

Minimising The Formation of 2378 TCDD and 2378 TCDF in Bleaching Effluents - A Laboratory Study

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ABSTRACT

Bleaching of pulps using chlorine is quite common in Indian Pulp and Paper Industry. Chlorination stage is responsible for generation of two very highly toxic compounds namely 2378 tetrachlorodibenzodioxin (2378 TCDD) and 2378 Tetrachlorobenzofuran (2378 TCDF). In order to reduce the generation of these two compounds bleaching process can be modified like splitting of chlorine dose in two stages, a oxygen stage prior to chlorination, replacement of chlorine by chlorine dioxide. In the present study levels of 2378 TCDD and 2378 TCDF have been estimated in bleaching effluents generated using different bleaching agents. These two compounds have also been estimated in some paper products of common use.

INTRODUCTION

Dioxin is the general term used by journalists, engineers and most non-chemists for 2378 tetrachlorodibenzo-p-dioxin (2378 TCDD). It is one of the family of 210 polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD and PCDF). The toxicity of individual members of the above mentioned family of PCDD and PCDF differ substantially. The most toxic 2378 TCDD is atleast 100,000 times more toxic than the least potent of them.

Dioxin has been an important issue in environmental and occupation health for almost two decades. This is shown by the fact that international symposium on the dioxins is held every year. During the last two decades scientists have developed isomer specific analytical procedures (1-3) in various environmental samples and have studied its possible impacts on exposed human populations and toxic effects on laboratory animals. As a result of this research effort, dioxin is now one of the best studied toxic

substances. A number of reports (4-7) books (8-10) and reviews (11-14) have appeared in recent years.

The main sources of the dioxins are thought to be burning of lead petrol and diesel fuel (15-16) in vehicles, burning of municipal waste (17-18) (incinerators), generations of electric energy through burning of coal (fly ash) (19-20) or oil industrial spillage's and some sewage treatment plants (21-22).

A series of PCDD'S and PCDF'S have now been identified in technical formulations and in various environmental samples such as human blood (23-24) and adipose tissue (25-26), fish tissue (27-28), bird eggs (29), beef fat (30), deer tissue (31), sediments (32), soil (33-34), fly ash (35-36) and other products from incineration or combustion process. The presence of

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these compounds have also been detected in phenoxy herbicide (37), chlorophenols (38-40) (used extensively as fungicides, mold inhibitors, disinfectants and insecticides), in polychlorinated biphenyl (PCB) (used as pesticides) (41).

The 2378 TCDD has been shown to be highly toxic, bioaccumulative, mutagenic and carcinogenic. The half life has been found to be 600 days in model aquatic environment (42), about 5 years in human system (43) and 10-12 years in soils. 50-60% of the original concentrations (1-100 ppm) remain unchanged even after weathering for one year in soil (44). Young Oats and soybeans grown on sandy loam (soil) contaminated with 60 ppb TCDD were found to accumulate 40 ppb (45). TCDD was also found to be present in cow milk and milk of exposed mothers (47,48) from contaminated area of Seveso, Italy. It shows strong mutagenicity with salmonella strain for most animals' (49) (mouse, rat, chicken, rabbit, monkey, and guinea pig). The LD values for guinea pig 0.6 µg/kg (50). Carcinogenic effects like high incidence of soft tissue sarcomas diseases among workers employed in US in the manufacture of phenoxy herbicide and chlorophenols (51) and three cases of Vietnam who were exposed to Agent Orange (52) (herbicide).

In 1985, trace levels of dioxin was reported in the fish samples from down stream of paper mills. In an effort to find the source, EPA tested mill sludge and found trace amounts of dioxin (53). Since then paper industries all over the world have come under tremendous pressure to measure the levels of dioxin, devise methods to reduce the generation of dioxins & furans if not altogether removed. Joint study groups were set up in U.S.A. and other developed countries comprising members from industry, research institutions, EPA and NCASI to study in depth the problem of dioxin formation. These studies have confirmed the presence of trace levels of 2378 TCDD and 2378 TCDF in bleached pulp, effluents, sludge and paper samples of common use (54,55).

During the last one decade a number of publications (56-68) have appeared on the dioxins pertaining to bleaching of pulp and paper industry. The studies have confirmed that these compounds are formed during chlorination of pulp (58). The quantity of dioxin depends upon quantity of chlorine charged (56). Among the various methods employed to reduce the formation of 2378 TCDD and 2378 TCDF are to reduce the quantity of chlorine charged by replacing partially or completely chlorine by chlorine dioxide or using oxygen stage prior to chlorination/chlorine dioxide

stage of pulp bleaching.

NCASI also examined the potential impact of inhalation of paper dust on mill employee's (69). The risk assessment studies shows that if the work place dust levels are at or below the current standard set by Occupational Safety and Health Administration, there is no dioxin related risk posed to workers through paper dust inhalation.

Indian paper industry still continues to use chlorine for bleaching. In India the use of chlorine is likely to continue for atleast one or two decades. In the present communication, we report results on the estimation of 2378 TCDD and 2378 TCDF in the chlorination, extraction and chlorine dioxide stage effluents generated in the laboratory by bleaching a mixed wood industrial kraft pulp and paper products of common use.

EXPERIMENTAL

REAGENTS

All solvents used were of HPLC grade. Aluminum oxide (basic, Brockman activity grade 1) and silica gel (60-120mesh) were obtained from Sisco Research Laboratory (Bombay, India). E. Merck (India) supplied activated carbon. Celite 545, laboratory reagent grade was procured from S.D. Fine Chemicals Ltd (India). Standard solutions of 2378 TCDD and 2378 TCDF (50 µg/ml in nonane) were supplied by Cambridge Isotope Laboratory (Massachusetts, USA). Fused silica capillary columns were procured from J&W Scientific (Folsom, California USA). The reagents used for bleaching of pulp were laboratory grade chemicals. All other chemicals used were analytical reagent grade.

Unbleached mixed wood pulp (eucalyptus + pine+ bamboo) was taken from a nearby paper mill. The Kappa number (residual lignin) of the pulp was determined (Tappi Test Method T_{236cm-85}) and was found to be 32.6. the chlorine demand was calculated from the equation:

$$\text{Chlorine demand (\%)} = 0.25 \times \text{kappa number}$$

Unbleached pulp (equivalent to 100g oven dried pulp) was bleached in the laboratory to generate effluents 70% of chlorine demand has been applied as elemental chlorine in chlorination and chlorine dioxide stages. The bleaching conditions and the volumes of the effluents generated (filtrate + washings) are shown Table-1.

Table-1
Bleaching conditions

Parameter	Bleaching stage			
	C	E	D ₁	O
Chlorine charge (%)	5.7	-	5.7*	-
NaOH (%)	-	3	-	2.5
Oxygen pressure (kg/cm ²)	-	-	-	8
Consistency (%)	3.5	10	10	10
pH	1.8-2.0	10	4-6	11
Temperature (°C)	Ambient	60	70	110
Time (min)	60	75	180	60
Effluent volume (l)	5.17	6.0	6.0	1.5

* as active chlorine

EXTRACTION PROCEDURE:

EFFLUENTS:

The entire effluent approx. 6l was divided into three 5l round bottomed flask and extracted for 16 hrs. with 400 ml of methylene chloride per liter of effluent. The organic extracts and washings were combined and concentrated to 10 ml in a synder column.

PAPER SAMPLES:

Homogenized paper sample equivalent to 100g oven dried paper was placed in 4 Soxhlets extraction apparatuses and extracted with 175ml each of 50:50 acetone benzene mixture for 16 hrs. The extracts and rincings were combined and concentrated to 10 ml in a synder column

CLEAN UP PROCEDURE

The following liquid chromatography columns were prepared.

SILICA COLUMN:

A glass chromatographic column 20mm OD x 230 mm long, tapered to 6mm at one end was packed successively with a plug of glass wool, 1g silica, 2g silica containing 28% (w/w) 1M NaOH, 1g silica, 4g silica containing 30% (w/w) H₂SO₄ and 2g silica

ALUMINA COLUMN:

Basic alumina (60-120mesh) was activated at 600°C

by placing it in a muffle furnace for 24 hrs. It was then cooled and stored in a desiccator. An alumina column was made by packing a plug of glass wool and then adding 3g of basic alumina.

CARBON/CELITE COLUMN:

A mixture of 5.35g carbon + 62.5g celite 545 was prepared and activated by placing in an oven at 130°C for 6 hrs. A 9-inch disposable Pasteur pipette was cut 1.25 cm above the tip. The glass wool was inserted into the tube and packed with activated carbon celite mixture up to 2cm height.

WASHING

The concentrated extracted sample (10ml) was washed successively by following wash solutions by shaking for 10min.

- (i) 30 ml of 20% aq. KOH solution.
- (ii) 30 ml of distilled water.
- (iii) 30 ml of conc. H₂SO₄.
- (iv) 30 ml of distilled water.

The washed extract was dried by adding 5g of anhydrous Na₂SO₄ to washed extract and the mixture was allowed to stand for 15 min. The extract was quantitatively transferred to a test tube and concentrated to 5ml by passing a stream of N₂ over extract maintained at a temperature of 55°C by placing the test tube in a water bath.

Table-2
GC conditions for analysis of 2378 TCDD and 2378 TCDF

Parameter	Capillary column	
	DB-5	DB-225
Detector	ECD	ECD
Detector range	10°	10°
Chart speed (cm/min)	10	10
Sample size (µl)	0.5	0.5
Carrier gas	N ₂	N ₂
Column dimensions	60 m x 0.25 mm	30 m x 0.25 mm
Film thickness (µm)	0.10	0.25
Injection & detector temp. (°C)	280	260
Column temp. programming		Isothermal
Initial temp. (°C)	190	
Initial time (min)	1	
Temp. programming rate (°C/min)	6	
Final temp. (°C)	260	
Final time (min)	20	

COLUMN CLEANING:

The sample was cleaned by passing through 5 different columns.

SILICA COLUMN:

The washed sample along with two 1ml rinsings of n-hexane was transferred to a silica column. The column was eluted with 90ml of hexane and the eluate was concentrated to 1-2ml.

ALUMINA COLUMN:

The concentrated eluate along with two 1ml rinsings were transferred to alumina column. The column was first eluted with 10 ml of 3% methylene chloride in hexane and then eluted with 15ml of 20% methylene chloride in hexane. Both the eluates were discarded. Finally the column was eluted with 15ml of 50% methylene chloride in hexane and the eluate was concentrated to 1ml.

ALUMINA COLUMN:

The concentrated eluate along with two 1ml rinsings were transferred to alumina column and eluted with 90 ml hexane. The eluate was concentrated to 1ml.

CARBON CELITE COLUMN:

The concentrated eluate along with two 1ml rinsings were transferred to a carbon celite column and eluted first with 2ml of 50:50 methylene chloride cyclohexane mixture and then with 2ml of 50:50 benzene ethyl acetate mixture. Both the eluates were discarded. Then the column was reversed (inverted) and was extracted with 4ml of toluene. The eluate was concentrated to 1ml.

ALUMINA COLUMN

The concentrated eluate along with 1ml rinsings were transferred to an alumina column and eluted with 15ml of 50% methylene chloride in hexane. The eluate was concentrated to 1ml.

The eluate was transferred to micro reaction vessel using two 1ml portions of methylene chloride to rinse the test tube. The solution was evaporated to dryness using a stream of N₂. The walls of micro reaction vessel were rinsed with 0.5ml methylene chloride and the solution was again evaporated to dryness. The residue was dissolved in 100µl of n-nonane and 0.5µl of this solution was injected into respective GC column.

GC STUDIES:

Gas chromatographic studies were performed on a Shimadzu Gas Chromatograph GC-9A model equipped with ECD detector. The fused silica column used for

Table-3
Retention time and extraction efficiency of 2378 TCDD and 2378 TCDF.

Compound	Column	RT	Percent extraction efficiency			
			Liquid samples at pH			Solid sample at pH
			2	7	11	7
2378 TCDD	DB-5	24.69	48.4	40.7	33.7	78
2378 TCDF	DB-225	22.73	62.5	42.5	31.5	80

the analysis of 2378 TCDD was DB-5 and for 2378 TCDF was DB-225. The injection was splitless mode (2 min). The gas chromatographic conditions are given in Table 2.

Standard solutions of 2378 TCDD and 2378 TCDF were prepared by diluting original solution of 50 µg/ml to 5ng/ml. These solutions were used for determination of retention time, response factor and extraction efficiency.

RESPONSE FACTOR DETERMINATION:

Retention time was determined by injecting 0.5 µl of a standard solution of 2378 TCDD or 2378 TCDF into respective GC column maintained as per conditions given in Table 2. From the peak area, the response factor was calculated by the equation:

$$\text{Response factor} = \frac{\text{Sample injected (pg)}}{\text{Peak area}}$$

EXTRACTION EFFICIENCY DETERMINATION:

10ng of 2378 TCDD or 2378 TCDF was added to 31 of distilled water or 20g equivalent of oven dried paper sample. The sample was extracted, purified and concentrated to 100 µl as per procedure outlined above. 0.5 µl of the extracted and non-extracted sample (containing 10ng/100µl) was injected into respective GC column and the peak area was determined in both the cases. The extraction efficiency (EF) was calculated from the equation:

$$\text{EF(\%)} = \frac{\text{Peak area of extracted sample} \times 100}{\text{Peak area of non-extracted sample}}$$

The values of retention time, response factor and extraction efficiencies are given in Table 3. 2378 TCDD and 2378 TCDF in various effluent and paper samples were identified by matching the retention time of the

peaks with those of pure standards. The quantity of 2378 TCDD and 2378 TCDF was estimated from the multi point calibration curve drawn between peak area and quantity of 2378 TCDD/2378 TCDF.

RESULTS AND DISCUSSION

The LD₅₀ values (Table-4) indicate that 2378 TCDD is highly toxic and carcinogenic. The concentrations of 2378 TCDD and 2378 TCDF in various bleaching effluents, are given in Table 5. The results (Tables-5) show that the concentration of 2378 TCDF is much higher than 2378 TCDD in all the effluents. The concentration being nanogram levels of TCDF and TCDD. The results (Table 5) further show that the concentrations of both TCDD and TCDF in extraction stage are much higher than their corresponding concentration in C_{stage} or D_{stage}.

Recent studies indicate that the formation of 2378 TCDD increases with increasing chlorine active multiple, the values being very low at chlorine active multiple of 0.16 and then increase substantially with increasing chlorine active multiple (58,59,67). The bleaching studies have been performed at chlorine active multiple of 0.175 (70% of 0.25). The results obtained in the present study are somewhat higher.

The results (Table 5) show that introduction of oxygen stage prior to C_{stage} results in reduction of concentration of total (C_{stage} + E_{stage}) TCDD by 77% and TCDF by 67%, the chlorine multiple still being 0.175. This indicates that the generation of TCDD and TCDF is not only a function of active chlorine multiple but also is a function of active chlorine charged.

When the total chlorine charged in C_{stage} is split into two equal doses, the generation of total (C_{stage} + E_{stage}) TCDD is reduced by 38% and TCDF by 22%. This is in agreement with the reported results.

When chlorine dioxide stage is used in place of C_{stage}, the generation of total (C_{stage} + E_{stage}) TCDD is

Table-4
Biological effects of 2378 TCDD.

Sample	Half life	LD ₅₀ value	Carcinogenic risk
Aquatic environment	6000 d	-	-
Soil	10-12 y	-	-
Human	5 y	-	-
Guinea pig	30 d	0.6 µg/kg	-
Rats	31 d	-	70 µg/kg/d
Monkey	1 y	-	1 pg/kg/d
Hamsters	-	5 mg/kg	-

Table-5
Concentration of 2378 TCDD and 2378 TCDF in various bleaching effluents.

Bleaching sequence	Effluent (stage)	2378 TCDD		2378 TCDF	
		ng/l	mg/t(pulp)	ng/l	mg/t(pulp)
CEH	C	5.03	0.260	173.30	8.96
	E	6.66	0.400	458.30	27.50
OCEH	C	0.54	0.028	21.66	1.12
	E	2.08	0.125	185.16	11.11
C ₁ C ₂ EH	C ₁ C ₂	2.24	0.116	148.55	7.68
	E	3.77	0.226	344.00	20.64
D ₁ ED ₂	D ₁	1.60	0.096	56.60	2.93
	E	2.53	0.152	229.17	13.75

Table-6
Concentration of 2378 TCDD and 2378 TCDF in different paper samples.

Paper sample	2378 TCDD		2378 TCDF	
	pg/g		pg/g	
Writing paper	26.8		5250	
Tissue paper	85.9		7690	
Paper plate	72.6		7960	

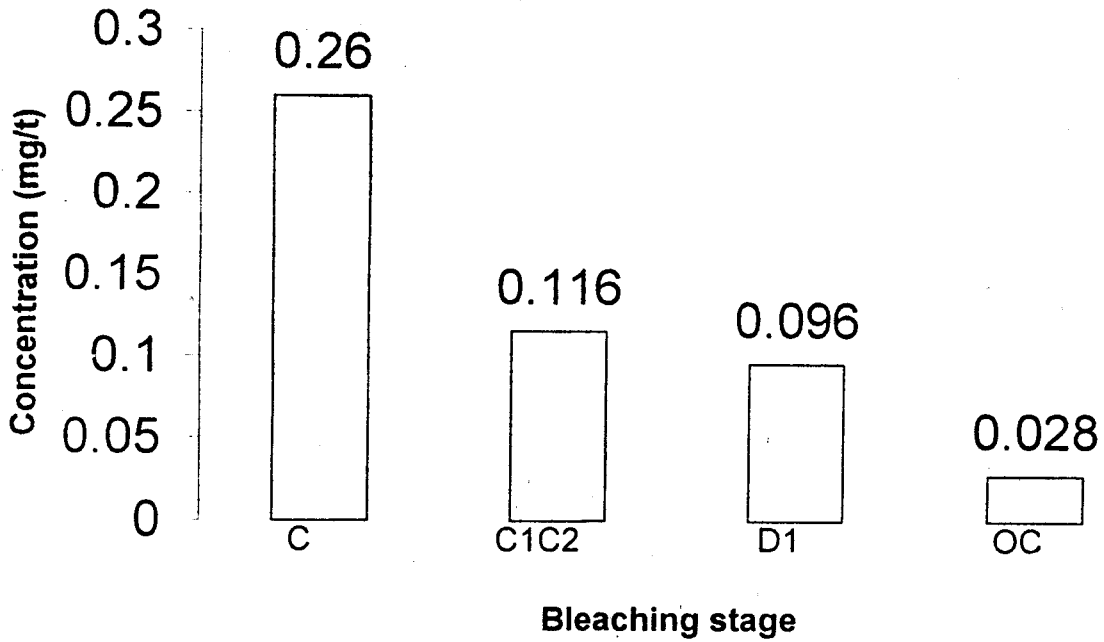
reduced by 62% and that of TCDF by 53%, the chlorine dioxide charged in D_{stage} being equivalent to active chlorine charged in C_{stage} is equivalent to 100% replacement of chlorine by chlorine dioxide in C_{stage}. The results are in agreement with the reported results (59, 67), which indicate that at 70%, or above substitution of chlorine by chlorine dioxide in C_{stage}, the formation of TCDD and TCDF becomes negligible. The percent reduction obtained in the present study is somewhat

lower than the reported results.

The results (Figs. 1-4) further indicate that the reduction in the concentration of TCDD and TCDF in the extraction stage following the respective OC, C₁C₂ or D_{stage} is of the similar order as observed with OC, C₁C₂ and D_{stage}.

Thus approx. 22-77% of TCDD and TCDF levels can be reduced by adopting changes in bleaching

FIG.1 Concentration of 2378 TCDD in various bleaching stages before 1st extraction stage



technology incorporating modern bleaching agents like in conventional C_{stage} oxygen, chlorine dioxide or even splitting chlorine dose

FIG.2 Concentration of 2378 TCDD in 1st extraction stage of different bleaching sequences.

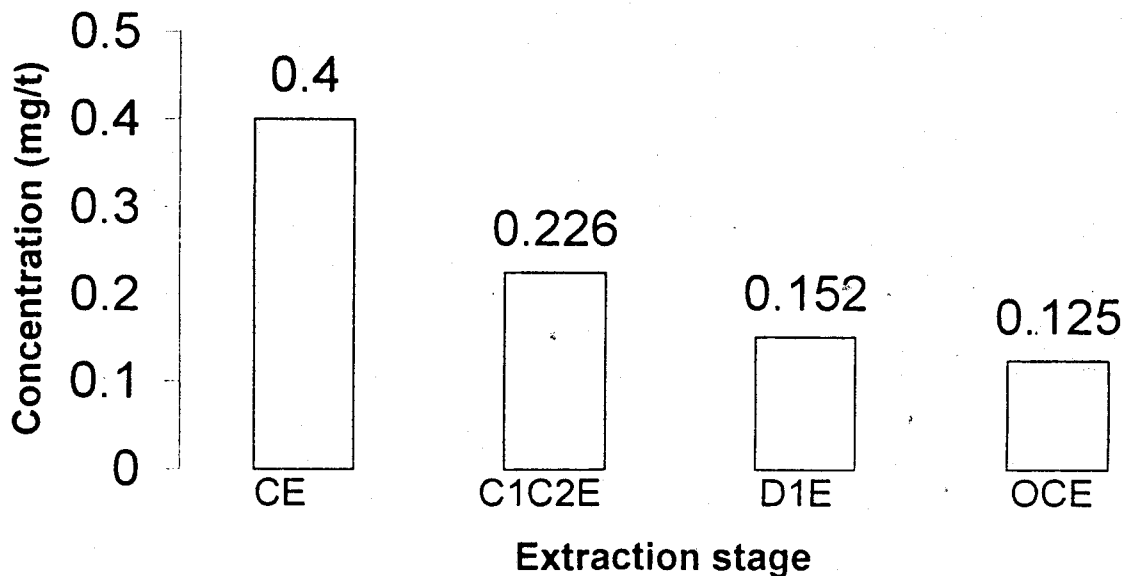
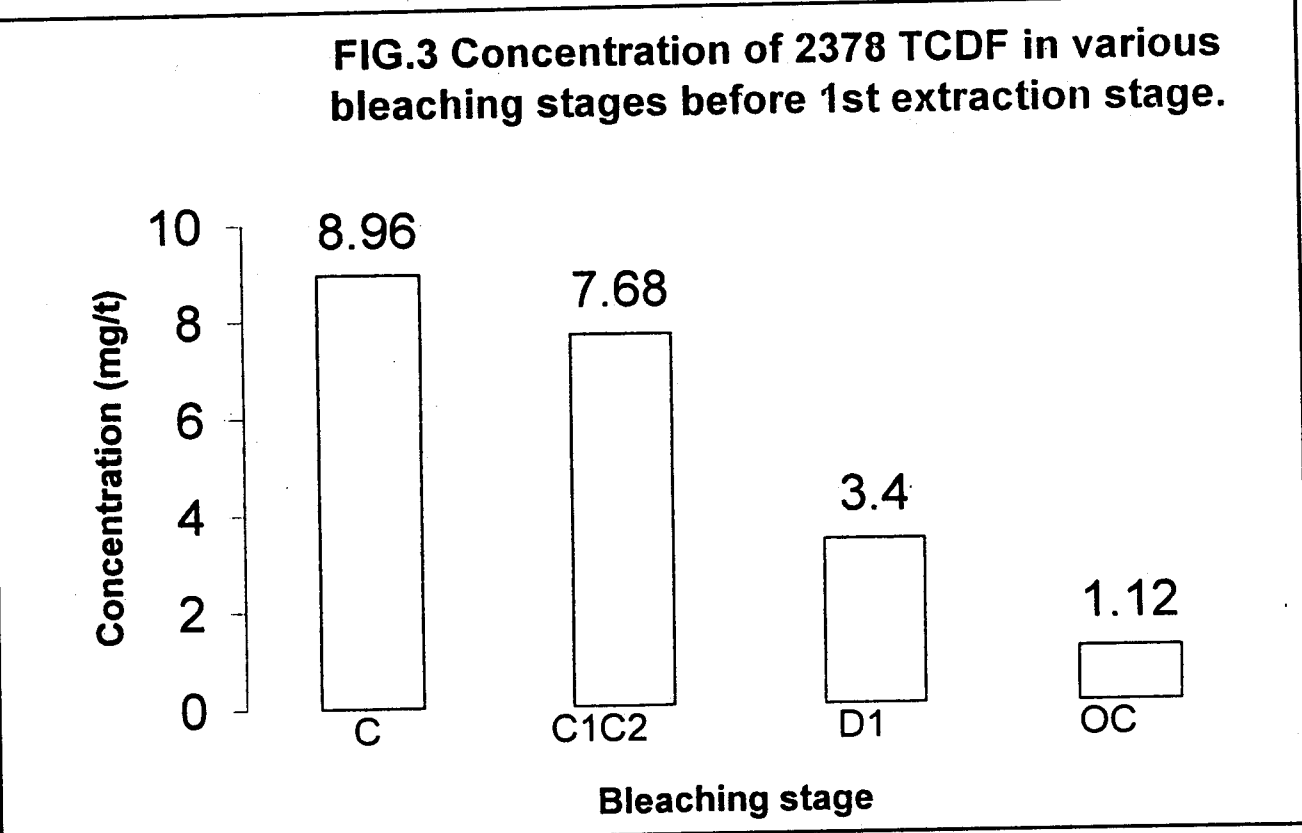
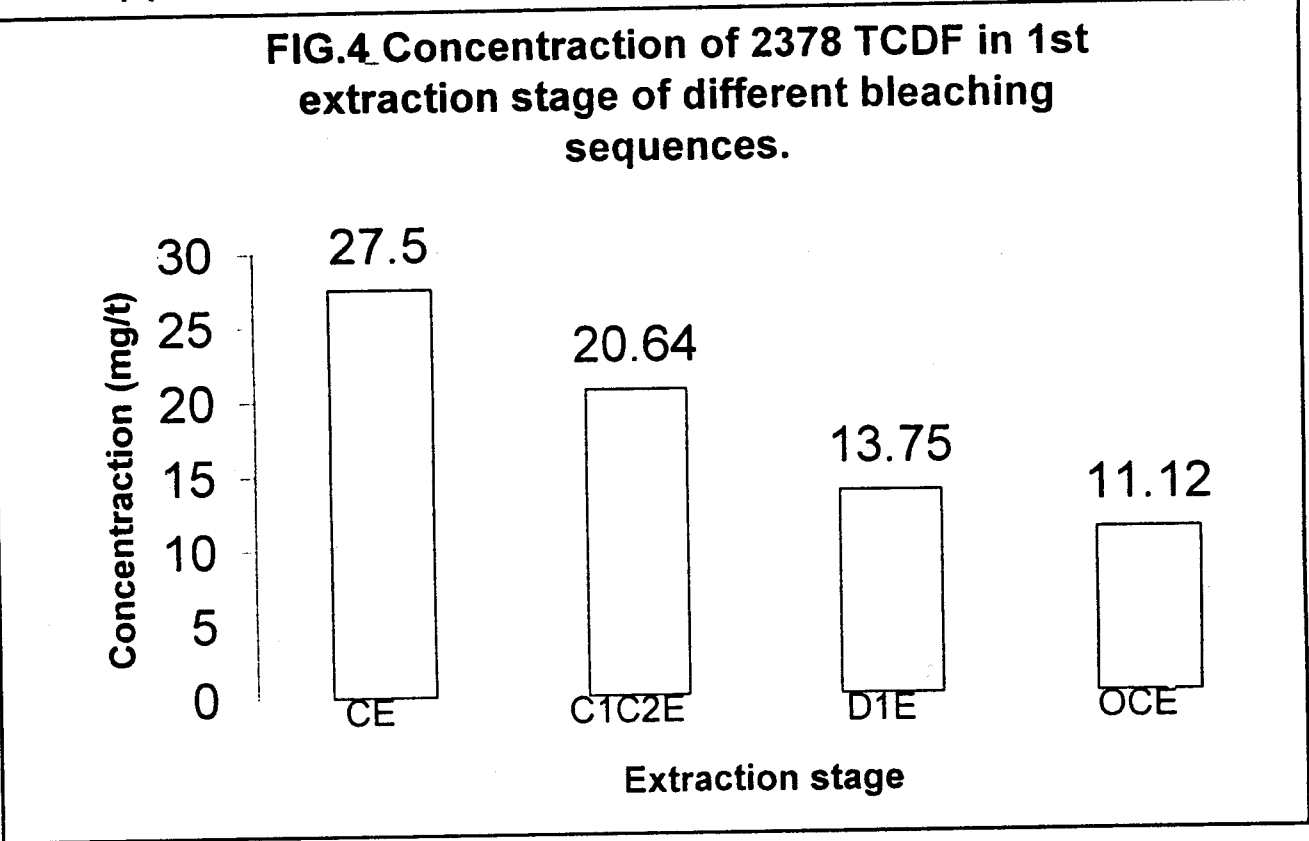


FIG.3 Concentration of 2378 TCDF in various bleaching stages before 1st extraction stage.



The concentration of 2378 TCDD and 2378 TCDF in various paper samples of common use is given in Table 6. The concentration of TCDF is much higher than TCDD, the concentration being nanogram levels

FIG.4 Concentration of 2378 TCDF in 1st extraction stage of different bleaching sequences.



of TCDF and picogram levels of TCDD. The concentration of TCDD and TCDF in tissue paper and paper are comparable but higher in comparison to writing paper. The values of TCDD and TCDF observed in the paper samples are somewhat higher than some reported results (61,70).

Because of high toxicity of TCDD and TCDF, internationally the trend is to either completely eliminate the formation of these two compounds or to bring their concentration to negligible levels (slightly above the detection limits). In India, no limit has been prescribed for the discharge of these two highly toxic compounds in paper mill wastewater but some countries have fixed very low discharge levels. Canada has specified that the concentration of 2378 TCDD and 2378 TCDF in the paper mill wastewater should not exceed 15 and 50 ppq respectively. There is a need to generate reliable information on the levels of discharge of these two compounds in Indian conditions for better monitoring and control.

CONCLUSIONS

1. The above laboratory studies clearly show that chlorination, dioxide and extraction stage effluents have detectable levels of 2378 TCDD and 2378 TCDF. The range of concentrations obtained are of concern.
2. Decreasing chlorine multiple in terms of splitting the C_{stage} or reducing chlorine usage (following an oxygen pre bleaching) or substituting chlorine stage by dioxide stage has significantly lower generation of 2378 TCDD and 2378 TCDF.
3. The level of use of chlorine in bleaching (or other bleaching agents) not only depend upon inlet pulp kappa number but is strongly influenced by the level of carry over of dissolved organics with pulp after washing, maintaining optimum operating conditions during bleaching, proper mixing of bleaching agent with pulp and sufficient time contact between pulp and bleaching agent in the bleach tower. All these operational parameters need to be carefully controlled to ensure least generation of 2378 TCDD and 2378 TCDF.

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