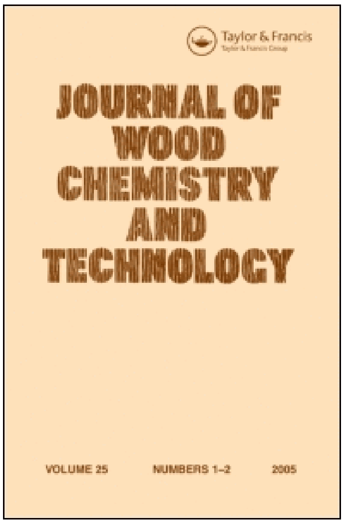

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# Kinetic Models for Peroxide Bleaching Under Alkaline Conditions. I. One and Two Chromophore Models

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# KINETIC MODELS FOR PEROXIDE BLEACHING UNDER ALKALINE CONDITIONS, PART 1. ONE AND TWO CHROMOPHORE MODELS.

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## ABSTRACT

Several kinetic models for alkaline peroxide bleaching of Eucalypt mechanical pulp have been examined. A previously reported kinetic model, developed to describe peroxide bleaching of softwoods, was found to be inadequate. The models proposed here assume two distinct categories of chromophores which are eliminated through first order processes, rather than the high orders for reaction processes suggested in previous kinetic analyses. Our model enables prediction of a maximum in the rate of bleaching in the range pH 11-12, whereas previous models imply that the rate of chromophore elimination increases continuously with hydroxide ion concentration.

## INTRODUCTION

Kinetic models for peroxide bleaching of mechanical pulps have received much less attention than many other processes involving reactions of lignin under alkaline conditions, such as oxygen bleaching[1,2] and alkaline pulping[3-5] for example. Moldenius and co-workers[6,7] have proposed a kinetic model based on studies of peroxide brightening of spruce pulps under conditions where the concentrations of reagents can be regarded as constant. In the present work, we have studied the kinetics of chromophore elimination during peroxide bleaching of a Eucalypt groundwood pulp. The results have been examined using the previously proposed kinetic model, and alternative models have also been examined.

## RESULTS AND DISCUSSION

In kinetic studies of bleaching involving lignin removal, the extent of reaction can be monitored by Kappa number measurements which determine the amount of residual lignin[10]. However, for bleaching of high yield pulps, such as with alkaline hydrogen peroxide, chromophoric groups are eliminated without delignification[11-13]. In order to study peroxide bleaching kinetics, the chromophore concentration must be monitored in some way. The Kubelka-Munk theory[14] predicts that the light absorption coefficient of a pulp (K) will be proportional to the concentration of chromophores at a fixed wavelength[8,10,15].

In this study, the effects of alkaline hydrogen peroxide on *E. regnans* were followed at 50°C by measuring changes in light absorption coefficient, while maintaining pH and peroxide concentration at constant levels during each experiment. These so called 'constant conditions' experiments are a well established technique for monitoring pulp bleaching kinetics[6-10,16]. Constant conditions are maintained by adding peroxide and alkali as they are consumed during the bleaching of a low consistency pulp. To enable comparison with other studies, light absorption coefficients were measured at a wavelength of 457 nm.

An example of the effects of peroxide concentration and reaction time on the rate of chromophore elimination, measured by the decrease in the light absorption coefficient (K), is shown in Figure 1 for bleaching at pH 10. This set of curves exhibits a rapid initial decrease in the light absorption coefficient, the rate of which depends on the concentration of peroxide. Following this initial phase, the rate decreases and appears to proceed at a rate which is independent of the peroxide concentration. It is worth noting that the peroxide bleaching chemistry of hardwood and softwood pulps will not be the same due to slight differences in their lignin structure which in turn will be reflected in bleaching kinetics. Although subtle differences in hardwood and softwood bleaching curves are evident, the general features observed for *E. regnans* in Figure 1 are consistent with those reported for constant pH peroxide bleaching studies using pulps prepared from northern hemisphere softwoods[6-9]. This would seem to indicate that differences between hardwood and softwood lignins do not strongly influence trends in kinetic behaviour.

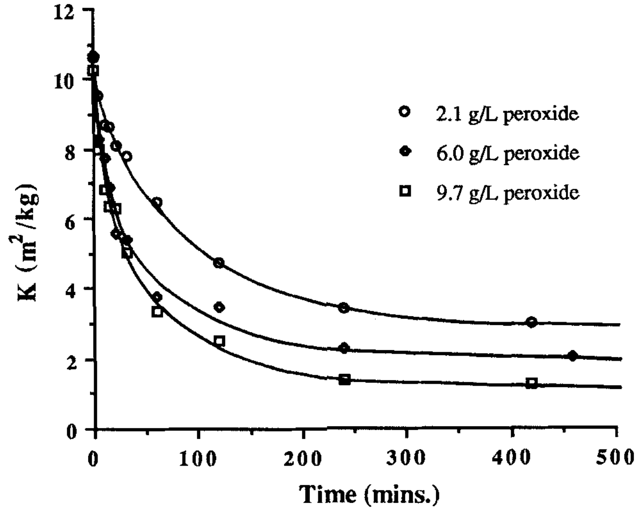


**Figure 1** : The effect of peroxide concentration on light absorption coefficient during bleaching (T = 50°C, pH 10).

## PEROXIDE BLEACHING MODELS

### Model I : Simple Empirical Expressions

Over the past decade there have been a number of attempts to formulate kinetic expressions which describe chromophore elimination during peroxide bleaching[6-10]. Using kinetic results from experiments at constant conditions, empirical expressions of the form

$$-\frac{d\,C_k}{dt} = k\,[OH^-]^a[H_2O_2]^b[C_k]^c \qquad (1)$$

have been formulated to describe the bleaching rate in terms of hydroxide, total peroxide and chromophore concentrations. Orders of reaction a, b, and c are determined experimentally and have been reported to have non-integer values.

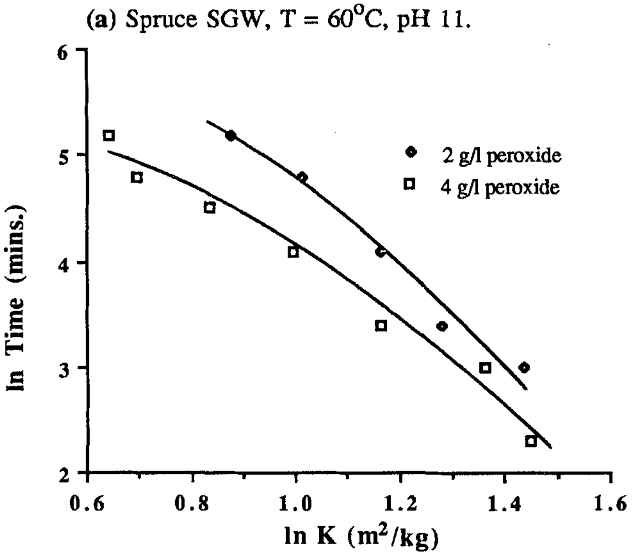


Figure 2 : Natural log of absorption coefficient vs. natural log of time from the data of Moldenius *et al* (a), Allison *et al* (b) and this study (c).

(continued)

Equation 1 predicts that, at constant pH and peroxide charge, the variation in chromophore concentration with time will be given by

$$-\frac{dC_k}{dt} = k\,[C_k]^c \qquad (2)$$

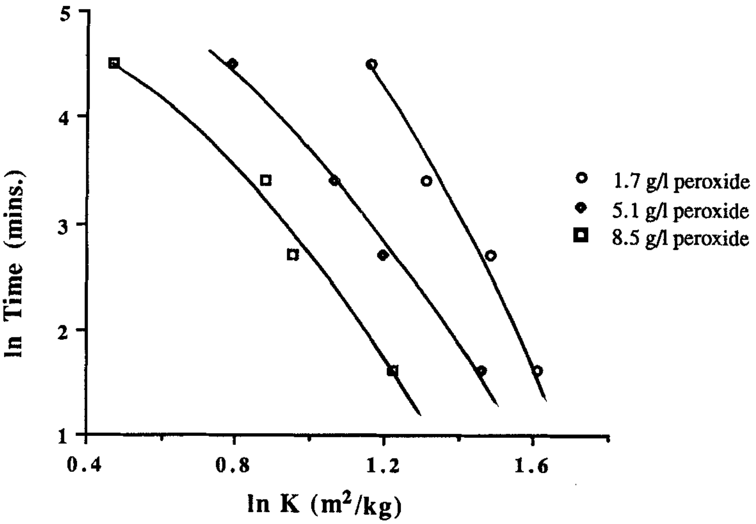
where k is a pseudo c-order rate constant which is dependent on pH and total peroxide concentration.

Upon integration of equation (2), the following expression is obtained,

$$C_k^{1-c} = (c-1)kt \qquad (3).$$

The reaction order, c, can be found from the slope of a plot of ln $C_k$ vs. ln t if a linear relationship is observed. These types of plots are depicted in Figure 2 for our results at pH 10, and also the results of Moldenius *et al*[7] and Allison *et al*[9]. Figure 2 clearly indicates that a linear fit of the data from our work is not satisfactory when this kinetic model is used. It is also clear that the data of Allison

(b) *P. radiata* TMP, T = 60°C, pH 10.



(c) T = 50°C, pH 10.

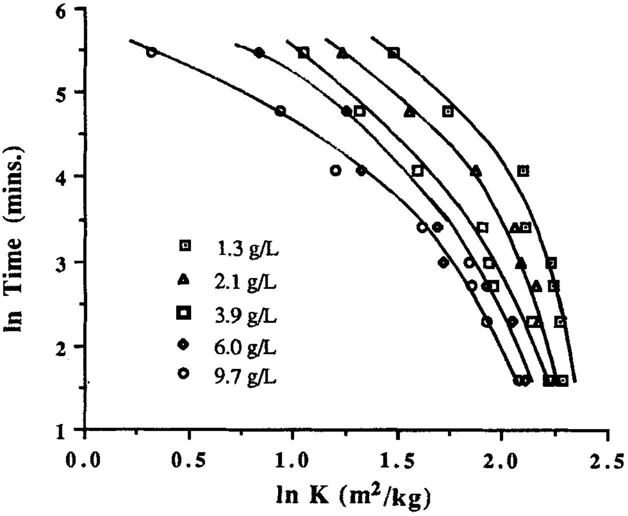


Figure 2 Continued

*et al* and Moldenius *et al* deviates from linear behaviour, particularly at longer bleaching times. This implies that the simple empirical model is only successful over a short range of time, with the behaviour at longer durations being poorly described.

In addition to a poor fitting with experimental results, a severe limitation of this empirical model is the lack of kinetic information it conveys. When applied to peroxide[6-10] and other bleaching processes[1,2,16-18], the empirical model results in high, non-integral reaction orders with respect to chromophore concentration. Several authors have pointed out that a sum of parallel processes of low order can imitate a single process of high order[10,16-18], while others[10,19-21] have taken the view that various heterogeneous processes, such as diffusion, are responsible for high reaction orders. Extremely complex mathematical treatments are the result of describing pulp bleaching reactions using various heterogeneous approaches[10,22], while if more than three parallel homogeneous reactions are considered, the number of independent parameters often becomes too large to be determined[16].

To achieve a better correlation between our experimental results and a theoretical expression, two alternative forms of model were investigated, and these are described below.

## Model II : The Two Chromophore Model

The experimental bleaching profiles shown in Figure 1 suggest the existence of at least two categories of chromophores which are responsible for light absorption at 457nm. The first type ($C_1$) is present during the initial bleaching stages and its rate of removal is strongly dependent on the concentration of peroxide present. This is clear from a comparison of initial rates of chromophore elimination if the peroxide concentration is increased by a factor of approximately 5 (Figure 1).

The effects of the second chromophoric type ($C_2$) become clearer during the latter stages of bleaching when $C_1$ has largely been removed. The rate of removal of $C_2$ is not strongly dependent on peroxide concentration. This is apparent from inspection of Figure 1 where the rate of chromophore removal becomes almost independent of peroxide concentration at long bleaching times. Similar conclusions regarding the existence of two distinct chromophore types can be drawn by inspection of similar plots for bleaching of softwood species under constant conditions[6-9].

At this stage of the development of a kinetic model, the two chromophoric groups are regarded as multi-component, lumped constituents which are classified solely on the basis of their kinetic behaviour. It is recognized that the assumption of two chromophoric types is a major generalization since many different chromophores have been shown to be present in lignin, each reacting via different routes[12,23-27]. Consideration of every individual chromophore in the lignin polymer and its subsequent reaction would result in a model of considerable complexity and so the two chromophore model has been formulated in an attempt to describe the bleaching process using a minimum number of kinetically meaningful parameters.

The model chromophore types are assumed to be present in initial concentrations of $C_1^0$ and $C_2^0$. Upon reaction with peroxide, each type gives rise to a group of colourless products, $C_p$, via two parallel first order processes as shown in Figure 3a. $C_1$ is assumed to react at a much faster rate than $C_2$ , hence $C_2$ can be identified with the latter part of the bleaching curves of Figure 1, while $C_1$ is largely responsible for the rapid initial rates.

## Calculations

To allow kinetic simulations to be carried out, evaluation of the two rate constants ($k_a$ and $k_b$) and initial chromophore concentrations ($C_1^0$ and $C_2^0$) was necessary.

Since the chromophore type $C_2$ was associated with the latter stages of bleaching and was assumed to follow first order kinetics, the rate constant ($k_b$) and initial chromophore concentration ($C_2^0$) were calculated by simultaneously solving the equation for first order decay

$$C_2 = C_2^0 e^{-k_b t} \qquad (4)$$

using the final two light absorption coefficients at each peroxide concentration.

The initial concentration of chromophore type $C_1$ ($C_1^0$) was easily calculated since

$$C_1^0 = C_{tot}^0 - C_2^0 \qquad (5)$$

where $C_{tot}^0$ is the total blank light absorption coefficient.

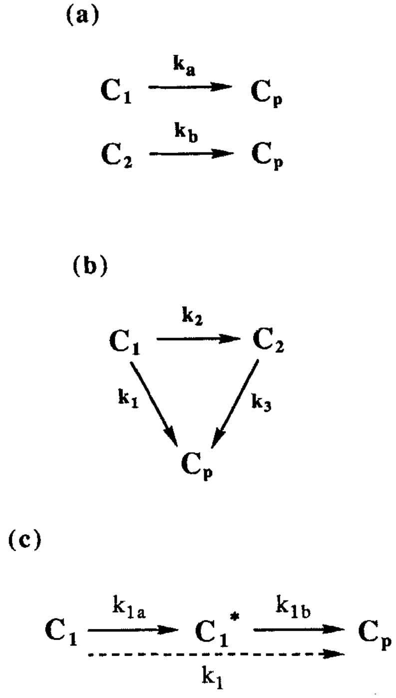


**Figure 3** : The two chromophore model (a), the two chromophore consecutive reaction model (b) and the proposed mechanism for $C_1$ to $C_p$ conversion (c).

The amount of $C_2$ present at 10 minutes was calculated using equation 4, and this allowed the corresponding amount of $C_1$ at 10 minutes to be calculated from equation 6,

$$C_1 = C_{tot} - C_2 \qquad (6)$$

where $C_{tot}$ is the total light absorption coefficient after 10 minutes bleaching.

The rate constant associated with the removal of $C_1$ ($k_a$) was then calculated in the same way as $k_b$ by using data points at 0 and 10 minutes to define an initial rate through equation 7.

$$C_1 = C_1^0 e^{-k_a t} \qquad (7)$$

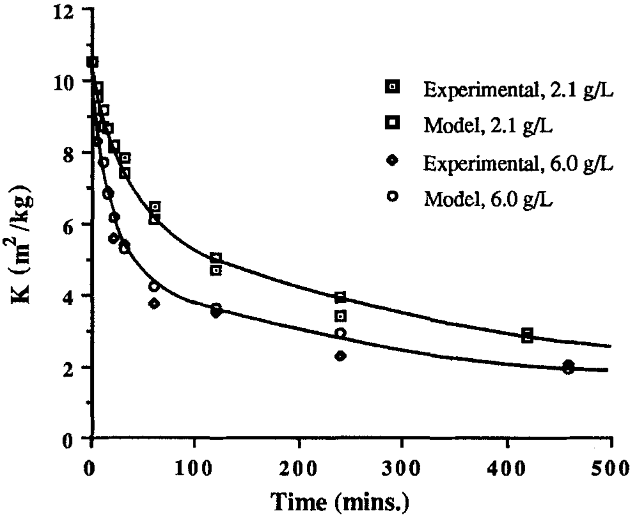


Figure 4 : Comparison of experimental and model bleaching profiles from this study. Simulated points generated using the two chromophore model, (T = 50°C, pH 10).

The validity of this model was tested by performing kinetic simulations using TUTSIM, a commercially available program for the simulation of continuous dynamic systems. A description of TUTSIM in relation to soda-additive delignification has been given previously[3]. Substitution of $C_1^0$, $C_2^0$, $k_a$ and $k_b$ into TUTSIM allowed plots of light absorption coefficient vs. time to be generated for comparison with experimental data. These comparisons at 2.1 g/L and 6.0 g/L peroxide are shown in Figure 4 from which it is evident that the model is successful in duplicating the experimental data. However, variations in the calculated initial chromophore concentrations ($C_1^0$ and $C_2^0$) with peroxide concentration are also required to obtain reasonable fits as shown in Table 1. This is in contradiction with the assumption that $C_1$ and $C_2$ should be present in a fixed ratio in the initial pulp sample.

## Model III : The Two Chromophore Consecutive Reaction Model

To overcome the limitations of the two chromophore model described above, a modified version was devised. While continuing with the idea of two

TABLE 1

Values of $C_1^0$ and $C_2^0$ with Varying Peroxide Concentration

| Peroxide Concentration (g/L) | $C_1^0$ (m$^2$/kg) | $C_2^0$ (m$^2$/kg) |
|---|---|---|
| 1.3 | 4.47 | 6.02 |
| 2.1 | 6.30 | 4.19 |
| 3.9 | 6.62 | 3.87 |
| 6.0 | 7.83 | 2.66 |
| 9.7 | 8.94 | 1.55 |

chromophore types, the possibility of $C_p$ being formed from $C_1$ via a consecutive reaction was considered (Figure 3b). It will be noted from Table 1 that the lower peroxide concentrations apparently correspond to lower initial ratios of $C_1 : C_2$. This phenomenon could be interpreted as corresponding to formation of $C_2$ from $C_1$ as the reaction proceeds. In this case there will be two competing parallel pathways for reaction of $C_1$: it can react to give a colourless product, $C_p$, or it can react to give the second type of chromophore, $C_2$. Obviously, the faster $C_1$ reacts to produce $C_p$ (ie. at higher peroxide concentrations) the smaller will be the opportunity for $C_2$ to accumulate.

Since the final sections of each bleaching profile (Figure 1) appear to approach a common limiting slope, a rate constant ($k_3$) was assigned as a parameter which is independent of peroxide concentration at pH 10. The parameters $k_3$ and $C_2^0$ were calculated from the final two points at 9.7 g/L peroxide concentration as this section of the curve best defined a limiting slope common to the bleaching profiles. The rate constant responsible for the rapid initial rate ($k_1$) was calculated, for each curve, from the initial slope which was defined by the points at 0 and 10 minutes bleaching, as in Model II. The remaining parameter ($k_2$) was adjusted to minimise the least squares fit of model and experimental data at each level of peroxide. Data for model III was generated using TUTSIM. An example of the comparison between experimental and simulated values is shown in Figure 5 while an example of variation in model chromophore concentrations with time is presented in Figure 6.

From Figure 5 it is evident that the second model is equally as effective at simulating the experimental results of this study while not changing the concepts of

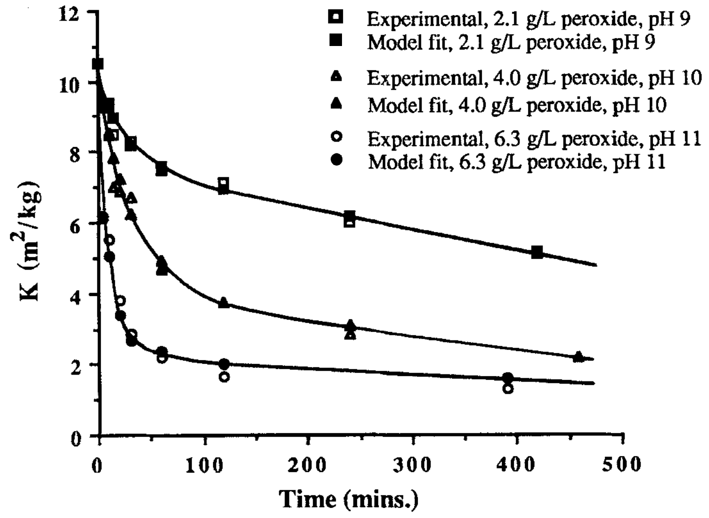


**Figure 5** : Some examples of model and experimental bleaching profiles from this study (T = 50°C).

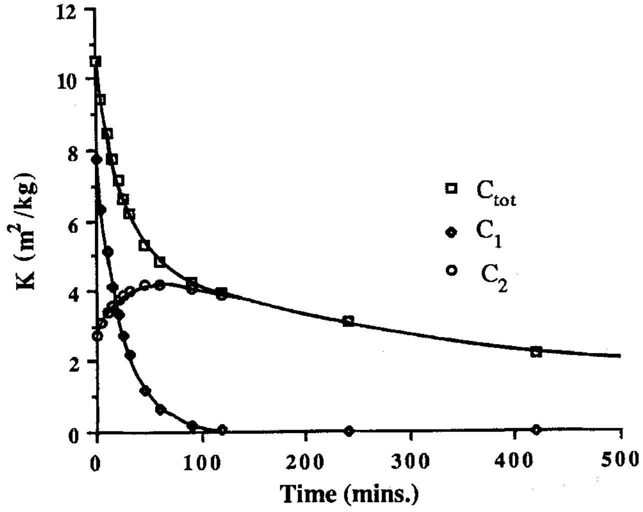


**Figure 6** : Contribution of the model chromophores $C_1$ and $C_2$ to the overall bleaching profile (T = 50°C, pH 10, 4 g/L peroxide).

TABLE 2

Comparison of Model Fits of Experimental Data at Various Peroxide Levels

| Peroxide Concentration (g/L) | MODEL II Std. Error ($m^2/kg$)[a] | MODEL III Std. Error ($m^2/kg$)[a] |
|---|---|---|
| 1.3 | 0.340 | 0.366 |
| 2.1 | 0.780 | 0.675 |
| 3.9 | 0.387 | 0.450 |
| 6.0 | 0.516 | 0.440 |
| 9.7 | 1.032 | 0.789 |

[a] Standard Error = [(sum of squares of residuals) / (N-1)]$^{1/2}$, where N = no. of data points.

$C_1^0$ and $C_2^0$. Table 2 shows comparisons of sum of squares of residuals for model II and model III. Figure 7 shows that model III can also be applied to results for bleaching profiles from other studies[7,9] at pH 10.

## pH Dependence

The effects of alkalinity on the two chromophore consecutive reaction model were investigated by carrying out bleaching experiments at pH 9 and pH 11. An identical procedure to that described for the pH 10 experiments was used to model this data. Examples of experimental and model comparisons (Figure 5) again indicate good model descriptions of the experimental points. The trends observed in other studies[6,7] are again evident in this study with the most extensive bleaching occurring at pH 11 and the least at pH 9 (Figure 8).

## Behaviour of Initial Rate Constant, $k_1$

At each pH level examined, the initial rate constant ($k_1$) increases with the total peroxide concentration (Figure 9a). It is evident that the process of converting the chromophore type $C_1$ to colourless product $C_p$ is not a simple first order process with respect to peroxide since the expected linear relationship between $k_1$ and peroxide concentration is not observed. Figure 9a shows that there is a 'falling off' in the response of $k_1$ to increasing peroxide concentration at higher levels of addition. This implies that the conversion of $C_1$ to $C_p$ does not take place in a single elementary step, but occurs through a more complex sequence of processes. Figure 9b shows that a plot of $k_1$ vs. $[H_2O_2]^{0.5}$ at pH 10 is close to linear, suggesting an expression of the form $k_1 \propto [H_2O_2]^a$. This type of kinetic expression can be explained by assuming a consecutive mechanism involving an intermediate, illustrated by Figure 3c where $k_{1a}$ and $k_{1b}$ represent respective individual rate constants for formation and removal of an intermediate species $C_1^*$, while $k_1$ represents the overall observed rate constant. Reaction processes of this type leading to apparent non-integer orders of reaction have been discussed for soda-additive delignification[3], and can explain features such as 'square root' relationships. A consecutive mechanism such as that in Figure 3c has also been proposed[28] to explain the enhancement of bleaching response during a two stage process.

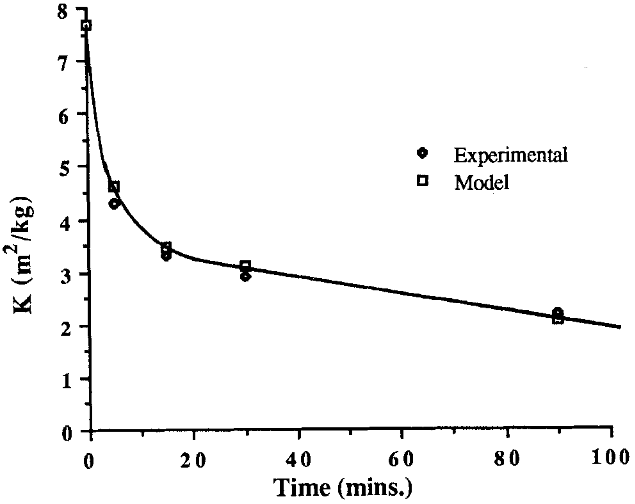
It is generally believed that the peroxide anion ($HO_2^-$) is the active species during peroxide bleaching[29], therefore kinetic expressions for chromophore elimination should preferably be formulated in terms of $HO_2^-$ rather than total peroxide concentration, as shown in Figure 9c. This shows that there is a progression in bleaching response over the pH range studied, with the action of the $HO_2^-$ anion having greatest effect at the lowest pH level. If the exclusive role of alkali was production of peroxide anions, then the rates at each pH would be expected to lie on a common curve when plotted against $HO_2^-$ concentration. Figure 9c shows this is not the case, and the alkali appears to have a retarding effect on the initial bleaching rate, in addition to its role of inducing peroxide ion formation. This observation is consistent with the results of experiments[6,7,29,30] which show that excess alkali inhibits peroxide bleaching.

The magnitude of $k_1$ is a function of both peroxide anion and alkali concentration and can be approximately represented by an empirical expression of the form,

$$k_1 = k' \frac{[HOO^-]^a}{[OH^-]^b} \quad (8).$$

Solving by least squares methods resulted in the following values for a, b and k' being obtained: a = 0.43, b = 0.27, $k' = 0.063\ min^{-1}$. By using equation 8 to

(a) *P. radiata* TMP, T = 60°C, pH 10, 5.1 g/L peroxide.



(b) Spruce SGW, T = 60°C, pH 10, 6 g/L peroxide.

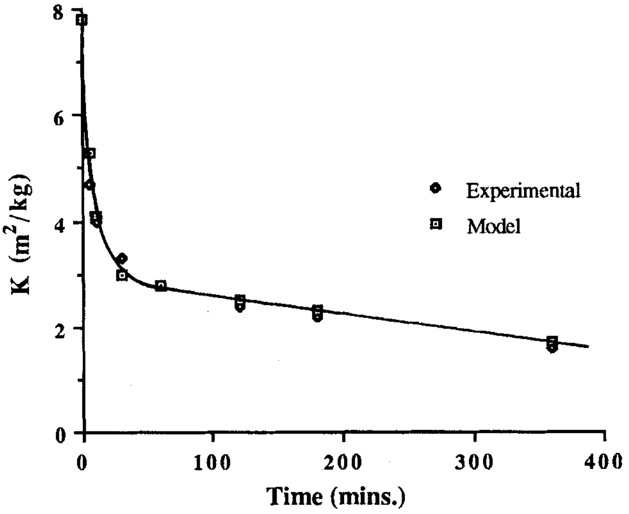


**Figure 7** : Comparison of model points with experimental points from Allison *et al* (a) and Moldenius *et al* (b).

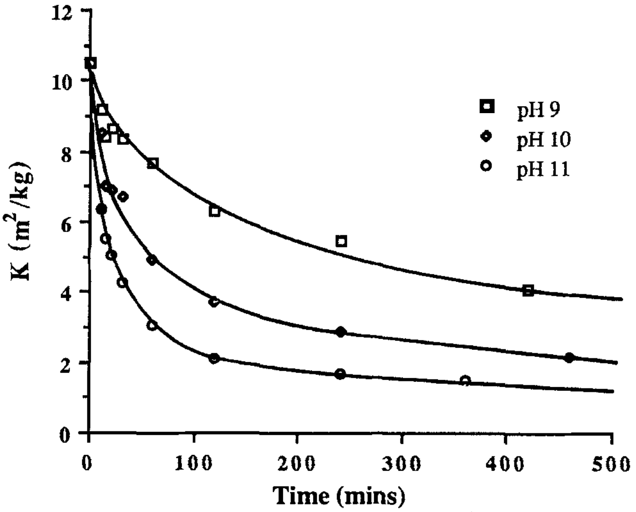


**Figure 8** : Variation in bleaching profiles with pH at constant peroxide dose (4 g/L, T = 50°C).

determine the variation in $k_1$ with pH, Figure 10 was constructed. This shows that our model predicts a maximum in the rate of chromophore elimination. Such a prediction is in agreement with observed trends reported at high pH levels[6,7,29]. This conclusion from our model suggests that there may be an optimum pH level to obtain maximum bleaching response, due to the inhibiting effect of alkali. This phenomenon is well known, although its cause has been associated with increased peroxide decomposition[12,24,29-33], rather than an actual inhibition of the bleaching reaction itself. Studies of peroxide bleaching under constant conditions with softwoods[6,7] have shown that the bleaching process is retarded at high pH (>11.5), and this effect cannot be explained on the basis of peroxide decomposition. It should also be noted that, while our model predicts a maximum response with pH, Model I would predict an indefinite increase in the rate of bleaching with pH.

## Behaviour of Rate Constant, $k_2$

The rate constant $k_2$ represents the ease with which chromophore type $C_1$ is converted into $C_2$, and was evaluated using the fitting procedure already described.

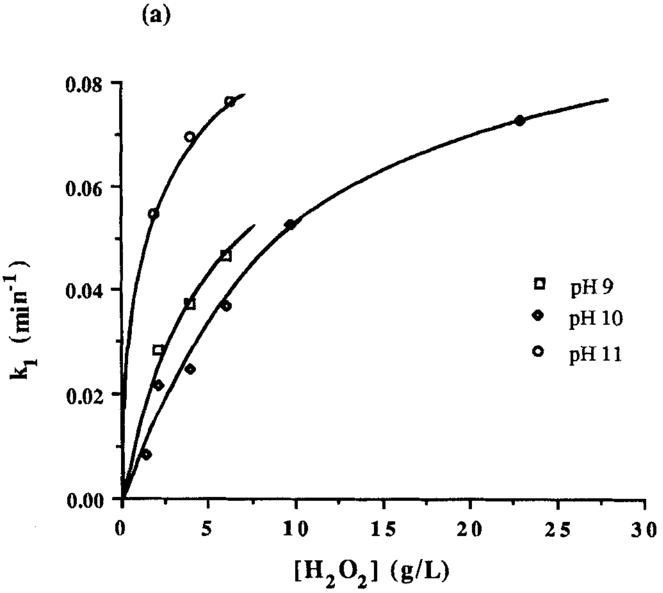


**Figure 9** : Variation in initial rate constant, $k_1$, with total peroxide (a), square root of total peroxide at pH 10 (b) and peroxide anion (c), (T = 50°C).

(continued)

Figure 11 shows the variation in $k_2$ with the concentration of $HO_2^-$ at the pH levels studied. This rate constant does not appear to be strongly dependent on either pH or peroxide concentration. In order to maximise the rate of chromophore elimination, it is desirable to reduce conversion of $C_1$ to $C_2$. However our model predicts that it is not possible to exert significant control over the rate of this process by variation in pH or peroxide anion concentration.

## Behaviour of Limiting Rate Constant, $k_3$

This limiting rate constant controls the rate at which chromophore type $C_2$ is converted to $C_p$. From the experiments at pH 10, the limiting rate constant ($k_3$) was assumed to be first order and independent of peroxide concentration. The limiting rate constants were obtained at pH 9 and 11 using an identical procedure to

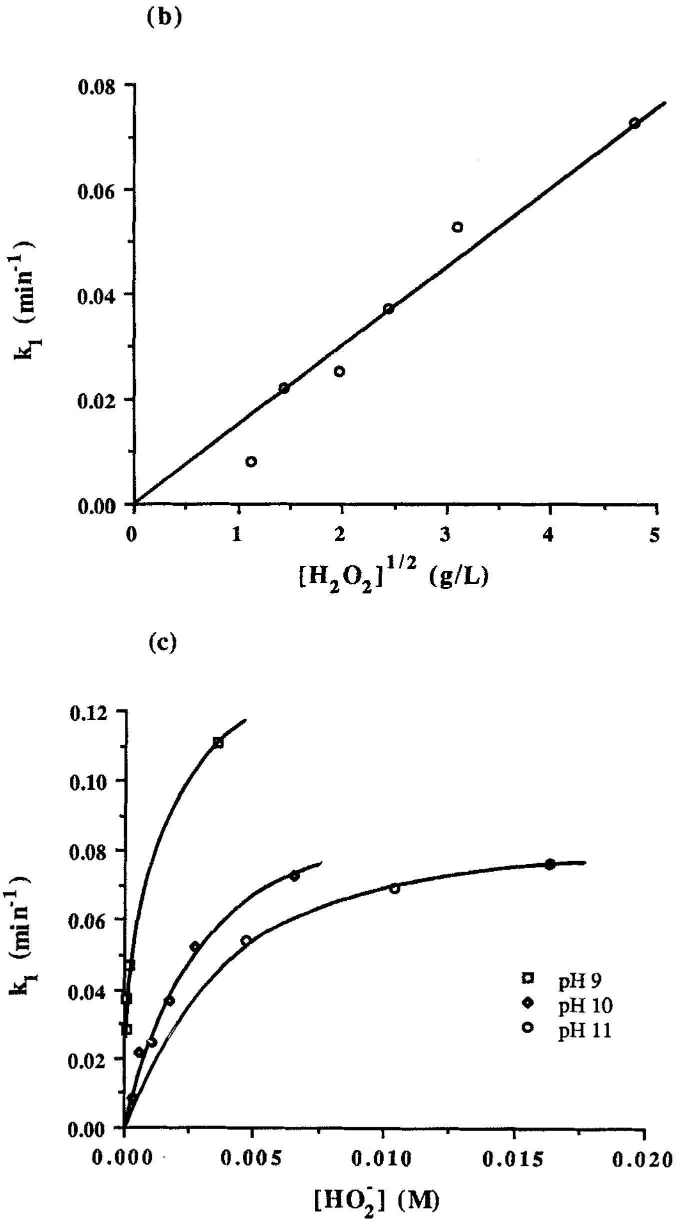


Figure 9 Continued

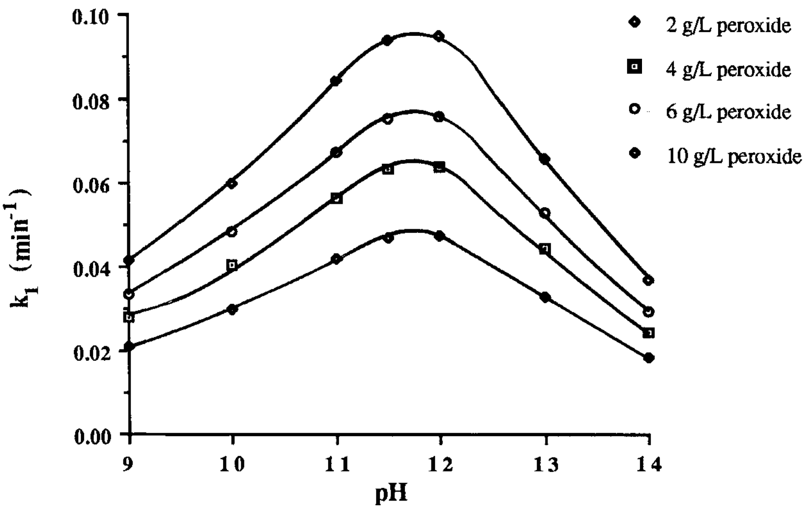


**Figure 10** : Variation in initial rate constant ($k_1$) with pH at constant hydrogen peroxide levels as predicted by the two chromophore consecutive reaction model.

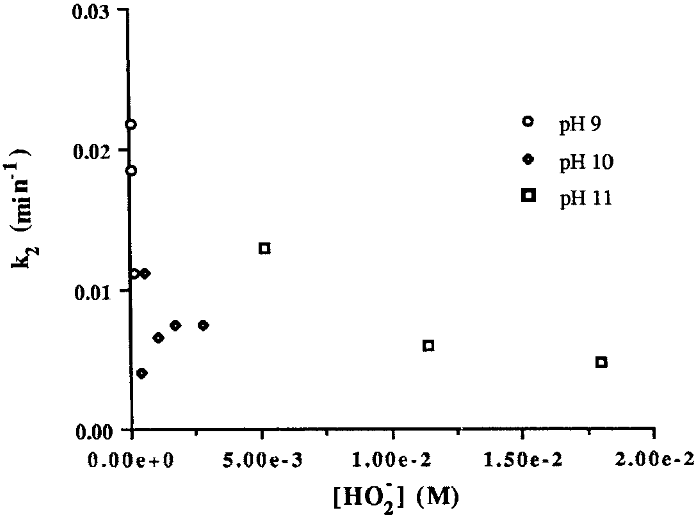


**Figure 11** : Variation in rate constant, $k_2$, with peroxide anion (T = 50°C).

**TABLE 3**

Rate Constants for Model III

| Rate Constant ($min^{-1}$) | pH 9 | pH 10 | pH 11 |
|---|---|---|---|
| $k_1$ [a] | 0.015 - 0.025 | 0.02 - 0.04 | 0.05 - 0.08 |
| $k_2$ [a] | 0.02 - 0.01 | 0.01 - 0.08 | 0.005 - 0.01 |
| $k_3$ | 0.001 | 0.0005 | 0.0015 |

[a] Rate constants over 2-6 g/L peroxide concentration range.

that described at pH 10. Due to the method of calculation, $k_3$ was found to be extremely sensitive to any error in the final two data points, which define $k_3$. For example, a 10% error in each of the final points was found to change $k_3$ by *ca.* 80% making accurate evaluation of $k_3$ difficult. As a consequence, the pH dependence of $k_3$ was difficult to ascertain. Table 3 suggests that $k_3$ is best regarded as a small, pH insensitive parameter at this stage of model development. The overall magnitude of $k_3$ implies that the conversion of $C_2$ to $C_p$ is the slowest of all the steps in Model III. Like $k_2$, the insensitivity of $k_3$ to both peroxide and alkali concentration means that very little can be done to accelerate $C_2$ to $C_p$ conversion by way of changing peroxide or alkali concentrations.

## CONCLUSION

Kinetic phenomena during bleaching of a Eucalypt mechanical pulp have been studied under constant conditions of pH and peroxide. Analysis of the results has shown that a model based on the assumption of two distinct chromophore types can be used to obtain adequate agreement between theory and experiment. The model developed gives a better fitting for our results than a previously proposed model, and has the advantage that the overall bleaching response is defined in terms of first order processes, rather than high reaction orders. The model developed here predicts the appearance of a maximum in the rate of bleaching at a pH in the range 11-12, rather than a continuous increase in bleaching rate without limit.

Furthermore, our model indicates that the dominant reaction during the initial stages of bleaching might occur through a sequential process involving an intermediate, the formation of which may be favoured by less alkaline conditions. This finding agrees with the results of recent studies on two stage acidic/alkaline peroxide bleaching.

This approach to kinetic modelling based on a network of parallel and/or consecutive first order processes will provide not only a better representation of experimental observations, but will ultimately yield fundamental information regarding the individual reactions involved. It cannot be stated that the models investigated here provide a unique solution to the experimental data, and more supporting chemical information must be obtained to differentiate between other possible reaction networks. However the approach taken will eventually provide much information on the mechanisms of bleaching processes and the behaviour of the chromophores present.

## EXPERIMENTAL

### Chemicals

Hydrogen peroxide (30%) and sulphuric acid (98%) were supplied by Ajax Chemicals. Semi-conductor grade sodium hydroxide (99.99%) obtained from Aldrich Chemicals was used as the alkali source to minimise the introduction of transition metal impurities.

### Procedure

Alkaline groundwood pulp was prepared from approximately 150 year old *E. regnans* blocks which were soaked in Milli-Q water for three days prior to grinding. The wood was ground in a dilute solution of sodium hydroxide using a lab-scale grindstone at Australian Newsprint Mills, Boyer. The resulting pulp was concentrated from 1.5% to 20% consistency by filtration and stored at 4°C until use.

Bleaching experiments were performed by adding sufficient *E. regnans* pulp to 6 L of Milli-Q water such that a pulp slurry of 0.3% consistency was achieved. The slurry was vigorously stirred in a polyethylene bucket immersed in a water bath to maintain a constant temperature of 50°C. Before each bleaching run, an aliquot of pulp was removed to make blank handsheets so that changes in the pulp, due to storage, could be monitored.

Bleaching was initiated by simultaneously adding enough alkali (1M NaOH) and hydrogen peroxide to reach the target conditions. Subsequently, constant pH was maintained by adding alkali from a pH controller supplied by Cole-Parmer. The concentration of peroxide was maintained at constant levels by periodic addition of the necessary amount of hydrogen peroxide calculated from iodometric titration[34].

After initiation of bleaching, aliquots of pulp slurry (400 mL) were removed at the desired times to make pulp handsheets. The bleaching reaction was quenched by acidifying the slurry to pH 2.5 with sulphuric acid (2.5 M), followed by filtering to remove the bleaching liquor. Handsheets having conditioned basis weights of 40-45 g.s.m were formed by filtering the required volume of re-dispersed pulp slurry onto Whatman No. 540 filter paper as described in the Appita Standard[35]. Using this procedure, 3 handsheets were obtained from each aliquot. The sheets were fan dried for several hours at room temperature and were then allowed to equilibrate at constant temperature (25°C) and humidity (50%) so that conditioned basis weights could be obtained.

After drying, black-backed and self-backed reflectance measurements were made on each sheet, at a wavelength of 457nm, using an Elrepho 2000 reflectance spectrometer. Individual opacity (W), scattering coefficient (S) and light absorption coefficient (K) properties were calculated from the Kubelka-Munk equation[14,15,36]. These properties were reported as the average per group of 3 handsheets.

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