AOX MITIGATION IN PULP BLEACHING EFFLUENTS USING ELEMENTAL CHLORINE FREE BLEACHING

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ABSTRACT

The pulping and bleaching are two major processes of prime environmental concern during paper manufacture due to the generation of highly polluted effluents. The bleaching is aimed at removing the residual lignin to achieve desired pulp brightness. Cl₂ or chlorine-based bleaching chemicals generate a variety of chlorinated organics, measured collectively as adsorbable organic halides (AOX), in the bleaching effluents. The disposal of bleaching effluents containing AOX poses an enormous threat to the aquatic organisms and public health. The environmental concern has led to the substitution of Cl₂ based conventional bleaching with elemental chlorine-free (ECF) and chlorine-free (TCF) bleaching to regulate AOX generation in the effluents. The present study is aimed at reducing AOX generation in the bleaching effluent by using eco-friendly ECF bleaching technology (i.e. replacement of elemental chlorine with ClO₂, H₂O₂ reinforced alkaline extraction and O₂ delignification). The mixed hardwood kraft pulp is bleached to 87% ISO target brightness using D/CED, DED, DE_pD, and ODED sequences under the controlled laboratory conditions. The ECF bleaching sequences (0.67, 0.55, and 0.34 kg/t OD pulp for DED, DE_pD, and ODED, respectively) can reduce AOX generation below the set regulatory standard (1 Kg/T OD pulp) as compared to D/CED sequence (2.6 kg/t OD pulp). ODED sequence saved 45% bleach chemical as compared to the D/CED sequence. The ECF bleaching sequences can cut NaOH dose by 30% during the alkaline extraction (E/E_p) stage as compared to D/CED sequence. ODED and DE_pD bleaching sequences are found appropriate to meet the AOX discharge standard.

Keywords: AOX, ECF, Bleaching, O₂ Delignification, Pulp, Economic Analysis.

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INTRODUCTION

The pulping and bleaching are two major processes during pulp and paper manufacture from wood or other lignocellulosic raw materials. They are of prime environmental concern due to the generation of highly polluted effluent streams. The considerable increase in awareness about the environmental impacts of pulp bleaching effluents during past decades has resulted in stricter statutory norms. This is a driving force that is moving the pulp and paper industry towards sustainability. The cleaner processes are being adopted to reduce the impact on the natural environment. The lignin which keeps cellulose fibers bound together in wood is an undesirable material during pulp and paper manufacture. The chemical pulp production involves the dissolution of a significant part of lignin by cooking wood chips at high temperature and pressure with chemicals. The pulp produced after pulping still contains residual lignin (2-5%)¹. The residual lignin produces unwanted dark color and causes photo-yellowing of pulp. The bleaching is aimed to remove the residual lignin to improve pulp brightness for the production of white paper. Bleaching improves the pulp brightness by either lignin removal or decolourization² with various chlorine or oxygen-based chemicals (oxidants). The bleaching is carried out in multiple stages for better chemical efficiency and protection of pulp strength. The individual pulp bleaching stages follow intermediate alkaline (NaOH) extraction stage which dissolves and remove lignin degradation products.

Cl₂ or chlorine-based chemicals used for bleaching generate a variety of chlorinated organics (chlorinated hydrocarbons, phenols, guaiacols, vanillins, resin acids, fatty acids, syringols, catechols, furans, and

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dioxins etc.) in the bleaching effluents which are estimated as adsorbable organic halides (AOX)^{3,4}. The residual lignin left in the pulp after pulping is assumed to be the major cause of AOX generation⁵. AOX generation is directly proportional to the consumption of Cl₂ or chlorine derived bleach chemicals⁶ and is influenced by the pulp's hexenuronic acid and hemicellulose content^{7,8}. The pulp and paper sector is one of the biggest users of water and generate about 20–100 m³ of effluent per metric ton of paper⁹. The effluent is characterized with high load of biochemical oxygen demand (BOD: 14-18 kg/t), chemical oxygen demand (COD: 25-40 kg/t), colour, chlorinated organics (AOX: 0–4 kg/t of pulp), suspended solids (SS: 10-15 kg/t), nitrogen (400-600 g/t), and phosphorus (100 g/t)¹⁰⁻¹². The hardwood pulps are reported to generate a lower amount of AOX (3-5 kg/t pulp) as compared to softwood pulps (5-10 kg/t pulp)¹³.

The discharge of bleaching effluents containing AOX poses an enormous threat to the aquatic organisms and human health. Chlorinated organics are bio-recalcitrant, carcinogenic, mutagenic, and toxic. They show long-distance mobility and bio-magnify through food chains to affect organisms at different trophic levels^{14,15}. Chlorine substitution of natural substances during bleaching decreases reactivity, water solubility, and increases the persistence of resultant compounds. This increases the bio-concentration potential of the compound into living tissues with greater toxicity¹⁶. The effluents from the paper industry are found to affect liver function, reduce gonad size, depress sex steroids, and affect the development of ovaries in fish¹⁷. The dark color and turbidity of effluent affect photosynthesis and bottom-feeding organisms in the aquatic ecosystems.

The paper industry is encouraged to upgrade and implement cleaner technologies to meet stricter environmental regulations and ensure global competitiveness in terms of the use of energy, fuel, and chemicals. The Central Pollution Control Board (India) has set an effluent discharge standard for AOX generation as 1 kg/t of paper produced with effect from 1st March 2008 for large pulp and paper industry (>24,000 MT/ annum)¹⁸. The environmental concern about the discharge of AOX in bleaching effluents has led to the substitution of Cl₂ based conventional bleaching with elemental chlorine (Cl₂) free (ECF) and total chlorine-free (H₂O₂ and O₃ etc.) (TCF) technologies¹⁹. The ECF bleached pulp (employing ClO₂) has dominated the world market (production 10 times of TCF) and demand continues to increase. The modern trend is towards a replacement of Cl₂ with ClO₂ to produce ECF pulp. The well-managed ECF pulp and paper industries are reported to have a negligible impact on aquatic ecosystems due to the absence of persistent and toxic organics in treated water². Yang *et al.* (2017)²⁰ reported a significant reduction (1.3–14.9 times) in the generation of polychlorinated dioxins and furans by substitution of Cl₂ bleaching by ClO₂ during a field investigation in a non-wood pulp and paper industry. Kaur *et al.* (2017)²¹ studied ClO₂ bleaching of rice straw pulp and reported 66% reduction in generation of AOX as compared with Cl₂ based bleaching sequences. ClO₂ based bleaching can improve effluent quality and decrease the volume of effluent by 30% as compared with Cl₂ bleaching²². The present study is aimed at reducing AOX generation in the bleaching effluents by using eco-friendly ECF bleaching technology. The process of economic analysis is also carried out to determine the appropriate bleaching sequence.

EXPERIMENTAL

Materials

NaClO₂ solution (40 g/L) is used for in-situ generation of chlorine dioxide (D or D/C stage). The alkaline extraction (E or E_p) stage is conducted using a solution of NaOH. H₂O₂ (30%) solution is used for peroxide reinforced alkaline extraction of pulp (E_p stage) along with NaOH solution. The pH of the pulp is adjusted with NaOH or H₂SO₄ solutions (1M). The chlorine bleach liquor (D/C stage) and unbleached mixed hardwood (Eucalyptus: Poplar, 70:30) kraft pulp (Kappa number: 15, brightness: 34.5% ISO, and viscosity: 13.9 cP) are received from a pulp and paper industry. The paper industry uses OCE_pHH bleaching sequence. The pulp is hand washed on a screen, air dried, and kept stored in plastic bags to be used for bleaching.

Pulp Bleaching

The pulp is bleached to a target brightness of 87% ISO following D/CED, DE_pD, DED, and ODED sequences under the controlled laboratory conditions (Table-1). The active chlorine multiple (aCl) required for pulp bleaching is estimated using the following equation:

$$\text{Chlorine demand } (\% \text{ aCl}^-) = \text{Kappa no.} \times \text{Kappa factor} \quad (1)$$

The 70% of the bleach chemical charge is given in D₁ or D/C (first) stage and 30% in D₂ (last) stage. All the experiments are performed in polythene bags except D/C stage which is carried out into plastic containers at room temperature with 200 g O.D. unbleached pulp. All the bleaching stages are carried out at 10% consistency except D/C stage (3%). The disintegrated pulp is first adjusted to the desired consistency and pH. This is followed by bleach chemicals addition, hand mixing, and placing in the water bath at the desired temperature. The pulp is well mixed by hand (poly bags) or shaking the bottle (D/C stage) throughout the bleaching. The pulp slurry is filtered and washed with distilled water after completion of bleaching using a Buchner funnel. The filtrate and washings are mixed before characterization (Fig.-1). All bleaching experiments are carried out in duplicate and average values reported.

Table-1: Pulp Bleaching Experimental Conditions

Parameters	D/CED			DE _p D			DED			ODED			
	D ₅₀ /C ₅₀	E	D	D ₁	E _p	D ₂	D ₁	E	D ₂	O	D ₁	E	D ₂
a Cl ⁻ Applied (%)	3.15 (50/50)	-	1.35	3.15	-	1.35	3.68	-	1.57	-	1.74	-	0.75
Residual aCl ⁻ (%)	Nil	-	0.23	Nil	-	0.04	Nil	-	0.03	-	Nil	-	Nil
NaOH (%)	-	1.0	-	-	0.7	-	-	0.7	-	2.0	-	0.7	-
O ₂ Pressure (kg/cm ²)	-	-	-	-	-	-	-	-	-	6	-	-	-
H ₂ O ₂ (%)	-	-	-	-	0.3	-	-	-	-	-	-	-	-
MgSO ₄ .7H ₂ O (%)	-	-	-	-	-	-	-	-	-	0.2	-	-	-
Temperature (°C)	Ambie nt	70	70	70	70	70	70	70	70	100	70	70	70
Time (min)	45	90	180	180	90	180	180	90	180	75	180	90	180
End pH	2.0	10. 5	3.5	3.5	10.5	3.3	3.4	11.5	3.5	-	3.5	11.4	3.2

Analysis

The pulp brightness is measured using TECHNIBRITE ERIC 950 (Technibrite Corporation, USA). The pulp viscosity is measured by the capillary viscometer method using 1 M cupriethylenediamine (CED) solution. The strength of NaClO₂ or Cl₂ bleach liquor, as active chlorine (aCl⁻), is determined by titrating against a standard solution of 0.1 N Na₂S₂O₃ using starch (0.5%) as an indicator. 10 mL KI (10%) and 10 mL acetic acid (10%) is added to 10 mL of diluted bleach liquor and the resulting solution is titrated against standard Na₂S₂O₃ solution. The endpoint is blue to colorless. The strength of the bleach liquor is calculated using the following formula:

$$\text{Strength of bleach liquor (g/l)} = \text{Normality of bleach liquor} \times 34.5 \quad (2)$$

The residual chlorine in the spent bleach liquor is determined by taking 100 mL of spent bleach liquor following the same procedure²³. The pulp bleaching effluents are characterized for AOX using a column method with an AOX analyzer (ECS 1200).

RESULTS AND DISCUSSION

The mitigation of bio-recalcitrant and hazardous compounds in the paper industry effluents can be achieved through either adoption of eco-friendly manufacturing technologies or end-of-pipe effluent treatment. The use of eco-friendly ECF bleaching technologies has gained momentum during past decades as an effective approach for at source mitigation of AOX generation. Hence, ECF bleaching (DED, DE_pD, and ODED) of hardwood kraft pulp has been investigated as compared with Cl₂ bleaching (D/CED), with 50 – 100% substitution of Cl₂ by ClO₂, for reduction of AOX generation in the bleaching

effluents. The O_2 pre-delignification and H_2O_2 application during alkaline extraction are also studied for the reduction of AOX generation during ECF bleaching. The O_2 delignification is targeted for 40-50% reduction in kappa number with a minimum drop in pulp viscosity. Almost 45% kappa number reduction is achieved with 12% viscosity drop at an optimum NaOH dose of 20 kg/t O.D. pulp in our previous study²⁴. O_2 is poorly selective at a high degree of delignification and may lead to a reduction in pulp quality and yield, if used extensively, by carbohydrate degradation²⁵.

Fig.-1: The Pulp Bleaching Sequences Flow Chart

Chlorine Demand Optimization

The optimum chlorine (a Cl^-) demand required to achieve 87% ISO target pulp brightness through D/CED, DED, DE_pD, and ODED bleaching sequences is found by varying kappa factor (KF) from 0.28 - 0.35 (Figure 2). A KF of 0.35 is found to be optimum for the DED sequence as compared with other sequences (KF 0.3). ClO_2 is much less effective at 100% substitution with low final brightness, hence a higher KF (bleach chemical charge) is needed to achieve the same target brightness²⁶. H_2O_2 , an eco-friendly oxidizing agent, participates in additional lignin oxidation reactions during alkaline extraction (E) stage of the DE_pD bleaching sequence and thus a lower KF (0.3) is required for a given target brightness. The O_2 pre-delignification stage reduced the initial kappa number of the pulp by 45%. Hence, a lower KF (0.3) is found optimum for the ODED bleaching sequence for the same target brightness.

AOX Mitigation

The major AOX load came from the first two bleaching (D/C or D₁ and E or E_p) stages for all the bleaching sequences (Table 3). The large quantity of organic material solubilized during chlorination and alkaline extraction stages, during kraft pulp bleaching²⁷. The increase in no of free phenolic hydroxyl and carboxyl groups and decreased molecular weight improve the solubility of lignin during following alkaline extraction stage. The highest amount of AOX is generated in D/CED sequence (50% ClO₂ and 50% Cl₂) effluents (2.60 kg/t O.D. pulp) as compared to DED, DE_pD, and ODED sequences (100% ClO₂). The pulp chlorination involves the binding of about 10% of chlorine applied to residual lignin to form chlorinated organics while the remainder (90%) is converted into chloride ion²⁸.

AOX generation in the effluent has been reported to decrease by 40-60% with 45-100% chlorine demand substitution by ClO₂²⁹. ClO₂ has five times higher oxidation power as compared to Cl₂. The proportion of oxidative reactions increases by application of ClO₂. This results in decreased generation of chloroorganics in the effluent^{3, 30}. The DED sequence is found to generate higher AOX in effluents (0.67 kg/t O.D. pulp) as compared to DE_pD and ODED sequences. This is due to the requirement of higher KF for achieving the same target brightness. ClO₂ is much less effective at 100% substitution, often resulting in higher CE lignin content and lower final brightness. Hence, the requirement of higher bleach chemical charge results in the generation of higher AOX in the effluent as compared with DE_pD and ODED sequences²⁶. H₂O₂ is an environmentally friendly and strong oxidizing agent for bleaching³¹.

Fig.-2 Chlorine Demand Optimization to Achieve 87% ISO Target Brightness for D/CED, DED, DE_pD, and ODED Bleaching Sequences

Table-3: AOX Generation (Kg/t O.D. pulp) during Different Bleaching Sequences

Bleaching Stage	D/CED	DED	DE _p D	ODED
D/C or D ₁	2.20	0.32	0.27	0.16
E or E _p	0.30	0.28	0.23	0.14
D/D ₂	0.10	0.07	0.05	0.04
Total	2.60	0.67	0.55	0.34

The application of H₂O₂ along with NaOH during E stage in the DE_pD sequence reduced the requirement of active chlorine multiple (KF 0.30) hence lower AOX is generated as compared to the DED sequence. H₂O₂ addition in E stage decreased the lignin content further by additional oxidation and thus allowed the KF for a given kappa target to be lowered. Hence, AOX generation in effluents decreased because of less chlorine demand in the first bleaching stage³². ODED sequence effluents are found to be having the lowest AOX load (0.34 Kg/t O.D. pulp) as compared to other sequences. This is because of the decrease (45%) of the initial kappa number of the pulp after O₂ delignification. This reduces aCl⁻ demand needed for the subsequent bleaching stages and AOX load³. The pulp with a lower kappa number can be bleached more easily, and the bleach chemicals consumption and the pollution load can be minimized³³.

Economic Analysis

The dose of various chemicals applied during different pulp bleaching sequences is summarized in Table-4. The total active chlorine consumption followed the order: DED > D/CED = DE_pD > ODED to achieve same target brightness of 87% ISO (Fig.-3).

Table-4: Chemical Dose (Kg/t O.D. pulp) Applied During Pulp Bleaching

Sequences	Stages	Cl ₂	ClO ₂	NaOH	H ₂ O ₂	O ₂	MgSO ₄ .7H ₂ O	Brightness (%ISO)
D ₅₀ /C ₅₀ ED	D/C	15.75	5.99	-	-	-	-	86.9
	E	-	-	10	-	-	-	
	D	-	5.13	-	-	-	-	
DE _p D	D ₁	-	11.98	-	-	-	-	87.3
	E _p	-	-	7	3	-	-	
	D ₂	-	5.13	-	-	-	-	
DED	D ₁	-	13.97	-	-	-	-	87.1
	E	-	-	7	-	-	-	
	D ₂	-	5.97	-	-	-	-	
ODED	O	-	-	20	-	20*	2	86.9
	D ₁	-	6.63	-	-	-	-	
	E	-	-	7	-	-	-	
	D ₂	-	2.84	-	-	-	-	

*3

Fig.-3: Chemical Consumption During Pulp Bleaching Sequences

The application of the O₂ delignification stage in the ODED sequence can reduce bleach (aCl⁻) chemical dose by 53% as compared to the DED sequence and 45% as compared to D/CED and DE_pD sequences. DED sequence required 14% higher bleach (aCl⁻) chemical dose to achieve 87% ISO target brightness as compared to D/CED and DE_pD sequences. There is required 30% less NaOH dose during bleaching with ECF (DED, DE_pD, and ODED) sequences as compared to the D/CED sequence. There has been reported a reduction in alkali charge during E stage during ECF bleaching sequences²⁶. The reduction of chemical requirements for pulp bleaching is important for process economy as well as for environmental protection.

The economic analysis of any process change can be assessed by considering operating cost or value addition. However, the economic value calculation is difficult for intangible benefits. The improved environmental performance, in such cases, can be considered for the assessment of process economic viability.

The process may face closure due to non-compliance with set statutory norms. Under such circumstances, the additional input costs for making the process operation can be considered as an investment cost and cost of closure due to non-compliance as an economic gain of investment. The bleaching economic analysis has been carried out by considering the costs associated with the following factors:³⁴

- The bleach chemical costs for different sequences (Table-5) as per 2018.

- AOX abatement costs: by bleaching modification and effluent treatment (adsorption and ion exchange: Rs 200/kg of AOX removed) have been considered as additional operating costs for meeting the regulatory standards.
- The intangible benefits, environmental compliance by bleaching modification, which would otherwise have been closed due to non-compliance, are not considered.
- The cost savings by alkali recovery from O₂ stage effluent recycling have not been considered, which will further reduce the cost of the ODED sequence.

The economic analysis of various pulp bleaching sequences as compared with the D/CED sequence is summarized in Table 6. The cost of the DED sequence is found to be the highest (2274 Rs/t O.D. pulp) followed by ODED, DE_pD, and D/CED sequences due to the requirement of higher bleach chemical charge to attain the same target brightness. If the additional costs associated with AOX abatement at source (Rs 683/-, 580/-, and 596/- for DED, DE_pD, and ODED sequences, respectively, as compared to D/CED sequence) and effluent treatment of AOX (amount reduced at source as compared to D/CED sequence) using adsorption and ion exchange technologies (Rs. 200/kg AOX removed)³⁵ are considered, then ODED sequence is found to be having Rs 144/- higher cost followed by DE_pD (Rs 170/-) and DED (Rs 297/-) sequences as compared to D/CED sequence. All ECF bleaching sequences (DED, DE_pD, and ODED) can reduce AOX generation below the set regulatory standard (1 kg/t of paper for large pulp and paper industry)¹⁸. DED sequence generated 74% lesser AOX as compared to the D/CED sequence.

Table-5: Cost of Chemicals (Rs/Kg) Used for Pulp Bleaching in India (2018)

Chemical	Cost (Rs/kg)
Chlorine (Cl ₂)	05
Chlorine Dioxide (ClO ₂)	100
Sodium Hydroxide (NaOH)	40
Hydrogen Peroxide (H ₂ O ₂)	60
Oxygen (O ₂)	07
Magnesium Sulphate (MgSO ₄ .7H ₂ O)	10

Table-6: Economic Analysis of Pulp Bleaching Sequences

Sequence	Bleaching Cost (Rs/T O.D. pulp)		AOX (kg/T O.D. Pulp)		AOX Abatement Cost (Rs/kg)		
	Pre-treatment	Bleach Chemical	Generation	Reduction at Source	At Source	ET*	Savings
D/CED	-	1591	2.60	-	-	-	-
DED	-	2274	0.67	1.93	+683	386	-297
DE _p D	-	2171	0.55	2.05	+580	410	-170
ODED	960	2187 [#]	0.34	2.26	+596	452	-144

*Effluent treatment cost of AOX (which is reduced at source) (200 Rs/kg)³⁵; # including the cost of O₂ pre-treatment.

The pulp and paper industry may look at O₂ pre-bleaching stage to meet AOX discharge standards and closing the bleach cycle with ~87% lower AOX generation at Rs 144/- higher cost as compared to D/CED sequence. The high capital cost is one of the major causes of not adopting the O₂ pre-delignification process, particularly in small industries. The pulp and paper industries which will not be able to install O₂ pre-bleaching stage can meet up effluent AOX discharge standards by adopting a DE_pD sequence with 79% lesser AOX generation at Rs 170/- higher cost as compared to D/CED sequence.

CONCLUSION

The following conclusions are drawn based on the results:

- All ECF bleaching sequences are found to decrease effluent AOX generation below the regulatory standard.
- The ECF bleaching sequences reduced alkali consumption by 30% as compared to the D/CED sequence.

- The economic analysis shows that ODED and DE_pD sequences can be adopted concerning meeting AOX discharge standards. DE_pD sequence is an alternative for the pulp and paper industries where O₂ plant installation is not possible.

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