

# Pulp bleaching by hydrogen peroxide activated with copper 2,2'-dipyridylamine and 4-aminopyridine complexes

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## Abstract

Oxygen-bleached kraft pulp (OKP) was bleached with H<sub>2</sub>O<sub>2</sub> activated with a copper complex coordinated with 2,2'-dipyridylamine (dpa) or 4-aminopyridine (4-ap) under alkaline conditions. Bleaching of OKP by H<sub>2</sub>O<sub>2</sub> activated with the Cu(II)–dpa complex decreased the kappa number (*k*) and viscosity (*v*) of the pulp by 26 and 0.7%, respectively. In contrast pulp bleaching without the coordinator resulted in a decrease in *k* and *v* values of 25 and 7.8%, respectively. Thus, selectivity for delignification, expressed by *k/v*, was increased 12-fold by the coordination with dpa. ESR demonstrated that the coordination with dpa suppressed the production of •OH by 57%. These results support the involvement of a hydroperoxo complex of Cu(II) formed by the reaction of <sup>-</sup>OOH with [Cu(II)(dpa)(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup>. When the OKP was bleached with H<sub>2</sub>O<sub>2</sub> activated with a Cu(II)–4-ap complex, selectivity (*k/v*) in pulp bleaching increased by 2.6-fold and production of •OH decreased by 47%. We conclude that Cu(II)–dpa is a catalyst potentially applicable to totally chlorine free (TCF) bleaching sequences due to its high selectivity for delignification.

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**Keywords:** Copper complex; Pulp bleaching; 2,2'-Dipyridylamine; 4-Aminopyridine; Lignin; ESR

## 1. Introduction

In paper-making mills, pulp bleaching has been performed conventionally by multistep sequences involving treatments with molecular chlorine or chlorine-based chemicals. Effluents from these processes contain chlorinated aliphatic and aromatic compounds that could be acutely toxic, mutagenic and carcinogenic. Environmental concerns about chlorinated organics and system closure requirements have created a need for new technologies to replace the use of chlorine in pulp bleaching operations. Therefore, totally chlorine free (TCF) bleaching sequences based on the use of oxygen, ozone, alkaline peroxide or enzymes have been developed. Environmentally friendly enzymatic pulp bleaching techniques such

as the laccase-mediator system and xylanase have been investigated extensively in recent years. In addition to enzymatic bleaching, oxidants produced by activation of H<sub>2</sub>O<sub>2</sub> with transition metal complexes have been proposed as a potential agent to achieve the selective delignification of pulps.

Hydrogen peroxide is generally recognized as an environmentally friendly oxidant. In alkaline media, the equilibrium of H<sub>2</sub>O<sub>2</sub> shifts to the formation of hydroperoxide anion (<sup>-</sup>OOH). The anionic active oxidant is widely used as a lignin-degrading agent in pulp bleaching although hydroxyl radicals are also produced in the alkaline-H<sub>2</sub>O<sub>2</sub> bleaching system. Except for the alkaline-H<sub>2</sub>O<sub>2</sub> system, little is known about the practical applications of activated H<sub>2</sub>O<sub>2</sub> to pulp bleaching. A major drawback of the use of H<sub>2</sub>O<sub>2</sub> in pulp bleaching is the limited delignification capability of the active oxidant. The most promising method to enhance the reactivities of H<sub>2</sub>O<sub>2</sub> for delignification is the use of activators. Several transition metal complexes are

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known to activate  $\text{H}_2\text{O}_2$ . For instance, Kuhne et al. [1] used a binuclear manganese complex,  $[\text{Mn(III)Mn(IV)}(\mu\text{-O})_2(\mu\text{-CH}_3\text{COO})_2]$ , 1,2-bis-(4-7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane $(\text{ClO}_4^-)_2$ . The manganese complex bleached OKP with a suppression in kappa number and viscosity decrease of 55 and 13%, respectively. In addition, the activation of  $\text{H}_2\text{O}_2$  with copper complexes is also a potential chemical system to degrade lignin. However, there have been few reports on the delignification of pulps using copper complexes. In 1998, we reported that  $\text{H}_2\text{O}_2$  activated by copper/pyridine complexes is able to depolymerize lignin in aqueous solutions at room temperature [2]. The activation of  $\text{H}_2\text{O}_2$  by copper/pyridine systems has been applied to pulp bleaching [3] and the decolorization of synthetic dyes such as Poly-R [4], Poly B-411, Phenol red, Tropaeolin, Evans blue and Eosin yellowish [5]. In copper/pyridine systems, the control of free radical production from organic hydroperoxides has also been investigated. The organic hydroperoxide system was found to delignify wood, leading to fiber separation as observed in wood decay by selective white rot fungi [6].

In the present paper, we report that the  $\text{Cu(II)-dpa}$  complex is a powerful delignifying agent for OKP as well as the  $\text{Cu(II)-4-ap}$  complex in combination with  $\text{H}_2\text{O}_2$  [3]. Catalytic functions of the  $\text{Cu(II)-dpa}$  complex for the bleaching of OKP are discussed in comparison with those of the  $\text{Cu(II)-4-ap}$  system.

## 2. Experimental

### 2.1. Materials and general methods

2,2'-Dipyridylamine (dpa) was obtained from Tokyo Chemical Industries (Tokyo, Japan). 4-Aminopyridine (4-ap),  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ , ethylenediamine tetraacetic acid (EDTA) were purchased from Wako Pure Chemical Industries (Osaka, Japan). A stable radical, which was used to calculate concentration of spin adducts from ESR intensity, 1,1-diphenyl-2-picrylhydrazyl (DPPH) was also purchased from Wako. Cupriethylenediamine and  $\text{CuCl}_2$  were obtained from Kanto Chemicals (Tokyo, Japan) and Nacalai Tesque (Kyoto, Japan), respectively. A spin trapping reagent,  $\alpha$ -(4-pyridyl-1-oxide)-*N-tert*-butylnitron (4-POBN) was from Labotec (Tokyo, Japan). Oxygen pre-bleached kraft pulp (OKP) (mixed hardwood) (A: kappa number, 10.7; viscosity, 1132 mL/g; ISO brightness, 55; B: kappa number, 9.8; viscosity, 888 mL/g; ISO brightness, 56) was used after a chelation (Q) treatment to remove the metal ions in the original pulp.

### 2.2. Preparation of copper complex

A stock solution of  $\text{Cu(II)-dpa}$  complex (1:1) was prepared by mixing 25 mM  $\text{CuCl}_2$  and 25 mM dpa. A stock solution of  $\text{Cu(II)-4-ap}$  complex was prepared by mixing 1 mM  $\text{CuSO}_4$  and 100 mM 4-ap. These solutions were kept for over 24 h in darkness before use.

### 2.3. Pulp bleaching

#### 2.3.1. Cu stage

All bleaching experiments were carried out in a 1 L glass reaction vessel equipped with an automatic controller for temperature, pressure and stirring speed. For pulp bleaching with  $\text{Cu-dpa}$ , all the experiments were performed with a  $\text{Cu-dpa}$  (1:1) (250  $\mu\text{M}$ ) complex at 5% pulp consistency in 100 mM sodium carbonate buffer (pH 10). Before reaction, the pulp suspension was heated to 60 °C. To this suspension,  $\text{H}_2\text{O}_2$  (1% o.p.) was added and allowed to react for 4 h with constant stirring. Bleaching experiments were also carried out with 1, 5 and 10% o.p. of  $\text{H}_2\text{O}_2$ . Experiments without coordinators were performed under the same conditions.

For pulp bleaching with  $\text{Cu-4-ap}$ , reactions were started by adding  $\text{H}_2\text{O}_2$  (1% o.p.) in an aqueous solution containing OKP, 10  $\mu\text{M}$   $\text{Cu(II)}$ , and 1 mM 4-ap, 4-hydroxybenzoic acid (0.1% o.p.) at 60 °C for 4 h with a 5% consistency of pulp under a oxygen atmosphere at 0.2 MPa.

#### 2.3.2. Chelation (Q)-stage

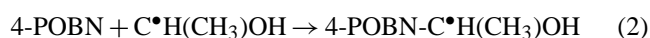
Air-dried OKP was treated with EDTA (0.5% o.p.) for one hour at 80 °C at 5% pulp consistency. After the reaction, the pulp was washed with 2 L of distilled water using a funnel. Q-treatment after the Cu-stage was performed according to the same procedure.

### 2.4. Determination of kappa number, viscosity and brightness

The determination of kappa number and viscosity of pulp was carried out according to Tappi T 236 cm-85 [7], and SCAN-CM 15:88 [8], respectively. Brightness of pulp was measured according to ISO standards 5351-1 [9].

### 2.5. Determination of hydroxyl radicals by ESR spin trapping method

An aliquot of the  $\text{Cu(II)}$  stock solutions, 0.1 M POBN, 1.0 M EtOH and 20 mM carbonate buffer (pH 11) were mixed in a glass vial. To the solution, 30%  $\text{H}_2\text{O}_2$  was added to start the reaction. The solution was immediately drawn into a quartz cell and put into an ESR cavity. Final concentrations of each reagent were 100 mM EtOH, 10 mM 4-POBN, 5%  $\text{H}_2\text{O}_2$  and 250  $\mu\text{M}$  of  $\text{Cu(II)-dpa}$  or  $\text{CuCl}_2$ . After 5 min, ESR spectra of 4-POBN- $\text{C}^\bullet\text{H}(\text{CH}_3)\text{OH}$  adduct, produced by reactions (1) and (2) were measured with a JEOL JES-FR30 Free Radical Monitor (Tokyo, Japan) at room temperature under the following conditions: frequency: 9.425 GHz; center field, 335.6 mT; sweep width, 5.0 mT; modulation width, 0.10 mT; receiver gain, 320; data points, 4096; time constant, 0.10 s; sweep time, 1.0 min; power, 4.0 mW.



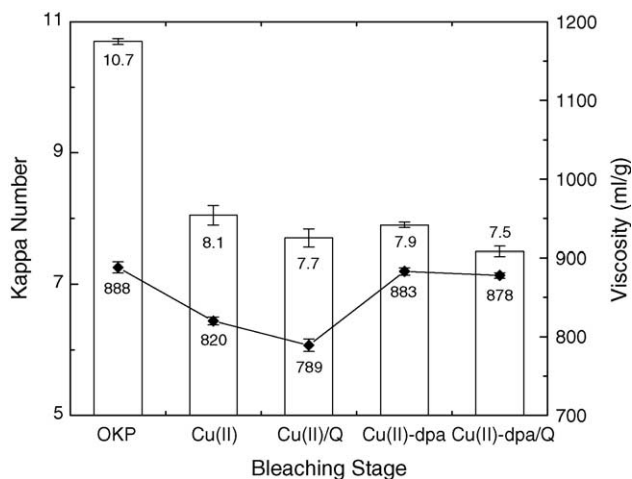


Fig. 1. Effects of dpa as a coordinator of Cu(II) on the decrease in kappa number and viscosity of OKP. Kappa number (□) and viscosity (◆).

The ESR intensity of each spectrum was converted to the concentration of the radicals using the intensity ratio between the Mn(II) marker and DPPH. Experiments were also carried out with a series of different H<sub>2</sub>O<sub>2</sub> concentrations, 1, 5 and 10%.

For the assay of •OH in the Cu–4-ap system, reactions were started by adding 1% H<sub>2</sub>O<sub>2</sub> in 10 mM sodium carbonate buffer (pH 11) containing 100 mM ethanol, 10 mM 4-POBN, 10 μM CuSO<sub>4</sub> and 1 mM 4-ap. Control experiments were carried out under the same conditions without 4-ap.

### 3. Results and discussion

The catalytic efficiency of H<sub>2</sub>O<sub>2</sub> activated with Cu(II)–dpa or Cu(II)–4-ap in the bleaching of OKP was evaluated by measuring the kappa number (*k*) and intrinsic viscosity (*v*) of the pulp. The selectivity for delignification was estimated with *k/v*. Bleaching of OKP with H<sub>2</sub>O<sub>2</sub> (1% o.p.) activated with the Cu(II)–dpa complex decreased the kappa number of the pulp by 26% (Fig. 1). In the bleaching reactions, the decrease in viscosity was 0.7%. Thus, high selectivity in pulp bleaching was achieved in the Cu(II)–dpa system under the conditions employed. In contrast, pulp bleaching by H<sub>2</sub>O<sub>2</sub> and Cu(II) without the coordinator resulted in a decrease in kappa number and viscosity by 25 and 7.8%, respectively. Thus, selectivity for delignification, expressed by *k/v*, was increased 12-fold by the coordination with dpa. Assays for hydroxyl radicals (•OH) by ESR spin trapping method revealed that coordination by dpa decreased the amount of •OH products from 8.44 to 3.64 μM in the reactions of Cu(II) and 5% H<sub>2</sub>O<sub>2</sub> (Fig. 2). This supports the involvement of a hydroperoxo–Cu(II) complex proposed by Robbins and Drago [10]. They speculated that [Cu(II)(dpa)(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> reacts with HOO<sup>–</sup> to form an equatorially bound Cu(II)–hydroperoxo complex, [Cu(II)(dpa)(H<sub>2</sub>O)<sub>3</sub>(OOH)]<sup>2+</sup>. The active oxidant then

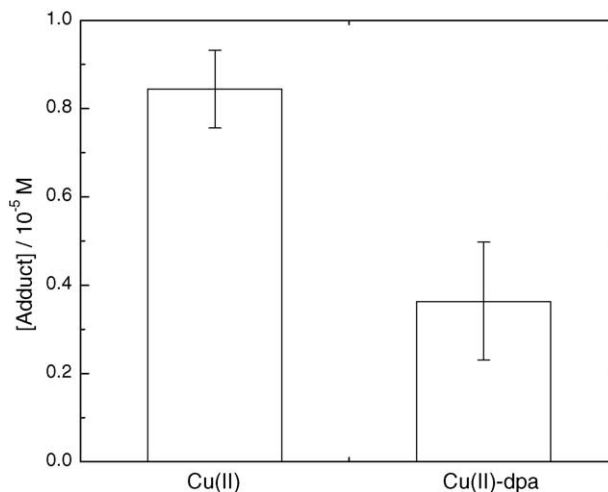
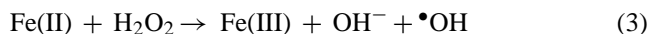


Fig. 2. Production of hydroxyl radicals in the reactions of H<sub>2</sub>O<sub>2</sub> with the Cu(II)–dpa complex or CuCl<sub>2</sub>.

oxidizes substrates, with concomitant reduction of the hydroperoxo intermediate to [Cu(II)(dpa)(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>. [Cu(II)(dpa)(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> is converted to [Cu(II)(dpa)(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> on dissociation of coordinated water from an axial position to complete the oxidation cycle. Hydroperoxo-copper intermediates have also been proposed for the multi copper [11,12] and copper amine [13] oxidases as well as copper–zinc superoxide dismutase [14].

The decomposition of hydrogen peroxide under alkaline conditions proceeds via two different pathways. One is a bimolecular reaction that results in the direct formation of molecular oxygen and water. The other, important pathway is a unimolecular reaction known as the Fenton reaction shown in reaction (3).



For unimolecular reactions, a one-electron transfer catalysis from transition metals to H<sub>2</sub>O<sub>2</sub> produces hydroxyl radicals (•OH). We observed production of •OH in the reaction of H<sub>2</sub>O<sub>2</sub> and Cu(II) without coordinators. This phenomenon is explained by the reduction of Cu(II) by H<sub>2</sub>O<sub>2</sub>, and a subsequent Fenton type reaction between Cu(I) and H<sub>2</sub>O<sub>2</sub>. The latter reaction generates •OH and Cu(II). In the reactions of copper complexes with H<sub>2</sub>O<sub>2</sub>, the reduction of Cu(II) by H<sub>2</sub>O<sub>2</sub> depends on the redox potential of the complex. For instance, when H<sub>2</sub>O<sub>2</sub> was mixed with Cu(II)–EDTA or Cu(II)–dtpa complex, no reaction occurred [15]. However, production of •OH was observed on addition of biological reductants such as cysteine and ascorbic acid. This is explained by the coordination by EDTA and dtpa of Cu(II) which changed the redox potential of Cu(II) toward H<sub>2</sub>O<sub>2</sub>. In the reaction of Cu(II)–dpa with H<sub>2</sub>O<sub>2</sub>, reduction of [Cu(II)(dpa)(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> to [Cu(I)(dpa)(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> by H<sub>2</sub>O<sub>2</sub> is disfavored because production of •OH is decreased by the coordination by dpa. This is advantageous for the delignification of pulps with high selectivity.

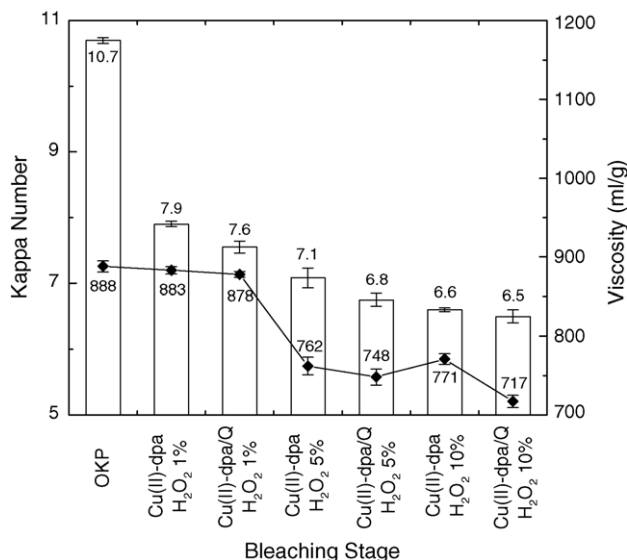


Fig. 3. Effects of hydrogen peroxide concentration on the decrease in kappa number and viscosity in bleaching of OKP by H<sub>2</sub>O<sub>2</sub> activated with Cu(II)-dpa complex. Kappa number (□) and viscosity (◆).

Fig. 3 shows effects of H<sub>2</sub>O<sub>2</sub> concentration on delignification and viscosity decrease. With 1% o.p. H<sub>2</sub>O<sub>2</sub>, the kappa number decreased by 2.8 points but the viscosity decrease was negligible. Thus, pulp bleaching with high selectivity was achieved with 1% o.p. H<sub>2</sub>O<sub>2</sub>. With 5 and 10% o.p. of H<sub>2</sub>O<sub>2</sub>, the delignification effect increased but a decrease in selectivity was observed. The amount of •OH generated at the different concentrations of H<sub>2</sub>O<sub>2</sub> is shown in Fig. 4. The amount of •OH produced at 1, 5 and 10% of H<sub>2</sub>O<sub>2</sub> was 2.24, 3.64 and 5.67 μM, correspondingly, so it is not proportional to the concentration of H<sub>2</sub>O<sub>2</sub>. The excess amount of H<sub>2</sub>O<sub>2</sub> resulted in increased production of a cellulolytic active oxygen species, •OH. With 1, 5 and 10% o.p. of H<sub>2</sub>O<sub>2</sub>, ISO

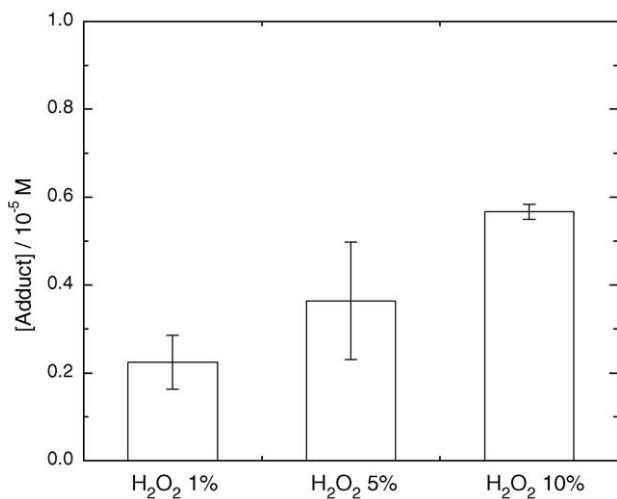


Fig. 4. Effects of hydrogen peroxide concentration on •OH production by the Cu(II)-dpa complex.

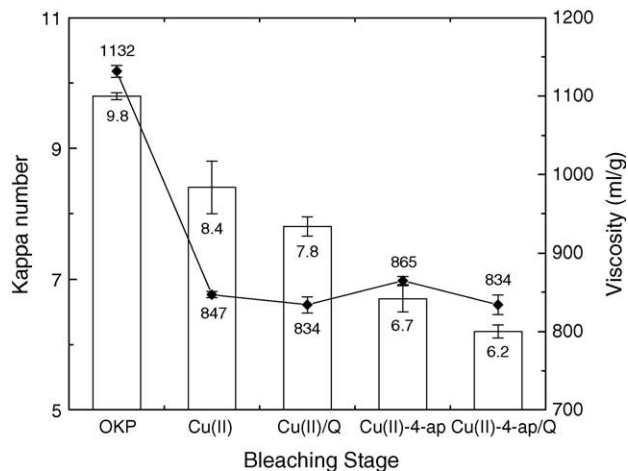


Fig. 5. Effects of coordination of Cu(II) with 4-ap on the decrease in kappa number and viscosity. Kappa number (□) and viscosity (◆).

brightness of the pulp increased from 55 to 60, 68 and 66, correspondingly.

In the present study, 4-ap was also examined as a bleaching agent (Fig. 5). Bleaching of OKP with the Cu(II)-4-ap complex resulted in a 32% decrease in kappa number and 24% decrease in viscosity. Under this condition, ISO brightness of the pulp increased from 56 to 68. The selective delignification with the Cu(II)-4-ap complex is in stark contrast to the pulp bleaching with copper without a coordinator. The reaction without the coordinator gave a 14% decrease in kappa number and 28% decrease in viscosity. These values are consistent with a previous report [3]. The use of 4-ap as a ligand for Cu(II) decreased the amount of •OH from 2.81 to 1.48 μM (Fig. 6).

The 4-ap system required a high concentration of ligand. The molar concentration of 4-ap is 100 times higher than that of Cu(II) ion. In contrast, pulp bleaching with the Cu(II)-dpa

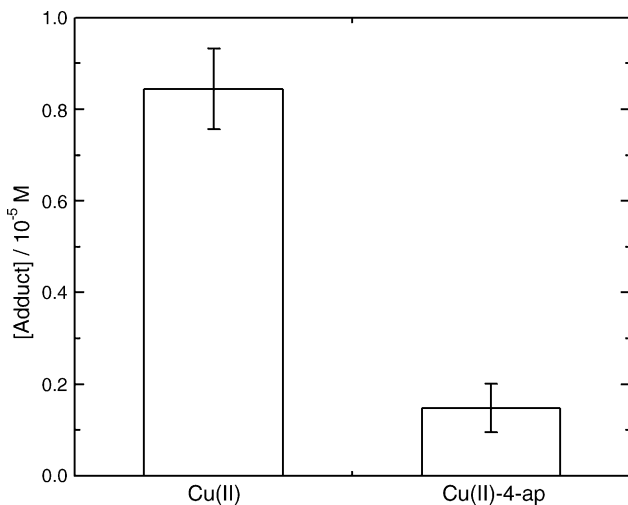


Fig. 6. Production of hydroxyl radicals in the reactions of H<sub>2</sub>O<sub>2</sub> with the Cu(II)-4-ap complex or CuCl<sub>2</sub>.

system can be carried out at much lower concentrations of ligand. This is advantageous for practical applications of the copper system. In the Cu–dpa and Cu–4-ap systems, pulp bleaching is performed in alkaline media where the phenolic group in lignin is converted to a reactive phenolate form. A bleaching sequence in combination with E-stage (alkaline treatment) can be easily designed due to the similar pH region between the E- and Cu-stages.

#### 4. Conclusion

The Cu(II)–dpa complex activated H<sub>2</sub>O<sub>2</sub> to delignify OKP in alkaline media. We conclude that Cu(II)–dpa is a catalyst potentially applicable to TCF bleaching sequences due to its high selectivity for delignification and requirement of low concentrations of coordinators. The ESR study supports that the major oxidant in the bleaching system is not •OH but a hydroperoxo copper complex.

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