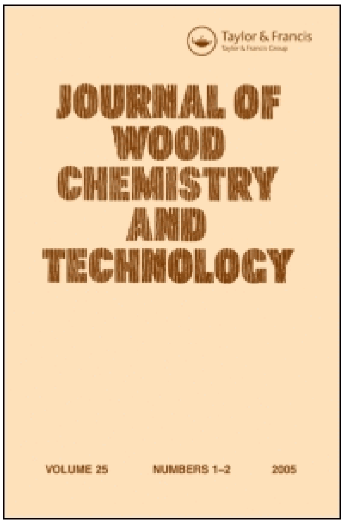

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Jeffrey Keating[a]; C. Ingemar Johansson[a]; John N. Saddler[a]; Rodger P. Beatson[b]
[a] Wood Science Department, University of British Columbia, Vancouver, BC, Canada [b] Advanced Papermaking Initiative, British Columbia Institute of Technology, Burnaby, BC, Canada

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Kinetics of Hydrogen Peroxide Brightening of Western Red Cedar (*Thuja plicata Donn*) CTMP

Jeffrey Keating,[1] C. Ingemar Johansson,[1] John N. Saddler,[1] and Rodger P. Beatson[2]

[1]Wood Science Department, University of British Columbia, Vancouver, BC, Canada
[2]Advanced Papermaking Initiative, British Columbia Institute of Technology, Burnaby, BC, Canada

Abstract: The use of western red cedar mechanical pulp is limited by its very low brightness. This article presents the kinetic expressions for hydrogen peroxide brightening of western red cedar chemimechanical pulp. The significance of the results for the reaction mechanism and for brightening under practical conditions is discussed. The kinetics of peroxide brightening of western red cedar chemimechanical pulp was monitored at the three absorption maxima—357 nm, 457 nm, and 550 nm—in the UV-visible spectra. The reaction order with respect to hydrogen peroxide was around 1 at all three wavelengths. The reaction order with respect to chromophores was approximately 2.4 at the higher wavelengths and 5 at 357 nm. The kinetic equations were successful in predicting brightness values obtained under practical conditions.

Keywords: Brightening, chromophores, hydrogen peroxide, kinetics, mechanism, reaction order, UV-visible, western red cedar

INTRODUCTION

Mechanical pulps have several advantages over chemical pulps in the preparation of light-weight printing papers. They are lower cost, obtained in a much higher yield from wood, and produce a more opaque sheet. Their use is limited

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Address correspondence to Rodger P. Beatson, British Columbia Institute of Technology, 3700 Willingdon Ave., Burnaby, BC, Canada V5G 3H2. E-mail: rodger_beatson@bcit.ca

by a relatively low strength, low brightness, and brightness instability. Developments in mechanical pulping technology have improved pulp strength and led to increased use of mechanical pulps in products such as newsprint and groundwood specialties. However, low brightness and brightness reversion are still major limiting factors in their use in higher grade papers. Western red cedar is a very low brightness wood and the difficulty in brightening mechanical pulps from western red cedar has precluded its use in even low brightness grades such as newsprint.

The fiber morphology of western red cedar has many good attributes for papermaking. The fibers are long and slender, and chemical pulp from western red cedar is capable of producing well bonded paper with high tensile strength and good surface properties.[1–5] These attributes are being exploited in the production of cedar kraft pulps for special applications. The long and slender fibers in western red cedar should also produce a superior mechanical pulp, especially in relation to the coarse fibered species from western Canada and northwestern United States such as Douglas fir and hemlock. Production of a high value, high yield mechanical pulp from western red cedar would be a much better utilization of this unique resource relative to production of cedar chemical pulps where the yields are only 38%.[5]

The major challenge in producing a high value mechanical pulp from cedar is the low brightness and difficulty in brightening. Previous attempts at peroxide brightening of western red cedar mechanical pulps, groundwood, and CTMP, have yielded unacceptable results.[6–9] Generally, the final brightness is in the mid 40% ISO. In an effort to develop procedures capable of efficiently brightening cedar mechanical pulp to high brightness levels we are conducting a fundamental investigation into the nature of the color in western red cedar mechanical pulps.[9–11] This article reports the results of our investigation into the peroxide brightening kinetics of western red cedar CTMP and the factors that limit its efficacy.

EXPERIMENTAL

Western Red Cedar CTMP Pulp

Cedar chips collected at Canadian White Pine were screened to remove fines and overs using a Dillon screen. CTMP pulp was made at the Paprican pilot plant (Vancouver Laboratory) using a 12″ Sunds Defibrator single-disc laboratory refiner where the conditions are detailed in what follows. The chips were pretreated using a 2% solution of sodium sulfite.

Refiner plates	Rotor, No. 3809, Stator, No. 3804
Pre-steaming time	20 min (atmospheric)
Pre-heater pressure	145 kPa

Pre-heating residence time	7 min
Refiner housing pressure	155 kPa
Prex compression ratio	3:1
Sodium sulfite, % on OD wood	3.2
Specific refining energy, MJ/kg	6.6
Freeness, mL CSF	276

Chelation

The pulp was made up to 1% consistency, pH adjusted to 5.5, stirred for 1 h, and readjusted to pH 5.5. The pulp was then filtered, and the fines recirculated twice in order to minimize yield loss. The chelation stage was performed at 50°C for 30 min at 3% consistency with a 1% EDTA (ethylenediaminetetraacetic acid) loading. After chelation, the pulps were filtered and filtrates were recirculated twice in order to retain the fines and then the pulps were washed in water at a 1% consistency.

Peroxide Brightening

Kinetic Studies

Twenty-five grams oven dried (OD) of chelated red cedar CTMP was manually broken up and charged into a polyethylene bag followed by the brightening liquor (0.1–0.25 M peroxide, 8% sodium silicate on OD pulp, sodium hydroxide, to adjust the pH 9 to 11.5, and 0.05% magnesium sulfate on OD pulp). Experimental conditions are given in Table 1.

Table 1. Experimental conditions for the peroxide brightening kinetics of western red cedar CTMP

Trial	Peroxide(M)	pH	Temp (°C)
1	0.1	10	55
2	0.15	10	55
3	0.20	10	55
4	0.25	10	55
5	0.20	9	55
6	0.20	10.5	55
7	0.20	11.5	55
8	0.20	10	40
9	0.20	10	80
10	0.20	10	65

The CTMP at 1% consistency was placed into a water bath. Both the pH and peroxide concentration were monitored and, if required, further peroxide or sodium hydroxide was added to maintain their initial levels throughout the experiment. At 5, 10, 20, and 30 min, 5 g OD pulp samples were removed and the peroxide quenched with sodium sulfite. Then the pH was adjusted to 5.5. At the end of the brightening (60 min) the remaining 5 g of pulp was treated similarly. The consistency of the 5 g samples was brought back up to about 30% and the fines recycled twice.

Laboratory Brightening

The pulp (12 g OD weight) was chelated as already explained. Four grams dry weight of pulp was removed for preparation of a pre-bleached handsheet. The pulp was concentrated to 30% consistency prior to bleaching. Each sample of 8 g dry weight red cedar CTMP was placed in a polyethylene bag. The bleaching liquor (0.2M H_2O_2, 4% Na_2SiO_3, 0.05% $MgSO_4$, and pH = 11.5) was mixed into the chelated pulp samples at room temperature at a 10% consistency. The mixture was allowed to react at 80°C for up to 1 h in a water bath. The pulp was then given a 1% water wash, the pH was adjusted to 5.5, and the pulp subsequently filtered. Two brightness handsheets were made (4 g each). For the constant pH and peroxide brightening run, peroxide and alkali were monitored every 2 to 5 min and the requisite amounts of sodium hydroxide and/or hydrogen peroxide were added, with mixing, in order to maintain their value as the reaction progressed.

Analytical Methods

The peroxide concentration was determined by titration with 0.1 N sodium thiosulphate to a colorless endpoint, after adding deionized water (50 mL), 10% sulfuric acid (10 mL), peroxide solution (1 mL), 10% potassium iodide (2 mL), 10% ammonium molybdate (3 drops), and 0.5% starch (10 drops), to a 300 mL Erlenmeyer flask. The peroxide concentration for bleaching was done in triplicate. Residual peroxide was determined in the same way, except that the 1 mL of hydrogen peroxide solution was replaced with 25 mL of filtrate after bleaching.

Handsheets and Brightness

Handsheets (4 g each) were prepared according to CPPA standard C.5 and optical handsheets were prepared at a basis weights in the range of 20 to 40 g/m^2. The basis weights of the optically thin handsheets were determined individually by measuring the OD weight of a known area.

The ISO brightness was determined using a Technibrite TB-1C instrument (Technidyne, New Albany, Indiana, USA). Diffuse reflectance UV-visible spectra were collected on a Varian Cary 1E spectrophotometer equipped with an integrating sphere and corrected according to manufacturer procedures.

RESULTS AND DISCUSSION

Results

A chemithermomechanical pulp (CTMP) was prepared on a pilot scale by sulfite pre-treatment of western red cedar chips followed by refining under pressure at a specific refining energy of 6.6 MJ/kg. The resulting CTMP had a freeness (CSF) of 276 ml and a brightness of 23% ISO. This pulp was used for all the peroxide brightening trials.

As in previous work with mechanical pulps from other species,[12,13] it was our hypothesis that the reaction of hydrogen peroxide with chromophores in western red cedar would show dependence on the concentration of chromophores in the pulp, and the concentration of alkali and hydrogen peroxide in the surrounding liquid phase. Thus, the reaction rate could be modeled by the following equation:

$$-\frac{dC_k}{dt} = k[\mathrm{H_2O_2}]^a[\mathrm{OH^-}]^b C_k^n \tag{1}$$

where $[\mathrm{H_2O_2}]$ = total peroxide concentration, $[\mathrm{OH^-}]$ = caustic concentration, a, b, n = reaction orders, C_k = concentration of chromphores (Kubelka-Munk absorption coefficient), and k = brightening rate constant.

Under constant reagent concentrations (hydrogen peroxide and caustic) Eq. (1) can be rewritten as:

$$-\frac{dC_k}{dt} = k_{obs} C_k^n \tag{2}$$

where the observed rate constant is $k_{obs} = k\ [\mathrm{H_2O_2}]^a[\mathrm{OH^-}]^b$.

Rearranging and integrating both sides of rate Eq. (2), gives the rate equation in a suitable form for analysis of the experimental data.

$$\frac{1}{C_k^{n-1}} = k_{obs}(n-1)t + C \tag{3}$$

where $C$is the constant of integration.

Peroxide brightening of western red cedar was performed at low consistency (1%) with constant pH and peroxide concentrations at temperatures of 40 to 80°C (Table 1). For each trial, 5-gram samples were drawn at 5, 10, 20, 30, and 60 min. From the 5 g removed, one thick handsheet (4 g) and one low basis weight handsheet (~0.3 g) were prepared. The optical data from both the thick and thin handsheets were used to calculate absorption coefficients according to the equations developed by Schmidt and Heitner.[14] The scattering coefficient (s) was determined at wavelengths above 600 nm and assumed to be constant throughout the UV-Visible spectrum.[15] Generally, the scattering coefficient was found to be around 42 m^2/kg for all samples at 700 nm. The scattering coefficient was found to be the same after alkaline peroxide brightening, consistent with previous work on peroxide brightening of TMP from radiata pine and spruce.[16,17] Absorption coefficients were determined at three wavelengths (357, 457, and 550 nm) corresponding to previously determined absorption maxima in the diffuse reflectance UV.[11]

Reaction Orders

Equation (3) is in a form such that the observed absorption coefficient (C_k) can be plotted against time and the reaction order n and rate constant k_{obs} can be evaluated. The reaction rate order n in Eq. (3) was solved graphically. The best value for n being the one that gave the maximum value of the correlation coefficient r^2 in the linear regression fit. Once linearization of the plots was achieved, k_{obs} was extracted from the slopes. Typical plots of Eq. (3), at the four experimental temperatures, are shown in Figure 1.

The reaction orders a and b can be determined from log plots of k_{obs} versus peroxide or caustic concentration respectively in trials where the concentration

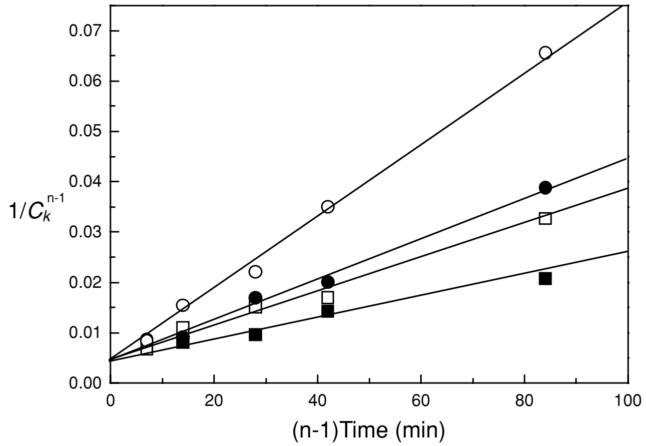

Figure 1. Typical fit of experimental brightening data to Eq. (3). Data shown is for trials 7 to 10 (Trial 8 = ■, Trial 7 = □, Trial 10 = ●, Trial 9 = ○).

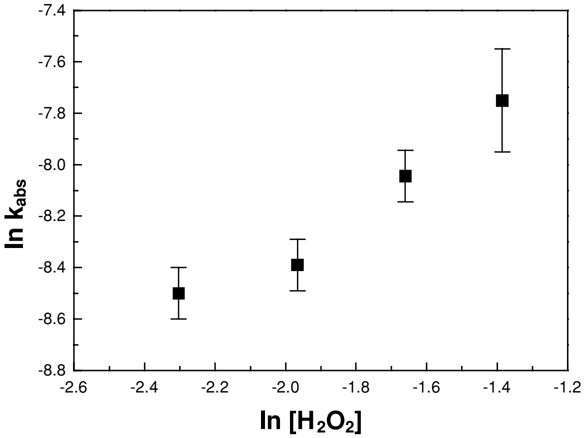

Figure 2. Determination of reaction order for peroxide brightening at 457 nm.

of the second component is held constant.

$$k_{obs} = k[\mathrm{H_2O_2}]^a[\mathrm{OH^-}]^b \tag{4}$$

$$\ln k_{obs} = a\ln[\mathrm{H_2O_2}] + b\ln[\mathrm{OH^-}] + \ln k \tag{5}$$

From the last equation, a plot of lnk_{obs} versus natural log of peroxide (or caustic) concentrations will give a slope equal to a (or b). Figure 2 shows the plot for the evaluation of the peroxide reaction order where the slope gave a value of 1.1 for a.

Temperature Dependence

The temperature dependence for the peroxide brightening kinetics was evaluated using the Arrhenius equation.

$$\ln k_{obs} = -\frac{E_a}{RT} + \ln A \tag{6}$$

whereE_a = energy of activation, T = temperature in degrees Kelvin,R = the gas constant, and A = a constant.

The kinetics of chromophore removal during the peroxide brightening was followed at the three predetermined wavelengths of 357, 457, and 550 nm and analyzed according to the equations discussed earlier. Table 2 gives the results for western red cedar CTMP and, in Table 3, the data for kinetics of western red cedar brightening (457 nm monitor wavelength) is compared with data on other mechanical pulps from the literature.

Table 2. Western red cedar CTMP alkaline peroxide brightening reaction rate orders and activation energies

$\lambda_{\max}$ nm	k_{obs} (10^{-3})	n	a	b	E_a (kJ/mole)
550	—	2.4 ± 0.2	1.0 ± 0.2	0.30 ± 0.08	41 ± 1
457	3.2 ± 0.3[1]	2.4 ± 0.2	1.1 ± 0.2	0.23 ± 0.04	33 ± 1
352	—	5.0 ± 0.5	1.1 ± 0.4	0.34 ± 0.04	53 ± 5

[1] Trial 4 conditions; Table 1.

Discussion

The general assumption in chemical kinetics studies is that the disappearance of reactants and/or the formation of products can be directly monitored, without interference, to obtain meaningful kinetic and thermodynamic data. This data can be used to develop process models for brightening and can also be used to help elucidate the reaction mechanism. In the case of pulp brightening kinetics it is difficult to directly monitor the individual reactions involved because of the complexity of the substrate.

The available techniques for monitoring brightening kinetics, brightness absorption at 457 nm, and diffuse reflectance UV-visible (DRUV) spectroscopy are limited by the fact that the UV-visible absorption bands for individual chromophores are broad and extensively overlapped, making it very difficult to follow the fate of a single entity. This was noted by Schmidt and Heitner,[14] who recommended following as much of the UV-visible spectrum as possible to help isolate the behavior of the individual chromophores.

In previous work,[11] we treated western red cedar mechanical pulp with borohydride, peroxide, and by acetylation and monitored the changes in both the UV-visible and diffuse reflectance infra-red spectra. This allowed us to identify three main components, with different absorption maxima in the UV-visible spectra, which contributed to the color in western red cedar. These

Table 3. Summary of alkaline peroxide brightening reaction rate orders for various mechanical pulps

Species/Pulp type	n	a	b	E_a (kJ/mol)
Spruce/GWD[13]	5.0	1.0	0.3	72
Spruce/GWD[20]	4.5–5.0	1.0	0.38–0.44	43–68
Spruce/TMP[20]	4.5–5.0	1.0	0.43–0.48	44–47
Radiata/TMP[16]	4.8	1.2	0.25	—
Red cedar/CTMP*	2.4	1.1	0.23	33

*This work.

colored components were coniferyl aldehyde ($\lambda_{\max} \sim 357$ nm) and two *ortho*-quinones ($\lambda_{\max} \sim 450$ nm and 550 nm). These three absorption maxima were monitored separately during the peroxide brightening in an attempt to obtain kinetic data for each of the components.

Effect of Hydrogen Peroxide Concentration on Brightening Rate

A typical plot of Eq. (5) at various pseudo-constant peroxide loadings, pH 10 and 55°C, is shown in Figure 2. The plots for all three chromophores gave reasonably good linear lines with slopes (a) between 1.0 to 1.1 (Table 2). These results indicate that a single peroxide molecule was involved in brightening each chromophore. However, we noted that the low peroxide loading point, when following the 357 nm and 457 nm monitors at low temperature, was always slightly above a line drawn through the other points. This slight variation was not outside the error bars (a straight could be drawn through all four points) but the observation hinted at a change in the brightening kinetics as the reaction progressed through its early stages. To ascertain whether this observation was a real phenomena or not, the details of DRUV spectra from the low temperature trials were inspected. At low peroxide concentrations and temperatures the band at 357 nm displayed a brightening latency time of about 10 minutes whereas the band in the visible region, the *ortho*-quinones, was apparently immediately brightened. This corresponds to a previously reported time delay of approximately 10 minutes for diffusion of alkaline peroxide into the fiber wall[18,19] and suggests an accessibility issue where the coniferyl aldehyde is less accessible than the other chromophores. At higher temperatures and/or peroxide concentrations, this time lag was not observed.

Effect of Alkali on Brightening Rate

The determined values for b, the alkali dependence of the brightening kinetics, of around 0.3 (Table 2), are lower than those reported for spruce mechanical pulps[13,20] but similar to that reported for radiata pine TMP,[16] as seen in Table 3. The reaction order b is not directly related to the brightening reaction. The main role of hydroxyl anions is to ionize hydrogen peroxide and not to react with the chromophores. Thus, the value of b does not have any easily identifiable physical significance.

Effect of Chromophores Concentration on Brightening Rate

For alkaline peroxide brightening, as monitored at the standard brightness wavelength of 457 nm, the best optimized linear line (Figure 1) gave values for the reaction order with respect to chromophores (n) of 2.4 ± 0.2. This value was valid for all peroxide concentration, pHs, and temperatures. This value of 2.4 was lower than found in other studies on alkaline peroxide brightening of mechanical pulps where the order with respect to chromophore concentration had a value of 5.[13,16] The reaction order *n* monitored at 550 nm was 2.4, the same as that determined at 457 nm (Table 2). The value of *n* at 357 nm was 5, about twice that found for the 457 and 550 nm monitors (Table 2). The apparent wavelength dependence of the reaction order *n* and the difference between the reaction order determined at 457 nm for western red cedar and other species (Table 3) requires an explanation.

Axegård et al.[12] pointed out that the major flaw in following brightening kinetics was the limitation of following brightness kinetics at a single wavelength. As eluded to earlier, UV-visible absorption bands are broad and extensively overlapped, thus the brightening kinetics follows the kinetics of several chromophores simultaneously. This complicates the brightening kinetics and the reaction order *n* becomes a function of several independent brightening reactions. Axegård et al. illustrated this point by mathematically simulating the brightening kinetics of three chromophores, with different reaction rates. The simulation showed that a reaction order around 5 could arise from three individual reactions each having a reaction order of 1. Similarly, if only two chromophores were being monitored during brightening, the overall reaction order would drop from 5 to 2–3.

From the aforementioned discussion, the results in Table 2 can be rationalized, and the wavelength dependence of the reaction order *n* can be explained as the follows. The 357 nm monitor is influenced by the presence of a minimum of three independent chromophores, one of which is coniferyl aldehyde. The identity of the remaining chromophores monitored at 357 nm is currently unknown but the 300–400 nm region can be a host for a large variety of chromophores[21] such as aryl ketones ($\lambda_{max} \sim 310$ nm) and stilbenes ($\lambda_{max} \sim 360$ nm). The 457 nm and 550 nm monitors are following the kinetics of the two *ortho*-quinones, which dominate the 400–600 nm visible spectrum. At these wavelengths, changes in weaker absorbances such as found in other species cannot be detected as they are overwhelmed by the intense quinone absorbances.

Temperature Dependence

The temperature dependence of the observed rate constants was quantified according to the Arrhenius equation and the results are given in Table 2. Excellent Arrhenius plots were observed that were wavelength dependent. The wavelength dependency is due to the fact that each kinetic monitoring wavelength is, to a large extent, following the reaction of a different chromophore. For the 457 nm monitor the calculated activation energy was 33 kJ/mole, which was lower than expected, based on studies on other softwood species, where the activation energies are above 40 kJ/ mole (Table 3). The low energy of activation for the 457 nm monitor indicates that the brightening rate of western red cedar CTMP does not increase with temperature as rapidly as with other mechanical pulps.

It is interesting to note that even though the reaction orders n, a, and b are similar at the 457 and 550 nm monitors, the energy of activation is not. This is consistent with the notion that different chromophores predominate at each wavelength.

Application of Kinetic Equations to Practical Bleaching Situations

Normal peroxide brightening is conducted under conditions significantly different to those used in the kinetic experiments. The consistency is higher, the peroxide charge on pulp is lower, and the concentration of peroxide and pH vary as brightening proceeds. To test the ability of the kinetic parameters to predict the behavior under practical conditions, western red cedar CTMP pulp was brightened at the higher consistency of 10% (80°C, pH 11.5, 0.2M, or 6% peroxide) under two sets of conditions. In the first, the pH and peroxide concentration were maintained at approximately their starting levels by monitoring their values every 2 to 5 min, then mixing in the requisite amount of peroxide and/or sodium hydroxide. In the second, the pH and peroxide concentration were allowed to change as the reaction proceeded.

The data was analyzed using the following equation, which is obtained by rearrangement of Eq. (1) and insertion of the previously determined reaction orders:

$$\frac{1}{C_k} \approx k_{obs}[\mathrm{H_2O_2}]^{1.1}[\mathrm{OH^-}]^{0.25}t + \frac{1}{C_{k,o}} \tag{7}$$

where $C_{k,o}$ is the absorption coefficient at zero time and t is the time in minutes.

The results from the data obtained at constant pH and peroxide concentration were used to obtain a value for k_{obs}valid at 10% consistency. This value of k_{obs} was then used to fit the data for the trial where both peroxide and pH were allowed to vary. An iterative process was used to account for the changing peroxide and pH levels. In this process, the pH and peroxide levels were monitored approximately every 2 min. The new values being substituted into the equation to predict the following brightness increase.

As seen in Figure 3, there was a reasonable fit of predicted and observed values of brightness for the data at constant pH and peroxide concentration, with brightness values reaching 52% ISO after 1 h at 80°C. The data and model indicate that the brightness will continue to increase with time. The model predicts that a brightness of 62% ISO would be achieved after 3 h under these conditions. The brightness predictions from the model, for the trial in which

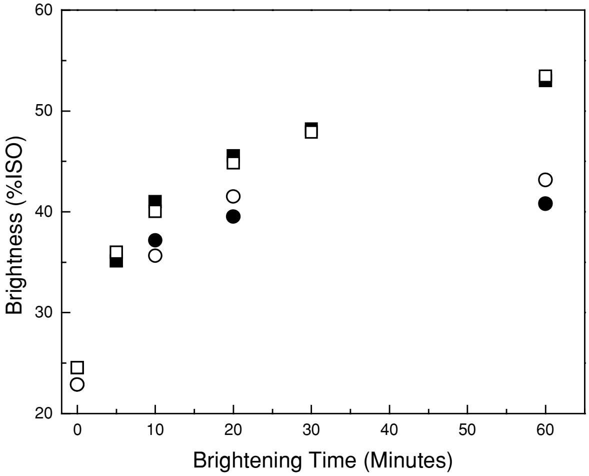

Figure 3. Laboratory brightening ([H_2O_2] = 0.2M, pH = 11.5, 80°C and 10% cs) and simulated brightening of western red cedar CTMP. Squares represent brightening at constant peroxide and pH, circles represent no addition of chemicals during brightening (experimental data closed points; simulated data open points).

the peroxide concentration and pH were allowed to vary, are not quite as good (Figure 3). However, the drop in brightness relative to the constant chemical trial is reasonably well reproduced with a plateau being observed around 42% ISO. This plateau is in the region of previously reported brightness limits for peroxide brightening of western red cedar mechanical pulps.[6–8] The good fits under both sets of conditions indicate that the reaction orders n, a, and b obtained from the kinetic study are valid under the conditions normally used in peroxide brightening of mechanical pulps. The reason for the low brightness value under the practical conditions was most likely related to the rapid decrease in peroxide concentration. After 1 h, the peroxide concentration was approximately 10% of the starting value. This drop in peroxide concentration could be a function of high peroxide consumption by the chromophores in the pulp, or more likely, the presence of moieties in the pulp that accelerate peroxide decomposition. A possible candidate for this is the presence of metal ions, especially Fe, which we have found to be abundant in the refined western red cedar and very difficult to remove by standard chelating procedures.[22]

The long time required to achieve a modest brightness under “ideal” conditions where peroxide concentration and alkalinity remain high is unusual. Chemimechanical pulps from other softwood species can reach brightness ceilings above 80% ISO during peroxide brightening. It appears that there are either some chromophores in western red cedar CTMP that are recalcitrant to peroxide brightening or, that during the brightening process recalcitrant chromophores are being generated. The latter observation is consistent with our previous finding that high alkalinity in the first stage of a two-stage peroxide brightening process of western red cedar, results in a much lower final brightness.[22]

CONCLUSIONS

The kinetics of peroxide brightening of western red cedar chemimechanical pulp can be monitored at the three absorption maxima, 357 nm, 457 nm, and 550 nm, in the UV-visible spectra using diffuse reflectance ultra violet spectroscopy. The reaction order with respect to hydrogen peroxide is around 1 at all three wavelengths, indicating that one molecule of hydrogen peroxide was involved in the rate determining step in the brightening reaction for each chromophore. The reaction order with respect to chromophores was approximately 2.4 at the higher wavelengths and 5 at 357 nm. This indicated that at the higher wavelengths, due to spectral overlap, the two *ortho*-quinones that absorb in this region were being monitored simultaneously. At 357 nm, the high reaction order of 5 indicates that at least two absorptions besides coniferyl aldehyde are also being monitored during the brightening. A reaction order of 5 with respect to chromophores is also found with other species at the standard brightness wavelength of 457 nm. The rate of brightening for western red cedar mechanical pulp is less sensitive to temperature than other softwood species.

The kinetic equations were successful in predicting brightness values obtained under practical conditions. A rapid decrease in peroxide concentration occurs under these conditions, probably caused by the high iron content of the pulps. In the presence of excess hydrogen peroxide, a brightness of 62% was predicted after 3 h bleaching at 80°C.

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