Effect of Bleaching Conditions on the Formation of Chloro-Organics in Bagasse Pulp.

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ABSTRACT: *The chlorinated organic compounds formed during bleaching of pulp are known for their toxicity to overall environment. The present paper highlights the level of chloro-organics as AOX formed during bleaching of bagasse pulp and the effect of kappa number & different active chlorine factor on the formation of chloro-organics. It is observed that elemental chlorine is mainly responsible for the formation of chloro-organics and the formation of chloro - organics can be reduced by lowering the pulp kappa number & using low active chlorine factor.*

INTRODUCTION

Bleach plant effluents have long been known for their toxicity to aquatic organisms. Chlorine & chlorine based chemicals are most widely used to bleach the pulps resulting in the formation of chlorinated organic compounds. Approximately 300 different compounds in kraft bleach plant effluent have been identified and about 200 of them are chlorinated organic compounds[1]. For a chlorine based bleaching process[2], about 70 - 80% of the organically bound chlorine is present with high molecular weight material and this high molecular weight mass is essentially non-aromatic and has been shown to have little or no acute toxicity perhaps because the molecules size are too large to penetrate the living cell membrane. But past evidences showed that this high molecular weight mass might be broken down in receipient waters or in sediments & converted into smaller biologically active compounds. While low molecular weight chlorinated organic compounds (< 1000 D) can penetrate the cell wall membrane of organisms and have been shown to exhibit acute & chronic toxicity to aquatic organisms, in some cases it persists and bioaccumulates in environment[3]. The distribution of different organohalides in effluent is shown in Fig-1.

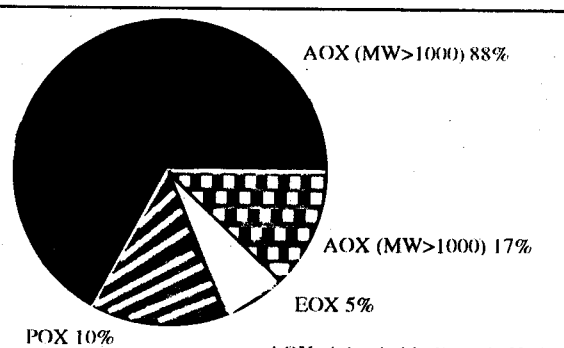

Fig.1. Distribution of organohalides in the straw pulp bleaching & combined mill effluent2.

The impact of bleach plant effluents from kraft & sulfite pulps on the metabolic activities of fish was reported first in Sweden[4&5]. The results of Swedish studies, however are in conflict with workdone in the United States where extensive testing of treated effluent from a bleached kraft mill showed there was little, if any, effect on fish and plant life in artificial streams[6&7]

With ever increasing concern with environmental

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issues all over the globe in recent years, there has been growing concern about chlorinated organic matter in bleach plant effluents. The environment hazards of pulp bleaching effluents are considered related to the use of chlorine containing chemicals especially molecular chlorine. The detrimental effects of the chlorine / chloro - organics has forced the industry to develop the ways or methods to reduce/ eliminate the use of elemental chlorine. Today atleast 10 countries have proposed the target for chloro-organics as AOX. The AOX level is currently in the range of 2-6 Kg./t. with higher value to kraft and lower to sulfite pulps. Germany, Sweden and parts of Canada already have limits in operation.

Recently Central Pollution Control Board has proposed the discharge limit for organically bound chlorine i.e. 2.0 Kg./t. product after external treatment for Indian Pulp & Paper industry. Almost all Indian Pulp & Paper mills are using chlorine & chlorine based chemicals for bleaching of pulps. No information/data are available so far regarding the generation and level of organically bound chlorine in Indian pulp & paper industry. In present paper an attempt has been made to quantify the level of chloro-organics as AOX in bleach effluent from bagasse pulp and the effect of different active chlorine factor & kappa number on the formation of chloro-organics was studied.

DISCHARGE LIMITS FOR TOTAL ORGANIC CHLORINE

COUNTRY	LIMIT Kg./t.	MODE
SWEDEN	1.5	TOCl
CANADA	1.5	AOX
GERMANY	1.5	AOX
INDIA	2.0	TOCl

Measurement of Chloro-Organics

The identification and quantification of individual chlorinated organic compound is exceedingly complex and so generic measurement is desirable. Whereby the total amount of chlorine bound to organic matter is quantitatively determined.

There are several techniques developed for the analysis of chlorinated organics. Some of these techniques are Total Organic Chlorine (TOCl), Total Organic Halogen (TOX), Extractable Organic Halogen (EOX), Purgeable Organic Halogen (POX) and Adsorbable Organic Halogen (AOX). The principle of all methods is same. In Sweden, a relatively complex method, known as TOCl[8] has been used to extablish much of the background data and basis for Swedish regulation. The AOX techinque[9,10&11] is considered to be the most suitable and most widely used, especially for bleached pulp mills. In sweden also, there is a move to adopt the easy AOX method instead of TOCl method. The AOX method has the following advantages over TOCl method--

- Better reproductibility.
- Lower detection limit.
- Higher percentage recovery of volatile chloro-organics.

The measurement of AOX is achieved in three steps

1. **Separation**

   Organic matter containing covalently bound chlorine atoms is adsorbed onto activated carbon followed by washing with nitrate to remove inorganic halides.

2. **Mineralization**

   The adsorbed organic matter onto activated carbon is combusted at higher temperature in presence of oxygen to convert organically bound chlorine to HCl.

3. **Analysis**

   The HCl produced is determined by microcoulometric titration.

EXPERIMENTAL

Bleaching of pulp

The bagasse soda pulps of different kappa number prepared in laboratory were bleached by CEH sequence using active chlorine factor of 0.10, 0.15, 0.20 & 0.25 in chlorination stage.

$$\text{Active chlorine factor} = \frac{\%\ \text{of } Cl_2 \text{ in C-stage on pulp basis}}{\text{Kappa number of unbleach pulp}}$$

The bagasse soda pulps of same kappa number were bleached with hypochlorite to achieve more or less the same pulp brightness level as in CEH sequences. The bleached pulps were evaluated for their physical strength properties.

Determination of AOX

The bleach effluents generated were analysed quantitatively for AOX as follows--

a. Pretreatment of sample

The bleach effluents collected were checked to reduce the free chlorine if any, followed by acidification with Nitric acid (AR grade) to pH 2 and stored in refrigerator at 4°C.

b. AOX measurement

The AOX was measured quantitatively according to DIN 38 409 H 14 (Flask procedure) method using Dohrmann TOX/AOX analyser.

100 ml. diluted bleach effluent sample was taken into 250 ml. stoppered conical flask containing 5 ml. nitrate solution. The pH was adjusted to 2 with nitric acid followed by one hour shaking to adsorb the halides onto activated carbon (50 mg.). After one hour the aliquote was filtered through polycarbonate membrane filter paper followed by nitrate wash to remove the inorganic halides. Thus, the filtered activated carbon along with membrane filter paper was combusted at 1000 °C in presence of oxygen followed by microcoulometric titration of produced HX (X-halides) against silver ions by using Dohrmann TOX/AOX analyser. The AOX was calculated as follows--

$$\text{AOX, } \mu g/l = \frac{A - B}{V \times Rf} \times D$$

Where--

A - µg reading of sample.

B - µg average of daily blank.

C - Volume of sample in litre.

D - Dilution factor.

Rf - Recovery factor from calibration standard.

RESULTS AND DISCUSSION

The bagasse soda pulps of different kappa number prepared by cooking of depithed bagasse with caustic in laboratory digester were bleached by using CEH & H-H bleaching sequences. The bleaching conditions used were as under--

Chlorination (C)	:	30 °C, 30 mins. & 3% consistency.
Alkali Extraction (E)	:	60 °C, 60 mins. & 8% consistency.
Hypo (H)	:	45 °C, 90-120 mins. & 8% consistency.

The Brightness target was maintained to achieve 75 ± 2% in all bleaching sequences. The bleach effluents collected from individual bleaching stages were analysed for pH, total solids, COD & colour.

The results reported in table 1,2 & 3 show that the alkali extraction stage bleach effluent is the main source of pollution load and contributes about 60-70% of total COD and 90-95% of total colour. The colour and COD loads reduced by 35-38% by using low active chlorine factor i.e. 0.10 (Table-3).

Table-1.

Characterisation of bleach effluents from bagasse pulp

UNBLEACH PULP KAPPA NO. 20 ACTIVE CHLORINE FACTOR 0.20

S.N.	Parameters	Bleaching sequence Chlorination	Extraction	Hypo
1.	pH	2.34	11.20	8.39
2.	Total Solids, g/l	1.79	4.82	2.25
3.	COD, mg/l	611	2446	245
4.	Colour, Pt.Co.	1614	8714	457

Final pulp brightness - 70%

Table-2.

Characterisation of bleach effluents from bagasse pulp

UNBLEACH PULP KAPPA NO. 16 ACTIVE CHLORINE FACTOR 0.20

S.N.	Parameters	Bleaching sequence Chlorination	Extraction	Hypo
1.	pH	2.0	11.0	9.5
2.	Total Solids, g/l	1.32	4.52	2.25
3.	COD, mg/l	475	2400	230
4.	Colour, Pt.Co.	579	7500	200

Final pulp brightness - 76%

Table-3.

Characterisation of bleach effluents from bagasse pulp

UNBLEACH PULP KAPPA NO. 16 ACTIVE CHLORINE FACTOR 0.10

S.N.	Parameters	Bleaching sequence Chlorination	Extraction	Hypo
1.	pH	2.65	11.30	9.5
2.	Total Solids, g/l	1.40	3.26	2.60
3.	COD, mg/l	230	1536	806
4.	Colour, Pt.Co.	291	4600	284

Final pulp brightness - 75%

Bleach effluents generated during bleaching of pulps were analysed for quantitative measurement of AOX and results are given in table 4 & 5. Table-4 shows that the level of AOX measured was 5.28 Kg./t. pulp at kappa number 24 with corresponding total chlorine consumption of 56.9 Kg.Cl_2/t. pulp. When total chlorine consumption was reduced to 42.2 Kg.Cl_2/t. pulp by lowering the pulp kappa number from 24 to 16, the AOX level measured reduced by 38% i.e. 3.23 Kg. AOX/t. pulp compared to value at kappa number 24 (Fig. 2).

Table-4.

Results of AOX in bleach effluents at different kappa No. of bagasse pulp

Unbleach pulp Kappa No.	AOX Kg./t. pulp CEH	Brightness %	Total Cl_2 Consumption Kg./t. pulp	HH	Brightness %
24	5.28	74	56.9	-	-
20	4.20	73	48.6	-	-
18	3.26	75	45.0	1.62	75
16	3.23	76	42.2	1.11	74

Table-5.

Results of AOX in bleach effluents at different chlorine factor in C-stage

Unbleach pulp kappa No. 16

Active Chlorine Factor	AOX Kg./t. pulp CE	H	CEH	Total Cl_2 Consumption Kg./t. pulp	Final pulp Brightness %
0.10	1.31	0.54	1.85	42.6	75
0.15	2.59	0.32	2.91	39.0	74
0.20	2.99	0.24	3.23	42.2	76
0.25	3.40	0.22	3.62	50.4	76

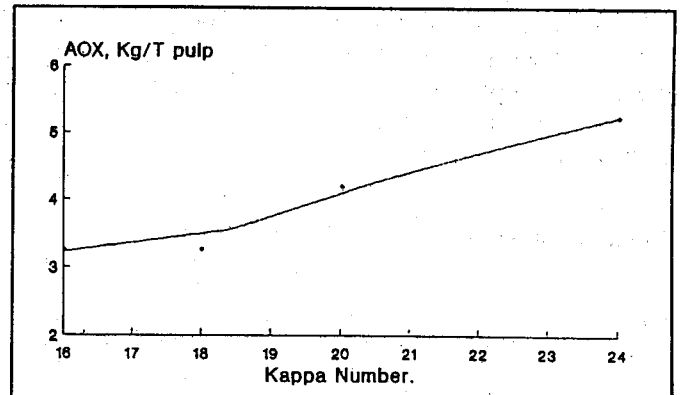

Fig.2. Quantity of AOX vs Kappa Number in Bagasse Pulp (CEH Sequence)

The pulps of kappa number 16 & 18, when bleached with hypochlorite (H-H) to get more or less the same brightness level as in CEH bleaching, the AOX level measured was 1.11 & 1.62 Kg. AOX/t. pulp respectively (Table-4). This clearly indicates that the AOX formation in H - H bleaching is less by 50-60% inspite of higher total chlorine consumption compared to CEH bleaching process. This may be because of oxidation/reduction reaction of chlorine with organics in hypochlorite bleaching.

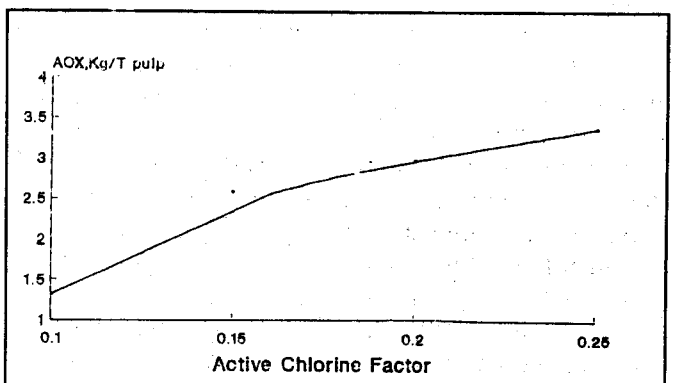

Fig.3. Formation of AOX in CE Stage at Different Active Chlorine Factor in Bagasse Pulp

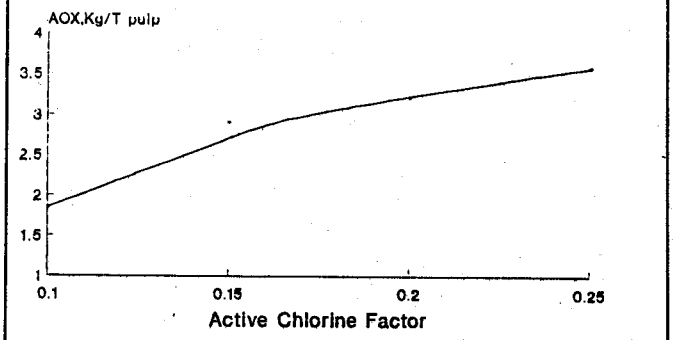

Fig.4. Quantity of AOX at different Active Chlorine Factor in Bagasse Pulp (CEH Sequence)

In another experiment, the bagasse soda pulp of kappa number 16 was bleached by CEH bleaching sequence using different active chlorine factor in C-stage to study the effect of elemental chlorine on the formation of AOX. The final pulp brightness target was set at 75 ± 2%. Table-5 indicates the level of AOX measured was 1.85, 2.91, 3.23 & 3.62 Kg. AOX/t. pulp at active chlorine factor of 0.10, 0.15, 0.20 & 0.25 in C-stage, respectively (Fig. 4).

The generation of AOX in chlorination - extraction stage at different active chlorine factor shown in Fig. 3, shows that about 70-95% of total AOX is originating only from chlorination-extraction stage. It is evident from results that the elemental chlorine is mainly responsible and culprit in the formation of AOX and about 8-10% of consumed elemental chlorine is being converted into AOX formation while in hypochlorite bleaching, about 2-4.5% of consumed chlorine is being converted into AOX formation. Fig.5 shows that about 7.0 to 9.5% of consumed total chlorine is ending up as AOX to raise the final pulp brightness of 75 ± 2%.

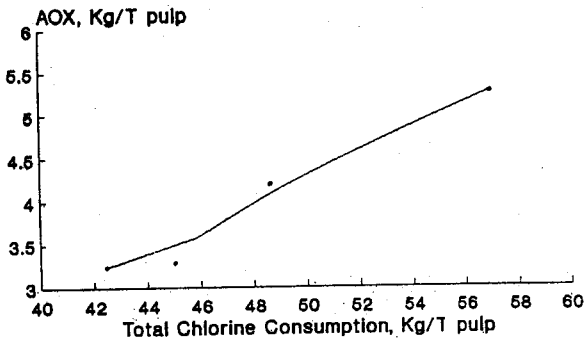

Fig.5. Quantity of AOX vs Total Chlorine Consumption in Bagasse Pulp (CEH Sequence)

The bleached bagasse pulps were evaluated for their strength properties. Table-6 indicates that the strength properties of hypo bleached pulp are 8 to 17% lower compared to the strength properties of pulp bleached by CEH bleaching using active chlorine factor of 0.10 & 0.20 in C-stage.

Table-6.

Strength properties of bleached bagasse pulp at 300 ml. C.S.F.

Pulp details	Burst Index ($KPam^2/g$)	Tensile Index (N.m/g)	Tear Index (mN.m/g)
C(0.20) E H	3.10	64	3.20
C(0.10) E H	3.25	62	3.95
H H	2.75	52	2.70

CONCLUSIONS

- The level of chloro-organics as AOX in bleach effluents from bagasse pulp bleached in laboratory ranges from 3.23 to 5.28 Kg. AOX/t. pulp at kappa number 16 to 24.
- The results show that CE-stage contributes about 70-80% of total-chloro-organics as AOX which means that elemental chlorine is mainly responsible for the formation of AOX.
- The formation of chloro-organics can be reduced effectively by lowering pulp kappa number & using low active chlorine factor in C-stage.
- The formation of chloro-organics in hypochlorite bleaching is 50-60% less compared to CE-stage.
- Strength properties of hypo bleached pulps are lower compared to strength properties of pulp bleached by CEH sequence.

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