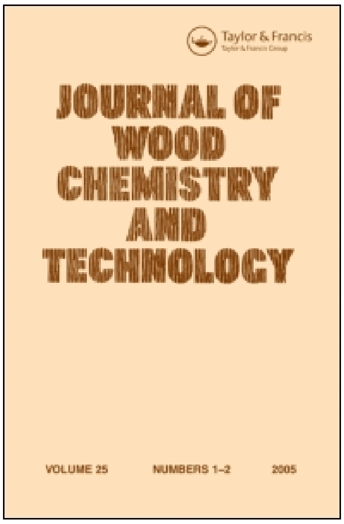

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KINETIC MODELS FOR PEROXIDE BLEACHING UNDER ALKALINE CONDITIONS, PART 2. EQUILIBRIUM MODELS.

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ABSTRACT

The validity of a previously proposed kinetic model for alkaline peroxide bleaching has been tested by changing reagent concentrations during bleaching. The model has been revised to account for experimental observations and now includes a reversible reaction between chromophoric and leucochromophoric groups. Analysis of model first order rate constants indicates that ionic and radical species may both play an important role in alkaline peroxide bleaching.

INTRODUCTION

There is currently widespread interest in the expansion of markets for mechanical and chemi-mechanical pulps bleached with hydrogen peroxide. In addition, there is also a growing potential for substitution of high brightness mechanical pulps into products traditionally manufactured from bleached chemical pulps. However, problems arising from reversion processes, for example after exposure to light, may limit the extent of replacement. It is now generally believed that radical induced processes participate in reversion reactions induced by both heat and light[1-6]. Reactions involving radical species have also been the subject of recent debate during the alkaline bleaching process itself. It is now thought that radicals, in particular the hydroxyl radical ($OH^{\cdot}$), may play an important role in bleaching[7-10] in addition to the perhydroxyl anion (HO_2^-) which has long been considered to be the active reagent[11]. However, there is conflicting evidence as to whether the involvement of radicals leads to brightening or darkening processes.

In part 1 of this study[12] we undertook an examination of the kinetics of alkaline peroxide bleaching processes under conditions of constant reagent concentrations at low consistency. Several plausible kinetic schemes were examined in detail, including a two chromophore consecutive reaction model. In the present paper we have extended our study to include a model which allows for a reversible reaction in which chromophores are created as well as removed. The analysis of peroxide bleaching kinetics in terms of a reversible reaction has also been considered in the context of identifying the possible contributions of radical induced processes in the overall reaction scheme.

RESULTS AND DISCUSSION

THE TWO CHROMOPHORE CONSECUTIVE REACTION MODEL

In the previous paper[12], the kinetic behaviour associated with the bleaching of *E. regnans* mechanical pulp was examined under constant reagent conditions by following the change in light absorption coefficient (K) with time. The light absorption coefficient has been found to be the the most suitable variable to monitor since it is known to relate proportionally to the chromophore concentration[13-16]. Analysis of bleaching behaviour led to the formulation of a peroxide bleaching model based on two distinct chromophore types (C_1 and C_2). Both chromophores were considered to be initially present in the pulp and, under bleaching conditions, were assumed to react via first order processes to yield colourless products (C_p) via the mechanism presented in Figure 1(a) (the other mechanisms outlined in Figure 1 will be discussed later).

Chromophore type C_1 was assumed to react rapidly via two routes, with rate constants k_1 and k_2, to form C_p and C_2 respectively. Hence the disappearance of C_1 was correlated with the rapid initial decrease in light absorption coefficient

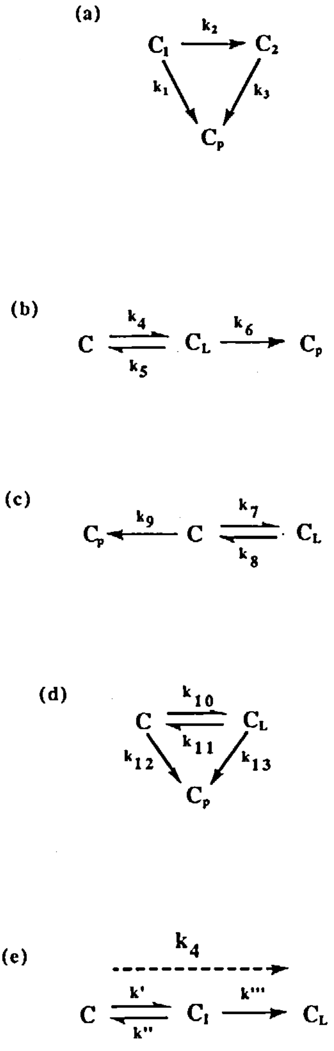


FIGURE 1 : Kinetic model reaction schemes. (a) The two chromophore consecutive reaction model, (b) & (c) 3 parameter equilibrium models, (d) 4 parameter equilibrium model (e) Postulated mechanism for C to C_L conversion.

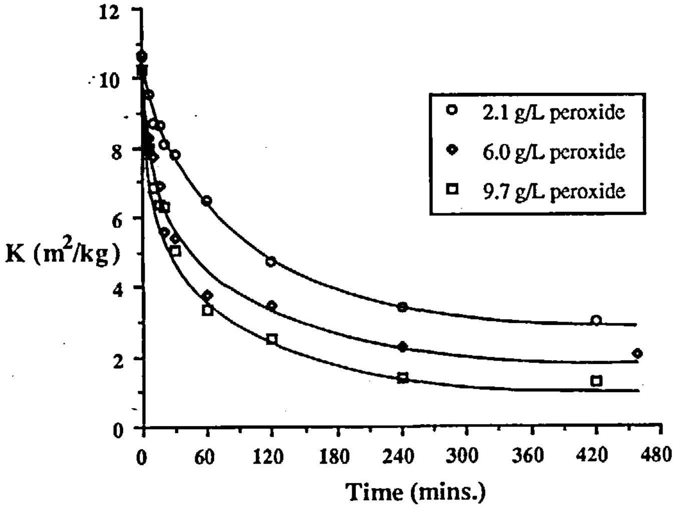


FIGURE 2 : Typical variation in light absorption coefficient (K) with time for an *E. regnans* pulp bleached under constant conditions (pH 10, 50°C, 0.3% pulp consistency).

which is evident during the first 30 minutes of bleaching (Figure 2). The chromophoric group C_2 was assumed to be more resistant to bleaching and was identified as being responsible for the much slower final bleaching phase. The rate constant associated with the conversion of C_2 to C_p (k_3) was found to be small and independent of reagent concentration and coincided with the levelling off in the rate of bleaching at longer times.

Computer evaluation of the rate constants (k_1, k_2 and k_3) allowed the features of the two chromophore consecutive reaction model to be examined in more detail. The model was initially favoured for several reasons. Firstly, a good fitting between experimental and theoretical data was obtained and secondly, the reaction steps could be defined in terms of chemically meaningful first order processes. Finally, a maximum bleaching rate in the pH range 11-12 was predicted which is in agreement with experimental observations[11,17,18], whereas previously published empirical models[15,17,18] predict a continuous increase in bleaching rate with pH.

Two Chromophore Consecutive Reaction Model Tests

Although the fitting obtained between experimental data and theoretical behaviour predicted by the consecutive reaction model was a significant improvement on previously proposed kinetic models, this is not sufficient to establish the validity of the proposed scheme[15]. As is the case with any complex multi-parameter kinetic model, an apparent adequate fitting of data points should not be used as the sole criterion of model validity. It is important to attempt to formulate tests to compare experimental behaviour with model predictions.

The experiments undertaken here to test the consecutive reaction model were essentially consecutive two stage bleaching sequences carried out under constant conditions at 50°C and 0.3% consistency. The aim of these experiments was to check the ability of the present model to predict the effects of sudden changes in reagent conditions.

(i) Increase in Peroxide Concentration at Constant pH

An *E. regnans* pulp was bleached under constant conditions (4 g/L peroxide, pH 11) for 3 hours at 50°C. Bleaching progress was monitored by following the decrease in the light absorption coefficient (K) with time. After 3 hours bleaching, enough hydrogen peroxide was added to raise the peroxide concentration to 6 g/L while maintaining the pH at 11. Light absorption coefficients were followed for a further 1 hour. The results of this bleaching procedure, shown in Figure 3(a), indicate that when the total peroxide concentration is increased at constant pH, the absorption coefficients slowly shift from the 4 g/L bleaching profile to the 6 g/L profile. In other words, increasing the peroxide concentration increases the rate of bleaching.

In terms of the two chromophore consecutive reaction model, this effect is unexpected. At the stage of bleaching when the peroxide concentration was increased (after 3 hours) the consecutive reaction model predicts chromophores would exist exclusively in the difficult to remove C_2 state (Figure 4). Therefore the decrease in absorption coefficient after 3 hours is a result of C_2 being converted to the colourless C_p type, the rate constant being represented by k_3. This rate constant had previously been shown[12] to be small and independent of alkali and peroxide concentration which is clearly in conflict with experimental observations.

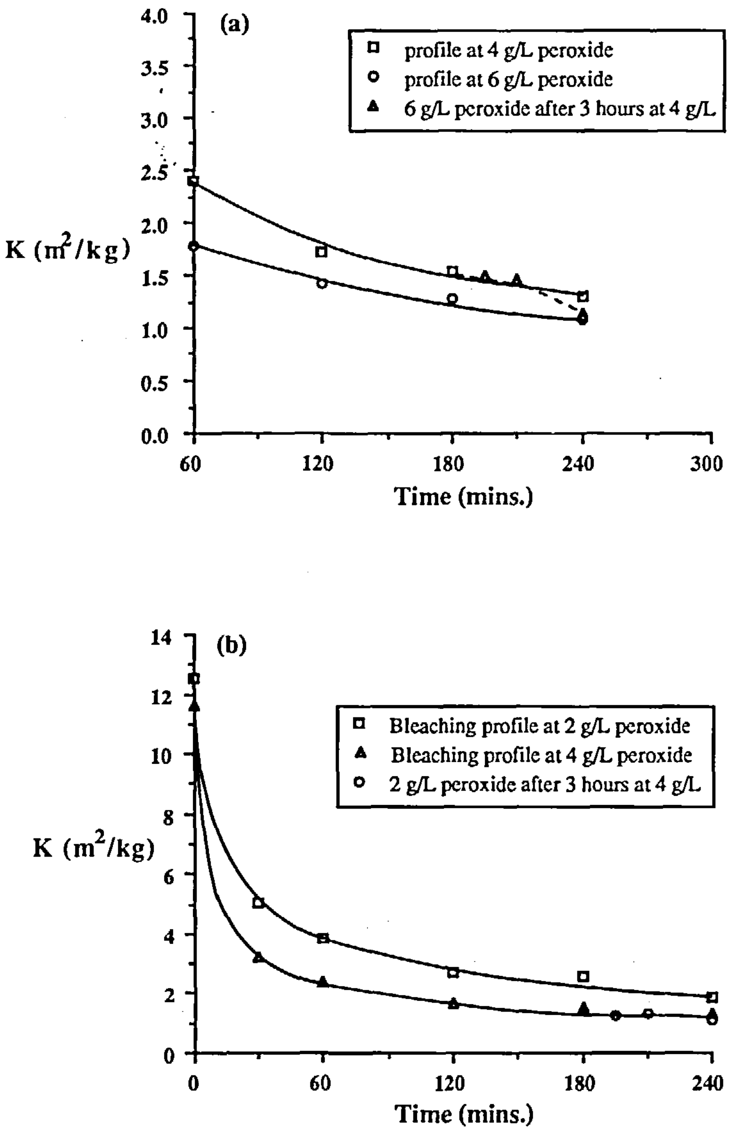


FIGURE 3 : Effect on light absorption coefficient (K) when reagent conditions are changed during bleaching. (a) Peroxide levels increased at constant pH, (b) Peroxide levels decreased at constant pH, (c) pH increased at constant peroxide concentration.

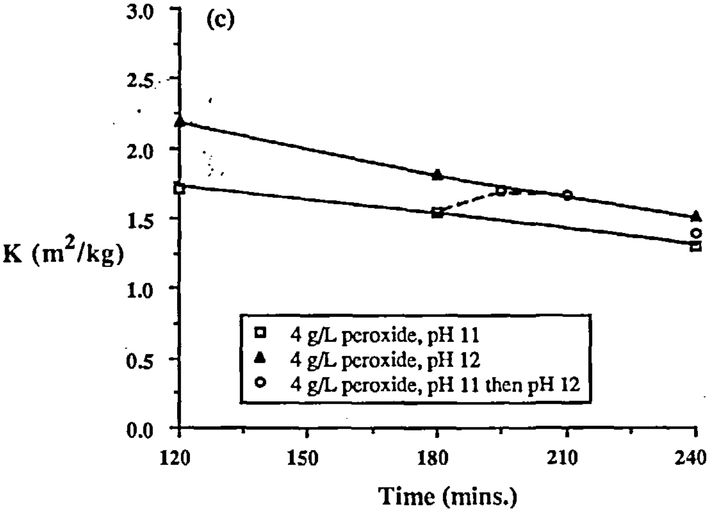


Fig. 3 (continued)

(ii) Decrease in Peroxide Concentration at Constant pH

An *E. regnans* pulp was bleached for 3 hours using an identical procedure to that in (i). After 3 hours the reaction was quenched by cooling and acidifying the slurry to pH 3, followed by filtration of the pulp. The pulp was then bleached at pH 11 and 2 g/L peroxide for a further hour and light absorption coefficients were followed.

Figure 3(b) shows that when peroxide levels are decreased at constant pH, light absorption coefficients tend to remain constant rather than shifting towards a bleaching profile corresponding to a lower amount of peroxide. This implies that reducing the amount of peroxide by half does not significantly impede bleaching rate. This observation has been noted before in the context of industrial peroxide bleaching[19]; as long as there is some residual peroxide present at the end of a bleaching stage the pulp will not darken. Figure 3(b) is also consistent with the predictions of the two chromophore consecutive reaction model since the rate constant which controls the removal of chromophore C_2 (k_3) has been shown to not be greatly influenced by a decrease in peroxide concentration.

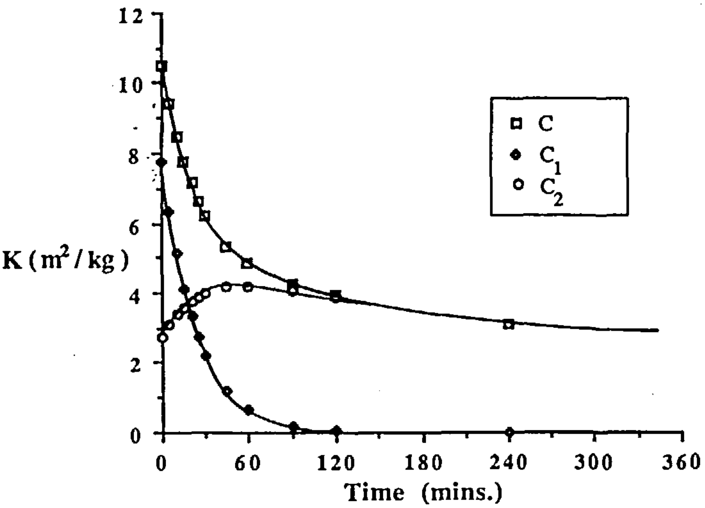


FIGURE 4 : Example of variation of two chromophore consecutive reaction model species C_1, C_2 and C_p with time. Points calculated from rate constants at pH 10, 4 g/L peroxide.

(iii) Increase in pH at Constant Peroxide Concentration

An *E. regnans* pulp was bleached for 3 hours under identical conditions to those in (i). After 3 hours the alkalinity was increased from pH 11 to pH 12 by addition of sodium hydroxide (2 M) and the reaction was allowed to proceed for a further hour. The change in light absorption coefficient with time is shown in Figure 3(c). From this figure it can be observed that when pH is increased from 11 to 12, absorption coefficients increase and move from the pH 11 bleaching profile to that at pH 12. This behaviour causes the pulp to darken. Such a darkening is somewhat surprising considering that formation of the active bleaching species[11], the perhydroxyl anion HO_2^-, is favoured by increasing pH (Table 1). This information implies that the action of (HO_2^-) is substantially impeded at high pH in agreement with studies, including this work, which show a maximum bleaching rate in the pH 11-12 range (Figure 5).

The darkening observed in Figure 3(c) is also indicative of a reversible reaction which cannot be explained in terms of the consecutive reaction model. The

TABLE 1

Effects of Increasing pH on the Formation of Perhydroxyl Ions at 50°C (Calculated from the Equation of Teder & Tormund[20]).

Concentration H_2O_2 (g/L)	pH	Concentration HO_2^- (M)
2.0	9	5.7 e-05
4.0	9	1.1 e-04
6.0	9	1.7 e-04
2.0	10	5.7 e-04
4.0	10	1.1 e-03
6.0	10	1.7 e-03
2.0	11	5.2 e-03
4.0	11	1.0 e-02
6.0	11	1.6 e-02
2.0	12	2.9 e-02
4.0	12	5.8 e-02
6.0	12	8.7 e-02

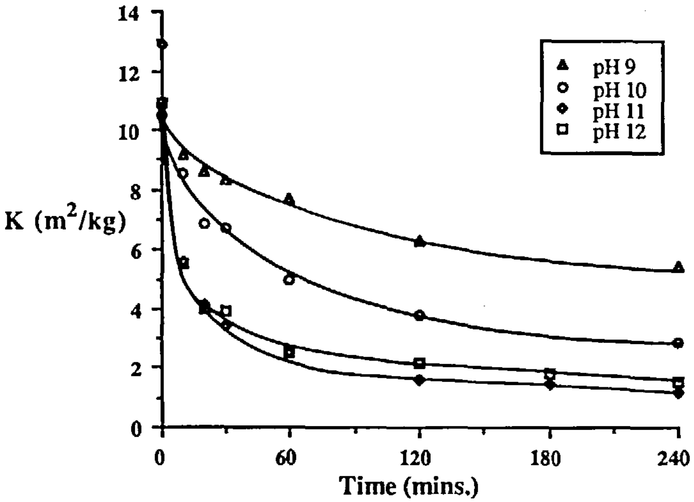


FIGURE 5 : Evidence for maximum bleaching rate in the pH range 11-12. *E. regnans* pulp bleached under constant conditions (4 g/L peroxide, 50°C, 0.3% pulp consistency).

model predicts that, after 3 hours, chromophore type C_1 will have been fully converted to C_2 and C_p. The darkening which occurs on increasing the pH suggests that C_1 is being somehow reformed from C_2 and C_p, a possibility which is not taken into account by the current model.

EQUILIBRIUM MODELS

The model tests mentioned above clearly illustrate some of the deficiencies in the two chromophore consecutive reaction model. Although this model appears to adequately describe the kinetics of chromophore removal under conditions of constant peroxide concentration and pH, it does not account for the observed effects which occur during changes in reagent concentration. Ultimately, if we wish to be able to describe peroxide bleaching behaviour under mill conditions, a valid kinetic model must account for behaviour under conditions where reagent concentrations are not maintained at constant levels.

In particular, the consecutive reaction model is unable to describe the darkening which occurs when pH is increased from 11 to 12 at constant peroxide levels. This observation suggests that a reversible step should be incorporated in the model. Several plausible models containing a reversible step are presented in Figures 1(b), 1(c) and 1(d). Light absorption coefficients also appear to reach approximately limiting values after long bleaching times, and these values are dependent on the amount of peroxide present (Figure 2). This type of behaviour can be explained by the concept of attainment of an equilibrium. Indeed, inconsistencies in the consecutive reaction model were recently noted in its application to the peroxide bleaching of *P. radiata* TMP at high temperatures[21], particularly with regard to explaining the effect of repeated bleaching cycles. As a result, a model involving an equilibrium between a chromophoric group (C) and a colourless leucochromophoric group (C_L) followed by an irreversible conversion to a colourless product (C_p) was postulated as a better description of experimental data (Figure 1(b)).

The equilibrium model outlined in Figure 1(b) was fitted to existing kinetic data[12] from the bleaching of *E. regnans* pulps under constant conditions at 50°C. The concentration of chromophores (C) present before bleaching was considered to correspond to the light absorption coefficient of unbleached handsheets while the

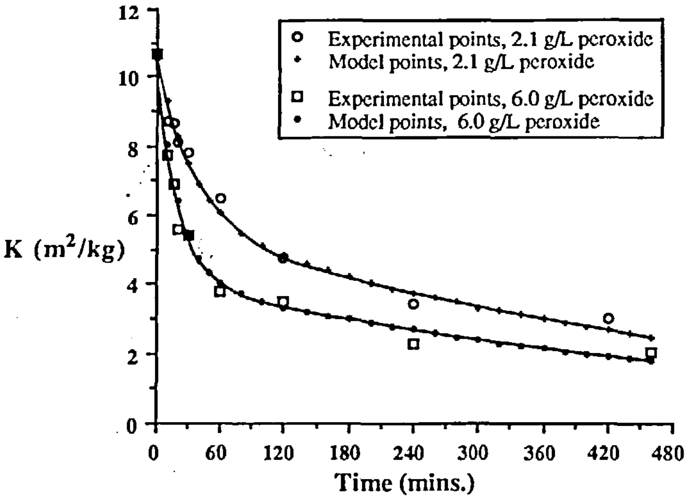


FIGURE 6 : Examples of equilibrium model fits of experimental bleaching curves. *E. regnans* pulp bleached under constant conditions (pH 10, 50°C, 0.3% pulp consistency).

initial concentrations of leucochromophores (C_L) and colourless products (C_P) were set to zero.

Differential equations describing the changes in C, C_L and C_P with time were solved by Laplace transformation to yield explicit equations for the variation in each of the chromophore types with time. The rate constants were computed using an iterative procedure whereby different combinations of k_4, k_5 and k_6 were substituted into the explicit equations to generate theoretical bleaching curves. Standard deviations between theoretical and experimental points were calculated and iterations were ceased once minimisation of standard deviations had occurred. The rate constants corresponding to the minimum standard deviation were regarded as the optimum solutions. Figure 6 illustrates some model fits of experimental data and from Table 2 it is evident that these fits are generally very good.

Features of the Equilibrium Model

A typical plot of the variation in equilibrium model species C, C_L and C_P with time is shown in Figure 7. An advantage of the equilibrium model over the

TABLE 2
Standard Deviations in the Fitting of the Equilibrium Model to Experimental Data from the Bleaching of *E. regnans* at 50°C.

	Standard Deviation in K (m^2 / kg)			
Peroxide dose (g/L)	pH 9	pH 10	pH 11	pH 12
2	0.207	0.323	0.354	0.186
4	0.294	0.337	0.389	0.308
6	0.307	0.374	0.391	0.167

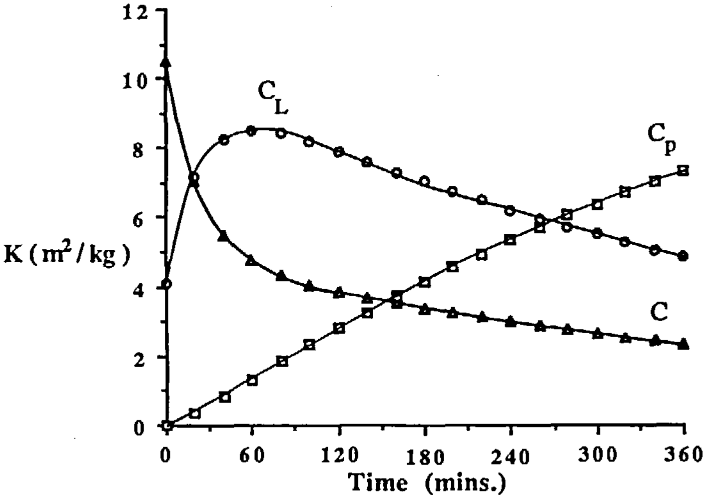


FIGURE 7 : Example of variation of equilibrium model species C, C_L and C_p with time. Points calculated from rate constants at pH 10, 4 g/L peroxide.

two chromophore consecutive reaction model is that the behaviour observed in Figures 3(a) and 3(c) when reagent conditions were changed part way through a bleach can now be described in terms of a model (Figures 8(a) and 8(c)). These figures show the predicted behaviour when either the peroxide concentration is increased at constant pH, or pH is increased at constant peroxide concentration. Theoretical lines have been generated corresponding to behaviour under constant conditions using values of the rate constants previously obtained by computer optimisation. The third line in each graph shows the predicted behaviour obtained by a sudden change in reagent concentration (ie. changing values of the rate constants) after 180 minutes. By comparison with Figure 3 it can be seen that the predicted response in terms of change in chromophore concentration is close to that observed experimentally.

Interestingly, the model also predicts that darkening should occur when peroxide levels are reduced at constant pH (Figure 8(b)), although this effect was not observed in the current work (Figure 3(b)). Further testing at lower peroxide concentrations than studied here may be required to investigate whether darkening can occur when peroxide levels are reduced at constant pH, as the model would predict.

(i) Behaviour of Rate Constant, k_4

Figure 9(a) shows the dependence of k_4, the dominant rate constant responsible for removal of colour, with the concentration of perhydroxyl ion (HO_2^-) which may be considered to be the primary active bleaching species.

It is apparent that the magnitude of k_4 increases with the concentration of HO_2^- at a given pH, but the relationship is non-linear and falls off at higher concentrations of the anion. At very high concentrations of HO_2^-, the rate constant appears to reach a limiting value (as shown here for pH 12). This behaviour suggests that the process described by the conversion of C to C_L does not take place in either a single step (ie. an elementary process in which HO_2^- reacts with C) or through a sequential mechanism in which only C and HO_2^- participate in a rate determining step.

It is also clear that the results at different pH levels in Figure 9(a) do not fall on a common curve. This shows that the dominant process for chromophore removal is strongly influenced by the hydroxide ion (OH^-) as well as the

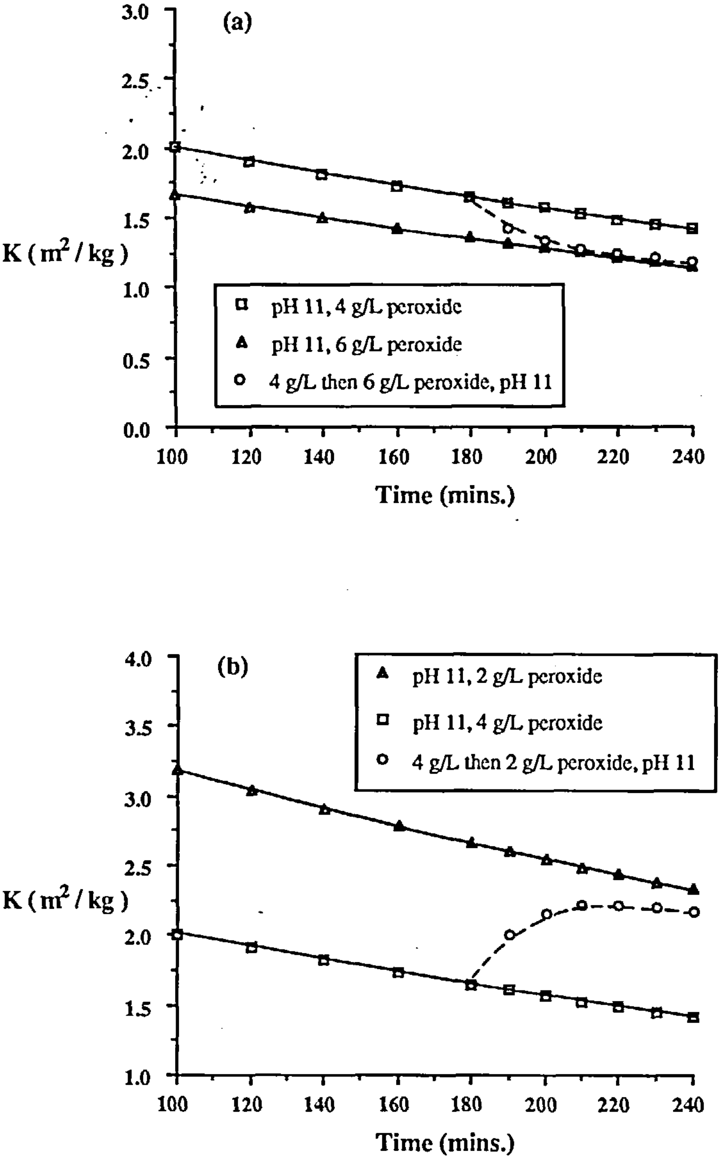


FIGURE 8 : Equilibrium model predictions of the change in light absorption coefficients when reagent concentrations are changed during bleaching. (a) Peroxide levels increased at constant pH, (b) Peroxide levels decreased at constant pH, (c) pH increased at constant peroxide concentration.

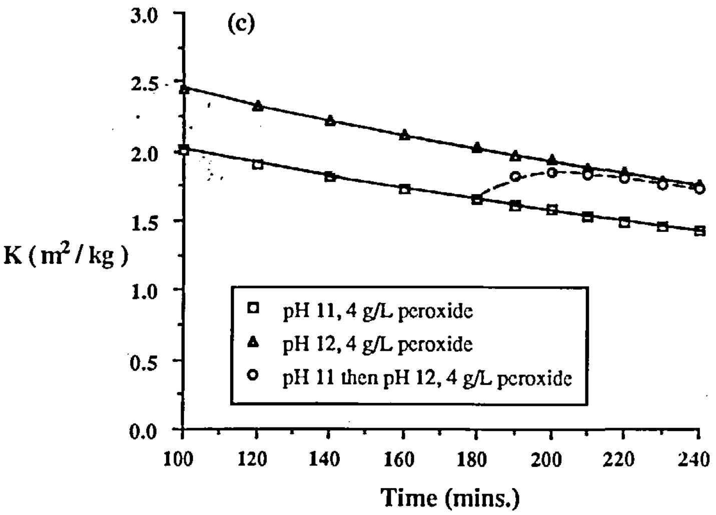


Fig. 8 (continued)

perhydroxyl anion (HO_2^-). The trend shown in Figure 9(a) implies that the forward reaction of C to C_L is promoted by the presence of HO_2^- and inhibited by the presence of OH^-.

A plausible mechanism to account for the kinetic behaviour of k_4 is shown in Figure 1(e). In this mechanism we postulate the formation of an intermediate species (C_I). The rate of formation of C_I is directly proportional to the concentration of HO_2^- (rate constant k') while the reverse process is proportional to the concentration of OH^- (rate constant k"). Formation of the leucochromophoric product (C_L) takes place in a single irreversible step (rate constant k"') which is assumed to be independent of HO_2^- and OH^-. Assuming this type of mechanism it is possible to generate a family of curves, as in Figure 9(b), which resemble the experimental curves in Figure 9(a). The postulated mechanism would explain the non-linear dependence of k_4 on HO_2^-, the limiting value of k_4 at very high HO_2^- concentrations and the inhibiting influence of the hydroxide ion.

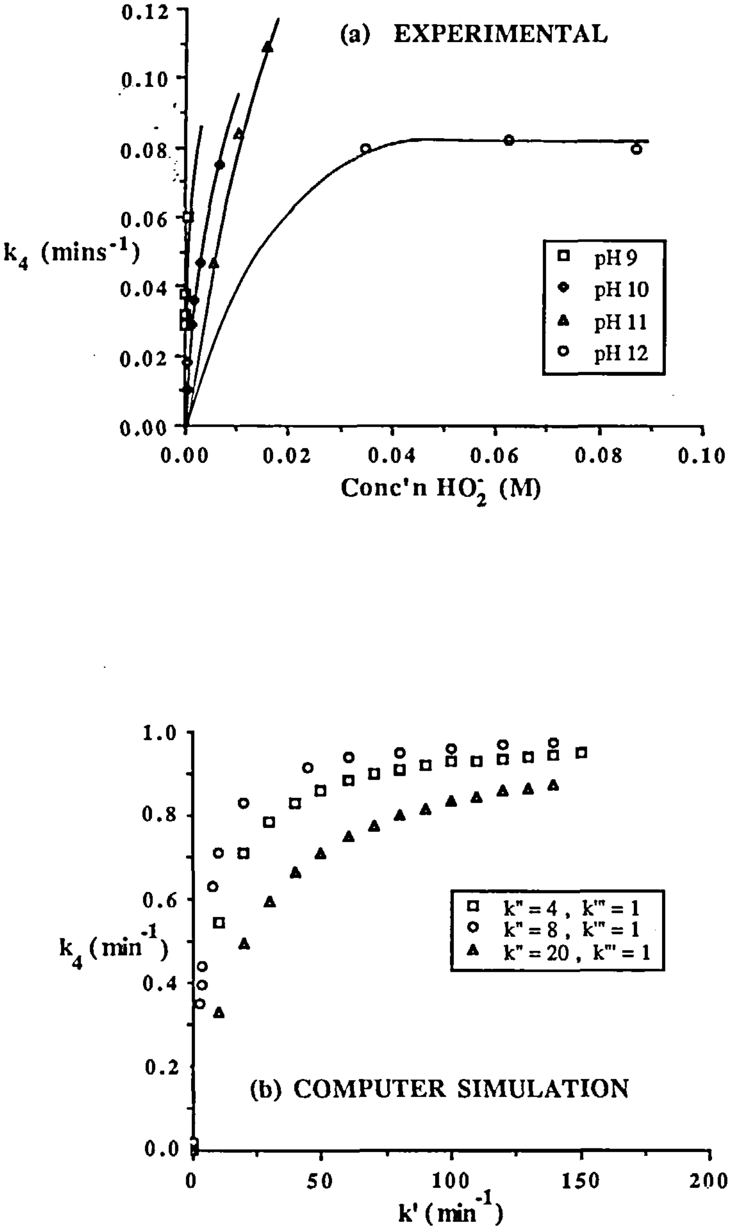
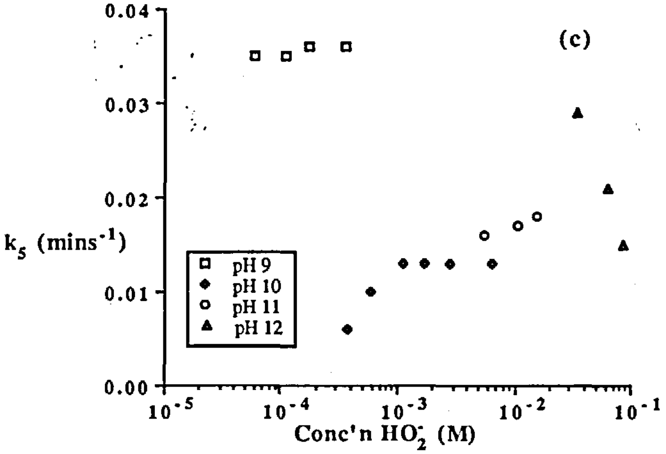


FIGURE 9 : Variation in equilibrium model rate constants with perhydroxyl ion concentration. (a) Rate constant k_4, (b) Simulation of behaviour of k_4, (c) Rate constant k_5, (d) Limiting rate constant k_6.



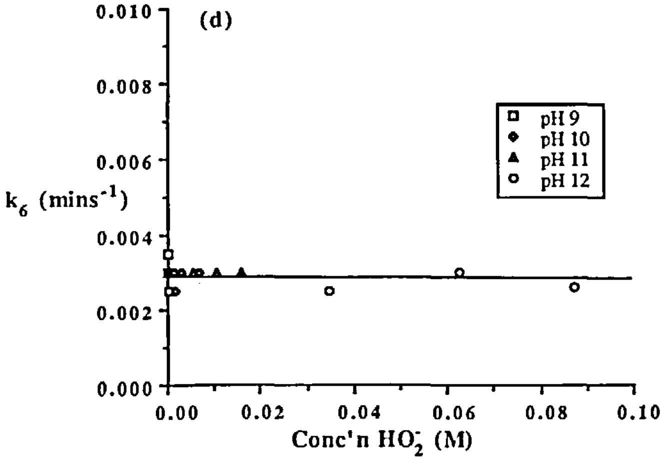


Fig. 9 (continued)

TABLE 3
Rate Constants and Standard Deviations for the Fitting of 4 Different Models to a Single Peroxide Bleaching Curve (pH 10, 3.9 g/L Peroxide).

Model Type	Figure 1(a)	Figure 1(b)	Figure 1(c)	Figure 1(d)
Rate Constants (min^{-1})	$k_1 = 0.025$ $k_2' = 0.021$ $k_3 = 0.002$	$k_4 = 0.030$ $k_5 = 0.014$ $k_6 = 0.003$	$k_7 = 0.025$ $k_8 = 0.016$ $k_9 = 0.006$	$k_{10} = 0.027$ $k_{11} = 0.014$ $k_{12} = 0.003$ $k_{13} = 0.002$
Std. Deviation (m^2/kg)	0.337	0.337	0.338	0.338

(ii) Behaviour of Rate Constants k_5 and k_6

The dependence of rate constant k_5 on perhydroxyl ion concentration is depicted in Figure 9(c) over the pH range 9-12. At constant pH, k_5 appears to be almost independent of perhydroxyl ion concentration. Despite the perhydroxyl ion and alkali concentrations varying by a factor of approximately 1000, Figure 9(c) shows that k_5 changes by a factor of about 3 in the pH range 10-12. From this observation it can be concluded that k_5 is much less sensitive to alkali and peroxide concentrations than k_4.

The rate at which the model leucochromophoric group (C_L) is irreversibly converted to a colourless product (C_P) is described by the rate constant k_6. This rate constant is reflected in the residual rate of reaction after equilibrium has been achieved. As was the case for the two chromophore consecutive reaction model, k_6 has been found to be considerably smaller than both k_4 and k_5 indicating that the conversion of C_L to C_P is the slowest step of all. The rate constant also appears to be insensitive to both alkali and peroxide levels (Figure 9(d)) suggesting that little can be done to accelerate this reaction step by way of changing reagent concentrations. Over the entire range of conditions examined, k_6 was invariably found to have a value between 0.0025-0.0030 min^{-1}.

PEROXIDE BLEACHING MECHANISMS

Table 3 shows that the adequacy of fitting obtained for the consecutive reaction model (Figure 1(a)), two 3 parameter equilibrium models (Figures 1(b) and

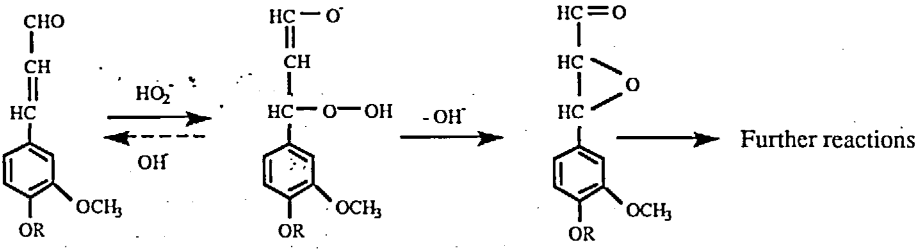


FIGURE 10 : Proposed mechanism for peroxide bleaching of lignin model compound, coniferaldehyde[23].

1(c)) and a 4 parameter equilibrium model (Figure 1(d)) are very similar. It is therefore impossible to distinguish between these models solely on the basis of fitting between experimental and theoretical points. However, as already demonstrated, the favoured equilibrium model (Figure 1(b)) can predict the response of a pulp under constant reagent conditions when the concentrations of either peroxide or hydroxide are increased. This model can apparently also explain behaviour when a pulp is repeatedly bleached in a series of consecutive stages with the same initial conditions[21].

Application of the equilibrium model under constant reagent conditions leads to the conclusion that the principle reaction leading to elimination of chromophores is controlled by ionic species as demonstrated by the behaviour of k_4. This reaction proceeds through an intermediate species the formation of which depends directly on the perhydroxyl anion and is retarded by the hydroxide ion. The existence of such an intermediate has recently been discussed in the context of two stage acid/alkaline peroxide bleaching[22]. A possible example of this type of reaction process might be envisaged for conjugated carbonyl groups[23] (Figure 10). This type of chromophore is believed to contribute a significant proportion of the colour in mechanical pulps, and is reactive towards alkaline peroxide. The mechanism shown illustrates how an intermediate species may be involved in the overall mechanism of chromophore removal. It is conceivable that the postulated intermediate would undergo elimination of hydroxide ion to produce the epoxide at a rate which is strongly dependent on the ionic species OH^- and HO_2^-. Detailed examination of the kinetic behaviour of selected model compounds in the presence of alkaline peroxide should be valuable in interpretation of the observed kinetic phenomena for mechanical pulps.

Our analysis also shows that the values of rate constants k_5 and k_6 in the equilibrium model are more or less insensitive to the concentrations of the OH^- and HO_2^- ions. A plausible explanation for this phenomena might be to assign these reactions to radical dependent processes. There has been considerable interest in the possible participation of radical species in peroxide bleaching reactions over the past decade[7-10]. Although it appears that the hydroxyl radical ($OH^\cdot$) may play a significant role, there is evidence that radical species may participate in both chromophore elimination and chromophore creation processes[9,10,24]. This is an interesting observation in view of our equilibrium model which may imply the participation of radical induced reactions in both brightening processes (k_6) and darkening processes (k_5).

Although the equilibrium model can apparently explain the behaviour of pulps under constant reagent conditions and when the concentrations of ionic reagents (HO_2^- and OH^-) are increased, the response to decreasing concentrations of these species is not predicted (Figure 8(b)). For example, a strict application of the model would predict that washing the pulp with water after prolonged bleaching should result in darkening ($k_4 \rightarrow 0$, k_5 independent of ion concentrations). This is not observed in practice but can possibly be rationalized in terms of a rapid quenching of radical processes associated with the conversion of C_L to C. Further studies will be required to provide supporting evidence for participation of ionic species and radicals as suggested by the present kinetic analysis.

CONCLUSION

The two chromophore consecutive reaction model for peroxide bleaching has been tested by carrying out a series of two stage bleaching experiments under constant reagent conditions. When peroxide levels or pH are suddenly increased during bleaching, the consecutive reaction model is unable to describe the resulting experimental behaviour. An equilibrium model was investigated and found to be capable of duplicating experimental observations while retaining the benefits of the consecutive reaction model in terms of adequacy of fitting between theoretical and experimental results.

The behaviour of the model rate constants indicate that initial chromophoric species, C, are converted to stable leucochromophores, C_L, through a series of steps which are dependent on ionic species. Furthermore, these leucochromophores can be eliminated to form colourless products (C_P) or they may be reconverted to coloured species (C). These processes can possibly be assigned to reactions involving radicals, in particular the hydroxyl radical ($OH^{\cdot}$).

The present model based on an equilibrium concept can adequately describe the kinetic behaviour of the chromophores in alkaline hydrogen peroxide under constant reagent conditions. It can also describe transient and final behaviour when increasing reagent concentrations to a new set of constant reagent conditions.

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 (~0.02 M) using a laboratory 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 such that a constant temperature of 50°C was maintained. Before each bleaching run, an aliquot of pulp was removed to make blank handsheets so that changes in pulp, due to storage, could be monitored.

Bleaching was initiated by simultaneously adding enough alkali (2 M 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 occasional addition of the necessary amount of hydrogen peroxide calculated from iodometric titration[25] of the bleaching liquor.

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 3 with sulphuric acid (2.5 M), followed by filtration to remove the bleaching liquor. Pulp handsheets of 40-45 g.s.m conditioned basis weight were formed by filtering the required volume of re-dispersed pulp slurry onto Whatman No. 540 filter paper[26]. 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 457 nm, 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[13,27]. These properties were reported as the average per group of 3 handsheets.

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