

Improving the efficiency of hydrogen peroxide bleaching of chemimechanical pulp by continuous replenishment of bleaching chemicals

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ABSTRACT: Hydrogen peroxide (H_2O_2) is commonly used to bleach chemimechanical pulp. A decrease in the concentrations of the bleaching reagents throughout the bleaching process results in low bleaching efficiencies. In this study, chemical solutions were continuously added into the pulp slurry during the bleaching process to maintain constant concentrations of H_2O_2 and total alkali in the bleaching system to improve bleaching efficiency. The results showed that when the H_2O_2 and total alkali concentrations were maintained at 4.5 g/L and 0.79 g/L, respectively, for 50 min, the bleaching efficiency reached 16.79 ($\Delta\%$ ISO brightness/ $\Delta\%$ H_2O_2 consumed [on oven-dry pulp]), which was significantly higher than 7.38 obtained by using the high-consistency bleaching method. The results confirmed that continuous replenishment of chemical solutions into the bleaching system to maintain the constant chemical concentrations improved the efficiency of H_2O_2 bleaching of the chemimechanical pulp.

Application: Continuous replenishment of H_2O_2 during chemimechanical pulp bleaching improves bleaching efficiency and reduces production costs.

Bleached chemimechanical pulp is an important fiber stock. It offers advantages of higher pulping yield, greater opacity, and higher bulk. It is commonly used in many kinds of paper products, including lightweight coated paper, supercalendered paper, and wallpaper [1]. Two primary processes for the production of bleached chemimechanical pulp are the pre-conditioning refiner chemical treatment, alkaline peroxide mechanical pulping process, and the bleached chemithermomechanical pulping process. Peroxide bleaching is used for brightening both types of pulps [2]. The advantages of peroxide bleaching include high brightening capabilities, less yellowing after bleaching, and low environmental impact of bleaching effluents. However, the bleaching efficiency, which can be defined as % ISO brightness/% hydrogen peroxide (H_2O_2) consumed (on oven-dry pulp), is very low [3]. In the bleaching process, H_2O_2 is primarily consumed by two simultaneously competing reactions: 1) the self-decomposition of H_2O_2 , and 2) the bleaching reaction of H_2O_2 with the chemimechanical pulp. The former reaction can consume a significant portion of the total H_2O_2 applied, which can result in low brightness gains [4,5]. Therefore, to improve the bleaching efficiency of H_2O_2 , the bleaching reaction should be selected to minimize H_2O_2 decomposition. An important factor affecting the selectivity of the reaction is the chemical concentration in the bleaching system.

An H_2O_2 bleaching solution is comprised of various chemical constituents. During the bleaching process, the concentrations of various chemicals, especially H_2O_2 and total alkali, decline to various degrees. In the bleaching system containing high concentrations of chemicals, the rate of the brightening reaction is high, but the rate of H_2O_2 decomposition is also high [6,7]. In the conventional high-consistency peroxide bleaching process, the concentrations of H_2O_2 and total alkali at the beginning are approximately 20 g H_2O_2 /L and 10 g sodium hydroxide (NaOH)/L (~12 pH or more), and the values at the end of the bleaching reaction are 5.0 g/L and 0.2 g NaOH/L (~9 pH) [8]. A previous study showed that the concentrations of these chemicals are not optimal for high bleaching efficiency (i.e., they are too high at the start and are too low at the end, which results in low bleaching efficiency) [9].

Reasonable control of the chemical concentration profiles during peroxide bleaching can be an effective method to improve brightening efficiency [3,10,11]. In the last stage of a traditional high-consistency peroxide bleaching process, a large amount of unreacted H_2O_2 often remains in the pulp because of insufficient alkali to activate the bleach. Zhao et al. [12] added additional NaOH midway during the bleaching process so that the residual H_2O_2 could be activated later during the bleaching stage. This study showed that the bleaching efficiency with the addition of NaOH increased by 0.61 ($\Delta\%$ ISO brightness/ $\Delta\%$ H_2O_2 consumed) when compared

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with that of the control. Wang [10] adopted the same method to bleach wheat straw pulp and observed similar results. The addition of extra alkali in the middle of the bleaching process enhanced the bleaching efficiency by increasing the alkali concentration in the latter portion of bleaching process. However, the alkali concentration in these bleaching systems still decreased when alkali was added midway through the bleaching stage, although it did result in a slight enhancement of bleaching efficiency (i.e., $\Delta\%$ ISO brightness/ $\Delta\%$ H_2O_2 consumed).

Two-stage peroxide bleaching is also an effective method for promoting brightening reactions while minimizing undesired reactions. The initial alkali and peroxide concentrations of both stages are lower than those of a single peroxide stage, and chemical consumption was decreased by 10%–20% [13]. Although two-stage peroxide bleaching can solve the excessively high chemical concentrations at the beginning of bleaching, the issue of insufficient chemical concentrations toward the end of the bleaching stage remains unsolved.

Displacement bleaching has also been studied in peroxide bleaching of chemimechanical pulp [14,15]. Zhao [3] studied a single displacement bleaching stage with a chemithermo-mechanical pulp (CTMP). Zhao [3] showed that under optimized peroxide bleaching conditions, the bleaching efficiency reached 10.79 ($\Delta\%$ ISO brightness/ $\Delta\%$ H_2O_2 consumed). The initial peroxide and alkali concentrations were lower in this process than those of conventional high-consistency peroxide bleaching.

Although the chemical concentrations in the peroxide bleaching system are balanced to a certain degree by these methods, the concentrations of bleaching reagents decrease throughout the reaction, which still results in low bleaching efficiencies. This study focused on improving bleaching efficiency by maintaining constant concentrations of bleaching reagents. We continuously replenished the chemicals to the bleaching stage to account for the chemicals consumed during the brightening reactions. We have termed this process as “continuous chemical supplement” (CCS) peroxide bleaching. CCS peroxide bleaching for poplar CTMP was studied.

A response surface methodology was used for the experimental design to determine the optimum H_2O_2 and total alkali levels of the CCS peroxide bleaching process. The impact of this process on peroxide bleaching efficiency (i.e., $\Delta\%$ ISO brightness/ $\Delta\%$ H_2O_2 consumed) was also assessed.

EXPERIMENTAL

Raw material

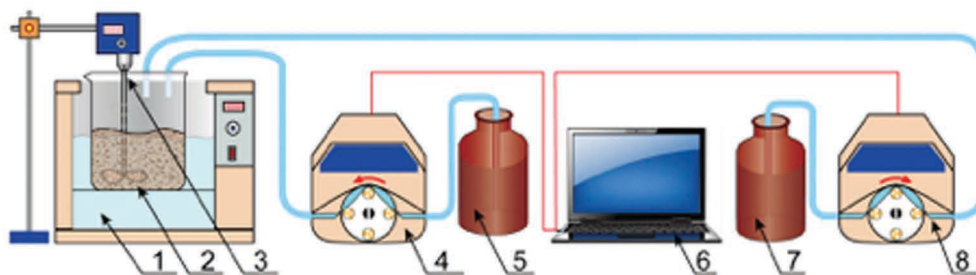
Unbleached poplar CTMP with an ISO brightness of 46.07% was obtained from a CTMP mill in Shandong Province, China. This pulp was first washed with deionized water, thickened to a consistency of about 30%, and stored in a cold room at approximately 4°C.

Chemicals

The following chemical reagents were used in this study: sodium silicate (Na_2SiO_3) (41° Bé) from China PQ (Tianjin) Silicates Technology Co. Ltd.; diethylenetriamine pentamethylenephosphonic acid (DTPMPA) from Chunjiang (Changzhou) Chemicals Co. Ltd., China; magnesium hydroxide ($\text{Mg}(\text{OH})_2$) slurry (80 g/L) from Haililong Magnesium Technology Co. Ltd., China; and diethylenetriaminepentaacetic acid (DTPA) from Akzo Nobel N.V. (Amsterdam, Netherlands). Hydrogen peroxide and NaOH were purchased from Jiangtian Chemical Co., Tianjin, China. All chemicals used were of analytical grade unless otherwise specified.

CCS experimental apparatus and process control

Figure 1 illustrates the CCS peroxide bleaching apparatus used in the present study. A 2000 mL beaker was placed into a constant temperature water bath and used as a bleaching reactor. A mixer with a speed range of 50–2000 rpm was used to mix pulp and chemicals in the beaker. Two peristaltic pumps set to a flow rate of 20 $\mu\text{L}/\text{min}$ continuously replenished the chemical solutions into the pulp slurry during the bleaching process. The bleaching chemicals that were replenished were stored in separate 500 mL plastic bottles. The flow rates of each peristaltic pump were controlled by a computer using the pump manufacturer’s software.



1. Apparatus for the continuous chemical supplement (CCS) bleaching process.

Note: 1 = thermostatic bath; 2 = reactor; 3 = stirrer; 4 = peristaltic pump for hydrogen peroxide (H_2O_2); 5 = plastic container for H_2O_2 ; 6 = computer; 7 = plastic container for sodium hydroxide (NaOH); 8 = peristaltic pump for NaOH .

CCS experimental procedure

The entire CCS bleaching process was divided into two phases: 1) the constant chemical concentration phase, and 2) the residual peroxide consumption phase. In the first phase, 40.00 g of oven-dried unbleached poplar CTMP was first placed in the reactor and then diluted to a pulp consistency of 5% at a stirring speed of 200 rpm. When the pulp reached a temperature of 75°C, the following bleaching chemicals were added to the pulp: 0.2% Mg(OH)₂, 0.3% DTPMPA, and 0.2% DTPA (on oven-dried unbleached pulp). Subsequently, according to the initial chemical concentrations in the experimental design, Na₂SiO₃, NaOH, and H₂O₂ were successively added to the pulp. Finally, the pulp was diluted to a consistency of 4.0% with deionized water, and the peristaltic pumps immediately started to replenish the consumed peroxide and alkali with 60 g/L H₂O₂ and 30 g/L NaOH solutions at set flow rates. The initial concentrations of the H₂O₂ and total alkali in the bleaching system remained constant for 50 min. When the reaction time reached 50 min, the pulp in the reactor was transferred to a cloth bag and thickened to a consistency of about 30%. The residual H₂O₂ concentration of the filtrate and the yield of bleached pulp were then measured.

In the residual peroxide consumption phase, 60.00 g of wet pulp (equivalent to about 18.0 g of oven-dried pulp) obtained in the CCS phase was immediately sealed in a plastic bag and quickly placed in a water bath at 90°C, and the bleaching reaction was continued for 70 min. After the bleaching reaction was completed, the concentration of the residual H₂O₂ and the pulp brightness were measured. The H₂O₂ consumption, *S*, was calculated according to the following equation:

$$S = \frac{40y \left(\frac{100}{c_1} - 1 \right) \cdot (c_2 - c_3) \cdot 10^{-5} + v_1 c_4 + 0.960 c_5 - (0.960 + v_1 + v_2) c_2}{40} \times 100\% \quad (1)$$

where

c_1 = thickened pulp consistency at the end of constant chemical concentration phase, %

c_2 = peroxide concentration at the end of the constant chemical concentration phase, g/L

c_3 = peroxide concentration at the end of the residual peroxide consumption phase, g/L

c_4 = concentration of H₂O₂ solution for replenishment, g/L

c_5 = initial H₂O₂ concentration in the constant chemical concentration phase, g/L

y = pulp yield in the constant chemical concentration phase, %

v_1 = volume of H₂O₂ solution for replenishment, L

v_2 = volume of NaOH solution for replenishment, L

The constant value of 0.960 is the initial volume of bleaching solution (L) and the constant value of 40 is the weight of oven-dried unbleached pulp (g). The bleaching efficiency was obtained by the following formula:

$$\text{Bleaching efficiency} = \frac{\text{brightness gains (\% ISO)}}{\text{H}_2\text{O}_2 \text{ consumption on pulp (\%)}} \quad (2)$$

Experimental design

We used a response surface methodology statistical software program, Design Expert 8.0.5b (State-Ease; Minneapolis, MN, USA), to optimize the parameters of the CCS bleaching process [16,17]. According to the results of preliminary experiments, the initial concentrations of H₂O₂ (x_1), NaOH (x_2), and Na₂SiO₃ (x_3) in the bleaching system were chosen as the independent variables. These variables were investigated at three levels. The response variables were the pulp brightness (Y_1) and bleaching efficiency (Y_2). According to a statistical Box-Behnken Design, there were a total of 17 experimental runs (**Table I**).

High-consistency peroxide bleaching experiment

To compare the effectiveness of the CCS peroxide bleaching process with that of a conventional high-consistency peroxide bleaching process, an experiment of high-consistency peroxide bleaching was made in the present work. The process conditions of the experiment were the same as those in the CTMP mill from which we obtained the CTMP sample. An equivalent of 40 g oven-dried CTMP was mixed with the following bleaching chemicals: 5.5% H₂O₂, 2.75% NaOH, 3% Na₂SiO₃, and 0.2% DTPA on oven-dried CTMP. The mixed pulp was adjusted to a consistency of 25% and sealed in a plastic bag. The bag was placed in a water bath at 90°C for 120 min [18].

Analysis and measurement

Brightness measurements were taken on bleached pulp samples made into handsheets in accordance with ISO Standard 3688: 1999 (E) "Pulps — Preparation of laboratory sheets for the measurement of diffuse blue reflectance factor (ISO brightness)." Brightness measurements were conducted on the handsheets according to ISO Standard 2470—1: 2009 "Paper, board and pulps — Measurement of diffuse blue reflectance factor — Part 1: Indoor daylight conditions (ISO brightness)." An AT-510 automatic titrator (Kyoto Electronics Mfg. Co. Ltd.; Kyoto, Japan) was used for the titration analyses of the chemical concentrations [19,20].

RESULTS AND DISCUSSION

Relationship between bleaching efficiency and pulp brightness

When the concentrations of H₂O₂ and total alkali in the bleaching system were maintained at constant values, the pulp brightness and bleaching efficiency varied significantly (**Table I**). The maximum bleaching efficiency was 18.00 (Δ% ISO brightness/Δ% H₂O₂ consumed) while obtaining an ISO brightness was 74.98%. However, the highest ISO brightness was 77.86%, with a bleaching efficiency of 10.83. A high pulp brightness was usually accompanied by a low bleaching efficiency value. The optimal bleaching efficiency, in fact,

Run	Independent Variables			Response Variables	
	x_i	x_j	x_k	Y_1	Y_2
	H ₂ O ₂ , g/L	NaOH, g/L	Na ₂ SiO ₃ , g/L	ISO Brightness, %	Bleaching Efficiency, Δ% ISO brightness / Δ% H ₂ O ₂ consumed
1	1.78	1.02	2.50	72.76	14.62
2	1.78	0.51	3.75	72.00	16.65
3	3.57	0.51	2.50	74.98	18.00
4	3.57	1.02	3.75	75.84	13.84
5	3.57	1.53	2.50	75.80	10.18
6	1.78	1.02	5.00	73.04	15.05
7	1.78	1.53	3.75	72.60	12.93
8	5.35	0.51	3.75	76.36	13.84
9	3.57	0.51	5.00	74.32	13.69
10	3.57	1.53	5.00	75.98	13.63
11	3.57	1.02	3.75	75.16	13.63
12	5.35	1.02	5.00	77.29	12.96
13	5.35	1.53	3.75	77.86	10.83
14	5.35	1.02	2.50	77.53	13.02
15	3.57	1.02	3.75	75.52	12.91
16	3.57	1.02	3.75	75.92	13.72
17	3.57	1.02	3.75	75.46	12.25

H₂O₂ = hydrogen peroxide; NaOH = sodium hydroxide; Na₂SiO₃ = sodium silicate.

I. Results from the Box-Behnken design-of-experiments.

hinges on the gain of the pulp brightness. The higher the pulp brightness, the lower the bleaching efficiency (**Fig. 2**).

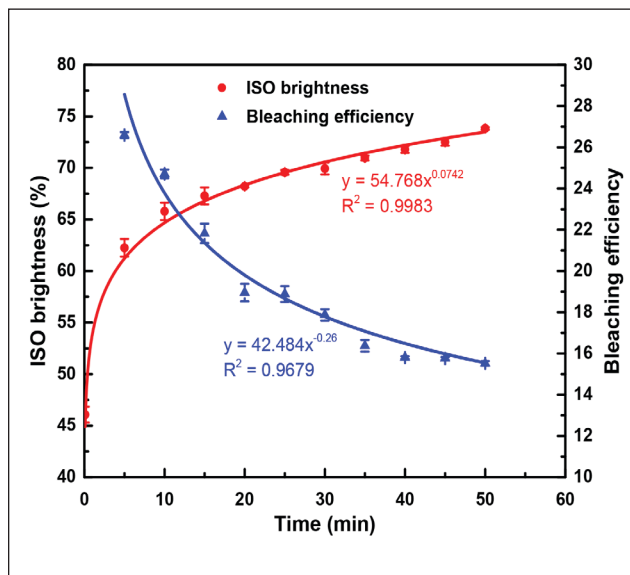
Establishment of the mathematical model for pulp brightness and bleaching efficiency

A second order multivariate regression analysis of the data in Table I was conducted, and two corresponding regression equations, Eqs. (3) and (4), with pulp brightness (Y_1) and bleaching efficiency (Y_2) as the response values were obtained (uncoded):

$$Y_1 = 68.46 + 2.38x_i + 1.99x_j - 0.51x_k + 0.25x_ix_j - 0.06x_ix_k + 0.32x_jx_k - 0.16x_i^2 - 1.46x_j^2 + 0.04x_k^2 \quad (3)$$

$$Y_2 = 31.23 - 0.60x_i - 15.69x_j - 2.96x_k + 0.19x_ix_j - 0.05x_ix_k + 3.04x_jx_k \quad (4)$$

The results of the analysis of variance (ANOVA) in **Tables II** and **III** show the significance of each factor and the degree of their influences on the response values. The p values of x_i and x_j elements were <0.0001 and 0.0005, respectively, which indicated a significant effect of H₂O₂ and NaOH concentrations on bleached pulp brightness. The influences of various factors on the pulp brightness were: H₂O₂ (x_i) > NaOH (x_j) > Na₂SiO₃ (x_k). The ANOVA result of the bleaching efficiency model in Table III revealed that the p values of x_j



2. Effect of bleaching time on the pulp brightness and bleaching efficiency.

Note: The bleaching conditions were as follows: 4.50 g/L H₂O₂, 0.50 g/L NaOH, and 2.50 g/L sodium silicate (Na₂SiO₃) in the bleaching system; 0.2% magnesium hydroxide (Mg(OH)₂), 0.3% diethylenetriamine pentamethylenephosphonic acid (DTPMPA), and 0.2% diethylenetriaminepentaacetic acid (DTPA) based on the weight of oven-dried unbleached pulp; 75°C, and 4% pulp consistency.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	p-value
Model	48.2500	9	5.3600	79.1000	<0.0001
x_i	43.4312	1	43.4312	640.7807	<0.0001
x_j	2.6221	1	2.6221	38.6855	0.0004
x_k	0.0242	1	0.0242	0.3570	0.5690
$x_i x_j$	0.2025	1	0.2025	2.9877	0.1275
$x_i x_k$	0.0676	1	0.0676	0.9974	0.3512
$x_j x_k$	0.1764	1	0.1764	2.6026	0.1507
x_i^2	1.0317	1	1.0317	15.2214	0.0059
x_j^2	0.6080	1	0.6080	8.9704	0.0201
x_k^2	0.0206	1	0.0206	0.3044	0.5983
Residual	0.4745	7	0.0678		
Lack of fit	0.0969	3	0.0323	0.3420	0.7977
Pure error	0.3776	4	0.0944		
Total*	48.7282	16			
	$R^2 = 0.9903$			$R_{adj}^2 = 0.9777$	

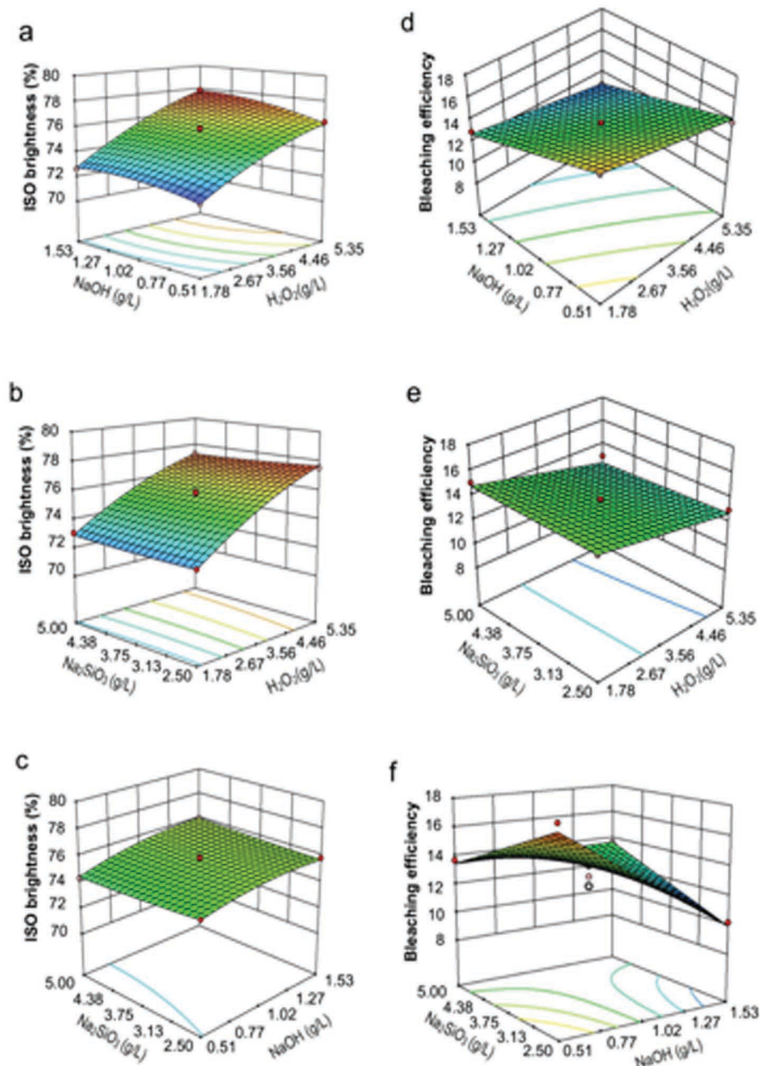
*Total corrected for the mean.

II. Analysis of variance (ANOVA) for the fitted quadratic polynomial model for bleached brightness. (Note: The responses were the mean values of three experiments with a relative deviation of $\pm 0.6\%$ – 4.0% .)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	p-value
Model	51.2000	6	8.5300	23.7500	<0.0001
x_i	9.2450	1	9.2450	25.7311	0.0005
x_j	26.6815	1	26.6815	74.2611	<0.0001
x_k	0.0300	1	0.0300	0.0835	0.7785
$x_i x_j$	0.1260	1	0.1260	0.3508	0.5668
$x_i x_k$	0.0600	1	0.0600	0.1671	0.6913
$x_j x_k$	15.0544	1	15.0544	41.9001	<0.0001
Residual	3.5929	10	0.3593		
Lack of fit	1.7659	6	0.2943	0.6444	0.7001
Pure error	1.8270	4	0.4568		
Total*	54.7899	16			
	$R^2 = 0.9344$			$R_{adj}^2 = 0.8951$	

* Total corrected for the mean.

III. ANOVA for the fitted quadratic polynomial model of bleaching efficiency.



3. Response surfaces showing the effects of different bleaching parameters ($x_1 = \text{H}_2\text{O}_2$ concentration, $x_2 = \text{NaOH}$ concentration, and $x_3 = \text{Na}_2\text{SiO}_3$ concentration) on the response brightness (Y_1) and bleaching efficiency (Y_2).

and x_i elements were also <0.0001 and 0.0005 , respectively, which indicated that the NaOH and H₂O₂ concentrations had a significant effect on bleaching efficiency as well. The p value of the quadratic term x_jx_k was <0.0001 , which indicated significant interactions between the concentrations of NaOH and Na₂SiO₃ on the bleaching efficiency. The influences of various factors on the bleaching efficiency were: NaOH (x_j) $>$ Na₂SiO₃ (x_k) $>$ H₂O₂ (x_i).

The significance and goodness-of-fit of the established models were assessed, as shown in Tables II and III. The p values of the brightness and bleaching efficiency models were all <0.0001 , indicating that a linear relationship generally existed between the independent variable expressed by these models and the response values. The coefficients of determination (R^2) for the brightness and bleaching efficiency models were 0.9903 and 0.9344 , respectively, showing that these mod-

els effectively reflected the actual relationship between the factors and response values, and that they could be used to predict the optimal process conditions.

Effect of constant chemical concentrations on pulp brightness and bleaching efficiency

The mathematical model generated by response surface model revealed the effects of various concentrations of individual chemicals and their interactive effects on the brightness and bleaching efficiency (Fig. 3). Within the investigated range of chemical concentrations (NaOH: 0.51 – 1.53 g/L, Na₂SiO₃: 2.5 – 5.0 g/L, and H₂O₂: 1.78 – 5.35 g/L), the brightness of the bleached pulp rapidly increased with increasing H₂O₂ concentration (Figs. 3a and b) and slightly improved with raising NaOH concentration (Figs. 3a and c). However, the bleaching efficiency exhibited a slight down-

	H ₂ O ₂ , g/L	NaOH, g/L	Na ₂ SiO ₃ , g/L	Bleaching Efficiency, Δ% ISO brightness/ Δ% H ₂ O ₂ consumed	ISO Brightness, %
Predicted value	4.50	0.52	2.50	16.86	75.99
Measured value	4.50	0.50	2.50	16.79	75.83

H₂O₂ = hydrogen peroxide; NaOH = sodium hydroxide; Na₂SiO₃ = sodium silicate.

IV. Comparison of the predicted model value and observed value obtained from validation experiment.

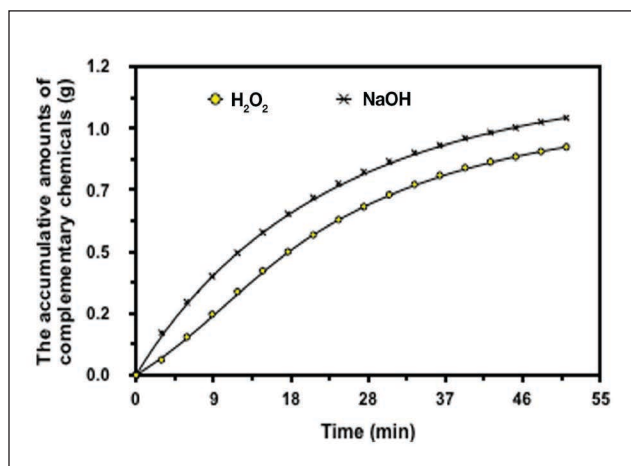
ward trend (Figs. 3d and e). These results can be explained by the fact that an increased H₂O₂ concentration accelerated the bleaching reaction rate because of the formation of the perhydroxyl anion (HOO⁻) from H₂O₂, the specie that is responsible for the bleaching effect. Although this ion increases the pulp brightness, it also accelerates the decomposition of H₂O₂, which hinders bleaching efficiency [21]. Therefore, the concentrations of H₂O₂ and NaOH should be maintained at a certain level to achieve the brightness target with a bleaching efficiency as high as possible.

Figure 3c shows that the brightness of the bleached pulp did not change appreciably when the Na₂SiO₃ concentration was varied from 2.5 g/L to 5 g/L. When the NaOH concentration increased from 0.51 g/L to 1.53 g/L, the bleaching efficiency changed from decreasing rapidly to increasing rapidly as the Na₂SiO₃ concentration increased (Fig. 3f). The results indicated that a significant synergistic effect existed between Na₂SiO₃ and NaOH. One reason for this synergistic effect could be that Na₂SiO₃ acts as a buffer [1,2] that stabilizes the total alkalinity of the bleaching system while inhibiting H₂O₂ decomposition and improving bleaching efficiency. It should be noted that Na₂SiO₃ could form complexes with transition metal ions, together with magnesium ions, thus inhibiting catalytic peroxide decomposition [1].

Prediction and validation of the optimal process conditions

Maximum bleaching efficiency was dependent on the target brightness of bleached pulp. In the current work, an ISO brightness target of 76% was set while achieving maximum bleaching efficiency. According to the mathematical model (Y_2), we predicted the optimal process conditions, and the response values of brightness and bleaching efficiency (**Table IV**). Based on the predicted conditions, the experimental conditions set for a validation experiment was: 4.50 g/L H₂O₂, 0.50 g/L NaOH, and 2.50 g/L Na₂SiO₃ (with an initial total alkali concentration of 0.79 g NaOH/L). The result of the validation experiment showed that the bleaching efficiency and pulp brightness were very close to the predicted values (Table IV). These conditions were considered as the optimal ones to obtain the maximum bleaching efficiency.

Figure 4 shows the cumulative totals of H₂O₂ and NaOH versus time for the optimized CCS bleaching process. The cumulative amounts of added H₂O₂ and alkali gradually increased with time, and the addition rates decreased with in-



4. Relationship between the accumulative amounts of complementary chemicals (on 40 g unbleached pulp) and bleaching duration.

creased bleaching reaction time toward the end of the bleaching stage.

Comparison between the CCS bleaching and high-consistency bleaching

Table V compares CCS bleaching and high-consistency bleaching (i.e., control). The pulp ISO brightness values in these two bleaching methods were relatively close. However, the bleaching efficiency of the CCS bleaching method was 16.79, which was much higher than the 7.38 of the high-consistency bleaching. Zhao [3] reported a bleaching efficiency of 10.79 with the displacement bleaching method. To our knowledge, Zhao's study produced the highest reported value. Thus, the CCS bleaching method exhibited the highest bleaching efficiency among the compared methods. The results confirmed that CCS bleaching was an effective method to improve hydrogen peroxide bleaching efficiency.

When the chemical concentrations and the H₂O₂ consumption in the bleaching system were compared, the initial H₂O₂ concentration and total alkali concentration in the CCS bleaching process were 4.50 g/L and 0.79 NaOH/L (pH 10.46). Those concentrations were significantly lower than the corresponding initial levels in the high-consistency bleaching process (H₂O₂ of 19.38 g/L and total alkali of 10.30 g NaOH/L). At the same time, the H₂O₂ consumption in the CCS bleaching process was only 1.77% on pulp, which was significantly

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	Bleaching Process	
	CCS Bleaching	High-consistency Bleaching
ISO brightness of the unbleached pulp, %	46.07	46.07
ISO brightness of the bleached pulp, %	75.83	76.42
Bleaching efficiency, $\Delta\%$ ISO brightness/ $\Delta\%$ H ₂ O ₂ consumed (on ovendry pulp)	16.79	7.38
H ₂ O ₂ concentration, g/L	4.50	19.50
Total alkali concentration, g/L	0.79	10.30
H ₂ O ₂ consumption, %	1.77	4.11
NaOH consumption, %	2.69	2.71
Pulp consistency, %	4	25
Bleaching temperature, °C	75	90

H₂O₂ = hydrogen peroxide; NaOH = sodium hydroxide.

V. Comparison between the continuous chemical supplement (CCS) peroxide bleaching and high-consistency peroxide bleaching of poplar chemithermomechanical pulp.

lower than the 4.11% on pulp with the high-consistency bleaching process. We concluded that the low initial chemical concentrations in the CCS bleaching could result in a low H₂O₂ consumption, and therefore, the bleaching efficiency was enhanced.

When comparing the two bleaching methods, lower reaction temperatures (i.e., 75°C) and use of multiple peroxide stabilizers, DTPMPA and Mg(OH)₂, were used in the CCS bleaching process. However, both of these process conditions with the CCS bleaching played an important role in inhibiting unproductive hydrogen peroxide decomposition.

CONCLUSIONS

This study examined using the CCS bleaching process to improve H₂O₂ bleaching efficiency of poplar CTMP. The pulp brightness was enhanced with the constant addition of H₂O₂ and total alkali solutions over time, but the bleaching efficiency decreased. The synergistic effect of Na₂SiO₃ and NaOH significantly affected the bleaching efficiency. The optimized chemical concentrations for CCS bleaching were 4.50 g/L H₂O₂, 0.50 g/L NaOH, and 2.50 g/L Na₂SiO₃. Under these conditions, the bleaching efficiency reached 16.79 ($\Delta\%$ ISO brightness/ $\Delta\%$ H₂O₂ consumed), which was significantly higher than the 7.38 of the high-consistency bleaching process (i.e., control). The low initial chemical concentrations in the CCS bleaching could result in low H₂O₂ consumption, and hence, the efficiency of the CCS bleaching was enhanced. In addition, low bleaching reaction temperature and the addition of multiple peroxide stabilizers could help improve bleaching efficiency. The CCS bleaching process can be an effective approach to improve the efficiency of peroxide bleaching of chemimechanical pulp. **TJ**

LITERATURE CITED

1. Sundholm, J., *Mechanical Pulping*, Papermaking Science and Technology, Book 5, Fapet Oy, Helsinki, 1999.
2. Ek, M., Gellerstedt, G., and Henriksson, G., *Pulp and Paper Chemistry and Technology: Pulping Chemistry and Technology*, Walter de Gruyter GmbH & Co., Berlin, 2009.
3. Zhao, Q., "Research on reinforced hydrogen peroxide bleaching of poplar CMP and bleaching mechanism," Ph.D. dissertation, Beijing Forestry University, Beijing, China, 2009.
4. Xu, E., *J. Pulp Pap. Sci.* 28(11): 379(2002).
5. Zhao, Q., Pu, J., Mao, S., et al., *BioResources* 5(1): 276(2010).
6. Fei, X., Yao, J., Du, J., et al. *Cellulose* 22(2): 1379(2015).
7. Zeinaly, F., Shakhes, J., Firozabdi, M.D., et al., *BioResources* 4(4): 1409(2009).
8. Behrooz, R., Ghasemi, S., Atoii, G.A., et al., *BioResources* 7(1): 161(2012).
9. Shen, K., "High-brightness bleaching of China fir CTMP pulp and its mechanism," Ph.D. dissertation, Chinese Academy of Forestry, Beijing, China, 2008.
10. Wang, R., "Studies on anaphase activation of peroxide bleaching of pulp," M.S. thesis, Northeast Forestry University, Harbin, China, 2004.
11. Hatam, A., Pourtahmasi, K., Resalati, H., et al., *Wood Sci. Technol.* 42(5): 353(2008).
12. Zhao, Q., Sun, D., Wang, Z., et al., *BioResources* 7(4): 4889(2012).
13. Suhr, M., Klein, G., Kourti, I., et al., *Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board*, European Integrated Pollution Prevention and Control Bureau, Seville, Spain, 2014. Available [Online] http://eippcb.jrc.ec.europa.eu/reference/BREF/PP_revised_BREF_2015.pdf <21 June 2017>.

14. Li, Z., Ni, Y., and van Heiningen, A., *Pulp Pap. Can.* 97(9): 46(1996).
15. Li, X., "Studies on hydrogen peroxide displacement bleaching processes and mechanisms of *E. globulus* CTMP," Ph.D. dissertation, South China University of Technology, Guangzhou, China, 2000.
16. Singh, G., Ahuja, N., Batish, M., et al., *Bioresour. Technol.* 99(16): 7472(2008).
17. Perincek, S., Duran, K., and Korlu, A.E., *Ozone: Sci. Eng.* 35(4): 316(2013).
18. Liu, W., Han, S., Xu, N., et al., *Ind. Eng. Chem. Res.* 53(8): 2897(2014).
19. Hietanen, T.M., Österberg, M., and Backfolk, K.A., *BioResources* 8(2): 2337(2013).
20. Karlsson, A., and Agnemo, R., *Nord. Pulp Pap. Res. J.* 25(3): 256(2010).
21. Mota, S.F., Paulo, J.G., Zeller, C.A.V., et al., *Nord. Pulp Pap. Res. J.* 22(1): 17(2007).

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Hydrogen peroxide (H_2O_2) is widely used in bleaching chemimechanical pulp. However, its bleaching efficiency is not high because of the self-decomposition of H_2O_2 in bleaching. Much research has focused on improving bleaching efficiency by balancing the chemical concentration in the bleaching system. Although bleaching efficiency has been improved to some extent, much further improvement could be made.

In this study, the authors made a great effort to improve the bleaching efficiency of H_2O_2 . A novel bleaching method was proposed by which constant chemical concentrations in the bleaching system were maintained.

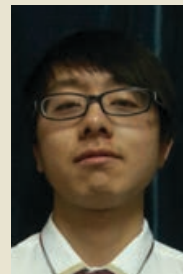
How to maintain the chemical concentrations was the difficult aspect of this research. The authors used two peristaltic pumps to continuously supplement H_2O_2 and sodium hydroxide solutions into the bleaching system to maintain constant concentrations of H_2O_2 and total alkali. Flows of the peristaltic pumps were accurately controlled and changed by



Sun



Zhang



Zhao



Hou

computer. A surprising find was that the bleaching efficiency gained in the study was extremely high.

To better understand the new bleaching method, the authors will further study the reaction kinetics and mechanism of peroxide bleaching under the conditions of constant chemical concentrations. Mills could use the bleaching method proposed in this study to reduce bleaching chemical costs. New equipment would be developed to meet the needs of practical production.

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