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DELIGNIFICATION KINETICS AND CHARACTERIZATION OF KRAFT PULP CONTAINING VARYING LIGNIN CONTENT WITH SODIUM PERBORATE AND SODIUM METAPERIODATE

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The study examined the use of chlorine free bleaching agents consisting of sodium perborate for removal of lignin found in kraft pulp under various process conditions, including temperature (ranging from 30 °C to 50 °C), sodium perborate dosage (ranging from 1 g to 3 g), and pulp consistency (ranging from 2% to 4%). The optimal kappa reduction occurred between 40 °C and 45 °C and a pulp consistency of 3% to 3.5%. Scanning electron microscopy images confirmed the lignin removal in the bleached pulp samples. FT-Raman spectroscopic analysis was employed to identify the blueprint of different molecules. Raman spectra indicated the Raman shift at 10 cm^{-1}, which resulted from the polymorphic transfer of cellulose I to II. The absence of significant peaks in the bleached pulp, compared to the unbleached pulp, confirmed the lignin removal. Fourier transform infrared spectroscopy provided information on the unbleached and bleached pulp functional groups. The reaction rate constant determined for the sodium perborate bleaching process is 0.00833 min^{-1}. The reaction constant calculated using sodium metaperiodate bleaching is 0.0083 min^{-1}, and the value of activation energy is 28.73 KJ/mol.

Keywords: kappa reduction, FT-Raman spectroscopy, scanning electron microscopy, kraft pulp, environmental impact

INTRODUCTION

The primary objective of the chemical delignification of kraft pulp is to remove lignin from cellulose fibers, with minimal structural and physical damage. Cellulose is a complex carbohydrate or polysaccharide that forms the fundamental component for all the plant cell walls.[1] Lignin is an amorphous biopolymer containing a cross-linked aromatic structure composed of phenylpropane units formed by an enzyme-initiated repetitive coupling of the monolignol precursors, sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol.[2-5] Lignin is the base material that provides structural strength to wood fiber by surrounding cellulosic fiber.[6] It protects cellulosic polymers from the attack of pathogens or microorganisms. The delignification process extracts lignin available in the cell walls of plants.[7]

As a bleaching agent, chlorine selectively removes lignin compounds, without causing significant damage to the pulp. The chlorinated organic compounds released during the bleaching process of pulp cause environmental damage due to toxic emissions, and the chlorinated organic substances percolate into marine systems, causing harm to aquatic organisms. The chlorine-based bleaching agents rise a lot of concerning issues regarding effluent discharge due to stringent regulations taken across the globe to keep the limits of discharge of adsorbable organic halogens (AOX) below 1.5 kg/tonne of effluents, opening a path for the search of other totally chlorine free (TCF) alternatives. Chlorine dioxide is a valuable alternative to chlorine, as it reduces the formation of organochlorines and the risk of bioaccumulation. The replacement of chlorine as a bleaching agent by TCF compounds reduces severe environmental impacts, and several studies in this area provide promising results.[8,9]

Oxidizing bleaching agents can selectively remove lignin, which is responsible for the coloration effect in the pulp. The delignification of

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pulp using various oxidizing agents disrupts lignin-carbohydrate bonds, allowing fragments to dissolve and break up the lignin molecule. Oxygen-based bleaching agents like peroxides can remove 50% of the lignin content in wood and cause significant chemical changes that reduce pulp strength.[10,11] Ozone reacts with lignin polymers and breaks the bonds, while maintaining pulp brightness at 80 °C. The performance of the bleaching process at such high temperatures results in the depolymerization of fibers present in cellulose.[12-14]

The delignification of pulp using peroxymonosulfuric acid and carbamide peroxide effectively removes lignin. The oxidizing tendency of peroxy acids is much larger than the oxidizing potential of oxygen and hydrogen peroxide, and hence, peroxy acids have more lignin-removing capacity. The process involving peroxy acids generates less effluent load and releases less toxic organic compounds.[15] The factors influencing the rate of the bleaching process are pH, temperature, oxidant concentration, and reaction time, which are responsible for cellulose degradation. The delignifying capacity of the process can be improved by pre-treatment, including acid washing.[16]

The sequential bleaching process involving hydrogen peroxide remains an effective technique for lignin removal by reducing the carbonyl groups, which are the cause of color in the pulp fibers.[17] The hydrogen peroxide bleaching step, in addition to elemental chlorine-free (ECF) bleaching sequences operated at temperatures between 60 °C and 75 °C, a reaction time of 1.5 to 2 hours and a pulp consistency of 10% to 15% yields more economical and effective removal of lignin from the pulp, resulting in superior brightness. The process suffers limitations at higher bleaching temperatures at 90 °C, resulting in inefficient bleaching due to excessive pulp brightness.[18] Hydrogen peroxide is an aqueous substance that is easy to store and handle without risk of contamination that could decompose the chemical agent at significant costs.[19,20]

Sodium perborate tetrahydrate ($Na_2H_4B_2O_8$) (SPB) is a white, odorless, water-soluble solid that, on hydrolysis, releases borate and H_2O_2.[21] The H_2O_2 produces hydroperoxyl anion in alkaline conditions, resulting in the oxidative bleaching of pulp.[22] The –B–O–O–B–O–O– ring adopts a chair chirality conformation with two OH groups coupled to each B atom that forms the perborate dianion $[(B(OH)_2OO)_2]^{2-}$. SPB finds applications as detergents, disinfectants, and cleaning products. SPB bleaches the pulp due to the production of active oxygen molecules.[23,24] SPB does not cause dye and textile fiber degradation during processing, compared to chlorine-based bleaching agents.[25]

Sodium metaperiodate (SMP) is a better substitution for peracid bleaching agents within the TCF bleaching and a novel replacement for the conventional bleaching techniques using chlorine and its derivatives. Being a white crystalline powder by nature, SMP dissolves in water and consists of four oxygen atoms bonded to an iodine atom that decomposes at slightly higher temperatures, it can release one nascent oxygen atom while absorbing two other hydrogen atoms into itself, making it an excellent oxidizing agent for removal of lignin.[26-28]

Xylanase enzymes act also as bleaching agents by removing xylan from the fiber surface and releasing the existing lignin during subsequent bleaching stages. The delignification rate achieved with xylanase is considerably higher than conventional bleaching methods.[29,30] The enzymatic delignification process efficiency is influenced by the pH and temperature of the bleaching process. However, the disadvantages of using enzymes as a bleaching agent in the bleaching process are the high cost involved in manufacturing enzymes and the difficulty of enzymes to sustain at the high temperature of bleaching operation.[31,32]

This study aims to estimate the influence of temperature, amount of bleaching agent used, and consistency of the kraft pulp on kappa reduction in the pulp. We used Fourier transform infrared spectroscopy (FTIR) and FT-Raman spectral analysis to observe the structural changes and changes in functional groups after the pulp bleaching. Scanning electron microscopy (SEM) was used to observe changes in the external surface morphology of bleached pulp.

EXPERIMENTAL

The bleaching study of pulp with SPB bleaching agent utilized softwood pulp from a pulp plant in Tamil Nadu, India. The bleaching studies of pulp with SMP utilized the raw unbleached pulp obtained from a pulp industry in Telangana, India. We procured the SPB bleaching agent from Nice Chemicals Ltd., India, and the SMP bleaching agent from Sigma Aldrich Ltd.

Mixing the chemical agent with the pulp is necessary for the bleaching process. However, applying mechanical force during the mixing weakens the fiber strength and leads to a high viscosity of the mixture. The ultrasonication bath facilitates mixing, since it can induce molecular-level mixing through vibrations. The mixing was done in ultrasonic bath sonicator manufactured by LABMAN, at a frequency of 33 KHz.

The study of pulp bleaching with SPB examined various process variables, including reaction temperature (low and high levels at 30 °C and 50 °C), pulp consistency (2% and 4%), and SPB dosage (1 g/100 g of pulp and 3 g/100 g pulp), and the response variable studied was kappa reduction. The pulp sample had an initial kappa number of 14.78.

The bleaching of pulp with SMP studied the variables: the pulp consistency (2% lower level, and 4% higher level), temperature (40 °C, 60 °C), and the SMP amount added (1 g/100 g pulp, 2.5 g/100 g pulp). The pulp sample had an initial kappa number of 27.

The amount of 0.1N $KMNO_4$ (mL) consumed by 1 g of pulp dried in an oven according to the conditions mentioned in TAPPI 1999 estimates the kappa number. The kappa measurement follows the T 236 om-99 (TAPPI 1999) standard procedure.

The variables studied in the SPB bleaching experiment were: pulp consistency (X_1), amount of SPB (X_2), and reaction temperature (X_3). The relationship between these variables and the kappa number (Y) was analyzed using the Box-Behnken design, consisting of fifteen runs of experiments. Box-Behnken design is a statistical tool used in response surface methodology to optimize processes to develop a quadratic model, avoiding the testing of all possible combination of variables. The design involves multiple factor interaction with a desired outcome. This design avoids including combinations where all factors are at their extreme values simultaneously to avoid unfeasible experimental conditions. This design helps to find the optimal conditions of the process with less experimental effort and provides a powerful insight of interaction of various variables. The resulting model equation used to measure the kappa number (Y) is as follows:[33,34]

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

where Y represents the kappa number, which is a response variable, X_1, X_2 and X_3 are various factors or parameters studied, β_0 is the model constant, β_1, β_2 and β_3 are the linear coefficients, β_{11}, β_{22} and β_{33} are the square or quadratic coefficients, and β_{12}, β_{13} and β_{23} are the interaction coefficients.

The experimental ranges of factors studied in the SMP bleaching are pulp consistency (X_1), temperature (X_2), and the SMP amount added (X_3) to estimate the kappa number (Y).

Fourier transform infrared spectroscopy (FTIR) analyses of the samples was performed using a Nicolet iS10 FTIR spectrometer (Thermo Scientific) in the 400-4000 cm^{-1} range. The dried and ground pulp sample was mixed with dry KBr and ground together to form a uniform powder. It was pressed into a clear pellet using a pellet press. FTIR was run in transmission mode for analysis.

The spectroscopic analysis of pulp samples was conducted using a Bruker RFS 27 stand-alone FT-Raman spectrometer. The pulp specimen was excited at 1064 nm using an Nd: YAG laser diode, covering the wavenumber range of 4000-50 cm^{-1}. The pulp sample was oven dried at 80 °C and ground into fine powder. A glass sample cup was filled with the ground pulp, the surface was compressed with a glass slide and the cup was placed directly under the Raman laser.

The changes in surface topography in dried pulp samples were observed using scanning electron microscopy (SEM) (SIGMA HV-Carl Zeiss with Bruker Quantax 200-Z10 EDX Detector).

RESULTS AND DISCUSSION

Modeling and contour regions for pulp delignification with SPB

The variables impacting the delignification of the pulp sample, such as pulp consistency (X_1), amount of SPB (X_2), and reaction temperature (X_3), and their effect on kappa number (Y_1), were analyzed using the Box-Behnken design of fifteen sets of experiments. Table 1 provides the experimental results of the kappa number for each experimental run.

The Minitab 17 software measures the regression correlation of the kappa number for the delignification of kraft pulp as follows:

$$Y_1 = 34.44 - 4.61X_1 - 0.002X_2 - 0.95X_3 + 0.62X_1^2 - 0.62X_2^2 + 0.009X_3^2 - 0.0025X_1X_2 + 0.013X_1X_3 + 0.055X_2X_3 \quad (2)$$

The individual effects of pulp consistency and temperature significantly impact kappa reduction, as indicated by P values. Additionally, the interaction between the amount of SPB and temperature is essential for two-way interactions. The Minitab 17 software obtains the contour plots for the delignification experiments.

Figure 1 illustrates the relationship between temperature and pulp consistency for kappa reduction. The pulp consistency range is from 2% to 4%, while the temperature conditions vary from 30 °C to 50 °C for a reduction in kappa number. The degradation study could achieve a 50% kappa reduction for the pulp consistency, which ranges from 2.5% to 4%, and the heating ranges from 35 °C to 50 °C. The optimal kappa reduction of pulp occurs when the pulp consistency is between 3% and 3.5% and the heating range is between 40 °C and 45 °C.

The contour plot of temperature *versus* the amount of SPB provides the kappa reduction to 6.5 for 3 g/100 g of pulp within 35 °C to 50 °C. The hydrolysis of SPB occurs closer to 50 °C, releasing nascent oxygen molecules. This reaction is endothermic and enhances the bleaching action of SPB. The optimal conditions for increasing bleaching yield are 40 °C to 45 °C, a pulp consistency of 3% to 3.5%, and 3 g of SPB per 100 g of pulp.

Table 1
Kappa numbers for delignification of pulp using SPB bleaching agent

Run	Pulp consistency (%) (X_1)	Amount of SPB (g/100g of pulp) (X_2)	Temperature (°C) (X_3)	Kappa number (Y_1)
1	4	3	40	6.57
2	2	3	40	7.12
3	2	2	30	9.85
4	3	3	30	7.12
5	3	2	40	6.57
6	2	1	40	7.66
7	3	1	50	6.57
8	3	2	40	7.66
9	3	3	50	7.12
10	4	2	50	7.66
11	4	2	30	8.76
12	4	1	40	7.12
13	3	1	30	8.76
14	2	2	50	8.21
15	3	2	40	7.12

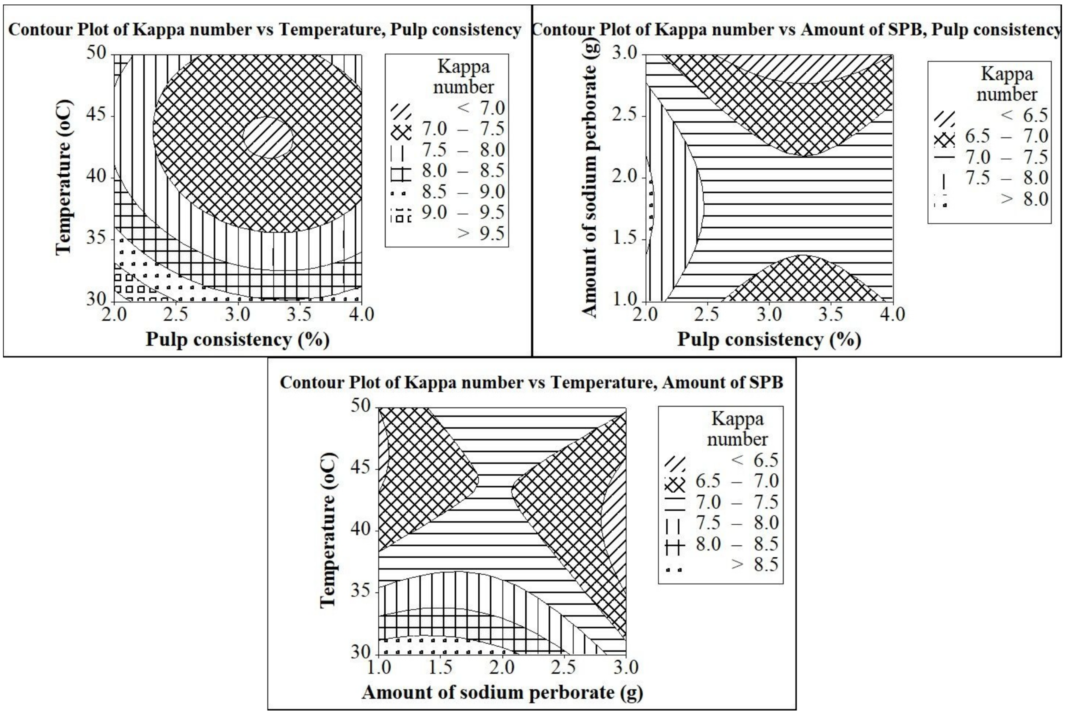

Figure 1: Contour plots of (1) temperature *vs* pulp consistency; (2) amount of SPB *vs* pulp consistency; (3) temperature *vs* amount of SPB

FTIR of pulp delignification using SPB

FTIR is an analytical tool to determine the vibrational spectrum of individual molecules. It gives information about chemical bonds and helps to identify different compounds in a sample.[35] Figure 2 shows the FTIR spectra of unbleached and SPB bleached pulp samples. The bands at 1000 cm^{-1} and 3000 cm^{-1}, which correspond to aromatic O-H stretch and cyclohexane rings, show a decrease in transmittance value. It indicates that the chromophoric groups responsible for the coloration of the pulp reduce significantly. An observable peak in the 3200-3450 cm^{-1} range shows the existence of polymeric OH stretches. The bands at 3475, 1600, 1430, and 1055 cm^{-1} were caused by the presence of the OH group, H-bonded OH stretch, alkynyl C-H stretch, methyl C-H asymmetric bend, and cyclohexane ring vibrations, respectively. Judging by the spectra, the difference in transmittance (or absorbance value) directly indicates the extent of lignin removal in the pulp.

The bleaching process does not result in any significant loss or structural damage to the cellulose fibers in the bleached samples. The transmittance value of the OH groups in the SPB bleached selection is slightly higher compared to that of the unbleached sample, indicating a considerable decrease in lignin content after bleaching. A higher transmittance value signifies that the pulp has lower absorptivity and, consequently, less reflecting power. Table 2 presents the FTIR results, highlighting the significance of relevant peaks.

FT-Raman spectroscopy analysis of pulp delignification using SPB

The spectroscopic analysis of pulp samples was conducted using a Bruker RFS 27 stand-alone FT-Raman spectrometer. The pulp specimen was excited at 1064 nm using an Nd: YAG laser diode, covering the wavenumber range of 4000-50 cm^{-1}. The aromatic stretching can be observed by examining the difference in peaks and heights at 3000 cm^{-1}. The size of this peak directly correlates with the lignin kappa number, with higher numbers indicating a stronger aromatic stretching band. Figure 3 displays the FT-Raman spectra for the bleached and unbleached pulp samples for the entire range of wavelengths.

The spectra at 3100-3000 cm^{-1} exhibit a C-H bond. In the 1700-1000 cm^{-1} range, peaks could be due to the cellulose and hemicellulose structures associated with lignin. The absence of significant peaks in the bleached pulp sample indicates the removal of lignin-containing groups. There is a noticeable increase at 3000 cm^{-1} in the raw pulp and at 3100 cm^{-1} in the bleached sample, suggesting a difference of 10 cm^{-1}. The peaks, including C-H stretch vibrations, are reduced due to self-absorption by the OH groups in the bleached pulp sample.

Short, broad peaks at 150 cm^{-1} for the bleached samples and at 200 cm^{-1} for unbleached samples indicate the presence of lattice vibrations in the crystal. In the span of 3200-3300 cm^{-1}, we can observe small peaks that are very narrow and closely spaced at that specific wavelength, suggesting the presence of C-H bonds. The bleached and unbleached samples' spectra overlap in this range, confirming that these C-H groups and other existing bonds are not significantly damaged and only the lignin-containing chromophoric groups are degraded.

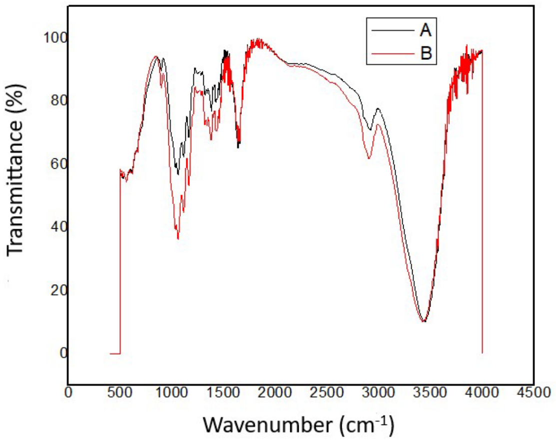

Figure 2: FTIR spectra of unbleached (A) and SPB bleached (B) samples over the wavenumber range of 500-4000 cm^{-1}

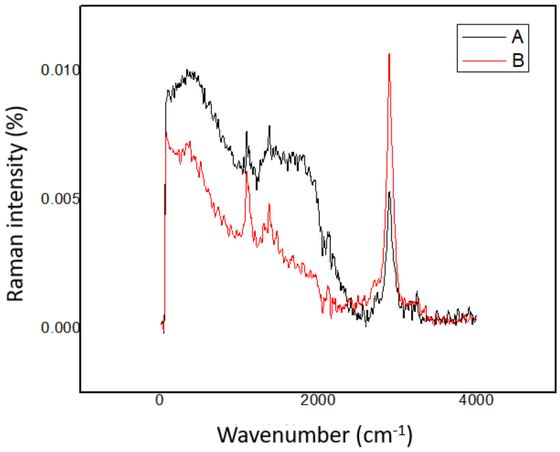

Figure 3: FT-Raman spectra of unbleached (A) and SPB bleached (B) samples over the wavenumber range of 50-4000 cm^{-1}

Table 2
FTIR interpretation data in relation with peak assignments

Wavenumber (cm^{-1}) (Unbleached pulp)	Peak assignment (Unbleached pulp)	Wavenumber (cm^{-1}) (SPB bleached pulp)	Peak assignment (SPB bleached pulp)
3475	Hydroxy group, H-bonded OH stretch	3200-3570	Hydroxy group, H-bonded OH stretch
3070-3130	Aromatic C-H stretch	2900-2800	Methylene C=H stretch
1600	Alkenyl C=C stretch	1620-1680	Alkenyl C=C stretch
1430	Methyl C-H asymmetric/ symmetric bend	1430-1470	Methyl C-H asymmetric/ symmetric bend
1000-1055	Cyclohexane ring vibrations	1000	Cyclohexane ring vibrations
890-915	Vinyl C-H out of plane bend	900	Vinyl C-H out of plane bend

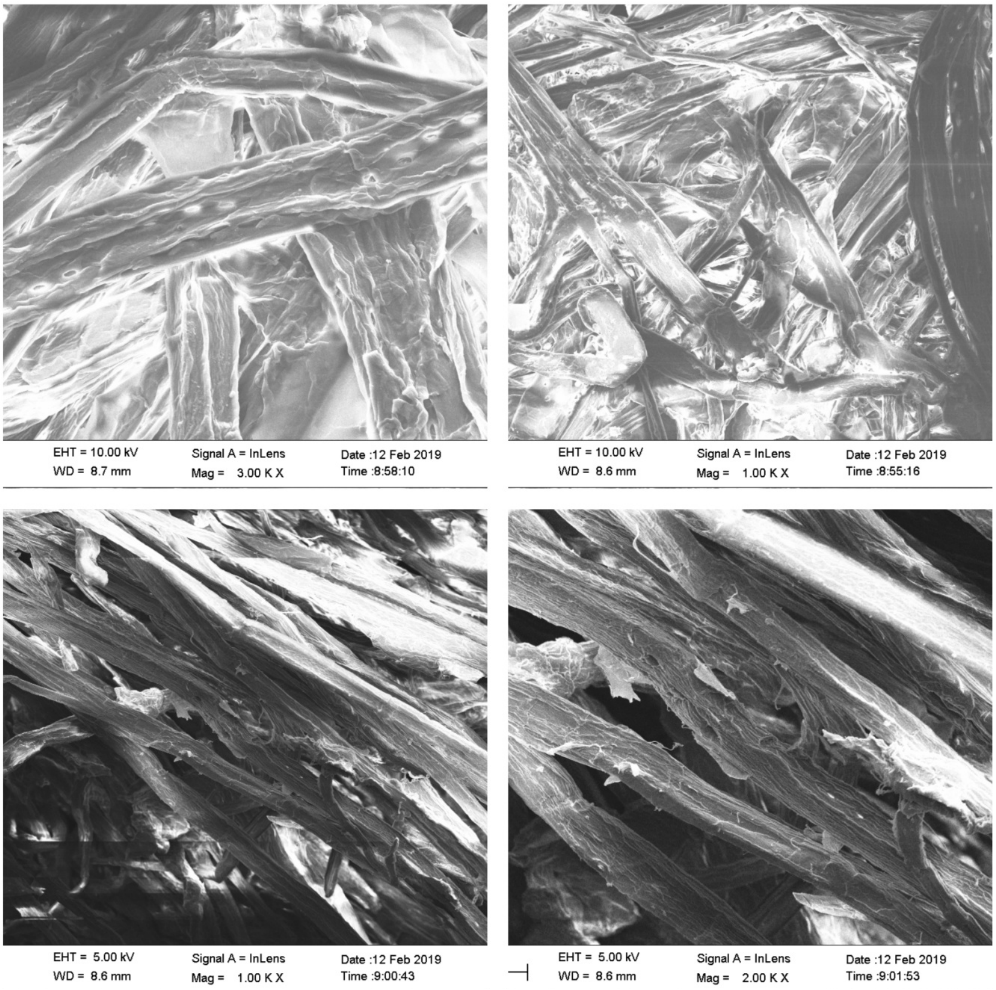

Figure 4: SEM images of unbleached (Top) and SPB bleached pulp (Bottom)

SEM analysis of pulp delignification using SPB

The changes in surface topography in pulp samples were observed using SEM. Figure 4 shows SEM images of raw pulp (top) and treated kraft pulp (bottom) at different resolutions. The unbleached pulp sample exhibits small networks of fibril structures that appear brighter and cover the surface of the cellulose fiber structures. These brighter structures are composed of lignin. The electrons that hit the sample generate backscattered electrons due to their scattering. These backscattered electrons are highly sensitive to the atomic number and molecular weight, resulting in a brighter shade. Lignin is a more complex structure than cellulose, which develops a cross-linked pattern in cellulosic fibers in kraft pulp, as observed in the images at magnifications ranging from 1 KX to 3 KX.

The bleached pulp samples demonstrate a noteworthy decrease in fibrillar lignin content compared to the unbleached pulp sample. In certain areas, the surface of cellulose fibers contains clusters of remaining lignin. As observed in the SEM images, the reduction in lignin content decreases the pulp binding strength, leading to a lack of cohesion between the individual fibers. Conversely, the bleached models exhibit a lignin-free, smooth surface of cellulose fibers, indicating the success of the delignification process.

Rate kinetics for the delignification reaction of pulp using SPB

The delignification kinetics of bleaching follow first-order kinetics in lignin removal.[20] The equation for first-order kinetics states $-r_A = kC_A$. The plot of $(-dC_A/dt)$ vs C_A is a straight line. Table 3 provides the reaction rate for delignification studies conducted for two hours. The slope corresponding to the plot of (dC_A/dt) vs. C_A is the reaction rate constant (k) from the above general equation. The value of the specific reaction rate (k) obtained at a temperature condition of 50 °C is 0.00833 min^{-1}.

Table 3
Rate of delignification reaction of pulp using SPB as bleaching agent*

S.No	Temperature (°C)	Pulp consistency (%)	Amount of SPB (g)	SPB concentration (mol/m^3)	Final kappa number	Final lignin concentration (mol/m^3)	$-r_A$ ($\text{mol/m}^3\text{.min}$)
1	50	3	1	21.66	6.57	8099.75	84.37
2	50	3	3	64.99	7.12	8774.73	78.74
3	50	4	2	43.33	7.66	9449.71	73.12
4	50	2	2	43.33	8.21	10124.69	67.49

*Initial Kappa number = 14.78; Initial lignin concentration = 1.82×10^4 mol/m^3)

Table 4
Kappa number for delignification of pulp using SMP bleaching agent

Run	Pulp consistency (%) (X_1)	Temperature (°C) (X_2)	Dosage of SMP (g/100g of pulp) (X_3)	Kappa number (Y)
1	4	40	2.5	17.40
2	2	40	2.5	15.10
3	2	60	1.0	14.14
4	2	60	2.5	10.64
5	4	40	1.0	23.88
6	2	40	1.0	22.91
7	4	60	2.5	11.30
8	4	60	1.0	17.82

Table 5
Analysis of variance for kappa number of SMP bleaching

Source	Degree of freedom	Sequential sum of squares	Adjusted sum of squares	Adjusted mean of squares	F	P
Main effects	3	161.69	161.69	53.89	22.79	0.153
2-way interactions	3	2.77	2.77	0.92	0.39	0.792
Residual error	1	2.36	2.36	2.36		
Total	7	166.83				

Process modeling for SMP delignification of pulp

The factors studied are pulp consistency (X_1), reaction temperature (X_2), and SMP dosage (X_3) for the response of kappa number (Y). Table 4 provides the kappa number for various experiments conducted for 2^3 factorial designs.

The analysis of the design of experiments for 2^3 full factorial designs yielded the following regression equation:

Kappa number: $Y = 43.508 + 0.775X_1 - 0.482X_2 - 6.765X_3 + 0.013X_1X_2 - 0.281X_1X_3 + 0.071X_2X_3$ (3)

Table 5 provides the analysis of variance (ANOVA) for SMP delignification. The total degree of freedom for the experiment is seven. The values of F indicate that the main effects have a higher F value that affects the kappa more than the 2-way interactions between the factors. The effect variance exceeds the error variance due to the small dataset indicated in the high value of F. The P values for individual main effects are much lower than the two-way interactions.

Figure 5 shows a plot of the dosage of SMP *versus* the consistency of pulp to achieve a kappa reduction to 16 for pulp consistency of 2% and dosage above 2.4 g. The contour plot for the dosage of SMP versus reaction temperature provides a kappa reduction below 12 for a dosage of 2.4 g and a reaction temperature of 60 °C.

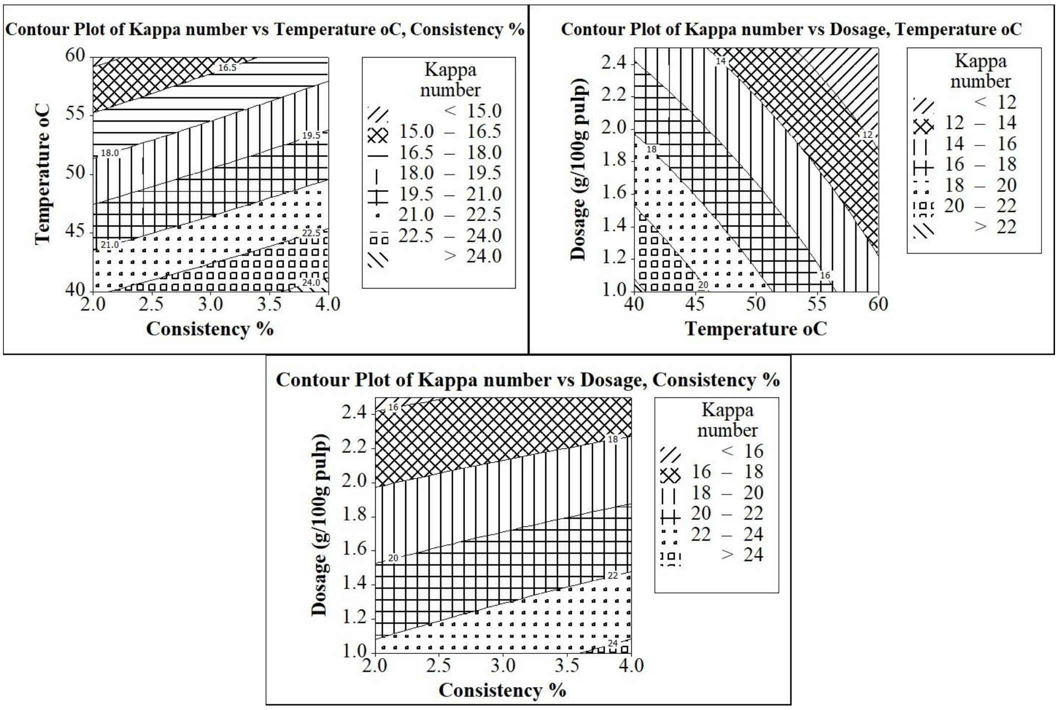

Figure 5: Contour plots of (1) temperature *vs* consistency of pulp for kappa reduction; (2) amount of SMP *vs* temperature for kappa reduction; (3) amount of SMP *vs* consistency of pulp for kappa reduction

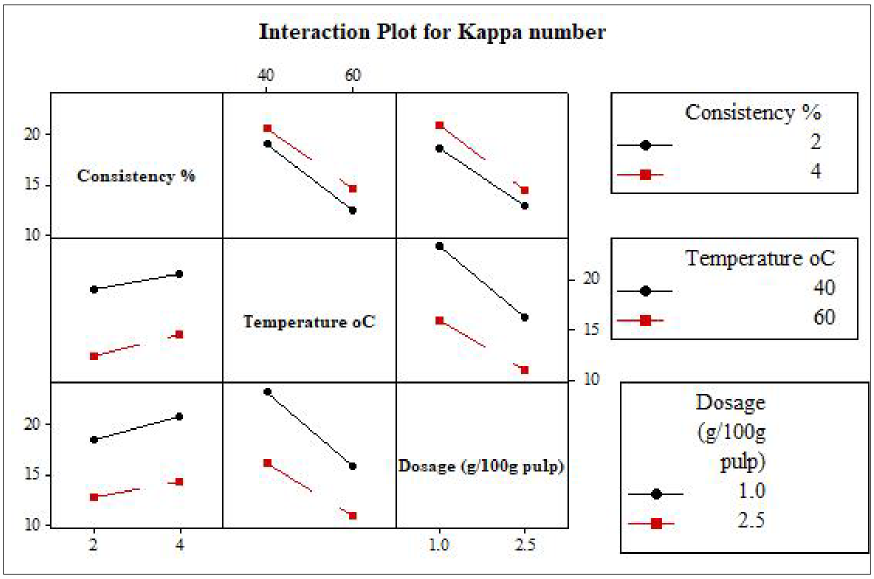

Figure 6: Interaction plot for kappa number using SMP

The contour plot for reaction temperature *versus* pulp consistency shows a trend comparable to the experimental results at higher dosages and high temperatures that reduce the kappa number more efficiently than at lower temperatures and lower dosage values across all different consistencies.

Figure 6 shows an interaction plot for the variation in the different reaction parameters. The kappa reduces to 10 with increasing temperature and dosage, while reducing the pulp consistency. The process achieves an optimal kappa reduction at a 2% pulp consistency for an SMP dosage of 2.5 g/100 g of pulp at 60 °C operating temperature.

Table 6
Rate of delignification reaction of pulp using SMP bleaching agent*

S.No	Pulp consistency (%)	Temperature (°C)	Dosage (g/100 g)	Kappa final	Final lignin concentration (mol/m^3)x10^4	$-r_A$ ($\frac{dC_A}{dt}$) (mol/m^{3}min)	C_A x10^4
1	2	60	2.5	10.64	3.06	392.02	3.06
2	4	60	2.5	11.30	3.25	376.18	3.25
3	2	60	1.0	14.14	4.07	308.02	4.07
4	4	60	1.0	17.82	5.13	219.70	5.13

*Initial Kappa number = 26.97; Initial lignin concentration = 7.76 X 10^4 mol/m^3

Table 7
Rate equation and rate constants for delignification of pulp*

S.No	Temperature (°C)	Kappa final	Final lignin concentration (mol/m^3) x 10^4	$-r_A = \frac{dC_A}{dt}$ (mol/m^3 min)	$\frac{1}{T}$ (1/K)	ln(k)
1	40	15.10	4.34	284.98	0.0031	-9.81
2	50	14.65	4.21	295.78	0.0030	-9.74
3	60	10.64	3.06	392.02	0.0030	-9.14

*Initial Kappa number = 26.97; Initial lignin concentration = 7.76 X 10^4 mol/m^3; Pulp consistency = 2%; Dosage = 2.5 g/100 g

Kinetics for SMP delignification

The kinetic study follows the first-order rate for lignin degradation.[20] The rate equation is given by $-r_A = kC_A$ where k is the rate constant and C_A is the lignin concentration, then a plot of $\frac{dC_A}{dt}$ vs C_A will be a straight line. Table 6 provides the calculated results for the rate constant. The straight-line graph proves the point that the reaction has first-order kinetics. The slope of the graph gives the specific reaction rate constant. From the slope of the graph, we can determine the rate constant as 0.0083 min^{-1}.

Using the Arrhenius equation $k = k_0 e^{\frac{-E_a}{RT}}$, where k_0 is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is temperature, we obtain:

$$\ln(k) = \ln(k_0) - \frac{E_A}{RT} \tag{4}$$

Plotting a graph between ln (k) vs $\frac{1}{T}$ for various temperatures will yield a slope of $\frac{E_A}{R}$ and intercept of ln (k_0). Table 7 provides the calculated results for the rate constant at different temperatures. The activation energy (E_A) value is 28.7365 KJ/mol, and the pre-exponential factor is 3.12 min^{-1}.

CONCLUSION

The optimum conditions for pulp delignification studies are an SPB dosage of 3 g per 100 g of pulp, temperature conditions between 40 °C to 45 °C, and a pulp consistency of 3% to 3.5%. These conditions resulted in a kappa reduction to 6.5. SEM images confirmed the absence of lignin in the cellulose fibers in the bleached pulp. FTIR spectral data provided insights into the structural groups present, and the similarity in the plot's close variation for both bleached and unbleached samples indicated that SPB could delignify the sample without causing significant damage to the cellulose matrix, thus preserving its structural integrity.

Conventional Raman spectroscopy analyses are problematic because of the fluorescence produced by laser beams, which interferes with the Raman signal and leads to errors. FT-Raman spectral analysis overcomes these limitations on the bleached samples. These spectra showed a Raman shift of 10 cm^{-1}, indicating the transformation of cellulose I to II. The absence of significant peaks in the bleached pulp indicates lignin removal.

The plot of both bleached and raw pulp samples demonstrated a reduction in peaks, including C-H stretch vibrations, causing the OH groups self-absorption in the sample. The delignification reaction using SPB follows the first-order reaction kinetics, with a specific reaction rate value of 0.00833 min^{-1} at 50 °C. Critically, the bleaching process did not result in substantial loss or structural damage to the existing cellulose fibers in the sample.

The optimal results for SMP bleaching of pulp for kappa reduction are a 2% pulp consistency for an SMP dosage of 2.5 g/100 g at 60 °C operating temperature. The rate constant for SMP bleaching is 0.0083 min^{-1}, the activation energy is 28.7365 KJ/mol, and the pre-exponential factor is 3.12 min^{-1}.

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