

## Assessment of Aox Content in Bleaching Effluent of Eucalyptus Tereticornis Kraft Pulps

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### Abstract

The research aim is to reduce the organochlorine content in bleach plant effluents by modifying conventional (CEHH) bleaching sequences. Majority of pulp and paper mills generally adopted CEHH or CEH bleaching sequences, using chlorine or chlorinated compounds to remove the color from pulps. Organochlorine compounds are mainly generated from chlorination and alkali extraction stages. The purpose of the study is to substitute elemental chlorine in bleaching with oxygen, chlorine dioxide, or peroxide. Investigations of AOX content of various traditional and innovative ECF bleaching sequences were conducted. In this study, kraft pulps of Eucalyptus tereticornis with kappa numbers of 44.91 and 26.46 and its oxygen-delignified pulps of kappa numbers 21.32 and 13.03 were used. In terms of AOX, various ECF bleaching sequences were compared to the reference sequence (CEHH). AOX value was 4.45, 3.42, 2.27 kg/tp for the pulp bleached adopting OCEH, ODEH, ODEP bleaching sequence and 9.24 kg/tp for the pulp bleached adopting CEHH bleaching sequence for the pulp corresponding to Kappa number 44.91. Similarly, the AOX value was 2.60, 1.78 1.24 Kg/tp for the pulps bleached adopting the OCEH, ODEH, ODEP bleaching sequence and 5.56 Kg/tp for the pulp bleached adopting the CEHH sequence for the pulp corresponding kappa number 26.46. Due to partial-delignification of oxygen, AOX production was reduced up to 50%.



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Organochlorine.

### Introduction


After pulping, the residual lignin is removed by bleaching to produce a high quality bright paper and pulp products.<sup>1</sup> Several chemicals and approaches are used during the bleaching process (delignification and brightness). In conventional

bleaching, chlorination/ alkali extraction/ Hypochlorite/ Hypochlorite(C/E/H/H), chlorine or chlorinated compounds are used to remove the color from the pulp. 45-50 kg of organic materials are dissolved out from pulp into the waste bleach liquor for every tone of pulp produced.<sup>2</sup>

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About 70-90 percent of this material is produced during the first two bleaching stages i.e. chlorination and alkali extraction.<sup>3</sup> Chlorination stage yields about 5-10 kg organically bounded chlorine with every tone of pulps in the form of high and low molecular weight compounds causing water pollution. These compounds contribute to significant biological and chemical oxygen demands (COD and BOD, respectively), consume the oxygen present in water, and reduce the available oxygen for aquatic life. The color of effluent reduces the light penetration, consequently photosynthetic activity and aesthetic quality of water. The toxicity of pulp and paper mill effluent has drawn more attention over the past decade.<sup>4</sup> Research efforts have been directed to identify and study the toxicity of various chemicals coming from the bleaching section of the pulp and paper industry.<sup>5</sup>

A large number of organochlorines, collectively called Adsorbable Organic Halides (AOX-for the effluent of Pulp and Paper Mills, X represents chlorine). Approximately, 250 different chlorinated and non-chlorinated compounds have been isolated in C and E- stage effluents.<sup>6</sup> The High molecular weight material contributes 80% by weight, but the chlorine content by 10 %. These are relatively hydrophilic mainly non-aromatic and do not permeate cell walls. Low molecular weight compounds contribute 20 % by weight but possess nearly 90% of chlorine. Out of 20% low molecular material, (19% are relatively hydrophilic, hydrolysable, and metabolisable). 0.9% relatively lipo-philic potentially toxic and bio-accumable. It is only a 0.1% chlorinated compound, mainly known as dioxin and furans, which contribute to 44% chlorine by weight. They are highly lipo-philic, bio-accumable, and acute geno-toxic. Because of their lipo-philic nature, they enter the food chain and cause geno-toxic effects.<sup>7</sup>

Several organochlorine substances are hazardous, mutagenic, persistent, bio-accumulative, and toxic to biological systems.<sup>8</sup> The compounds are recalcitrant to microbial degradation due to their toxicity. Hence chlorine bleaching is banned in developed countries and is substituted by the process of bleaching with total and elemental chlorine-free (ECF/TCF), to improve effluent characteristics and reduce the formation of dioxin and furan.<sup>11</sup> But these processes are not economically feasible, particularly for small and medium-sized pulp- and paper-making mills

in developing nations, and hence they find it difficult to bring down AOX content within the permissible limit. In India, the permissible limit for discharge of AOX was 2.0 kg/ton in the year 1992 which is now narrowed down to 1.5 kg/ton of paper produced (Central Pollution Control Board, Government of India). Removal methods are expensive and not very effective. Nowadays, research in this field is largely focused on optimizing pulping and bleaching procedures. More effective pulping techniques decrease the quantity of residual lignin passing to the bleaching process, and alternative bleaching procedures are being investigated to produce pulp. The objective of the present study is to partially or completely modify the existing bleaching trends with oxygen, chlorine dioxide, and peroxide.

#### Material and Methods

The *E.tereticornis* logs were collected from the campus of Forest Research Institute, Dehradun. The middle portion of the logs was chipped and stored for the experiment. Chips had 13 % moisture content. Wood chips were pulped in an air bath pulping unit using 14% and 18 % active alkali as Na<sub>2</sub>O at a maximum temperature of 1650C and were kept constant for 60 minutes in both cases.<sup>9</sup> Kraft pulp produced using 14% and 18% active alkali corresponding to Kappa numbers 44.91 and 26.46, were treated with oxygen 8 Kg/cm<sup>2</sup> oxygen pressure at 100 °C temperatures. Kappa number of kraft pulps was reduced up to 21.32 and 13.03 respectively through oxygen pre-bleaching.

Chlorination was carried out at an ambient temperature and 3% consistency for 30 minutes. Alkali extraction was carried out at 65+2 °C and 8% consistency for 60 minutes. Hypochlorite treatment was carried out at 42+2 °C and 8% consistency for 120 minutes pH 9.5+0.5 was maintained throughout the hypochlorite treatment. Chlorine dioxide stage, Chlorination was carried out at an ambient temperature and 3% consistency for 30 minutes. In the hydrogen peroxide stage, hydrogen peroxide charge was 1.0%, consistency 8.0 %, reaction temperature 65+2 °C, and one-hour duration for both pulps of *E.tereticornis*. Certain metal ions such as Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup> act as a catalyst in the decomposition of hydrogen peroxide so MgSO<sub>4</sub> 1.0 %, sodium silicate 1.5%, and ethylene di-amine tetra acetic acid (EDTA) 0.25 % on oven dry pulp, were added to deactivate these metal ions and

to mitigate carbohydrate degradation by oxygen under alkaline conditions. AOX content of different bleaching sequences like CEHH, OCEH, ODEH,

and ODEP was investigated. In all cases, chemical charges were maintained to obtain the desired brightness of 85% ISO.<sup>10</sup>

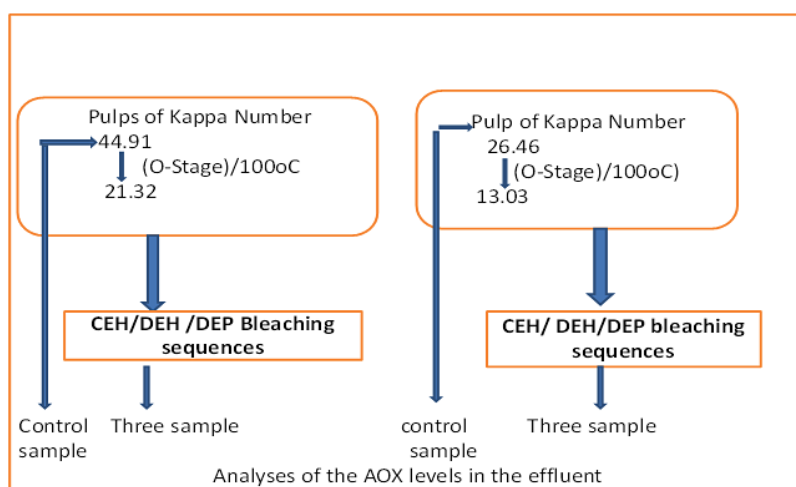
**Table 1: Bleaching conditions of *E. tereticornis* kraft pulps**

SN	Sequences	CEHH		OCEH		ODEH		ODEP	
1.	Active Alkali, %	14	18	14	18	14	18	14	18
	Kappa number (unbleached pulps)	44.91	26.46	44.91	26.46	44.91	26.46	44.91	26.46
2.	Oxygen stage(O)								
	Alkali charge	-	-	3.75	2.50	3.75	2.50	3.75	2.50
	Kappa no.			21.32	13.03	21.32	13.03	21.32	13.03
3.	Chlorination stage (C)								
	Chlorine,%	6.60	4.00	3.25	2.25	--	--	--	--
4.	Chlorine dioxide (D)	-	-	-	-	2.75	1.75	2.75	1.75
5.	Alkali extraction (E)	1.75	1.25	0.75	0.50	0.50	0.50	0.50	0.50
6.	Hypochlorite stage-1(H)	2.60	1.60	2.00	1.00	1.00	1.00	--	--
7.	Hypochlorite stage-II (H)	1.80	1.00	--	--	--	--	--	--
8.	Peroxide (P)	--	--	--	--	--	--	1.00	1.00

**Effluent Collection and Storage**

Effluent samples from the bleaching unit were separately collected for a particular bleaching sequence. Effluent from various stages was

collected, combined, and kept for two hours in sunlight to escape the residual chlorine if any. Discard the effluent of the oxygen treatment stage as it may be, recycled in the chemical recovery system.



**Fig. 1: Analyses of AOX levels in the effluent of different bleaching sequence**

**Aox Analysis of Bleach Effluents**

AOX of the effluent of each bleaching sequence was determined separately, using the given procedure. AOX is the amount of organic halogen that

adsorbs on activated carbon, after the combustion of activated carbon-containing halides with oxygen at about 950°C, halides converted into hydrochloric acid are detected by microcoulometric titration and

measure the amount of chlorine generated from the effluent adsorbed on the activated charcoal and gives a graph on the calibrated printer/plotter, which directly give the amount of AOX in the effluent. The real value of AOX is computed considering the dilution factor.

### Result and Discussion

The aim of this study was to investigate the influence of oxygen delignification on the AOX formation

in the subsequent ECF bleaching. Two pulps with kappa number 44.91 and 26.46 were therefore oxygen delignified to kappa numbers 21.32 and 13.03 respectively. Pulps of two different kappa number then bleached in a CEH, DEH and DEP sequence. (Table 2) The AOX levels in the generated effluents were compared with nonoxygen delignified pulps. (Fig.1.)

**Table 2: Kappa number, bleaching sequences and Adsorbable organic halides of effluents after bleaching.**

Active Alkali, %	Kappa numbers	Bleaching sequences	AOX, kg/tp	Bleached pulp yield, %	Brightness, % ISO	Burst Index kPam <sup>2</sup> /g	Tensile Index Nm/g	Tear Index, mNm <sup>2</sup> /g
14 %	44.91	CEHH	9.24	42.37	72.20	4.30	60.00	7.55
		OCEH	4.45	41.96	72.91	4.85	67.50	6.65
		ODEH	3.42	41.03	72.83	3.55	51.60	6.35
		ODEP	2.27	40.65	73.62	3.51	51.06	6.15
18%	26.46	CEHH	5.56	42.39	73.50	4.10	61.80	6.95
		OCEH	2.60	41.45	76.00	4.25	64.43	6.25
		ODEH	1.78	40.33	79.02	3.43	47.95	5.85
		ODEP	1.24	40.10	82.30	3.12	45.24	5.51

In Table 2 the AOX values of different bleaching sequences were recorded, excluding the effluents generated in oxygen stage bleaching as they could be recycled in a chemical recovery system. AOX value was 4.45 kg/tp for the pulp bleached adopting OCEH and 9.24 kg/tp for the pulp bleached adopting CEHH bleaching sequence for the pulp corresponding to Kappa number 44.91. Similarly, the AOX value was 2.60 Kg/tp for the pulps bleached adopting the OCEH sequence and 5.56 Kg/tp for the pulp bleached adopting the CEHH sequence for the pulp corresponding kappa number 26.46.

AOX value was 3.42 kg/tp for the pulp bleached adopting ODEH and 2.27 kg/tp for the pulp bleached adopting ODEP bleaching sequence for the pulp corresponding to Kappa number 44.91. Similarly, the AOX value was 1.78 Kg/tp for the pulps bleached adopting the ODEH sequence and 1.24 Kg/tp for the pulp bleached adopting the ODEP sequence for the pulp corresponding to kappa number 26.46.

AOX values were highest for CEHH followed by OCEH, ODEH, and OD EP. Since the AOX values

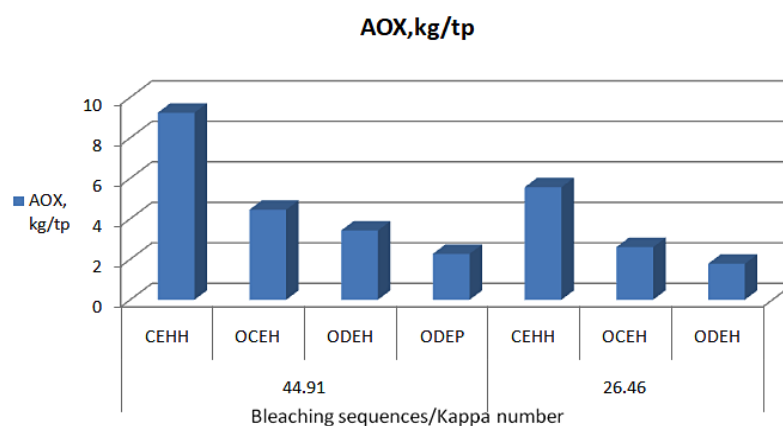
are more or less dependent on the residual lignin in pulp. Thus, these values were decreased on oxygen treatment before further bleaching. Decreases in these values more or less correspond to the remaining lignin present in the pulps, as expected. The kraft pulps were treated in alkaline media with oxygen bringing about oxidative changes primarily in residual lignin in pulps. The reaction with molecular oxygen results in a considerable breakdown of these fractions (lignin degrading oxidative bleaching). During the oxygenation of lignin in an alkaline medium, hydrogen peroxide is generated by auto-oxidation of enediol structure which in turn generated the hydroperoxide. The oxidation with alkaline hydroperoxide under normal condition does not degrade lignin to any appreciable extent but remove chromophores (lignin retaining oxidative bleaching).

During reaction with oxygen, the lignin structure is broken up between the aromatic nuclei and propyl side chain forming various carbonyl and carboxylic acids from the side chain as well as para-quinones from the aromatic part. Para-quinones

are the colored structure that can transform into the colorless structure with the help of a small amount of  $H_2O_2$  formed during bleaching and ring-opening reactions making the lignin more hydrophilic and more easily dissolved as well as de-methylation reactions sometimes open the ring, which has less effect on the degradation of lignin, but may increase its solubility. This is because aromatic ring opening produces water-soluble di-carboxylic acids, such as muconic or succinic acid.<sup>11</sup>

Chemical charges to different bleaching sequences are presented in Table 1. OCEH bleaching sequence reduces about 40% of net chlorine usage to the reference, CEHH. After pretreatment with oxygen and replacement of the chlorine stage with  $ClO_2$  and hypochlorite with peroxide in the last stage, i.e.

ODEH and ODEP resulted in a 45% to 50% reduction in elemental chlorine consumption.<sup>12</sup> A considerable reduction of elemental chlorine improves the quality of effluent because effluent quality mainly depends upon the consumption of the elemental chlorine either in the form of chlorine or hypochlorite to achieve the desired targeted brightness. Since most chlorinated compounds are generated during the chlorination/hypochlorite stage, are phenolics. Chlorinated phenolics are the biggest threat due to their toxicity.<sup>13</sup> Partial delignification of the pulps with oxygen influenced the adsorbable organic halogen (AOX) formation and hexenuronic acid content (HexA) in the elemental chlorine free (ECF) bleaching effluent. The HexA content of the pulps had a major impact on the AOX formation.



**Fig. 2: Adsorbable organic chlorine (AOX) in effluent adopting different bleaching sequence.**

The amount of AOX in different bleaching sequences was calculated and illustrated in Fig-1. Based on data collected, it could be concluded that partial replacement of Conventional (CEHH) bleaching sequence to ODEH bleaching sequence is expected to be more beneficial, for reducing the organochlorine content and genotoxicity of effluents as well as maintaining the pulp properties. At an early stage, the use of oxygen bleaching substantially reduces the chlorine content of the bleach plant effluent. As a result, a sizeable portion of effluent can be recycled into the process corresponding to reducing the discharge to the recipient water.<sup>14</sup> The environmental benefits from (ODEH) compared to ODEP were marginal but pulp yield and strength properties were decreased.

Although, effluent generated from the pulp bleaching of kappa number 26.46 contain less value of AOX as compared to effluent generated from the pulp bleaching of kappa number 44.91 the strength properties of pulp were also lower. Under the optimum conditions of pulping and bleaching based on the strength properties and effluent load of OCEH (oxygen treatment at 100oC) was 4.45 kg/tp. This value is quite in limit and can further be brought down in effluent treatment plants of pulp and paper mills.

### Conclusion

Based on the experiment carried out on bleaching of pulp using CEHH, OCEH, ODEH, and ODEP, it was observed that the OCEH bleaching

of pulp produced using 14 % alkali during pulping corresponding to kappa number 44.91, has high pulp yield as compared to other pulps. AOX generated under these bleaching conditions had CEHH (9.24 kg/tp), OCEH, ( 4.45 kg/tp), ODEH( 3.42 kg/tp), and ODEP( 2.27 kg/tp). AOX generated under these bleaching conditions had CEHH ( 5.56 kg/tp), OCEH, ( 2.60 kg/tp), ODEH( 1.78 kg/tp), and ODEP (1.24 kg/tp) for the pulp produced using 18% alkali during pulping corresponding to kappa number 26.46.

Oxygen pre-delignification / pre-bleaching followed by conventional bleaching sequence results in the reduction of about 50% in AOX and pulp yield is 42.16+0.21 % in OCEH. Based on data collected it could be concluded that OCEH bleaching may be preferred in high kappa number (44.91) pulp

at cost of pulp yield and strength properties. In lower kappa number (26.46) a significant drop in yield and strength properties was observed with any gain in effluent quality.

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#### Conflicts of Interest

Nil

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