

ORIGINAL ARTICLE

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Enhancement of the reaction between pulp components and hydroxyl radical produced by the decomposition of hydrogen peroxide under alkaline conditions

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Abstract Experiments on alkaline hydrogen peroxide treatments with stepwise addition and oxygen pressurization were performed to determine whether they enhance the reaction between pulp components and hydroxyl radicals produced by the decomposition of hydrogen peroxide. In this study the degradation of methyl β -D-glucopyranoside (MGP), a model compound of pulp components, was an indicator of the progression of the reaction between pulp components and hydroxyl radicals. When comparing the degradation of MGP in the stepwise and one-time addition systems, MGP was degraded more in the stepwise addition system than in the one-time addition system when Fe^{3+} was added. This result indicates that the hydroxyl radical produced by the decomposition of hydrogen peroxide efficiently attacks MGP in the stepwise addition system. MGP was degraded to the same degree in the stepwise addition system as in the one-time addition system when Fe^{2+} or Mn^{2+} was added. Aggregation and precipitation of metal ions might affect their catalysis. Oxygen-pressurized hydrogen peroxide treatment caused almost no enhancement of the degradation of MGP compared to the treatment under atmospheric pressure. Instead, high stability of hydrogen peroxide was produced by oxygen-pressurized hydrogen peroxide treatment. Such high stability can result in frequent attacks of the hydroperoxide anion, the conjugate base of hydrogen peroxide, against some chromophores and quinones.

Key words Hydrogen peroxide · Hydroxyl radical · Oxygen pressure · Transition metal · Methyl β -D-glucopyranoside

Introduction

Although hydrogen peroxide has become one of the major bleaching chemicals in elementary chlorine free (ECF) and total chlorine free (TCF) sequences, the mechanism of hydrogen peroxide reaction with pulp components is not clearly understood. It is generally believed that not only the hydroperoxide anion, the conjugate base of hydrogen peroxide, but also hydroxyl radicals produced by the metal-catalyzed decomposition of hydrogen peroxide plays a role in the degradation of pulp components during alkaline hydrogen peroxide bleaching.^{1,2}

In a previous report, we examined the decomposition of hydrogen peroxide and the degradation of a coexisting model compound, methyl β -D-glucopyranoside (MGP), under alkaline conditions in the presence of metal ions.³ The production and reaction of hydroxyl radicals originating from metal-catalyzed decomposition of hydrogen peroxide was evaluated in this experiment. A significant observation in the previous report was that the degradation of MGP was accelerated when the concentration of hydrogen peroxide decreased. This phenomenon suggests that hydroxyl radical produced by the decomposition of hydrogen peroxide preferentially reacts with hydrogen peroxide itself rather than with MGP under the conditions employed. The high reactivity of hydroxyl radicals toward hydrogen peroxide under alkaline conditions was reported in some other studies.^{2,4} This is a waste of the chemical. Hydroxyl radicals must react more frequently with pulp components than with hydrogen peroxide.

The objective of this paper is to examine whether alkaline hydrogen peroxide treatments with stepwise addition and oxygen pressurization can enhance the reaction between hydroxyl radicals and MGP. The degradation of MGP in both treatments is compared with those seen with the one-time addition of hydrogen peroxide.

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In this research, MGP is used as a model compound because it reacts only with hydroxyl radicals among the species working in the system, and hence the degradation of MGP reflects the action of hydroxyl radicals produced by the decomposition of hydrogen peroxide. Superoxide anion radical, which is also produced by the decomposition of hydrogen peroxide, does not oxidize general organic substrates including MGP, and therefore its action cannot be examined in this system.⁵ Molecular oxygen (both singlet and triplet) also cannot oxidize MGP. Therefore, the enhanced degradation of MGP, even though it is generally used as a cellulose model compound, is considered not to be unfavorable but to be the result of the efficient action of hydroxyl radicals.

Materials and methods

Materials

MGP was purchased from Tokyo Kasei Kogyo (Tokyo, Japan) and was recrystallized twice from ethanol. Transition metals used in this work were Fe^{3+} , Fe^{2+} , and Mn^{2+} because these metals are generally contained in pulps in large amounts. Mg^{2+} was also used in some experiments. All the metal ions were in the form of chloride salts and were purchased from Kishida Chemicals (Osaka, Japan). Hydrogen peroxide solution for the atomic absorption analysis (assay 30%–35%, contained no stabilizer) was purchased from Wako Pure Chemical Industries (Osaka, Japan), and sodium hydroxide of ultra-high purity (99.99 + %) was purchased from Aldrich Chemical (Milwaukee, WI, USA). Water was deionized and purified by an ultra-high pure water generator (Japan Organo, Tokyo, Japan).

Alkaline hydrogen peroxide treatment under atmospheric pressure

A sodium hydroxide solution (33.3 mmol/l) containing one of the transition metal ions [Fe^{3+} (0.36 mmol/l), Fe^{2+} (0.36 mmol/l), or Mn^{2+} (1 $\mu\text{mol/l}$)] and MGP (4 mmol/l) was prepared. The volume of the reaction solution was 300 ml. The solution was transferred to a three-necked 500-ml glass flask equipped with a condenser, stirrer, and thermometer. The flask was heated to 70°C in a waterbath. When one-time addition of hydrogen peroxide treatment was performed, 0.3 ml of the hydrogen peroxide solution was added (initial concentration ca. 11 mmol/l), and the reaction was started. When stepwise addition of hydrogen peroxide was conducted, 20 μl of the hydrogen peroxide solution was added 15 times over a span of 30 min.

Alkaline hydrogen peroxide treatment under oxygen or nitrogen pressure

A sodium hydroxide solution (33.3 mmol/l) containing Fe^{3+} (0.36 mmol/l), Mg^{2+} (0.72 mmol/l), and MGP (4 mmol/l) was

prepared. The volume of the reaction solution was 300 ml. The solution was transferred to a Teflon-coated reaction vessel⁶ (vessel is shown in Yokoyama et al.'s paper⁶) and was heated to 70°C under 1.1 MPa of oxygen or nitrogen pressure. After raising the temperature the pressure was released, and 0.3 ml of the hydrogen peroxide solution was added (initial concentration ca. 11 mmol/l). The reaction was started at this point. As soon as possible, the solution was repressurized to 1.1 MPa.

Analysis of residual MGP and hydrogen peroxide

A portion of the reaction solution (2 ml) was withdrawn and neutralized by excess addition of acetic acid. Oxygen or nitrogen pressure was kept at the same level when the solution was withdrawn. After adding an internal standard (myoinositol), the solution was concentrated and vacuum-dried. The dried sample was acetylated using sodium acetate and acetic anhydride at 100°C for 2 h. The residual MGP was determined by gas chromatography (GC).

The residual concentration of hydrogen peroxide was determined by iodometric titration. A portion of the reaction solution (10 ml) was withdrawn and poured into a titration solution. The titration solution contained 5 ml of sulfuric acid solution 5 mol/l and 10 ml of potassium iodide solution 5 mol/l; the total volume was about 90 ml. After 4 min of stirring, the iodine liberated was titrated with sodium thiosulfate solution 2 mmol/l under a nitrogen current.

Results and discussion

Decomposition of hydrogen peroxide under alkaline conditions

The proposed mechanisms for hydrogen peroxide decomposition mentioned in this section are shown in Fig. 1. The decomposition of hydrogen peroxide under alkaline conditions generally consists of two types⁵: One is a bimolecular reaction that results in direct formation of molecular oxygen and water ([1] in Fig. 1); the others are unimolecular reactions catalyzed by transition metals and often involving the formation of hydroxyl and superoxide anion radicals ([2]–[9] in Fig. 1).^{2,5} Hydrogen peroxide is also degraded by hydroxyl and superoxide anion radicals, as a chain-type reaction ([8] and [9] in Fig. 1) in the latter case.

For unimolecular reactions, the mechanism is roughly categorized into three types. The first is a one-electron transfer catalysis by transition metals, which involves the formation of hydroxyl and superoxide anion radicals ([2] and [3] in Fig. 1). Consecutive two-electron transfers from or to transition metal(s) can result in the formation, respectively, of two hydroxide anions or molecular oxygen ([4]–[7] in Fig. 1). Finally, a chain-type reaction caused by the attack of hydroxyl or superoxide anion radicals on hydrogen peroxide itself is anticipated ([8] and [9] in Fig. 1). This chain-type reaction is involved in the one-electron transfer decomposition mechanism of hydrogen peroxide ([2] and

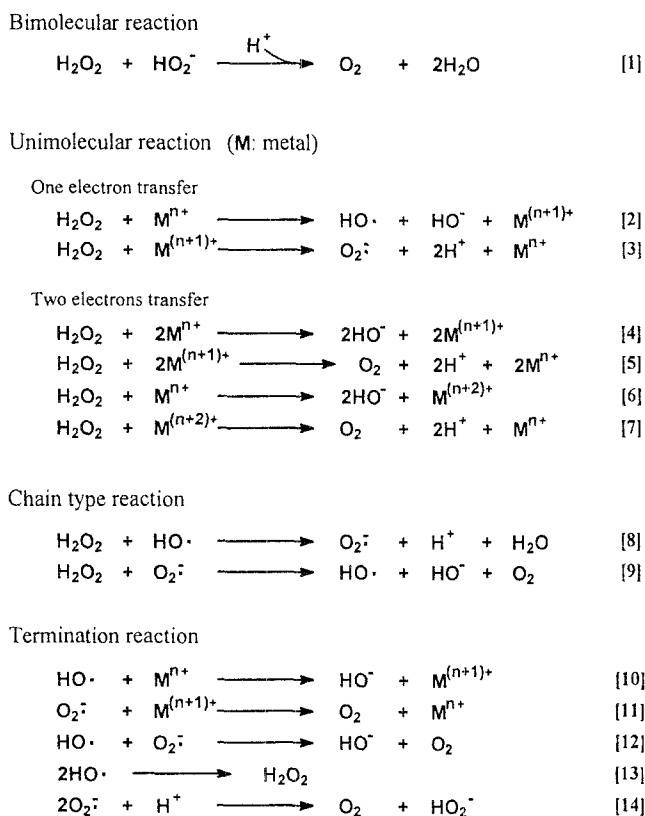


Fig. 1. Postulated decomposition mechanisms of hydrogen peroxide

[3] in Fig. 1). Termination reactions of radical species produced are shown in [10]–[14] in Fig. 1.

Effect of stepwise addition of hydrogen peroxide on the degradation of MGP

The degradation of MGP during the stepwise addition of hydrogen peroxide is compared with that during one-time addition. The stepwise addition should reduce the decomposition of hydrogen peroxide operated by the chain type ([8] and [9] in Fig. 1) because of the low concentration of hydrogen peroxide, and thus the hydroxyl radicals produced should attack MGP more efficiently during the stepwise addition than during the one-time addition. Based on this, the enhanced degradation of MGP in the stepwise addition system compared to the one-time addition system suggests that the hydroxyl radical is frequently produced by decomposition of hydrogen peroxide catalyzed by the one-electron transfer mechanism ([2] and [3] in Fig. 1). In contrast, the lack of enhanced degradation of MGP shows that radical species do not work extensively in the system.

Figures 2a, 3a, and 4a show the time courses of the decomposition of hydrogen peroxide during both the stepwise and one-time addition systems when Fe^{3+} , Fe^{2+} , and Mn^{2+} , respectively, were added. The decomposition of hydrogen peroxide when Mn^{2+} was added was much faster than when Fe^{3+} or Fe^{2+} was added, and the decomposition time course could not be followed. Therefore, the concentration of Mn^{2+} was set at $1/360$ of Fe^{3+} and Fe^{2+} to slow down

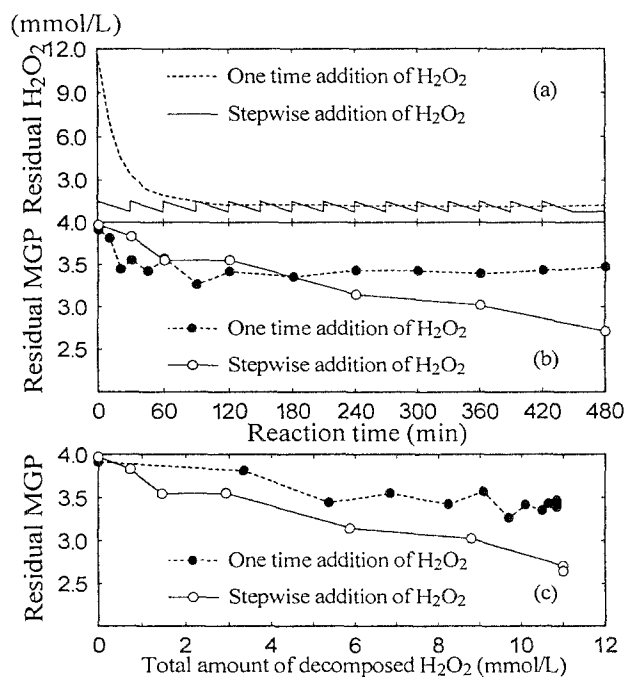


Fig. 2. Effect of stepwise addition of hydrogen peroxide when Fe^{3+} was added. **a** Residual concentration of hydrogen peroxide versus reaction time. **b** Residual concentration of methyl β -D-glucopyranoside (MGP) versus reaction time. **c** Residual concentration of MGP versus total amount of degraded H_2O_2

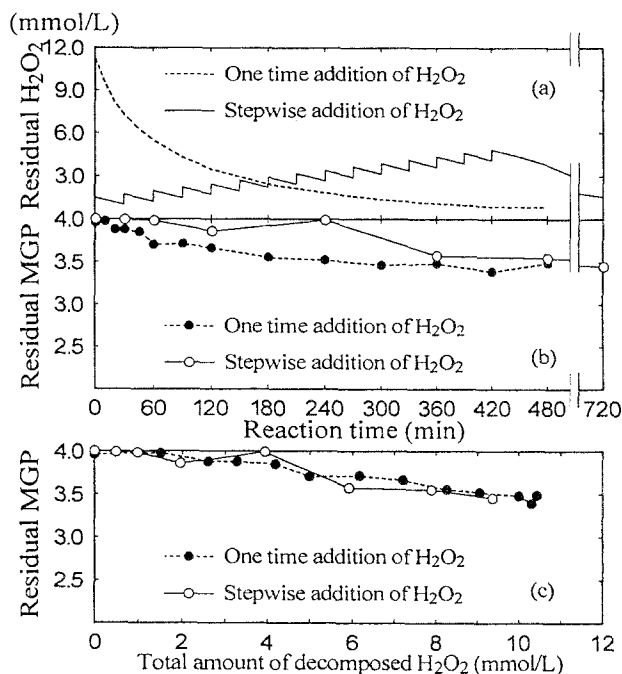


Fig. 3. Effect of stepwise addition of hydrogen peroxide when Fe^{2+} was added. **a** Residual concentration of hydrogen peroxide versus reaction time. **b** Residual concentration of MGP versus reaction time. **c** Residual concentration of MGP versus total amount of degraded H_2O_2

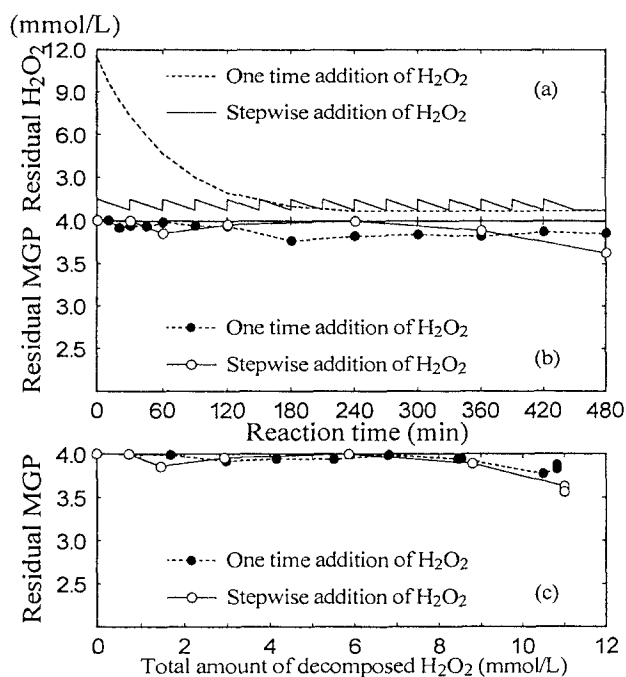


Fig. 4. Effect of stepwise addition of hydrogen peroxide when Mn^{2+} was added. **a** Residual concentration of hydrogen peroxide versus reaction time. **b** Residual concentration of MGP versus reaction time. **c** Residual concentration of MGP versus total amount of degraded H_2O_2

the decomposition catalyzed by Mn^{2+} . Figures 2b, 3b, and 4b show the time courses of the residual concentration of MGP; and Figs. 2c, 3c, and 4c illustrate the residual concentrations of MGP per unit of decomposed hydrogen peroxide in the same systems.

The effect of stepwise addition of hydrogen peroxide on the degradation of MGP was clearly observed when Fe^{3+} was added (Fig. 2c). The decomposition of 3 mmol of hydrogen peroxide resulted in degradation of 0.4 mmol of MGP in the stepwise addition system, whereas decomposition of 3 mmol of hydrogen peroxide caused degradation of only 0.2 mmol of MGP in the one-time addition system. (The y-axes in the figures show the residual concentration.) This result indicates that the hydroxyl radical is frequently produced and oxidizes MGP more efficiently in the stepwise addition system than in the one-time addition system due to the low concentration of hydrogen peroxide when Fe^{3+} is added. Therefore, it is suggested that one of the major decomposition mechanisms of hydrogen peroxide is one-electron transfer catalysis ([2] and [3] in Fig. 1) when Fe^{3+} is added to the reaction solution. Although the first species produced by the one-electron transfer from hydrogen peroxide to Fe^{3+} is superoxide anion radical ([3] in Fig. 1), this electron transfer converts Fe^{3+} to Fe^{2+} , and the catalytic decomposition of hydrogen peroxide by Fe^{2+} affords hydroxyl radicals ([2] in Fig. 1). Furthermore, the attack of the superoxide anion radical on hydrogen peroxide also results in the formation of hydroxyl radicals ([9] in Fig. 1).

The effect of the stepwise addition was not clearly observed at the final stage of the reaction when Fe^{2+} was added. This result seems to show that hydrogen peroxide

decomposes only via the bimolecular reaction ([1] in Fig. 1) and the consecutive two-electron transfers ([4]–[7] in Fig. 1). However, because the amount of degradation of MGP when Fe^{2+} was added was the same as that when Fe^{3+} was added in the one-time addition system, the decomposition mechanism of hydrogen peroxide via the one-electron transfer ([2] and [3] in Fig. 1) should be operative. Furthermore, although the catalytic effect of Fe^{2+} should be similar to that when Fe^{3+} is added because Fe^{2+} and Fe^{3+} are converted to each other by catalyzing the decomposition of hydrogen peroxide, the catalytic effect of Fe^{2+} was different from that of Fe^{3+} . These phenomena, i.e., no enhancement of the degradation of MGP in the stepwise addition system when Fe^{2+} is added and the different catalytic effect of Fe^{2+} from Fe^{3+} , cannot be explained by this experiment, but a possible explanation is as follows. Transition metals including Fe^{2+} and Fe^{3+} generally aggregate, forming hydroxyl-bridged polynuclear species, or precipitate when they are added to alkaline solutions.⁷ Precipitates formed when Fe^{2+} is added to the solution catalyze the one-electron transfer decomposition reaction of hydrogen peroxide ([2] and [3] in Fig. 1) without the occurrence of the consequent chain-type reaction ([8] and [9] in Fig. 1), whereas those formed when Fe^{3+} is added to the solution catalyze the decomposition of hydrogen peroxide via one-electron transfer ([2] and [3] in Fig. 1) involving the chain-type reaction ([8] and [9] in Fig. 1).

The stepwise addition of hydrogen peroxide did not affect the extent of the degradation of MGP compared with the one-time addition; the amount of degradation of MGP was small when Mn^{2+} was added. It is concluded that hydrogen peroxide is decomposed via the bimolecular reaction ([1] in Fig. 1), the consecutive two-electron transfer system ([4]–[7] in Fig. 1), or both, by the catalysis of manganese ion; and no radical species are produced. The lack of radical species production when Mn^{2+} is added is consistent with the result obtained by Lachenal and coworkers.⁸ Concerning the mechanism of the consecutive two-electron transfers, it is unclear which species (Mn^{3+} , Mn^{4+} , or both) is present as the high valence state of manganese ion in the reaction solution.

Effect of oxygen-pressurized hydrogen peroxide treatment on the degradation of MGP

When the decomposition of hydrogen peroxide occurs without the presence of other substrates and transition metals work only as catalysts, one molecule of oxygen and two molecules of water are stoichiometrically formed by the decomposition of two molecules of hydrogen peroxide, regardless of its decomposition mechanism (Fig. 1). The amount of molecular oxygen and water formed, however, is small when the hydroxyl radical produced by the decomposition of hydrogen peroxide reacts with substrates other than hydrogen peroxide.⁹ Based on this consideration, the reaction of hydroxyl radical with MGP might be enhanced by treatment with oxygen-pressurized hydrogen peroxide. The reason why the reaction might be enhanced is that high

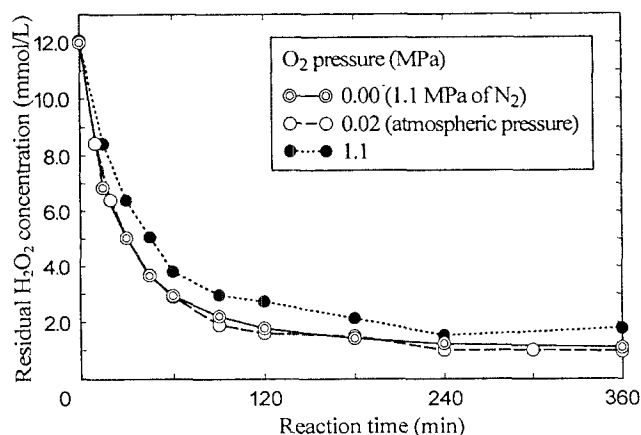


Fig. 5. Effect of oxygen pressure on the decomposition of hydrogen peroxide. Fe^{3+} 0.36 mmol/l; Mg^{2+} 0.72 mmol/l; initial MGP 4 mmol/l

oxygen pressure should lead to the decomposition of hydrogen peroxide via routes in which the production of molecular oxygen is suppressed (i.e., frequent occurrence of the reaction between hydroxyl radicals and MGP). It is pointed out, however, that oxygen-pressurized treatment can also suppress the formation of molecular oxygen via another method (i.e., stabilization of hydrogen peroxide). In this case, the reaction of the hydroxyl radical with MGP is not enhanced. Therefore, we must evaluate whether the degradation of MGP is enhanced and hydrogen peroxide is stabilized by oxygen-pressurized hydrogen peroxide.

The degradation of MGP in the oxygen-pressurized hydrogen peroxide system was examined under 0, 0.02, or 1.1 MPa. In the case of 0 MPa of oxygen, 1.1 MPa of nitrogen was used. In the case of 0.02 MPa of oxygen, the pressure was atmospheric. The reactions were performed in the presence of Fe^{3+} 0.36 mmol/l and Mg^{2+} 0.72 mmol/l because previous experiments showed that the difference in the extent of MGP degradation could be visualized under this metal profile.³

Figure 5 shows the time course of the residual concentration of hydrogen peroxide under three different oxygen pressures. The decomposition of hydrogen peroxide was clearly suppressed by the higher oxygen pressure. The half-life of hydrogen peroxide can be estimated by the reaction time when the residual concentration of hydrogen peroxide is around 6.5 mmol/l. (All the curves in Fig. 5 seem to start from 12 mmol/l and end at 1 mmol/l, and therefore the half-concentration is 6.5 mmol/l.) The value under 1.1 MPa of oxygen pressure is about 1.5 times greater than that under 0 or 0.02 MPa. Figure 6 shows the residual concentration of MGP when a unit of hydrogen peroxide decomposes. Only minimal enhancement of the degradation of MGP was observed with the increase in oxygen pressure, and this difference is insufficient to conclude that the reaction of the hydroxyl radical with MGP is enhanced by higher oxygen pressure.

Thus, the effect of the oxygen-pressurized hydrogen peroxide treatment is mainly to stabilize hydrogen peroxide. It is known that another kind of bleaching reaction, the action

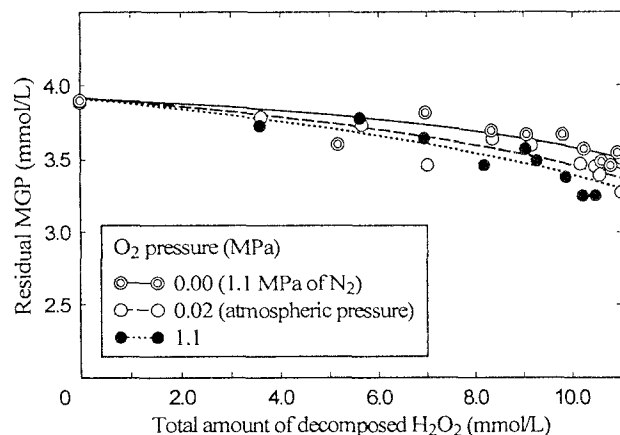


Fig. 6. Effect of oxygen pressure on the degradation of MGP during alkaline hydrogen peroxide treatment. Fe^{3+} 0.36 mmol/l; Mg^{2+} 0.72 mmol/l

of hydroperoxide anion (HOO^-), can operate more frequently under higher oxygen pressure due to the high stability of hydrogen peroxide. However, the occurrence of this reaction cannot be analyzed by the methods reported herein (i.e., analysis of MGP degradation). Chromophores and quinone-type structures in residual lignin are degraded by hydroperoxide anion. This could be one of the mechanisms of priority for delignification during oxygen-pressurized hydrogen peroxide bleaching.^{10,11} A further experiment in which a carbonyl-containing lignin model compound, such as vanillin or acetoguaiacone, is subjected to oxygen-pressurized alkaline hydrogen peroxide treatment could make it possible to elucidate whether this treatment gives hydroperoxide anion a more frequent chance to attack carbonyl-containing structures.

Conclusions

The reaction between MGP and hydroxyl radicals produced by decomposition of hydrogen peroxide in the stepwise addition system was enhanced compared with that in the one-time addition system when Fe^{3+} was added. This shows that the hydroxyl radical can frequently attack MGP, and therefore hydrogen peroxide is used efficiently as a bleaching reagent in the stepwise addition system. On the other hand, the degradation of MGP was not affected by stepwise addition of hydrogen peroxide when Fe^{2+} or Mn^{2+} was added. It is postulated that the precipitates of metal ions formed when these ions are added to the reaction solution could affect their catalytic ability. Precipitates formed when Fe^{3+} or Fe^{2+} is added could catalyze the decomposition of hydrogen peroxide via one-electron transfer with or without, respectively, the chain-type reaction. The decomposition of hydrogen peroxide produces no radical species when Mn^{2+} is added due to the tendency of Mn^{2+} to catalyze the decomposition of hydrogen peroxide via the bimolecular reaction or consecutive two-electron transfers.

Oxygen-pressurized hydrogen peroxide treatment did not significantly enhance the reaction between hydroxyl radicals and MGP but stabilized hydrogen peroxide. The stabilization of hydrogen peroxide by high oxygen pressure results in the more frequent action of hydroperoxide anion by the attack on chromophores and quinone-type structures.

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