

ENVIRONMENTAL ASPECTS AND EFFICACY OF PERACETIC ACID TREATMENT TO IMPROVE ELEMENTAL CHLORINE FREE BLEACHING PROCESSES

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The pulp bleaching process is mainly responsible for the generation of toxic substances in the whole paper making process. The modification of conventional ECF (elemental chlorine free) bleaching was studied using an oxygen stage, a peracetic acid stage and an oxygen followed by peracetic acid stage in the following bleaching sequences: OD₀E_{OPD}, PaaD₀E_{OPD}, OPaaD₀E_{OPD} and QOPaaD₀E_{OPD}. The PaaD₀E_{OPD} sequence reduced the COD, BOD, color, TDS and AOX by 36.8, 37.0, 52.4, 39.8 and 53.9%, respectively, in comparison with D₀E_{OPD}. Moreover, PaaD₀E_{OPD} has better optical effluent properties, compared to the OD₀E_{OPD} sequence. OPaaD₀E_{OPD} reduced the chlorophenols, chloroguaiacols by 73.3 and 89.3%, and improved the brightness and whiteness by 1.7 and 3.1 units, respectively, in comparison with the D₀E_{OPD} bleaching sequence. The QOPaaD₀E_{OPD} sequence improved the pulp viscosity by 0.8 units in comparison with OPaaD₀E_{OPD}. The amendment of the conventional bleaching sequence was found to be effective for achieving an improvement in optical properties and effluent quality at reduced dose of chlorine dioxide.

Keywords: peracetic acid, Kappa number, viscosity, AOX, chlorophenolic compounds, FTIR

INTRODUCTION

Paper manufacturing involves the pulp bleaching process, which is responsible for the generation of the most toxic substances in the whole paper making process. Global environmental awareness accelerated the need of clean and low impact bleaching processes. The paper manufacturing units are now focusing on exploring potential environment-friendly bleaching reagents that allow reducing toxic pollutants and improving the pulp properties during bleaching.

The bleaching process includes the lignin removal from unbleached pulp, which improves its brightness using different bleaching chemicals. The effluent released after the bleaching process is rich in BOD, COD and chlorophenolic compounds.^{1,2} The chlorinated products are the results of several reactions of bleaching chemicals with lignocellulosic biomass that impart high toxicity to the discharged effluent.³ Chlorophenolic compounds called adsorbable organic halides (AOX) are persistent in nature and

cause kidney and liver damage, and also bring hormonal changes in many living beings.⁴ Because of their lipophilic property and strong C-Cl bond, chlorinated compounds are not easily degradable.⁵ The release of effluent from the bleaching plant pollutes the water bodies, as well as impacts the life of aquatic animals and disturbs together monetary and societal assets of society. This has caused massive pressure on pulp and paper manufacturing units to reduce the discharge of toxic substances by advanced wastewater treatment methods.⁶

Many advanced wastewater treatment technologies are available for the degradation of AOX content, but cannot meet the norms for effluent discharge using conventional bleaching processes.¹ Therefore, pulp and paper manufacturing units are under immense stress to switch towards cleaner and greener bleaching processes. To cut down the AOX content, the pulp manufacturing units are now more dependent on the elemental chlorine free (ECF) bleaching

technique.^{7,8} The ECF bleaching replaces the elemental chlorine by chlorine dioxide and consequently reduces the AOX content significantly; the quantity of PCDD/Fs toxic compound was found inferior by a multiple of 1.3–14.9, in comparison with the chlorine based bleaching sequence.⁹ ECF is a foremost bleaching technology and about 95% of the total bleached pulp in the world is produced by this process.¹⁰ However, due to the use of chlorine dioxide, some chlorinated compounds are still formed during ECF bleaching of pulp.¹¹

In addition to ECF bleaching, some new developments have also been evaluated for environmental benefits, with improvement in pulp quality. By utilizing oxygen, ozone and hydrogen peroxide, it is possible to reduce the pollutants from the bleaching process, as well as the effluent volume to be treated in the effluent treatment plant.^{8,12} The AOX content is associated to the use and consumption of chlorine and its derivatives in a bleaching sequence.⁴ Hart and Santos revealed that pulp with higher kappa number entering the bleach plant tends to form higher AOX and toxic pollutants.¹³ Peracetic acid has also been recognized as a promising bleaching agent with capabilities to reduce the pollution load and effluent volume from the pulp bleaching process.¹⁴ In previous studies, it was found that the oxidation potential of peracetic acid was higher than that of chlorine and chlorine dioxide; it can oxidize the lignin and reduce the kappa number of unbleached pulp before the pulp enters the bleaching plant.

Peracetic acid has been extensively utilized in various industrial sectors due to its versatile nature and degradation into non-toxic substances.¹⁵ It efficiently removes the lignin and is capable to enhance the brightness and whiteness of pulp.^{16,17} Peracetic acid has also been proved as a proficient bleaching reagent for agro pulp, without adversely affecting the pulp properties.¹⁸ It is successfully utilized in pre- and post-bleaching processes for enhancement of optical properties.^{10,19} Also, it has the capability to substitute or decrease the quantity of chlorine based and other bleaching chemicals to get targeted pulp brightness. Fiskari *et al.* used peracetic acid for partial substitution of hydrogen peroxide in the bleaching process.²⁰ However, little literature evidence is available on the reduction of the pollution load by the use of peracetic acid in pulp bleaching. The present study focused on finding a suitable ECF bleaching

sequence for mixed hardwood pulp by incorporating oxygen and peracetic acid. The study also emphasized the importance of using peracetic acid for lignin content reduction, with simultaneous reduction of toxic pollutants in the pulp bleaching effluent, which consequently reduces the load on the effluent treatment plant. Bleaching sequences were compared in terms of the pulps' optical and strength properties, and wastewater load generation; in addition, comparative analysis of FTIR spectra of differently bleached pulp samples was also performed.

EXPERIMENTAL

Materials

For the experiments, unbleached pulp was collected from a mixed hardwood mill in northern India. For consistency, throughout the study, the pulp was mixed thoroughly, shredded and kept in polythene bags. The pulp was analyzed in terms of kappa number, brightness and viscosity, using standard methods. Peracetic acid was kindly provided by Mars Chemicals, Anand, Gujarat.

Pretreatment of mixed hardwood pulp by oxygen and peracetic acid

Oxygen bleaching

Oxygen bleaching (O-stage) was carried out in a lab fabricated reactor of 3.5 L capacity, provided with an oxygen gas injection system, with high shear mixing of the pulp. The high shear mixing ensures better contact of the oxygen gas and the pulp throughout the reaction. The specifications maintained during O-stage were according to Tripathi *et al.*¹² as given in Table 1.

Peracetic acid treatment

Peracetic acid treatment (Paa-stage) of pulp was carried out using 1.0% dose of commercially available peracetic acid on oven dry basis of pulp, 10.0% pulp consistency for 60 min kept at 80 °C temperature.

Oxygen treatment followed by peracetic acid treatment

For oxygen treatment followed by peracetic acid treatment (OPaa-stage), O-stage was carried out on unbleached pulp according to the specifications given in Table 1. After uniform washing, Paa-stage was carried out using the above given specifications.

Diethylenetriamine pentaacetate (DTPA) treatment

DTPA treatment (Q-stage) of the pulp was carried out as per the specifications reported by Shen *et al.*,²¹ as shown in Table 1. After each treatment, the pulp samples were washed properly and analyzed for brightness, kappa number and viscosity as per Tappi

test methods. Brightness, kappa number and viscosity of the pulp were characterized by T 525, T 236 and T 230, respectively. Statistical study of variance (ANOVA) was used for brightness, kappa number and viscosity data, with the help of software Origin 6.1.

ECF bleaching

Bleaching of unbleached mixed hardwood mill pulp was performed by the conventional ECF bleaching sequence $D_0E_{OP}D$; where D_0 – bleaching with chlorine dioxide in the first step to oxidize the lignin content remaining after pulping, E_{OP} – in this step extraction was carried out on chlorine dioxide bleached pulp using sodium hydroxide, oxygen and hydrogen peroxide to dissolve the lignin and improve the brightness of pulp, and D – chlorine dioxide was used in the final stage of the bleaching sequence to improve pulp brightness.

Optimization of bleaching chemicals

In D_0 , to calculate the optimum dose of chlorine dioxide, different kappa factors: 0.20, 0.22, 0.24, 0.26, 0.28 and 0.30, were studied. The alkaline extraction

stage (E_{OP}) of bleaching sequences $D_0E_{OP}D$, $PaaD_0E_{OP}D$, $OD_0E_{OP}D$ and $PaaD_0E_{OP}D$ was carried out in the reactor having temperature control software and with high shear mixing throughout the reaction. To calculate the optimum dose of chlorine dioxide in D , for bleaching sequences $D_0E_{OP}D$, $PaaD_0E_{OP}D$, $OD_0E_{OP}D$ and $OPaaD_0E_{OP}D$, the doses of 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0% were applied. The purpose of bleaching is the extraction of the lignin content left behind in pulp after the pulping process. The D -stage was executed in plastic bags in a temperature-controlled water bath; the desired temperature and pH were maintained during bleaching. After each stage of bleaching, the pulp was washed thoroughly to remove residual chemical and reaction products. Constant conditions were maintained during the bleaching of pulps for each sequence (Table 1). All sets of bleaching experiments were executed in triplicate and the averages of the results were reported. The efficacy of bleaching of the pulp was evaluated by comparison of optical properties, such as brightness, whiteness and yellowness of pulp.

Table 1
Specifications maintained for the bleaching study

Parameter	O	D_0	E_{OP}	D	P_{aa}	Q
Pulp consistency (%)			10			5
Temperature (°C)	100.0	55.0	80.0	75.0	80.0	60.0
Reaction time (h)	1.00	1.25	2.00	3.00	1.00	1.00
Oxygen pressure (kg/cm ²)	3.5	--	3.0	--	--	--

FTIR-ATR spectroscopy of pulp samples

Pulp samples bleached by different bleaching sequences were analyzed by FTIR to see the impact of oxygen, peracetic acid treatments on functional groups. A Frontier MIR spectrometer (PerkinElmer, UK) was utilized to record the ATR-FTIR spectra of pulp samples. The FTIR spectra of all the pulp sheets were acquired in the range of 4000 to 400 cm^{-1} wavelength to elucidate the changes. In the ATR cell, the refractive index (RI) of the diamond was used (from PIKE Technologies).

Analysis of bleaching effluent

A representative sample of effluent was prepared for each stage of the ECF bleaching sequence by adding effluent in the respective volume according to the consistency of each stage of bleaching. Representative samples were evaluated as per the standard test methods of Indian Standards (IS) and American Public Health Association (APHA). Chemical oxygen demand (COD) in the samples was evaluated as per IS: 3025 (Part 58). Total dissolved solids (TDS) of the samples were evaluated as per the test method IS: 3025 (Part 16). BOD_3 was evaluated by the method IS: 3025 (Parts 38 and 44). Color was evaluated as per the method APHA 2120. AOX was

evaluated by an AOX analyzer as per the test method ISO: 9562.

Chlorophenolic compounds analysis

The samples of all bleaching sequences were evaluated for chlorophenolic compounds using a gas chromatograph (GC Varian 450 GC) having electron capturing detector. 1 L of all samples was extracted separately and derivatized in accordance with the method provided by Lindstrom and Nordin (1976). Initially, the samples were acidified using sulphuric acid to attain a pH close to 2.0. The acidified sample was introduced into a separating funnel and about 200 mL of solvent was added – a mixture of diethyl ether and acetone in the 90:10 ratio. The sample was mixed thoroughly and left for 48 h with periodical mixing.

After separation of the layers, the solvent part of the sample was collected into another separating funnel. The extract was washed with 2.5 mL of sodium bicarbonate solution (0.5 M) to make the layer acid free. Sodium hydroxide (0.5 M) was mixed in the separating funnel and the mixture was shaken for another 5 minutes. The aqueous NaOH layer was separated with extracted chlorophenolic compounds; the layer was washed with fresh diethyl ether and collected in a glass tube with a tight screw cap. For

maintaining the pH, 0.5 mL of disodium hydrogen phosphate buffer (0.5 M) was added. For conversion of chlorophenols into their derivatives, 0.5 mL of acetic anhydride (AR grade) was added and was shaken for 5 min, then 4 mL of hexane (HPLC grade) was added as well.

For reference, 21 isomers of different chlorophenolic compounds procured from Sigma Aldrich, USA, were also derivatized using the same procedure. The reference compounds were used for identification of each chlorophenolic component by matching their retention time (± 0.5 min).

The specifications for the gas chromatograph are given below in Table 2.

Table 2
Specifications of the gas chromatograph

Column type	Capillary column VF-1 ms
Dimensions	30 m X 0.25 mm I.D. with 0.25 μ m thickness
Sample size (μ L)	1
Detector	ECD
Temperature profile	
Detector	290 °C
Injector	270 °C
Column temperature (°C)	Initial 100 °C for 3 min
	100–180 °C at 4 °C/min
	180°C for 10 min
	180–270°C at 15 °C/min
	270 °C for 2 min
Column pneumatics	1 mL/min
Nitrogen flow	28 mL/min
Split ratio	1:20

RESULTS AND DISCUSSION

Effects of oxygen, peracetic acid and chelating reagent treatment on pulp properties

Unbleached mixed hardwood pulp was treated by oxygen (O-stage), peracetic acid (Paa-stage), oxygen followed by peracetic acid (OPaa-stage) and chelating reagent followed by oxygen and peracetic acid (QOPaa-stage), as per the specifications given in Table 1. The effects of O, Paa, OPaa and QOPaa stages on pulp properties and variance are given in Table 3. It was found that O-stage enhanced the pulp brightness by 12.6 points, with a decline in kappa number and viscosity by 46.3 and 20.0%, respectively, in comparison with unbleached pulp. The results are in agreement with those reported in the study of Bajpai,²³ who established that the oxygen stage can reduce the kappa number of pulp by up to 50%, and further than this, excessive carbohydrate destruction occurred.²³ In the Paa-stage, pulp brightness was improved by 13.9 points, with a decline in the kappa number and

Efficiency of extraction

To calculate the efficiency of extraction for reference chlorophenolic compounds, these were also extracted and derivatized by the same procedure as described above. The sample was identified by its peak and the peak area was used for concentration calculation. The quantity of chlorophenolics in the extracts was calculated by using the peak area through the formula:²²

$$\text{Extraction efficiency \%} = \frac{\text{Peak area of extracted sample}}{\text{Peak area of nonextracted sample}} \times 100 \quad (1)$$

viscosity by 48.9 and 18.8% respectively, in contrast to unbleached pulp. Peracetic acid degrades the lignin more, as it causes considerable demethylation of lignin in pulp, leaving quinone and muconic acid type rich structures and lower biphenyl and biphenyl ether structure pulp, compared to oxygen treated pulp.²⁴ These chemical changes led to improved bleachability in subsequent stages.

After the OPaa-stage, the pulp brightness was improved by 25 points and the kappa number and viscosity were reduced by 70 and 24.4%, respectively, compared to unbleached pulp. The lignin removal by peracetic acid treatment may be the reason that, owing to the breaking of side chains, the hydrophilicity of lignin increased.¹⁹ During the peracetic acid treatment, a number of reactions occurred, including ring opening, side chain cleavage, hydroxylation, β -ether bond cleavage, demethylation and epoxidation.²⁵ After the OPaa-stage, the decline in viscosity was more pronounced in comparison with that of the O-

stage. The results are in line the literature, as the presence of metal ions converts the aliphatic hydroxyl groups to carbonyl groups, resulting in declined viscosity of pulp.²⁴ Therefore, a chelating stage was added prior to the OPaa-stage; the addition of the chelating stage prior to peracetic acid treatment can remove the metal ions and improve the selectivity of peracetic acid treatment.²¹ Therefore, when the pulp was treated with DTPA (Q-stage), viscosity was preserved as DTPA removed the metal ions. After the QOPaa-

stage, the pulp was less degraded and had 0.8 cP higher viscosity value in comparison with that of the OPaa-stage, with approximately the same kappa reduction.

Besides pulp properties, the benefit of oxygen and peracetic acid bleaching is also that the wastewater from these stages can be recycled in a recovery process, as there is no chloride ion present, which, consequently, reduces the pollution load for the effluent treatment plant.

Table 3
Effects of oxygen, peracetic acid and chelating reagent on pulp properties

Pulp sample	Brightness (%ISO) (mean)	Variance	Kappa number (mean)	Variance	Viscosity (cP) (mean)	Variance
Unbleached pulp	29.0	0.023	19.0	0.090	16.0	0.043
O-stage	41.6	0.010	10.2	0.130	12.8	0.063
Paa-stage	42.9	0.023	9.7	0.010	13.0	0.023
OPaa-stage	54.0	0.040	5.7	0.023	12.1	0.070
QOPaa-stage	54.5	0.013	5.6	0.093	12.9	0.093
	F= 75.94 P= 2.35		F= 7.68 P= 0.024		F= 111.73 P= 5.60	

At the 0.05 level, the means of brightness, kappa number and viscosity for different treatments are significantly different

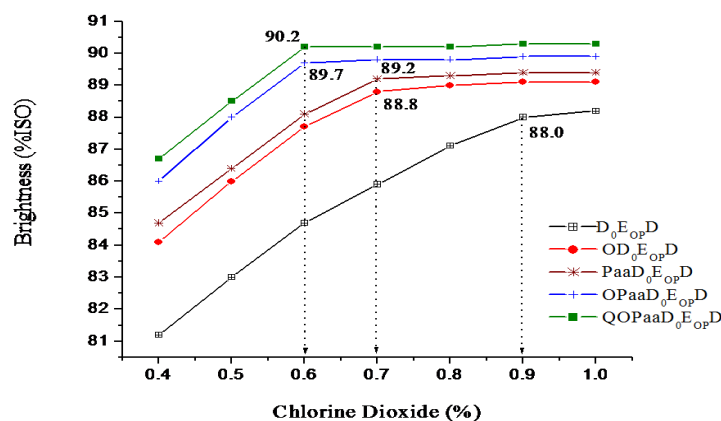


Figure 1: Optimization of chlorine dioxide dose for different bleaching sequences

Bleaching chemical dose optimization for pulp bleaching

The bleaching chemicals dosage was optimized on bone dry basis of pulp for bleaching sequences D₀E_{OP}D, PaaD₀E_{OP}D, OD₀E_{OP}D and OPaaD₀E_{OP}D. For the optimum dose of chlorine dioxide for D₀ stage, the kappa factor was varied from 0.22 to 0.30. From the study, 0.28, 0.24, 0.24 and 0.23 kappa factors were found to be optimum for D₀E_{OP}D, PaaD₀E_{OP}D, OD₀E_{OP}D and OPaaD₀E_{OP}D, respectively. Above these kappa factors for different bleaching sequences, the

residual quantity of chlorine dioxide was amplified manifolds in the effluents, which showed the perimeter for chlorine dioxide dose in the D₀ stage. The quantity of chlorine dioxide for the D₀ stage during bleaching of mixed hardwood pulp was calculated according to Kaur *et al.*⁸ by the formula (2):

$$\text{Requirement of chlorine (\%)} = \text{Kappa number} \times \text{Kappa factor}$$

The optimization study for the D stage was based on brightness improvement; the increment in brightness was observed to evolve linearly up to a certain dose of chlorine dioxide, afterwards,

the increment in brightness was found to be negligible (Fig. 1).

The residual chlorine dioxide content increased manifolds above these doses of chlorine dioxide for all bleaching sequences. So, it was observed that the optimum doses of chlorine dioxide were 0.9, 0.7, 0.7 and 0.6% for D₀E_{OPD}, PaaD₀E_{OPD}, OD₀E_{OPD} and OPaaD₀E_{OPD}, respectively. On further raising the chlorine dioxide dose above the optimum dose, no improvement in brightness was observed, but the highest residual content of chlorine dioxide was obtained. For the QOPaaD₀E_{OPD} sequence, the chemicals were applied according to the OPaaD₀E_{OPD} sequence.

Analysis of bleached pulp properties

After the O-stage, Paa-stage and OPaa-stage, the requirement of chlorine dioxide for bleaching was reduced by 44.2, 45.5 and 62.3%, respectively, in comparison with conventional bleaching. The conventional bleaching sequence DE_{OPD} had obtained 88.0% ISO brightness and 77.8 CIE whiteness of final bleached pulp, and the results were in agreement with those reported by Tripathi *et al.*¹² for mixed hardwood pulp (Table 4). Brightness and whiteness improved by 0.8, and 1.1 points, respectively, whereas the post color number (P.C. no.) reduced by 20.0% for OD₀E_{OPD} in comparison with DE_{OPD} bleaching sequence. Further improvement was found for PaaD₀E_{OPD} bleached pulp in comparison with ODE_{OPD} sequence. An improvement in brightness and whiteness by 1.2 and 1.6 points,

respectively, and a reduction in P.C. no. by 23.5% were found. By combination of oxygen and peracetic acid treatment improved the optical properties significantly. The pulp brightness and whiteness for OpaaD₀E_{OPD} was enhanced by 1.7 and 2.3 points, respectively, whereas P.C. no. also reduced by 27.6% in comparison with DE_{OPD}. The brightness improvement with Paa treatment due to increased hydrophilicity of lignin during peracetic acid treatment, therefore, the residual lignin content was detached without difficulty in successive bleaching stages.²⁵ Krizman *et al.*²⁶ revealed that, when peracetic acid was used as bleaching reagent in the initial stage for cotton fiber, the brightness of the pulp was enhanced. Bleaching with oxygen is not lignin selective, and also reacts with the carbohydrates present in the pulp.²⁷

Our results were also in agreement with that OD₀E_{OPD} had lower pulp viscosity value compared to pulp viscosity of PaaD₀E_{OPD} bleached pulp. With OPaaD₀E_{OPD} sequence final pulp viscosity was observed to be 10.5 cP which is less than OD₀E_{OPD}. Peracetic acid does not harm the cellulose directly, but with the presence of transition metals the degradation of cellulose takes place during peracetic acid treatment. With addition of Q-stage prior to OPaaD₀E_{OPD} sequence, pulp viscosity was improved. In addition, QOPaaD₀E_{OPD} sequence obtained more than 90 %ISO brightness and excellent whiteness improvement in comparison to D₀E_{OPD} sequence.

Table 4
Optical properties of final bleached pulp

Parameter	D ₀ E _{OPD}	OD ₀ E _{OPD}	PaaD ₀ E _{OPD}	OPaaD ₀ E _{OPD}	QOPaaD ₀ E _{OPD}
Brightness %ISO	88.0	88.8	89.2	89.7	90.2
Whiteness	77.8	78.9	79.4	80.1	81.0
P.C. Number	0.45	0.36	0.34	0.33	0.32
Viscosity (cP)	12.1	11.0	11.3	10.5	11.4

FTIR analysis

For recording FTIR spectra, the lab prepared pulp handsheets were pressed against a diamond ATR crystal. All spectra were measured against a background spectrum, in the absence of the sample. All the spectra were collected in the spectral range of 500–4000 cm⁻¹.

The impact of different bleaching sequences on functional groups of the pulp was studied by the ATR-FTIR spectra, as shown in Figure 2. The

peak at 897 cm⁻¹ represents the cleavage of the glycosidic bond. The peak at 897 cm⁻¹ for the QOPaaD₀E_{OPD} bleaching sequence showed minimum absorbance, which indicates that the treatment with the chelating agent preserves the carbohydrates from degradation. The spectra at 1200 cm⁻¹ and 1100 cm⁻¹ represent the region of hemicelluloses. Meanwhile, the peak at 1030 cm⁻¹ corresponds to the C-O stretching, denoting the cellulose,²⁸ and it was the highest in the spectrum

for the QOPaaD₀E_{OP}D sequence. The band at 1243-1317 cm⁻¹ shows the skeletal vibrations of lignin guaiacyl.²⁹ The peak for syringyl nuclei in hardwood lignin was found at 1595 cm⁻¹.²⁸ The absorption bands at 1512 cm⁻¹, 1620 cm⁻¹, found to be associated with functional groups in lignin, were absent in the spectra of all the sequences, which showed that most of the lignin was removed through bleaching. The peak around 1316 cm⁻¹ is assigned to the crystallized cellulose;³⁰ the maximum peak was found for QOPaaD₀E_{OP}D, followed by PaaD₀E_{OP}D, OD₀E_{OP}D and OPaaD₀E_{OP}D, compared to D₀E_{OP}D. Zhang *et al.* revealed that the band at 1429 cm⁻¹ was found to represent the syringyl and

guaiacyl groups of lignin.³¹ The decline in these peaks was found in the following order: QOPaaD₀E_{OP}D, OPaaD₀E_{OP}D, PaaD₀E_{OP}D and OD₀E_{OP}D bleaching sequences, which strengthen the elimination of syringols and guaiacols groups. The peak at 1640 cm⁻¹ was attributed to stretching of C=C and C=O in the lignin aromatic ring and was correlated with lignin degradation.³² The C-H symmetrical stretch was characterized by the peaks at ~2900 cm⁻¹ due to aliphatic and aromatic structures in polysaccharides.^{33,34} The peak present at ~3400 cm⁻¹ corresponds to O-H stretching vibrations associated with intermolecular H-bond.

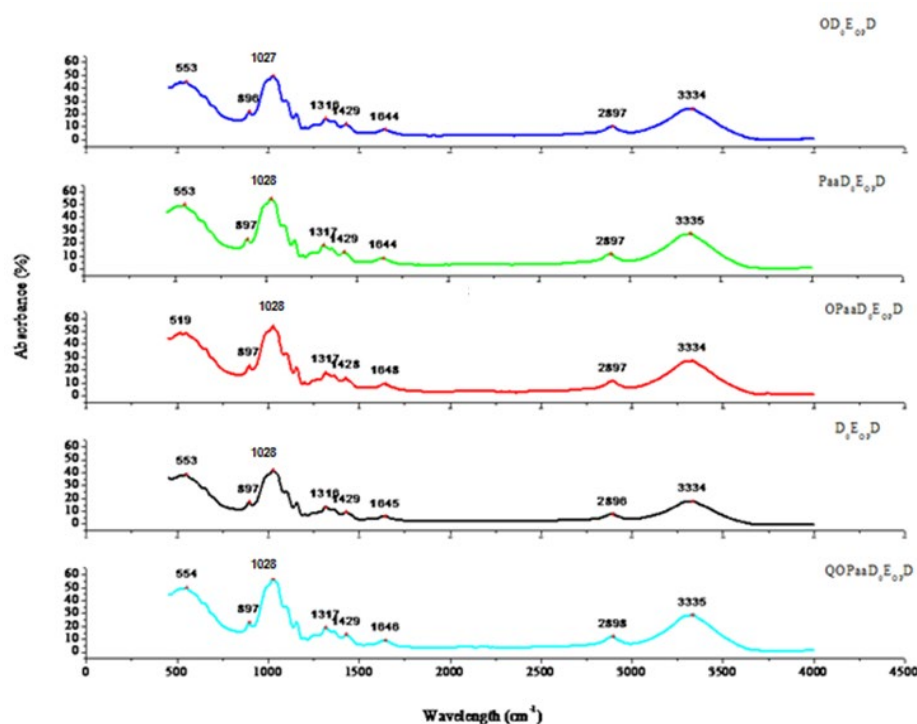


Figure 2 FTIR-ATR spectra of pulps bleached by different bleaching sequences

Table 5
Effect of bleaching sequences on effluent characteristics

Parameters	D ₀ E _{OP} D	OD ₀ E _{OP} D	PaaD ₀ E _{OP} D	OPaaD ₀ E _{OP} D	QOPaaD ₀ E _{OP} D
pH	5.5 ± 0.1	5.7 ± 0.1	5.8 ± 0.1	5.7 ± 0.1	5.6 ± 0.1
COD (mg/L)	1139.7 ± 23.0	823.5 ± 12	720 ± 22	540 ± 16	404.4 ± 12
BOD (mg/L)	230 ± 17	165 ± 11	145 ± 7	101 ± 5	100 ± 4
Color (PCU)	536 ± 11	291 ± 9	255 ± 6	125 ± 7	119 ± 8
AOX (mg/L)	24.1 ± 0.5	12.2 ± 0.3	11.1 ± 0.2	5.4 ± 0.2	5.0 ± 0.1
TDS (mg/L)	3412 ± 63	2410 ± 58	2055 ± 41	1689 ± 32	1580 ± 29

Effluent analysis

All sequences with O, Paa, OPaa and QOPaa stages prior to ECF bleaching were superior to traditional ECF bleaching alone in terms of

reducing toxic pollutants. With the analysis of the bleaching effluent for all bleaching sequences, it was found that minimum pollutants were generated by the QOPaaD₀E_{OP}D bleaching

sequence (Table 5). Different studies also revealed that a pretreatment of unbleached pulp prior to ECF bleaching diminished the effluent load, compared to ECF bleaching alone.^{12,35} By inclusion of the O-stage prior to the D₀E_{OPD} bleaching sequence, the COD, BOD, Color and TDS were reduced by 27.7, 28.3, 45.7 and 29.4%, respectively, and the results were also in agreement with those of an earlier research study reported by Tripathi *et al.*¹²

For the PaaD₀E_{OPD} bleaching sequence, the COD, BOD, Color, TDS and AOX were reduced by 36.8, 37.0, 52.4, 39.8 and 53.9%, respectively, in comparison with those of D₀E_{OPD}. These reductions were higher than those of the OD₀E_{OPD} sequence. Sharma *et al.*¹⁴ also reported that the AOX content was reduced by 54.7% by incorporating the Paa stage prior to ECF bleaching. The study by Nie *et al.*³⁶ revealed that the AOX compounds were produced during chlorine dioxide bleaching when the generated hypochlorous acid reacted with the lignin present in the pulp. The reduction in pollutants was increased significantly with the oxygen and peracetic acid treatment. It was observed that for the OPaaD₀E_{OPD} sequence, the COD, BOD, Color and TDS were reduced by 52.6, 56.1, 76.7 and 50.5%, respectively, in comparison with those of D₀E_{OPD}. The main consequence of integrating the OPaa stage prior to ECF bleaching was the reduction of AOX compounds. About 77.6% reduction in AOX was found in the sequence OPaaD₀E_{OPD}, when compared with the sequence D₀E_{OPD}. In the same manner, pollutants were reduced for the QOPaaD₀E_{OPD} bleaching sequence, in comparison with those of D₀E_{OPD}. A significant amount of AOX content was reduced upon incorporation of O, Paa, OPaa and QOPaa stages prior to ECF bleaching, as these stages reduce the lignin content prior to bleaching. The amount of AOX generated in pulp bleaching depended on the nature of the bleaching chemicals and the content of residual lignin.^{12,37}

Effects of bleaching sequences on generation of chlorophenolic compounds

Different organohalides were found in the effluents produced through the bleaching of pulp with different bleaching sequences. Chlorophenolic compounds include the isomers of chlorosyringols (CS), chlorophenols (CP), chlorocatechols (CC), chloroguaiacols (CG), dichlorosyringaldehyde (CSA) and chlorovanillins (CV). The total chlorophenolic compounds

generated in the D₀E_{OPD} bleaching sequence were 539.5 mg/t of pulp, and these were reduced to 300.6, 278.4, 180.2 and 175.35 mg/t for sequences OD₀E_{OPD}, PaaD₀E_{OPD}, OPaaD₀E_{OPD} and OPaaD₀E_{OPD}, respectively (Table 6). There was significant reduction in chlorophenolic compounds by the oxygen and peracetic acid treatment. This may correspond to a reduction in kappa number by these treatments before applying bleaching chemicals. The D₀E_{OPD} bleaching effluent contained chlorocatechols (193.08 mg/t), chlorovanillins (145.66 mg/t), chloroguaiacols (10.09 mg/t), chlorosyringols (25.15 mg/t) and chlorophenols (84.45 mg/t), respectively (Table 6). After incorporation of the O-stage, the chloroguaiacols and chlorovanillins were reduced significantly. Kaur *et al.*³⁸ also claimed that after the addition of the O-stage before ECF bleaching of rice straw pulp, chloroguaiacols and chlorovanillins reduced drastically. The reduction was increased further with the peracetic acid treatment, as chloroguaiacols content reduced for PaaD₀E_{OPD} to 83.75%, which perked to 89.30% for OPaaD₀E_{OPD} sequence, in comparison with the D₀E_{OPD} sequence.

Also, it was established that the generation of chlorovanillins declined to 60.2, 65.5 and 73.3% in OD₀E_{OPD}, PaaD₀E_{OPD} and OPaaD₀E_{OPD} sequences, respectively, in comparison with the D₀E_{OPD} sequence. 2,3,4,5-Trichlorophenol, the chief patron of chlorophenolics in the D₀E_{OPD} sequence (57.49 mg/t), declined considerably in the OPaaD₀E_{OPD} sequence (11.66 mg/t). Through integrating the O- stage prior to D₀E_{OPD}, the results showed that pentachlorophenol was reduced by 88%, and by addition of Paa and OPaa-stages, it entirely disappeared in the bleaching effluent. This was attributed to the reduction in initial kappa number after the treatment, which declined the generation of chlorophenolic compounds. These results were also according to Kaur *et al.*³⁸ and Kumar.³⁹ It was also observed that 2,6 DBP was reduced by 98.4% in the OPaaD₀E_{OPD} sequence in comparison with the D₀E_{OPD} sequence. For the QOPaaD₀E_{OPD} sequence, the reduction in chlorophenolics was found in the same trend as for OPaaD₀E_{OPD}.

Table 6
Generation of chlorophenolic compounds in different bleaching sequences

Component	RT (min)	EE (%)	Chlorophenolic compounds concentration (mg/t)				
			1	2	3	4	5
3-chlorocatechols (3-CC)	5.85	103	25.75 ± 0.7	21.73 ± 0.7	19.72 ± 0.7	13.37 ± 0.5	12.37 ± 0.5
5-chloroguaiacols (5-CG)	6.89	52	3.22 ± 0.2	3.03 ± 0.2	1.34 ± 0.1	0.82 ± 0.1	0.80 ± 0.1
6-chloroguaiacols (6-CG)	7.14	52	ND	ND	ND	ND	ND
2,6-dichlorophenol (2,6-DCP)	7.79	63	12.14 ± 0.6	8.82 ± 0.4	7.94 ± 0.2	4.02 ± 0.1	4.00 ± 0.1
2,6-dibromophenol (2,6-DBP)	7.91	51	4.55 ± 0.2	4.55 ± 0.2	1.30 ± 0.1	0.07 ± 0.0	0.07 ± 0.0
2,5,6-trichlorophenol (2,5,6-TCP)	8.17	52	9.63 ± 0.5	7.84 ± 0.4	7.75 ± 0.3	0.29 ± 0.0	0.30 ± 0.0
3,4-dichlorocatechol (3,4-DCC)	8.34	56	60.39 ± 0.3	37.93 ± 0.4	37.70 ± 0.4	27.45 ± 0.4	26.95 ± 0.4
3,5-dichloroguaiacol (3,5-DCG)	9.74	60	0.49 ± 0.1	0.11 ± 0.0	0.11 ± 0.0	0.11 ± 0.0	0.11 ± 0.0
3,4,6-Tetrachlorocatechol (3,4,6-TCC)	10.11	62	83.69 ± 3.9	28.59 ± 1.2	30.62 ± 1.2	13.40 ± 0.7	13.22 ± 0.6
2,3,4,5-trichlorophenol (2,3,4,5-TCP)	10.8	12	57.49 ± 2.3	31.27 ± 1.2	27.09 ± 1.0	11.66 ± 0.5	11.53 ± 0.5
5-chlorovanillin (5-CV)	10.86	41	8.00 ± 0.4	0.19 ± 0.0	0.06 ± 0.0	0.05 ± 0.0	0.05 ± 0.0
4,5-dichlorocatechol (4,5-DCC)	11.27	49	20.63 ± 1	19.80 ± 0.9	19.32 ± 0.8	17.52 ± 0.7	17.50 ± 0.7
3,4,5-trichlorovanillin (3,4,5-TCV)	11.71	77	28.49 ± 1.4	6.14 ± 0.3	7.39 ± 0.3	6.90 ± 0.3	6.89 ± 0.3
4,6-dichloroguaiacol (4,6-DCG)	13.1	44	6.38 ± 0.2	0.20 ± 0.0	0.19 ± 0.0	0.15 ± 0.0	0.12 ± 0.0
3-chlorosyringol (3-CS)	13.3	98	17.45 ± 0.7	14.50 ± 0.6	13.38 ± 0.5	4.82 ± 0.2	4.68 ± 0.2
3,4,5-Tetrachlorocatechol (3,4,5-TCC)	14.27	8	2.62 ± 0.1	2.18 ± 0.9	1.92 ± 0.7	1.75 ± 0.7	1.75 ± 0.6
Pentachlorophenol (PCP)	14.43	74	5.19 ± 0.2	0.62 ± 0.0	0.00 ± 0.0	0.00 ± 0.0	0.00 ± 0.0
5,4-dichlorovanillin (5,4-DCV)	14.56	52	60.53 ± 2.8	24.78 ± 1.1	22.15 ± 1.0	22.15 ± 1.0	22.0 ± 1.0
3,5-dichlorosyringol (3,5-DCS)	14.97	78	7.70 ± 0.4	2.22 ± 0.8	2.16 ± 0.8	2.13 ± 0.8	2.18 ± 0.8
2,6-dichlorosyringaldehyde (2,6-DCSA)	18.65	74	76.57 ± 3.4	59.21 ± 2.5	57.57 ± 2.3	43.89 ± 1.8	42.0 ± 1.5
Tetrachlorovanillin (TCV)	20.32	30	48.64 ± 2.3	26.89 ± 1.2	20.68 ± 0.8	9.67 ± 0.4	8.83 ± 0.4

RT – retention time, EE – extraction efficiency; 1 – D₀E_{OP}D, 2 – OD₀E_{OP}D, 3 – PaaD₀E_{OP}D, 4 – OPaaD₀E_{OP}D, 5 – QOPaaD₀E_{OP}D

It was additionally noticed that the chlorocatechol components did not change significantly by treating the pulp prior to bleaching; it may possibly correspond to oxidative demethylation, which leaves the catechols on the residual lignin. For the reduction of chlorophenolic compounds, the peracetic acid treatment was a better option compared to the oxygen treatment. Van den Berg *et al.* also revealed that chlorocatechols were formed in higher concentration and stayed enclosed to chlorolignins.⁴⁰

CONCLUSION

The use of peracetic acid in pulp bleaching is an eco-friendly approach for paper industry. Peracetic acid has the capability to bleach the pulp with elemental chlorine free based bleaching practices. Peracetic acid treatment was acknowledged as the most effective, considering that it declined the bleaching chemical dosage and the pollutants in the bleaching effluent, while also enhancing optical properties. Peracetic acid can be a better option in comparison with oxygen treatment, due to ensuring better optical properties and brightness stability of the pulp, with low degradation of the cellulose content. Chlorophenolic compounds were also reduced more for PaaD₀E_{OPD}, in comparison with the OD₀E_{OPD} bleaching sequence.

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