Rationalization of the Use of TAED During Activated Peroxide Delignification and Bleaching. Part I: Kinetic Model

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A kinetic model has been built to predict the generation of peracetic acid (PAA) during the reaction between tetraacetylethylenediamine (TAED) and hydrogen peroxide (perhydrolysis). The effect of pH, temperature, reactant concentrations and reaction time was studied. In alkaline medium (pH >10), the peracetate anion is formed almost instantaneously at a high yield, but it is unstable and is rapidly decomposed by hydrolysis. At mid-alkalinity (pH 7.5–8.5), the formation of PAA is much slower, and the yield is limited by PAA disproportionation and by peracetolysis (reaction of TAED and peracetate anion). At acidic pH (pH 3.5–6), the decomposition of PAA is very slow, and good generation conditions can be found by increasing temperature and reactant concentrations. In the latter case, modelling is particularly useful and offers the possibility of controlling the time–concentration profile of the reacting species and the PAA release during a bleaching stage.

Le mécanisme réactionnel de génération d'acide peracétique (PAA) par réaction entre le peroxyde d'hydrogène et le tetra-acétyle ethylène diamine (TAED) a été modélisé cinétiquement. Le pH, la température, la concentration en réactif et le temps de réaction ont été étudiés. En milieu alcalin (pH >10), l'anion peracetate est formé quasi-instantanément avec un haut rendement, mais il est instable et rapidement décomposé par hydrolyse. En milieu faiblement alcalin (pH 7.5–8.5), la génération de PAA est beaucoup plus lente, et le rendement est limité par dismutation du PAA, ainsi que par la réaction de peracétolyse (reaction entre le TAED et l'anion peracetate). A pH acide (pH 3.5–6), l'acide peracétique est stable, et de bonnes conditions de génération peuvent être trouvées en augmentant la température et la concentration des réactifs. Dans ce dernier cas, la modélisation s'avère particulièrement utile pour prédire et contrôler l'évolution des espèces réactives dans le milieu ainsi que la vitesse de formation d'acide péracétique.

INTRODUCTION

Alkaline hydrogen peroxide is used widely in the pulp industry to bleach lignin-rich pulps to brightness levels of 80–83% ISO without substantial delignification. The bleaching effect of hydrogen peroxide has been attributed to its ability to react with various coloured carbonyl-containing structures in lignin [1]. In the last few years, the interest in totally chlorine free processes has stimulated research on ways to use hydrogen peroxide as a delignifying agent. The advantages of using hydrogen peroxide are the low investment cost and the accompanying strong bleaching effect. However, hydrogen peroxide is a rather poor delignifying agent compared to chlorine dioxide or oxygen. Therefore, the way to activate hydrogen peroxide for pulp bleaching has recently been the subject of numerous investigations.

Since the 1980s, tetraacetylethylenediamine (TAED) has been adopted widely in Europe for use in powdered detergent compositions as an activator for peroxygen bleaching agents [2]. Application to the bleaching of sulphite pulps [3], mechanical pulps [4,5] or recycled pulps [6] is more recent and has not reached industrial acceptance yet. Potential benefits are improved yields, reduced corrosion (by reduced residence time, temperature and pH) and improved pulp brightness [4,7]. Croud and Tompsett [8] and Croud [9] have proposed to work at acidic pH to get maximum benefit from the delignifying action of peracetic acid (PAA) which would be the active species. Despite the slow reaction between TAED and hydrogen peroxide, improved delignification results were obtained and the process was patented [10,11]. However, there is no evidence that other conditions should not be preferable.

The action of hydrogen peroxide on esters or N-acyl donors can be depicted by reaction (1).

Mechanistic aspects and kinetic data relative to this type of reaction have been described in detail in the work of Favier [12], Becker [13] and Hofmann et al. [14]. Compounds structurally similar to TAED, such as N,N′-diacetyl N,N′-dimethylurea, pentaacetyl glucose, tetraacetylglycoluryl and 1,5-diacetyl-2,4-dioxohexahydro-1,3,5 triazine (see Fig. 1) have also been studied.

According to this mechanism, the active species would be the generated PAA or peracetate anion. Several studies of the use of PAA in pulp bleaching have defined the optimum conditions for this chemical. However, nothing indicates that these conditions should be also the best for the TAED–H_2O_2 system. In

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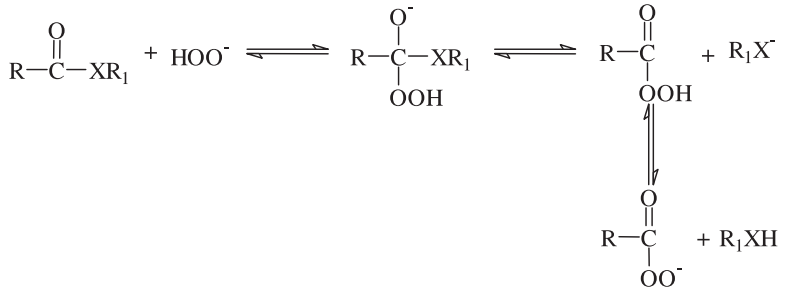
Reaction 1



where

X = O^-–, $\underset{|}{N}$ – CO – R_2, ...

R, R_1, R_2 = H, CH_3, ...

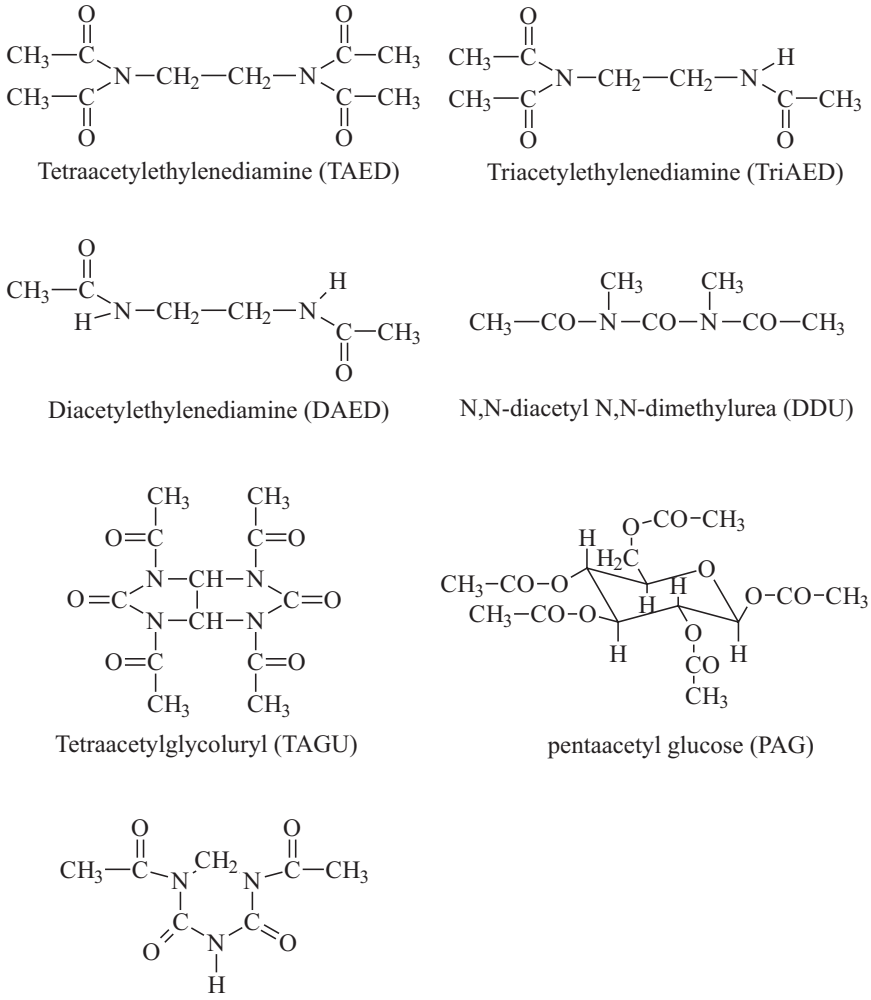


Fig. 1. Structure of the N-acyl donors used in stain bleaching.

fact, in this latter case, PAA first has to be produced at a sufficient rate before reacting with lignin. Moreover, one can expect that PAA produced progressively in the medium and kept at low concentration during bleaching should be decomposed less than during a batch PAA bleaching stage [15,16].

The purpose of this paper is to present a theoretical work in which available kinetic data concerning the TAED–H_2O_2–PAA reaction system are gathered to establish a mathematical model aimed at selecting optimal conditions for delignification or bleaching of chemical pulps. The kinetic data used in this work are taken from studies by Davies et al. [17] and Ni et al. [15,16] where transition metal influences were negated as much as possible. In real pulp bleaching experiments, transition metal cations may interfere. Nevertheless, the accuracy and usefulness of the simplified kinetic model presented herein are demonstrated in the second paper of this series, in which the results of kraft pulp bleaching tests using the TAED–H_2O_2 system will be evaluated and discussed.

DEVELOPMENT OF A KINETIC MODEL

Reaction Mechanism and Kinetic Equations

We will assume that the active species in a TAED–hydrogen peroxide bleaching system is the PAA or the peracetate anion generated by the reaction between hydrogen peroxide and TAED or triacetylethylenediamine (TriAED). However, competitive reactions take place: hydrolysis and peracetolysis of TAED and TriAED; and decomposition of PAA.

Perhydroxyl or hydroxyl anions react with TAED (perhydrolysis or hydrolysis) to form consecutively TriAED and diacetylethylenediamine (DAED) with the release of two molecules of PAA or acetic acid (reactions 2–5). A maximum of 2 mol of PAA or acetic acid and 1 mol of DAED can be produced per mole of TAED.

$$\text{TAED} + HOO^- \rightarrow \text{TriAED} + AcOO^- \quad (2)$$

$$\text{TriAED} + HOO^- \rightarrow \text{DAED} + AcOO^- \quad (3)$$

$$\text{TAED} + OH^- \rightarrow \text{TriAED} + AcO^- \quad (4)$$

$$\text{TriAED} + OH^- \rightarrow \text{DAED} + AcO^- \quad (5)$$

Since the above reactions are elementary, their rate expressions can be expressed by :

$$r_2 = k_2 \cdot [\text{TAED}] \cdot [HOO^-] \quad (6)$$

$$r_3 = k_3 \cdot [\text{TriAED}] \cdot [HOO^-] \quad (7)$$

$$r_4 = k_4 \cdot [\text{TAED}] \cdot [HO^-] \quad (8)$$

$$r_5 = k_5 \cdot [\text{TriAED}] \cdot [HO^-] \quad (9)$$

Davies [17] has measured, by ultraviolet spectrometry, the disappearing rates of TAED and TriAED at pH = 9.6 and 30°C, in a medium containing hydrogen peroxide in excess. At this pH, the TAED and TriAED are not likely to

react with hydroxyl anions, competitors of perhydroxyl anions, because of the lower nucleophilicity of OH^- compared to that of HOO^- and the difference in concentration between these two species.

The following rate expressions were found:

$$r_2 = k_{obs(2)} \cdot [\text{TAED}] \cdot [H_2O_2]_0 \quad (10)$$

and

$$r_3 = k_{obs(3)} \cdot [\text{TriAED}] \cdot [H_2O_2]_0 \quad (11)$$

where

$k_{obs(2)} = 3.35\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$

and

$k_{obs(3)} = 1.16\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$

Since $k_{obs(i)}$ is pH dependent, the following expression can be deduced:

$$k_i = k_{obs(i)} \cdot \frac{Ka_1 + [H^+]}{Ka_1} \quad (12)$$

where $i = 2$ or 3, and Ka_1 is the acidity constant of hydrogen peroxide.

With the data $Ka_1 = 2.511 \times 10^{-12}$ at 30°C, the values of k_2 and k_3 are found equal to 339 and 118 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively, at 30°C.

The decomposition rates of TAED and TriAED (hydrolysis) were also measured at pH = 9.6 and 30°C in the absence of hydrogen peroxide. Similar expressions as for perhydrolysis were found:

$$r_4 = k_{obs(4)} \cdot [\text{TAED}] \quad (13)$$

and

$$r_5 = k_{obs(5)} \cdot [\text{TriAED}] \quad (14)$$

where

$k_{obs(4)} = 1.4 \times 10^{-4}\ \text{s}^{-1}$

and

$k_{obs(5)} = 5.0 \times 10^{-5}\ \text{s}^{-1}$

Introducing

$$K_i = k_{obs(i)} \frac{[H^+]}{Kw} \quad (15)$$

where $i = 4$ or 5, and Kw is the ionic product of water, the values of k_4 and k_5 were found to be 3.52 and 1.26 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively, at 30°C.

In the molecules DAED, TriAED and TAED, the reactivity towards nucleophiles increases with the number of acetyl groups present in the molecule. This reflects the electron-withdrawing effect of additional acetyl groups in the molecule. In TAED, the delocalization of the nitrogen lone pair occurs over each carbonyl function, hence reducing the strength of the N–C bonds in the molecule, whereas in TriAED, just one pair of carbonyl groups is reactive. The low reactivity of DAED is typical of amides and due to resonance stabilization of the amide bond.

With the formation in the medium of the peracetate anion ($AcOO^-$), peracetolysis may also occur:

$$\text{TAED} + AcOO^- \rightarrow \text{reaction products} \quad (16)$$

$$\text{TriAED} + AcOO^- \rightarrow \text{reaction products} \quad (17)$$

The rate of reaction (16) has been measured by Davies [17]:

$$r_{16} = k_{16} \cdot [\text{TAED}] \cdot [AcOO^-] \quad (18)$$

where $k_{16} = (3.8 \pm 1.6) \times 10^{-2}\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ at 30°C.

The rate constants of reactions (2)–(5) are much greater than that of reaction (16). This may be attributed either to a lower nucleophilicity of the peracetate anion compared to that of hydroxyl or perhydroxyl anions, or to steric hindrance due to molecular size. Since TriAED is less reactive than TAED with hydroxyl or perhydroxyl, it was assumed in the model that the rate of TriAED peracetolysis (reaction 17) was negligible compared to the rate of reactions (2)–(5) and (16).

The stability of the PAA or peracetate anion formed in the medium is also pH dependent. In a pure system (no metal ions present), the decomposition of PAA occurs in two ways: PAA disproportionation (reaction 19) at pH ~pKa_2, the acidity constant of PAA (pKa_2 = 8.2 at 25°C), and hydrolysis in an alkaline medium (reactions 24,25).

Hautal et al. [18] and Ni et al. [15] have proposed a disproportionation mechanism for PAA. It is postulated that the decomposition reaction involves a nucleophilic attack of the peracetate anion on the peracid molecule (reaction 19).

$$AcOOH + AcOO^- \rightarrow AcOH + AcO^- + O_2 \quad (19)$$

The rate of that reaction is given by:

$$r_{19} = k_{19} \cdot [AcOOH] \cdot [AcOO^-] \quad (20)$$

where

$$k_{19} = 9.21 \times 10^{13} \exp\left(-\frac{94\,273}{RT}\right)$$

The mechanism of the reaction is given by reaction (21).

In another paper, the same authors [16] have described a mechanism for PAA hydrolysis (reactions 24,25). OH^- reacts with either peracetate anion or PAA, following reactions (22) and (23), which can be summarized as:

$$AcOO^- + HO^- \rightarrow AcO^- + HOO^- \quad (24)$$

$$AcOOH + HO^- \rightarrow AcO^- + H_2O_2 \quad (25)$$

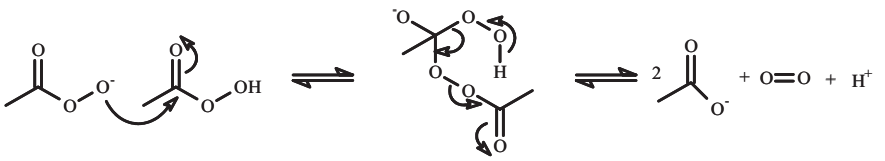
The rate of reactions (24) and (25) is therefore expressed by the sum of two terms:

$$r_{24,25} = k_{24}\,[AcOO^-] \cdot [OH^-] + k_{25}\,[AcOOH] \cdot [OH^-] \quad (26)$$

where

$$k_{24} = 2.32 \times 10^8 \exp\left(-\frac{62\,263}{RT}\right)$$

Reaction 21



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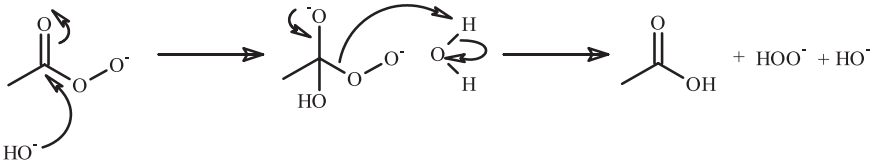

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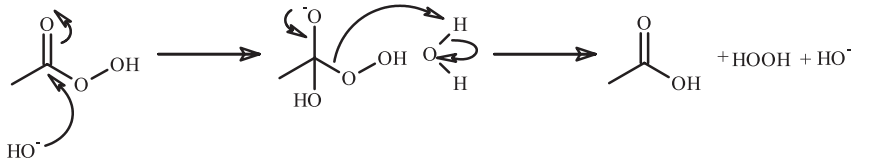

and

$$k_{25} = 1.19 \times 10^{9} \exp\left(-\frac{49\,082}{RT}\right)$$

Transformation of the Rate Equations

One can express:

$$\left[HOO^{-}\right] = \left[H_2O_2\right]_T \cdot \frac{Ka_1}{Ka_1 + \left[H^{+}\right]} \quad (27)$$

and

$$\left[H_2O_2\right] = \left[H_2O_2\right]_T \cdot \frac{\left[H^{+}\right]}{Ka_1 + \left[H^{+}\right]} \quad (28)$$

where $Kw = [OH^-] \cdot [H^+]$ is the ionic product of water,

$$Ka_1 = \frac{\left[HOO^{-}\right] \cdot \left[H^{+}\right]}{\left[H_2O_2\right]}$$

is the dissociation constant of hydrogen peroxide, and $[H_2O_2]_T$ is the sum of hydrogen peroxide and perhydroxyl anion concentrations.

Similarly

$$\left[AcOO^{-}\right] = \left[AcOOH\right]_T \cdot \frac{Ka_2}{Ka_2 + \left[H^{+}\right]} \quad (29)$$

and

$$\left[AcOOH\right] = \left[AcOOH\right]_T \cdot \frac{\left[H^{+}\right]}{Ka_2 + \left[H^{+}\right]} \quad (30)$$

where

$$Ka_2 = \frac{\left[AcOO^{-}\right] \cdot \left[H^{+}\right]}{\left[AcOOH\right]}$$

is the dissociation constant of PAA and $[AcOOH]_T = [AcOOH] + [AcOO^-]$.

The rate expressions of reactions (2)–(5), (16), (19), (24) and (25) are given in Table I.

Differential Equations

The reaction rate of TAED, which is consumed in reactions (2), (4) and (16), is given by:

$$\begin{aligned}
&\frac{d\left[TAED\right]}{dt} \\
&= -r_2 - r_4 - r_{16} \\
&= -k_2\left[TAED\right]\left[H_2O_2\right]_T \frac{Ka_1}{Ka_1 + \left[H^{+}\right]} \\
&\quad - k_4\left[TAED\right]\frac{Kw}{\left[H^{+}\right]} \\
&\quad - k_{16}\left[TAED\right]\left[AcOOH\right]_T \frac{Ka_2}{Ka_2 + \left[H^{+}\right]}
\end{aligned} \quad (31)$$

Similarly, the variation of [TriAED], $[H_2O_2]$ and $[AcOOH]_T$ can be expressed by:

$$\begin{aligned}
&\frac{d\left[TriAED\right]}{dt} \\
&= r_2 - r_3 + r_4 - r_5 \\
&= k_2\left[TAED\right]\left[H_2O_2\right]_T \frac{Ka_1}{Ka_1 + \left[H^{+}\right]} \\
&\quad - k_3\left[TriAED\right]\left[H_2O_2\right]_T \frac{Ka_1}{Ka_1 + \left[H^{+}\right]} \\
&\quad + k_4\left[TAED\right]\frac{Kw}{\left[H^{+}\right]} - k_5\left[TriAED\right]\frac{Kw}{\left[H^{+}\right]}
\end{aligned} \quad (32)$$

$$\begin{aligned}
&\frac{d\left[H_2O_2\right]_T}{dt} \\
&= -r_2 - r_3 + r_{24,25} \\
&= -k_2[TAED][H_2O_2]_T \frac{Ka_1}{Ka_1 + \left[H^{+}\right]} \\
&\quad - k_3[TriAED][H_2O_2]_T \frac{Ka_1}{Ka_1 + \left[H^{+}\right]}
\end{aligned}$$

TABLE I
REACTION RATE EXPRESSIONS USED IN THE MODEL. VALUES OF ACTIVATION ENERGIES AND EXPONENTIAL COEFFICIENTS

Reaction	Rate	k ($L \cdot mol^{-1} \cdot s^{-1}$) at 30°C	E_a ($kJ \cdot mol^{-1} \cdot K^{-1}$)	A ($L \cdot mol^{-1} \cdot s^{-1}$)
2	$k_2 \cdot [TAED] \cdot [H_2O_2]_T \cdot \frac{Ka_1}{Ka_1 + [H^+]}$	339	110	3.06×10^{21}
3	$k_3 \cdot [TriAED] \cdot [H_2O_2]_T \cdot \frac{Ka_1}{Ka_1 + [H^+]}$	118	110	1.06×10^{21}
4	$k_4 \cdot [TAED] \cdot \frac{Kw}{[H^+]}$	3.53	110	3.17×10^{19}
5	$k_5 \cdot [TriAED] \cdot \frac{Kw}{[H^+]}$	1.26	110	1.13×10^{19}
16	$k_{16} \cdot [TAED] \cdot [AcOOH]_T \cdot \frac{Ka_2}{Ka_2 + [H^+]}$	3.81×10^{-2}	110	3.42×10^{17}
19	$k_{19} \cdot [AcOOH]_T^2 \cdot \frac{Ka_2 \cdot [H^+]}{(Ka_2 + [H^+])^2}$	5.25×10^{-3}	94.273	9.21×10^{13}
24	$k_{24} \cdot [AcOOH]_T \cdot \frac{Kw \cdot Ka_2}{[H^+] \cdot (Ka_2 + [H^+])}$	4.34×10^{-3}	62.263	2.32×10^{8}
25	$k_{25} \cdot [AcOOH]_T \cdot \frac{Kw}{Ka_2 + [H^+]}$	4.15	49.082	1.19×10^{9}

For reactions (2)–(5) and (16), rate constants at 30°C were taken from Davies et al. [17], and activation energies and exponential coefficients were calculated by fitting the data of Mathews and Croud [3,7], assuming an equal value for activation energies. Data of reactions (19), (24) and (25) were taken from Ni et al. [15,16].

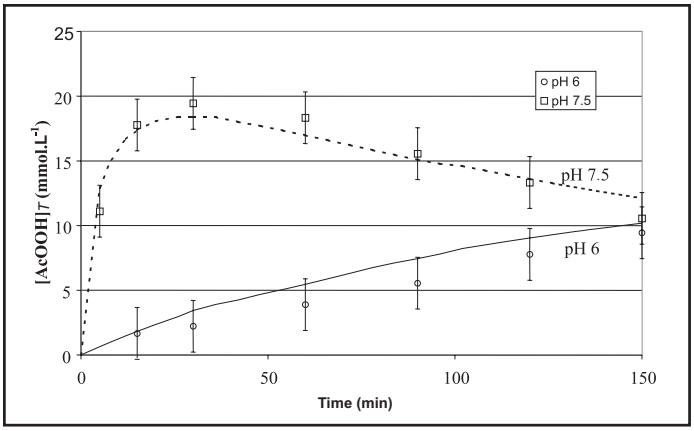

Fig. 2. Generation of PAA: comparison of kinetic predictions of the model (lines) and experimental data (points) of Croud and Mathews [3] at 40°C. $[H_2O_2]_0$ = 0.02941 mol·L^{-1} and $[TAED]_0$ = 0.01314 mol·L^{-1}. The precision was estimated to be 0.002 mol·L^{-1} (by cerimetric titration).

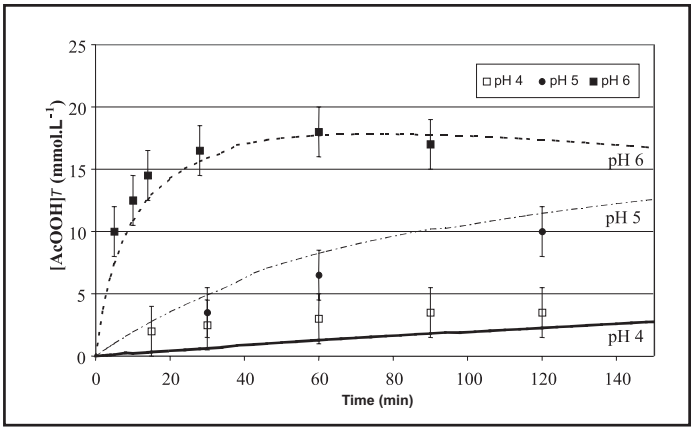

Fig. 3. Generation of PAA: comparison of kinetic predictions of the model (lines) and experimental data (points) of Croud and Mathews [7] at 60°C. $[H_2O_2]_0$ = 0.02941 mol·L^{-1} and $[TAED]_0$ = 0.01314 mol·L^{-1}. The precision was estimated to be 0.002 mol·L^{-1} (by cerimetric titration).

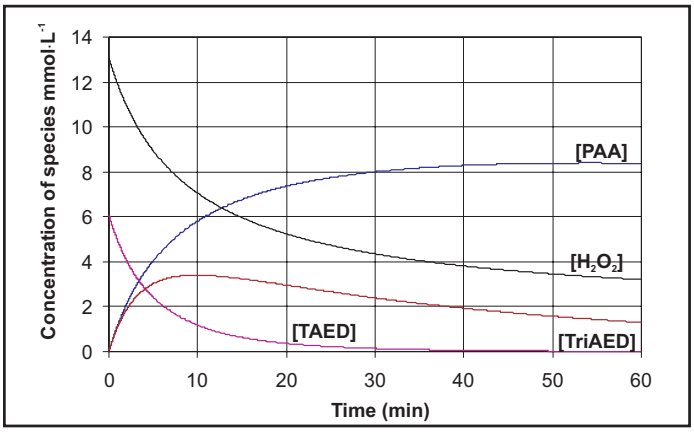

Fig. 4. Simulation of the reaction between TAED and H_2O_2 at pH 7, 50°C. $[H_2O_2]_0$ = 0.013072 mol·L^{-1}, $[TAED]_0$ = 0.006087 mol·L^{-1}.

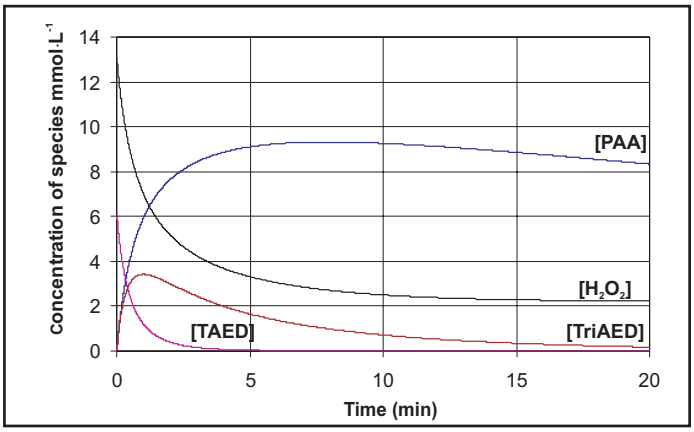

Fig. 5. Simulation of the reaction between TAED and H_2O_2 at pH 8, 50°C. $[H_2O_2]_0$ = 0.013072 mol·L^{-1}, $[TAED]_0$ = 0.006087 mol·L^{-1}.

$$+ k_{24}[\mathrm{AcOOH}]_T \frac{KwKa_2}{\left[\mathrm{H^+}\right]\left(Ka_2 + \left[\mathrm{H^+}\right]\right)}$$
$$+ k_{25}[\mathrm{AcOOH}]_T \frac{Kw}{Ka_2 + \left[\mathrm{H^+}\right]} \qquad (33)$$

$$\frac{\mathrm{d}\left[\mathrm{AcOOH}\right]_T}{\mathrm{d}t}$$
$$= r_2 + r_3 - r_{16} - 2r_{19} - r_{24,25}$$
$$= k_2[\mathrm{TAED}][\mathrm{H_2O_2}]_T \frac{Ka_1}{Ka_1 + \left[\mathrm{H^+}\right]}$$
$$+ k_3[\mathrm{TriAED}][\mathrm{H_2O_2}]_T \frac{Ka_1}{Ka_1 + \left[\mathrm{H^+}\right]}$$
$$- k_{16}[\mathrm{TAED}]\left[\mathrm{AcOOH}\right]_T \frac{Ka_2}{Ka_2 + \left[\mathrm{H^+}\right]}$$
$$- 2k_{19}\left[\mathrm{AcOOH}\right]_T^2 Ka_2 \frac{\left[\mathrm{H^+}\right]}{\left(Ka_2 + \left[\mathrm{H^+}\right]\right)^2}$$
$$- k_{24}\left[\mathrm{AcOOH}\right]_T \frac{KwKa_2}{\left[\mathrm{H^+}\right]\left(Ka_2 + \left[\mathrm{H^+}\right]\right)}$$
$$- k_{25}\left[\mathrm{AcOOH}\right]_T \frac{Kw}{Ka_2 + \left[\mathrm{H^+}\right]} \qquad (34)$$

This set of four differential equations with four variables is solved numerically, and compared graphically with experimental data.

Fitting Rate Constants

The missing activation energies (E_a) in reactions (2)–(5) and (16) have to be estimated. Because of the similarities of the reaction mechanisms, the activation energies were assumed to be identical. Fitting the data of Croud and Mathews [3,7], a value of E_a = 110 kJ·mol^{-1}·K^{-1} was found (Figs. 2,3).

The variation of the ionic product of water, Kw, with temperature was also accounted for by applying:

$$Kw = \exp\left(-\frac{\Delta H_{diss} - T \cdot \Delta S_{diss}}{RT}\right) \qquad (35)$$

where T is the absolute temperature, ΔH_{diss} is the dissociation enthalpy of water (56583.65 J·mol^{-1}) and ΔS_{diss} is the dissociation entropy of water (–78.27 J·mol^{-1}·K^{-1}).

RESULTS AND DISCUSSION

The data that will be examined to evaluate the reaction pattern and kinetics are:

- The PAA molar yield, defined as the number of moles of PAA formed at a given time, divided by the maximum possible number (equal to twice the number of moles of TAED);
- The time at which the maximum molar yield is reached; and
- The molar yield at a given time (60 or 120 min) as a good indicator of PAA stability.

Reaction at Neutral or Alkaline pH

The reaction pattern in this range of pH is well illustrated by Figs. 4–6, in which values that were chosen for the initial reactant concentrations would correspond to bleaching tests using 0.4% H_2O_2, 1.25% TAED and a pulp consistency of 10%. These conditions correspond to a molar ratio H_2O_2:TAED of 2.15, a value slightly greater than the stoichiometric ratio of 2.

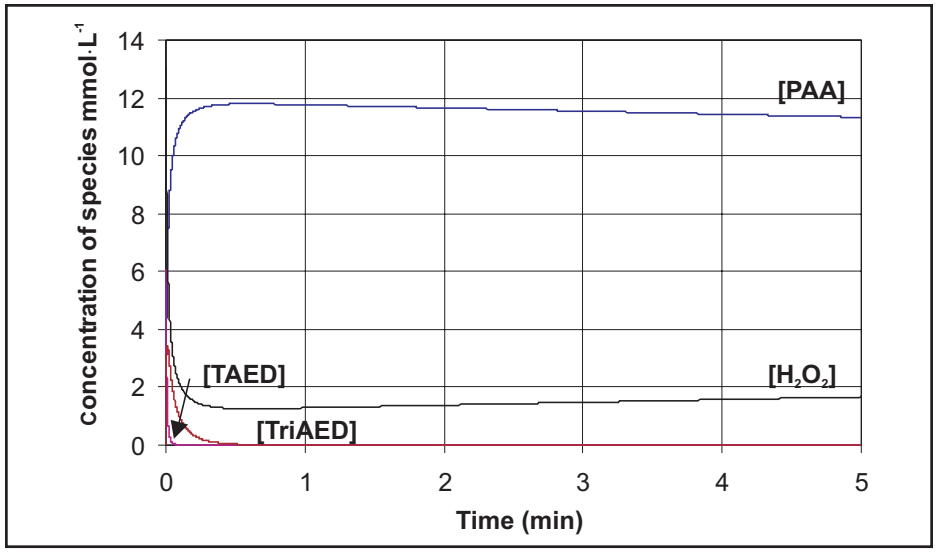

Fig. 6. Simulation of the reaction between TAED and H_2O_2 at pH 10, 50°C. $[H_2O_2]_0$ = 0.013072 mol·L^{-1}, $[TAED]_0$ = 0.006087 mol·L^{-1}.

TABLE II
EFFECT OF pH AND TEMPERATURE ON THE MOLAR YIELD OF PAA GENERATION AT NEUTRAL OR SLIGHTLY ALKALINE pH

		With peracetolysis			Neglecting peracetolysis	
pH	Temp. (°C)	Maximum molar yield of PAA (%)	Time to reach the maximum molar yield (min)	Molar yield after a reaction time of 60 min (%)	Maximum molar yield of PAA (%)	Time to reach the maximum molar yield (min)
7	30	56.1	1018	16.4	62.3	1006
7	50	69.0	54.2	68.9	73.2	53.7
7	70	78.0	4.0	27.6	80.7	4.0
8	30	65.2	150.5	57.9	70.6	148.1
8	50	75.6	7.9	41.9	79.9	7.7
8	70	83.7	0.57	3.4	85.7	0.57
10	30	97.1	15.6	94.3	97.4	15.8
10	50	96.9	0.59	56.4	97.1	0.59
10	70	95.6	0.03	0.6	95.7	0.03

Right two columns: simulations artificially assuming a zero rate of peracetolysis (reaction 16). $[H_2O_2]_0$ = 0.013072 mol·L^{-1}, $[TAED]_0$ = 0.006087 mol·L^{-1}.

TABLE III
EFFECT OF pH AND TEMPERATURE ON PAA GENERATION AND DECOMPOSITION, AND ON HYDROGEN PEROXIDE (H_2O_2) RECOVERY FROM PAA DECOMPOSITION AT ALKALINE pH

pH	Temp. (°C)	Maximum PAA molar yield (%)	Time to reach the maximum molar yield (min)	PAA formed at maximum molar yield (mmol·L^{-1})	PAA decomposed from maximum concentration level at a reaction time of 120 min (mmol·L^{-1})	H_2O_2 recovered from PAA decomposition at a reaction time of 120 min (mmol·L^{-1})
8.2	50	79.7	6.1	9.70	7.03	1.49
8.2	80	87.6	0.1	10.67	10.67	4.66
9.5	30	94.4	30.9	11.49	0.75	0.44
9.5	50	95.7	1.3	11.65	7.86	6.07
9.5	80	94.6	<0.1	11.51	11.51	10.05
10.5	30	98.0	6.8	11.93	0.93	0.88
10.5	50	97.1	0.3	11.82	8.27	8.08
10.5	80	93.6	<0.1	11.40	11.40	11.27

$[H_2O_2]_0$ = 0.013072 mol·L^{-1}, $[TAED]_0$ = 0.006087 mol·L^{-1}

TAED and TriAED are consumed by H_2O_2 (perhydrolysis) with the formation of PAA. At the same time, PAA decomposes, which explains the presence of a maximum yield. This maximum occurs very quickly under some of the conditions tested (Fig. 6).

The simulation data reported in Table II show that pH and temperature have a great influence on the rate and molar yield of PAA generation, as well as on PAA stability.

At pH 7 or 8, raising the temperature allows a significant reduction of the PAA generation time, while increasing the molar yield. However, PAA appears to be unstable above room temperature.

At pH 10, the generation of peracetate is quite fast even at room temperature, with no significant decomposition. Increasing the temperature slightly affects the molar yield of peracetate, but strongly increases its decomposition.

As described above, PAA or peracetate decomposition in pure water may follow two patterns: disproportionation (reaction 19), leading to the formation of acetate and oxygen; or alkaline hydrolysis, forming acetate and hydrogen peroxide. The data reported in Table III show clearly the former mechanism at slightly alkaline pH (~p*Ka* of PAA), whereas the latter dominates above pH 9.5.

This has a major consequence for bleaching. If bleaching and decomposition reactions occur at similar rates, a slightly alkaline pH will lead to an important loss of hydrogen peroxide whereas, in stronger alkaline medium, the bleaching action of hydrogen peroxide at least will be preserved, but with an important loss in the activation effect of TAED.

Effect of Peracetolysis

As described above, the competing TAED peracetolysis reaction (reaction 16), i.e. the reaction of TAED with the generated peracetate anion, might penalize the TAED–H_2O_2 activation system. Although the rate constants of perhydrolysis (k_2 or k_3) measured by Davies et al. [17] were found to be ~10^3–10^4 times that of peracetolysis (k_{16}), the difference in the reaction rates might be significantly less, since it is also related to the difference in the p*Ka*'s of PAA and hydrogen peroxide (8.2 and 11.6 at 25°C, respectively).

It is difficult, therefore, to draw definite conclusions about the effect of peracetolysis, since it should also be considered that TAED as an activator usually is present in stoichiometrically lower quantities than H_2O_2, and that TAED and peracetate are not likely to be present simultaneously in the medium for any extended period.

Therefore, to assess the effect of peracetolysis, the kinetic model was used and simulations artificially assuming a zero rate of peracetolysis were compared to regular simulations. It can be seen from the results reported in the right two columns of Table II that peracetolysis would contribute a rather small part to the loss of PAA. As expected from p*Ka* values, increasing the pH in this range tends to

accelerate perhydrolysis more than peracetolysis, therefore improving the molar yield of PAA. Raising the temperature also decreases the effect of peracetolysis, which can be explained by a shorter reaction time for the total consumption of TAED. Thus, the complementary loss of PAA (i.e. the difference from 100% yield) can be attributed to decomposition reactions (19), (24) and (25).

Effect of the Ratio H_2O_2:TAED

This effect is illustrated well by Fig. 7. Both rate and molar yield of PAA are affected significantly by the initial molar ratio of the reactants. However, the relative importance of the latter is attenuated with an increase in pH or temperature, i.e. conditions enhancing a faster generation of PAA.

Classification of Factors that Affect the Molar Yield and Stability of PAA

This was done by applying a 2^4 factorial design, with the following choice of parameters:

— pH in the range 7–10
— Temperature in the range 40–80°C
— TAED concentration in the range $2.5 \times 10^{-3} - 10^{-2}$ mol·L^{-1}
— H_2O_2:TAED ratio in the range 2.5–10.

Results of the factorial design are given in Table IV, in which the maximum PAA molar yield, the yields attained at times 60 and 120 min, and the percentage of PAA decomposition at time 120 min from maximum yield have been reported.

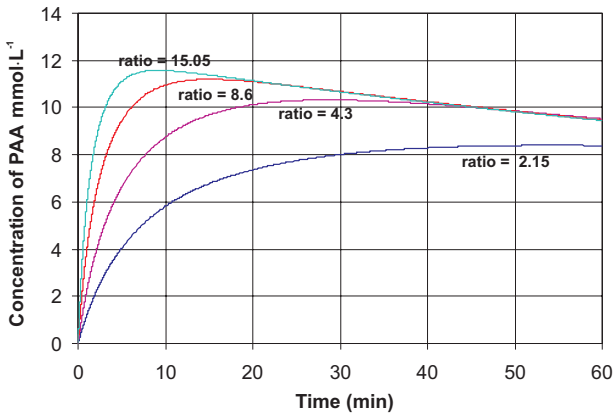

Fig. 7. Effect of the initial molar ratio H_2O_2:TAED at pH 7, 50°C. $[TAED]_0$ = 0.006087 mol·L^{-1}. Ratios were chosen to correspond to 0.4, 0.8, 1.6 and 2.8% H_2O_2/pulp, 1.25% TAED/pulp and 10% pulp consistency.

TABLE IV
RESULTS OF A 2^4 FACTORIAL DESIGN TO CLASSIFY THE EFFECTS OF pH, TEMPERATURE, TAED CONCENTRATION AND MOLAR RATIO H_2O_2:TAED ON MOLAR YIELD AND STABILITY OF PAA AT NEUTRAL OR MID-ALKALINE pH

pH	Temp. (°C)	TAED conc. (mmol·L^{-1})	H_2O_2: TAED molar ratio	Max. PAA molar yield (%)	PAA molar yield at time 60 min (%)	PAA molar yield at time 120 min (%)	PAA decomposed from maximum yield at a reaction time of 120 min (%)
7	40	2.5	2.5	65.8	35.1	49.6	–
10	40	2.5	2.5	96.4	83.9	72.5	24.8
7	80	2.5	2.5	82.1	18.2	6.7	91.9
10	80	2.5	2.5	92.0	0.0	0.0	100.0
7	40	10	2.5	68.1	62.5	68.1	–
10	40	10	2.5	98.8	83.3	70.4	28.8
7	80	10	2.5	86.3	6.7	2.2	97.4
10	80	10	2.5	97.7	0.0	0.0	100.0
7	40	2.5	10	89.1	78.8	88.7	–
10	40	2.5	10	99.5	85.9	74.2	25.5
7	80	2.5	10	96.3	18.6	6.8	93.0
10	80	2.5	10	98.7	0.0	0.0	100.0
7	40	10	10	90.3	87.9	78.0	13.7
10	40	10	10	99.8	83.9	70.9	29.0
7	80	10	10	97.4	6.7	2.2	97.7
10	80	10	10	99.7	0.0	0.0	100.0

NOTES: PAA stands for peracetic acid or peracetate anion. The symbol (–) in the right column corresponds to experiments for which the maximum yield is not attained at time 120 min, and therefore its decomposition yield cannot be calculated at that time.

The following multilinear regression equations can be derived:

maximum PAA molar yield

$$= 91.1 + 6.7\,X_1 + 2.6\,X_2 + 1.1\,X_3 + 5.2\,X_4 - 3.5\,X_1X_2 - 3.6\,X_1X_4 + 0.4\,X_2X_3 - 1.0\,X_2X_4 - 0.7\,X_3X_4 + 1.5\,X_1X_2X_4 \quad (36)$$

PAA yield at time 120 min

$$= 36.9 - 34.6\,X_2 + 3.2\,X_4 - 2.9\,X_1X_4 - 3.2\,X_2X_4 + 2.9\,X_1X_2X_4 \quad (37)$$

where X_i are normalized centred variables standing for true variables x_i (i.e. x_1 = pH, x_2 = temperature, x_3 = TAED concentration, x_4 = H_2O_2:TAED ratio), calculated as:

$$X_i = -1 + 2\frac{x_i - a_i}{b_i - a_i} \quad (38)$$

where a_i and b_i are lower and upper interval limits, respectively, for each variable x_i.

The results show that both pH and reactant ratio produce the highest maximum yield increase, despite a negative but smaller interaction between these two parameters. Increasing reactant concentration has the smallest influence, slightly reinforced by the positive interaction with temperature, but negatively affected by an increase in the reactant ratio. Temperature alone has a small but positive influence on the maximum PAA yield, but it interacts negatively with pH and reactant ratio in a greater way. However, its major effect is to decrease PAA stability, and therefore it appears that the best conditions for PAA generation would be at a rather low temperature and a pH of ~9–10.

At higher pH, peracetate formation is almost instantaneous even at low temperature, and the maximum molar yield approaches 100%, except above 80°C, because of the increased competition of TAED hydrolysis (see Fig. 8A). However, a severe limitation of alkaline bleaching will be the instability of peracetate at high temperature, as shown in Fig. 8B, unless delignification or bleaching reactions take place more rapidly than alkaline hydrolysis of peracetate.

The conclusion is that activation by TAED is probably justified at rather low temperatures (below 50°C) and at mid-alkaline pH (~9–10), provided good delignification or bleaching action of the peracetate anion can be expected under these conditions, as in the case of textile bleaching. At higher pH, peracetate appears unstable, and a successful use of the TAED–H_2O_2 activation system will rely on whether or not very short residence times are sufficient for significant action of peracetate on pulp, compared to that of non-activated hydrogen peroxide.

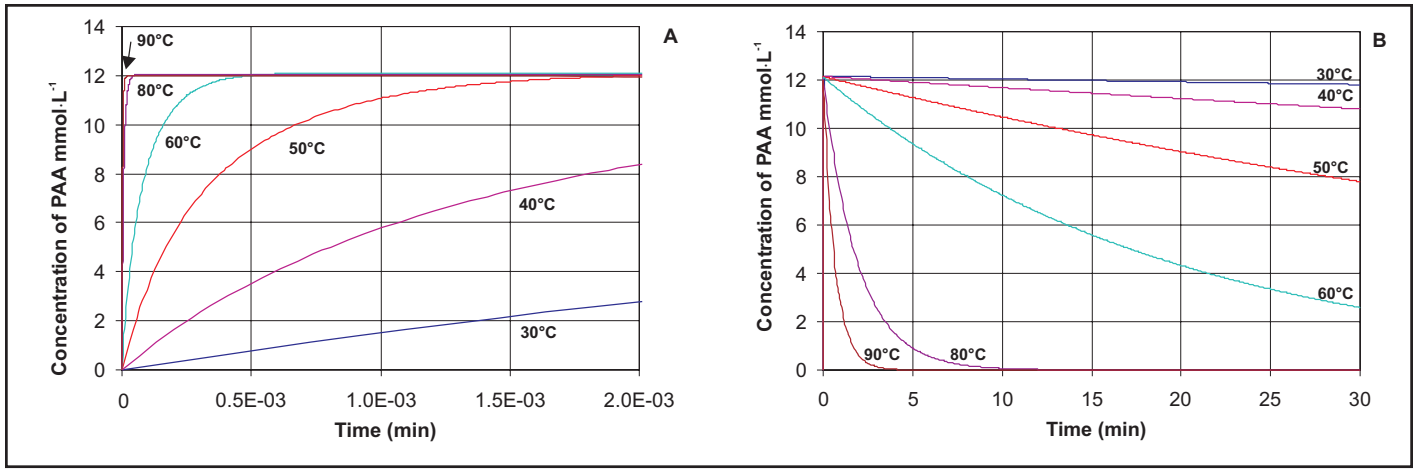

Fig. 8. Simulations at pH 11, effect of temperature. (A) short times; (B) long times. $[TAED]_0 = 0.006087$ mol·L^{-1}, $[H_2O_2]_0 = 0.06536$ mol·L^{-1}. Concentrations were chosen to correspond to 2% H_2O_2/pulp, 1.25% TAED/pulp and 10% pulp consistency.

Reaction in Acidic Medium

A mildly acidic pH range may be interesting to consider, since it meets standard conditions for PAA bleaching. However, a severe limitation comes from the low rate of PAA generation. Such a drawback might be turned to advantage if one considers that, compared to standard PAA bleaching, the TAED-activated system may induce a slow release of PAA in the pulp, i.e. a time-controlled action. Another possibility would be to pregenerate PAA at higher reactant concentrations in a separate mixture, prior to its introduction into the pulp.

Results of some simulations at different pH, temperature and reactant concentrations are presented in Table V. It is shown that PAA can be generated at an appreciable rate without important decomposition by decreasing pH and increasing temperature, if the concentration of reactants is sufficiently high. However, it may be preferable during a pregeneration step to avoid significant acidification, and it is shown that interesting conditions are also found at a pH of ~6–6.5 and a medium temperature (50°C). During a PAA pregeneration step, one can discuss the advantages or disadvantages of partial generation to keep a reserve of bleaching power in the form of unreacted TriAED prior to pulp introduction.

The best way to use pregeneration and to control time–concentration profiles during bleaching stages will be presented and discussed in a second paper on this subject.

TABLE V
SIMULATION IN ACIDIC MEDIUM; EFFECT OF pH, TEMPERATURE AND CONCENTRATION OF REACTANTS ON THE MOLAR YIELD AND STABILITY OF PAA

pH	Temp. (°C)	[TAED] (mmol·L^{-1})	[H_2O_2] (mmol·L^{-1})	Maximum molar yield of PAA (%)	Time to reach the maximum molar yield (min)	Time to reach 90% molar yield (min)	Molar yield after a reaction time of 120 min (%)
6	50	6.087	65.36	93.0	120	50	93.0
6	70	6.087	65.36	96.3	7.1	2.6	65.7
6	90	6.087	65.36	97.7	0.55	0.2	19.8
6.5	50	6.087	65.36	93.1	38.4	15.8	83.8
6	50	23.50	252.1	93.4	31.9	13.0	81.7
5.5	50	23.50	252.1	93.3	100.5	41.4	93.0
6.5	40	23.50	252.1	90.6	47.1	20.6	82.2
5.5	60	23.50	252.1	95.3	23.4	9.0	82.7
5	60	23.50	252.1	95.3	74	28.6	93.8
5	70	23.50	252.1	96.7	18.6	6.7	84.6
4.5	80	23.50	252.1	97.6	15.8	5.5	87.1
4	90	23.50	252.1	98.2	14.4	4.7	89.7
3.5	90	23.50	252.1	98.2	45.9	14.8	96.4

Note about the choice of reactant concentrations: the low-concentration series corresponds to 1.25% TAED on pulp, 2% H_2O_2 on pulp, 10% pulp consistency; the high-concentration series corresponds to 30% pulp consistency. Such an elevated aqueous concentration might be used during a PAA pregeneration step in a separate liquid volume prior to pulp introduction.

CONCLUSIONS

The activation effect of TAED during hydrogen peroxide delignification or bleaching stages is due to the generation of PAA (or peracetate anion at pH above 8.2, the p*Ka* of PAA at 25°C). Available data relative to the reaction mechanism and kinetics have allowed the construction of a mathematical model to predict generation rate and optimal operating conditions. The reactions taken into account are valid for a pure water system in which the influence of metal ions is negated.

High-yield generation of PAA is almost instantaneous in alkaline media (at pH above 10) but, because of the poor stability of the peracetate anion which is decomposed by hydrolysis (reactions 24,25) at elevated temperatures, the main benefit of activation would occur at rather low temperatures. However, applying these conditions to delignification or bleaching also relies on the reactivity of the peracetate anion towards pulp, which should be evaluated and compared with that of non-activated hydrogen peroxide.

At medium alkalinity (pH ~8.2), significant generation of PAA can be obtained by raising the temperature above ambient, but PAA is unstable and decomposed by disproportionation (reaction 19). This not only induces a loss of PAA, but also a loss of hydrogen peroxide that is not regenerated during the decomposition process, contrary to hydrolysis at alkaline pH.

Under acidic conditions, generation of PAA is slow. However, this might be considered an advantage, since it allows a time-controlled release of PAA during bleaching. A preliminary PAA generation step at slightly acidic pH in a separate mixture, prior to pulp introduction, may also be envisaged. By increasing the reactant concentrations, this procedure promotes a higher generation yield in a reasonable time.

Finally, it was shown that mathematical modelling is a useful tool to predict optimal operating conditions for a hydrogen peroxide bleaching system activated by TAED.

NOMENCLATURE

TAED	tetraacetylethylenediamine
TriAED	triacetylethylenediamine
DAED	diacetylethylenediamine
PAA	Peracetic acid or peracetate anion (or their sum in a mixture of the two compounds)

AcOOH	Peracetic acid
$AcOO^-$	peracetate anion
r_i	reaction rate of reaction *i* ($mol \cdot L^{-1} \cdot s^{-1}$)
k_i	reaction rate coefficient of reaction *i* ($L \cdot mol^{-1} \cdot s^{-1}$)
$k_{obs(i)}$	observed reaction rate coefficient for the reaction *i*
$[i]$	concentration of species *i* ($mol \cdot L^{-1}$)
T	temperature (K)
R	constant (8.3143 $J \cdot mol^{-1} \cdot K^{-1}$)
Kw	ionic product of water
Ka_1	acidity constant of hydrogen peroxide
Ka_2	acidity constant of peracetic acid
$[H_2O_2]_T$	sum of hydrogen peroxide and perhydroxyl anion concentration ($mol \cdot L^{-1}$)
$[AcOOH]_T$	sum of PAA and peracetate anion concentration ($mol \cdot L^{-1}$)
$[H_2O_2]_0$	initial concentration of hydrogen peroxide introduced in the medium ($mol \cdot L^{-1}$)
$[TAED]_0$	initial concentration of TAED introduced in the medium ($mol \cdot L^{-1}$)
Ea	activation energy ($J \cdot mol^{-1}$)
A	exponential factors ($L \cdot mol^{-1} \cdot s^{-1}$)
ΔH_{diss}	molar dissociation enthalpy ($J \cdot mol^{-1}$)
ΔS_{diss}	molar dissociation entropy ($J \cdot mol^{-1} \cdot K^{-1}$)

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KEYWORDS: MODELS, REACTION KINETICS, PEROXIDE BLEACHING, HYDROGEN PEROXIDE, PERACETIC ACID, ETHYLENEDIAMINE, VARIABLES, REACTION MECHANISMS.