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Efficient total halogen-free photochemical bleaching of kraft pulps using alkaline hydrogen peroxide

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ABSTRACT

Total halogen-free bleaching of kraft pulps was conducted by an oxidative photochemical process at room temperature using alkaline hydrogen peroxide. Selection of an appropriate wavelength of light was crucial for effective bleaching and avoiding degradation of cellulose. The wavelength of the light has to be selected so that the light is absorbed only by the colored compounds in the pulps and not by the bleaching reagents or the pulp itself. When a long-wavelength black-light fluorescent lamp was used in combination with aqueous hydrogen peroxide solution at pH 11, the bleaching efficiency for hardwood and softwood kraft pulps reached the same level as that obtained by conventional two-stage elemental chlorine-free processes.

1. Introduction

Bleaching is an important process in the paper industry for producing high-quality white paper. A large proportion of paper is produced from kraft pulp that is made by delignification of wood (chemical pulping), but the pulp thus produced still contains a small amount of colored compounds that have to be removed or decolorized by bleaching [1–3]. The bleaching process is a degradation and/or decolorization of the colored compounds adsorbed or chemically bound to kraft pulps. Although the chromophores of the colored compounds are not well defined, they are reported to be olefins conjugated with quinones, quinone methides, and aromatic rings [2]. The colored compounds are most probably formed from lignin during chemical reactions in pulping processes because lignin itself has only a faint color.

Conventional bleaching of pulps was generally conducted by multi-step processes using molecular chlorine in long high-temperature processes, during which it had been revealed that the toxic chlorinated organic compounds (adsorbable organic halogens, AOXs) were generated and released into the environment [2]. To avoid this release of AOXs, chlorine bleaching has been gradually replaced by elemental chlorine-free (ECF) processes that use ClO_2 and by total chlorine-free (TCF) processes [4,5].

With the optimization of ECF processes, recent assessments of their effluents have reported no significant differences between ECF and TCF processes in terms of their biological effects on aquatic environments [5]. However, significant amounts of halogenated hydrocarbons, such as $CHCl_3$ and chlorophenols, are still generated from ECF processes [2,6].

To achieve complete suppression of AOX emissions, TCF processes have advantages over ECF processes. Present TCF processes in production sites are thermal processes that use oxygen, hydrogen peroxide, or ozone [2,3]. As an alternative to thermal reactions, photochemical TCF bleaching of various pulps has been reported [3]. Although a simple irradiation of pulps with light was found to be inefficient [7], a photochemical reductive bleaching using sodium borohydride was found to be effective [8]. As for oxidative bleaching, photochemical bleaching of softwood kraft pulp using molecular oxygen has been reported, but without any information on the brightness of the bleached pulps [9]. Recently, pulps have been bleached by photochemically activated molecular oxygen using photosensitizers [10], photocatalysts [11], or both [12], in which the reactive species is believed to be singlet oxygen.

Instead of using photosensitizers or photocatalysts as additional reagents, we have reinvestigated photochemical oxidative bleaching using alkaline hydrogen peroxide [13] to simplify the process and to increase its efficiency. This paper reports a considerable improvement in oxidative photochemical bleaching of kraft pulps using alkaline hydrogen peroxide, achieving the same bleaching efficiency as conventional two-stage ECF processes. The improvement was based mainly on the proper selection of

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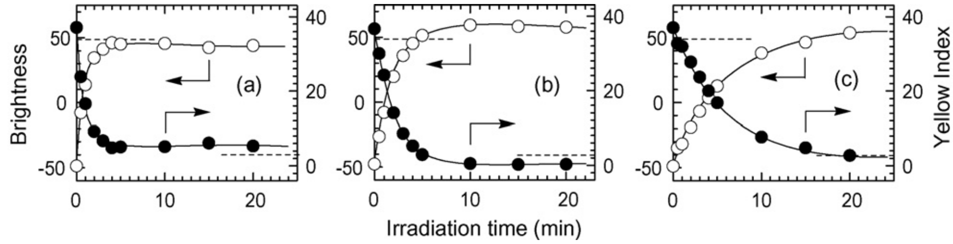

Fig. 1. Wavelength dependence on the brightness and yellow index of excimer laser-bleached NOKP sheets by an aqueous $Na_2CO_3 \cdot 1.5H_2O_2$ solution as a function of irradiation time [14]. Utilized lasers, (a) KrF, (b) XeCl, and (c) XeF excimer lasers. Brightness: white symbols and yellow index: black symbols. Laser bleaching condition: 40 mJ cm^{-2} pulse^{-1}, 5 Hz, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature. Number of pulp sheets: 1 sheet. Brightness and yellow index of a pulp sheet prepared from conventionally bleached commercial-grade NBKP are shown in the figures as broken horizontal lines.

the light wavelength, which proved to have a crucial effect on bleaching.

2. Results and discussion

2.1. Laser bleaching of softwood kraft pulp sheets

Aqueous solutions of five oxidizing reagents were tested to select an optimal bleaching reagent; the reagents tested were hydrogen peroxide (H_2O_2), sodium peroxocarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$), sodium peroxide (Na_2O_2), sodium peroxoborate ($NaBO_3$), and urea hydrogen peroxide addition compound ($H_2NCONH_2 \cdot H_2O_2$). A XeCl excimer laser (308 nm) was used to irradiate a sheet of softwood kraft pulp (NOKP), and bleaching efficiency was assessed by the measurements of the brightness and the yellow index of the laser-irradiated NOKP sheets; efficient bleaching is indicated by a higher brightness and a lower yellow index [14].

The best reagent was found to be $Na_2CO_3 \cdot 1.5H_2O_2$, an alkaline hydrogen peroxide, with bleaching efficiency almost as high as that achieved with conventionally bleached NOKP (NBKP; commercial-grade bleached NOKP by a conventional two-stage ECF process using ClO_2 and H_2O_2) after 20 min irradiation. Reference experiments conducted without laser irradiation showed only a small bleaching effect, indicating that both laser irradiation and an oxidizing reagent are necessary for sufficient bleaching [15]. The effect of light irradiation can be explained by a facilitation of electron transfer between the bleaching reagents and the excited state of the colored compounds in the pulps during the initial stage of the bleaching, which increased the reactivity of the colored compounds towards bleaching reagents that were less reactive in their ground states (thermal reactions).

Optimization of laser bleaching with $Na_2CO_3 \cdot 1.5H_2O_2$ was then conducted. Firstly, the wavelength effect of the lasers was investigated using KrF (248 nm), XeCl, and XeF (351 nm) excimer lasers. Fig. 1 shows the brightness and the yellow index of the laser-bleached NOKP sheets as a function of laser irradiation time. The bleaching proceeded faster with a shorter wavelength laser, but the brightness and the yellow index leveled off before reaching the level of NBKP when the KrF laser was used. With the other lasers, the brightness and the yellow index were better than those of NBKP.

Fig. 2 shows the brightness and the yellow index of the laser-bleached NOKP sheets as a function of the laser pulse energy. The total energy irradiated into a unit area was kept constant in this experiment, which means that the number of laser pulses decreased with increasing laser pulse energy. In the case of XeCl laser irradiation, the bleaching efficiency was not affected by the laser pulse energy, but was determined by the total dosage of photon energy per unit area. However, in the case of the KrF laser, irradiation with lower pulse energy gave better bleaching efficiency at the same total dosage of photon energy per unit area; the opposite effect was observed in the case of the XeF laser.

The effect of the concentration of $Na_2CO_3 \cdot 1.5H_2O_2$ was also studied. Considerable improvements in brightness and the yellow index were obtained by increasing the reagent concentration, but they leveled off at the concentrations over 10 wt.% [15].

2.2. Laser bleaching of hardwood kraft pulp sheets using sodium peroxocarbonate

Laser bleaching of hardwood kraft pulp (LOKP) sheets showed a similar trend to that of NOKP. The pulp sheets made only from LOKP were too fragile to be used in experiments; therefore, pulp sheets prepared from a 1:1 mixture of LOKP and NBKP (LOKP/NBKP) were used for the experiments. Fig. 3 shows the results of laser bleaching of the LOKP/NBKP sheets using KrF, XeCl, and XeF lasers. For all lasers, the brightness and the yellow index exceeded those of commercial-grade LBKP/NBKP (1:1) sheets (LBKP: commercial-grade bleached LOKP by a conventional two-stage ECF process using ClO_2 and H_2O_2) within short irradiation times. A slight discoloration was observed during KrF laser bleaching with prolonged irradiation, similar to that observed in NOKP sheets.

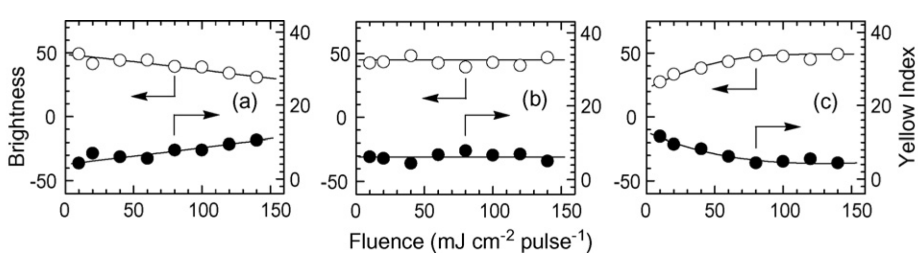

Fig. 2. Laser fluence dependence on the brightness and yellow index of excimer laser-bleached NOKP sheets by an aqueous $Na_2CO_3 \cdot 1.5H_2O_2$ solution as a function of laser pulse energy [14]. Utilized lasers, (a) KrF (total energy: 48 J/cm^2), (b) XeCl (total energy: 60 J/cm^2), and (c) XeF (total energy: 120 J/cm^2) excimer lasers. Brightness: white symbols and yellow index: black symbols. Laser bleaching condition: 5 Hz, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature. Number of pulp sheets: 1 sheet.

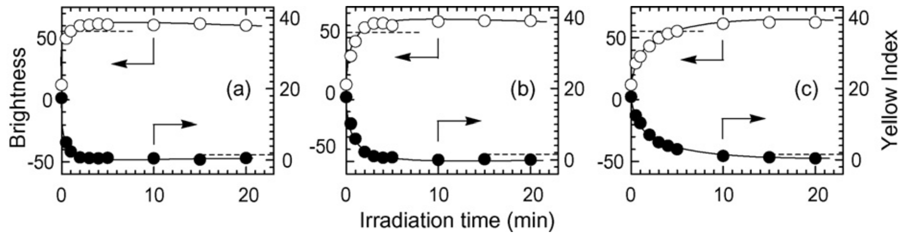

Fig. 3. Brightness and yellow index of KrF excimer laser-bleached LOKP/NBKP (1:1) sheets by an aqueous $Na_2CO_3{\cdot}1.5H_2O_2$ solution as a function of irradiation time [14]. Irradiation condition: (a) KrF, (b) XeCl, and (c) XeF excimer lasers. Brightness: white symbols and yellow index: black symbols. Laser bleaching condition: 40 mJ cm^{-2} pulse^{-1}, 5 Hz, 6 wt.% $Na_2CO_3{\cdot}1.5H_2O_2$ (aq), room temperature. Number of pulp sheets: 1 sheet. Brightness and yellow index of pulp sheets prepared from a 1:1 mixture of conventionally bleached commercial-grade LBKP and NBKP are shown in the figures as broken horizontal lines.

2.3. *Photochemical bleaching of kraft pulp sheets with conventional light sources using sodium peroxocarbonate*

Laser intensity effects on the bleaching of NOKP sheets showed that the efficiency depended mainly on the total energy of light irradiation per unit area (cf. Fig. 2), which implies that sufficient bleaching can also be accomplished by conventional lamp irradiation if the irradiation is continued for a sufficient time. Fig. 4 shows the brightness and the yellow index of photochemically bleached NOKP and LOKP/NBKP sheets obtained using two conventional lamps: a low-pressure mercury lamp (major emission: 254 nm) and a standard black-light fluorescent lamp (cf. Fig. 5). The bleaching proceeded faster with the low-pressure mercury lamp than with the standard black-light fluorescent lamp but a slight discoloration was observed with prolonged irradiation, which was consistent with the results for the wavelength effect using KrF and XeF lasers (Figs. 1a vs. 1c, and 3a vs. 3c).

In the case of the bleaching of LOKP/NBKP sheets using a low-pressure mercury lamp (Fig. 4c), the brightness and the yellow index exceeded those of conventional bleaching within a 20-min irradiation. However, in other cases (Fig. 4a, b and d), the bleaching efficiency did not reached the level obtained with conventional bleaching within 90 min irradiation. However, when a standard black-light fluorescent lamp was used as the light source, a continuous increase in the brightness and a continuous decrease in the yellow index were observed for both NOKP and LOKP/NBKP sheets, suggesting that a bleaching efficiency comparable to that obtained

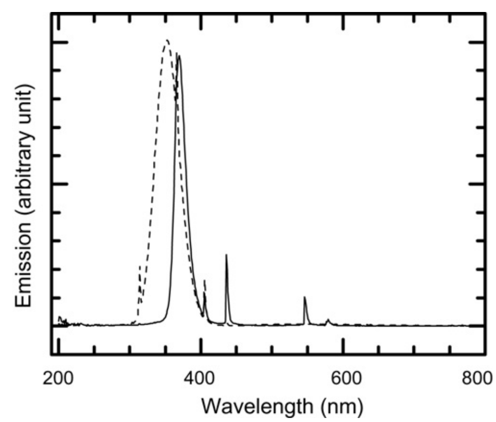

Fig. 5. Emission spectra of standard (broken line) and long-wavelength (solid line) black-light fluorescent lamps.

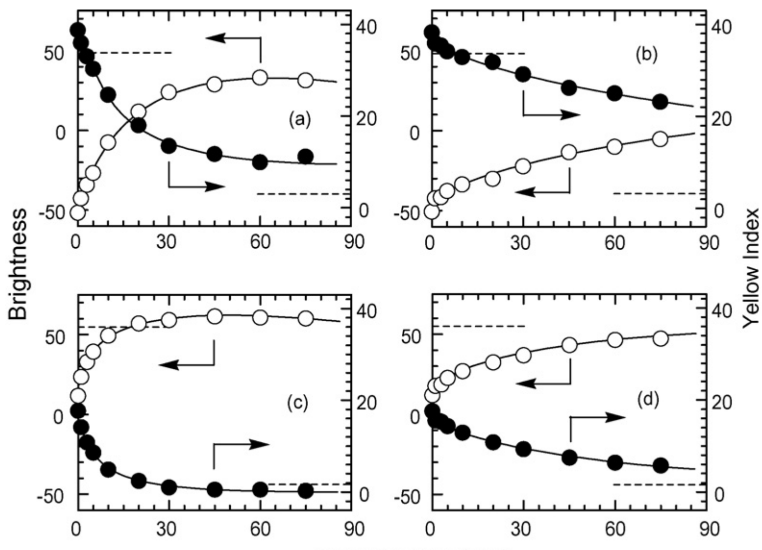

Fig. 4. Brightness and yellow index of photochemically bleached pulp sheets by an aqueous $Na_2CO_3{\cdot}1.5H_2O_2$ solution as a function of irradiation time [14]. Irradiation condition: (a) and (c) low-pressure Hg lamp (2.41 mW cm^{-2}) or (b) and (d) standard black-light fluorescent lamp (1.53 mW cm^{-2}). (a) and (b) NOKP and (c) and (d) LOKP/NBKP (1:1). Brightness: white symbol and yellow index: black symbols. Irradiation condition: 6 wt.% $Na_2CO_3{\cdot}1.5H_2O_2$ (aq), room temperature. Number of pulp sheets: 1 sheet. Brightness and yellow index of pulp sheets prepared from conventionally bleached commercial-grade NBKP and a 1:1 mixture of LBKP and NBKP are shown in the figures as broken horizontal lines.

with a conventional two-stage ECF process can be obtained with prolonged irradiation.

2.4. Degree of polymerization and discoloration of photochemically bleached pulp sheets

It is important to know the changes in the properties of pulps by bleaching. Table 1 shows the weight loss and the change in the degree of polymerization (DP) of kraft pulps as a result of photochemical bleaching. Although the weight losses due to the photochemical bleaching were small, a considerable decrease in DP was observed in some cases, which depended much on the wavelength and intensity of the irradiated light. Larger decreases in DP were observed with shorter wavelengths of light and with the use of lasers.

The effect of wavelength on DP can be explained by the generation of hydroxyl radicals by photochemical decomposition of $Na_2CO_3{\cdot}1.5H_2O_2$. With shorter wavelength (KrF and XeCl lasers and low-pressure mercury lamp), significant amounts of hydroxyl radicals were generated due to considerable absorption of light by $Na_2CO_3{\cdot}1.5H_2O_2$, which resulted in a degradation of cellulose initiated by the hydroxyl radicals [16]. This is consistent with the report on a rapid decrease in the tensile strength of pulps that are bleached by alkaline H_2O_2 using a medium-pressure mercury lamp [13(c)]. In contrast, with longer wavelength light (XeF laser and standard black-light fluorescent lamp), the decrease of DP was smaller because the generation of hydroxyl radicals can be avoided due to the lack of absorption of $Na_2CO_3{\cdot}1.5H_2O_2$ at these wavelengths. As for the effect of light intensity on DP, a larger decrease was observed with high-intensity light (cf. Table 1, KrF laser vs. low-pressure mercury lamp and XeF laser vs. standard black-light fluorescent lamp).

Table 1 also shows the results for the discoloration of the photochemically bleached NOKP and LOKP/NBKP sheets, which was studied by the tests on the color fastness to light. In the cases of photochemical bleaching of NOKP, the degree of discoloration was comparable to that observed in conventional bleaching when lasers were used as the light sources. The degree of discoloration of photochemically bleached LOKP/NBKP sheets varied depending on the light source, but the brightness and the yellow index after the discoloration tests were better than or the same as those of conventionally bleached pulp sheets in most cases.

2.5. Optimization of photochemical bleaching of NOKP sheets using conventional light sources

Although the properties of photochemically bleached LOKP/NBKP sheets using a standard black-light fluorescent lamp and aqueous $Na_2CO_3{\cdot}1.5H_2O_2$ solution reached almost the level of conventional two-stage ECF bleaching, NOKP could not be sufficiently bleached under the same conditions. Therefore, further optimization of the bleaching conditions was conducted with conventional light sources.

Firstly, instead of using $Na_2CO_3{\cdot}1.5H_2O_2$ as a source for an alkaline H_2O_2 (pH 10.6) solution, pH effect on bleaching efficiency was studied using aqueous H_2O_2 with the pH adjusted with NaOH. Fig. 6 shows a dependence of the bleaching of NOKP sheets on pH. An increase in the rate of photochemical bleaching was observed with an increase of the pH of the solution from 10 to 12. However, a considerable decrease in the DP of the pulp was observed when the pH was increased to 12. This result was consistent with the reported decrease in the viscosity of photochemically bleached pulp using H_2O_2, which was observed when the pH of the solution was increased from 11 to 12, indicating the decrease of DP at pH 12 [13(b)]. From these results, the optimal pH of the solution for photochemical bleaching was found to be 11.

This decrease in DP was attributed to the photochemical generation of hydroxyl radicals; a red shift in the absorption of the H_2O_2

Table 1
Weight loss, viscosity-average degree of polymerization, and discoloration of bleached pulp sheets using sodium peroxocarbonate [14,18].

Bleaching method	Pulp sheets (bleaching time/min)	Weight loss by bleaching (%)[a]	Degree of polymerization	Before test[b]		After test[b]	
				Brightness[a]	Yellow index[a]	Brightness[a]	Yellow index[a]
KrF laser[c]	NOKP (4)	6.6	550	49	3.1	42	5.7
	LOKP (4)[d]	8.3	270	60	0.3	49	4.5
XeCl laser[c]	NOKP (10)	5.7	530	56	0.1	50	2.4
XeF laser[c]	NOKP (20)	5.8	660	57	2.2	53	3.3
	LOKP (10)[d]	3.8	980	60	1.2	58	2.2
Hg lamp[e]	NOKP (60)	2.6	700	37	8.3	36	8.9
	LOKP (60)[d]	6.3	400	61	0.3	56	2.4
Black-light[f]	NOKP (75)	2.4	1020	2.4	21	−1.1	22
	LOKP (75)[d]	2.6	1020	49	5.1	51	5.0
Thermal[g]	NOKP (75)	0	1130	−30	31	−27	31
	LOKP (75)[d]	0	1330	29	12	28	12
Conventional[h]	NBKP	–	1220	48	3.6	42	6.0
	LBKP[i]	–	1340	55	2.3	51	3.8
None	NOKP	–	1280	−49	38	−44	36
	LOKP[d]	–	1350	11	18	13	17

[a] Average of three independent runs.

[b] Test method for color fastness to xenon arc lamp light (lamp irradiation time: 12 h). The irradiation by the xenon arc lamp and the measurements of both brightness and yellow index were performed on the same side as the irradiation of light during bleaching (number of pulp sheets: 1 sheet).

[c] Bleaching condition: 40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 6 wt.% $Na_2CO_3{\cdot}1.5H_2O_2$ (aq), room temperature.

[d] 1:1 mixture of LOKP and NBKP.

[e] Bleaching condition: low-pressure Hg lamp (2.41 mW cm^{-2}), 6 wt.% $Na_2CO_3{\cdot}1.5H_2O_2$ (aq), room temperature.

[f] Bleaching condition: standard black-light fluorescent lamp (1.53 mW cm^{-2}), 6 wt.% $Na_2CO_3{\cdot}1.5H_2O_2$ (aq), room temperature.

[g] Bleaching condition: 60 min, 6 wt.% $Na_2CO_3{\cdot}1.5H_2O_2$ (aq), room temperature.

[h] Commercial-grade pulps bleached by a conventional ECF process using ClO_2 and H_2O_2 from a paper mill.

[i] 1:1 mixture of LBKP and NBKP.

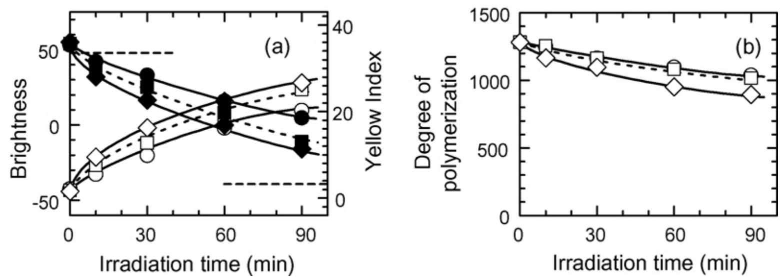

Fig. 6. pH dependence on the (a) brightness (white symbols) and yellow index (black symbols), and (b) degree of polymerization of photochemically bleached NOKP sheets by H_2O_2 solution as a function of irradiation time [14,18]. Irradiation condition: 2 wt.% H_2O_2 (aq), standard black-light fluorescent lamp (1.53 mW cm^{-2}), room temperature, pH (adjusted by NaOH): 10 (○, ●), 11 (□, ■) and 12 (◇, ♦). Number of pulp sheets: 1 sheet. Brightness and yellow index of a pulp sheet prepared from conventionally bleached commercial-grade NBKP are shown in the figures as broken horizontal lines.

solution [15] occurred with the increase of pH of the solution, and this red shift resulted in considerable overlapping of the absorption of the H_2O_2 solution and the light wavelength used (cf. Fig. 5), which in turn caused a photochemical decomposition of H_2O_2 to form hydroxyl radicals.

Although the decrease in DP at pH 11 was smaller than at pH 12, a further attempt was made to suppress the decrease of DP by changing the light source to a long-wavelength black-light fluorescent lamp (cf. Fig. 5) to prevent overlapping of the absorption of the H_2O_2 solution and the light wavelength. Fig. 7a shows the brightness and the yellow index of the bleached NOKP sheets using a long-wavelength black-light fluorescent lamp and an aqueous H_2O_2 solution at pH 11. Although a slight decrease in the rate of bleaching was observed compared with that obtained with a standard black-light fluorescent lamp, the decrease in the DP of the bleached NOKP was significantly reduced, as shown in Fig. 7b.

To increase the rate of bleaching, the effect of H_2O_2 concentration was investigated [15]. Similarly to the case of laser bleaching, the rate of photochemical bleaching increased with the increase of the H_2O_2 concentration. The decrease in DP in the photochemically bleached NOKP was very small and not dependent on the pH of the solution.

The effect of additives on bleaching efficiency was also investigated because some additives have been found to be effective in the bleaching of cotton fabrics [17]. The additives tested were sodium gluconate, sodium malate, sodium tartrate, sodium citrate, and sodium sulfate. However, these additives caused a slight reduction in bleaching efficiency for NOKP sheets [15].

2.6. Photochemical bleaching of pulps in suspensions using a long-wavelength black-light fluorescent lamp

A large difference in the brightness and the yellow index between the front- and back-sides of the pulp sheets in conventional-light bleaching, particularly in the case of NOKP sheets, implies that the light intensity was not sufficient to enable efficient penetration of light through the pulp sheets. A simple solution to this problem is to provide light irradiation on both sides of the pulp sheets. However, we have tested another approach to solve this problem; bleaching of pulps suspended in aqueous bleaching solutions.

Fig. 8 shows the results on the bleaching of NOKP and LOKP/NBKP in suspension in aqueous alkaline H_2O_2. As shown in Fig. 8a and b, bleaching efficiency reached the levels of conventional two-stage ECF bleaching after 8 and 2 h irradiation for NOKP and LOKP/NBKP, respectively, using a 20-W long-wavelength black-light fluorescent lamp.

Fig. 8c and d shows the changes in DP in the course of photochemical bleaching. Some drop in DP was observed with prolonged irradiation for both NOKP and LOKP/NBKP. This drop in DP is most probably due to the alkaline hydrolysis that occurred with prolonged alkaline treatment [18]. Therefore, this problem can be avoided by shortening the bleaching time by increasing the intensity of the light.

Table 2 shows the results for discoloration of photochemically bleached NOKP and LOKP/NBKP using a long-wavelength black-light fluorescent lamp. As seen in the table, the degree of pulp discoloration was the same as that observed in conventional bleaching.

2.7. UV–vis spectra of photochemically bleached pulps

Fig. 9 shows the absorbance of NOKP sheets (**OP**), laser-, lamp-, and thermally bleached NOKP sheets (**LP**, **PP**, and **TP**, respectively), and **LP**, **PP**, and **TP** after the test of color fastness to light (**LPT**, **PPT**, and **TPT**, respectively). The efficiency of the laser bleaching exceeded the levels of the conventional ECF process (**CP**) particularly in the UV region (**LP**–**CP** in Fig. 9a–c). Fig. 9A–C shows that a larger decrease in absorption was obtained by irradiation with shorter wavelength light. However, greater discoloration of the

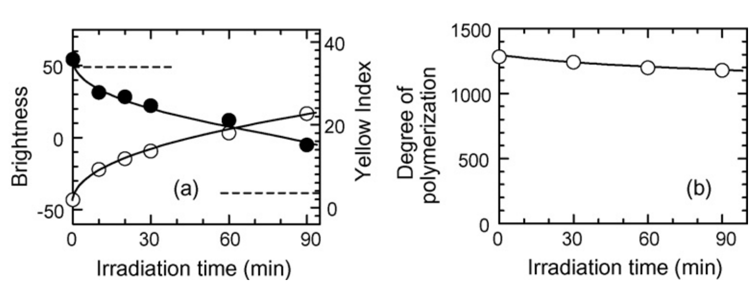

Fig. 7. (a) Brightness (white symbols) and yellow index (black symbols), and (b) degree of polymerization of photochemically bleached NOKP sheets by a H_2O_2 solution as a function of irradiation time [14,18]. Irradiation condition: 2 wt.% H_2O_2 (aq), long-wavelength black-light fluorescent lamp (1.53 mW cm^{-2}), room temperature, pH (adjusted by NaOH): 11. Pulp sheets were padded in the 2 wt.% H_2O_2 (aq) solution every 15 min during irradiation. Number of pulp sheets: 1 sheet. Brightness and yellow index of a pulp sheet prepared from conventionally bleached commercial-grade NBKP are shown in the figures as broken horizontal lines.

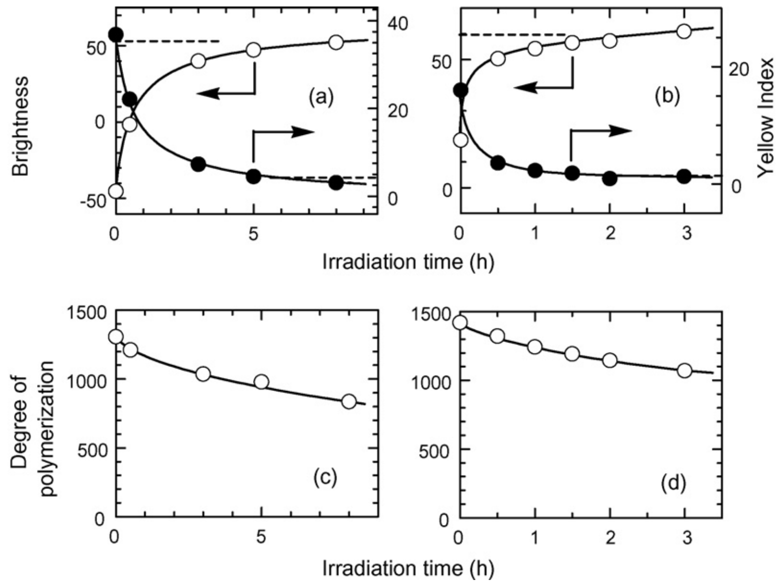

Fig. 8. (a) and (b) Brightness and yellow index, and (c) and (d) degree of polymerization of (a) and (c) NOKP and (b and d) LOKP/NBKP (1:1) photochemically bleached in a suspension in a H_2O_2 solution as a function of irradiation time [14,18]. (a) and (b) Symbols, white: brightness, black: yellow index. Irradiation condition: 6 wt.% H_2O_2 (aq), long-wavelength black-light fluorescent lamp (2.41 mW cm^{-2}), room temperature, pH (adjusted by NaOH): 11. Number of pulp sheets: 1 sheet. Brightness and yellow index were measured with pulp sheets prepared after the bleaching. Brightness and yellow index of a pulp sheet prepared from conventionally bleached commercial-grade (a) NBKP and (b) a 1:1 mixture of LBKP and NBKP are shown in the figures as broken horizontal lines.

bleached pulps was observed from the test of color fastness to light for the pulp sheets bleached with shorter wavelength lasers, which showed the generation of a new absorption at 270 nm together with an increase in absorption at longer wavelength after the test.

In contrast to laser bleaching, the efficiency of bleaching using the standard black-light fluorescent lamp and heat was lower than that of conventional bleaching (**PP**–**CP** and **TP**–**CP** in Fig. 9e and f). In the case of the low-pressure mercury lamp, the bleaching efficiency was better in the UV region but poorer in the visible region (**PP**–**CP** in Fig. 9d). However, discoloration of the bleached pulp after the test was much less than in the case with the KrF laser whose emission wavelength was similar to that of the major emission wavelength of the low-pressure mercury lamp. A similar trend was observed in the bleaching of LOKP/NBKP [15].

When the bleaching was conducted in suspension using a long-wavelength black-light fluorescent lamp, the brightness and the yellow index of photochemically bleached NOKP and LOKP/NBKP were practically the same as those obtained in conventional two-stage ECF bleaching but their absorption spectra were slightly different from each other. As shown in Fig. 10a and b, **PP**–**CP** of photochemically bleached NOKP and LOKP/NBKP showed better bleaching efficiency around 350 nm but poorer around 240 nm compared with the conventional process. A small increase in absorption after the discoloration test appeared at wavelength greater than 300 nm, but the brightness and the yellow index remained essentially unchanged compared with those of conventionally bleached pulps after the same test.

The difference absorption spectra (**OP**–**LP**, **OP**–**PP**, and **OP**–**TP** in Figs. 9 and 10) indicates that colored compounds have broad absorption from UV to visible regions. The absorption was decreased by photochemical bleaching, which indicates decomposition and/or shortening of the extended π-electron systems of the colored compounds. The decrease in absorption in the UV region by photochemical bleaching was larger than that in the conventional ECF process (**PP**–**CP** and **PP**–**CP** in Figs. 9 and 10). The decreases in absorption around 250–270 nm indicate the decrease of chromophores having mononuclear aromatic moieties that are a part of the phenolic phenylpropane unit of lignin, most probably catechol and hydroquinone moieties [2].

Table 2
Discoloration of pulp sheets prepared from pulps bleached by irradiation with a long-wavelength black-light fluorescent lamp of aqueous suspensions of pulps in alkaline hydrogen peroxide solution [14].

Bleaching method	Pulp sheets (bleaching time/h)	Before test[a]		After test[a]	
		Brightness[b]	Yellow index[b]	Brightness[b]	Yellow index[b]
Black-light[c]	NOKP (8)	54	1.6	45	4.7
	LOKP (3)[d]	60	1.1	57	2.5
Conventional[e]	NBKP	52	3.6	48	5.3
	LBKP[f]	59	2.1	56	3.3

[a] Test method for color fastness to xenon arc lamp light (lamp irradiation time: 12 h). The irradiation by the xenon arc lamp and the measurements of both brightness and yellow index were performed on the same side as the irradiation of light during bleaching (number of pulp sheets: 1 sheet).
[b] Average of four independent runs.
[c] Bleaching condition: long-wavelength black-light fluorescent lamp (2.41 mW cm^{-2}), 6 wt.% H_2O_2 (aq), pH 11 (adjusted by NaOH), room temperature.
[d] 1:1 mixture of LOKP and NBKP.
[e] Commercial-grade pulps bleached by a conventional ECF process using ClO_2 and H_2O_2 from a paper mill.
[f] 1:1 mixture of LBKP and NBKP.

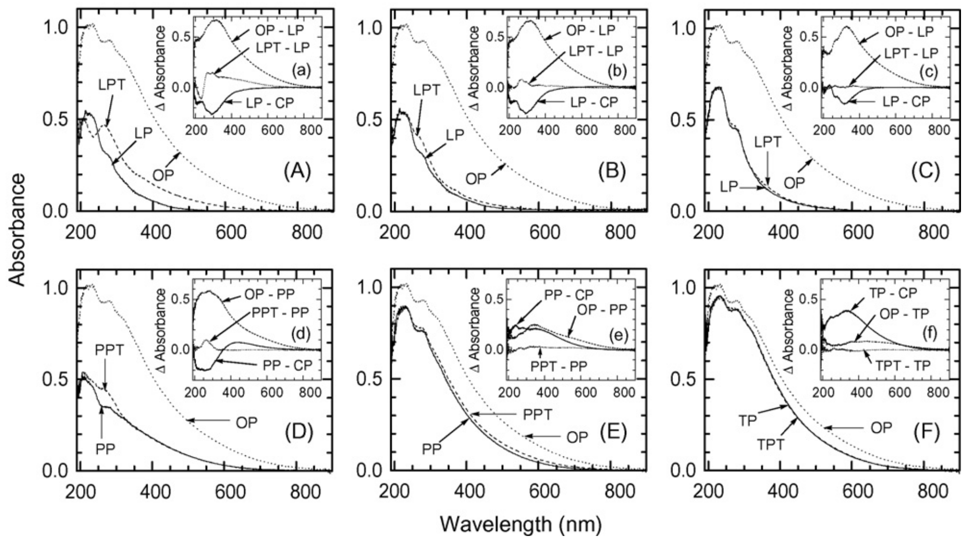

Fig. 9. Absorption (A)–(F) and absorption difference (a)–(f) spectra of NOKP sheets. Bleaching condition: (A) and (a) KrF laser [40 mJ cm^{-2} pulse^{-1}, 5 Hz, 4 min, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature], (B) and (b) XeCl laser [40 mJ cm^{-2} pulse^{-1}, 5 Hz, 10 min, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature], (C) and (c) XeF laser [40 mJ cm^{-2} pulse^{-1}, 5 Hz, 20 min, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature], (D) and (d) low-pressure Hg lamp [2.41 mW cm^{-2}, 60 min, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature], (E) and (e) standard black-light fluorescent lamp [1.53 mW cm^{-2}, 75 min, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature], (F) and (f) thermal [75 min, 6 wt.% $Na_2CO_3 \cdot 1.5H_2O_2$ (aq), room temperature]. (A)–(F) (···) NOKP sheets (**OP**), (—) laser-bleached (**LP**) or photochemically bleached (**PP**) or thermally bleached (**TP**) NOKP sheets, (- - -) **LP** or **PP** or **TP** after the test of color fastness to light (**LPT**, **PPT**, **TPT**, respectively). (a)–(f) (—) **LP–CP** or **PP–CP** or **TP–CP** (**CP**: a pulp sheet prepared from conventionally bleached commercial-grade NBKP), (- - -) **OP–LP** or **OP–PP** or **OP–TP**, (···) **LPT–LP** or **PPT–PP** or **TPT–TP**. Number of pulp sheets: 3 sheets.

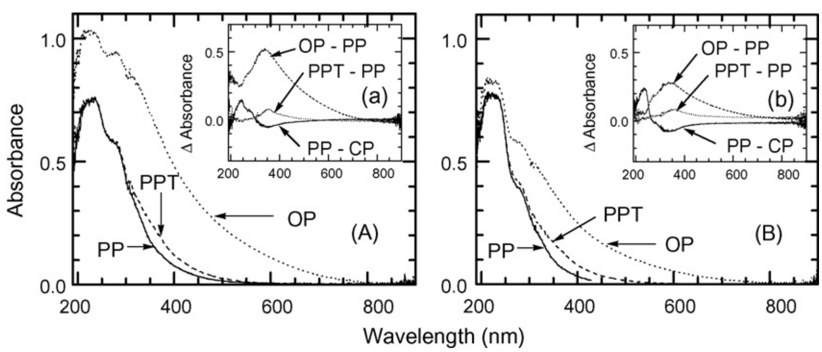

Fig. 10. Absorption (A) and (B) and absorption difference (a) and (b) spectra of NOKP (A) and (a) and LOKP/NBKP (B) and (b) sheets. Bleaching condition: long-wavelength black-light fluorescence lamp [2.41 mW cm^{-2}, 6 wt.% H_2O_2 (aq), pH 11 (adjusted by NaOH), room temperature, 8 h (A) and (a) and 3 h (B) and (b)]. (A) and (B) (···) NOKP and LOKP/NBKP sheets (**OP**), (—) photochemically bleached NOKP or LOKP/NBKP sheets (**PP**), (- - -) **PP** after the test of color fastness to light (**PPT**). (a) and (b) (—) **PP–CP** (**CP**: a pulp sheet prepared from conventionally bleached commercial-grade NBKP or LBKP/NBKP), (- - -) **OP–PP**, (···) **PPT–PP**. Number of pulp sheets: 3 sheets.

3. Conclusions

Total halogen-free oxidative photochemical bleaching of kraft pulps was conducted using alkaline hydrogen peroxide at room temperature. The selection of an appropriate wavelength of light was found to be crucial for effective bleaching of pulps. The light wavelength must be selected so that the light is absorbed only by the colored compounds in the pulps and not by bleaching reagents or the pulp itself. The wavelength of light, irradiation time, pH and the concentration of the aqueous H_2O_2 solution were optimized using excimer lasers. Once the optimum bleaching conditions were obtained, the laser was replaced by various conventional light sources, and the process was further improved. The optimal bleaching conditions involved light irradiation using a long-wavelength black-light fluorescent lamp in combination with aqueous H_2O_2 solution at pH 11. These conditions gave bleaching efficiency and the properties of pulps similar to those obtained by conventional two-stage ECF processes for both hardwood and softwood kraft pulps.

4. Experimental

4.1. Light sources

The light sources used were Lambda Physik LPX210i [KrF (248 nm) and XeF (351 nm)] and Lambda Physik COMPex102 [XeCl (308 nm)] excimer lasers, a 15-W low-pressure mercury lamp (National Germicidal Lamp GL-15), a 15-W standard black-light blue fluorescent lamp (National FL15BL-B), and a 20-W long-wavelength black-light blue fluorescent lamp (Toshiba FLR20S·B-DU-37C/M). The pulse energy of the lasers was measured by a Gentec ED-500 joulemeter and a Gentec SOLO PE Monitor. The light intensities of both the low-pressure mercury lamp and the black-light fluorescent lamps were measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with either an UVD-S254 (for the GL-15 lamp) or UVD-S365 (for the FL15BL-B and FLR20S·B-DU-37C/M lamps) photo detector. The emission spectra of the lamps were measured by an Ushio USR-40D Spectroradiometer.

4.2. Bleaching of pulp sheets

Paper sheets of oxygen-bleached softwood kraft pulp (NOKP) (68 g/m^2) and a 1:1 mixture of oxygen-bleached hardwood kraft pulp (LOKP) and commercial-grade bleached softwood kraft pulp (NBKP) (LOKP/NBKP; 62 g/m^2) from a paper mill were used for the bleaching experiments. A pulp sheet (2 cm × 3 cm) was padded in aqueous solutions of bleaching reagents [hydrogen peroxide (H_2O_2), sodium peroxocarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$), sodium peroxide (Na_2O_2), sodium peroxoborate ($NaBO_3$), urea hydrogen peroxide, addition complex ($H_2NCONH_2 \cdot H_2O_2$), and alkaline hydrogen peroxide (H_2O_2 + NaOH)]; the uptake of the solutions by the 1-g sheet was approximately 5 g. The sheet was then irradiated with a light source at room temperature for appropriate time, perpendicular to the surface of the sheet, washed with water, and dried. Thermal bleaching at room temperature was conducted similarly without irradiation.

4.3. Bleaching of pulps in suspension

A sample (45 mg) of an oxygen-bleached softwood kraft pulp (NOKP) or a 1:1 mixture of oxygen-bleached hardwood kraft pulp (LOKP) and commercial-grade bleached softwood kraft pulp (NBKP) (LOKP/NBKP) paper sheets from a paper mill was suspended in 13 mL of water in a test tube and filtered through a glass filter (diameter: 2.6 cm) to form a paper sheet. The sheet was then dried in a vacuum oven at room temperature over-night, and its weight, brightness, and yellow index were measured. The sheet and 13 mL of an aqueous alkaline hydrogen peroxide (H_2O_2 + NaOH) solution were then added to a quartz glass tube (internal diameter: 2.0 cm), and the pulp was suspended by stirring. The suspension was irradiated with a long-wavelength black-light blue fluorescent lamp (2.41 mW cm^{-2}) for an appropriate time and then filtered through a glass filter (diameter: 2.6 cm) to form a paper sheet. The sheet was then thoroughly washed with water, dried in a vacuum oven at room temperature over-night, and its weight, brightness, and yellow index were measured.

Reference paper sheets of commercial-grade bleached softwood pulp (NBKP) and 1:1 mixture of commercial-grade bleached hardwood kraft pulp (LBKP) and NBKP (LBKP/NBKP) were prepared in a similar manner to the NOKP and LOKP/NBKP sheets, but without the bleaching procedure.

4.4. Measurements of pulps

Brightness, yellow index, and absorption spectrum of the paper sheets were measured by a UV–vis spectrophotometer (Shimadzu UV-2400PC), equipped with an integration sphere (Shimadzu ISR-2200) using $BaSO_4$ (Merck, for white standard DIN 5033) as a reference. The brightness (JIS Z 8715; ISO 105-J02) and the yellow index (JIS K 7103) were calculated from measured UV–vis spectra using software for color measurements (Shimadzu P/N 206-65207). Color fastness to light was measured by "test method for color fastness to xenon arc lamp light" using a xenon long life fade meter (Suga Test Instruments Co., Ltd., FAL-25AX). The viscosity-average degree of polymerization was calculated from limiting viscosity [19] that was obtained by the measurements in cupriethylene diamine solutions using a viscometer (LAUDA, Viscosity Measuring System PVS 1) according to JIS P8215:1998 (ISO 535H:1981). The pH of the aqueous solutions was measured by a Sartorius PT-15 Portable Meter equipped with a pH/ATC electrode [standardized by pH buffer solutions (DKK-TOA Corp.) at pH 4.01, 6.86, and 9.18].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.09.006.

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