The Role of the Hydroxyl Radical in Peroxide Bleaching Processes

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THE ROLE OF THE HYDROXYL RADICAL IN PEROXIDE BLEACHING

PROCESSES

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ABSTRACT

The kinetics of N,N-dimethyl-4-nitrosoaniline (DMNA) oxidation in alkaline and acidic hydrogen peroxide have been studied at 50°C. Based on the premise that DMNA is a specific acceptor for the hydroxyl radical during the oxidation process, the effects of transition metal ions and stabilizing agents on steady state concentrations of the radical species have been determined. Using these kinetic formulations, it has been inferred that the hydroxyl radical has little influence on alkaline peroxide bleaching of mechanical wood pulp at low consistency. However, using a two-stage acid/alkali peroxide bleaching process a correlation exists between the calculated relative hydroxyl radical concentration in the acidic stage and the final pulp brightness after the alkaline stage.

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INTRODUCTION

Hydrogen peroxide has been used as a bleaching reagent in the pulp and paper industry for over 40 years, mainly to achieve higher brightness of mechanical pulps. Approximately 90% of the hydrogen peroxide currently supplied in Canada is used for this purpose and is becoming the dominant chemical for mechanical pulp bleaching[1]. It has traditionally been thought that the active species present under alkaline bleaching conditions is the perhydroxyl anion, HO_2^- [2-6]. Oxidative reactions involving nucleophilic attack of this species on specific chromophore types such as $\alpha-\beta$ unsaturated aldehydes, α-carbonyls and quinones have been described as the major route for elimination of chromophores[7-15]. Over the past decade there has been a growing awareness that other species, particularly the hydroxyl radical (OH˙) may also play an important role during peroxide bleaching processes[13,14,16-19]. There are, however, contradictory reports in the literature concerning whether this radical species leads to beneficial or detrimental effects during chromophore elimination[13,14,16-20].

The use of hydrogen peroxide is also expected to increase very significantly over the next decade as a bleaching agent for chemical pulps[21-24]. Traditionally, high brightness chemical pulps (e.g. Kraft pulps) have been obtained using reagents such as chlorine and chlorine dioxide to remove residual lignin and achieve the high brightness levels required for market pulp. Increasingly, however, environmental concerns are applying pressure on industry to move toward chlorine-free processes using agents such as oxygen, ozone and hydrogen peroxide. The reactions occurring in these processes are as yet ill-defined, but their understanding is of enormous potential economic importance. Under conditions where selective lignin removal is required, as in bleaching of chemical pulps, it is possible that processes involving the hydroxyl radical play a very significant role[21]. However, it is also known that attack on the carbohydrate component of the pulp by this radical species can also lead to depolymerisation[25], resulting in unacceptably low mechanical strength properties. The controlled activity of this radical species as a selective reagent could therefore be crucial in moving to chlorine-free bleaching.

Recently[26] a kinetic analysis of peroxide bleaching has also shown the possibility of a dual mechanism. Of these two mechanisms one can be associated with the perhydroxyl anion while the second can be related to the presence of radical

species. Several two-stage acid/alkali peroxide bleaching processes[26-31] have been developed to test this kinetic analysis and also investigate alternate peroxide bleaching sequences.

Recent interest in the hydroxyl radical has arisen in other areas of chemistry and biochemistry, as for example, the interaction of hydroxyl radicals with DNA[32]. Modelling of atmospheric chemistry[33] usually includes hydroxyl radicals as an important part of these systems. The self-purification of natural waters is also related to the presence of hydroxyl radicals[34-36].

A number of methods have been developed to measure hydroxyl radical concentrations in aqueous systems. These include using phthalic hydrazide as a trap and detection via chemiluminescence of the species formed[37], UV determination of radicals formed by the interaction of hydroxyl radicals with thiocyanate[38]or bicarbonate ions[39] and ESR techniques. A simple spectrophotometric method based on the oxidation of N,N-dimethyl-4-nitrosoaniline (DMNA) has been demonstrated to be specific for hydroxyl radicals in alkaline media[40-41]. Kraljic et al.[40] showed that the hydroxyl radical is the only species which reacts with DMNA, even in the presence of other potential oxidants. Attempts have been made to identify products, but most are unstable, with N,N-dimethyl-4-nitroaniline observed as a major product[41]. The method has been applied to studies of the influence of metal ions in neutral and mild alkaline solutions of hydrogen peroxide[35-36,42-44]. In this study we have used pH conditions typical of industrial bleaching (pH 11), as well as mild acidic conditions, and developed a kinetic analysis to show the influence of both transition metal additives and stabilizing reagents commonly encountered in commercial bleaching processes.

Using this analysis we have attempted to elucidate the effects of hydroxyl radicals in single stage alkaline peroxide bleaching and two-stage acid/alkali peroxide bleaching processes by a correlation of the calculated relative steady state hydroxyl radical concentrations with the final brightness response of the pulp.

EXPERIMENTAL

Hydrogen peroxide (30%) was obtained from Ajax Chemicals. Nitrates of copper, iron, magnesium, manganese and chromium (all 99%), diethylenetriamine-

pentaacetic acid (DTPA) (97%), *N,N*-dimethyl-4-nitrosoaniline (DMNA) (97%), potassium hydroxide of semiconductor purity (99.99%) and sodium silicate solution (30%) were obtained from Aldrich Chemicals. Methanol was distilled before use.

All experiments were performed in polyethylene reaction vessels immersed in a constant temperature water bath maintained at 50°C throughout the experiment. Milli-Q water[45] was used to minimize the level of introduced transition metal ions. The pH was maintained at either 5.8 or 11.0 throughout all experiments by addition of either potassium hydroxide or dilute sulfuric acid.

UV-Visible spectra were recorded on a Varian DMS 100 spectrophotometer. DMNA concentrations were determined from the absorbance at 440nm. Experiments were ceased when approximately 30% of the initial DMNA charge was consumed due to the influence of reaction products which have significant absorptions close to 440nm. In the absence of peroxide, DMNA solutions at pH 11.0 decolourize slowly. This has been taken into consideration in all cases. Peroxide residuals were determined by iodometric titration of samples. The samples were added to sulfuric acid, excess potassium iodide and ammonium molybdate. The liberated iodine was then titrated with sodium thiosulfate to a starch endpoint.

Bleaching experiments were performed in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. All bleaching was under conditions of constant pH 11.0 to allow comparison with solution studies. In two-stage bleaching processes the pH of the first stage was maintained at 5.8. The pulp used was *E. regnans* SGW, prepared on a small scale grindstone at Australian Newsprint Mills Boyer mill. The pulp, after filtration and washing, was stored at 20% consistency and 4°C until used. Experiments were performed at 1% pulp consistency with a peroxide charge of 12% on oven dried pulp. Samples were taken at 30 minute intervals for determination of peroxide residuals and brightnesses (%ISO). For bleaching under constant conditions of alkali and peroxide concentration, additions of chemicals were made when deviation from the initial conditions were observed. This was achieved by regular determination (10-15 minute intervals) of the peroxide concentration and continuous pH measurement.
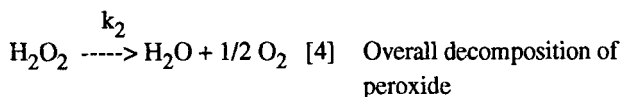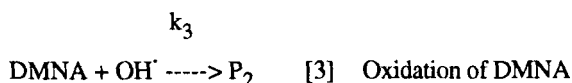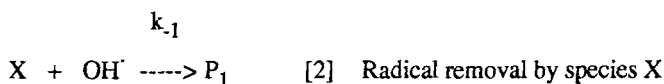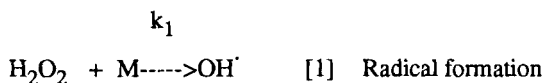
The brightness of the unbleached pulp was regularly monitored to allow calculation of brightness gains and to determine if any changes occurred with storage. The brightness of the unbleached pulp was 53-55 %ISO. Pulp brightnesses were measured using a Elrepho 2000 (as %ISO) after making standard handsheets.

RESULTS AND DISCUSSION

Kinetic Model Development

Previous studies have shown that DMNA reacts specifically with the hydroxyl radical in the presence of hydrogen peroxide[40-41].

Simplified kinetic expressions for oxidation of DMNA can be developed as follows:

$$H_2O_2 \ + \ M \xrightarrow{\ k_1\ } OH^{\cdot} \qquad [1] \quad \text{Radical formation}$$

$$X \ + \ OH^{\cdot} \xrightarrow{\ k_{-1}\ } P_1 \qquad [2] \quad \text{Radical removal by species X}$$

$$DMNA + OH^{\cdot} \xrightarrow{\ k_3\ } P_2 \qquad [3] \quad \text{Oxidation of DMNA}$$

$$H_2O_2 \xrightarrow{\ k_2\ } H_2O + 1/2\ O_2 \quad [4] \quad \text{Overall decomposition of peroxide}$$

where: - M is a metal species.

- X are species (other than DMNA) which can trap hydroxyl radicals.

- DMNA is N,N-dimethyl-4-nitrosoaniline.

- P_1 and P_2 are oxidation products.

- k_1, k_{-1}, k_2 and k_3 are the respective rate constants

The rate of removal of DMNA[35] is given by:

$$\frac{-d[DMNA]}{dt} = k_3[DMNA][OH^{\cdot}] \qquad\qquad [5]$$

The steady state concentration of hydroxyl radicals is given by:

$$\frac{-d[OH^.]}{dt} = k_3[DMNA][OH^.] - k_1[H_2O_2][M] + k_{-1}[OH^.][X] = 0$$

$$[6]$$

Two limiting cases can be considered:

Case 1:

Reaction with DMNA is the dominant reaction leading to the removal of radicals:

i.e $k_3[DMNA][OH^.] \gg k_{-1}[OH^.][X]$
so that:

$$[OH^.] = \frac{k_1[H_2O_2][M]}{k_3[DMNA]}$$

$$[7]$$

and: $\quad \frac{-d[DMNA]}{dt} = k_1[M][H_2O_2]$

$$[8]$$

Case 2:

Reaction with other species (X) is the dominant termination reaction for hydroxyl radicals. In our system X could be metal species[19], hydrogen peroxide[35] or another radical species[17].

Under this condition $\quad k_{-1}[OH^.][X] \gg k_3[DMNA][OH^.]$
leading to

$$[OH^.] = \frac{k_1[H_2O_2][M]}{k_{-1}[X]}$$

$$[9]$$

and : $\quad \frac{-d[DMNA]}{dt} = \frac{k_1 k_3[DMNA][H_2O_2][M]}{k_{-1}[X]}$

$$[10]$$

On integrating the kinetic expressions are:

Case 1:

$$[DMNA]_t = [DMNA]_0 - k_1[M][H_2O_2].t \qquad [11]$$

Case 2:

$$\ln\frac{[DMNA]_t}{[DMNA]_0} = k_1k_3[DMNA][M][H_2O_2].t \qquad [12]$$

The derived kinetic expressions [11] and [12] indicate first-order dependence on concentrations of metal ion species and peroxide concentrations. It is well known that the nature of the metal ion species present in aqueous systems is strongly dependent on the pH of the medium[46]. For studies carried out at constant pH, [M] could be regarded as constant throughout a particular experiment. Maintaining the peroxide concentration at a constant level throughout an experiment is difficult, particularly in the presence of significant concentrations of catalytic species where the rate of decomposition is appreciable. Instead, it is preferable to take account of the continuous decline in peroxide concentration with time in the kinetic expression, by assuming first-order decomposition:

$$-\frac{d[H_2O_2]}{dt} = k_2[H_2O_2] \qquad [13]$$

on integrating we have:

$$[H_2O_2] = [H_2O_2]_0 e^{-k_2 t} \qquad [14]$$

This leads to the kinetic expressions

Case 1:

$$[DMNA]_t = [DMNA]_0 - k_1[M][H_2O_2]_0 e^{-k_2 t}.t \qquad [15]$$

Case 2:

$$\frac{\ln[DMNA]_t}{[DMNA]_0} = \frac{k_1 k_3 [DMNA][M][H_2O_2]_0 e^{-k_2 t} \cdot t}{k_{-1} k_2 [X]} \qquad [16]$$

Case 1 requires a zero-order dependence on [DMNA], while a first-order dependence is predicted in case 2. It should be easily established which model is preferable by observing whether the rate of removal of DMNA depends on the initial amine concentration. Thereafter, the validity of the proposed model can be further tested by examining plots of the appropriate [DMNA] function against the time variable $te^{-k_2 t}$.

Kinetic Phenomena under Alkaline Conditions

Experiments were performed to follow the rate of removal of DMNA in alkaline peroxide solutions at 50°C, under conditions of constant pH = 11.0. The concentration of DMNA was measured spectrophotometrically, while decomposition of hydrogen peroxide was measured by periodic titration of samples. The effect on kinetic phenomena of introducing transition metal ions, including iron, manganese and copper were observed, as well as the influences of adding stabilizers such as sodium silicate, magnesium nitrate and DTPA.

The development of the kinetic models as shown in the previous section assumes that the rate of peroxide decomposition is first-order with respect to peroxide concentration. This was found to be a reasonable assumption for each of the systems investigated, with linear logarithm-time relationships as shown in Fig. 1. Addition of transition metal ions or stabilizers to the alkaline peroxide solution changed the magnitude of the rate constant for peroxide decomposition (k_2) as shown in Table 1 .

Experiments also showed that the rate of DMNA removal is dependent on the initial amine concentration, as shown in Fig. 2. This demonstrates that the kinetic expression developed as Case 1 cannot be valid under these conditions. Analysis of kinetic phenomena was therefore based on testing the validity of equation [16] (Case 2).
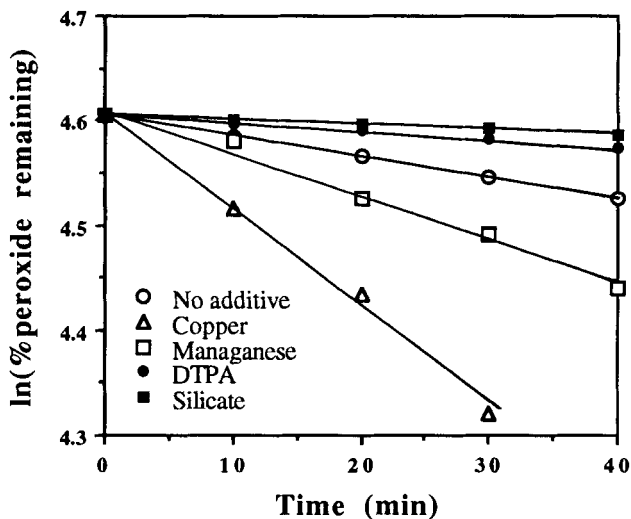
FIGURE 1. First-order rate plots for hydrogen peroxide decomposition in the presence of various catalysts and stabilizers. Peroxide concentration = 0.0353M, pH 11.0, 50°C, copper = 8.02 x 10^{-6}M, manganese = 9.14 x 10^{-6}M, DTPA = 5.09 x 10^{-5}M and silicate = 4.00 x 10^{-2}M

TABLE 1.

Rate Constants for Peroxide Decomposition in the Presence of added Transition Metal ions and Stabilisers at 50°C.

Additive	Concentration (x 10^{-5} M)	k_2 (x 10^{-3}/min)
None	-	2.00
Copper	0.40	6.56
Manganese	0.91	4.18
Iron	0.90	1.65
Magnesium	6.63	0.33
DTPA	25.4	0.55
Silicate	2000	1.33
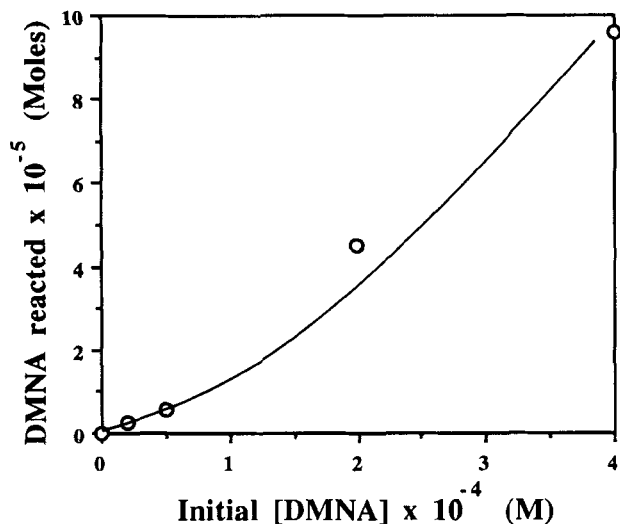
FIGURE 2. Relationship between the initial DMNA concentration and the quantity reacted after 20 minutes.

Fig. 3 shows that, in the the absence of added transition metal ions or stabilizers, plots of $\ln[DMNA]_t/[DMNA]_0$ against the time function te^{-k_2t} are linear, with values of the correlation coefficient (R^2) close to unity. This is consistent with equation [16], assuming that the concentration of radical terminating species [X] can be regarded as constant for a particular system.

The slopes of the plots illustrated in Fig. 3 can be related to the value of the rate constant for removal of DMNA defined by

$$K = \frac{k_1 k_3}{k_{-1} k_2} \tag{17}$$

The Influence of Added Transition Metal Ions

The transition metals commonly reported to have most influence on hydrogen peroxide stability during industrial bleaching of mechanical pulps are manganese,
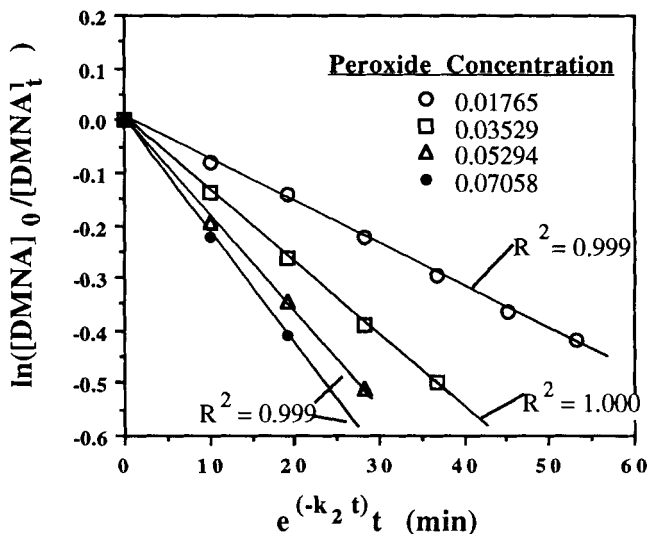
FIGURE 3. Model fit for various levels of peroxide concentration. DMNA concentration = 2.00 x 10^{-5}M.

iron and copper[46-49]. The presence of manganese in particular is a concern under conditions normally encountered during bleaching[50]. Traces of these transition metal impurities are derived either from the wood itself, or are introduced during pulp processing[47]. In industrial bleaching processes chelating agents such as DTPA are often used to modify the catalytic activity of these metals towards peroxide decomposition[46]. In the present work, we have not added combinations of metals and chelating agents as we wish to separate out the individual behaviour due to each additive.

The influence of copper, manganese and iron addition on the kinetics of peroxide decomposition and DMNA oxidation was investigated at pH 11.0 and 50°C. The validity of equation [16] was tested in the presence of introduced metal ions by plotting $\ln[DMNA]_t/[DMNA]_0$ against the time function $te^{-k_2 t}$. In all cases tested, adequate linear relationships were obtained, as illustrated in Fig. 4. Using the slopes of these plots, values of K were plotted as a function of metal additive concentrations as shown in Fig. 5. The magnitude of K gives the rate constant for the removal of DMNA in each case. This term also reflects the relative ratio of
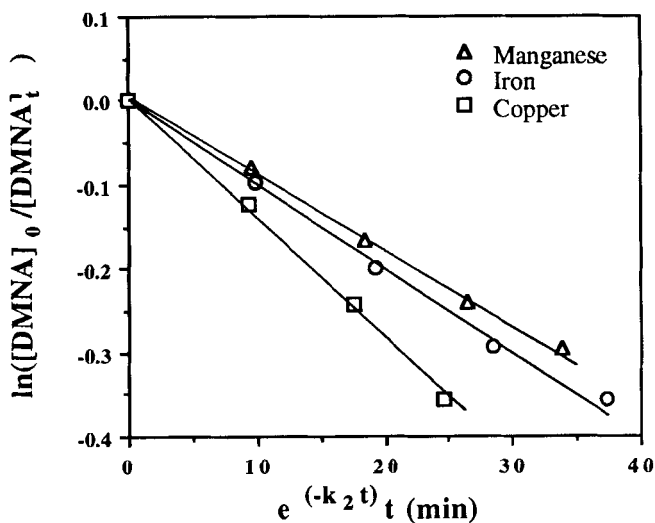
FIGURE 4. Model fit for the addition of transition metal ion catalysts. Conditions as in Fig. 1, DMNA concentration = $5.00 \times 10^{-5}M$, copper = $4.01 \times 10^{-6}M$, manganese = $9.14 \times 10^{-6}M$, iron = $4.49 \times 10^{-6}M$

k_1/k_{-1} and is directly proportional to the steady state concentration of radicals (equation [9]).

Previous studies by Ernestova et al. on the DMNA-peroxide system have been reported at 70°C at pH 7[35]. Their results showed that addition of iron(III) had no effect on DMNA oxidation[35], and concluded that micro-colloidal iron particles present do not contribute to the formation or disappearance of hydroxyl radicals. Other studies have concluded that iron does not decompose peroxide via a radical mechanism (34). Fig. 5a shows that K is not significantly affected by increasing the amount of iron in the system. In fact, it appears that the addition of iron causes a slight reduction in K compared to the system where no iron is introduced.

In contrast, the addition of copper to the alkaline peroxide system produces a significant increase in the values of K as illustrated in Figure 5. Hydroxyl radical concentrations as measured by K are almost directly proportional to the levels of copper introduced. Our observations are in agreement with previous studies [34-36]
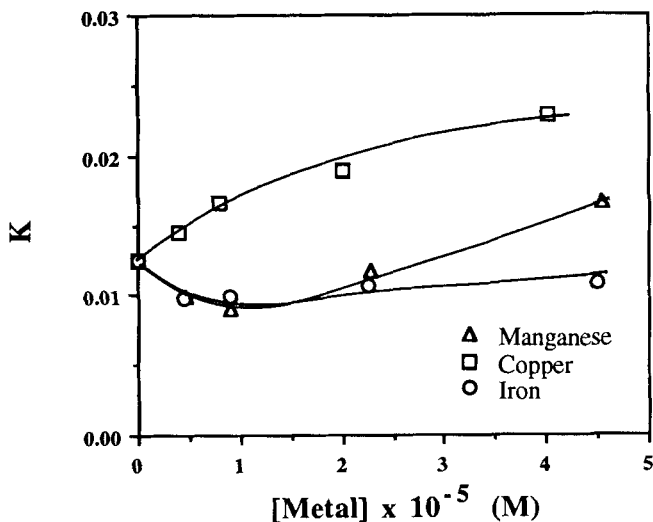
FIGURE 5. Plots showing the variation in the rate constant K for the addition of copper, iron and manganese.

where addition of Cu(II) was found to produce a proportionate increase in the rate of oxidation of DMNA. These workers also reported that the effects of added Mn(II) were similar to those of iron, with manganese addition producing little influence on the formation or removal of hydroxyl radicals. Other studies have concluded that the catalytic decomposition of hydrogen peroxide in the presence of Mn(II) does proceed via a chain mechanism involving hydroxyl radicals[43]. Our results at low levels of manganese addition show little influence of manganese on hydroxyl radical concentration as shown in Fig. 5.

The Influence of Added Stabilizing Agents

Stabilizing agents commonly used in the peroxide bleaching of mechanical pulps are magnesium salts[46,51-52], sodium silicate[3,46,51-52] and chelating agents such as DTPA and EDTA[2,3,46,50,52]. The addition of these reagents aims to reduce the catalytic decomposition of hydrogen peroxide, leaving higher levels of peroxide

available for pulp bleaching. Peroxide decomposition in the presence of these stabilizers follows first-order kinetics and the values of k_2 are reported in Table 1. In all cases stabilization of peroxide is achieved and plots of $\ln[DMNA]_t/[DMNA]_0$ against te^{-k_2t} again showed adequate linear correlations. Calculated values of K from these plots for the addition of magnesium, DTPA and silicate are shown in Fig. 6.

The effect of the of magnesium addition is shown in Fig. 6a. The value of K is decreased markedly at low levels of magnesium and further addition does not affect the value significantly. The mechanism of stabilization of alkaline peroxide solutions by magnesium involves either the interruption of free radical processes that are initiated by the residual transition metal ions present in the solution[46], or deactivation of the catalytically active species in some way[46].

The addition of DTPA, as shown in Fig. 6b shows very similar trends for K as magnesium. The value is reduced to low levels compared to unstabilized peroxide solutions at low stabilizer addition, and further addition of stabilizer has little or no effect. It has previously been proposed[50] that the mechanism of DTPA stabilization of alkaline peroxide solutions is related to the ability of DTPA to bind and deactivate the residual transition metal ions in solution, thus reducing the catalytic decomposition.

The effect of sodium silicate addition, as shown in Fig. 6c, differs from that of magnesium and DTPA. The value of K, which is a measure of the hydroxyl radical concentration available for reaction with DMNA, does not decrease on addition of silicate.

The Influence of Methanol

Alcohols, particularly methanol and ethanol, are known to be effective hydroxyl radical traps[36]. Figs. 7a and b show the effect of methanol concentration on peroxide decomposition and the calculated steady state concentration of hydroxyl radicals. Fig. 7a shows that increasing the concentration of methanol leads to an increase in the rate of peroxide decomposition. The reason for this is not clear, but could relate to transition metal ion impurities introduced with methanol. Fig. 7b shows that increasing the proportion of methanol in solution significantly decreases the value of K. Fig. 7c shows the effect of increasing hydrogen peroxide
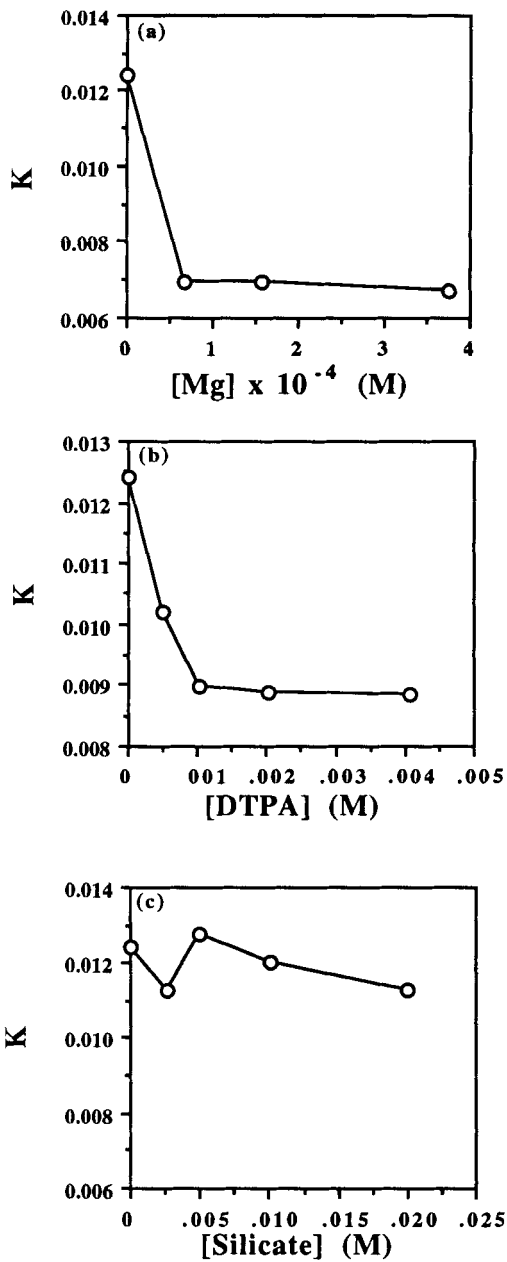
FIGURE 6. Plots showing the variation in the rate constant K for (a) magnesium, (b) DTPA and (c) silicate. Conditions as in Fig. 4.
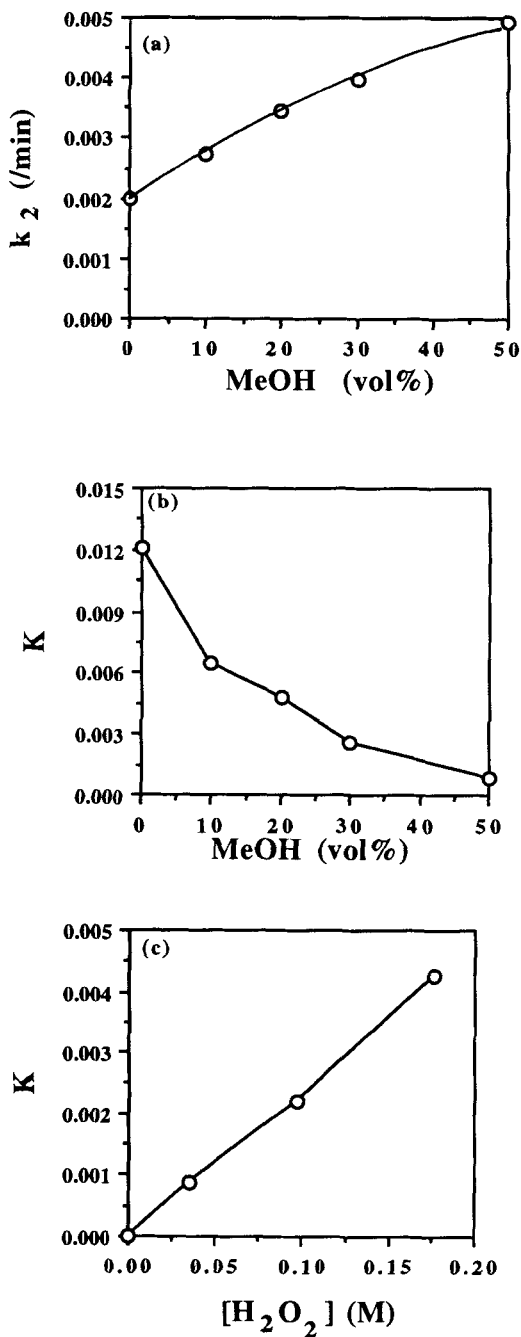
FIGURE 7. The effect of methanol addition on (a) peroxide decomposition rate, (b) K. (c) The effect of varying peroxide concentration on K in 1:1 methanol:water. pH 11.0, other conditions as in Fig. 4.
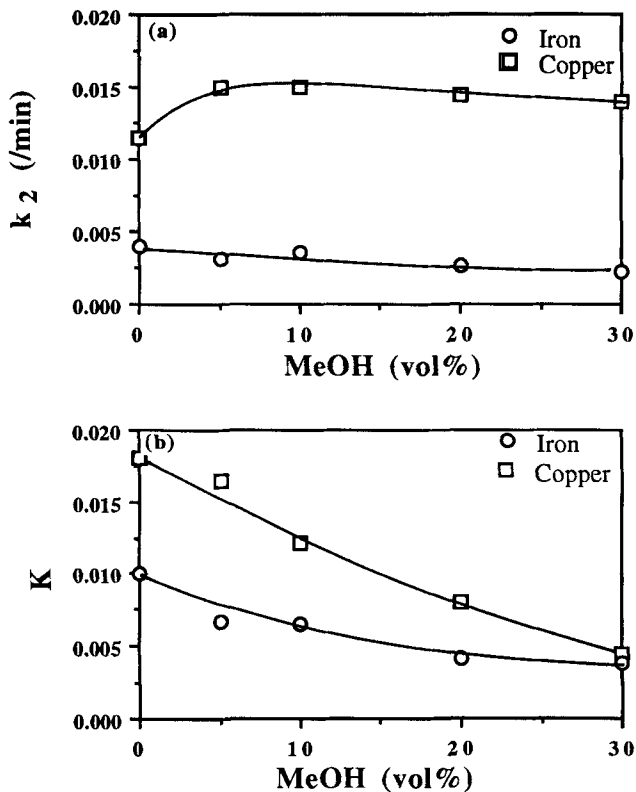
FIGURE 8. The effect of methanol addition on (a) k_2 and (b) K in the presence of added copper (1.003×10^{-5}M) and iron (1.113×10^{-5}M). pH 11.0, other conditions as in Fig. 4.

concentration on the value of K in 1:1 methanol:water. As expected, higher concentrations of hydrogen peroxide result in higher values of this constant.

Figs. 8a and b show the effect of increasing the methanol to water ratio in the presence of added iron and copper. The effect of methanol on the rate of peroxide decomposition, as shown in Fig. 8a, is small. Increasing the proportion of methanol in the solution markedly decreases the rate of DMNA decolorization (Fig. 8b) and thus the calculated concentration of hydroxyl radicals.

Bleaching Studies under Alkaline Conditions

In theory it is possible to examine the influence of hydroxyl radical concentration during alkaline peroxide bleaching by following DMNA oxidation in the presence of pulp. Brightness gain could then be correlated with the radical concentration profile for each system. However, this approach has the drawback that DMNA, being highly coloured, may directly affect the brightness of the pulp by adsorption onto the fibres. Fig 9 shows the effect of DMNA concentration on brightness gain during alkaline peroxide bleaching and also in the absence of peroxide under alkaline conditions. Clearly, DMNA itself can influence the optical properties of the pulp.

It is therefore preferable to draw correlations between the calculated radical concentrations from our solution studies with the results of peroxide bleaching experiments in the absence of DMNA. However, it is first necessary to determine whether the presence of the pulp affects the oxidation of DMNA under our experimental conditions, as reflected by the calculated parameters. Table 2 shows that the calculated values for K are very similar in the presence and absence of pulp. Values of k_2 are increased in the presence of pulp in the case of magnesium addition and with no additive present, due to the consumption of peroxide by bleaching processes. Table 2 also shows that the values of K, which reflect availability of hydroxyl radicals, give similar trends with additives introduced, both in the presence and absence of pulp. It therefore appears reasonable for us to correlate values of K from our solution studies (in the absence of pulp) with the observed bleaching response of the pulp in the absence of DMNA.

Figure 10a shows results obtained for the addition of various amounts of magnesium nitrate to peroxide bleaching of pulp. The final brightness of the pulp is not significantly affected by the presence of magnesium or the implied reduced concentration of hydroxyl radicals. A slight reduction in peroxide consumption was achieved with the introduction of magnesium, but the brightness gains in the presence and absence of magnesium are similar. Bleaching studies in the presence of varying quantities of methanol, illustrated in Fig. 10b, also show that pulp brightness is not significantly affected by the presence of a radical trap, thus supporting the results obtained with magnesium.

Figure 11 shows negative effects of additions of iron, copper and manganese on brightness gain during peroxide bleaching experiments. However, it is difficult
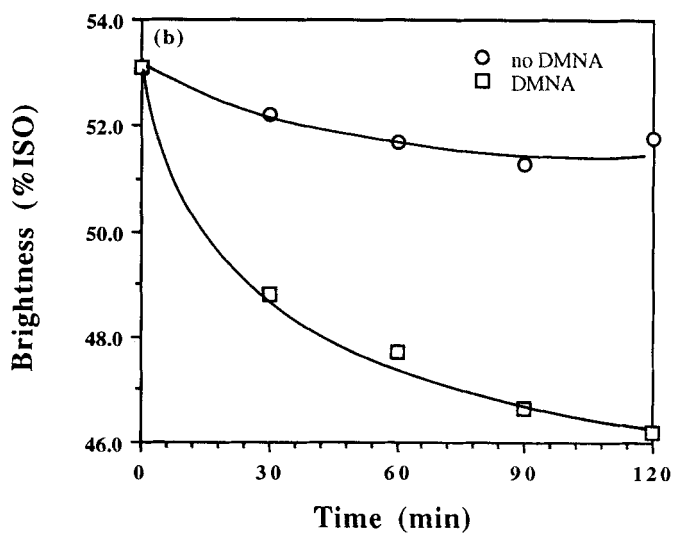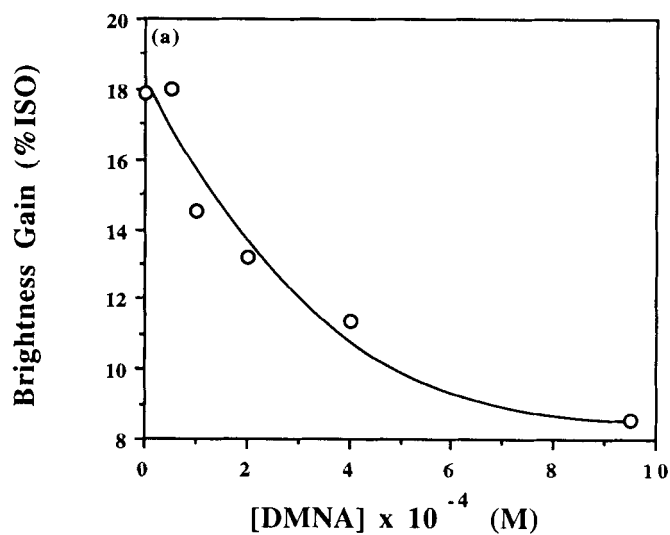
FIGURE 9. The effect of DMNA concentration on (a) the bleaching response of pulp and (b) alkali darkening. Conditions: pH 11.0, 50C, 1% consistency, (a) 12% peroxide on o.d. pulp, (b) [DMNA] 2×10^{-4}M.

TABLE 2

Values of Rate Constants in the Presence and Absence of Pulp. Conditions: 50°C, 1% consistency, pH 11.0, 0.0353M peroxide.

Additive		k_2 ($\times 10^{-3}$ /min)	K ($\times 10^{-2}$)
none	solution	2.00	1.24
copper	solution	13.3	1.89
magnesium	solution	0.36	0.67
none	pulp	3.10	1.27
copper	pulp	9.17	1.71
magnesium	pulp	1.29	1.28

to isolate the influences of radical concentration in these experiments, as the concentration profile for total peroxide is also strongly dependent on the introduction of these additives. For this reason experiments were performed under conditions where both the pH and peroxide concentration were maintained at constant levels [53]. Table 3 shows that for the introduction of either transition metal ions or stabilisers under constant conditions there is no significant difference in brightness gain, even though the solution studies indicate that significantly different concentrations of hydroxyl radicals would be available.

Our results are in agreement with those of Reitberger *et al.* who used a method based on chemiluminescence of solutions after addition of phthalic hydrazide[37] to follow generation of hydroxyl radicals during peroxide bleaching. They reported that copper was particularly efficient in formation of hydroxyl radicals from alkaline hydrogen peroxide, while silicate, DTPA and magnesium sulfate reduced their concentration[54]. Their method also showed that at low pulp consistencies (2.5%) there were no positive effects due to enhanced formation of hydroxyl radicals during alkaline peroxide bleaching of a mechanical pulp.

However, other investigations have concluded that peroxide decomposition products can have either positive or negative effects on brightness gain. Sjogren *et*

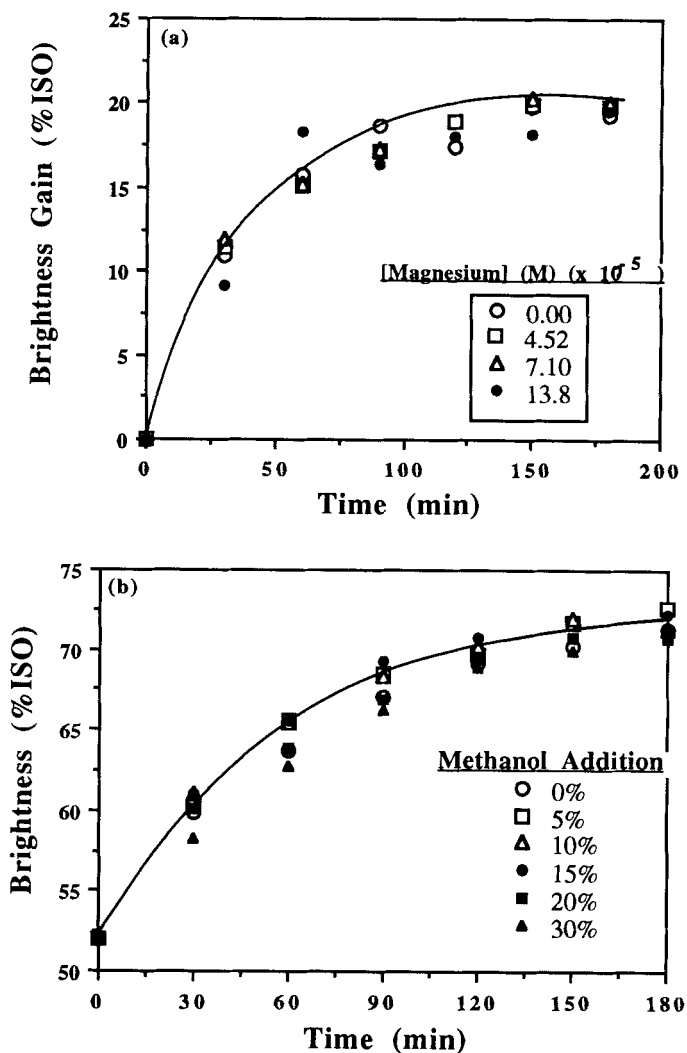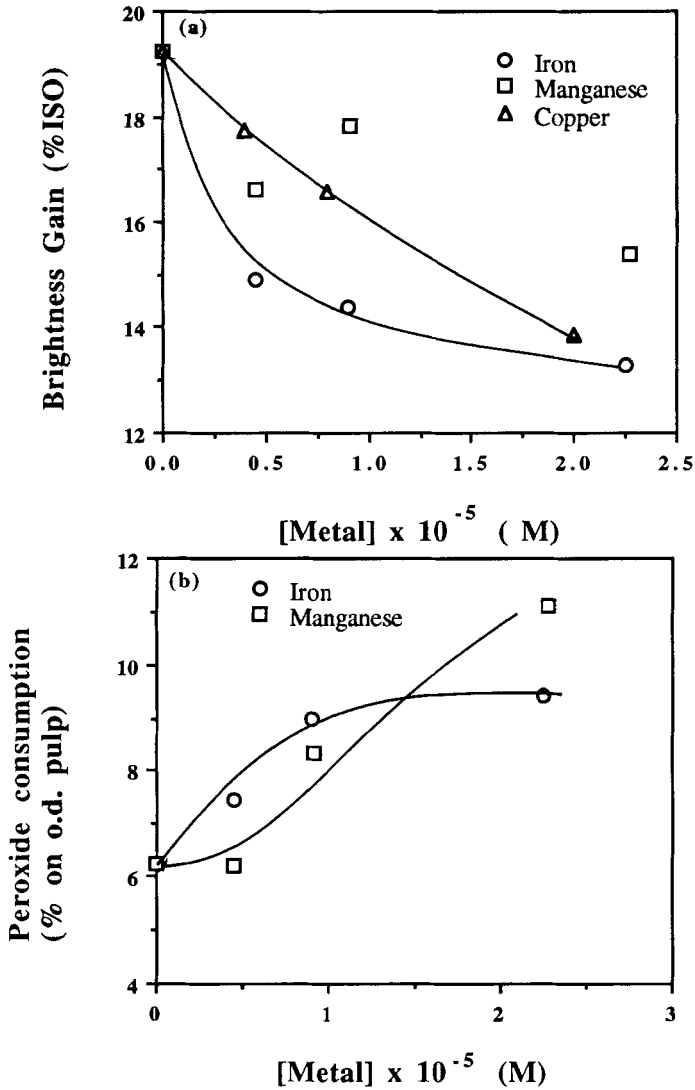**FIGURE 10.** The brightness response of *E. regnans* SGW in the presence of (a) magnesium and (b) methanol. pH 11.0, 12% peroxide on oven dry pulp, 1% stock consistency, 50°C.

FIGURE 11. The change in a) final brightness and b) peroxide consumption for bleaching in the presence of added transition metal ions. Conditions: 1% pulp consistency, 50°C, pH 11.0, 12% peroxide on o.d. pulp, duration of bleach:180 minutes.

TABLE 3.

Bleaching response of *E. regnans* pulp under conditions of constant concentration of peroxide (12% on oven dry pulp) and alkali (pH 11.0). Other conditions as in Fig. 10a.

Additive	Concentration (x 10^{-5} M)	Brightness Gain (%ISO)		K (x 10^{-2}/min)
		60 minutes	180 minutes	
None		11.9	18.4	1.24
Copper	1.00	10.6	17.6	1.70
Manganese	1.14	12.7	17.5	0.90
Iron	1.12	12.1	18.3	1.05
Magnesium	7.98	10.6	17.2	0.70
Silicate	2000	11.5	18.1	1.20

al.[55] have reported positive effects of hydroxyl radicals produced by irradiation with γ rays during peroxide bleaching of a mechanical pulp. Kutney *et al.*[20] observed brightness reversion when a bleached pulp was exposed to alkaline peroxide in the presence of catalysts including iron, manganese and copper, and attributed the effects to peroxide decomposition products.

The apparent inconsistencies in these observations regarding the influence of the hydroxyl radical during alkaline peroxide bleaching of mechanical pulps may lie in the experimental conditions used, for example pulp consistency. From an analysis of the kinetics of chromophore removal during peroxide bleaching, Moldenius *et al.*[56] postulated that the effects of short lived species become much more apparent as the pulp consistency is increased, as these active intermediates could more easily migrate between fibres. Reitberger[54] also found that at increased pulp consistency positive effects of hydroxyl radicals become apparent.

Kinetic Phenomena under Acidic Conditions

Some transition metals exhibit maximum catalytic activity towards peroxide decomposition under acidic conditions[26,30], although the rate of decomposition of

TABLE 4.

Rate constant for peroxide decomposition in the presence of added chromium at 50°C.

[Cr] $(\times 10^{-5} M)$	k_2 $(\times 10^{-4}/min)$
0.00	4.20
2.49	6.00
4.97	9.86
9.95	16.0

peroxide is usually low without added catalysts at low pH. Table 4 shows first-order rate constants for decomposition of hydrogen peroxide in the presence of added chromium. Again the model (equation [16]) gives adequate linear correlations and peroxide decomposition follows first-order kinetics. Fig. 12a shows that the rate of removal of DMNA and the steady state concentration of hydroxyl radicals both increase with the addition of chromium.

The addition of methanol to acidic solutions of hydrogen peroxide containing chromium results in marked decrease in K at much lower levels of methanol than required for alkaline solutions (Fig. 7b), as shown in Fig. 12 b. The peroxide decomposition rate is greatly reduced in the presence of methanol, compared to the small changes noted in alkaline solution. The addition of magnesium under acidic conditions has a similar effect on K as shown in figure 12c.

Bleaching Studies under Acidic Conditions

Previous investigations[26,30-31] have shown that under acidic pH conditions addition of chromium to peroxide bleaching liquors can improve the subsequent response of mechanical pulps under conventional alkaline bleaching conditions. These studies showed that although no brightness gain was observed under acidic bleaching conditions, the chromophores present are rendered more susceptible to
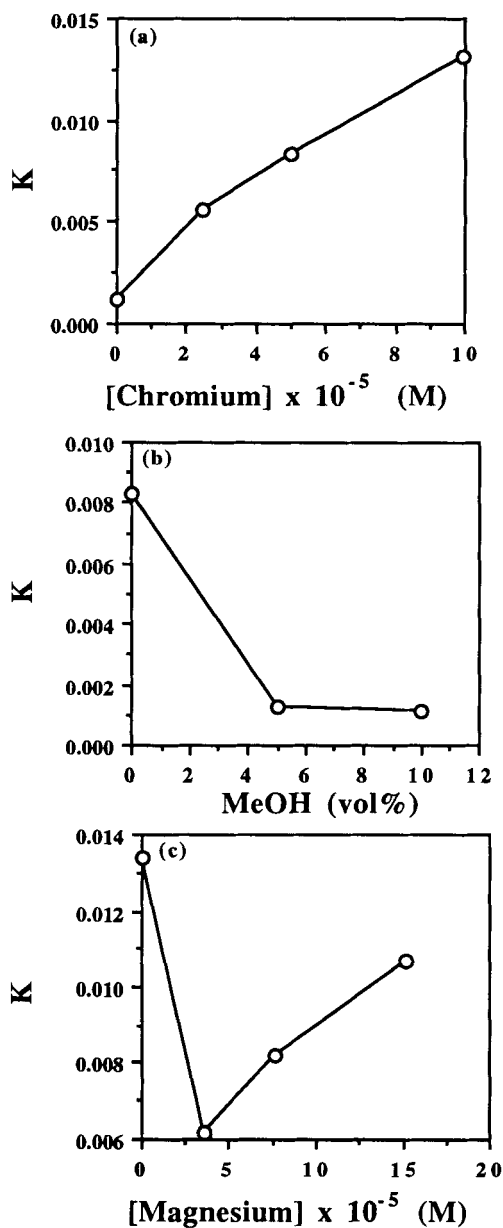
FIGURE 12. Plots showing the variation in K for the addition of (a) chromium, (b) chromium and methanol and (c) chromium and magnesium. Conditions: pH = 5.8, [DMNA] = 5 x 10^{-5}M.
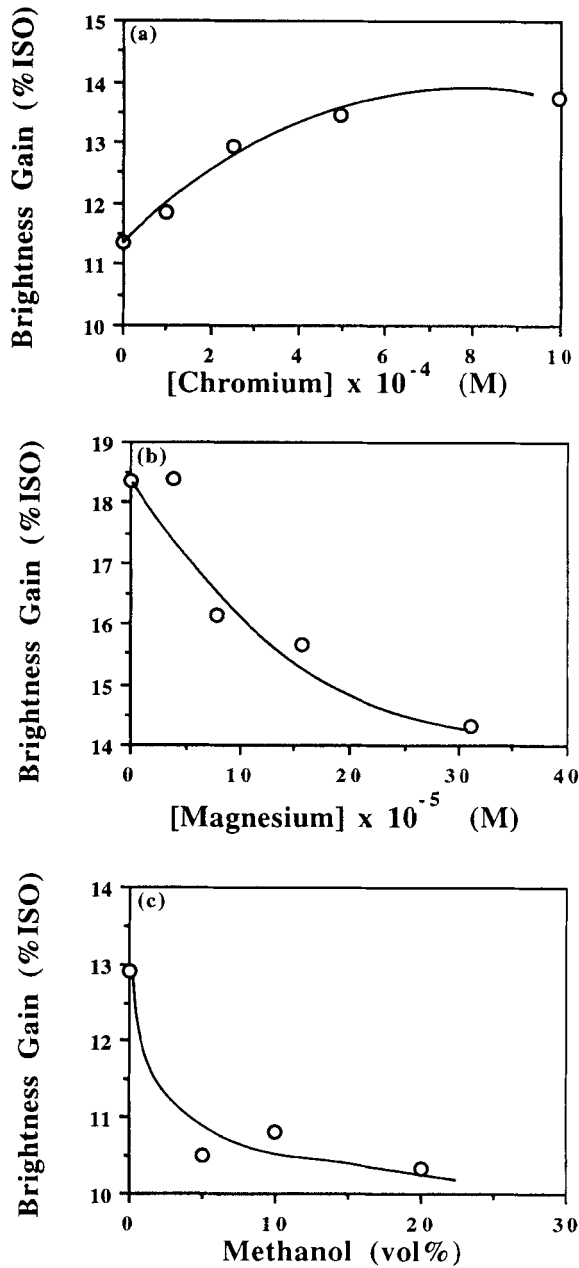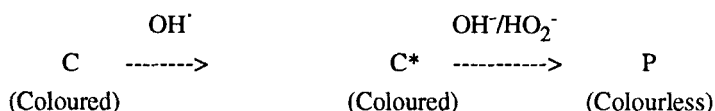
FIGURE 13. The effect of (a) chromium, (b) chromium and methanol and (c) chromium and magnesium addition on the brightness response during a two-stage bleaching process. Conditions: 1% pulp consistency, 50°C, 12% peroxide on o.d. pulp, acidic stage: 15 minutes, pH 5.8; alkaline stage 120 minutes, pH 11.0.

bleaching in an alkaline peroxide medium. This implies that hydroxyl radicals may have a positive effect on bleaching, provided the pulp is exposed to radicals under acidic conditions.

Figure 13a shows the bleaching response after the two-stage acid/alkali process in the presence of added chromium in the first stage. This can be compared to figure 12a showing the calculated hydroxyl radical concentrations. By increasing the hydroxyl radical concentration in the acidic stage of a two-stage process, the final brightness of the pulp can be increased. This process has[26,30] been explained previously in terms of a dual mechanism of peroxide bleaching, with bleaching being related to both the presence of the perhydroxyl anion and the hydroxyl radical, and these results support such a mechanism.

In the presence of stabilisers to reduce the hydroxyl radical concentration (Figure 12b and c), a decrease in brightness may be anticipated. Figures 13b and 13c show that for the addition of methanol or magnesium, a decrease in brightness is indeed observed after the alkaline stage. Clearly, as the radical concentration is reduced the brightness gain also decreases, indicating that the presence of hydroxyl radicals can result in an increased brightness response. This cannot be associated with a change in radical concentration in the alkaline stage as has previously been shown (Table 4, Figs. 10a and 10b)

Bleaching under acidic conditions in the presence of the hydroxyl radical enhances the final brightness of the pulp after the alkaline stage. However, no change in brightness is observed after the acidic stage[26,30-31]. This indicates that changes occur within the lignin structure that do not cause a change in colour of the pulp, but increases the susceptibility of the chromophores to elimination in the subsequent alkaline stage, as outlined below.

$$\begin{array}{ccccc} & OH^{\cdot} & & OH^-/HO_2^- & \\ C & \text{-------->} & C^* & \text{----------->} & P \\ (Coloured) & & (Coloured) & & (Colourless) \end{array}$$

The reason for the hydroxyl radical not having an influence under alkaline conditions may be related to the oxidation potential of this species. Under alkaline conditions the oxidation potential of the hydroxyl radical is significantly lower than under neutral or acidic conditions[19], thus lowering the reactivity. Furthermore, the pK_a of the hydroxyl radical is 11.4[19], producing the oxyl radical, $^{\cdot}O^-$, which has a

significantly lower oxidation potential than the hydroxyl radical, and is therefore less likely to be a major bleaching species.

Under acidic conditions, the oxidation potential of the hydroxyl radical is increased compared to alkaline conditions (2.72V under acidic conditions compared to 2.32V under neutral conditions)[19] and, therefore, the effect of hydroxyl radicals under acidic conditions may be more easily observed. Several two-stage peroxide bleaching processes have been reported[26-31] under acidic conditions followed by alkaline conditions, and the effects have been attributed to the action of the hydroxyl radical.

CONCLUSION

Concentrations of hydroxyl radicals available for reaction in alkaline or acidic solutions of hydrogen peroxide can be calculated from an analysis of DMNA oxidation kinetics. Similar parameters relating to radical concentration are obtained both in the presence and absence of pulp. These parameters can be correlated with bleaching response in the absence of DMNA. The present studies show that a wide range of concentration levels of hydroxyl radical are available depending on whether metal ions or stabilisers are present during bleaching. However, the final pulp brightness at low consistency under alkaline conditions is not significantly affected by reactions involving the hydroxyl radical. For two-stage bleaching processes, where the pulp is first subjected to acidic conditions, the availability of hydroxyl radicals at low pH can significantly influence the final pulp brightness achieved after subsequent alkaline bleaching.

ACKNOWLEDGMENTS

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