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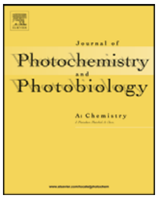

# Efficient total halogen-free photochemical bleaching of kraft pulps using alkaline hydrogen peroxide

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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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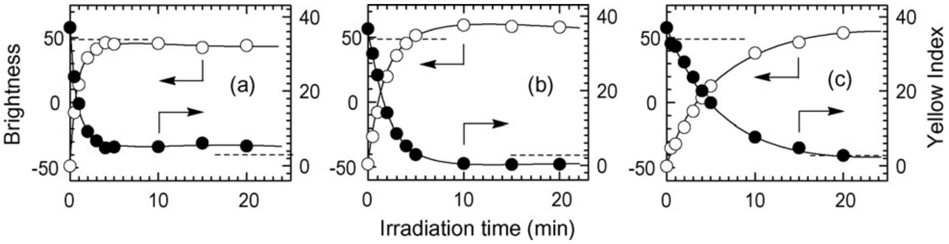

**Fig. 1.** Wavelength dependence on the brightness and yellow index of excimer laser-bleached NOKP sheets by an aqueous $Na_2CO_3 \cdot 1.5H_2O_2$ solution as a function of irradiation time [14]. Utilized lasers, (a) KrF, (b) XeCl, and (c) XeF excimer lasers. Brightness: white symbols and yellow index: 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.

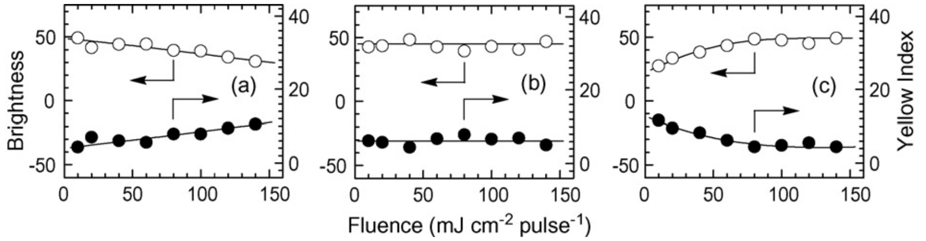

**Fig. 2.** Laser fluence dependence on the brightness and yellow index of excimer laser-bleached NOKP sheets by an aqueous $Na_2CO_3 \cdot 1.5H_2O_2$ solution as a function of laser pulse energy [14]. Utilized lasers, (a) KrF (total energy: 48 J/cm$^2$), (b) XeCl (total energy: 60 J/cm$^2$), and (c) 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.