RESPONSE SURFACE METHODOLOGY FOR OPTIMIZATION OF PERACETIC ACID PRETREATMENT OF PULP TO REDUCE POLLUTANTS FROM BLEACHING EFFLUENT

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Pulp bleaching processes emit many toxic substances. Peracetic acid (PAA) has been long recognized as an efficient bleaching agent for cellulose pulps. In the present study, 20 runs were conducted using response surface methodology (RSM) through central composite design for optimization of peracetic acid treatment of hardwood pulp, as a pretreatment step before applying conventional bleaching. Three factors, namely temperature (50-80 °C), time (0.5-2.0 h) and PAA dose (0.5-2.0%), were investigated to find out their impact on the kappa number, yield, brightness and viscosity of the pulp. The findings revealed that the peracetic acid dose of 1.0% at 80 °C for 1.0 h was the most suitable to obtain pulp of kappa number 10.2, yield of 96.87%, brightness of 43.6% ISO and viscosity of 11.7 cP. FTIR analysis revealed that the peracetic acid pretreatment of the pulp led to lower lignin content, compared to untreated pulp, but also reduced the bleaching effluent parameters, such as BOD, COD, TDS, color and AOX, by 43.0%, 55.7%, 31.9%, 51.4% and 51.1%, respectively.

Keywords: peracetic acid, Kappa number, viscosity, yield, FTIR, AOX

INTRODUCTION

Paper is a very valuable product for society due to its versatility and use in various application areas. The manufacturing of paper involves the consumption of large amounts of chemicals, water and energy, along with the discharge of toxic pollutants.[1] The conventional bleaching process based on chlorine is the root cause for the release of toxic substances into pulp and paper mill wastewater. The bleaching effluent contains high color load, COD (chemical oxygen demand), BOD (biological oxygen demand), suspended solids, lignin derived and chlorinated compounds generated during the bleaching process as a result of different chemical reactions taking place between bleaching chemicals and lignocellulosic biomass.[2] Chlorinated compounds are non-biodegradable and have an adverse impact on aquatic animals.[3] Chlorine based bleaching sequences generate about 500 different chloroorganic compounds, including chlorophenolic compounds, chlorinated resins, fatty acids *etc*.[4] Due to strict environmental legislation, the pulp and paper manufacturing units are under pressure to reduce the amount of toxic compounds released in the bleaching effluent.[5]

To reduce the concentration of toxic substances in the bleaching effluent, mainly two bleaching processes – elemental chlorine free (ECF) and total chlorine free (TCF) – have been reported in the literature. ECF bleaching is a leading process for bleaching chemical pulps; thus, more than 90% of the bleached pulps worldwide are obtained by this method.[6] This process significantly reduces the chlorinated compounds in the bleaching effluent, but not completely.[7] The kinetic study of AOX formation in ECF pulp bleaching was also studied previously.[8] Chlorinated compounds present in the bleaching effluent are persistent in nature and their amount magnifies in the sludge during wastewater treatment. Many researchers have sought ways to reduce the toxicity of bleaching effluents by bleaching process amendments and

reducing the effluent volume.[9-10] A number of promising bleaching agents, such as oxygen, ozone, hydrogen peroxide and peracids, have been reported in previous studies for both elemental chlorine free (ECF) and total chlorine free (TCF) bleaching practices.

Peracetic acid (PAA) is a promising bleaching agent that can reduce or totally replace chlorine and chlorine based bleaching chemicals due to its strong oxidizing effect. PAA is a potent oxidant and has higher oxidation potential in comparison with chlorine and chlorine dioxide.[11] PAA not only has the ability to improve the quality of the bleaching effluent, but also produces pulp with improved pulp qualities. A previous study revealed that PAA has high potential to enhance the optical properties of printing grade pulp.[12] Due to the degradation of PAA into harmless and easily degradable products, it has a wide range of applications. It can be transformed into acetic acid and hydrogen peroxide, which can again decompose into carbon dioxide, oxygen and water. PAA can be applied in any stage of pulp bleaching sequences, even after final bleaching, to improve the optical properties.[13] Danielewicz and Slusarska used PAA for improving the results of the oxygen delignification stage using pine kraft pulp and birch kraft pulp.[14-15] As reported in previous studies, PAA was found to be an effective bleaching agent for agro-residue pulps.[16-17] Therefore, Bajpai suggested the need of a detailed study on optimizing PAA dosage during pulp bleaching.[18]

The optimization of process parameters through response surface methodology (RSM) is a common practice and widely utilized in various research fields,[19-21] being suitable for delignification and bleaching studies as well.[22] In comparison with traditional methods, RSM can minimize the number of experiments and save time. The objective of the present work was to optimize the specifications for PAA pretreatment of pulp before it is subjected to a conventional bleaching procedure. The parameters studied included the dose of PAA, temperature and time during PAA treatment, focusing on their impact on pulp properties, *viz.* kappa number, yield, brightness and viscosity.

EXPERIMENTAL

Materials

A wood-based mill from the northern part of India provided mixed hardwood unbleached pulp. The pulp was thoroughly mixed and shredded, and then kept in a polythene bag to retain uniform moisture throughout the study. Peracetic acid was kindly provided by Mars Chemicals, Gujarat, India.

Optimization of peracetic acid pretreatment of pulp

Peracetic acid is commercially available as an acidic solution of hydrogen peroxide, acetic acid and water; it is unstable, so it needs standardizing before use in the study. The optimization of the PAA stage of pulp bleaching was conducted via response surface methodology (RSM), Design Expert® Version 9.0, Stat-Ease, Inc.

The full factorial central composite design (CCD) was constructed involving three independent process variables: reaction temperature, time and PAA dose, coded as A, B and C, respectively. RSM using CCD generated a set of 20 runs of experiment shown in Table 1, with the response being pulp properties, such as viscosity, kappa number, yield and brightness.

The peracetic acid (PAA) treatment was carried out in polyethylene bags. The desired pulp consistency was maintained by adding water, after addition of peracetic acid, the polythene bag was immediately sealed with a rubber band. The sealed polyethylene bags were hand kneaded for about one minute and then kept at the desired temperature in a water bath. During the reaction time, pulp samples were hand kneaded again for ten seconds after every fifteen minutes.

Analysis of pulp samples by FTIR spectroscopy

FTIR analyses were carried out on PAA treated and untreated pulp samples to study the effect of the peracetic acid treatment on functional groups. A Frontier MIR LiTa/KBr/AI spectrometer (PerkinElmer, UK) was used to record the FTIR spectra. The spectra of both pulp samples were obtained from 4000-400 cm^{-1}, at a resolution of 8 cm^{-1}, to explain any changes after peracetic acid treatment. In the ATR cell, 2.4 was the refractive index of the diamond (from PIKE Technologies); incident radiation fell at an angle of 45° onto the samples.

Bleaching of peracetic acid treated and untreated pulp samples

The mixed hardwood unbleached pulp and PAA treated pulps were bleached by the conventional ECF bleaching sequence $D_0E_{OP}D$, as per the conditions given in Table 2, where D_0 stands for bleaching with chlorine dioxide initially; E_{OP} – after oxidation of lignin by chlorine dioxide, oxidized lignin was solubilized in the extraction stage with the help of alkali, oxygen and hydrogen peroxide; D – final bleaching with chlorine dioxide. The flow diagram for both sequences $D_0E_{OP}D$ and $PaaD_0E_{OP}D$ is shown in Figure 1. The final bleached pulps were analyzed for brightness, whiteness, P.C. (post color) number and viscosity.

In the initial stage, chlorine dioxide was added as per the calculation:[23]

$$\text{Chlorine demand (\%)} = \text{Kappa number} \times \text{Kappa factor} \quad (1)$$

The extraction stage was carried out in a pressurized vessel to maintain oxygen pressure during the reaction. After each stage of bleaching, the pulp was squeezed in a Buchner funnel and the effluent was collected for analysis; after washing the pulp was analyzed for pulp properties.

Table 1
RSM experimental design for peracetic acid pretreatment of unbleached pulp

Run	Factor A: Temperature (°C)	Factor B: Time (h)	Factor C: Dose (%)
1	50.00	0.50	2.00
2	80.00	0.50	0.50
3	65.00	1.25	1.25
4	90.23	1.25	1.25
5	80.00	2.00	0.50
6	80.00	0.50	2.00
7	65.00	1.25	1.25
8	65.00	2.51	1.25
9	50.00	2.00	2.00
10	39.77	1.25	1.25
11	65.00	1.25	1.25
12	65.00	1.25	1.25
13	50.00	0.50	0.50
14	65.00	1.25	2.51
15	65.00	1.25	1.25
16	65.00	1.25	1.25
17	80.00	2.00	2.00
18	65.00	1.25	1.25
19	65.00	1.25	1.25
20	50.00	2.00	0.50

Table 2
Conditions maintained during the pulp bleaching processes

Parameters	$D_0E_{OP}D$	$PaaD_0E_{OP}D$
D_0 (consistency – 10%, temperature – 55 °C, time – 45 min, kappa factor – 0.25)		
Chlorine dioxide (%)	1.85	0.92
E_{OP} (consistency – 10%, temperature – 80 °C, time – 120 min)		
Hydrogen peroxide (%)	0.7	0.7
Sodium hydroxide (%)	1.9	0.97
D (consistency – 10%, temperature – 75 °C, time – 180 min)		
Chlorine dioxide (%)	0.6	0.6

Pulp analysis

TAPPI test method T 236 was used for estimating the kappa number of pulp. Kappa number represents the delignification of pulp after treatment. The brightness of the pulp samples was analyzed as per ISO 2470. Brightness is a measurement of reflectance of light from the sample at the wavelength of 457 nm. Viscosity of unbleached and bleached pulp samples was analyzed as per TAPPI test method T 230 om-08. Unbleached pulp of kappa number 19.5, brightness 30.5% ISO and viscosity 15.5 cP was used for the study.

Effluent analysis

From every stage of bleaching, effluent samples were collected for analysis. The respective volumetric proportions were respected to prepare a composite sample. The American Public Health Association (APHA) and Indian standard (IS) test methods were used for analysis of effluent samples. IS: 3025 (Part 38 and 44) was used for BOD_3 estimation by measuring the quantity of oxygen required by microorganisms for degradation of organic matter present in the samples. COD of effluent samples was analyzed by the open reflux method as per IS: 3025 (part 58), in which organic matter was oxidized by potassium dichromate. After oxidation, the excess of potassium dichromate was titrated with ferrous ammonium sulfate and the oxidisable organic matter was calculated in terms of oxygen equivalent. Color in effluent samples was evaluated according to method APHA 2120 C. AOX of effluent samples was analyzed as per test method ISO:

9562, using an AOX analyzer. Effluent samples were also characterized for total dissolved solids (TDS) as per test method IS: 3025 (Part16).

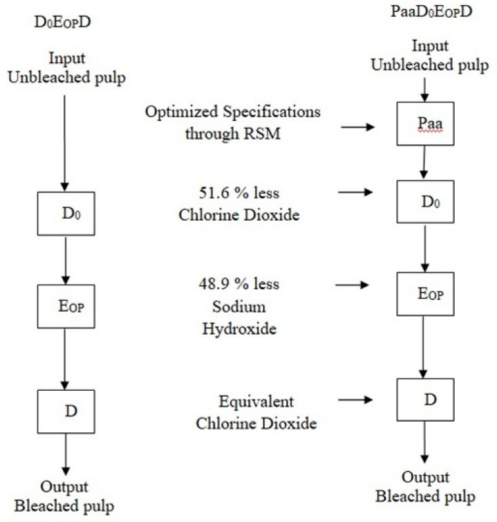

Figure 1: Flow diagram for bleaching sequences $D_0E_{OP}D$ and $PaaD_0E_{OP}D$

RESULTS AND DISCUSSION

Optimization of specifications for peracetic acid pretreatment of pulp

The three variables, viz. PAA dose, temperature and time, were optimized to find the most efficient treatment parameters through their response on kappa number, yield, brightness and viscosity. The experimental results for all four responses by CCD, with six replications of the central point and six axial points, are shown in Table 3.

Table 3
CCD responses for pulp properties obtained in experimental runs

Run	Response 1 Kappa no.	Response 2 Yield (%)	Response 3 Brightness (%ISO)	Response 4 Viscosity (cP)
1	10.1	96.0	41.7	12.0
2	11.0	96.4	39.4	12.7
3	8.1	94.8	49.4	10.6
4	5.1	94.09	54.7	8.6
5	8.2	95.0	48.0	10.6
6	6.7	94.1	53.0	9.7
7	8.1	94.7	49.4	10.6
8	8.1	94.8	49.4	10.6
9	7.7	94.5	48.5	10.1
10	11.0	96.7	39.1	12.8
11	8.1	94.8	49.4	10.6
12	8.1	94.8	49.4	10.6
13	14.4	99.6	32.1	15.2
14	8.1	94.8	49.4	10.6
15	8.1	94.8	49.4	10.6
16	8.1	94.8	49.4	10.6
17	4.6	93.83	57.2	8.5
18	8.1	94.8	49.4	10.6
19	8.1	94.8	49.4	10.6
20	11.7	96.8	39.0	13.2

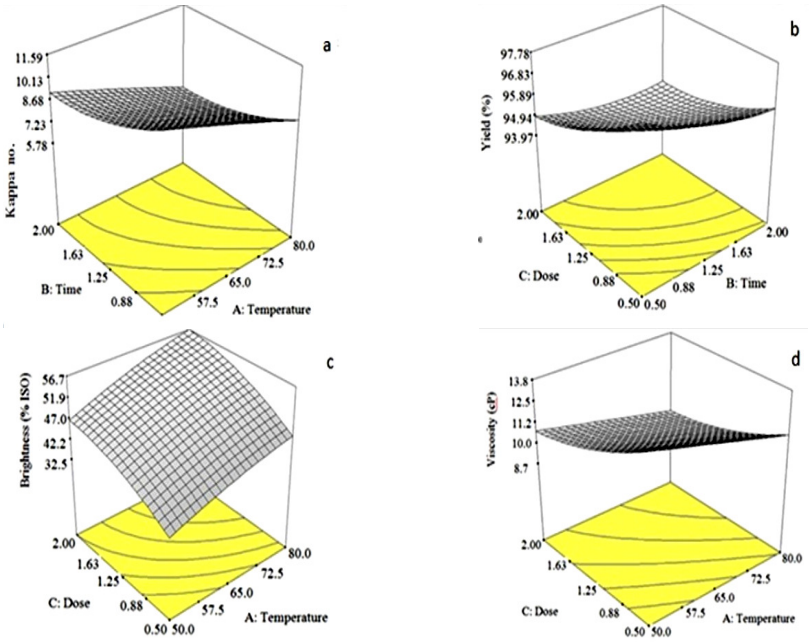

Figure 2: Response surface plots for kappa number (a), pulp yield (b), brightness (c) and viscosity (d) under variable conditions of peracetic acid treatment

Figure 2 presents the response surface plots for the combined effect of time and temperature on kappa number, for the combined effect of dose and time on pulp yield, for the combined effect of dose and temperature on pulp brightness and for the combined effect of dose and temperature on pulp viscosity.

Statistical analysis for kappa number

The analysis of variance for the response kappa number is shown in Table 4. The quadratic model was suggested by the response surface methodology for optimization of PAA treatment and the value of "predicted R-squared" is in concurrence with the value of "adjusted R-squared". Adequate precision measures the noise ratio and a ratio greater than 4 is desirable. The model showed that the temperature and time of peracetic acid treatment had a significant impact on the reduction of kappa number.

The following equation in terms of coded factors explains the predicted model:

$$Kappa\ no\ = +8.11 - 1.71A - 1.20B - 1.97C + 0.064\ A^2 + 0.62\ B^2 + 0.73C^2 + 0.025AB + 0.050AC + 0.013BC \quad (2)$$

Zhao *et al*. also claimed that peracetic acid reaction time and temperature had a significant impact on the delignification of the raw material.[24] PAA removes lignin by cleaving the bonds between carbon–oxygen, carbon–carbon and β-aryl ether.[25] Ma *et al*. and Park *et al*. also found that PAA removes lignin from complex biomass by degrading it to lower micro-molecules.[26-27] The impact of the variables, *i.e.* temperature, time and dose, on kappa number is shown in Figure 3.

Statistical analysis for yield

ANOVA analysis for the response yield is given in Table 5. The "F-value" obtained for the model indicates that the model was significant for the study. The yield was calculated by the following equation (using coded factors):

$$Yield\ = +94.79 - 0.87A - 0.71B - 1.14C + 0.19\ A^2 + 0.38B^2 + 0.46C^2 + 0.32AB + 0.30AC + 0.30BC \quad (3)$$

The response surface plot of CCD for yield showed that an increase in PAA dose and reaction time slightly reduced the yield after the treatment. Barbash *et al*. also revealed that, with an increase in PAA treatment process time, the pulp yield reduced.[28] The effect of peracetic acid dose and reaction time on the pulp yield is illustrated in Figure 2. Zhao *et al*. and Nada *et al*. claimed that pulp yield was affected during the peracetic acid treatment by the dose of peracetic acid.[24,29] With an increase in PAA dose more efficient lignin removal was noted, while temperature and time were fixed, but also deeper degradation of carbohydrates was found because of the acid hydrolysis and oxidation process. The results obtained in the present study are in agreement with those reported by Zhao *et al*. and Barbash *et*

al., confirming that yield was most affected by the dose of peracetic acid (Fig. 4).[24,28]

Table 4
Analysis of variance for kappa number

	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Quadratic	0.18	0.9967	0.9938	0.9498	4.73	Suggested
Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	93.93	9	10.44	337.25	<0.0001	Significant
A	39.83	1	39.83	1287.07	<0.0001	
B	12.51	1	12.51	404.28	<0.0001	
C	33.96	1	33.96	1097.34	<0.0001	
A^2	0.059	1	0.059	1.90	0.1977	
B^2	2.99	1	2.99	96.66	<0.0001	
C^2	4.11	1	4.11	132.97	<0.0001	
AB	0.005	1	0.005	0.16	0.6962	
AC	0.020	1	0.020	0.65	0.4401	
BC	0.13	10	0.13	4.04	0.0722	

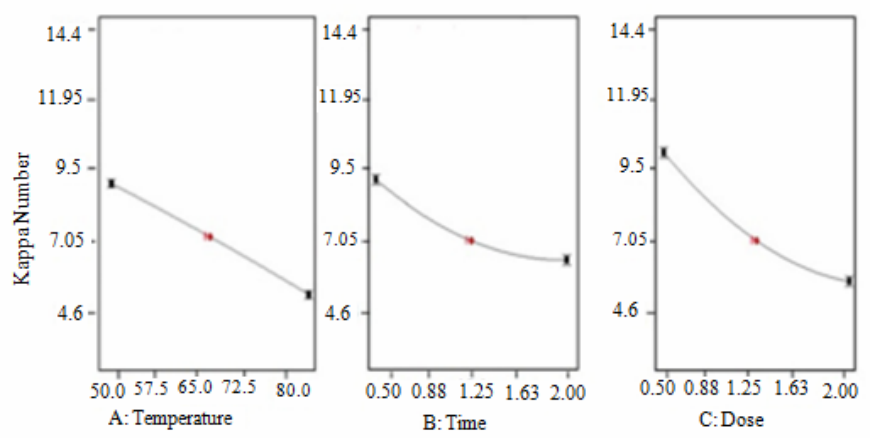

Figure 3: Effect of variables temperature, time and PAA dose on kappa number of pulp

Table 5
Analysis of variance for pulp yield

	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Quadratic	0.13	0.9948	0.9900	0.9283	2.37	Suggested
Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	32.91	9	3.66	210.75	<0.0001	Significant
A	10.40	1	5.08	26.71	<0.0001	
B	4.45	1	8.16	9.82	<0.0001	
C	11.32	1	13.15	15.94	<0.0001	
A^2	0.52	1	0.52	29.91	0.0003	
B^2	1.13	1	1.13	65.20	<0.0001	
C^2	1.63	1	1.63	93.74	<0.0001	
AB	0.84	1	0.84	48.33	<0.0001	
AC	0.71	1	0.71	41.15	<0.0001	
BC	0.71	1	0.71	41.15	<0.0001	

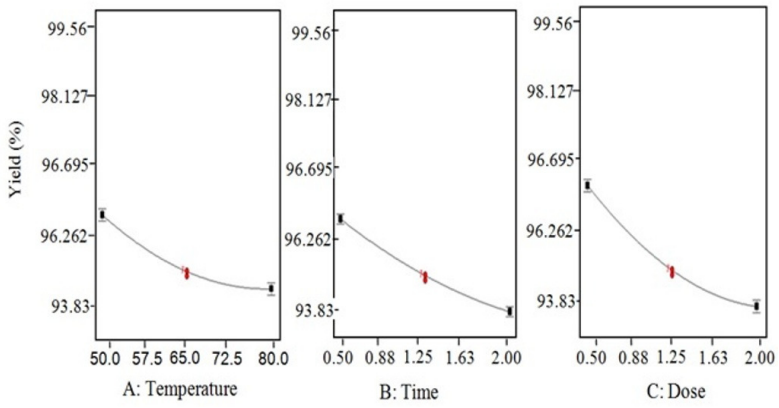

Figure 4: Effect of variables temperature, time and dose on pulp yield

Table 6
Analysis of variance for pulp brightness

	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Quadratic	0.54	0.9959	0.9922	0.9159	59.55	Suggested
Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	705.56	9	78.40	269.23	< 0.0001	Significant
A	286.36	1	286.36	983.44	< 0.0001	
B	91.42	1	105.75	11.94	< 0.0001	
C	232.56	1	232.56	798.68	< 0.0001	
A2	9.51	1	9.51	32.66	0.0002	
B2	24.93	1	24.93	85.62	< 0.0001	
C2	32.72	1	32.72	112.36	< 0.0001	
AB	0.10	1	0.10	0.35	0.5685	
AC	1.71	1	1.71	5.88	0.0358	
BC	2.53	1	2.53	8.69	0.146	

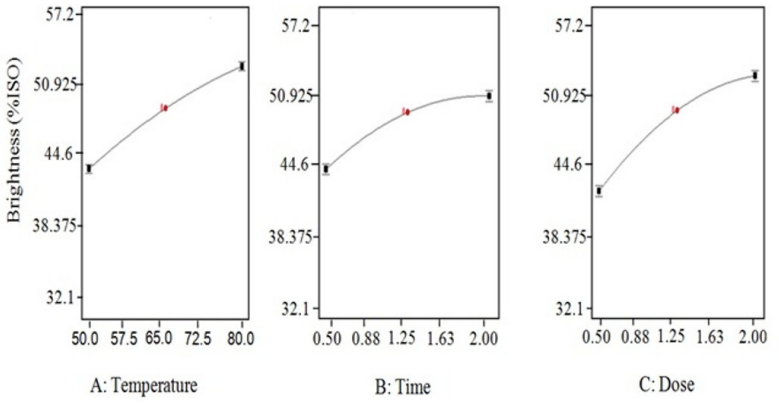

Figure 5: Effect of variables temperature, time and dose on pulp brightness

Statistical analysis for brightness

The data obtained by ANOVA for brightness are listed in Table 6, with an "F-value" indicating that the model was significant. The model showed that temperature, time and dose had a significant impact on pulp brightness. The final equation (4)

for brightness, in terms of coded factors, is given below:

$$Brightness = 49.39 + 4.58A + 3.24B + 5.16C - 0.82\,A^2 - 1.79\,B^2 - 2.05C^2 - 0.11AB + 0.46AC - 0.56BC$$

The response surface plot of CCD for brightness showed that pulp brightness improved significantly with an increase in PAA dose and temperature (Fig. 2). Thus, the results showed the same trend as in the case of yield, indicating that temperature and PAA dose have the highest impact on the brightness of pulp (Fig. 5).

Statistical analysis for viscosity

The data obtained by ANOVA analysis for the response viscosity are presented in Table 7, revealing that temperature, time and dose have a significant impact on pulp viscosity. The final equation for viscosity, in terms of coded factors, is given below:

$$Viscosity = +10.61 - 1.18A - 0.87B - 1.39\,C + 0.46\,B^2 + 0.49\,C^2 - 0.15\,AC + 0.12BC \quad (5)$$

Viscosity is an important pulp property, affecting physical strength properties. However, peracetic acid does not attack carbohydrates directly, as it is a lignin selective reagent.[30] During the treatment with peracetic acid, transition metal ions present in the pulp catalyze the degradation of peracetic acid and carbohydrates.[11] Zhao *et al*. revealed that the dose of peracetic acid and reaction temperature had the most significant impact on the viscosity of pulp.[24] Thus, pulp viscosity declined with an increase in temperature and PAA dose, as may be remarked in Figure 2.

Table 7
Analysis of variance for viscosity

	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Quadratic	0.15	0.9950	0.9905	0.9164	3.93	Suggested
Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	46.78	7	6.68	285.26	<0.0001	Significant
A	18.89	1	18.89	806.51	<0.0001	
B	6.64	1	6.64	283.63	<0.0001	
C	17.12	1	17.12	730.71	<0.0001	
A^2	1.91	1	1.88	80.12	0.0002	
B^2	1.64	1	1.64	70.10	<0.0001	
C^2	1.86	1	1.86	79.35	<0.0001	
AB	0.16	1	0.16	7.05	0.0253	
AC	0.18	1	0.18	7.68	0.0169	
BC	0.12	1	0.12	5.34	0.0395	

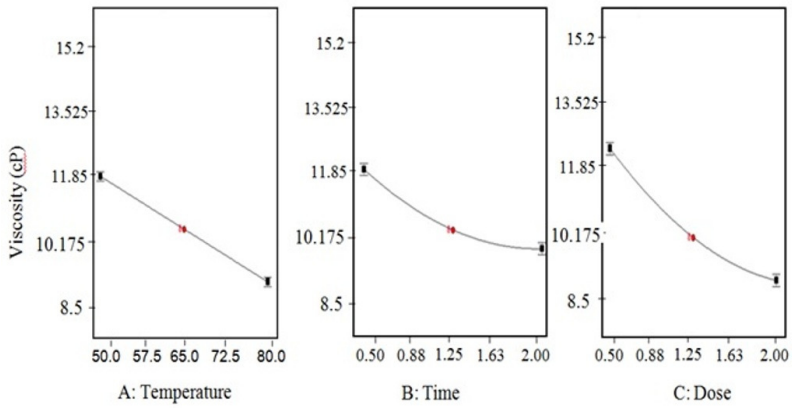

Figure 6: Effect of variables temperature, time and dose on pulp viscosity (cP)

The response surface plot of CCD for viscosity showed that, with an increase in the dose of peracetic and reaction temperature, the viscosity of the pulp samples was more affected than in the case of an increase in reaction time, and was reduced more significantly(Fig. 6).

From the results of the study, it was found that the peracetic acid dose, followed by temperature, most affected certain pulp properties, causing a reduction in kappa number and viscosity, as well as an improvement in pulp brightness, whereas the peracetic acid dose, followed by time, most significantly affected pulp yield. The choice of different process parameters during peracetic acid treatment of the pulp can lead to the desired results, for example, at a particular peracetic acid dose, with either low temperature and long time or high temperature with short time, minimum kappa number can be obtained, with optimum yield, brightness and viscosity of the pulp. The optimized process parameters for the peracetic acid pretreatment of the pulp were found as follows: 80 °C temperature, 1.0 h and 1.0% PAA dose. The final pH of the pulp sample pretreated with peracetic acid under the optimized conditions was 5.0. Under these optimized conditions, the pretreatment yielded pulp with kappa number 10.2, yield of 96.87%, brightness of 43.6% ISO and viscosity of 11.7 cP.

FTIR analysis of untreated and PAA treated pulps

The FTIR spectra of untreated and PAA treated hardwood pulps are shown in Figure 7. The spectra exhibit a broad stretching band at 3300-4000 cm^{-1} attributed to O-H stretching, a band at 2800-3000 cm^{-1} corresponding to C-H stretching in methyl and methylene groups and discrete absorption in the region from 1000 to 1700 cm^{-1}.[31] The bands at 1200 cm^{-1} and 1100 cm^{-1} belong to hemicelluloses and cellulose showed a peak around 1030 cm^{-1} due to C-O stretching,[32] which was intense for the peracetic acid treated pulp. The peak around 1316 cm^{-1} is assigned to the cellulose constituent, and is related to the contents of crystallized and amorphous cellulose.[33] Peracetic acid treated pulp showed a higher peak around 1316 cm^{-1}, compared to untreated pulp, which might be due to a decrease in the lignin content in the PAA treated pulp. This is in agreement with Zhao *et al*.[24]

Hardwood lignin consists of guaiacyl and syringyl units, thus, the band at 1595 cm^{-1} can be assigned to high content of guaiacyl units.[32] The intensity of this band was lower in the spectrum of peracetic acid treated pulp, compared to that of untreated samples, indicating a reduction in the lignin content in pulp after PAA treatment. The peak located between 2800 and 2900 cm^{-1} corresponds to C-H stretching due to aliphatic and aromatic structures. CH asymmetrical stretching vibration, in CH_3, CH_2 and CH groups is indicated by the peak at approximately 2892 cm^{-1}.[34] The band at 1640 cm^{-1} is due to C=C and C=O stretching in the aromatic ring of lignin, whereas the peak at 1428 cm^{-1} is attributed to deformation of CH_2 and CH_3. The peak around 3330 cm^{-1} was assigned to the O-H bond associated with intermolecular H-bonds.

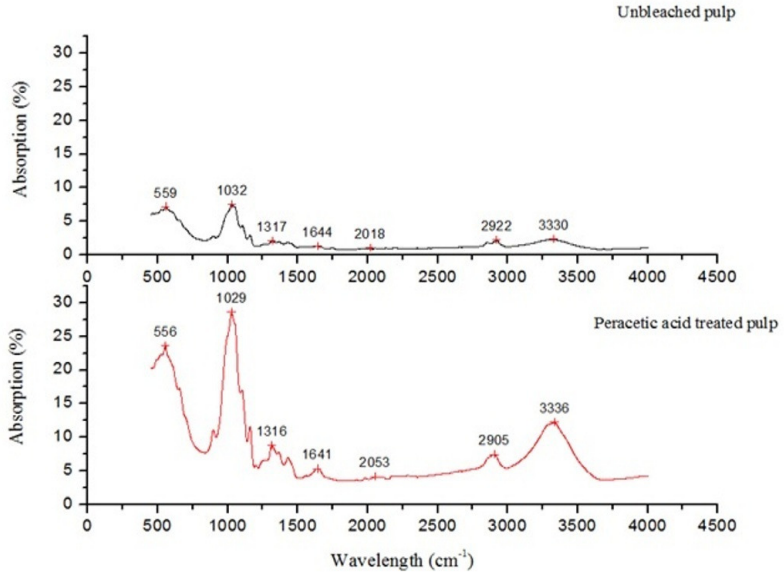

Figure 7: FTIR spectra of PAA treated and untreated pulp samples

Effect of peracetic acid treatment on optical properties

PAA treated pulps were further bleached by the conventional bleaching sequence $D_0E_{OP}D$. it was noticed that, with PAA pretreatment, a reduction in kappa number by 50.3% was achieved; consequently, the consumption of bleaching chemicals in the next step was also reduced significantly, by 52.8%, in comparison with the bleaching process without peracetic acid pretreatment of the pulp, as shown in Table 2. Lee *et al*. also revealed that after peracetic acid treatment, a significantly lower content (by 50%) of chlorine dioxide was necessary to bleach the PAA treated pulps, compared to untreated pulp.[35] Barros *et al*. also claimed that bleaching costs were significantly reduced by replacing the high dose of hydrogen peroxide with PAA.[36] Fiskari *et al*. revealed that PAA has the potential to replace hydrogen peroxide in the TCF bleaching sequence.[37] After PAA treatment, the residual lignin removal in the subsequent bleaching stage becomes easy due to increased solubility.[25] It might be explained by the fact that, after PAA treatment, the hydrophilicity of lignin augmented due to cleavage of side chains and increased amount of acidic groups.[36]

A considerable improvement in the optical properties of the pulps was observed after the $PaaD_0E_{OP}D$ sequence, in comparison with the conventional pulp bleaching sequence $D_0E_{OP}D$. Pulp brightness was improved by 1.5 points and whiteness by 2.2 points, while the P.C. number was reduced by 22%. The results obtained were in agreement with those reported in the study by Krizman *et al*., who utilized PAA as an initial stage of bleaching and found high optical properties of the pulp.[38] The viscosity of the pulp sample slightly declined after the PAA treatment of the pulp (Table 8). The presence of metal ions is responsible for carbohydrate degradation and this can be avoided by prior removal of metal ions.

Table 8
Impact of PAA treatment on bleached pulp properties

Parameters	$D_0E_{OP}D$	$PaaD_0E_{OP}D$
Brightness (% ISO)	88.1	89.6
CIE whiteness	78.8	82.0
P. C. no.	0.50	0.39
Viscosity (cP)	8.2	8.1

Table 9
Impact of PAA treatment on bleaching effluent properties

Parameters	$D_0E_{OP}D$	$PaaD_0E_{OP}D$
Effluent volume (m^3)	27	27
pH	5.2 (±0.1)	5.5(±0.1)
BOD (mg/l)	207 (±20)	118 (±22)
COD (mg/l)	779 (±23)	345 (±22)
TDS (mg/l)	3215 (±45)	2189 (±44)
Color (PCU)	370 (±8)	180 (±5)
AOX (mg/l)	22.5 (±0.4)	11.0 (±0.3)

Effect of peracetic acid treatment on effluent properties

A very desirable aspect of using PAA for pulp bleaching is the ease of recycling the effluent from this stage due to the absence of chloride. Thus, the pollution load, including indices such as BOD, COD and TDS reduced by 43.0, 55.7% and 31.9%, respectively, for $PaaD_0E_{OP}D$ in comparison with $D_0E_{OP}D$. The value of color in the effluent of the bleaching sequence $PaaD_0E_{OP}D$ was significantly cut down by 51.4%, compared to the conventional bleaching sequence $D_0E_{OP}D$. The AOX content was also tremendously reduced, by 51.1%, for $PaaD_0E_{OP}D$, in comparison with $D_0E_{OP}D$ (Table 9).

Many other studies also revealed that pretreatment of pulp prior to bleaching can reduce the pollution load.[9,39-41] For example, Sharma *et al*. concluded that the use of PAA treatment prior to bleaching improved the effluent quality and led

to an increment in optical properties.[40] Haider *et al*. used the electrocoagulation method for the treatment of the bleaching effluent, which reduced the fresh water consumption by utilizing treated water in the pulp bleaching process. The prepared paper had comparable strength properties and acceptable ISO brightness level.[39] In a recent study, the hypochlorous acid bleaching of eucalyptus kraft pulp was found appealing, following the ECF bleaching sequence. The results obtained from bleaching using an H mild stage (hypochlorus acid) showed that the use of hypochlorous acid decreased the kappa number of the pulp more efficiently than chlorine dioxide, without raising the AOX content in the effluent.[42] Among chlorophenolics, 2,3,7,8-TCDD and 2,3,7,8-TCDF are the dominant substances formed when elemental chlorine is used in the pulp bleaching process. By replacing elemental chlorine with chlorine dioxide, it was possible to eliminate the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF during the bleaching process.[43]

It should be highlighted that the pretreatment reduces the kappa number of the pulp before it is subjected to bleaching, and therefore it requires a lower amount of bleaching chemicals and consequently, the pretreatment leads to a reduction of toxic pollutants. The findings of the study revealed the PAA pretreatment of the pulp offers dual benefits, reducing the pollution load of the bleaching process and providing better optical properties of the pulp, in comparison with the conventional bleaching sequence.

CONCLUSION

The RSM central composite design was used to optimize the specifications for peracetic acid pretreatment of pulp as a preceding step before conventional bleaching. The optimum conditions to obtain minimum kappa number, with maximum yield, brightness and viscosity were found as follows: 80 °C temperature, 1.0 h and 1.0% PAA dose. Under the optimized conditions, the pulp produced had kappa number 10.2, the yield of 96.87%, and pulp brightness of 43.6% ISO and viscosity of 11.7 cP. The FTIR spectra of peracetic acid treated and untreated pulps indicated that peracetic acid treatment caused lignin degradation. The use of PAA under optimized conditions, prior to conventional bleaching ($PaaD_0E_{OP}D$), reduced the BOD, COD, TDS, color and AOX of the bleaching effluent by 43.0, 55.7%, 31.9%, 51.4% and 51.1%, respectively, in comparison with the corresponding parameters of the conventional bleaching effluent without PAA pretreatment of the pulp.

Most of pulp and paper manufacturing units in developed countries have switched to cleaner production techniques with improved bleaching practices. The scale of operation and high capital investment are the major problems that restrict the Indian pulp and paper manufacturing units to implement these new technologies. Thus, an approach with peracetic acid pretreatment of pulp can be recommended to be adopted by Indian mills to reduce the AOX level and toxicity of bleaching plant effluent.

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