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Identification And Advanced Oxidation Of Chloro - Organics From Bleaching Wastewater Of Pulp And Paper Mill

Abstract

This study evaluates the effectiveness of ozonation process for the treatment of pulp and paper mill wastewater from bleaching section. The wastewater was characterized for different chloro-organic compounds i.e. adsorbable organic halides (AOX), chlorophenolics, and chloro resin & fatty acids (cRFA). Six categories of chlorophenolics (chlorophenols (CP), chlorocatechols (CC), chloroguaiacols (CG), chlorosyringol (CS), chlorosyringaldehyde (CSA), and chlorovanilline (CV)) and four cRFA were detected in the bleaching wastewater. For ozonation studies, optimization of process variables including initial pH of wastewater and ozone dosage was done in terms of chemical oxygen demand (COD) and color removal efficiency. Under optimized conditions of pH (9.0) and dosage of ozone (1.3 mg O_3/mg COD), the removal efficiency for AOX, chlorophenolics, and cRFA was 73, 89, and 92%, respectively. After ozonation, the biodegradability of wastewater was increased about two times. This process proved to be more effective for the removal of cRFA and highly chlorinated chlorophenolics.

Keywords: *Advanced oxidation process, AOX, bleaching wastewater, chloro-organics, color, ozonation.*

Introduction

The Indian pulp and paper mill discharges large volume of high pollution load wastewater to the environment which may cause harmful environmental impacts upon discharge to receiving water bodies. The main sources of pollution in pulp and paper industry are wood preparation, pulping, pulp washing, bleaching and coating operations [1, 2]. Among these operations, pulp bleaching generates various toxic and bio-refractory chloro-

organic compounds in the paper mill wastewater [3, 4]. The mills in developed countries have reduced the pollution level below the prescribed limits but the Indian mills have continued using elemental chlorine for bleaching due to techno economic reasons. The bleaching process is essentially being chlorination (C) followed by alkali extraction (E) and calcium hypochlorite (H). Bleaching sequences like CEH, CEHH or CE$_p$HH are common. As a consequence the bleach plants have become a major source of environmental pollution contributing to high chloro-organics release with high biochemical oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halides (AOX) and color loads. More than 500 different chloro-organic compounds have been identified including chlorate, chloroform, chlorophenolics (chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols, chlorosyringaldehydes, and chlorovanillins) chloro resin and fatty acids (RFA), dioxins and furans, etc. [5-8]. In wastewater, these chloro-organic compounds are estimated collectively as AOX. Many of these compounds are toxic, mutagenic and are slowly degraded in the environment [9-11]. Chlorophenolics are formed primarily as a result of chlorination of the lignin remaining in the pulp after pulping process [11]. The chloro resin & fatty acids (cRFA) found in bleach plant effluent originate from the fibrous raw material and their quantity depends on the type of wood species, bleaching chemical charge applied and on the degree of washing of the unbleached pulp. The chlorophenolics and cRFA are the major contributors to toxicity of pulp and paper mill effluents to aquatic organisms [12]. These are hydrophobic in nature and have been shown to bioaccumulate in aquatic organisms [13]. The conventional treatment for Indian pulp and paper mills include primary and secondary (aerobic/anaerobic biological systems) treatment processes which are not effective for the degradation of many of these chloro-organic compounds and color from the pulp and paper mill wastewaters. It has been observed that the secondary treated wastewater still contains high organic load, color, and chloro-organics that impart toxicity to the wastewater. In order to protect wastewater receiving bodies and to meet increasingly stringent standard discharge limits, it is necessary to reduce the pollution load of pulp and paper mills wastewater.

Advanced oxidation processes (AOPs) are among the promising technologies that have received increasing interest for industrial wastewater treatment. The AOPs were developed and used as powerful methods capable of transforming the recalcitrant pollutants into harmless compounds [14]. AOPs are based on the generation of extraordinarily non-selective oxidizing species such as the hydroxyl radicals (OH). [15]. Ozonation as an AOP, has been extensively studied in the treatment of pulp and paper mill wastewater since the seventies [1, 14, 16, 17]. Ozone (O_3) is a very powerful oxidant agent (E^0= 2.08 V) and in the aqueous phase, it could be decomposed to hydroxyl radical species which reacts with the organic compounds with rate constants generally in the order of $10^6 10^9 M^{-1} s^{-1}$. [18]. A number of studies have carried out on ozone application for the improvement of wastewater quality both preliminary and tertiary treatment depending on the application purposes. Ozone application in preliminary treatment is advantageous with respect to the improvement of wastewater biodegradability before being subjected to biological treatment, which further results in improvement of the efficiency of treatment process. Several authors have reported the removal of toxic compounds, COD, and color from pulp and paper mill wastewater by ozone treatment [19-21]. Chloro-organics such as chlorophenolics, cRFA are not fully degraded by biological processes which require advanced oxidation before biological treatment to reduce color and refractory organics of the pulp and paper mill wastewater [18, 22].

The main objective of this study was to identify the chloro-organics present in the bleaching wastewater of pulp and paper mill wastewater and to treat the wastewater by advanced oxidation process (Ozonation). Optimization of the process parameters (initial pH of the wastewater and ozone dose) was done in terms of COD and color removal efficiency. The removal efficiency for other parameters such as BOD, AOX, chlorophenolics, and cRFA was determined under optimized conditions.

Materials and Methods

(a) Wastewater and Chemicals

For ozonation studies, wastewater samples were collected from bleaching section (chlorination (C) and alkali extraction (E) stage) of a pulp and paper mill which uses $OCE_{OP}HH$ (O-oxygen delignification stage, C-chlorination stage, $E_{OP}-O_2$ and H_2O_2 reinforced extraction stages, H-hypochlorite stage) bleaching sequence for brightening the mixed hardwood (Eucalyptus and Poplar) kraft pulp. The wastewater samples were collected in clean containers and stored in a refrigerator below $4^{\circ}C$ till use. The chlorophenols and 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 (Richmond, B.C. Canada). All the standards were of highest purity commercially available. Solvents i.e. acetone, *n*-hexane, methanol, tertiary butyl methyl ether, used were HPLC grade and other solvents i.e. ethanol,
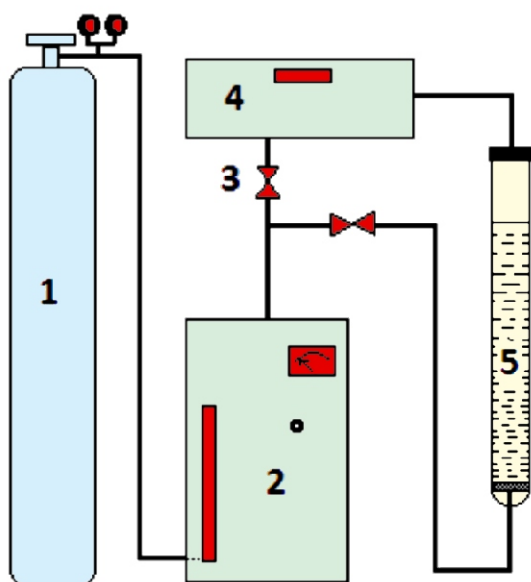

Fig. 1: Experimental set-up for the ozone wastewater treatment: (1) oxygen gas cylinder; (2) ozone generator; (3) on/off valve; (4) ozone monitor and destructor; (5) ozone bubble reactor

and diethyl ether, used were Laboratory grade.

(b) Experimental procedures

A schematic diagram of the laboratory-scale ozone reactor is depicted in Fig. 1. Ozone treatments were performed in a 1 L cylindrical vertical glass bubble reactor. The initial pH of the wastewater was adjusted using solution of either NaOH or H_2SO_4. Ozone was produced from pure oxygen in a laboratory ozone generator (Model: OGL-20, Expotech USA, INC.). The actual ozone production rate was controlled by the current input and the air flow rate. The ozone produced was bubbled through the reactor with different rates using a diffuser. The bottom of the reactor was equipped with diffuser to produce fine ozone bubbles. The flow rate of (oxygen + ozone) was continuously monitored with a rotameter incorporated into the ozone monitor and was set at 12 L/h. The concentration of ozone feed to the wastewater of the ozone reactor was measured by an ozone monitor (Model: BMT-964, BMT-Messtechnik, Berlin). Excess ozone leaving the reactor was destroyed by the in-built ozone destruction unit in ozone monitor. All the experiments were carried out in batch mode on a sample volume of 500 mL for 1 h. The wastewater was characterized before and after ozone treatment in terms of pH, AOX, BOD, COD, chlorophenolics, and cRFA. The change in biodegradability ratio (BOD/COD) of the wastewater was also investigated for assessing the biodegradability of organic pollutants.

(c) Analytical methods

Wastewater samples were analyzed immediately in the laboratory for pH, COD, BOD, color, AOX, chlorophenolics, and cRFA. Color measurement was performed spectrometrically on Analytic Jena spectrophotometer (model Spekol 2000). COD and BOD estimation was done by the standard methods [23]. 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 [24] 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 [25]. 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 were given some where else [26]. 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 [27]. 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 [28]. 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 were given some where else [29]. 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

I. Optimization studies

(a) Wastewater characteristics

The characteristics of the bleaching wastewater (C+E stage) used for the optimization of process parameters for ozonation studies are given in the Table 1. During the optimization studies the wastewater was characterized in terms of pH, COD, and color.

Table 1 : Characteristics of bleaching wastewater (C+E) used for optimization studies

Parameters	Average Value* ± SD
pH	5.5 ± 0.42
COD (mg L^{-1})	826 ± 164
Color (Pt-Co mg L^{-1})	1289 ± 84

*average of three value

(b) Effect of initial pH

The performance of the ozonation process is significantly affected by the reaction pH [30]. The ozonation of wastewater at various initial pH values (3.0-12.0) was examined on the removal of COD and color, respectively, at ozone dosage of 600 mg L^{-1} at the time interval of 60 minutes (Fig. 2). Initially, it was observed that COD and color removal efficiency decreased as the initial pH of the wastewater increased from 2.0 to 5.0. As the initial pH increased from 5.0 to 9.0, COD and color removal increased proportionally. But further increase in initial pH from 9.0 to 12.0, COD and color removal efficiency increased slightly by giving maximum values of 46 and 72%, respectively at pH 12.0. It was observed that both COD and color removal efficiency increased with increasing pH due to the self decomposition of ozone into free hydroxyl radicals under basic pH conditions, which were able to oxidize the organic compounds more actively [31, 32].
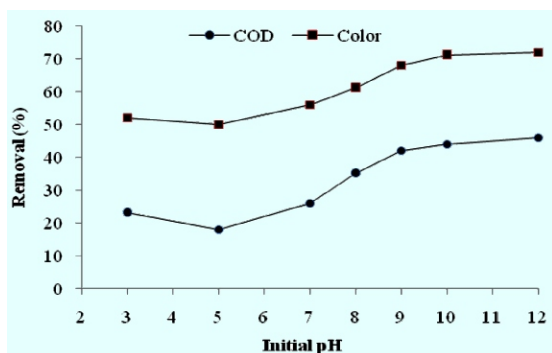
Fig. 2: Effect of initial pH on the removal of COD and Color from wastewater (ozone dose 600 mg L^{-1}, reaction time 1 h)

At lower pH, ozone is slowly decomposing and oxidizes organic matter selectively [33]. Under acidic pH conditions ozone exists in molecular state (O_3) and its decomposition into highly reactive species like HO°, HO°$_2$ and HO°$_3$ only occurs in an alkaline pH conditions [34]. Among these species, the reaction rate of HO° is 10^6 to 10^9 times faster than that of the reaction rate of molecular ozone [35]. Therefore, the initial pH of the wastewater is an important factor determining the efficiency of ozonation process as it can alter the degradation kinetics and pathways [36]. In wastewater, there are several compounds that are capable of the initiation (such as OH$^-$, H_2O_2/HO_2^-, Fe^{2+}, humic substances), promotion (R_2CHOH, aryl(R), formate, humic substances) or inhibition (CH_3COO^-, alkyl(R), HCO^{3-}/CO3^{2-}) of the radical chain reaction process. The inhibitors are capable of consuming hydroxyl radicals which also affects the treatment efficiency of the process [37].Tünay et al. reported oxidation of pulp and paper wastewater by using molecular ozone at pH 8.5 yielded around 80% COD removal in 2 h [38].

On the basis of above COD and color removal results, initial pH of 9.0 was chosen as optimum pH for the further experiments.

(c) Effect of ozone dosage

In order to determine the optimum dosage for the removal of COD and color from pulp and paper mill wastewater, different dosages of ozone were used (600 to 2400 mg L^{-1}) for 1 h. The initial pH value of the wastewater samples was adjusted to 9.0 before ozonation.

Fig. 3 shows the effect of ozone dosage on COD and color removal efficiency. It was observed that percent COD and color removal increased as the ozone dosage increased from 600 to 2400 mg L^{-1} (0.6-2.5 mg O_3/mg of COD) giving maximum COD and color removal efficiency of 68 and 87%, respectively. The rate of COD and color removal was higher as the ozone dosage increased from 600 to 1200 mg L^{-1} (0.6-1.3 mg O_3/mg of COD). But further increase in ozone dosage from 1200 to 2400 mg L^{-1}, the rate of COD and color removal was not proportional as only 10 and 11% additional COD and color removal was observed, respectively.

This could be explained as the more refractory compounds formed at more advanced reaction times [39]. After the initial oxidation stage, the easily oxidizable sites became less available for further ozone oxidation reactions. The ozone competing reaction between the remaining organic matter and chromophoric structures became more dominant. This behavior could be explained by the higher selectivity of ozone towards oxidizing the easily degradable organic compounds (present initially in the wastewater) compared with the ozone selectivity towards reacting with the remaining organic compounds [31]. Tünay et al. (2008) reported up to 80% of COD removal from pulp and paper mill wastewater by using ozone as an oxidant [38].

On the basis of above results and discussion, 1.3 mg O_3/mg of COD was selected as the optimum dosage for subsequent studies.
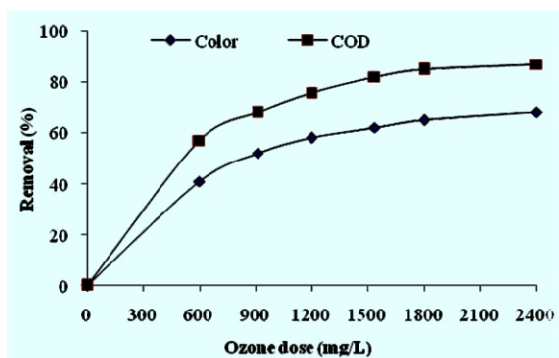

Fig. 3: Effect of ozone dosage on the removal of COD and color (at initial pH 9.0, reaction time 1 h)

II. Treatment of wastewater under optimized conditions

On the basis of optimization results, treatment of bleaching wastewater was conducted under optimum conditions of initial pH (9.0) and dosage of ozone (1.3 mg O_3/mg COD) to know the treatment efficiency of ozone for the removal of AOX, BOD, COD, color, chlorophenolics, and cRFA from the wastewater. The corresponding GC chromatograms for laboratory prepared mixture of 26 standard chlorophenolic compounds, and 4 standard cRFA are shown in Fig. 4 and 5, respectively. Fig. 6 (a-d) shows the chromatogram of chlorophenolics and cRFA in untreated and ozone treated wastewater.

(a) Wastewater characteristics

The characteristics of the bleaching wastewater used for ozone treatment studies are given in the Table 2. The untreated wastewater pH, COD, color, BOD, AOX, chlorophenolics, and cRFA values were 5.2 ± 0.14, 1017 ± 33 mg L^{-1}, 1381 ± 12 Pt-Co units, 228 ± 8 mg L^{-1}, 28.4 ± 1.3 mg L^{-1}, 574.3 ± 12.35 µg L^{-1}, and 645.8 ± 15.27 µg L^{-1}, respectively. The BOD/COD ratio of the wastewater was low (0.224). This indicates that bleaching wastewater contains significant amount of non-biodegradable compounds. Table 3 and 4 shows the concentration of individual chlorophenolics and cRFA detected in the bleaching wastewater, respectively.

Table 2 : Characteristics of untreated bleaching wastewater used for ozonation

Parameter	Average value ± SD
pH	5.2 ± 0.14
COD (mg L^{-1})	1017 ± 33
Color (Pt-Co mg L^{-1})	1381 ± 12
BOD_5 (mg L^{-1})	228 ± 8
AOX (mg L^{-1})	28.4 ± 1.3
Chlorophenolics (µg L^{-1})	574.3 ± 12.35
cREFA (µg L^{-1})	645.8 ± 15.27
BOD/COD	0.224 ± 0.016

Table 3 Removal of chlorophenolics from bleaching wastewater by ozone

S.No	Name of compound	Concentration (µg L^{-1}) ± SD	Removal (%)
1.	3-CP	1.32 ± 0.94	-127
2.	4-CP	0.53 ± 0.38	-310
3.	2,6-DCP	0.56 ± 0.06	85
4.	2,5-DCP	19.22 ± 0.86	90
5.	2,4-DCP	7.28 ± 1.46	83
6.	2,3-DCP	0.08 ± 0.01	ND
7.	3,4-DCP	0.22 ± 0.02	ND
8.	4-CG	1.05 ± 0.06	-50
9.	2,4,5-TCP	27.3 ± 3.26	95
10.	2,3,6-TCP	0.10 ± 0.03	ND
11.	2,3,5-TCP	0.22 ± 0.12	ND
12.	2,4,6-TCP	0.08 ± 0.06	ND
13.	4,5-DCG	23.21 ± 3.95	80
14.	2,3,4-TCP	0.64 ± 0.12	ND
15.	4,6-DCG	78.50 ± 3.77	87
16.	3,6-DCC	90.73 ± 3.63	88
17.	3,5-DCC	4.05 ± 0.58	65
18.	3,4,6-TCG	5.98 ± 1.21	97
19.	3,4,5-TCG	40.61 ± 1.08	91
20.	4,5,6-TCG	9.55 ± 1.59	84
21.	5,6-DCV	12.89 ± 1.14	ND
22.	PCP	3.88 ± 0.38	ND
23.	TeCG	44.13 ± 0.51	ND
24.	TCS	107.69 ± 4.44	94
25.	TeCC	1.09 ± 1.12	ND
26.	2,6-DCSA	93.38 ± 28.24	89
	Total	574.31 ± 12.35	89

D-di; T-tri; Te-tetra; P-penta; CP-chlorophenol; CG-chloroguaiacol; CC-chlorocatechol; CV-chlorovanilim; CSA-chlorosyringaldehyde
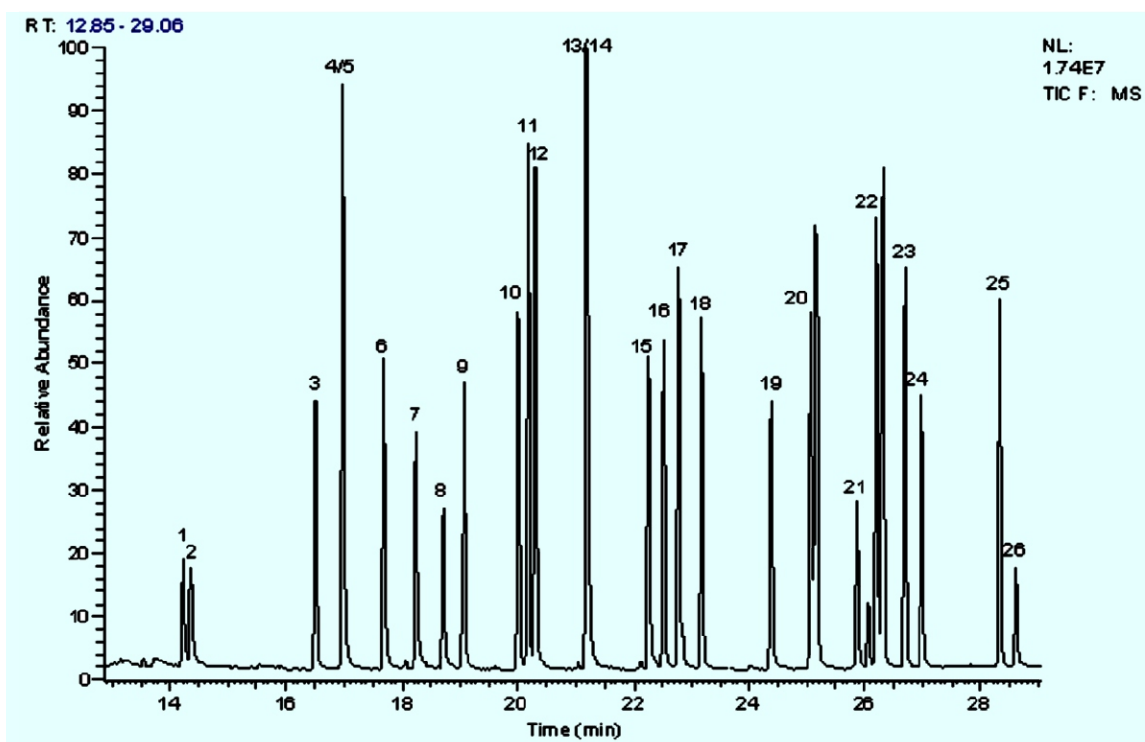
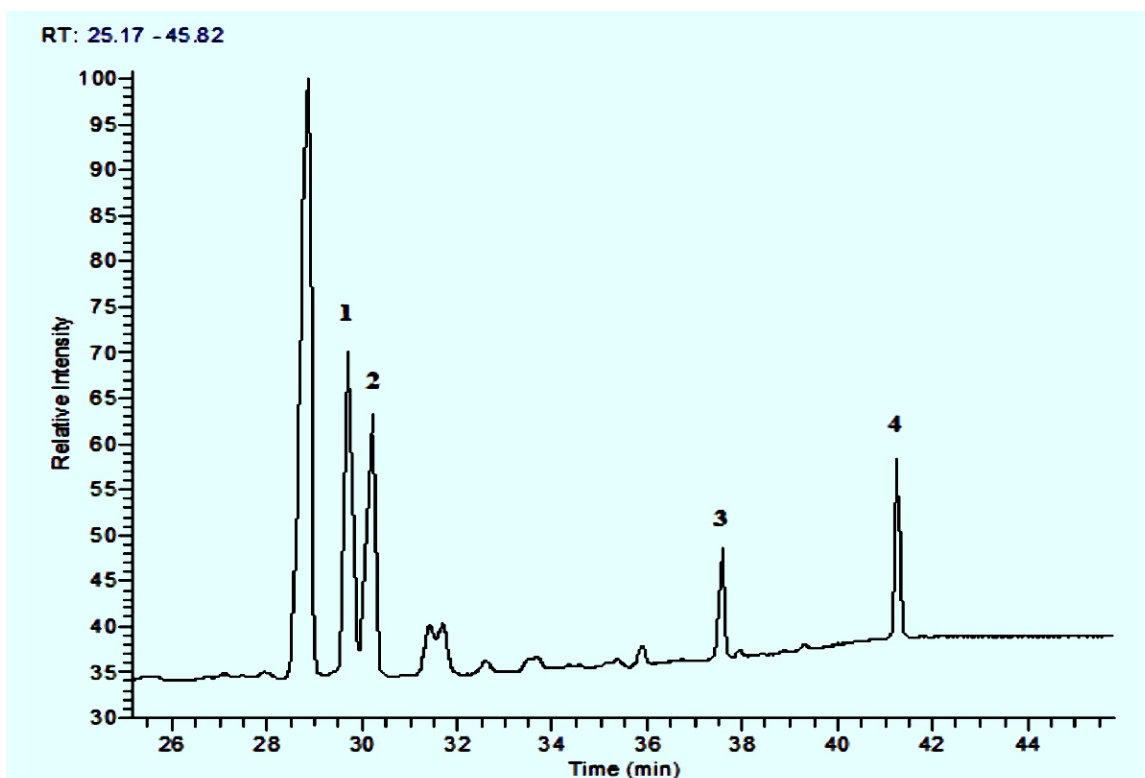Fig. 4: Chromatogram of a mixture of pure standards of chlorophenolic compounds
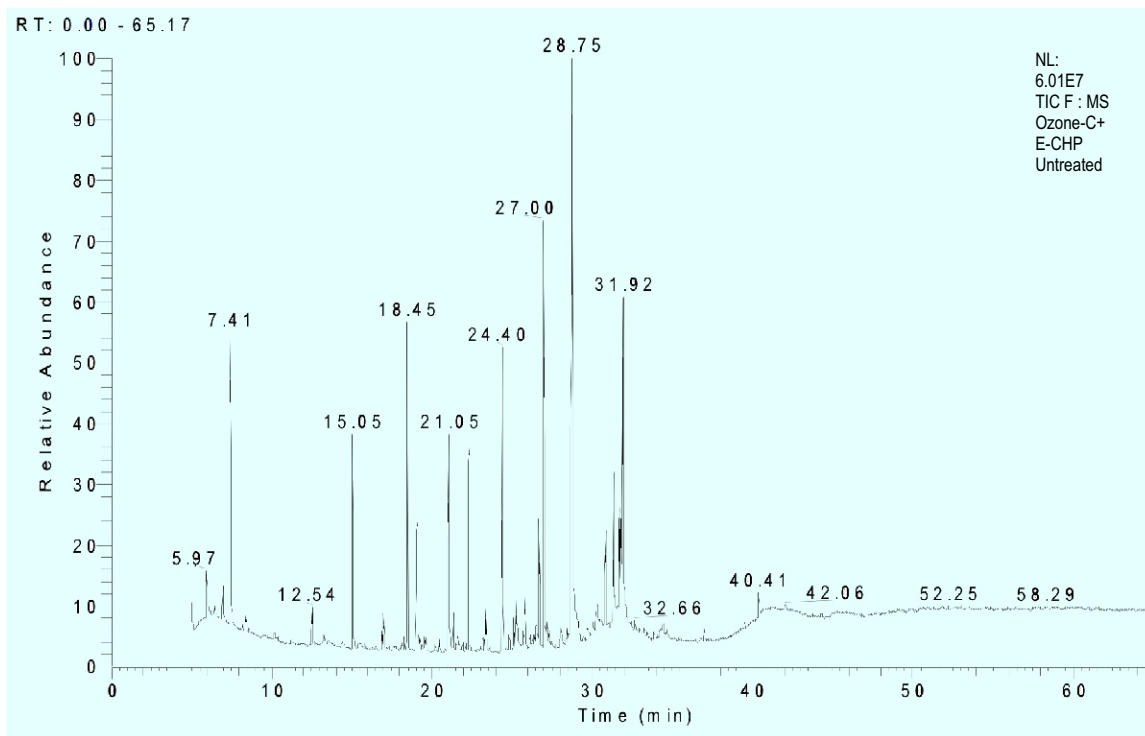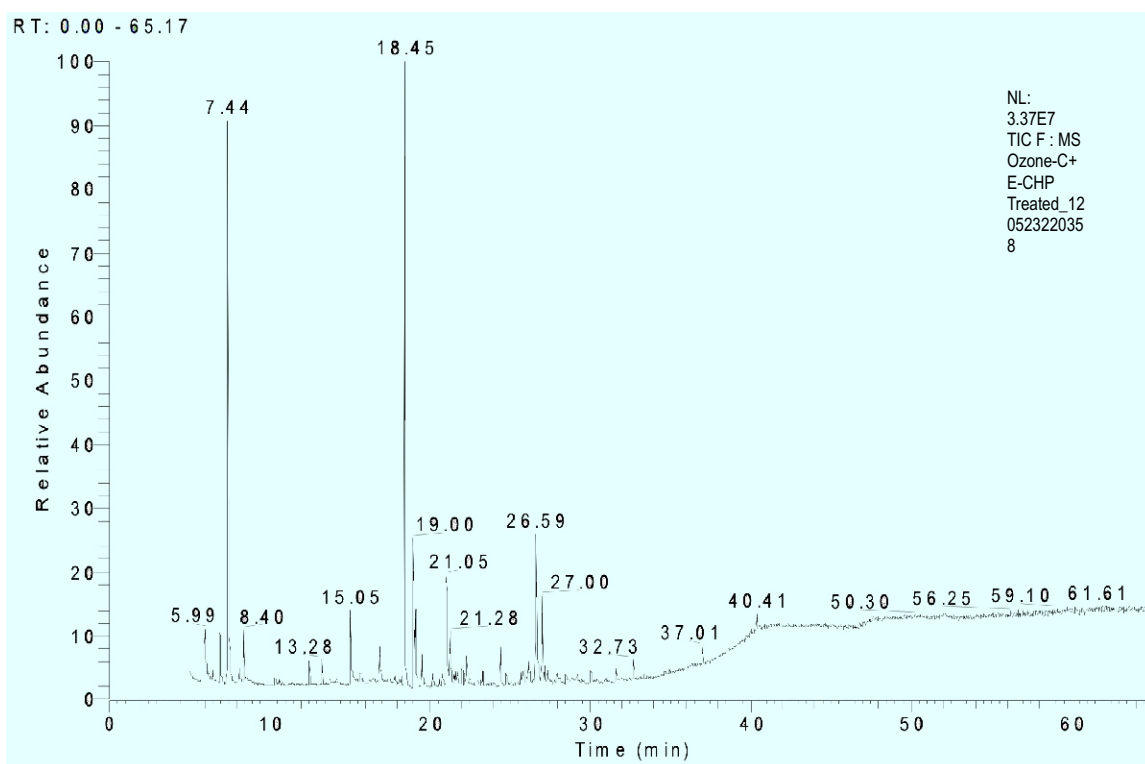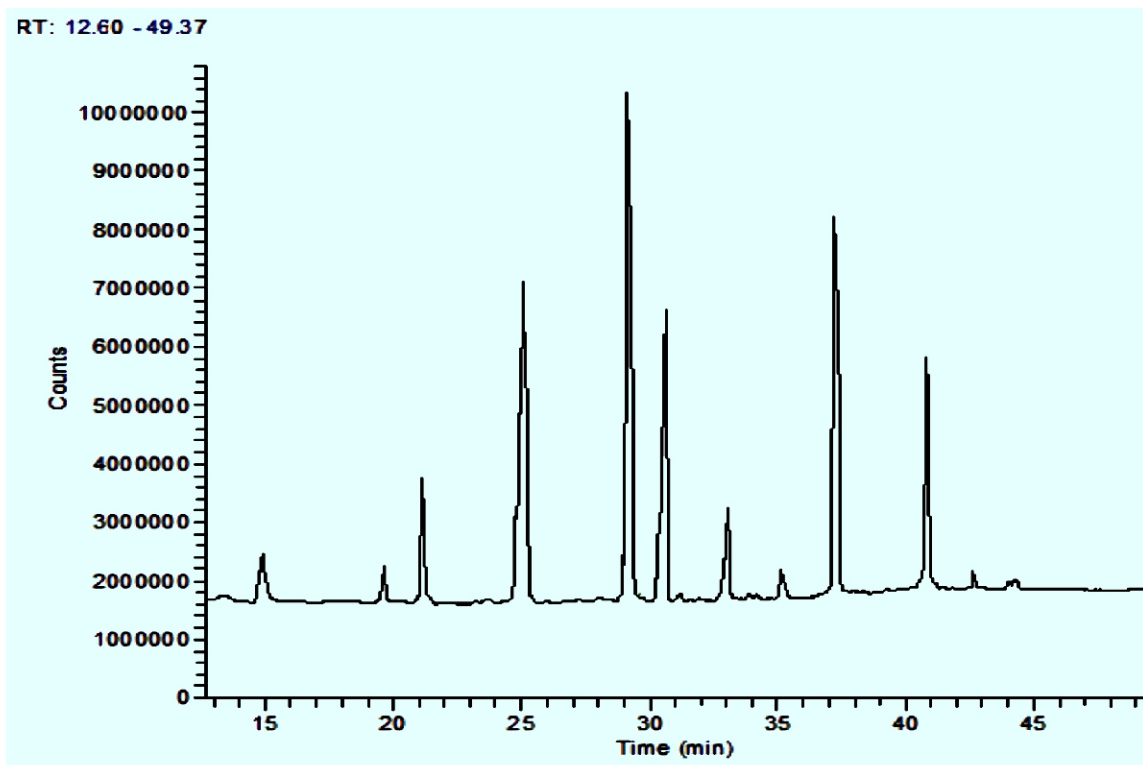

Fig. 5: Chromatogram of a mixture of pure standards of cRFA
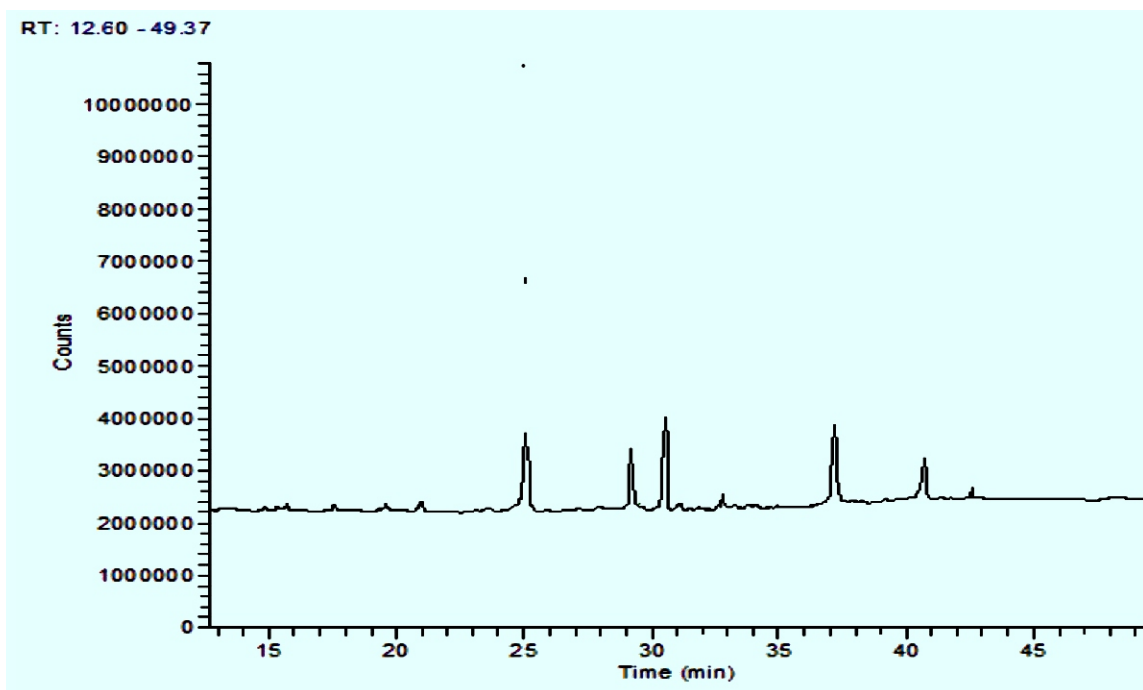
(a)

(b)

(c)

(d)

Fig. 6: Chromatogram of chlorophenolics (a) and cRFA (c) in untreated bleaching wastewater;
chromatogram of chlorophenolics (b) and cRFA (d) in ozone treated wastewater.

Table 3 shows that six categories of 26 chlorophenolic compounds (chlorophenols (CP), chlorocatechols (CC), chloroguaiacols (CG), chlorosyringol (CS), chlorosyringaldehyde (CSA), and chlorovanilline (CV)) were detected in the untreated wastewater. Among the various chlorophenolics, TCS contributed the highest concentration (107.69 µg L^{-1}) followed by 2,6-DCSA (93.38 µg L^{-1}), 3,6-DCC (90.73 µg L^{-1}), 4,6-DCG (78.50 µg L^{-1}), TeCG (44.13 µg L^{-1}), 3,4,5-TCG (40.61 µg L^{-1}), 2,4,5-TCP (27.32 µg L^{-1}), 4,5-DCG (23.21 µg L^{-1}), and 2,5-DCP (19.22 µg L^{-1}). The concentration of other chlorophenolics was below 10 µg L^{-1}. Examination of data of total chlorophenolics content reveals that CG contributed the highest share with 35.4% followed by CS (18.8%), CC (16.7%), CSA (16.3%), CP (10.7%), and CV (2.2%). The percentage of chlorophenolics as per chlorine atom substitution. Dichlorophenolics (DCP) contributed the highest share with 57.5% followed by trichlorophenolics (TCP) (33.5%), tetrachlorophenolics (TeCP) (7.9%), pentachlorophenolics (PCP) (0.7%), and monochlorophenolics (MCP) (0.5%).

The results indicate that about 99% of the identified compounds in the untreated bleaching wastewater were DCP, TCP, and TeCP compounds. The relative quantities of various chlorophenolics present in the wastewater mainly depends on the bleaching conditions (bleach chemical dose, temperature for bleaching, pulp consistency), nature and characteristics of lignin, wood species and type of pulp employed in bleaching by the paper mill [10].

The quantities of various cRFA detected in the untreated wastewater are shown in Table 4. Two chloro fatty acids (cFA) i.e. 9,10-dichlorostearic acid (DCSA) and 9,10,12,13-tetrachlorostearic acid (TCSA) and two chloro resin acids (cRA) i.e. chlorodehydroabietic acid (CDAA) and 12,14-dichlorodehydroabietic acid (DCDA) were identified in the untreated bleaching wastewater. Among the cRFA, the concentration of DCSA was found to be highest (184.50 µg L^{-1}) followed by CDAA (171.53 µg L^{-1}), DCDA (158.22 µg L^{-1}), and TCSA (131.57 µg L^{-1}). cRA and cFA contributed to 51.1 and 48.9%, respectively, of the total cRFA content.

(b) Wastewater treatment by ozone

The treatment efficiency of the ozonation process was examined by monitoring various pollution parameters in the untreated and treated wastewater, and the obtained results are given in Tables 2-4 and shown in Fig. 7-10. The final pH of wastewater after ozonation treatment process was observed to decrease significantly (end pH 8.1). This can be attributed to the formation of acidic compounds (such as oxalic acid, fumaric acid) during the ozonation process [40].
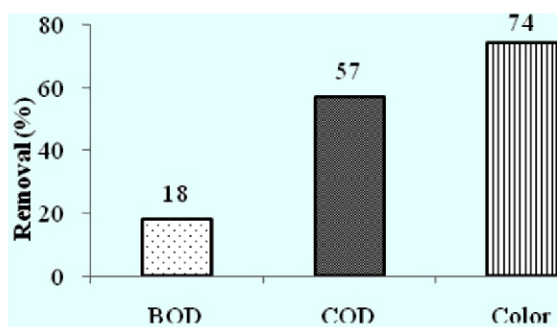
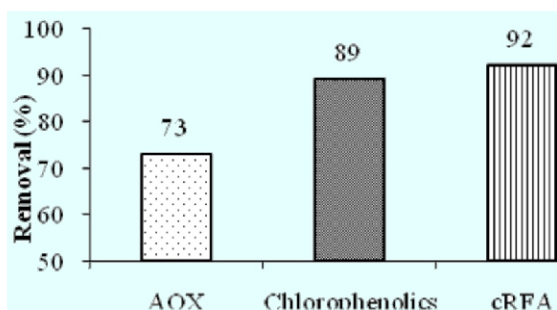

Fig. 7: BOD, COD, and Color removal by ozone

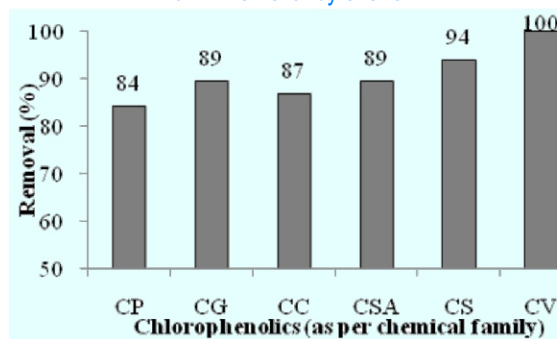Fig. 8: AOX, chlorophenolics and cRFA removal by ozone

Fig. 9: Removal of chlorophenolics from bleaching wastewater by ozone treatment
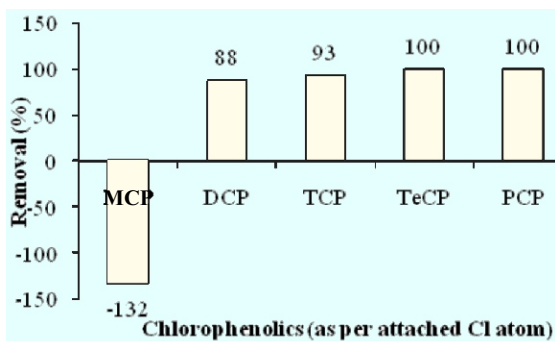
Fig. 10: Removal of MCP, DCP, TCP, TeCP and PCP by ozone treatment

Fig. 7 shows the average percent removal of BOD, COD, and color from bleaching wastewater by ozone treatment process. For BOD, COD, and color, removal efficiency of the process was 18, 57, and 74%, respectively. It was observed that the removal efficiency for color was higher in comparison to BOD and COD. This may be due to two probable reasons, first is the preferential attack of ozone on lignin as compared to carbohydrates in bleaching wastewater [41].

Secondly, higher color removal was probably due to the partial oxidation of unsaturated bonds of chromophoric groups responsible for color. However, partially oxidized products contributed to COD until their final degradation [42]. Pokhrel and Viraraghavan also reviewed several experiments, indicating that the ozonation was highly efficient for decolorization (95-97%) of pulp and paper mill wastewater [1]. Kreetachat et al. investigated the effect of ozonation process on pulp and paper mill wastewater. The results indicated that after 45 min, the ozonation of wastewater yielded over 90% decolorization efficiency [31].

After ozonation, the BOD/COD ratio of wastewater increased from 0.224 to 0.432. The increase in biodegradability produced by ozonation results both from transformation of high molecular mass fraction into low molecular mass fraction and increased biodegradability of the high molecular mass matter [41]. Fig. 8 shows the average percent removal of AOX, chlorophenolics and cRFA. The removal of AOX, chlorophenolics and cRFA obtained by the

treatment process was 73, 89, and 92%, respectively. Among chloro compounds the highest removal was observed for cRFA.

After ozone treatment process, 16 chlorophenolic (out of 26) compounds were detected in the wastewater. 65-100% removal of chlorophenolics was achieved except MCP (3-CP, 4-CP, and 4-CG) for which higher concentrations were observed in treated wastewater (Table 3). The chlorophenolics i.e., 2,3-DCP, 3,4-DCP, 2,3,6-TCP, 2,3,5-TCP, 2,4,6-TCP, 2,3,4-TCP, 5,6-DCV, PCP, TeCG, and TeCC were not detected after treatment. Examination of the data shows that the removal efficiency of ozone treatment was 100% for CV, 94% for CS, 89% for CG & CSA, 87% for CC, and 84% for CP (Fig. 9). Lowest removal was observed for CP and highest for CV. Figure10 shows the removal of chlorophenolics (as per Cl atom attached) by the ozone treatment. Percentage removal of DCP, TCP, TeCP, and PCP was 88, 93, 100, and 100%, respectively. Highest removal was observed for TeCP and PCP followed by TCP, and DCP. No positive removal was observed for MCP after the treatment. The removal efficiency for different cRFA was from 88-97% (Table 4). The highest removal was observed for DCSA (97%) followed by TCSA (95%), DCDA (89%), and CDAA (88%). Treatment efficiency of ozone was better for the removal of cRA (96%) than cFA (89%).

Table 4 : Removal of cREA from bleaching wastewater by zone

S.No	Name of compound	Concentration ($\mu g\,L^{-1}$) ± SD	Removal (%)
1.	DCSA[a]	184.50 ± 4.44	97
2.	CDAA[b]	171.53 ± 6.94	88
3.	DCDA[b]	158.22 ± 8.33	89
4.	TCSA[a]	131.57 ± 4.42	95
	Total	645.81 ± 15.27	92

a-chloro fatty acids, b-chloro resin acids

The degradation of chlorophenolics is favored at high pH [43]. The faster degradation of these compounds in alkali media can be due to the fast production of HO radicals and the dissociation of

chlorophenolics to chlorophenolate ions that are able to react with ozone faster than non dissociated species. After treatment with ozone, the complete removal of CV was observed. This was due to lowest share of CV (2.2%) in untreated wastewater comparative to other categories. Examination of data (Fig. 10) shows that the removal of higher chlorinated chlorophenolics was more as compared to lower chlorinated chlorophenolics. This is due to the following two reasons, first is the conversion of higher chlorine substituted chlorophenolics to the lower chlorine substituted chlorophenolic compounds which further increases the concentration of lower chlorine substituted chlorophenolics in the treated wastewater. Second is the lower content of TeCP and PCP in the untreated wastewater. Removal of higher chlorinated chlorophenolics (PCP, TeCP, and TCP) by ozone also favours to reduce the toxicity of bleaching wastewater as these compounds are more toxic in comparison to lower chlorinated chlorophenolics (MCP and DCP). During ozonation, organic chlorine is converted to chloride with high yields (up to 90%) depending upon the position of the chlorine atom with respect to the OH group [44]. Trapido et al. have also reported that an increase in the number of chlorine atoms in the aromatic ring favors the degradation rate of chlorophenols [45]. Similar findings were also reported by Benıtez et al. [43]. Reynolds et al. reported the complete removal of PCP (70 mg L^{-1}) by ozone within 15 min. of contact time [46]. Wright et al. reported the removal of abietic (70%) and linoleic acid (85%) by ozone doses above 2.5 mg L^{-1} under alkaline pH conditions [47].

After treatment, the BOD and COD values of the wastewater were still above the Indian standard of BOD and COD discharge limits of 30 mg L^{-1} and 250 mg L^{-1}, respectively but BOD/COD ratio increased from 0.224 to 0.432 due to the higher removal of COD (57%) load in comparison to BOD (18%). Lower BOD removal was due to the conversion of recalcitrant compounds into biodegradable compounds which further increased the biodegradable content in untreated wastewater. On the other hand, the removal of highly chlorinated chloro-organics was higher as compared to lower ones, which reduced the toxicity of bleaching wastewater. There was no specific standard discharge limits for color and different chloro-organics.

Conclusion

Based on the present investigation, it can be concluded that ozonation is an effective process for the treatment of bleaching wastewater. The removal of color and COD by ozonation increases as the initial pH of the wastewater and ozone dosage increases till it attains equilibrium. Ozonation also increases the biodegradability of wastewater. It results in the complete removal of CV and TeCP & PCP from wastewater. It is more effective for the removal of cRFA and highly chlorinated chlorophenolics as compared to lower chlorinated. The results of this study indicates that the ozone treatment alone is not sufficient to discharge the pulp and paper mill wastewater directly into surface water and further treatment is required to meet out the discharge limits. Ozone treatment of bleaching wastewater makes it suitable for biological treatment by increasing the biodegradability and decreasing considerably wastewater toxic compounds. Therefore ozonation process is recommended as pretreatment before biological treatment.

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