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PEROXIDE BLEACHING REACTIONS UNDER ALKALINE AND ACIDIC CONDITIONS

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ABSTRACT

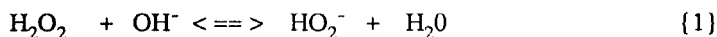
An examination of previously reported kinetic expressions describing peroxide bleaching of wood pulp under alkaline conditions reveals that the overall process can be considered as a combination of two parallel reaction routes. The first route corresponds to a reaction involving direct participation of the perhydroxyl anion in chromophore elimination. This mechanism can be identified with the classical explanation for peroxide bleaching. The second route can be associated with reactions in which chromophores are eliminated through the action of free radical intermediate species. New experimental evidence is presented to show that processes catalysed by transition metal ions can lead to enhancement of bleaching. A two stage peroxide bleaching sequence, initially under acidic conditions in the presence of chromium, followed by alkaline conditions produces an acceleration in bleaching rate, without significant additional consumption of peroxide.

INTRODUCTION

Alkaline hydrogen peroxide is used extensively for bleaching of mechanical pulps (1-6). Although the relative proportion of mechanical pulp bleached with peroxide (approximately 8%) is significantly smaller than that bleached with hydrosulfite (7), this proportion is expected to increase. Hydrogen peroxide is also used under alkaline conditions during production of fully bleached chemical pulps (8). A peroxide stage is often used as the final stage after a conventional multistage

bleaching sequence (8) when several extra points of brightness are required. With increasing environmental concerns, there has also been recent interest in the possibility of replacing chlorinated reagents with hydrogen peroxide during production of bleached chemical pulps (9,10).

For many years the action of alkaline hydrogen peroxide as a bleaching agent has been explained through the action of the perhydroxyl anion HO_2^- (1,2,5), which can be produced according to the equation:



It was believed that this anion was the principal active species involved in the elimination of chromophores in lignin structures (1,2,5). This explanation is consistent with the observation that bleaching activity is generally enhanced by increasing the pH, up to approximately pH 11 (1). Decreased bleaching efficiency at higher pH levels can be explained on the basis of reactions leading to increased peroxide decomposition, particularly those involving the catalytic effects of transition metal ions (11-13). It is also believed that at high pH levels competing reactions producing new chromophores become important (1), giving rise to the "alkali darkening" effect (13).

During the past decade the bleaching action of peroxide has been an active area for research, with many workers concluding that these systems are much more complex than once thought. In particular, it is now believed that various radical species including OH^\cdot and $\text{O}_2^{\cdot-}$ can participate in chromophore elimination (14-17). Furthermore, there has been consideration of possibilities for bleaching processes over a much wider range of pH conditions than used in conventional peroxide bleaching, including neutral and acidic conditions (19-21). In the present work we have examined parallel pathways for peroxide bleaching using a range of pH conditions. We have also undertaken further experimental work aimed at providing additional evidence for this dual mechanism, and discussed our results in the context of the literature pertaining to active species in peroxide bleaching.

There have been two basic approaches to formulating models to simulate the kinetics of alkaline peroxide bleaching (6,22-26). One approach is to relate brightness increase to variables such as initial pH and peroxide charge, temperature, stock concentration etc. (6,26). This type of formulation may be useful in predicting final brightness of a pulp using a given set of conditions, particularly under mill

conditions. The other type of kinetic formulation can be closely associated with the approaches of standard chemical kinetics. In this case, too, kinetic expressions must also be regarded initially as empirical expressions. However, these expressions should reflect the net result of many concurrent elementary processes which occur during bleaching. By analysis of such expressions, particularly if they are formulated directly in terms of the concentrations of the active species, a better understanding of mechanisms involved should be achieved. We have therefore also attempted to further analyse kinetic expressions reported in the literature (22-25) to show how these can be reconciled with our observations concerning bleaching mechanisms.

EXPERIMENTAL

Hydrogen peroxide (30%) and sulfuric acid (98%) were obtained from Ajax Chemicals. Chromium(III) nitrate (99%), DTPA (97%) and potassium hydroxide (99.99%) of semiconductor purity were supplied by Aldrich Chemicals. Semiconductor grade potassium hydroxide was used as the source of alkali in these studies as this introduces very low levels of transition metal impurities (27,28).

All bleaching studies were performed in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. Blocks of *Eucalyptus Regnans* wood were soaked in Milli-Q water for three days prior to grinding. The wood was ground in the presence of dilute aqueous sodium hydroxide, using a small scale grindstone at Australian Newsprint Mills, Boyer, Tasmania. The pulp was filtered to increase the consistency from 1.5% to approximately 20% and stored at 4°C until used.

Bleaching experiments were performed by adding sufficient *E. Regnans* pulp to a solution prepared by adding the required amount of hydrogen peroxide, chromium nitrate and acid or alkali (for pH control) as required to give a total volume of 500 mL with addition of Milli-Q water (26-27). All experiments were carried out at 1% pulp consistency and the solutions were stirred (29) throughout the bleaching runs. For bleaching under acidic conditions the pH was adjusted to 6.0 with either potassium hydroxide or sulfuric acid. After the prescribed time, sufficient potassium hydroxide was added to give a pH of 11.0 for the alkaline bleaching phase. The acidic treatment was performed for 30 minutes and followed by an alkaline phase for 30 - 120 minutes.

Chelated pulps were prepared by treating the pulp with 0.2% DTPA (on o.d. pulp) at 2% consistency for 15 minutes, then filtering and washing the pulp thoroughly.

Iodometric determinations of hydrogen peroxide were performed before the pulp was added, and to the initial filtrate, at the completion of the bleaching run. After addition of acidified potassium iodide and a few drops of ammonium molybdate solution, the liberated iodine was titrated against sodium thiosulfate solution (30). The initial concentration of hydrogen peroxide was 0.10M.

The brightness (%ISO) of the handsheets prepared were then measured using a Zeiss Elrepho with a 457nm filter. Blanks were regularly prepared to monitor any changes in the original pulp with storage time and to allow brightness gains to be calculated.

RESULTS AND DISCUSSION

Kinetic Models

Kinetic phenomena during peroxide bleaching of wood have been much less extensively reported than for many other important reactions, particularly alkaline pulping processes (31-33). Several recent studies (22-25) have considered kinetic behaviour during alkaline peroxide bleaching of mechanical pulps. Kinetic expressions obtained under conditions of constant concentrations of peroxide and alkali, usually obtained at low consistency, are most appropriate to a consideration of reaction mechanisms. Under such conditions the rate of removal of chromophores has been described by the expression:

$$\frac{-d[C_k]}{dt} = k [H_2O_2]_{tot}^a [OH^-]^b [C_k]^c \quad (2)$$

where $[C_k]$ = concentration of chromophores
 $[H_2O_2]_{tot}$ = total concentration of peroxide
 $[OH^-]$ = hydroxide ion concentration

It has been reported (22-25) that the orders of the reaction had the following values: a (1.0), b (0.3 - 0.5) and c (4 - 5). Specific values were found to depend on the particular pulp studied. Although this expression has been derived for conditions of low consistency and constant concentrations of reactants, it has also been applied to typical bleaching situations found for mill conditions (4,34).

Many of the difficulties with interpretation of this type of kinetic expression are identical to those encountered when considering expressions describing alkaline pulping processes (31-33). These include the heterogeneous nature of the reaction, uncertainties in the importance of diffusion processes and questions regarding the validity of defining species within the lignin macromolecules on a molar concentration basis (33). However, accepting these possible limitations, it is possible to proceed with an analysis of this kinetic expression.

The high apparent order of reaction with respect to chromophore concentration would be expected to occur for a set of chromophores with a wide variation in susceptibility to peroxide bleaching. High apparent orders with respect to lignin during pulping and bleaching processes have been discussed previously (32,33). This effect is similar to that found for other heterogeneous systems involving complex components, as often encountered for processes of industrial importance. For example, during cracking of hydrocarbons, while simple reaction orders are found for single components (35) high reaction orders are calculated applying a kinetic model to complex mixtures (gas-oils) containing a wide diversity of chemical structures with different reactivity (36).

The dependence on the rate of chromophore elimination in equation {2} is expressed in terms of the total peroxide concentration, which remains constant during the reaction and is given by

$$[\text{H}_2\text{O}_2]_{\text{tot}} = [\text{H}_2\text{O}_2] + [\text{HO}_2^-] \quad \{3\}$$

where $[\text{H}_2\text{O}_2]$ and $[\text{HO}_2^-]$ are the concentrations of undissociated hydrogen peroxide and perhydroxyl anion respectively. As these species probably differ significantly in their activity in bleaching processes, and many studies have suggested that the presence of the anion has the dominant influence, we have rearranged equation {2}, taking values of a, b and c as 1.0, 0.5 and 5.0 respectively, and using the relationships (22):

$$\frac{[\text{H}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]} = K_a = 10^{-11} \quad \{4\}$$

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14} \quad \{5\}$$

to give the following kinetic expression:

$$\frac{-d[\text{C}_k]}{dt} = k ([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5}) [\text{HO}_2^-] [\text{C}_k]^5 \quad \{6\}$$

Equation {6} shows that the rate of chromophore elimination is directly proportional to the concentration of perhydroxyl anions. The dependence of the rate on alkalinity of the solution is a more complex function, however, consisting of the sum of two terms. The first term increases with alkalinity while the second decreases with increasing pH of the medium. Fig 1a shows the behaviour of the two components of this expression as the pH is changed.

This formulation can be interpreted by assuming chromophore elimination can arise through two parallel pathways following different mechanisms and hence

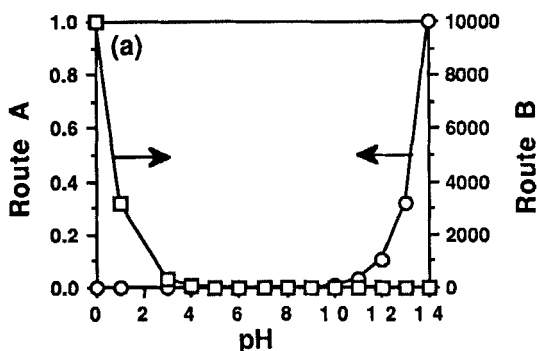


FIGURE 1a. Plots of the two pH dependent terms of the rate expression $([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5})$ against pH. Rates have been calculated based on the appropriate concentration of hydroxide ion.

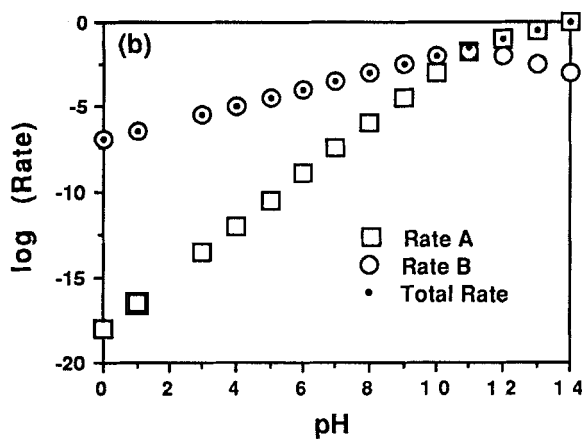


FIGURE 1b. Logarithmic plot of the two components of the rate expression $([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5}) [\text{HO}_2^-]$ and the total rate as the pH is varied. Rates have been calculated based on the appropriate concentration of hydroxide ion and using $\text{p}K_a = 10^{-11}$ for H_2O_2 .

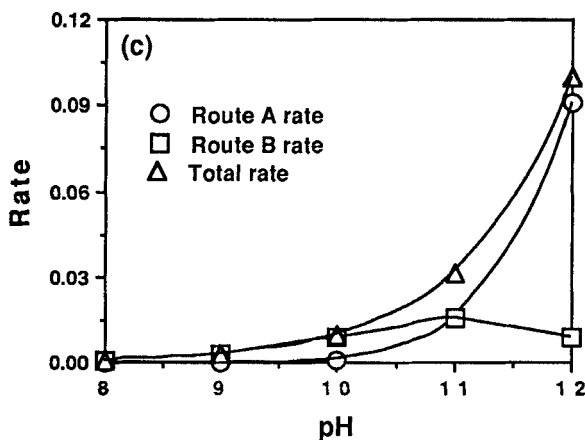


FIGURE 1c. Plots of the two components of the rate expression as in Figure 1b, and the sum of the two rates in the pH range 8 - 12. Rates have been calculated based on the appropriate concentration of hydroxide ion and using $\text{p}K_a = 10^{-11}$ for H_2O_2 .

leading to distinct kinetic behaviour. Route A is favoured by the presence of OH^- and HO_2^- , while route B is favoured by the presence of HO_2^- and H^+ . Fig 1b shows the variation in the in the two components of the expression $([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5})[\text{HO}_2^-]$ as the pH is varied. A small magnitude is associated with both components under neutral and acidic conditions. Under alkaline conditions the rate for route A increases with pH, while a maximum rate is observed for route B at approximately pH 11. It is apparent that, according to this analysis, both routes are of importance in the pH range 8 - 12 normally encountered in conventional peroxide bleaching (Fig 1c), with route A dominant at pH > 11 and route B dominant at pH < 11. At pH 11.0 which would be a typical initial pH value in peroxide bleaching the relative contribution from the two routes would be very similar.

Mechanisms and Active Species

Route A

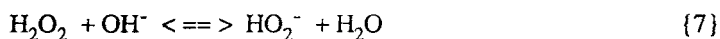
The classical explanation for the action of alkaline hydrogen peroxide is given in terms of the perhydroxyl anion as the active species (1,8). This anion is thought to act as a nucleophile, preferentially attacking centres of low electron density in the lignin structure (14). These reactions would include addition of the perhydroxyl anion to a double bond in a conjugated structure derived from a quinone methide intermediate at the C_2 position of the side chain, at unsubstituted positions in the ring (14) or at the carbonyl group (15). Addition to carbonyl groups in the alpha position of the side chain has also been suggested (9). Most mechanisms presented to illustrate these types of process involve a series of sequential steps, some of which may depend on the presence of hydroxide ions, either during formation of a quinone methide structure (9), or during breakdown of a perhydroxyl intermediate (15).

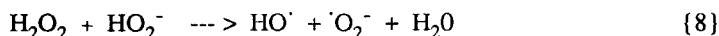
It would appear reasonable to identify this type of mechanism with route A in our kinetic model, where the rate of chromophore elimination depends on $[\text{OH}^-]^{0.5}$, $[\text{HO}_2^-]$ and $[\text{C}_k]^{0.5}$. The appearance of three concentration terms in the rate expression and the non-integer order of the hydroxide ion is consistent with the proposal of a sequential mechanism, in which the perhydroxyl anion and the hydroxide ion interact with the chromophore in different steps of the overall mechanism.

It is apparent that the predicted bleaching rate via route A would increase continuously with pH, so that the total rate of bleaching would not exhibit a maximum value. Most bleaching studies have been reported under conditions where the peroxide concentration falls as the reaction progresses, and in most cases (1) a maximum bleaching rate is found in the range pH 11-12. This could be attributed to an increased rate of peroxide decomposition at high pH levels (5). However, a maximum in bleaching rate is also observed at approximately pH 11 when the peroxide charge is maintained at a constant level throughout (23). This has been explained by the alkali darkening effect, which has been attributed to competing alkali induced creation of new chromophores at high pH levels.

Route B

It has been known for many years that decomposition of aqueous hydrogen peroxide to produce molecular oxygen can occur through free radical intermediates (21), particularly when the process is catalysed by the presence of transition metal ions (21). Those processes have traditionally been regarded as detrimental to peroxide bleaching efficiency, leading to loss of the bleaching agent. Consequently, additives such as sodium silicate, DTPA and magnesium salts are routinely incorporated into bleaching systems to retard decomposition (1,11). During the past decade, however, there has been an increasing awareness that free radicals derived from peroxide decomposition may, in fact, play an important role in the bleaching reactions of wood pulp (14-17,37,38). In the absence of metal ion catalytic species, hydroxyl and superoxide radicals can be produced as follows (39):



$$k_1$$


Taking equations {7} and {8} as the principal route to generation of free radicals, and including a termination step (40):

$$k_2$$


we have a simple overall mechanism for decomposition of hydrogen peroxide to produce molecular oxygen. The final step in which two free radicals combine is very fast (40) compared to the overall rate of reaction (41). Assuming that equilibrium has been established according to equation (7) and $k_2 \gg k_1$ the steady state concentration of free radicals (42) established will depend on the pH of the solution. The kinetic behaviour of this system can be modelled by computer methods (31) using a dynamic simulation program to give a profile of the variation in steady state total free radical concentration with pH as shown in Fig 2a. It is apparent that this profile has a maximum at approximately pH 11, and is similar to that describing the magnitude of route B in Fig 1b. These distributions can also be compared with Fig 2b, which shows the reported (17) variation in rate constant with pH for oxidation of alpha-methyl syringyl alcohol with hydrogen peroxide at 30°C. The rate of alkaline peroxide oxidation for this lignin model compound also exhibits a maximum at approximately pH 11, and the mechanism for this process has been discussed in terms of free radical intermediates derived from hydrogen peroxide (17).

Consequently, it is proposed that the generation of free radical species which can interact with chromophores in the lignin structure give rise to route B in the kinetic model. A number of studies have concluded that it is the hydroxyl radical rather than the superoxide radical that is active in reactions with lignin (21,43-45). The hydroxyl radical is a strong oxidant (38) and is thought to add to aromatic rings in the lignin structure as an electrophile (14).

In the presence of transition metal ions which can catalyse peroxide decomposition we might expect the steady state concentrations of free radical species would be increased, and this has indeed been observed (42). Furthermore, it has been found that the position of the maximum rate occurs at a pH which depends on the metal present under both homogeneous (11) and heterogeneous (46,47) conditions. The metal ions most commonly present in wood pulp which are also active towards peroxide decomposition are manganese, copper and iron. These ions have been found to produce maxima in the pH range 9 -12 (42) as illustrated for manganese in Fig 3a. This range includes the pH at which maximum brightness is usually observed for peroxide bleaching (15). Other metal ions, not normally present in pulp in high concentrations, can exhibit maxima under neutral or acidic conditions as for example with cobalt and chromium (11). Fig 3b shows that for chromium the maximum initial activity occurs at pH 5.8. This observation is useful,

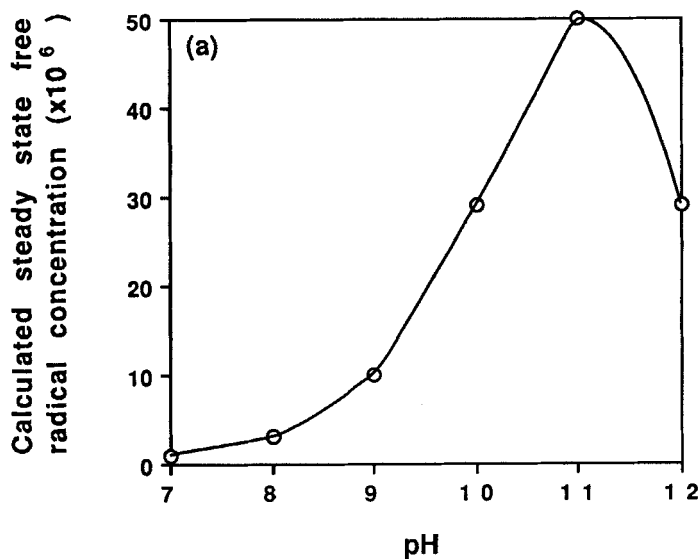


FIGURE 2a. Plot of the variation of steady state free radical concentration with pH. Values calculated using TUTSIM dynamic simulation program (31) with $k_1 = 10^{-3} \text{ s}^{-1}$ and $k_2 = 10^6 \text{ s}^{-1}$.

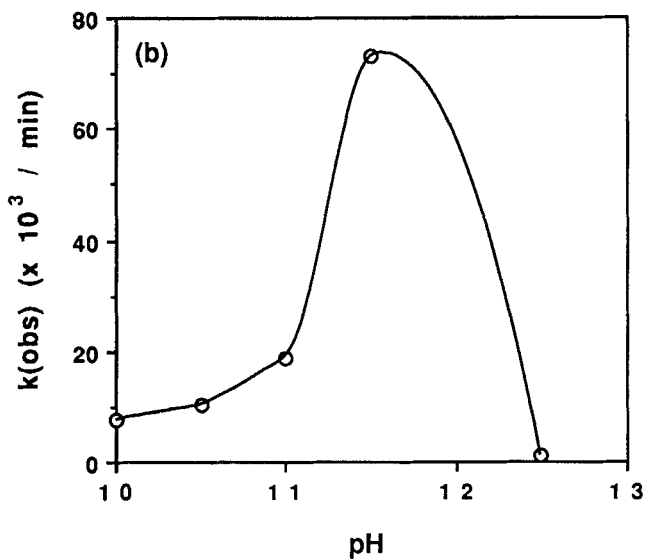


FIGURE 2b. Plot of the variation in the rate constant for the oxidation of alpha-methyl syringyl alcohol by hydrogen peroxide as a function of pH (17).

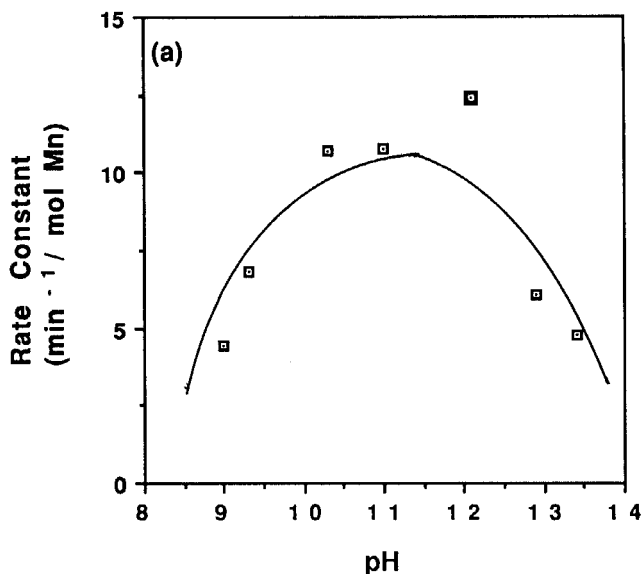


FIGURE 3a. Plot of the variation in the rate of decomposition of hydrogen peroxide in the presence of manganese against pH at 20°C. Initial concentration of hydrogen peroxide 0.10M; initial concentration of manganese nitrate 4.4×10^{-6} M.

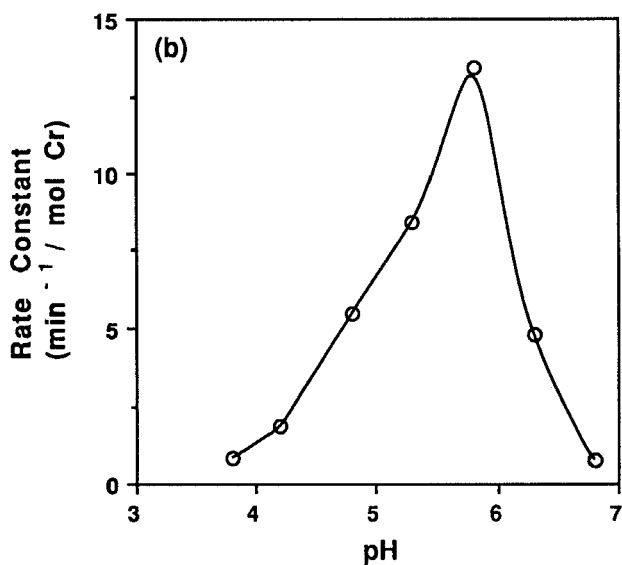


FIGURE 3b. Plot of the variation in the rate of decomposition of hydrogen peroxide in the presence of chromium against pH at 20°C. Initial concentration of hydrogen peroxide 0.10M; initial concentration of chromium nitrate 2.5×10^{-4} M.

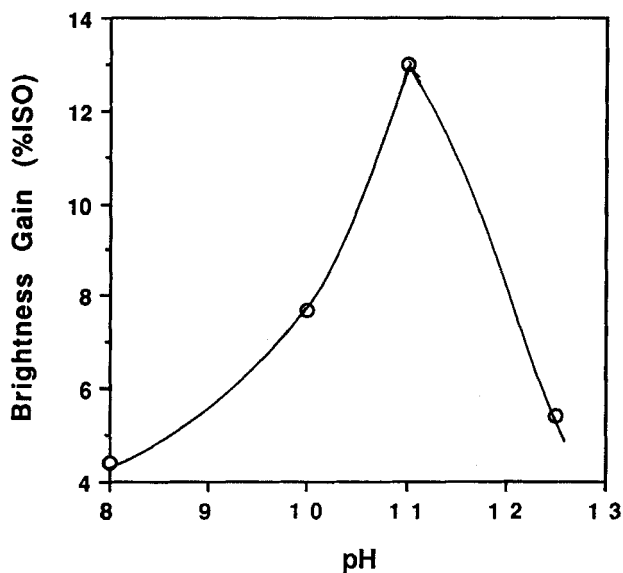


FIGURE 4. Plot of brightness gain against pH for samples of *E.Regnaans* bleached for 120 minutes at 1% consistency, 50°C, with 30% peroxide (w/w on o.d. pulp). Initial brightness of pulp : 53.2 (%ISO).

as it may enable us to expose pulp samples to high concentrations of radical species under conditions where the perhydroxyl ion concentration is low, and the contribution from route A should be very small.

Several recent studies have discussed the possibility of catalytic effects due to the presence of transition metal ions leading to increased rates of delignification with alkaline hydrogen peroxide (12,17). Other investigations have shown that acidic peroxide treatment of pulp can have beneficial effects (48-53), and there are indications that these may be promoted by the presence of metal ions acting as catalysts (50). These observations, coupled with our interpretations of kinetic phenomena led us to undertake further bleaching studies under both acidic and alkaline conditions, and the results of these observations are described below.

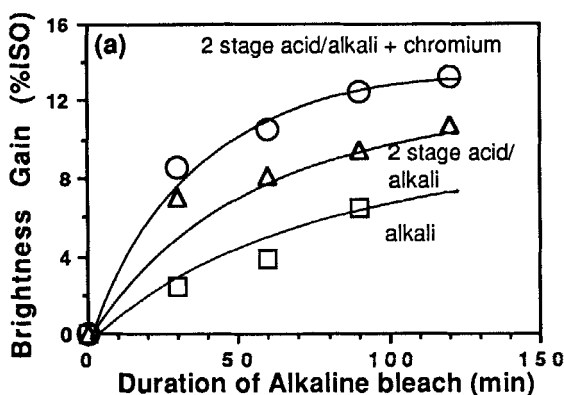


FIGURE 5a. Comparison of one and two stage bleaching processes showing the brightness gain for *E.Regnans* bleached at 1% consistency, 50°C, with 30% peroxide (w/w on o.d. pulp) under various conditions; Initial brightness of pulp : 56.0 (%ISO).

E) 30 minute acid bleach with 2.5×10^{-4} mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

C) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

G) alkaline bleach at pH 11.0 (no acidic treatment).

Bleaching Studies with *Eucalyptus Regnans*

Experimental studies were undertaken with *Eucalyptus Regnans* groundwood. Bleaching was carried out at 50°C at constant pH levels using 1% consistency and 30% hydrogen peroxide (on o.d. pulp). Under these conditions the peroxide concentration did not decrease to low residual levels during the bleaching runs, but it was possible to measure the amount of peroxide consumed. Fig 4 shows the the influence of pH on the brightness of the pulp after bleaching for a period of 2 hours in a single stage alkaine process. For single stage bleaching at pH 6.0 there was no significant increases in brightness of the pulp, even after 10 hours.

Fig 5a shows the increase in brightness of the groundwood pulp under alkaine conditions (initial pH 11.0) over a period of 2 hours for three different bleaching processes. The brightness increase for a standard one stage alkaine

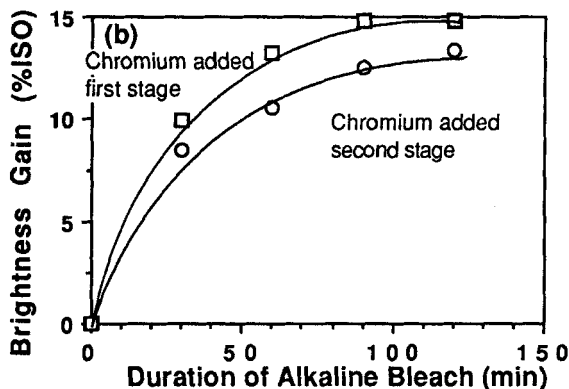


FIGURE 5b The influence of addition of chromium during the first and second stages (conditions as Figure 5a). Initial brightness of pulp : 55.6 (%ISO).

G) 30 minute acid bleach with 2.5×10^{-4} mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

E) 30 minute acid bleach with no added chromium followed by an alkaline bleach with 2.5×10^{-4} mol/L chromium nitrate at pH 11.0.

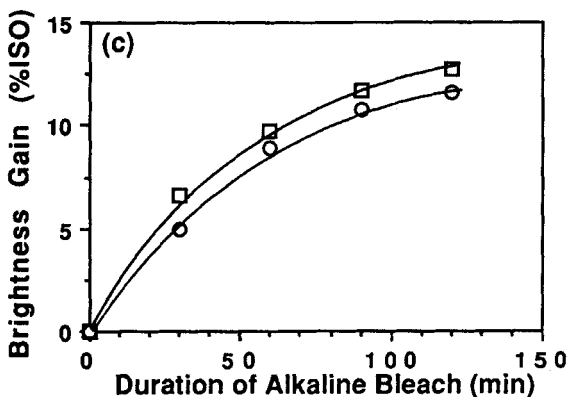


FIGURE 5c The influence of pulp chelation on two stage acid/alkali bleaching sequence in the presence of chromium (conditions as Figure 5a). Initial brightness of pulp : 55.6 (%ISO).

G) 30 minute acid bleach with 2.5×10^{-4} mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

E) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

bleaching process gives the lowest brightness improvement at any particular time. The figure also shows the effect on brightness increase for two-stage processes with prior acid treatment of the pulp at pH 6.0, both with and without addition of a catalytic amount of chromium nitrate (1.0% on o.d. pulp). For these two stage bleaching experiments the duration of the acid treatment was 30 minutes in each case, after which the pH of the solution was adjusted to 11.0 by addition of potassium hydroxide. Fig 5a shows that the rate of brightness enhancement is increased by an acid treatment prior to alkaline peroxide bleaching at pH 11.0. The addition of chromium to the system at pH 6.0 increases the effect of the first stage acid treatment. Our results can be compared to a previously reported study in which a two stage peroxide bleaching sequence was used for brightening an oxygen bleached hardwood kraft pulp (50). In that study compounds of tin, vanadium or titanium were introduced during the first stage under acidic conditions at pH 4-6, followed by an alkaline bleaching stage. Another study (51) has described an improved bleaching response with a two stage acid/alkali peroxide treatment without addition of a catalyst.

Figure 5b shows that the chromium is active in the first stage of the two stage bleaching sequence. When chromium is added to the alkaline stage of a two stage bleaching sequence significantly less brightness gain is achieved. Comparing these curves with figure 5a, it is apparent that when chromium is present only in the alkaline stage, the response is approximately the same as when no chromium is added, thus further supporting the view that the chromium is having an effect during the first stage of the bleaching sequence.

Figure 5c shows the influence of chelating and washing the pulp prior to a two stage acid/alkali bleaching sequence in the presence of chromium. Table 1 shows that this procedure has a significant effect on reducing the levels of transition metal ions in the pulp. The results in figure 5c show that there is a reduced brightness enhancement when metal ions are removed from the pulp, and it appears that the effects of chromium and the other transition metal ions in the pulp are additive. We have also shown that the removal of transition metal ions from *Pinus Radiata* TMP by chelation and washing reduces the effectiveness of two stage acid/alkali peroxide bleaching (52).

It would appear that the acidic peroxide treatment results in changes in the lignin structure promoted by the species formed by the catalytic decomposition of hydrogen peroxide (18,54). This can happen even when no catalyst is introduced

TABLE 1. Metal ion content of Pulps used in this work.

Wood type	Metal ion (ppm) ¹		
	Iron	Manganese	Copper
<i>Eucalypt</i> SGW	32	8	72
Chelated <i>Eucalypt</i> SGW	32	1	32

1) Concentration determined by atomic absorption after digestion of pulp.

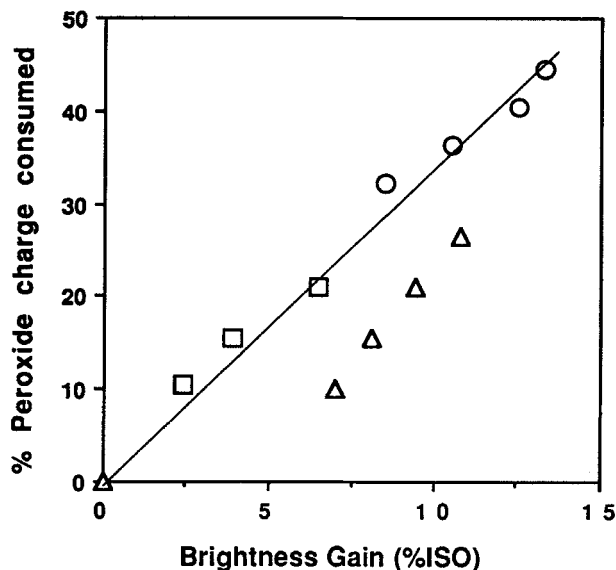


FIGURE 6. Plot of the peroxide consumption against brightness gain for pulps bleached at 1% consistency, 50°C and 30% peroxide (on o.d.pulp) under various conditions:

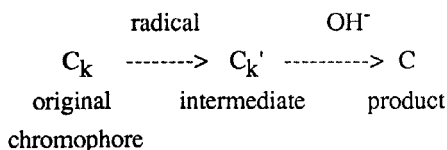
E) 30 minute acid bleach with 2.5×10^{-4} mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

G) alkaline bleach at pH 11.0 (no acidic treatment).

C) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

(55), as metal ions from the wood itself may be active. A number of studies have indeed shown that lignin structures are reactive under acidic conditions (14,20,48,49), most likely through processes involving free radicals (14), although little enhancement in brightness may be achieved (19) as expected from our kinetic analysis. We can regard the initial product of reaction between a radical species and a lignin chromophore as an intermediate, the formation of which does not in itself improve pulp brightness. The rate of formation of the intermediate will depend primarily on the concentration of free radical species as shown in Fig 2b.

In order to observe an increase in brightness a second step is required in the overall mechanism to eliminate the chromophore, which depends directly or indirectly on the presence of the hydroxide ion :



Under acidic conditions where $[\text{OH}^-]$ is low the intermediate is formed, and its production is enhanced by the presence of catalysts which promote radical formation. Under alkaline conditions, this intermediate species may again be produced, but it rapidly reacts in the presence of hydroxide ions leading to elimination of the chromophore.

Fig 6 shows the consumption of hydrogen peroxide plotted against the increase in pulp brightness for pulps bleached by a one stage alkaline process (initial pH 11.0) and the two stage acid/alkali process both in the presence and absence of chromium. Comparing the single stage alkaline bleach and the two stage bleach in the presence of chromium, it is apparent that the brightness gain achieved in each case is approximately proportional to the amount of peroxide consumed. It is also clear that use of a two stage process without added chromium can increase the efficiency of bleaching under the conditions employed in this study.

CONCLUSION

This study has provided further evidence for a dual mechanism for chromophore elimination during peroxide bleaching. Analysis of a previously

reported kinetic expression leads to the conclusion that the two parallel routes for bleaching correspond to: [1] a reaction which depends upon the direct participation of the perhydroxyl anion; [2] a reaction in which free radical species participate in chromophore elimination. Our analysis shows that both routes are important at pH levels normally encountered in conventional bleaching of wood pulp with hydrogen peroxide. Although the rate of chromophore elimination is very slow under acidic conditions, reactions occur which render the chromophores present more susceptible to subsequent reaction under alkaline conditions. Formation of these reactive intermediates is promoted by the formation of free radical species produced through catalytic decomposition of peroxide by transition metals such as chromium.

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