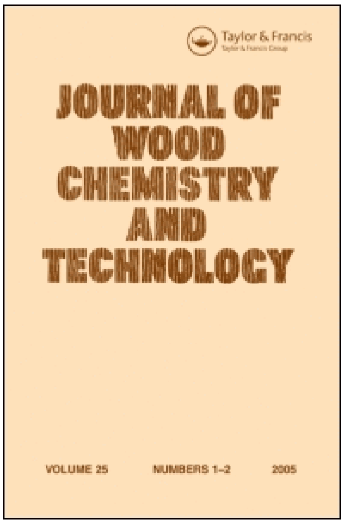

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

A Kinetic Model for Peracetic Acid Brightening of an Ozone Delignified Softwood Kraft Pulp

Z. Yuan[a]; Y. Ni[a]; A. R. P. van Heiningen[a]
[a] University of New Brunswick Fredericton, Canada

To cite this Article Yuan, Z. , Ni, Y. and van Heiningen, A. R. P.(1998) 'A Kinetic Model for Peracetic Acid Brightening of an Ozone Delignified Softwood Kraft Pulp', Journal of Wood Chemistry and Technology, 18: 1, 83 — 105
To link to this Article: DOI: 10.1080/02773819809350127
URL: http://dx.doi.org/10.1080/02773819809350127

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 18(1), 83-105 (1998)

A KINETIC MODEL FOR PERACETIC ACID BRIGHTENING OF AN OZONE DELIGNIFIED SOFTWOOD KRAFT PULP

Z. Yuan, Y. Ni, A.R.P. van Heiningen
University of New Brunswick
Fredericton, Canada, N.B., E3B 6C2

ABSTRACT

A kinetic model of peracetic acid brightening of a solvent-assisted ozone delignified pulp was developed. The model consists of three parallel and one consecutive reaction, and is based on reaction pathways reported for lignin model compounds with peracetic acid. An optimization search algorithm was used to find the kinetic parameters of the model. The kinetic model provides an adequate description of the disappearance rate of the chromophores in pulp at constant pH and peracetic acid concentration.

INTRODUCTION

Peracids have recently emerged as a potential alternative to chlorine containing chemicals for bleaching of chemical pulps.[1-13] It has been shown[1-2,13-16] that peracetic acid is a good delignifier when used in the prebleaching stages. In addition, peracetic acid (Pa) can also be applied in the later brightening stages as a substitute for chlorine dioxide.[2,8-10] We have shown[17] that an optimised Pa stage can effectively and selectively increase the brightness of a conventional softwood kraft pulp as part of a ZnEoPaEop bleaching sequence, in which Zn represents a solvent-assisted ozone stage. For example, a ZnEo delignified Hemlock kraft pulp with a brightness of 56.5%, kappa no. of 5.8 and viscosity of 28.4 mPa.s is bleached by the Pa stage to a brightness of 82.7% while maintaining a viscosity of 26.6 mPa.s with only about 1.5% peracetic acid by weight as peracetic acid, or 0.66% as hydrogen peroxide.[17] In the present paper, a kinetic model is developed for the peracetic acid brightening of a methanol-assisted ozone delignified and subsequently alkaline extracted (i.e. ZnE) pulp.

The constant condition method of kinetic experimentation in which the bleaching chemical concentrations, pH and temperature are held constant during the course of reaction was used in the present study. The kinetic data was obtained by following the light absorption coefficient of the bleached pulp. A similar experimental approach has been used to develop the kinetics of hydrogen peroxide bleaching of mechanical pulps[18-22] as well as that of chlorine dioxide bleaching of chemical pulps.[23,24]

The kinetic model presented in this paper consists of three parallel reactions and one consecutive reaction, all representing reaction pathways identified in lignin model compound studies with peracetic acid. First order reaction behaviours with respect to the chromophore and peracetic acid (or peracetate anion) concentrations were assumed. This approach is different from that of other studies[18-20,23,24] for which the prime objective was to develop an empirical equation based on its ability to represent the experimental data rather than on fundamental understanding of the detailed reaction mechanism.

The Hooke and Jeeves search algorithm[25] was used to find the kinetic parameters of the model by minimizing the sum of the squares of the differences between experimental and model predicted values of the light absorption coefficient. The initial values were estimated from the data at conditions when only one or two reactions dominated the brightening development.

EXPERIMENTAL

Equilibrium peracetic acid and ultra-pure grade NaOH were purchased from Aldrich (Milwaukee, USA). The equilibrium peracetic acid consists of about 34% w/w peracetic acid, 5% w/w hydrogen peroxide and 40% w/w acetic acid with the remainder being water. Distilled and deionized water was used in all experiments. Its metal ion content was below the detection limits of the atomic absorption (AA) spectroscopic analysis method used in this study.

An ozonated and alkaline extracted softwood kraft pulp of 8.43 m^2/kg absorption coefficient, 47.5% ISO brightness, 6.7 kappa number and 27.1 mPa·s viscosity was used in this study. Ozone bleaching (Zn) was carried out on a Hemlock kraft pulp impregnated with 70% methanol-water of pH 2, following an earlier described procedure.[26] The ozone charge was 1.6% (by weight on o.d. pulp) of which 90% was consumed. A subsequent alkali extraction stage (E) was performed at pH 11.0, 77°C, 10% pulp consistency for 45 minutes.

The peracetic acid bleaching experiments at constant peracetic acid concentration were carried out in a 1000 mL four-neck, well stirred, round-bottom flask immersed in a constant temperature bath. 3 grams o.d. pulp was used in each experiment and the pulp consistency was 0.3%. The pulp slurry was preheated to the desired temperature. A suitable amount of NaOH was then added to adjust pH to the desired level. Subsequently, the required amount of peracetic acid solution was added to initiate the bleaching. The pH was kept constant with an automatic titrator by addition of 10 mol/L NaOH. Preliminary bleaching runs were conducted to determine the rate of peracetic acid consumption. Subsequently, the desired amount of peracetic acid was charged to the reaction mixture at regular time intervals to maintain a constant peracetic acid concentration. The maximum change in peracetic acid concentration was less than 10%. The bleaching reaction was quenched by injecting an excess amount of KI dissolved in dilute sulfuric acid. The pulp was immediately washed with deionized water, and two hand sheets were made according to Tappi test method T272 om-92.

The peracetic acid and hydrogen peroxide concentrations were determined following the iodometric method developed by Greenspan and Mackellar.[27] The pulp brightness was determined following TAPPI method

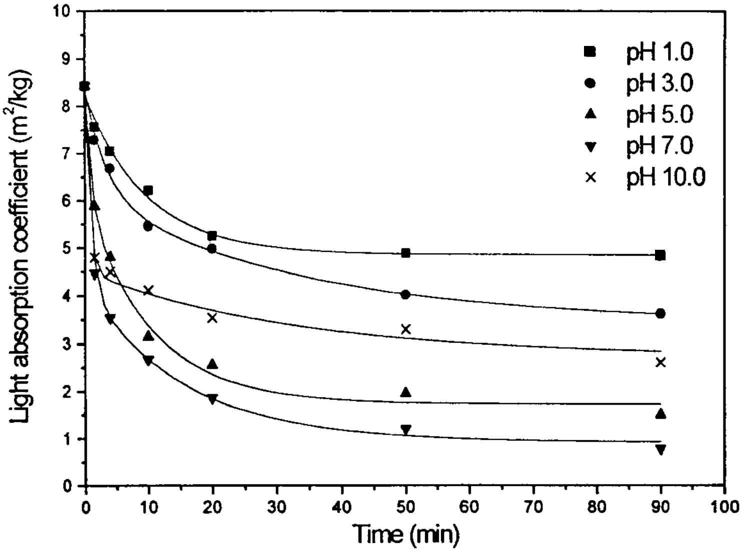

FIGURE 1. The effect of pH on the light absorption coefficient during the Pa brightening of ozone delignified softwood kraft pulp (50°C, [CH_3CO_3H] of 0.0493 mol/L)

T452 om-92. The light absorption coefficient was determined on a Technibrite Model TB-1 at 457nm. The viscosity and kappa number were determined in accordance with T230 om-89 and T236 cm-85 respectively.

RESULTS AND DISCUSSION

Since the light absorption coefficient of pulp is directly proportional to its chromophore concentration, the kinetics of peracetic acid brightening are described in terms of the rate change in the light absorption coefficient. Figure 1 shows the results obtained at different pHs but a constant peracetic acid concentration of 0.0493 mol/L and temperature of 50°C. It is evident that the light absorption coefficient decreases rapidly at the beginning, but that the decrease becomes increasingly slower as the reaction continues. A similar

TABLE 1.
The Development of the Light Absorption Coefficient at pH 6.0, 50°C and Different Peracetic Acid Concentrations

Time (min)	C_k (m^2/kg) at different peracetic acid concentrations		
	[Pa]: 0.0329 mol/L	[Pa]: 0.0493 mol/L	[Pa]: 0.0658 mol/L
0	8.43	8.43	8.43
1.5	5.10	4.80	4.47
4.0	4.44	4.08	3.66
10.0	3.57	3.21	2.79
20.0	2.58	2.34	2.13
50.0	2.07	1.80	1.53
90.0	1.83	1.53	1.23

behaviour has been observed for chlorine dioxide bleaching of chemical pulps and hydrogen peroxide bleaching of mechanical pulps.[18-24] As in these two other cases, this pattern could be explained by large differences in reactivity of the different chromophore structures.

It is noted that pH has a significant effect on both the chromophore disappearance rate and the final degree of chromophore removal. When the pH increases from 1 to 7, both of the above two parameters increase. However, as the pH increases further from 7 to 10, the initial chromophore disappearance rate is unchanged while the final degree of chromophore removal is reduced. These results are consistent with the general knowledge that the optimum pH of a peracetic acid brightening stage is in the neutral range.[8,14,28]

The development of the light absorption coefficient at pH 6.0 and different peracetic acid concentrations varying from 0.0329 to 0.0658 mol/L was also determined. The results are listed in Table 1. It shows that the chromophore disappearance rate and the final degree of chromophore removal are increased at a higher peracetic acid concentration. The results listed in Table 1 as well as those in Figure 1 form the data base for the determination of the kinetic parameters during peracetic acid brightening of the ZnE pulp.

Development of the Kinetic Model

Typical chromophoric structures in pulps include conjugated lignin macromolecules, α-carbonyl aromatic moieties and quinones.[29-30] The oxidation of lignin-like material by peracetic acid has been studied, mostly with model compounds.[29-38] The overall reaction pathways which occur during peracetic acid bleaching of wood pulps can be summarized by the following three general categories:

1. Hydroxylation of the aromatic rings of lignin by electrophilic substitution, resulting in the formation of hydroquinones.[30-34] The hydroquinones can either be destroyed to colourless water soluble products via electrophilic ring opening[30,31] or be further oxidized to conjugated quinones, which represent another chromophoric structure.[31-34] Kawamoto et al.[31] studied the oxidation of biphenyl lignin model compounds with peracetic acid at pH 5.5. They found that highly conjugated quinones were formed and that further destruction of these conjugated quinones was a relatively slow process. These highly conjugated quinones may be formed by condensation of quinonoid intermediates via a Diels-Alder mechanism.[39]
2. Conjugated quinones, both originally present, and formed from Route 1 above can be further oxidized to usually colourless and water soluble carboxylic acids via the Baeyer-Villiger reaction.[31-33]
3. Lignin structures containing an α-carbonyl group are oxidized via the Baeyer-Villiger reaction.[35-38] It has been found[35] that esters and their hydrolysis products were formed during the peracetic acid oxidation of α-carbonyl containing lignin model compounds. It was also found that a ketone is somewhat less reactive than an aldehyde. For example,

acetoguaiacone is significantly less reactive than vanillin due to the methyl substituent on the carbonyl carbon which sterically hinders the Baeyer-Villiger oxidation and/or retards nucleophilic attack by peracetic acid or peracetate anion. The etherification of a phenolic hydroxyl group or the presence of an extra methoxyl in the aromatic nucleus appears to have little or no influence on the reaction rate.[35]

It is important to point out that depending on the process conditions both nucleophilic and electrophilic mechanisms may contribute to the brightness increase during peracetic acid treatment. Peracetic acid (CH_3CO_3H) is a strong electrophile.[29,30,34,39] When pH is in the range of 1 to 6, peracetic acid, rather than peracetate anion ($CH_3CO_3^-$) is the dominant species (the pKa of peracetic acid is 8.2). Therefore, electrophilic attack is the main mechanism. When the pH is substantially higher than 8.2, the strongly nucleophilic peracetate anion ($CH_3CO_3^-$)[33,35,40-42] is the dominant species. As a result, a nucleophilic attack is expected to be the main reaction mechanism at high pH. It was established that hydroxylation of the aromatic rings proceeds via the electrophilic mechanism,[30-34] while the Baeyer-Villiger reaction takes place through a nucleophilic attack.[35-38] Because of these facts, it is understandable that the best brightening is obtained at a neutral pH range where both peracetic acid and peracetate anion are present in significant quantities.

In principle, the Baeyer-Villiger oxidation could take place at general acidic conditions. However, experimental results show that a high concentration of strong acid is required. For example, it was reported[43-46] that high concentrations of sulfuric acid and perchloric acid catalyse the Baeyer-Villiger reaction. However, in the absence of a high concentration of strong acid, the Baeyer-Villiger oxidation is expected to be slow under acidic conditions due to the low nucleophilicity of the undissociated peracid. This is supported by the results that the oxidation of benzophenone by peracetic acid in glacial acetic acid proceeds very slowly and that the addition of concentrated sulfuric acid greatly increases the reaction rate.[44] Sarkanen and Suzuki[47] found that the amount of

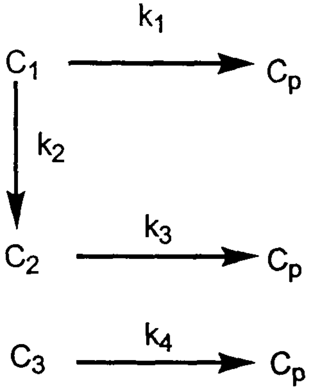

FIGURE 2. The proposed kinetic model for peracetic acid brightening of ozone delignified softwood kraft pulp

side-chain oxidation via the Baeyer-Villiger oxidation remains small at a low pH when they treated Douglas-fir meal with 10% peracetic acid in an aqueous solution. Similarly, Ishikawa et al.[37] treated acetoguaiacone with 8% peracetic acid (as weight percent on lignin model compound) at 35°C and found that the oxidation of acetoguaiacone was quite slow. However, at a high peracetic acid concentration, high temperature, and an extended reaction time, the Baeyer-Villiger reaction may account for part of the substrate consumed, as was observed by Nimz and Schwind.[35] Because of these results, it follows that peracetate anion, not peracetic acid, is mainly responsible for the Baeyer-Villiger oxidation in the system we studied.

Based on these identified reaction pathways, the kinetic model shown in Figure 2 is proposed for peracetic acid brightening of ozone delignified softwood kraft pulp.

The model in Figure 2 shows that the chromophoric lignin macromolecule C_1, is electrophilically attacked by peracetic acid CH_3CO_3H via the hydroxylation route, leading to the formation of either colourless products (Cp) or conjugated quinones (C_2), as discussed previously. Therefore, C_1 is consumed in two competitive reactions, with k_1 and k_2 as their rate constants respectively. The conjugated quinones, C_2, both the newly formed and those originally present, are oxidized to water soluble carboxylic acids via the Baeyer-Villiger reaction by peracetate anion $CH_3CO_3^-$, represented by the rate constant k_3. Finally, the α-carbonyl containing chromophores, C_3, are destroyed via the Baeyer-Villiger mechanism by $CH_3CO_3^-$, with a rate constant of k_4.

It is assumed that the reactions discussed in Figure 2 are first order with respect to the peracetic acid concentration and the chromophore concentration. This hypothesis is supported by the results of McDonough[33] that the kinetics of the oxidation of creosol by peracetic acid is first order both in peracetic acid and creosol concentrations. Therefore, based on the model described in Figure 2, the following rate equations of peracetic acid brightening are obtained:

$$-\frac{dC_1}{dt} = (k_1 + k_2)C_1[CH_3CO_3H] \tag{1}$$

$$-\frac{dC_2}{dt} = k_3C_2[CH_3CO_3^-] - k_2C_1[CH_3CO_3H] \tag{2}$$

$$-\frac{dC_3}{dt} = k_4C_3[CH_3CO_3^-] \tag{3}$$

Peracetic acid concentration, $[CH_3CO_3H]$, and peracetate anion concentration, $[CH_3CO_3^-]$, are related to the total titrable peracetic acid concentration $[CH_3CO_3H]_t$ as in Equations (4) and (5), with M being the ratio of the proton concentration to the dissociation constant of peracetic acid, i.e. $[H^+]/K_a$.

$$[CH_3CO_3^-] = [CH_3CO_3H]_t/(1+M) \tag{4}$$

$$[CH_3CO_3H] = M\,[CH_3CO_3H]_t/(1+M) \tag{5}$$

Since the concentration of peracetic acid, $[CH_3CO_3H]$, and that of peracetate anion, $[CH_3CO_3^-]$, are constant at a fixed pH and temperature, Equations (1) to (3) can be simplified as:

$$-\frac{dC_1}{dt} = (k_1' + k_2')C_1 \tag{6}$$

$$-\frac{dC_2}{dt} = k_3'C_2 - k_2'C_1 \tag{7}$$

$$-\frac{dC_3}{dt} = k_4'C_3 \tag{8}$$

where

$$k_1' = k_1\frac{M}{1+M}[CH_3CO_3H]_t \tag{9}$$

$$k_2' = k_2\frac{M}{1+M}[CH_3CO_3H]_t \tag{10}$$

$$k_3' = k_3\frac{1}{1+M}[CH_3CO_3H]_t \tag{11}$$

$$k_4' = k_4\frac{1}{1+M}[CH_3CO_3H]_t \tag{12}$$

Equations (6) to (8) can be solved analytically as:

$$C_1 = C_{1i}e^{-(k_1+k_2)t} \tag{13}$$

$$C_2 = \frac{k_2'C_{1i}}{k_3'-k_2'-k_1'}e^{-(k_1+k_2)t} + \left[C_{2i} - \frac{k_2'C_{1i}}{k_3'-k_2'-k_1'}\right]e^{-k_3t} \tag{14}$$

$$C_3 = C_{3i}e^{-k_4t} \tag{15}$$

Also the sum of all the different chromophore concentrations at any time during the course of the peracetic acid treatment equals to the total chromophore concentration, C, which is known experimentally, i.e.

$$C = C_1 + C_2 + C_3 \tag{16}$$

With the knowledge of the disappearance rate of total chromophore concentration under different conditions, it is possible to determine the rate constants and the initial concentration of each of the three chromophores by an optimization technique which utilizes the Hooke and Jeeves search algorithm.[25] The same technique was applied to determine the kinetics of chlorination.[48,49]

Equations (13) to (15) show that there are seven unknown variables: k_1', k_2', k_3', k_4', C_{1i}, C_{2i} and C_{3i}. In order to start the search algorithm, it is needed to provide initial values for six of the variables, with the seventh being restricted by Equation (16).

Estimation of the Initial Values

Estimation of C_{3i} and k4

Figure 1 shows that the initial rate of the chromophore disappearance is strongly dependent on the pH. Since the concentration of peracetate anion increases dramatically while that of peracetic acid is essentially the same when the pH increases from 1 to 7, the higher initial reaction rate in this pH region must be related to the higher peracetate anion concentration. Since it has been shown that α-carbonyl compounds, represented by C_3, react easily with peracetate anion according to the Baeyer-Villiger mechanism,[35-38] while the oxidation of conjugated quinones proceed slowly in aqueous solutions,[31] it was assumed that in the initial phase the Baeyer-Villiger oxidation of α-carbonyl chromophoric structures is the dominant reaction.

In order to better quantify the initial reaction rate, further experiments were done to characterize the light absorption coefficient development during the first 4 minutes at pH 7.0 and 50°C. The results in Figure 3 suggest that the Baeyer-Villiger oxidation is very fast since the first data point obtained at 5 seconds, the shortest time possible with our experimental set-up, shows that the light absorption coefficient decreases rapidly from 8.43 to 5.25 m^2/kg. Therefore, the initial α-carbonyl group concentration, C_{3i}, was estimated as 2.88 m^2/kg from the difference of the initial total chromophores, C_i, of 8.43 m^2/kg and the sum of C_{1i} and C_{2i} of 5.55 m^2/kg estimated by extrapolating the initial four points in Figure 3 to zero time.

Only a rough estimate of the rate constant k_4' can be obtained from the data in Figure 3, because the reaction of the α-carbonyl chromophores with

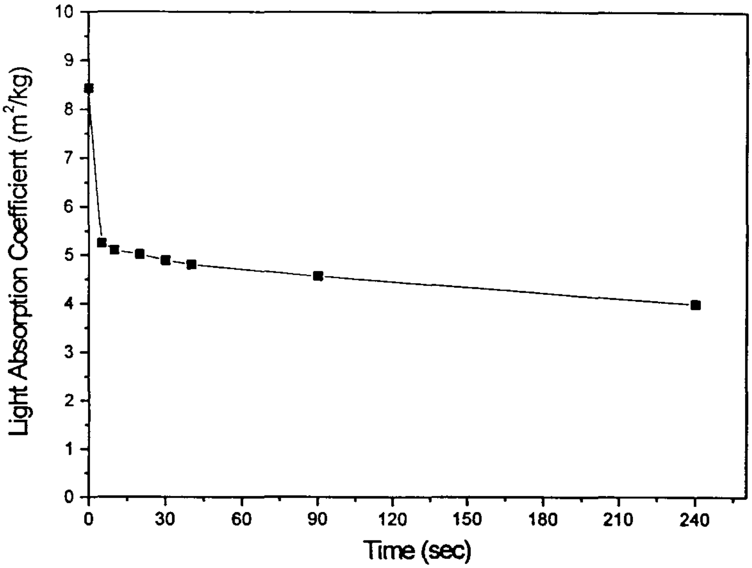

FIGURE 3. Estimation of C_{3i} and k_4 (50°C, pH 7.0, $[CH_3CO_3H]$ of 0.0493 mol/L)

peracetic anion appears to be essentially complete at the first data point of 5 seconds. However, in order to generate a first estimate of the initial value of k_4' for the optimization procedure it was assumed that 99% of the α-carbonyl chromophores initially present, C_{3i}, disappeared in the first five seconds. Following Equation (15), we estimated k_4' of 60 min^{-1}. Furthermore, we calculated that k_4 is approximately 3.33×10^2 L/mol·s, by taking into consideration of the pKa, pH and the total peracetic acid concentration. Since it is realized that the calculated value of k_4 of 3.33×10^2 L/mol·s is only a first estimate, the initial value of k_4 for the optimization procedure will be varied by two orders of magnitude around 3.33×10^2 L/mol·s in order to evaluate the sensitivity of the procedure to this initial guess value of k_4.

Estimation of C_{2i} and k_3

Since oxidation of both conjugated quinones, C_2, and α-carbonyl containing chromophores, C_3, at pH 1.0 is insignificant due to the very low peracetate anion concentration, the hydroxylation, which is achieved by peracetic acid and represented by reactions k_1 and k_2, can be considered as the only reaction pathway to remove chromophores at this pH. Figure 1 shows that the chromophore removal is negligible after 50 minutes of reaction at pH 1.0, so it is reasonable to assume that the hydroxylation reaction is completed within 50 minutes at this condition. Also because the actual concentration of peracetic acid is essentially the same when the pH is increased from 1.0 to 6.0, it is assumed that the hydroxylation reaction at pH 6.0 is also completed within 50 minutes. As discussed earlier, the Baeyer-Villiger oxidation of α-carbonyl containing chromophores is a fast reaction with k_4 being about 3.33×10^2 L/mol·s so that it takes less than one minute to complete this oxidation at pH 6.0. Based on the above analysis, it can thus be concluded that after 50 minutes at pH 6.0 the decrease in the light absorption coefficient is mainly due to the destruction of conjugated quinones, C_2, by reaction with peracetate anion, $CH_3CO_3^-$, i.e. Equations (6),(7) and (8) reduce to:

$$-\frac{dC_2}{dt} = k_3'C_2 \qquad (17)$$

Therefore, the initial concentration of conjugated quinones, C_{2i}, and the rate constant k_3' can be estimated by plotting lnC against time t at pH 6.0 for the data points obtained beyond 50 minutes. From this plot shown in Figure 4 it follows that C_{2i} is 1.71 m^2/kg and k_3' is 0.00145 min^{-1}. Substitution of k_3' to Equation (11) yields k_3 of 7.83×10^{-2} L/mol·s. With C_{3i} of 2.88 m^2/kg (shown in the previous section) and C_{2i} of 1.71 m^2/kg, the estimate for C_{1i} is calculated as 3.84 m^2/kg.

Estimation of k_1 and k_2

The values of k_1 and k_2 were estimated using the results obtained at pH 1.0, shown in Figure 1. Since the peracetate anion concentration, $[CH_3CO_3^-]$, is extremely low at pH 1.0, both of the Baeyer-Villiger pathways can be neglected,

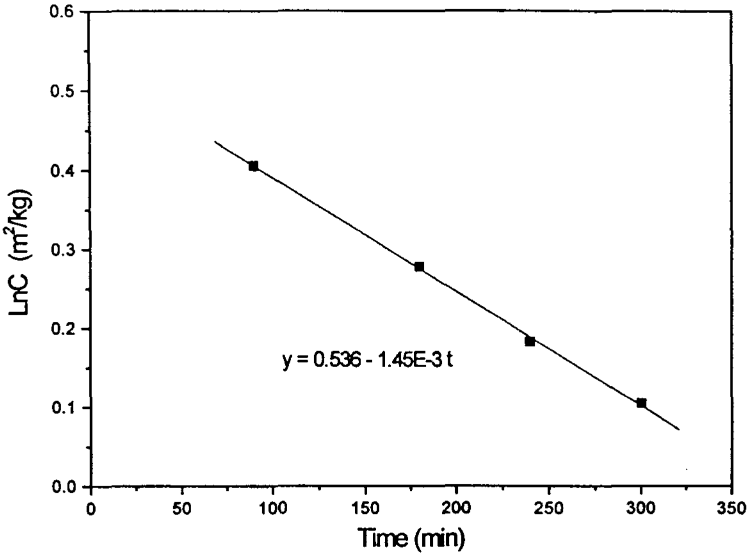

FIGURE 4. Estimation of C_{2i} and k_3 (50°C, pH 6.0, $[CH_3CO_3H]$ of 0.0493 mol/L)

as discussed earlier. Therefore, both k_3' and k_4' will be set equal to zero at pH 1.0. As a result, Equation (16) can be simplified to:

$$C = C_{2i} + C_{3i} + \frac{k_2'}{k_1' + k_2'} C_{1i} + \left[1 - \frac{k_2'}{k_1' + k_2'}\right] C_{1i} e^{-(k_1' + k_2')t} \tag{18}$$

An application of the exponential decay data fitting technique yields Equation (19) to model the data points at pH 1.0 in Figure 1 as:

$$C = 4.806 + 3.615\ e^{-0.106t} \tag{19}$$

From a comparison of Equations (18) and (19), it follows that:

$$k_1' + k_2' = 0.106 \tag{20}$$

and

$$\left[1 - \frac{k_2'}{k_1' + k_2'}\right] C_{1i} = 3.615 \tag{21}$$

By solving Equations (20) and (21), one obtains a k_1' of 0.100 min^{-1} and a k_2' of 0.0062 min^{-1}. Taking into consideration the pH and the total concentration of peracetic acid in Equations (9) and (10), k_1 and k_2 are estimated as 3.38×10^{-2} and 2.1×10^{-3} L/mol·s respectively.

Modelling Results

With the estimation of the initial values of C_{1i}, C_{2i}, C_{3i}, k_1, k_2, k_3 and k_4, it is now possible to determine the optimal value of these kinetic parameters using the data base shown in Figure 1 and Table 1 following the Hooke and Jeeves search algorithm.[25] The approach is to minimize the sum of squares of the difference between the experimental values of the total chromophore concentration and that of the model predictions. The procedure was considered converged when, for each data set at a fixed pH and peracetic acid concentration, the sum of squares changed by less than 0.1% between iterations. To ensure that the optimised set of parameters indeed represented the unique solution of the kinetic model for the present data, the most uncertain parameter, k_4, was varied by two orders of magnitude around the estimated value, while the other rate constants were varied by a factor of two. It was found that the values of the optimised parameters were independent of the variations in the initial guess values.

The optimized results are listed in Table 2. It shows that k_4 is much higher than the other rate constants, confirming that the oxidation of α-carbonyl containing chromophores, C_3, is a fast reaction. This is in agreement with the findings by McDonough[33] that acetoguaiacone reacts much faster than apocynol and vanillyl alcohol during peracetic acid treatment at a pH of 6 to 9. Table 2 also shows that k_3 is comparable to k_1, so their reaction rates largely depend on the concentrations of CH_3CO_3H and $CH_3CO_3^-$. Thus it is expected that the oxidation of conjugated quinones, C_2, proceeds slowly due to the lower concentration of $CH_3CO_3^-$ at a pH lower than 7.0, as was supported by Kawamoto et al.[31] who showed that further oxidation of the conjugated quinones

TABLE 2.
The Kinetic Parameters Obtained by the Hook and Jeeves Search Algorithm at 50°C for the Brightening of ZE Pulp

	Initial chromophore concentration (m^2/ kg)			Rate constants (L/mol·s)			
	C_{1i}	C_{2i}	C_{3i}	k_1	k_2	k_3	k_4
Estimated	3.84	1.71	2.88	3.38×10^{-2}	2.1×10^{-3}	7.83×10^{-2}	3.33×10^{2}
Optimized	3.78	1.62	3.03	4.03×10^{-2}	2.83×10^{-3}	5.55×10^{-2}	2.95×10^{-2}

formed via the hydroxylation pathway to colourless products is quite slow at pH 5.5.[31]

An example of a comparison between calculated and measured light absorption coefficients at pH 7.0 is given in Figure 5. It is apparent that the proposed kinetic model gives a good description of the development of the light absorption coefficient during peracetic acid brightening of the ozone delignified pulp used in this study.

With the optimized kinetic parameters, the concentration-time profiles of the three different chromophores, C_1, C_2, C_3 and the total chromophore concentration C was predicted at a pH of 3.0, 7.0 and 10.0. The results are plotted in Figures 6 to 8 respectively. At pH 3 in Figure 6 the destruction of chromophores C_1 is completed after about 50 minutes while around 40% of the α-carbonyl containing chromophores, C_3, are destroyed at 90 minutes. However, the concentration of the conjugated quinones, C_2, increases slightly over the course of the reaction. The behaviour of the C_3 chromophores is in agreement with the results by Nimz and Schwind[35] that about 42% acetoguaiacone is oxidized via the Baeyer-Villiger reaction at pH 3 and 60°C over a period of 60 minutes. At pH 7.0 in Figure 7, the oxidation of the α-carbonyl containing chromophores, C_3, is accomplished within a few seconds, while the C_1 chromophores are also removed within one hour. The degradation of conjugated

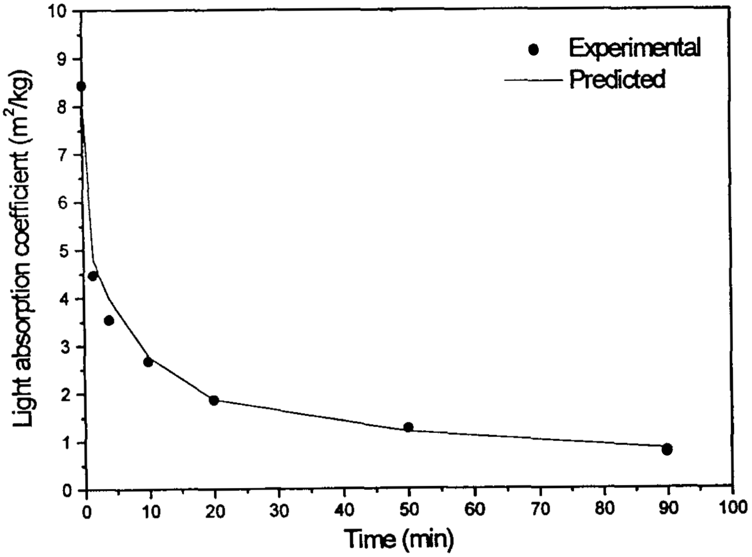

FIGURE 5. Comparison of model predictions and experimental results (50°C, pH 7.0, [CH_3CO_3H] of 0.0493 mol/L)

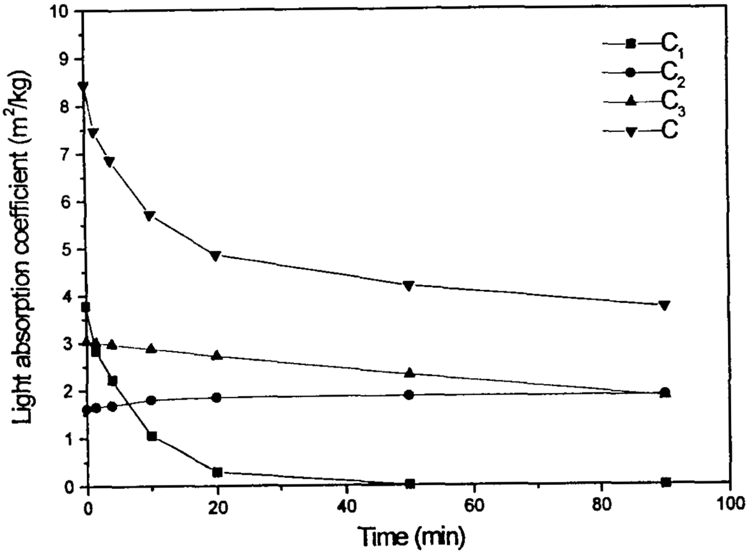

FIGURE 6. Predictions of the development of C_1, C_2, C_3 and C (50°C, pH 3.0, [CH_3CO_3H] of 0.0493 mol/L)

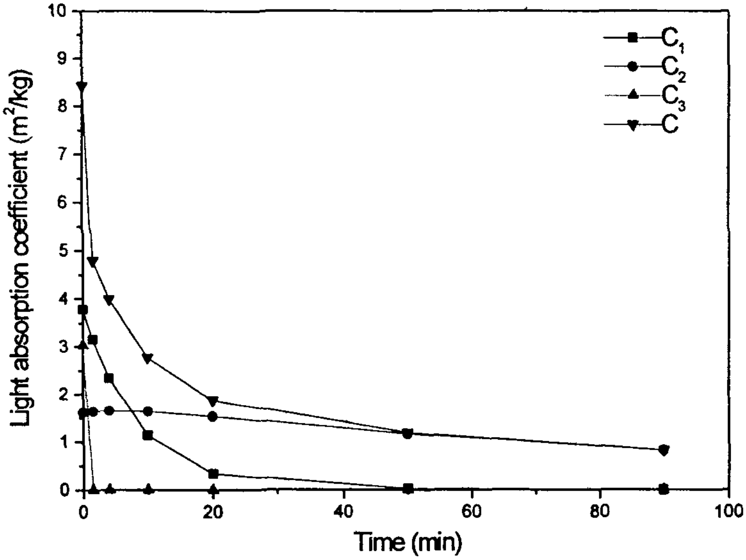

FIGURE 7. Predictions of the development of C_1, C_2, C_3 and C (50°C, pH 7.0, [CH_3CO_3H] of 0.0493 mol/L)

quinones, however, is still incomplete at 90 minutes at pH 7. At a higher pH of 10 in Figure 8, it can be seen that now the oxidation of conjugated quinones, C_2, is complete in almost 20 minutes. A higher pH favours the degradation of conjugated quinones relative to at pH 3 which is in agreement with the finding by Nimz and Schwind.[35] It can also be noticed that at pH 10 the destruction rate of chromophores C_1 is significantly reduced due to a much lower concentration of peracetic acid. Thus, although both quinones, C_2 and α-carbonyl containing chromophores, C_3, are efficiently removed at pH 10, the overall degree of chromophore removal is much less than that at pH 7.0 because the initial concentration of C_1 chromophores is larger than that of the C_2 chromophores. This explains the experimental fact that optimum brightness gain can be obtained at a neutral pH range.

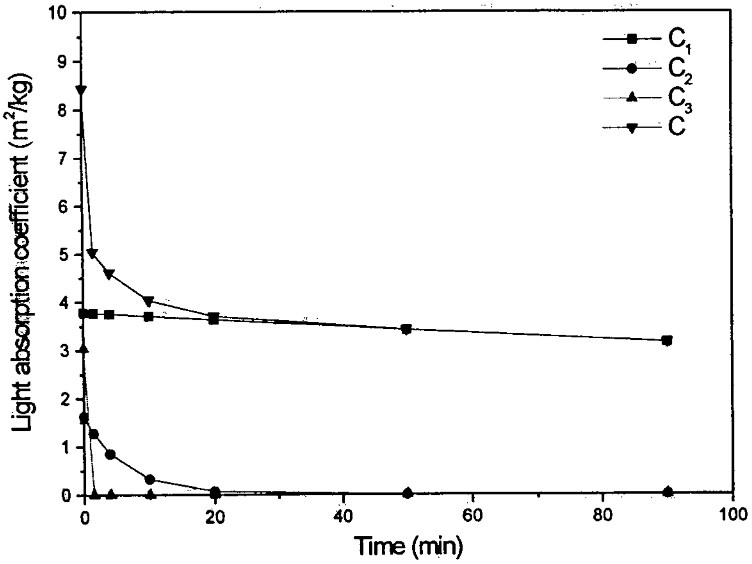

FIGURE 8. Predictions of the development of C_1, C_2, C_3 and C (50°C, pH 10.0, $[CH_3CO_3H]$ of 0.0493 mol/L)

CONCLUSIONS

Based on reaction pathways identified in literature, a kinetic model for peracetic acid brightening of a solvent-assisted ozone delignified pulp has been developed. The kinetic equations can adequately describe the development of the light absorption coefficient of pulp under conditions of constant pH and peracetic acid concentration. The model includes three parallel reactions, namely hydroxylation, oxidation of conjugated quinones, and oxidation of carbonyl containing lignin structures, which are responsible for the overall removal of chromophores, and thus for the decrease in the light absorption coefficient of the bleached pulp. The reaction rate of each of the three reactions is dependent on the pH during the peracetic acid treatment. At pH 3 only hydroxylation is significant. At pH 7, both the hydroxylation and oxidation of carbonyl containing lignin structures are complete, while only the conjugated quinones are remaining when the treatment is extended beyond 50 minutes at 50°C. A further increase in pH to 10.0 significantly retards the hydroxylation rate, which explains the smaller removal of chromophores at this pH as compared to that at pH 7.0.

ACKNOWLEDGMENT

The authors thank NSERC for financial support in the form of a Strategic Grant.

REFERENCES

1. R. T. Hill, P.B. Walsh, and J. A. Hollie, TAPPI 1992 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 1219.
2. J. R. Anderson, B. Amini, and W. Wilkinson, Preprints, the 81st CPPA Annual Meeting, Tech. Sect., CPPA, Montreal, 1995, p. B59.
3. J.Basta, L. Holtinger, P. Lundgren, H. Fasten, and R. Fredriksson, Proceedings, 1994 International Non-chlorine Bleaching Conference, Amelia Island, FL, sec. 11-3.
4. B.Amini and J. Webster, TAPPI 1994 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 371.
5. N. Liebergott, Proceedings, Preprints, the 81st CPPA Annual Meeting, Tech. Sect., CPPA, Montreal, 1995, p. B157.
6. J. Song, Ph.D thesis, North Caroline State University, USA, 1992.
7. E. L. Springer and J. D. McSweeny, Tappi J., 76(8):194 (1993).
8. N. Liebergott, Pulp & Paper Canada, 97(3):73 (1996).
9. N. Troughton, F. Desprez, and J. Devenyns, Proceedings, 1994 International Non-chlorine Bleaching Conference, Amelia Island, FL, sec. 10-1.
10. J. Devenyns, F. Desprez, and N. Troughton, TAPPI 1993 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 341.

11. B.Swan, Proceedings, 1996 International Non-chlorine Bleaching Conference, Hyatt Orlando, FL, sec. 13-2.

12. N. Nimmerfroh and H. U. Suss, Proceedings, 1996 International Non-chlorine Bleaching Conference, Hyatt Orlando, FL,sec. 5-4

13. C. W. Bailey and C. W. Dence, Tappi J., 49(1):9 (1966).

14. C. B. Christiansen and W. F. Parker, Preprint, TAPPI Annual Meeting, 1965, p132.

15. W. H. Rapson and C. B. Anderson, 1985 International Pulp Bleaching Conference, Quebec, 1985, p. 227.

16. G. Gellerstedt, Preprint, 1993 Workshop on Emerging Pulping and Chlorine-Free Bleaching Technology, Raleigh, N.C., March 3, 1993.

17 Z. Yuan, Ph.D thesis, Univ. of New Brunswick, Canada, 1997.

18. M. Lundqvist, Svensk Papperstidn., 82(1):16 (1979).

19. S. Moldenius and B. Sjogren, J. Wood Chem. Tech., 2(4):447 (1982).

20. R.W. Allison and K. L. Graham, JPPS, 15(4):J145 (1989).

21 P. Wright and J. Abbot, J. Wood Chem. Tech., 11(3): 349 (1991).

22. P. Wright, Y. Ginting, and J. Abbot, J. Wood Chem. Tech., 12(1):111(1992).

23. A. Teder and D. Tormund, Trans. Tech. Sect. CPPA, 3, 41 (1977).

24 U. Germgård and A. Teder, Trans. Tech. Sect., CPPA, 6, TR31(1980).

25. R. Hooke and T.A. Jeeves, J. Assoc. Comp. Mech., 8(2):212 (1961).

26 G. J. Kang, Y. Ni, and A. R. P. van Heiningen, Preprints, the 82nd CPPA Annual Meeting Preprints, Tech. Sect., CPPA, Montreal, 1996, p. B303.

27. F. P. Greenspan and D. G. Mackellar, Analy. Chem., 20(11):1061 (1948).

28. W. H. Rapson, Tappi J., 39(5):284 (1956).

29. H.M. Chang and G.G. Allan in Lignins, Edited by K. V. Sarkanen and C. H. Ludwig, p.459-462, Wiley Interscience, New York, 1971.

30. J. Boeseken and R. Engleberts, Proc. Acad. Sci. Amsterdam, 34:1292 (1931); 35:750 (1932).

31. H. Kawamoto, H. Chang, and H. Jameel, Proceeding, the 8th International Symp. on Wood and Pulping Chemistry, Helsinki, Finland, 1995, p.383.

32. G. Strumila and H. Rapson, Pulp & Paper Canada, 76(9):72 (1975).

33. T. J. M. McDonough, Ph.D Thesis, University of Toronto, Canada, 1972.

34. G.G. Henderson and R. Boyd, J. Chem. Soc., 97:1659 (1910).

35. H. H. Nimz and H. Schwind, Cellulose Chem. Technol., 13:35 (1979).

36. H. Hatakeyama, J. Nakano, and N. Migita, J. Chem. Soc. Japan, Ind. Chem. Sect., 68:972 (1965).

37. H. Ishikawa, T. Oki, and K. Ohkubo, J. Japan Tappi, 20, 435 (1966).

38. Y. Kinoshita, T. Oki, and H. Ishikawa, J. Japan. Wood Res. Soc., 13:319 (1967).

39. J. C. Farrand, Ph.D. Thesis, Institute of Paper Chemistry, Appleton, Wisconsin, USA, 1969.

40. W. P. Jencks and J. Carriuolo, J. Am. Chem. Soc., 82:1778 (1960).

41. C. H. Hassall, In Organic Reactions, Vol. 9, p.73, A. Roger (ed.), John Willey & Sons Ltd., New York, 1957.

42. S. Yasuhiko, In Organic Peroxides, p.437, W. Ando, (ed.), John Willey & Sons Ltd., New York, 1992.

43. J. E. Leffler, J. Org. Chem., 16:1785 (1951).

44. W. von E. Doering and L. Speers, J. Am. Chem. Soc., 72(12):5515 (1950).

45. S. L. Friess, J. Am. Chem. Soc., 71(7):2571 (1949).

46. R. E. Marker, E. Rohrmann, H. M. Crooks, E. L. Whittle, E. M. Jones, and D.L. Turner, J. Am. Chem. Soc., 62(2):525 (1940).

47. K. V. Sarkanen and J. Suzuki, Tappi J., 48(8):459 (1965).

48. J. Mackinnon, M. Eng. Thesis, McGill Univ., Canada, 1989.

49. Y. Ni, G. J. Kubes, and A.R.P. van Heiningen, JPPS, 21(1):J30 (1995).