Cooperative Decomposition of Hydrogen Peroxide by Lignin-combined Transition Metals in Pulp Bleaching

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The effects of lignin-combined manganese ion, iron ion, and lignin-combined iron and manganese on the decomposition of hydrogen peroxide were investigated. Elemental analysis and inductively coupled plasma-atomic emission spectrometry were used to analyze the chemical features of the lignin composites and the amount of metal ions present in the solution or adsorbed on lignin, respectively. The results showed that the main transition metal elements remaining in the precipitated lignin were Fe, Mn, and Cu. The hydrogen peroxide decomposition in the presence of lignin-combined transition metal was represented by pseudo-first-order kinetics, and the pseudo-first-order rate constant (k_{obs}) of peroxide decomposition with lignin-combined iron was 0.0068 min^{-1}, while it was 0.0063 min^{-1} in the presence of lignin-combined manganese. A synergistic effect of manganese and iron combined with lignin on peroxide decomposition was demonstrated, and a k_{obs} value of 0.0053 min^{-1} was obtained. The mixed addition of magnesium sulfate ($MgSO_4$), sodium silicate (Na_2SiO_3), and ethylene diamine tetraacetic acid disodium salt (Na_2EDTA) resulted in an optimal reduction in peroxide decomposition when single lignin-combined metal ion existed. However, adding Na_2EDTA alone had an optimal effect on the reduction of peroxide decomposition in the presence of lignin-combined iron and manganese, with a k_{obs} value of 0.0004 min^{-1}.

INTRODUCTION

With the increasing awareness in society of environment protection issues, elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching technologies have become important trends in the field of pulp bleaching. Hydrogen peroxide is the most important total-chlorine-free bleaching agent and is widely used for pulp bleaching due to its higher efficiency, lower cost, and better operability (Sixta 2006). Unfortunately, transition metals present in pulp are active in catalysis of the decomposition of hydrogen peroxide under certain bleaching conditions. Several studies involving transition metal induced peroxide decomposition have been conducted to try and control the unwanted decomposition of peroxide in the bleaching process, especially for iron ions and manganese ions (Wekesa and Ni 2003, 2011; Popov *et al*. 2007; Zhang *et al*. 2015, 2016).

Previous studies have shown that transitional metals are present in many different states during the bleaching process. These states include the "non-equilibrium" suspended particles, oligomer dynamic equilibrium with carboxylic groups of fiber, and

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the oligomer chelated with residual lignin by forming coordinate bonds with phenolic groups (Cardona-Barrau *et al*. 2001; Norberg *et al*. 2001; Zhang *et al*. 2010; Wekesa *et al*. 2011). In the case of high yield pulping, peroxide bleaching is performed together with the pulping process, with a certain content of dissolved lignin in waste liquor or residual lignin in pulp. Lignin is an amorphous, polyphenolic, highly cross-linked polymer consisting of certain numbers of active carboxyl and hydroxyl (phenolic or non-phenolic) sites that can be available for complexation with metal ions. According to several studies, lignin has been found to be suitable for transition metal removal from wastewater (Guo *et al*. 2008; Li *et al*. 2015). Various studies have investigated the mechanisms of interaction between transition metal and lignin (Merdy *et al*. 2002; Huang *et al*. 2015; Lin *et al*. 2016). Lignin can adsorb Fe (III) strongly at low pH (<3) while Mn(II) forms far less stable surface complexes at pH = 8.0. Redox processes take place as the metal ions are adsorbed onto lignin (Merdy *et al*. 2002). An outer-sphere complex is formed between Cr(III) and lignin, with the carbonyl groups as the predominant sites. In contrast to Cr(III), a reduction reaction has occurred in the case of Cr(VI) with the carbonyl and phenolic groups in lignin (Lin *et al*. 2015). Metal ions bound to lignin show less catalytic activity than the corresponding free ions in the solution (Zhang *et al*. 2016). The effect of different stabilizers on peroxide in the presence of both dissolved lignin and transition metals might change with the external conditions. For instance, the presence of calcium ion can decrease the adsorption of manganese onto lignin (Merdy *et al*. 2002), which may alter the catalytic action of peroxide decomposition. Therefore, further understanding of the effects of complexation between transition metals and lignin on decomposition of peroxide is important for the accurate characterization and effective control of the invalid decomposition of peroxide during the bleaching process.

In this study, lignin was prepared from the black liquor of a eucalyptus pulping process using hydrochloric acid without further purification, to simulate the dissolved lignin in the bleaching process. Ethylene diamine tetraacetic acid disodium salt (Na_2EDTA), sodium silicate (Na_2SiO_3), and magnesium sulfate ($MgSO_4$) were chosen as stabilizers for peroxide. The chemical composition of the precipitated lignin was studied using modern analytical methods, and the effects of different lignin-combined transition metals and different stabilizers on hydrogen peroxide decomposition were studied.

EXPERIMENTAL

Materials

All the reagents used in this study were of analytical grade and used without further purification. Manganese sulfate ($MnSO_4 \cdot H_2O$) and ammonium ferric sulfate ($NH_4Fe(SO_4)_2 \cdot 12H_2O$) were supplied by Dongguan Dongjiang Chemical Reagent Co., Ltd. (Dongguan, China). The black liquor was purchased from Guangxi Jingui Pulp & Paper Co., Ltd. (Qinzhou, China). The pH level was adjusted by a standard sodium hydroxide solution. Milli-Q (Millipore Corporation, Billerica, MA, USA) deionized water was used throughout the experiments.

Methods

Separation of precipitated lignin

In the initial experimental process, precipitated lignin was separated from the black liquor of eucalyptus pulping. Firstly, the black liquor was diluted to 10%

concentration by deionized water. Then, the black liquor was screened to obtain 400-mesh fraction. The filtrate was acidified to a pH of 2 to 2.5 using hydrochloric acid, and then stirred for 1 h. The liquid-sediment suspension was then transferred to a centrifugal tube, and the acid liquor was separated at a centrifugal speed of 5000 rpm. The solid was freeze dried under a vacuum. The dried solid was washed with deionized water (20 g•L^{-1}), shaken on an end-over-end shaker for 3 h, separated by centrifugation, and then freeze-dried. This washing and drying procedure was repeated twice, and the solid obtained was termed "precipitated lignin", which was used throughout the experiments.

Processing-complexation reaction of transition metal by precipitated lignin

The suspension of the precipitated lignin sample was magnetically and vigorously stirred for 2 h to hydrate the sample prior to the introduction of the metal ion. A standard stock solution of manganese ion was prepared by dissolving manganese sulfate into deionized water with 0.1 M HCl solution. A complexation process of metal ions by precipitated lignin took place prior to the peroxide decomposition reaction. The complexation reaction was conducted under the following conditions: metal concentration of 2 ppm, precipitated lignin concentration of 5 g•L^{-1}, reaction temperature of 60 °C, and 160 r•min^{-1} for 24 h. The mixed solutions were cooled sequentially to room temperature using a mixture of ice and water.

Decomposition of hydrogen peroxide

All hydrogen peroxide decomposition processes were conducted in 50-mL polyethylene bottles maintained in a constant temperature water bath at a temperature of 60 °C. The decomposition processes were performed under the following conditions: pH level of 11.0, initial hydrogen peroxide concentration of 2.777 g•L^{-1} (2.5% on oven-dry (o.d.) pulp at 10% consistency), metal concentration of 2 ppm, precipitated lignin concentration of 5g•L^{-1}, or without any precipitated lignin.

Decomposition of hydrogen peroxide with stabilizers

The stabilities of the additives during the hydrogen peroxide decomposition process were studied. Magnesium sulfate ($MgSO_4$) (0.25% on o.d. pulp at 10% consistency), sodium silicate (Na_2SiO_3) (2.5% on o.d. pulp at 10% consistency), and Ethylenediamine-tetraacetic acid disodium salt (Na_2EDTA) (0.05% on o.d. pulp at 10% consistency) were selected as stabilizers to inhibit the decomposition of hydrogen peroxide, either individually or in combination. The addition-sequence of these chemicals was as follows: Na_2EDTA, Na_2SiO_3, $MgSO_4$, and hydrogen peroxide. There was a 5 min interval and some stirring between the addition of each chemical.

Measurements and Characterization

The content of C, H, N, and S elements in the precipitated lignin was quantified by dry combustion in an autoanalyzer (Vario MAX cube, Elementar Analysensysteme GmbH, Hanau, Germany). X-ray diffraction (XRD; D/max-IIIA, Rigaku Corporation, Tokyo, Japan) was used to identify the crystalline structure of the freeze-dried samples. The amount of metal was determined using inductively coupled plasma-atomic emission spectrometry with an iCAP6300 (ICP-AES; Thermo Electron Corporation, Waltham, MA, USA). The peroxide concentration was measured according to standard iodometric titration using ammonium molybdate solution as a catalyst.

RESULTS AND DISCUSSION

Elemental Analysis of Precipitated Lignin

The concentrations of metal ions in the lignin precipitate are shown in Table 1. The elemental analysis and inductively coupled plasma-atomic emission spectrometry showed that the precipitated lignin had the following percentage composition: C, 41.66%; H, 4.92%; N, 0.90%; S, 2.21%; ash, 23.16%; Ca, 0.254%; Mg, 0.06%; Fe, 0.02%; Cu, 0.0022%; and Mn, 0.0074%. The results were different from those recorded in related literature. In one study, the target lignin contained Ca, 0.06%; Na, 1.4%; Mg, 0.01%; Fe, 0.007%; and Al, 0.03% (Guo *et al*. 2008). In another study, the target lignin contained Ca, 0.18%; Mg, 0.019%; Fe, 0.0058%; and Mn, 0.0057% (Svärd *et al*, 2016). These differences are likely due to the different pulping chemicals and process water. Table 1 also showed clearly that the main transition metal elements in the precipitated lignin were Fe, Mn, and Cu, which may have been adsorbed strongly onto lignin through chelation.

Table 1. Characterization of Precipitated Lignin

Analysis (mg•kg^{-1})	Value		
	PS[1]	Guo *et al*. 2008	Svärd *et al*. 2016
Ca (mg•kg^{-1})	2540.99	600	1800
Mg (mg•kg^{-1})	601.45	100	190
Fe (mg•kg^{-1})	208.53	70	58
Cu (mg•kg^{-1})	22.26	-[b]	1.2
Mn (mg•kg^{-1})	74.46	-[b]	57
Co (mg•kg^{-1})	-[a]	-[b]	0.1
C (%)	41.66	60.8	57.4$\pm$0.2
H (%)	4.92	5.8	4.9$\pm$0.4
N (%)	0.90	1.3	0.2
S (%)	2.21	2.1	4.6$\pm$0.8
O (%)	50.31	-[b]	-[b]
Ash content (%)	23.16	5.5	-[b]

[a]- Trace amounts of Co were absent in the hydrochloric acid precipitated lignin

[b]- not mentioned

[1]: present study

XRD of Fresh Manganese and Fresh Iron

It is well known that Mn^{2+} starts to hydrolyze when the pH level is greater than 8, forming $Mn(OH)_2$ precipitate or mixed manganese precipitate in the presence of O_2 (Morgan 2005). The results of the XRD phase analysis of fresh manganese precipitates are given in Fig. 1. The phases present in the fresh manganese sample were identified in accordance with the powder diffraction data contained in the portable document format (PDF) cards. The XRD powder patterns of fresh manganese were ascribed to Mn_3O_4 according to the Joint Committee Powder Diffraction Standards (JCPDS card 75-1560), Mn_3O_4 (JCPDS card 18-0803), $7Mn(OH)_2 \cdot 2MnSO_4 \cdot H_2O$ (JCPDS card 18-0788), and $Mn(OH)_2$ (JCPDS card 73-1133). The patterns indicated that the precipitates of fresh manganese were mixed crystal, composed of Mn_3O_4, $Mn(OH)_2$, and $7Mn(OH)_2 \cdot 2MnSO_4 \cdot H_2O$, and consisted of two kinds of Mn-OH.
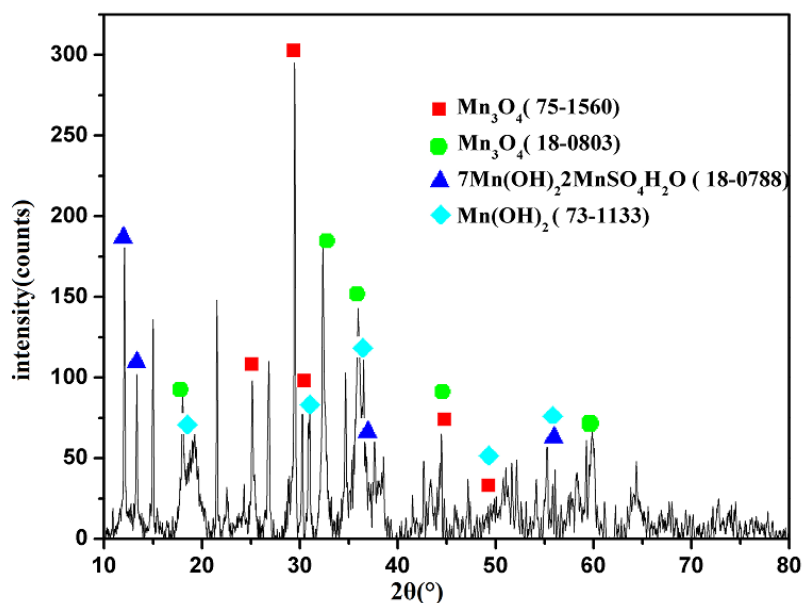
Fig. 1. XRD of fresh manganese

Generally speaking, the iron ion starts to hydrolyze when pH value exceeds 1; $Fe(OH)_i^{3-i}$ is formed initially, and then polynuclear hydrolyzed species are formed within milliseconds (Schneider 1988; Deng 1997). The iron ions precipitated in the early stage are gradually transformed to crystalline iron (III) hydroxides. Additionally, different kinds of mononuclear or polynuclear complexes can be generated at a higher pH. As a result, different states of iron can be formed during the hydrolysis and oxidizing process, such as $FeO(OH)$ and Fe_2O_3. The results of the XRD phase analysis of fresh iron precipitates are presented in Fig 2.
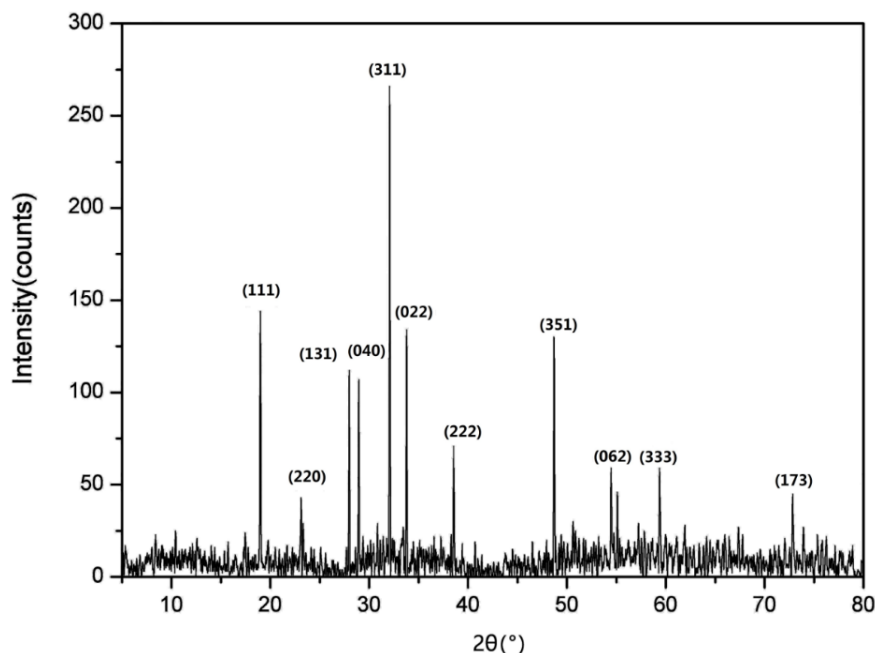

Fig. 2. XRD of fresh iron

The XRD powder patterns were just ascribed to thenardite (JCPDS card 37-1465), without any XRD of iron appearance, which indicated that the hydrolysis products of the iron ion were only amorphous iron without any crystalline phases. The result is similar to the previous studies; that is, there was not enough time to transform from amorphous iron to crystalline iron (III) hydroxides (Deng 1997).

Decomposition of Alkaline Hydrogen Peroxide with Manganese and Lignin

To quantify the invalid decomposition of hydrogen peroxide induced by metal ions combined with lignin, a kinetic model was firstly proposed. Under alkaline conditions, hydrogen peroxide decomposition in the presence of manganese or iron was represented by pseudo-first-order kinetics (Ni *et al.* 2000; Saisaha *et al.* 2013; Zeineb *et al.* 2015),

$$\ln([H_2O_2] / [H_2O_2]_0) = -k_{obs}t \tag{1}$$

where k_{obs} is the pseudo-first-order rate constant for the decomposition of hydrogen peroxide and t is time (min).

Table 2. Pseudo-first-order Rate Constant for the Decomposition of Hydrogen Peroxide with Manganese and in presence of Lignin

Presence of Mn and difference stabilizers	k_{obs} (min^{-1})
Mn-OH	0.0063
Mn-EDTA-OH	0.0013
Mn-Si-Mg-OH	0.0012
Mn-Si-Mg-EDTA-OH	0.0010
Note: Mn- manganese ion, 2 mg·L^{-1}; the addition of the additives was in the following order, Na$_2$EDTA, Si, Mg, OH, and H$_2$O$_2$, with a 5 min interval between every two additions	

The crystallization of manganese hydroxides showed noticeable activity in the hydrogen peroxide decomposition in the previous research (Ryabova *et al.* 2016). At high pH value (pH>10), the Mn(Ⅱ) can be oxidized by H$_2$O$_2$ to form MnO$_2$ (Calull *et al.* 1988). The pseudo-first-order rate constants for the decomposition of hydrogen peroxide with manganese and lignin at pH level of 11.0 are illustrated in Table 2. The results showed that the stabilizers had a positive effect on decreasing peroxide decomposition whether they were added individually or at the same time. Lignin is also a complex organic ligand, which would form stable complex such as [lignin-Mn-OH], and would promote the catalytic decomposition of hydrogen peroxide (Calull *et al.* 1988). The mixed addition of MgSO$_4$, Na$_2$SiO$_3$, and Na$_2$EDTA had the most positive effect on the reduction of peroxide decomposition with free manganese ions, having a k_{obs} value of 0.0010 min^{-1}. The k_{obs} for the decomposition of alkaline hydrogen peroxide with manganese and lignin without any additives was 0.0063 min^{-1}.

Decomposition of Alkaline Hydrogen Peroxide with Iron and Lignin

The pseudo-first-order rate constants for the decomposition of hydrogen peroxide with iron and lignin are presented in Table 3. It was confirmed that the addition of Na$_2$EDTA, MgSO$_4$, and Na$_2$SiO$_3$, in combination or individually, improved the stability of peroxide under alkaline conditions. The addition of a mixture of MgSO$_4$, Na$_2$SiO$_3$, and

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Na$_2$EDTA had the most positive effect on reducing peroxide decomposition, with a k_{obs} value of 0.0006 min^{-1}. The k_{obs} of decomposition of alkaline hydrogen peroxide was only 0.0068 min^{-1} with the existence of lignin-combined iron, which was higher than 2.2×10^{-3} min^{-1} in the presence of magnetite particles under different conditions (Zebardast *et al.* 2013). In addition, the present results revealed that iron (III) caused more catalytic decomposition than Mn(II), which was in good agreement with the effect in peroxide bleaching process in the presence of pulp (Lapierre *et al.* 1995; Körlü *et al.* 2008).

Table 3. Pseudo-first-order Rate Constant for the Decomposition of Hydrogen Peroxide with Iron and Lignin

Presence of Fe and difference stabilizers	k_{obs} (min^{-1})
Fe-OH	0.0068
Fe-EDTA-OH	0.0014
Fe-Si-Mg-OH	0.0008
Fe-Si-Mg-EDTA-OH	0.0006
Note: Fe- iron ion, 2 mg•L^{-1}; the addition of the additives was in the following order, Na$_2$EDTA, Si, Mg, OH, and H$_2$O$_2$, with a 5 min interval between every two additions	

Decomposition of Alkaline Hydrogen Peroxide with Iron, Manganese, and Lignin

The pseudo-first-order rate constants for the decomposition of hydrogen peroxide with mixed addition of iron, manganese, and lignin are shown in Table 4. A synergistic effect between manganese and iron combined with lignin on peroxide decomposition was demonstrated. The pseudo-first-order rate constant (k_{obs}) in the absence of any stabilizers was 0.0053 min^{-1}, which was less than the k_{obs} value of 0.0063 min^{-1} in the presence of lignin and manganese and the k_{obs} value of 0.0068 min^{-1} in the presence of lignin and iron. This might be attributed to the positive effect between manganese and iron on the adsorption of lignin, or the stronger ligands were formed, which were more stable for hydrogen peroxide. It could also be concluded that decomposition of alkaline hydrogen peroxide in the presence of mixed metals and lignin, including stabilizers, was different from that in the presence of single metal and lignin. The addition of Na$_2$EDTA individually had the most positive effect on reducing peroxide decomposition in the presence of iron and manganese, having a k_{obs} value of 0.0004 min^{-1}.

Table 4. Pseudo-first-order Rate Constant for the Decomposition of Hydrogen Peroxide with Iron, Manganese, and Lignin

Presence of Mn/Fe and difference stabilizers	k_{obs} (min^{-1})
Mn/Fe-OH	0.0053
Mn/Fe-EDTA-OH	0.0004
Mn/Fe-Si-Mg-OH	0.0005
Mn/Fe-Si-Mg-EDTA-OH	0.0009
Note: Mn/Fe- mixed addition of iron ion, 1 mg•L^{-1}, and manganese ion, 1 mg•L^{-1}; the addition of the additives was in the following order, Na$_2$EDTA, Si, Mg, OH, and H$_2$O$_2$, with a 5 min interval between every two additions	

CONCLUSIONS

1. The precipitated lignin was separated from the black liquor of eucalyptus pulping without further purification. The precipitated lignin still included transition metal elements such as Fe, Mn, and Cu according to the results of elemental analyses. The precipitates of fresh manganese ion were mixed crystal, containing Mn_3O_4, $Mn(OH)_2$, and $7Mn(OH)_2 \cdot 2MnSO_4 \cdot H_2O$, and consisted of two kinds of Mn-OH, as indicated by the results of XRD. The hydrolysis products of the fresh iron ion were only amorphous iron without any crystalline phases.

2. The pseudo-first-order rate constant for the decomposition of hydrogen peroxide in the presence of manganese was 0.0053 min^{-1}, which was the smallest rate constant compared to that in the presence of lignin-combined iron or lignin-combined manganese.

3. The addition of Na_2EDTA, $MgSO_4$, and Na_2SiO_3, in combination or individually, had favorable effect on peroxide stability in the presence of transition metals and lignin under alkaline conditions. Mixed addition of $MgSO_4$, Na_2SiO_3, and Na_2EDTA had the most positive effect on reducing the decomposition of peroxide in the presence of single metal ion and lignin. The k_{obs} was 0.0010 min^{-1} for manganese and 0.0006 min^{-1} for iron. The best effect on the reduction of peroxide decomposition in the presence of iron and manganese occurred when Na_2EDTA was added individually, with a k_{obs} value of 0.0004 min^{-1}.

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