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The effects of chelating agents on radical generation in alkaline peroxide systems, and the relevance to substrate damage

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Abstract

A spin-trapping EPR technique has been employed to explore the generation of hydroxyl radicals from reactions between a series of first row transition metal ions and aqueous hydrogen peroxide at pH 10, and with a range of chelating agents (EDTA, DTPMP and the readily biodegradable ligands S,S-EDDS and IDS). In the absence of these chelating agents only Cu(II) generates a significant level of hydroxyl radicals; in their presence with Cu(II) EDTA and IDS give similar behaviour whereas EDDS and DTPMP inhibit hydroxyl radical generation. For Fe(II), EDTA, DTPMP and IDS significantly enhance $^{\cdot}OH$ production under these conditions whereas EDDS does not. Results from model cellulose damage experiments broadly confirm the findings for copper, though experiments with Fe(II) lead to somewhat contrasting results. Our findings are discussed in terms of binding constants and implications for alkaline peroxygen bleaching systems.

Keywords: *Hydroxyl radical, hydrogen peroxide, chelating agents, cellulose, copper*

Introduction

Alkaline peroxygen systems play an important part in our daily lives, especially in pulp bleaching, textile bleaching and laundry detergents. The consumption of hydrogen peroxide for pulp bleaching in the US alone is around 250,000 tonnes per annum. The active species in pulp and textile bleaching is the hydroperoxide anion HOO^-, which carries out nucleophilic attack on chromophores such as conjugated carbonyl structures [1]. Household laundry detergents typically contain a bleach activator such as tetra-acetyl ethylenediamine (TAED); peracetic acid is believed to be the active species at the normal wash-temperatures of around 40°C, but the hydroperoxide anion is also present.

Alkaline hydrogen peroxide is not stable for any length of time so commercially it is supplied at acid pH or as a solid peroxygen-containing compound, such as sodium percarbonate. Once made alkaline it rapidly decomposes to oxygen and water, and trace levels of transition metals are believed to catalyse this decomposition [2]. In order to reduce the loss of hydrogen peroxide, metal-chelating agents are used. EDTA (**1**) and DTPMP (**2**) were chosen for this study because they are the most important members of the aminocarboxylate and phosphonate group of chelating agents, respectively, in terms of volumes sold. There are environmental concerns over using traditional chelating agents because of their poor biodegradability, so new, more readily biodegradable agents

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such as EDDS (**3**) and IDS (**4**) are now being considered for these applications [3,4] and these were also added into this study.

For transition metals in alkaline peroxide systems the generation of reactive oxygen species may be relevant. The hydroxyl radical in particular is extremely reactive, causing oxidation of most other species it encounters via hydrogen abstraction or addition to unsaturation and is believed to be the main species responsible for degradation of cellulose in pulp bleaching [5,6]. Hydroxyl and hydroperoxyl/superoxide radicals may also contribute toward dye damage during laundry washing, leading to fading or changing of colour.

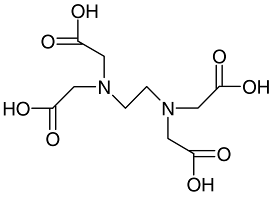
It has been claimed that addition of chelating agents to peroxide systems prevents the generation of radicals by sequestering of transition metals from the system. However, this is not necessarily true; e.g. with Fe^{2+}, addition of chelating agents can greatly accelerate the generation of hydroxyl radicals (see Ref. [7] and references therein).

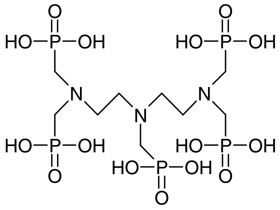
The purpose of the work reported here is to compare systematically the variation of hydroxyl radical generation under alkaline hard water conditions with a range of common transition metals and commercial chelating agents, and to investigate any correlation with cellulose damage. Our approach involved firstly the use of a spin-trapping technique in conjunction with EPR spectroscopy: it was intended to utilise the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO **5**) and its reaction with $^{\cdot}OH$ to give the well-known and long-lived adduct (**6**), detectable by its characteristic spectrum. Similarly, $^{\cdot}OOH$ (or $O_2^{\cdot-}$) gives the adduct (**7**). The appearance and intensity of the signals were to be noted as a function of added metals and chelating agents. We also designed a model experiment involving the gravimetric assessment of damage to cellulose.

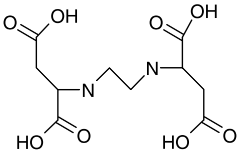
Materials and methods

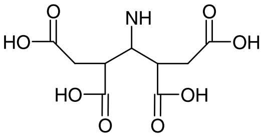
Chemicals

All solutions were made up with demineralised water. Calcium and transition metal salts were all chlorides and were laboratory reagent grade from Fisher Scientific or Acros Organics. Hydrogen peroxide was 100-volume laboratory reagent grade from Fisher Scientific. Ethylenediamine tetra-acetic acid, tetra-sodium salt (EDTA, **1**) was from BASF under the trade name Trilon® B Liquid. Diethylenetriamine penta-methylphosphonic acid, sodium salt (DTPMP, **2**) was from Solutia Inc under the trade name Dequest® 2066. Ethylenediamine disuccinic acid, tri-sodium salt (EDDS, **3**) was from Innospec under the trade name Octaquest® E30. Sodium iminodisuccinate (IDS, **4**) was from Bayer under the trade name Baypure® CX-100. DMPO (**5**) was from Sigma–Aldrich.


EDTA (**1**)

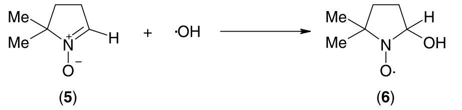

DTPMP (**2**)


EDDS (**3**)

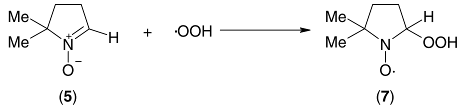

IDS (**4**)

EPR spin trapping: Comparison of signal intensities

The method employed the spin-trap (DMPO, **5**) to trap short-lived free radicals generated to give relatively stable spin-adducts ($t_{1/2}$ of the order of minutes), Reactions 1 and 2. The DMPO-OH radical adduct (**6**) has a characteristic EPR spectrum with $a_N = a_H = 14.85$ G. The hydroperoxyl adduct (**7**) has $a_N = 13.9$ G and $a_H = 10.85$ G. EPR spectra were recorded on Bruker ESP-300E spectrometer equipped with an X-band microwave bridge and TE102 cavity. The solution to be analysed was placed in an quartz aqueous flat-cell which was then put into the cavity of the spectrometer. The spectrum sweep was started 2 min after mixing of solutions. Typical spectrometer conditions were centre-field 348.0 mT, sweep width 10 mT, modulation amplitude 0.1 mT, microwave frequency ~ 9.77 GHz, microwave power 10 mW, time constant 160 ms, scan time 167 s. Relative intensities were estimated from peak heights in the first derivative spectra. Typical concentrations were as follows: Solution 1: Transition metal (150 mg/kg, ~ 2.6 mM,) with optional chelating agent (5 mM), (dosed in using a 0.25 M stock solution) and pH adjusted to 10 with NaOH immediately prior to addition to reaction mixture. In the case of Fe(II) the solution was sparged with nitrogen before and during the pH adjustment. Solution 2: Hydrogen peroxide (30 mM) containing calcium (7.5 mM, 300 mg/kg), adjusted to pH 10 with NaOH on the morning of the experiment. It was separately established that decomposition of this solution is < 1% over 16 h at RT. Solution 3: DMPO (100 mM).



(Reaction 1)



(Reaction 2)

For each experiment, equal volumes of H_2O_2 (Solution 2) and DMPO (Solution 3) were mixed and then the transition metal solution containing optional chelating agent (Solution 1) was added. The EPR spectrum of the resultant mixture was obtained 2 min after addition of Solution 1. Therefore, concentrations after mixing were: transition metal 50 mg/kg (approximately 0.9 mM), calcium 100 mg/kg (2.5 mM), optional chelating agent 1.7 mM, H_2O_2 10 mM and DMPO 33 mM.

The 150 mg/kg solutions of transition metals were made up 24 h before use at the pH of make-up (in all cases acidic) in stoppered volumetric flasks, in order to mimic ageing effects in real systems. With $FeCl_2$ this meant that partial oxidation of Fe(II) to Fe(III) would have occurred as evidenced by a slight colour change from pale green to a green with a yellowish tinge, but NaSCN testing indicated that the degree of oxidation to Fe(III) was $<2\%$. All solutions were at room temperature throughout. Although industrial peroxide bleaching processes are carried out between 40 and 60°C higher temperatures would have reduced reactive species' lifetimes and the use of a temperature control probe in these experiments would have dropped sensitivity too much and prevented easy mixing of the solutions.

Accelerated cellulose damage experiments

Mixed polyester–cotton was chosen as the substrate because the polyester maintains the integrity of the swatches even when the cellulose portion is badly degraded, allowing the extent of degradation to be easily determined by weight loss. An 8 cm-square of white 50–50 polyester–cotton cloth was dried at 40°C for 2 h and weighed (weight A). The cloth was then dosed with transition metal in the following way: For experiments in the absence of chelating agents 0.50 g of a 58 mM solution (29 mmol) of the appropriate transition metal chloride was dropped evenly around the cloth and the cloth was then dried at 40°C for 3 h. For experiments with chelating agents the metal complex was first formed separately by adding the appropriate amount of chelating agent to 5.0 g of a 58 mM solution of the transition metal whilst stirring. The mole ratio of chelating agent to metal was 1:1 in all experiments. The amount of metal complex solution required to give 29 mmol of transition metal was then spotted evenly around the cloth and the cloth was then dried at 40°C for 3 h. For Fe(II) experiments the cloths were quite yellow after drying, indicating that some oxidation to Fe(III) had occurred.

A total of 310 g of a solution of hydrogen peroxide (5% by weight, 1.47 M) and calcium chloride (100 mg/kg, 2.5 mM) was stirred with a 65 mm diameter polypropylene U-shape stirrer at 70 rpm in a 500 ml Pyrex beaker. The temperature was brought up to 90°C, at which point the mixture was adjusted to pH 10.0 with 20% NaOH. The appropriate dried cloth was then added and stirring was continued for 1 h. The temperature was maintained at 90°C but the pH was not controlled after the start and tended to drift upwards as hydrogen peroxide was used up. Losses in liquid volume by evaporation were made good by additions of demineralised water. Small aliquots were taken periodically and titrated against potassium permanganate to determine the hydrogen peroxide concentration. After 1 h, the cloth was washed by stirring in a bath of demineralised water, and then dried at 40°C for 3 h and reweighed (weight B). The loss in weight compared with the original clean cloth, (A–B)/A, was then calculated. Attenuated total reflectance infra-red spectroscopy confirmed that it was largely the cellulose portion that was destroyed.

Peroxide decomposition experiments

Water (to give a final volume of 150 ml) and appropriate metals (as chloride ions) were mixed and heated to 40°C. Hydrogen peroxide was then added to give a concentration of 5% by weight (1.47 M). The pH was adjusted immediately to 10.0 using 10% NaOH and the clock started. Aliquots of solution were taken periodically up to 60 min and titrated against potassium permanganate to determine the remaining hydrogen peroxide concentration. Temperature was maintained at 40°C throughout the experiment but pH was not controlled after the start and drifted upwards as decomposition progressed.

Results and discussion

Spin-trapping experiments

Hydroxyl radicals are formed via the "Fenton"-type reaction in which transition metal is subjected to a 1-electron oxidation by hydrogen peroxide (Reaction 3). Hydroperoxyl radicals can be generated via the 1-electron reduction of transition metal by peroxide anion (Reaction 4), or by the reaction of hydroxyl radical with hydrogen peroxide (Reaction 5). This is particularly established for Fe [8,9]

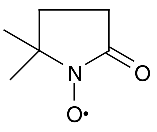
$$\mathrm{M}^{n+} + \mathrm{H_2O_2} \rightarrow \mathrm{M}^{(n+1)+} + {}^{\cdot}\mathrm{OH} + \mathrm{OH}^{-} \quad \text{(Reaction 3)}$$

$$\mathrm{M}^{(n+1)+} + \mathrm{HO_2^-} \rightarrow \mathrm{M}^{n+} + {}^{\cdot}\mathrm{OOH} \quad \text{(Reaction 4)}$$

$$\mathrm{H_2O_2} + {}^{\cdot}\mathrm{OH} \rightarrow \mathrm{H_2O} + {}^{\cdot}\mathrm{OOH} \quad \text{(Reaction 5)}$$

There have been many previous studies of radical generation in hydrogen peroxide but they have tended to be at neutral or acidic pH [7,10]. Moreover, these studies have usually been in de-mineralised water whereas real industrial systems contain $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$ (hardness ions). This work used 100 mg/kg (2.5 mM) calcium as a typical medium level of hardness; we also avoided the use of buffers as they contain good metal complexing ligands such as phosphate.

Types of radical detected. EPR experiments were conducted, as described above, with a range of metals and chelating agents in the presence of DMPO at pH 10. The formation of the $^{\cdot}$OH adduct, very pronounced in some cases as described below, is recognisable by the characteristic 1:2:2:1 pattern which arises from the equivalence of the nitrogen and hydrogen hyperfine splittings: an example is shown in Figure 1, together with a typical background trace. For a series of experiments, the relative $^{\cdot}$OH adduct intensities are shown in Table I. Some data from when hydrogen peroxide is not present is given in column 2, which gives information on any direct reaction of transition metal with DMPO. Whilst the variation in the DMPO-OH adduct (**6**) intensities is described below, attention is drawn to three other types of radical observed in certain cases. In some experiments, clear signals from the DMPO-OOH adduct (7) were also detected; exceptionally, signals were detected from DMPOX (**8**), which is believed to result from further oxidation (e.g. by the metal) of the $^{\cdot}$OH adduct or direct oxidation of the spin trap.


(**8**)

In a small number of experiments, formation of carbon-centred-radical adducts was recognised by signals with a_H 1.8–2.0 G, due presumably to radical attack on the chelating agent.

Reactions of uncomplexed ions. Significant radical chemistry, as judged by the observation of DMPO-OH radical adducts is only evident with Cu(II) and Fe(II). Unchelated Co(II), Cr(III) and Mn(II) do not generate significant levels of radicals and addition of chelating agents does not change this; no signals were observed for unchelated Ni(II). Unchelated Mn gives extensive decomposition of $\mathrm{H_2O_2}$ at pH 10 and 40°C (see later), and decomposition with unchelated Co(II) was evident from effervescence in the EPR cell, but no $^{\cdot}$OH adducts were observed for either metal. The mechanisms of peroxide decomposition in these cases are presumably by 2-electron rather than 1-electron processes. This is in general agreement with prior studies at lower pH; for instance only Fe and Cu are recommended for commercial applications of the Fenton-type reaction for cleaning up chemical pollutants [11].

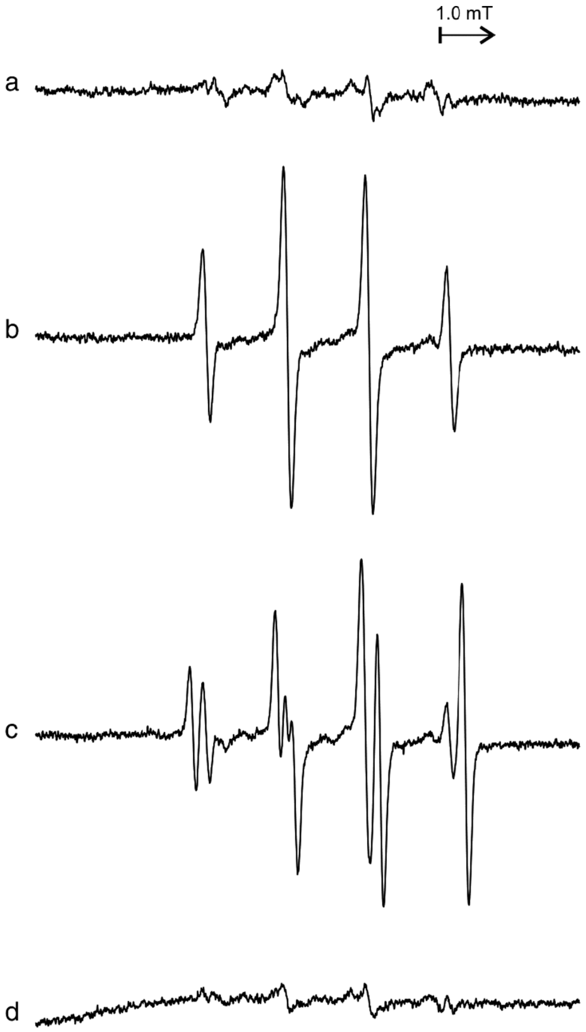


Figure 1. EPR spectra obtained on reaction of metal ions, ligands and hydrogen peroxide in the presence of the spin-trap DMPO. (a) without metal ions; (b) with Cu(II); (c) with Cu(II)/EDTA; (d) with Cu(II)EDDS.

It is slightly surprising that Cu(II) generates more hydroxyl radicals than Fe(II) since it is often considered that the reverse is true. Cu(II) needs to be reduced down to Cu(I) in order to carry out the

Table I. Relative intensities of ˙OH radical adduct.

		10 Mm H_2O_2 and 100 ppm Ca^{2+} at pH 10				
Transition metal (50 ppm)	No peroxide, calcium or chelating agent; at pH 10	None	EDTA	EDDS	DTPMP	IDS
None		0.5				
Co^{2+}		1.0		1.2⋆	2.0†	
Cr^{3+}	0.7	0.6	1.6	0.8	0.5	1.1
Cu^{2+}	2.6‡	9.4	7.4⋆	0.9⋆	1.1⋆	6.7
Fe^{2+}	7.5‡	0.9†	133.0	1.9¶	418.0	91.6
Mn^{2+}		1.1		0.0¶	1.4	4.0

⋆ Carbon-centred radicals also observed (initial intensity for Cu-EDTA system about 8.0 but growing during the scan, intensity for Cu-EDDS and Cu-DTPMP ~ 1.0); † Superoxide adduct also observed; ‡ DMPO-OH also observed, formed by direct oxidation of the spin-trap by the metal ion [i.e. Cu(II) or Fe(III)]; ¶ DMPOX radical, $a_N = 7.2$ G, $a_{2H} = 4.1$ G, also observed.

Fenton reaction; the process is generally slow unless there are some good reducing agents present, such as thiols; the reductants here are presumably HOO^- (by way of Reaction 4) and perhaps the spin trap itself. However, previous work at pH 7 in phosphate buffer using benzoate hydroxylation to detect ˙OH radicals, [12] and at pH 10.8 with no buffer using benzene hydroxylation [2], also showed unchelated Cu(II) produces a significantly higher flux of ˙OH radicals than unchelated Fe(II). In industrial systems reducing agents for Cu(II) are likely to be present, e.g. some of the Na_2S used in the production of Kraft pulp carries forward to the pulp bleaching stage.

Reactions of chelated copper. Addition of chelating agents to the Cu system gives rise to some interesting differences. When EDTA or IDS is added to the Cu system significant ˙OH radicals are still generated, as well as additional carbon-centred radical adducts for the former (Figure 1). The result for EDTA is surprising because at pH 7.2 in phosphate buffer and no added calcium it is reported to inhibit ˙OH radical generation [12,13]. The carbon-centred radicals are presumably formed by ˙OH attack on the chelating agent molecule (either complexed to metal or free). In contrast, EDDS and DTPMP inhibit the generation of ˙OH radicals (Figure 1). These differences may reflect differences in stability constants and speciation effects (Table II). The inability of IDS to quench radical generation is probably due to its relatively low binding constant with Cu(II). EDTA does have a high binding constant for copper but it may be significant that it has poorer specificity for copper over calcium as typified by the difference between the two conditional stability constants in the 4th column.

Reactions of chelated iron. Addition of EDTA, DTPMP or IDS to the Fe(II) system causes a very large increase in ˙OH adduct intensity. This is in line with earlier results at lower pHs: e.g. the rate constant of the Fenton reaction (Reaction 1) for Fe(II) EDTA complex is 100 times greater, and for Fe(II) DTPMP 500 times greater, compared with uncomplexed Fe(II) [7]. Addition of these types of chelating agents generally depress the Fe(III)/Fe(II) redox potential, e.g. for Fe-EDTA it is 0.12 V compared with 0.77 V for hexaaqua Fe, thereby making the Fenton reaction more thermodynamically favourable. However, the ˙OH adduct intensity for the Fe(II) EDDS system is very low. This is quite surprising: other aminocarboxylate chelating agents such as NTA (nitrilotriacetic acid) and DTPA, in addition to EDTA, [7] all greatly accelerate the Fenton reaction. Nor is there an obvious relationship with binding constants: IDS has relatively poor binding with iron compared with EDDS (Table II) but it still accelerates the Fenton reaction. The behaviour of EDDS may be due to differences in the Fe(III)/Fe(II) redox potentials, but this value is not known for the EDDS complexes.

Accelerated cellulose damage experiments

The hydroxyl radical is believed to be the main species responsible for degradation of cellulose in alkaline peroxide systems [5,6]. Further reactions of the first-formed carbohydrate radical can lead to de-polymerisation [5,14]. In pulp bleaching this could lead to loss of fibre strength and consequent web breakages on the paper machine, or to unsightly "spotting" on the paper. In textile bleaching and laundry washing cellulose breakdown leads to loss of strength or thinning of the fabric [15,16]. It is believed that the superoxide radical does not attack cellulose directly,

Table II. Conditional stability constants at 25°C and pH 10⋆.

	Cu(II)	Ca(II)	Cu(II)−Ca(II)	Fe(II)	Fe(III)
EDTA	16.0	10.2	5.8	13.3	10.3
EDDS	15.9	5.0	10.9	9.9	7.5
DTPMP	18.4	10.1	8.3	15.1	13.0
IDS	11.0	3.5	7.5	6.6	0.9

⋆ EDTA and EDDS values calculated from log *K* values in: Martell AE, Smith RM. Critical Stability Constants vol 1, Plenum Press, New York, 1974; DTPMP and IDS values from suppliers literature.

Table III. Weight loss in polyester–cotton swatches after bleaching at 90°C.

Metal solution	Weight loss (%)	Time for peroxide level to reach zero (min.)
No metal	0.2	$>60^{\star}$
Co(II) no chelator	0.0	4
Cr(III) no chelator	2.0	$>60^{\star}$
Cu(II) no chelator	17.4	40
Fe(II) no chelator	6.1	31
Mn(II) no chelator	0.2	6
Ni(II) no chelator	1.7	22
Cu(II)-EDTA (1:1)	7.5	37
Cu(II)-EDDS (1:1)	3.7	35
Cu(II)-DTPMP (1:1)	2.4	13
Cu(II)-IDS (1:1)	12.0	36
Fe(II)-EDTA (1:1)	4.0	18
Fe(II)-EDDS (1:1)	5.1	15
Fe(II)-DTPMP (1:1)	3.3	14
Fe(II)-IDS (1:1)	4.7	18

*Concentration of hydrogen peroxide after 1 h in these two experiments was 3.3%.

but can contribute to degradation by further reaction with carbohydrate radical species that have been formed by hydroxyl-radical attack [6]. An acclelerated cellulose damage experiment was designed to confirm whether the metals or metal/chelating agent systems that give the highest flux of hydroxyl radicals cause the most damage. Initially, the experiment listed in Table III using copper and no chelator was carried out at 40°C, but no weight loss was detected after 2 h (only 10% of the peroxide had disappeared after this time) so all subsequest experiments were carried out at 90°C. The decomposition times are also noted (Table III), the importance of which are to demonstrate that there is no relationship between them and weight loss.

Results with unchelated metals. As expected, untreated cloth suffers very little damage and decomposition of peroxide is slow. Of the metals containing no chelating agent, significant damage occurs with just Fe(II) and Cu(II), with Cu(II) being much worse than Fe(II). Again, these results support the view that these are the two metals that can readily undergo 1-electron catalysed decomposition of hydrogen peroxide. The peroxide decomposition times indicate that Mn(II) and Co(II) are much more active as decomposition catalysts, but they give very little cellulose damage, so presumably decomposition takes place via a non-radical mechanism. The high weight loss seen with Cu(II) was confirmed in a separate experiment in which 500 g of 5% peroxide was used instead of 310 g, with all other conditions kept the same. The weight loss in this instance was 28.8% (a sample of untreated cloth gave 1.2% weight loss using the same conditions). Assuming that only cotton is degraded and the polyester remains intact, then over 50% of the cotton was destroyed in this experiment. The intensity of the cellulose hydroxyl band at 3300 cm^{-1} in the infra-red spectrum had also decreased by 62% compared with the initial cloth, confirming that severe degradation had occurred. It has been reported that the active species in DNA damage in $\text{Cu/H}_2\text{O}_2$ systems is a Cu(I)OOH complex, rather than free hydroxyl radical [17,18] but there have not been any suggestions that such a species plays a role in the degradation of cellulose, which is a more robust a polymer than DNA, under alkaline bleaching conditions. So the extensive cellulose damage with Cu(II) most likely reflects the conclusion from the spin-trap experiments that, of the unchelated metals, it gives the highest rate of $^{\cdot}$OH radical formation.

Although these experiments are exaggerated with respect to industrial systems in terms of higher temperatures and higher copper levels than would normally be encountered, it should be noted that significant loss of strength in the cellulose fibres would be expected long before total dissolution of the polymer occurred.

Results with chelated copper. When the cloths are stained with Cu(II)-chelator complexes the damage is generally reduced. Nevertheless, EDTA and IDS give significantly more damage than EDDS and DTPMP, which is again in agreement with the spin-trap experiments.

Results with chelated iron. The cloths stained with the Fe(II)-chelator complexes suffer less damage than unchelated Fe(II) and have broadly similar weight losses, with DTPMP having the lowest weight loss. There is no sign of the much enhanced radical damage expected with DTPMP, IDS and EDTA that would be expected from the spin-trap experiments. It is difficult to rationalise this, but one issue is the form of the iron chelate complex on the cloth after drying could be very different to the Fe(II) complex in solution in the EPR experiments. It is well known that wet Fe(II) salts oxidise and hydrolyse rapidly upon drying in air, and the colour of the cloths turned very yellow upon drying, indicating significant oxidation. Cu(II) salts and complexes on the other hand have much lower tendency to hydrolyse than those of iron.

Peroxide decomposition and the role of calcium

Since commercial applications contain significant levels of hardness ions (Ca^{2+} and Mg^{2+}, with generally more of the former than the latter), the role of calcium on the rate of decomposition of peroxide was investigated. The results in Table IV demonstrate a stabilising effect of calcium on alkaline

Table IV. Effect of transition metal and calcium on peroxide decomposition at pH10, 40°C, in the absence of chelating agents.

Transition metal and concentration (mg/kg)	Calcium concentration (mg/kg)	Percentage of decomposition after 60 min
None	None	5
Fe(II) 4	None	60
Fe(II) 4	40	18
Fe(II) 4	200	15
Cu(II) 5	None	12
Cu(II) 5	100	4
Mn(II) 5	None	43
Mn(II) 5	100	72

hydrogen peroxide which has been dosed with Fe(II) or Cu(II), and a de-stabilising effect with Mn(II).

The authors have not found any prior studies on the role of calcium in these systems, but magnesium sulphate is a well-established additive into textile bleaching and pulp bleaching in order to reduce decomposition of hydrogen peroxide. Previous studies on Mg show similar behaviour to our results with Ca: it reduces the rate of decomposition where caused by Fe and Cu, but increases it with Mn [19]. The workers in reference [19] concluded that Mg inhibited free radical chain decomposition by stabilising superoxide radicals, but this mechanism is controversial and good evidence has been provided of a separate soluble species being formed at Mg: Fe molar ratios >6 which is a lot less active a decomposition catalyst than Fe alone [20].

Conclusions

The spin-trapping results confirm that, of the unchelated metal ions, Cu(II) leads to the most effective generation of hydroxyl radicals from H_2O_2 at pH 10; The cellulose damage experiments provide parallel findings. In the presence of the chelating agents EDDS and DTPMP, the rate of generation of $^{\cdot}OH$ (and cellulose damage) is much reduced; on the other hand, EDTA and IDS exert little protective effect as judged by both sets of experiments. This strongly suggests that, in these cases at least, damage to the substrate is $^{\cdot}OH$ radical-induced.

In contrast, for the iron-containing systems, the spin-trapping and cellulose damage experiments give results which differ. Thus, for the spin-trapping experiments, the chelating agents EDTA, DTPMP and IDS considerably enhance the generation of hydroxyl radicals by the Fenton reaction (Reaction 1), as noted previously [7]; this may reflect more favourable E^0 values. Conversely, these ligands have little effect on the extent of cellulose damage (indeed, the damage is generally reduced in each case).

For the other metals tested, lack of significant hydroxyl-radical generation parallels the lack of cellulose damage, despite significant peroxide decomposition with cobalt, nickel and manganese.

The contrast between the behaviour of copper and iron is notable. The differences observed between the spin-trapping results versus cellulose damage may well reflect the different time-scales of the homogenous (EPR) and heterogeneous (cellulose damage) experiments, the greater propensity for iron to hydrolyse and oxidise (e.g. during the preparation of the iron-doped cloths), and the lower stability constants of the iron complexes compared with copper (Table II).

These observations may have implications for substrate damage in real peroxygen bleaching systems. Hydroxyl radicals can be generated at transition-metal sites either in solution or heterogeneously on a surface, and in real systems metals may enter as soluble or fine colloidal species in the make-up or tap water, or they may already be bound to a polymeric substrate. If the metals enter in the water they may still tend to absorb onto the substrate (and in the case of laundry washing there could be a gradual build up over multiple wash-cycles). Pulp fibres are well known to bind transition metals and greater degradation of cellulose fibres has been associated, for example, with higher iron levels actually bound to the pulp fibres [21]. Damage to the substrate is actually more likely when transition metals capable of carrying out the Fenton-type reaction are precipitated or bound onto the substrate. For instance, copper has been found to give greater hydroxyl-radical degradation of proteins and DNA than iron, and this effect has been associated with copper specifically binding to these biopolymers [12,13]. Copper is also known to bind to the protein polymers in hair and subsequently cause degradation when the hair is treated with hydrogen peroxide containing oxidative hair dyes [22].

The studies detailed here provide evidence for, and details of, some of the likely mechanisms involved in substrate damage in peroxygen-based systems. Thus in particular, the use of EDTA, a widely used chelating agent in the pulp and textile bleaching industries, may be unsuitable under certain conditions; EDDS (and possibly DTPMP) may offer advantages for some applications, as noted in reference [22] for the prevention of hair damage.

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