48	0.48	0.23	1.57	0.04	2.24
16.	3,6-DCC	ND	3.57	ND	ND	7.67	6.75	2.03	7.27
17.	3,5-DCC	ND	ND	ND	ND	ND	ND	ND	1.04
18.	3,4,6-TCG	0.09	0.20	0.27	0.24	0.36	0.33	ND	0.35
19.	3,4,5-TCG	0.02	0.49	0.27	6.69	0.34	0.83	ND	0.75
20.	4,5,6-TCG	ND	0.11	0.22	0.14	0.23	0.27	ND	3.68
21.	5,6-DCV	ND	ND	0.51	ND	ND	0.18	ND	0.14
22.	PCP	ND	ND	ND	ND	0.17	ND	ND	ND
23.	TeCG	0.13	1.35	0.85	0.62	1.25	1.25	ND	0.85
24.	TCS	0.05	1.70	1.14	1.67	3.92	ND	ND	1.17
25.	TeCC	ND	1.18	4.82	1.07	0.75	1.63	0.16	3.04
26.	2,6-DCSA	ND	6.11	19.26	3.28	2.42	3.40	0.27	10.51
	Total	**10.0**	**35.9**	**47.9**	**167.7**	**22.6**	**37.4**	**3.6**	**117.6**

ND = not detected

Chloro-organics

The AOX value for different mills varied from 4.1-18.5 mg L^{-1} (Table 8). The concentration of chlorophenolics ranged from 3.6-167.7 µg L^{-1}, for different mills (Table 8). The results indicate that six categories of 26 chlorophenolic compounds (CP, CC, CG, CS, CSA, and CV) were detected in the treated wastewater of paper mills. The concentration of chlorophenolic compounds is shown in Table 9.

Highest concentration of chlorophenolics was observed in Mill D and H wastewater samples. The lowest concentration of chlorophenolics was observed for Mill G. 2,5-DCP, 2,4-DCP, 2,4,5-TCP, and 4,6-DCG, were detected in all the wastewater samples. The highest concentration of 2,4,5-TCP (5.06 µg L^{-1}), 2,5-DCP (9.75 µg L^{-1}), 2,6-DCSA (19.26 µg L^{-1}), 2,4-DCP (71.43 µg L^{-1}), 3,6-DCC (7.67 µg L^{-1}), 2,5-DCP (9.46 µg L^{-1}), 3,6-DCC (2.03 µg L^{-1}), and 2,4,5-TCP (27.40 µg L^{-1}), was observed in the wastewater of Mills A, B, C, D, E, F, and G, respectively.

Table 10 shows the concentration of chlorophenolics (according to category) in pulp and paper mill wastewater after biological treatment. Examination of data reveals that CP contributed the highest share among all categories except Mill E and G in which CC contributed to the highest share. CP and CG were detected in all the mill samples. The concentration of CP, CG, CC, CS, CSA, and CV were from 0.87-152.87, 0.30-32.92, 1.07-11.35, 0.05-3.92, 0.27-11.96, and 0.14-0.51 µg L^{-1}, respectively. Table 11 shows the concentration of chlorophenolics (according to Cl atom substitution) in paper mill wastewater after biological treatment. Data show that MCP, DCP, TCP, and TeCP were detected in all mills samples. PCP was only detected in Mill C, D, and E wastewater samples. DCP contributed the highest share of the total chlorophenolics content except Mill A in which TCP contributed the highest share. The concentration of MCP, DCP, TCP, TeCP, and PCP was from 0.01-12.49, 2.95-95.21, 0.25-57.93, 0.13-3.89, and 0.10-0.34 µg L^{-1}, respectively.

Table 10 : Chlorophenolics (category wise) in paper mill wastewater after biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Chlorophenols (CP)	8.66	19.30	22.45	152.87	5.06	20.49	0.87	61.47
Chloroguaiacols (CG)	1.28	4.08	3.51	8.76	2.79	4.94	0.30	32.92
Chlorocatecols (CC)	ND	4.74	8.24	1.07	8.41	8.38	2.19	11.35
Chlorosyringols (CS)	0.05	1.70	1.14	1.67	3.92	ND	ND	1.17
Chlorosyringaldehyde (CSA)	ND	6.10	11.96	3.28	2.42	3.40	0.27	10.51
Chlorovanilline (CV)	ND	ND	0.51	ND	ND	0.18	ND	0.14
Total	**10.0**	**35.9**	**47.9**	**167.7**	**22.6**	**37.4**	**3.6**	**117.6**

Table 11 : Chlorophenolics (based on Cl atom) in paper mill wastewater after biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Monochlorophenolics (MCP)	0.23	0.51	0.10	12.49	0.01	0.45	0.27	7.59
Dichlorophenolics (DCP)	4.40	25.91	22.48	95.21	12.53	27.84	2.95	71.20
Trichlorophenolics (TCP)	5.24	8.29	21.68	57.93	7.89	6.23	0.25	34.89
Tetrachlorophenolics (TeCP)	0.13	1.29	3.56	1.69	2.00	2.87	0.16	3.89
Pentachlorophenolics (PCP)	ND	ND	0.10	0.34	0.17	ND	ND	ND
Total	**10.0**	**35.9**	**47.9**	**167.7**	**22.6**	**37.4**	**3.6**	**117.6**

Table 12: Concentration of cRFA in paper mill wastewater after biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
DCSA[a]	13.53	8.96	9.73	42.80	ND	3.80	2.73	24.94
CDAA[b]	ND	9.05	ND	52.30	1.73	19.21	3.55	8.89
DCDAA[b]	3.05	6.31	7.23	13.49	5.61	9.53	6.69	9.43
TCSA[a]	27.96	11.34	10.11	2.13	18.93	15.02	5.94	24.85
Total	**44.5**	**35.7**	**27.1**	**110.7**	**26.3**	**47.6**	**19.2**	**68.1**

a-chloro fatty acid; b-chloro resin acid

Table 13: cRA and cFA in paper mill wastewater AFTER biological treatment

Name of Compound	Concentration (µg L^{-1})							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
cFA	41.49	20.30	19.84	44.93	18.93	18.82	8.67	49.79
cRA	3.05	15.36	7.23	65.79	7.34	28.74	10.51	18.32

Table 14 : Removal efficiency of biological treatment process in paper mills

Parameter	Removal (%)							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Color	58.9	43.3	62.5	58.8	69.1	56.4	72.7	65.2
COD	73.1	52.3	65.7	66.0	72.3	74.6	66.7	73.7
BOD	90.9	74.8	88.2	87.3	90.3	91.7	85.5	89.7
AOX	41.7	37.3	30.6	42.7	33.3	39.6	44.6	42.3
Chlorophenols	32.4	37.4	39.1	29.8	58.5	35.0	68.4	42.1
cRFA	22.9	67.2	37.2	29.5	55.6	32.4	47.4	35.9
2,3,7,8-TCDD	ND	39.9	ND	21.6	ND	–	ND	–

ND= not detected

The total concentration of cRFA was from 19.2 to 110.7 µg L^{-1} (Table 8). Four cRFA compounds, i.e. CDAA, DCDAA, DCSA, and TCSA were detected in the treated pulp and paper mill samples (Table 12). Highest concentration of cRFA was observed in Mill D wastewater sample and lowest was observed for Mill G. DCDAA and TCSA were detected in all the mill samples. The concentration of DCSA, CDAA DCDAA, and TCSA was from 2.73-42.80, 1.73-52.30, 3.05-13.49, and 2.13-27.96 µg L^{-1}, respectively, for different mills. DCSA was not detected in Mill E sample. Among cRFA, highest concentration of TCSA was observed in the treated wastewater of Mill A, B, C, and E.

Table 13 shows the concentration of cRA and cFA in paper mill wastewater after biological treatment. The concentration of cFA and cRA was from 8.67-49.79 and 3.05-65.79 µg L^{-1}, respectively. The concentration of cFA was higher in the samples of Mill A, B, C, E, and H while concentration of cRA was higher in the samples of Mill D, F, and G. The share of cFA and cRA was 39.6-93.2 and 6.8-60.4%, respectively.

The treated wastewater of six paper mills was analyzed for 2,3,7,8-TCDD and it was only detected in the samples of Mill B and D (Table 8). The concentration of 2,3,7,8-TCDD was 2.26 and 4.22 ng L^{-1} for Mills B and D respectively.

Performance of biological treatment process in paper mills

The removal efficiency of biological treatment process for different parameters of wastewater collected from eight mills is shown in Tables 14-18.

Removal of general parameters

Results show that the removal of color ranged from 43.3 to 72.7% (Table 14). Lowest color removal was observed for Mill B (43.3%) and highest for Mill G (72.7%). For Mill A, D, and F, the color removal efficiency observed was near about same (56-59%). The COD and BOD removal efficiency varied from 52.3-74.6% and 74.8-91.7%, respectively (Table 14). The lowest COD and BOD removal was observed for Mill B where as highest removal was observed for Mill F. The removal of BOD was generally more than 85% for all the mills except Mill B which showed 74.8%.

Removal of chloro-organics

These data do not explain the mechanism by which chloro-organic compounds are removed from the wastewaters. The possible mechanisms are biodegradation and adsorption on wastewater treatment sludge. The removal of AOX for different mills varied from 30.6-44.6%. The removal of chlorophenolics varied from 29.8-68.4% from different paper mill wastewater (Table 14). Generally, the removal of chlorophenolics was observed between 30-42% except two mills i.e. Mill E (58.5%) and G (68.4%). The highest removal was observed in case of Mill G (68.4%) and lowest for Mill D (29.8%). This is due to very low concentration of chlorophenolics in the untreated wastewater of Mill G as compared to Mill D in which highest load of chlorophenolics was observed. Table 15 shows the percent removal of chlorophenolics (according to category) from paper mill wastewater after treatment. The removal of CP, CG, CC, CS, CSA, and CV ranged from 7-91.8, 42-79.3, 30.9-85.5, 38.8-58.8, 14.1-54.5, and 9.6-62.9%, respectively, of the total chlorophenolics content. All the mills showed comparatively higher CG removal efficiency of 58-80% except Mills F and G which showed lower values of 45 and 42% respectively. CC was removed to a lower extent 38-50% except Mills D and G which showed higher values of 85.5 and 71.3% respectively. CSA was removed from 40-54% except Mills C and E which showed lower removal efficiencies of 14.1 and 34.45 respectively. CV was removed up to 60-63% except Mill C which had a lower value of 9.6%.

Table 16 shows the removal of chlorophenolics (as per Cl atoms substitution) from paper mill wastewater after treatment. The removal was 14.0-99.4, 20.5-69.5, 4.9-88.2, 20.7-75.8, and 10.4-43.8%, respectively for MCP, DCP, TCP, TeCP, and PCP. Highest

removal of MCP was observed from wastewaters of Mill A, C, E, F, G, and H while the removal of TeCP was highest for Mill B and D. The removal of DCP, TCP, and PCP was comparatively low. Another study has also shown that highly chlorine substituted compounds are more difficult to biodegrade [20].

The removal of cRFA varied from 22.9-67.2% (Table 14). Less than 40% removal was observed for Mill A, C, D, F, and H while for Mill B, E, and G the removal was 67.2, 55.6, and 47.4%, respectively. Table 17 shows the percent removal of DCSA, CDAA, DCDAA, and TCSA from paper mill wastewater after treatment. The removal varied from 23.7-66.8, 15.4-55.4, 27.5-65.9, and 8.9-68.1% for DCSA, CDAA, DCDAA, and TCSA, respectively.

Table 18 shows the percent removal of cRA and cFA in paper mill wastewater after treatment. The removal of cFA and cRA varied from 17.8-73.3 and 22.3-57.9%, respectively. The removal of cFA was higher for Mill B, C, D, F, and G while removal of cRA was higher for Mill A, E, and H.

The removal of 2,3,7,8-TCDD varied from 21.6-39.9% (Table 14). For Mill D, the removal is low as compared to Mill B which may be due to comparatively high concentration of 2,3,7,8-TCDD in untreated wastewater.

A wide variation in the removal of target chloro-organics was observed among different mills. The removal of chloro-organic compounds from wastewater not only depends on the biodegradation but also on the adsorption on sludge. The removal of chloro-organics by the biological treatment process generally depends on the initial load, type of compounds, toxicity and the process operation of the treatment system. It was observed that the removal of chloro-organics was low by ASP and the treated wastewater still contains significant amount toxic compounds.

Table 15 : Category wise removal of chlorophenolics from biologically treated paper mill wastewater

Name of Compound	Removal (%)							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Chlorophenols (CP)	14.1	7.0	91.8	21.9	70.3	25.0	65.6	41.0
Chloroguaiacols (CG)	72.7	71.2	78.5	64.2	79.3	45.0	58.6	42.0
Chlorocatecols (CC)	ND	49.5	30.9	85.5	38.5	42.3	71.3	48.4
Chlorosyringols (CS)	ND	39.3	55.4	58.8	38.8	ND	ND	39.1
Chlorosyringaldehyde (CSA)	ND	40.9	14.1	53.6	34.4	45.3	54.5	53.1
Chlorovanilline (CV)	ND	ND	9.6	ND	ND	62.9	ND	59.8

Table 16 : Chlorophenolics removal (based on Cl atom) from biologically treated paper mill wastewater

Name of Compound	Removal (%)							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
Monochlorophenolics (MCP)	92.8	66.3	91.7	14.0	99.4	54.9	76.3	51.3
Dichlorophenolics (DCP)	25.7	20.5	52.4	21.7	59.5	37.1	69.5	40.6
Trichlorophenolics (TCP)	4.9	53.9	88.2	41.0	54.9	26.6	38.7	44.4
Tetrachlorophenolics (TeCP)	46.0	75.8	44.1	60.3	52.5	24.0	37.3	20.7
Pentachlorophenolics (PCP)	ND	ND	43.8	10.4	ND	ND	ND	ND

Table 17: Removal of cRFA from paper mill wastewater after biological treatement

Name of Compound	Removal (%)							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
DCSA	31.5	66.8	23.7	34.9	ND	59.3	62.4	39.5
CDAA	ND	35.8	ND	15.4	55.4	33.6	40.1	44.2
DCDAA	51.4	65.9	31.3	41.0	53.8	27.5	42.7	35.5
TCSA	8.9	76.9	58.9	68.1	24.5	20.6	46.7	28.0

Table 18: Removal of cRA and cFA in paper mill wastewater after biological treatment

Name of Compound	Removal (%)							
	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F	Mill G	Mill H
cFA	17.8	73.3	46.9	37.9	48.1	33.4	52.9	34.2
cRA	57.9	52.9	31.3	22.3	54.2	31.7	41.9	40.1

Toxicity

$^{96}LC_{50}$ is a parameter which represents the toxicity of a particular compound. It is defined as the lethal concentration at which 50% of the test organism will get killed when the test organism is exposed to the toxicant for a period of 96 hours under standard test conditions. To know whether the effluent is toxic, the concentrations of the individual pollutants are compared with $^{96}LC_{50}$ values. Reported $^{96}LC_{50}$ (Tables 19 and 20) indicate that chlorophenolics, resin acids, unsaturated fatty acids and chlorinated resin and fatty acids are toxic. The lower $^{96}LC_{50}$ values indicate that resin acids are more toxic than unsaturated fatty acids.

Table 19 : LC_{50} value for various chlorophenolics and 2,3,7, 8-TCDD[21-24]

Name of Compound	$^{96}LC_{50}$ value(mg/L)
Di cholorocatechol	0.5-1.0
Di choloroguaiachol	2.3
2,4, Dicholorophenol	2.8
2,5 Dichlorophenol	1.7
Penta cholorophenol	0.096
3,4 Dichorocatechol	2.7
2,4,6 Tricholorophenol	0.45 - 2.6
Tetra cholorocatechol	0.25 - 1.5
3,4,5 Tri cholorocatechol	0.89 - 1.5
Tri choloroguaiacol	0.7 - 1.0
Tetra choloroguaiacol	0.2 - 1.7
2,3,7,8 - TCDD	0.0006

Table 20 : LC_{50} value for various resin and fatty acids [21-24]

Name of acid	$^{96}LC_{50}$ value(mg/L)
Palmitic	> 20
Heptadecanoic	N.A
Stearic	N.A
Oleic	3.2 - 8.0
Linoleic	2.0 - 4.5
Linolenic	3.0 - 6.0
Pimaric	0.7 - 1.2
Sandaracopimaric	0.4
Isopimaric	0.4 - 1.0
Palustric	0.5 - 0.6
Abietic	0.7 - 1.5
Dehydroabietic	0.8 - 1.7
Neoabietic	0.6 - 0.7
Chlorodehydro abietic	0.6 - 0.9
12, 14 Chlorodehydro abietic	0.6 - 1.2
9, 10 Dicholoro stearic	0.6 - 1.2

The quantities of various chlorophenolics, cRFA present in untreated effluents from different paper mills have been compared with reported $^{96}LC_{50}$ values. The concentrations of various cholorophenols, cRFA determined (Tables 3, 6, 9, 12) are below the respective $^{96}LC_{50}$ values. The $^{96}LC_{50}$ values describe the toxicity of a particular compound when present alone. However a number of compounds are present, interfering effects may be observed. Substantial evidence now exists which indicate that the threshold concentration is approximately 0.05-0.10 of $^{96}LC_{50}$ values. At this concentration or below this concentration range no sub lethal stresses have been reported.

Concentrations of all the chlorophenolics, cRFA for different paper mills investigated are below their respective threshold concentration for both untreated and biologically treated effluents. So it can be inferred that the untreated spent bleach liquor generated in the laboratory is of environmental concern. Presence of 2,3,7,8 TCDD, a very highly toxic compound was not detected in mill samples from mills A, C, E and G (Tables 2 and 8). Mills F and G were not tested for 2,3,7,8 TCDD as effluent sample was insufficient. It was detected in both untreated and biologically treated effluents from paper mills B and D but its concentration was below the threshold concentration (approximately 0.05-0.10 of $^{96}LC_{50}$ values).

Presence of a large number of chlorophenolics, cRFA and 2,3,7,8 TCDD at concentrations below threshold concentration have been detected in biologically treated paper mill effluents which is of environmental concern.

Conclusions

The major conclusions are as follows:

1. 26 chlorophenolics and 4 cRFA at µg L^{-1} and 2,3,7,8-TCDD at ngL^{-1} levels detected.
2. Concentration of chlorophenolics, cRFA, and 2,3,7,8-TCDD detected in untreated wastewater of paper mills was 12-239 µgL^{-1}, 37-157 µg L^{-1}, and 0-5.4 ng L^{-1}, respectively and in treated waste water was 4-170 µg L^{-1}, 19-111 µg L^{-1}, and 0-4.2 ng L^{-1}, respectively.
3. Chlorophenols contribute maximum share in both untreated and treated wastewaters.
4. 2,4-dichlorophenol, 2,5-dichlorophenol, and 2,4,5-trichlorophenols are the dominant compounds detected among chlorophenols.
5. Dichlorophenolics are the major group of compounds detected.
6. Among cRFA, cFA was present in higher proportion.
7. The removal efficiency of biological treatment of different paper mills are
   - BOD (87-92%); COD (66-73%); Color (60-72%); AOX (30-45%)
   - Chlorophenolics (28-59%); cRFA (30-37%); 2,3,7,8-TCDD (22-40%)
8. Concentrations of chlorophenolics, cRFA and 2,3,7,8 TCDD detected in untreated and biologically treated paper mill effluents are below their respective threshold concentration of toxicity.

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