Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 172 (2005) 231–240

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Dechlorination of pulp bleaching plant E-1 effluent by ArF* and KrF* excimer laser photolysis

Part 2. Dechlorination of polychlorinated oxylignins

Tian-yan Xie[a,b], Chen-Loung Chen[a,*], Josef S. Gratzl[a]

[a] *Department of Wood and Paper Science, North Carolina State University, Raleigh, NC 27695-8005, USA*
[b] *Appleton Paper Inc., Locks Mill, Combined Locks, Wisconsin, USA*

Received 25 June 2004; received in revised form 16 November 2004; accepted 29 November 2004

Abstract

The E-1 effluent from bleaching of pine kraft pulp was fractionated by ultrafiltration to obtain polychlorinated oxylignin fractions, PCOL-1, PCOL-2, PCOL-3 and POCL-4 with relative molecular mass (M_r) of 6500, 6000, 5500 and 3500, respectively. These PCOLs were characterized by elemental and functional group analyses, and gel permeation chromatography. The PCOLs were decolorized and dechlorinated in the presence of H_2O_2 in O_2-saturated solution at 20 °C by ArF* (193 nm) excimer photolysis. The results showed that both the decolorization and dechlorination were dependent on both the initial pH and concentration of H_2O_2 per substrate in the reaction mixture. In general, the decolorization increases with increasing pH and concentration of added H_2O_2. At pH 10.5 with 8% H_2O_2 per substrate to the initial reaction mixture, approximately 70% of chromophoric structures were degraded within the initial 60 min irradiation of ArF* (193 nm) laser radiation, then leveled off. The dechlorination reactions followed first order reaction law; first order with respect to total organically bound chlorine; first order overall. The dechlorination rates increase with increasing both pH and concentration of H_2O_2 per substrate. The quantum yields (Φ) for the generation of chloride ions from PCOLs in the presence of 2% H_2O_2 were appreciably lower than the values observed for the monomeric chlorophenols, in the range of approximately 0.03 versus 0.9. The ArF* excimer laser photolysis of PCOLs were also monitored by gel permeation chromatography. PCOL-2 was degraded into fragments with relative molecular mass (M_r) of approximately 1500. Similarly, PCOL-3 and PCOL-4 were degraded into fragments with M_r of approximately 4000 and 3000, respectively. In contrast, the M_r of PCOL-1 was increased to approximately 6500, indicating the occurrence of condensation among the degraded fragments.

Keywords: Pulp bleaching plant E-1 effluent; Polychlorinated oxylignins; Ultrafiltration; Advanced oxidation processes; ArF* (193 nm) eximer laser photolysis; Decolorization; Dechlorination; Oxygen; Hydrogen peroxide; Kinetics

1. Introduction

In previous investigations [1,2], some of the chlorophenols identified in the bleaching plant effluent from alkaline extraction (E-1 effluent) were dechlorinated in the aqueous solution at pH 7 and 10.5 in N_2- and O_2-saturated solutions at 20 °C by ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses. These chlorophenols included 4,5-chloroguaiacol (**1**) 3,4,5,6-tetrachloroguaiacol (**2**), 2,4,6-trichlorophenol (**3**) and 2,3,4,5-chlorophenol (**4**). The dechlorination reactions of **1**–**4** were determined to follow first order law; first order with respect to the total organically bound chlorine of substrate, first order overall. The efficiency of dechlorination was found to depend on the initial pH of reaction, the wavelength of excimer laser radiation and the substitution pattern of functional groups in the chlorphenenols investigated. The dechlorination rate of a substrate increased with increasing initial pH. In addition, the ArF* (193 nm) excimer laser photolysis was more effective than the KrF* (248 nm) excimer laser photol-

---

* Corresponding author. Tel.: +1 919 515 5749; fax: +1 919 515 6302.
E-mail address: chen-loung_chen@ncsu.edu (C.-L. Chen).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.11.018

ysis and UV-photolysis with 254 nm radiation in dechlorinating the chlorinated phenols. The dechlorination rate constant for each of the chlorophenols investigated was almost the same in N_2- and O_2-saturated solutions in the ArF* (193 nm) excimer laser photolysis. However, when 2% H_2O_2 per substrate was added to the initial reaction mixture of **4** in the O_2-saturated solution, the dechlorination rate constant increased appreciably.

Quantum yield (Φ) for the generation of chloride ions from **1**–**4** were determined on ArF* laser photolysis of these compounds in both N_2- and O_2-saturated solutions. In general, the quantum yields in O_2-saturated solution were slightly higher than the corresponding values in N_2-saturated solution under the same reaction conditions. However, on addition of 2% H_2O_2 per substrate in O_2-saturated solution, the quantum yield for the generation of chloride ions increased appreciably.

As presented in the previous paper [2], the polychlorinated oxylignins are highly toxic and persistent, and regarded as priority pollutants, for which efficient chemical treatment is required. Despite the large number of papers published in this field, very few high quality kinetic studies can be found in [3].

Two decades ago, Shimada [4] investigated on the UV-photolysis of polychlorinated oxylignin from bleaching effluent of red pine kraft pulp. The bleaching effluent was acidified, and the resulting precipitate was purified to give a polychlorinated oxylignin (PCOL) preparation, which was degraded in O_2-saturated alkaline solution with UV-photolysis using 254 nm radiation that was emitted from a low pressure mercury lamp. The degradation of PCOL increased with increasing pH that resulted in formation of low relative molecular mass substances with concomitant dechlorination, *O*-demethylation and cleavage of aromatic moieties. When the UV-photolysis was conducted in N_2-saturated alkaline solution, dechlorination and *O*-demethylation were observed, but not cleavage of aromatic moieties. In addition, the relative molecular mass of the PCOL was slightly increased with darkening of the color of the reaction mixture. However, no comprehensive investigation on the characterization of the POCL preparation and the UV-photolysis of POCL in O_2-saturated alkaline solution with addition of hydrogen peroxide were carried out. Recently, Archibald and Roy-Arcand [5] showed that absorbable organic halide (AOX) from elemental chlorine-free (ECF) bleaching plant effluents placed in remote lake was largely but not completely mineralized in 4 months by sunlight-dependent processes. In contrast, chromophores in the effuents were more rapidly and completely degraded by sunlight than the AOX under the same conditions.

The paper and pulp industry worldwide are move towards application of elemental chlorine-free (ECF) bleaching technologies [6–8]. Bjoerklund et al. [9] bleached softwood kraft pulps with different kappa numbers directly or after O_2 delignification with a bleaching sequence D(EO)D(EP)D and O(PO)TP to determine the effect of varying kappa numbers on the effluent properties, e.g., chemical oxygen demand (COD) and soluble lignins. Since chlorine dioxide (D) was used in the bleaching, the highly toxic polychlorinated oxylignins (PCOLs) should have been present in the E-1 and E-2 effluents even through ECF bleaching process was used for the bleaching of the softwood kraft pulps [10].

Consequently, the over all objective of the present investigation is to decolorize and dechlorinate the polychlorinated oxylignins in the pulp bleaching plant E-1 effluent obtained from bleaching of Loblolly pine kraft pulp with a bleaching sequence of C_DEPDD with 15.2% chlorine dioxide substitution in the chlorination stage. Specific objectives are (a) to fractionate the E-1 effluent to obtain polychlorinated oxylignins (PCOLs) by ultrafiltration, (b) to characterize the purified PCOL fractions by elemental analysis and relative molecular mass distribution pattern, and finally (c) decolorization and dechlorination of these fractions by ArF* (193 nm) excimer laser photolysis under the aforementioned optimum condition.

2. Experimental

2.1. E-1 effluent

The E-1 effluent was obtained from the Bleached Board Division of Westvaco Corporation at Covington, Virginia, USA. A Loblolly pine kraft pulp (kappa number 31.2) was bleached successively with Cl_2 with 15.2% chlorine dioxide substitution (C_D stage), extracted with a NaOH solution (E-1 stage), H_2O_2 (P stage), then twice with ClO_2 (DD stage), employing a chlorine factor of 0.16, i.e., bleaching sequence of C_DEPDD. The alkaline extraction (E-1 stage) was conducted at 65 °C. The effluent from the alkaline extraction is called E-1 effluent.

2.2. Fractionation of organics in E-1 effluent

The effluent from extraction stage (E-1 effluent; 20 l; pH 10.5; organic content: 3.2 g/l) was acidified with conc. H_2SO_4 to pH 3. The ppt was centrifuged, washed thoroughly with deionzed water, then suspended in deionized water and freeze-dried to obtain crude PCOL-1. The supernatants were combined and then fractionated by ultrafiltration using an Amicon model TC5E (Amicon Corp., Billerica, MA, USA) with working volume of 20 l and YM3, YM1, YC05 membranes with molecular mass cut-off value of 3000 and 1000, and 500 Dalton, respectively. The operating pressure was 55 psi (3.5 kg/cm^2). The combined supernatant was passed through 3000 Dalton membrane to obtain retentate 1 and permeate 1. The retentate 1 was suspended in deionized water, then freeze-dried to obtain crude PCOL-2. The permeate 1 was then pass through 1000 Dalton membrane to obtained retentate 2 and permeate 2. The retentate 2 was treated with Me_2CO to obtain Me_2CO-soluble and

Me_2CO-insoluble parts (yield of the latter 13%). The solvent was removed from the Me_2CO-soluble part under deduced pressure, then the resulting solid mass was suspended in deionzed water, and freeze-dried to obtained crude POCL-3. The permeate 2 was passed through 500 Dalton membrane to obtained retentate 3 and permeate 3. The retentate 3 was treated with dioxane to obtain dioxane-soluble and dioxane-insoluble parts (yield of the latter 3.8%). The dioxane-soluble part was then freeze-dried to obtain crude PCOL-4. The permeate 5 was concentrated under reduced pressure to obtain crude PCOL-5 that was found to be consisting mostly of inorganic materials. The crude PCOL-1, PCOL-2, PCOL-3 and PCOL-4 were individually purified by dissolving in dioxane-H_2O (96:4, v/v), then precipitating by addition of 10 times the volume of Et_2O. This procedure was repeated three time to obtain purified PCOL-1, PCOL-2, PCOL-3 and PCOL-4 with yield of 12.5, 20, 17 and 20% per the organic content in the original E-1 effluent, respectively. Both the Me_2CO-insoluble and dioxane-insoluble parts were not further investigated.

2.3. ArF* excimer laser photolysis

The 193 nm photons were produced by an ArF* excimer laser (Lumonics Series TE-860-3, Lumonics Inc., Ont., Canada). The laser beam was directed through the sample by a 1″-diameter, 45° flat 95% reflector (Acton Research Corp., Acton, MA, USA). The laser photolysis was carried out in a glass reactor having a 5 mm thick quartz window (Suprasil) and a side arm with a septum for sampling.

The ArF* (193 nm) excimer laser photolysis of PCOL preparations were carried out in O_2-saturated solution with the initial concentration of 450 mg/l. The reactor was filled with 500 ml solution of PCOLs. The average power of the laser beam was measured (Scientech 362 power meter, Scientech Inc., Boulder, CO, USA) every 5, 10 or 20 min during the experiment period. Small amount of samples (2 or 3 ml) were withdrawn at appropriate times during the experiment, and analyzed for chloride content, color, UV spectra and relative molecular mass distribution pattern.

2.4. Analytical methods

2.4.1. Determination of color

A Bausch and Lomb Spectronic 20 instrument measuring the absorption at 465 nm comparing it with a platinum–cobalt standard [11] measured the color. The color concentration is reported as equivalent Platinum–Cobalt Units (PCU). Experimental errors were ±2%.

2.4.2. Determination of relative molecular mass distribution

Relative molecular-mass distribution of the PCOLs was determined by gel permeation chromatography using FPCL system (Pharmacia LKB Biotech, Piscataway, NJ, USA). The samples were chromatographed on a Superdex G-75 gel column according to the procedure of Chen et al. [12]. Experimental error was ±3%. The standard lignin samples of known molecular mass were used for the calibration of the column. The function for calibration is: $\log M_r = -0.1242 \times [\text{elution volume (ml)}] + 5.3317$; $R^2 = 0.9997$.

2.4.3. Determination of organically bound chlorine (OCl) and chloride anion (Cl^-)

The organically bound chlorine (OCl) and chloride anion (Cl^-) were determined by the procedures described by Xie et al. [2].

2.5. Chemical compositions of polychlorinated oxylignins (PCOLs)

2.5.1. Elemental analysis

Elemental analyses of PCOL preparations were carried out by E and R Microanalytical Laboratory Inc. (Corona, NY). All samples analyzed were purified to an ash content of less than 0.1% and dried [13].

2.5.2. Functional group analysis

2.5.2.1. Determination of methoxyl group content. A modified procedure of Vieböck and Schwappach as described by Chen [14] was employed for determination of methoxyl content. The methoxyl groups in the samples react with a constant boiling HI (56%)-red phosphorus mixture to form MeI. The volatile MeI was stripped and reacted with Br_2 to give MeBr and IBr, the later of which further reacted with Br_2 in the presence of H_2O to HIO_3. The remaining Br_2 was reduced to HBr by HCOOH, and the HIO_3 produced was converted to I_2 by reaction with KI under acidic conditions. The released I_2 was determined by titration with $Na_2S_2O_3$ using starch or thiodyne as end-point indicators.

2.5.2.2. Determination of carboxylic group content. Carboxylic group content was determined by E & R Microanalytical Laboratory Inc. (Corona, NY). An acid-base back titration procedure was used for the determination.

2.5.2.3. Determination of total hydroxyl group contents. The total hydroxyl groups were determined based on the acetyl content (Ac%) of the acetylated samples as described by Chen [15]. In general, the total hydroxyl content of a lignin sample was acetylated with pyridine-acetic anhydride reagent (1:1, v/v) followed by saponification of the resulting acetate. The resulting acetic acid was stripped by distillation, then titrated with a standard 0.01 N NaOH solution using phenolphthalein solution as indicator.

2.6. Experimental errors

All experiments were conducted at least in triplicate. The experimental errors were then determined in term of accuracy, i.e., the average deviation (AD) of a mean value. It was calculated from the average deviation of a single determination (a.d.) divided by the square root of the number (n) of determination made: A.D = a.d./n$^{1/2}$.

3. Results and Discussion

3.1. Fractionation of the organics in the E-1 effluent

As reported previously, the E-1 effluent contained 92l mg/l of total chlorine, of which 245 mg/l was the organically bounded chlorine (OCl). Approximately 5% of the OCl were ether-extractable. Thus, it is evident that the majority of organically bound chlorine (OCl) was present in the E-1 effluent as ether-insoluble high relative molecular mass fraction that consisted mostly of toxic polychlorinated oxylignins. The gel permeation chromatogram showed that this fraction had a relative molecular mass (M_r) of approximately 5000 Dalton [1,2].

In order to characterize the polychlorinated oxylignins (POCLs), the E-1 effluent (20 l; pH 10.5; organic content: 3.2 g/l) was fractionated by ultrafiltration. The E-1 effluent was acidified with concentrated sulfuric acid to pH 3. The acid precipitate was centrifuged off to give crude fraction PCOL-1. The supernatant was then fractionated by ultrafiltration to give PCOL-2, PCOL-3, PCOL-4 and PCOL-5 fractions. The PCOL-5 contained mostly inorganics and did not be further investigated. The PCOL-1, PCOL-2, PCOL-3 and PCOL-4 fractions were individually purified by dissolving in dioxane-water (96:4, v/v), then precipitating by addition of 10 times the volume of diethyl ether. The yield of PCOL-1, PCOL-2, PCOL-3 and PCOL-4 are 12.5, 20, 17 and 20% per the organic content in the original E-1 effluent, respectively, and have the relative molecular mass of 6500, 6000, 5500 and 3500, respectively (Table 1, Fig. 1). Purification of these fractions prior of to the investigation on decolorization and dechlorination was necessary because the inorganic contaminants would cause difficulties in quantitative analysis of samples and evaluation of the results of ArF* excimer laser photolysis.

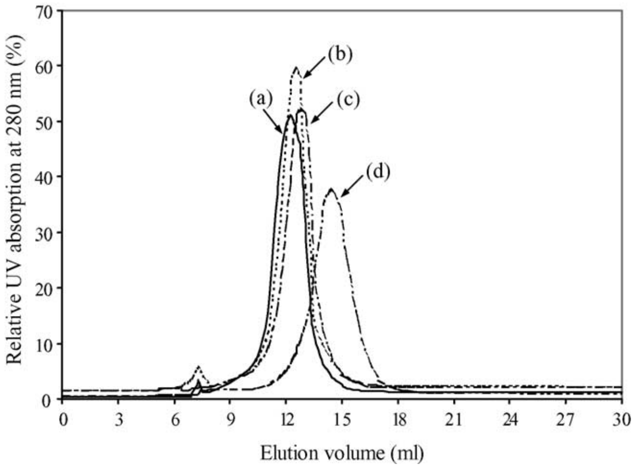

Fig. 1. Relative molecular mass of polychlorinated oxylignins, PCOL-1, PCOL-2, PCOL-3 and PCOL-4, determined by gel permeation chromatography. — (a) PCOL-1 (6500); - - - (b) PCOL-2 (6000); −−−−− (c) PCOL-3 (5500); −−−−−−− (d) PCOL-4 (3500). Calibration: $\log M_r = -0.1242 \times$ [elution volume (ml)] + 5.3317.

3.2. Chemical composition and functional group analysis of the polychlorinated oxylignin (PCOL) fractions

The PCOLs were acetylated with acetic anhydride–pyridine reagent, then methylated with ethereal diazomethane as described by Chen [15]. The acetylated, methylated PCOLs were then subjected to elemental analyses (C, H, O, S, Cl). The total hydroxyl contents of the PCOLs were calculated from acetyl content of the corresponding acetylated and methylated derivatives, while the COOH contents were calculated from the increase in methoxyl contents. The methoxyl group contents were determined by the modified procedure of Viehbock and Schwappach as described by Chen [14].

The elemental compositions of PCOLs using Cl content as unity are summarized in Table 1. The results show that the PCOLs have the C/Cl ratio in the range of 17.72–24.44.

Table 1
Molecular formulae of polychlorinated oxylignin (PCOL) preparations based on chlorine as unity

Preparations	Molecular formulae based on chlorine as unity	Functional group content (mole/Cl)			Relative molecular mass (M_r)
		OCH_3	COOH	Total OH	
PCOL-1	$C_{24.44}H_{25.67}O_{14.63}S_{0.09}Cl$	$(OCH_3)_{1.22}$	$(COOH)_{0.94}$	$(OH)_{3.22}$	6500
PCOL-2	$C_{21.52}H_{25.98}O_{13.54}S_{0.09}Cl$	$(OCH_3)_{0.91}$	$(COOH)_{1.49}$	$(OH)_{2.26}$	6000
PCOL-3	$C_{22.26}H_{22.07}O_{13.71}S_{0.11}Cl$	$(OCH_3)_{0.91}$	$(COOH)_{1.41}$	$(OH)_{2.24}$	5500
PCOL-4	$C_{17.72}H_{21.32}O_{10.15}S_{0.10}Cl$	$(OCH_3)_{1.43}$	$(COOH)_{0.90}$	$(OH)_{2.22}$	3500
PCOL[a]	$C_{14}H_{15}O_8Cl$; $C_{14}H_{10}O_9Cl$	ND	ND	ND	ND
E-1-1[b]	$C_{13.8}H_{9.8}O_{9.1}Cl$	$(OCH_3)_{1.77}$	ND	ND	>25000
E-1-2[b]	$C_{13.1}H_{9.5}O_{9.3}Cl$	ND	ND	ND	25000 – 10000
E-1-3[b]	$C_{14.3}H_{10.7}O_{12.4}Cl$	ND	ND	ND	10000 – 1000
E-1-4[b]	$C_{14}H_{17.3}O_{6.2}Cl$	ND	ND	ND	<1000
E-2-1[b]	$C_{118}H_{132}O_{68}Cl$	$(OCH_3)_{2.96}$	ND	ND	<1000

ND = not determined.

[a] Adopted from Bennett et al. [7].

[b] Adopted from Lindström and Österber [8].

Table 2
C_9-units of polychlorinated oxylignin (PCOL) fractions

Fraction	C_9-unit formulae	Functional group content (mole/C_9)		C_9-unit weight	Relative molecular mass (M_r)
		COOH	Total OH		
PCOL-1	$C_9H_{8.53}O_{5.2}S_{0.04}Cl_{0.39}(OCH_3)_{0.47}$	0.36	1.25	229.6	6500
PCOL-2	$C_9H_{10.15}O_{5.52}S_{0.04}Cl_{0.44}(OCH_3)_{0.4}$	0.65	0.99	252.09	6000
PCOL-3	$C_9H_{8.15}O_{5.4}S_{0.05}Cl_{0.42}(OCH_3)_{0.38}$	0.59	0.94	247	5500
PCOL-4	$C_9H_{9.41}O_{4.82}S_{0.06}Cl_{0.55}(OCH_3)_{0.79}$	0.5	1.23	252.48	3500
Kraft Lignin[a]	$C_9H_{7.98}O_{2.28}S_{0.08}(OCH_3)_{0.77}$	0.3	1.6	179.09	ND

ND = not determined.

[a] Adopted from Wang et al. [10].

These values are considerably higher than the reported values, the C/Cl ratios of 13–14 for the POCLs from the E-1 effluent obtained with alkaline extraction of acidic chlorine bleaching by Bennett et al. [16] and Lindström and Österberg [10]. However, they are appreciably lower than the C/Cl ratio of 118 found for the PCOL from the E-2 effluent obtained by alkaline extraction of chlorine dioxide bleaching effluent [10]. In addition, the PCOLs have the O/Cl ratio in the range of 10.15–14.63, which increase with increasing relative molecular mass (M_r). These values are also higher than the values for the O/Cl ratios of 8–9 and 6–12 [10,16], but appreciably lower than the O/Cl ratio of 68 found for PCOL from E-2 effluent [10]. Thus, it is evident that the higher C/Cl and O/Cl ratios found were caused by the fact that the E-1 bleaching effluent used in this investigation employed 15.2% chlorine dioxide substitution in the acidic chlorine bleaching stage. This implies that the used of 15.2% chlorine dioxide substitution in the chlorine bleaching results in an appreciable decrease in the formation of organically bound chlorine (OCl) in the bleaching.

The elemental compositions of PCOLs are also summarized in term of C_9-unit using that of kraft lignin as comparison (Table 2). The use of C_6-C_3 units (phenylpropane units) in expressing the composition of lignin preparations is a common practice in lignin chemistry for sake of comparison in spite the fact that most of the PCOLs do not have a complete C_9-unit. The relative frequencies of organically bound chlorine (OCl) in the different relative molecular mass fractions of PCOLs show that the Cl/C_9 ratio is in the ranging of 0.39–0.55 Cl/C_9, no appreciable difference (Table 2). PCOL-1 has the lowest OCl content while PCOL-4 the highest, 0.39 Cl/C_9 versus 0.55 Cl/C_9. In addition, the PCOLs have a relatively low total hydroxyl group content, in the range of 0.94–1.25 OH/C_9, as compared to 1.5 OH/C_9 for kraft lignin [17,18]. In general, the COOH group content of the PCOLs is in the range of 0.36–0.65 COOH/C_9, considerably higher than that of kraft lignin, 0.3 COOH/C_9. Most of the COOH groups in PCOLs were probably produced via oxidative cleavage of aromatic rings by chlorine in the chlorination stage of bleaching process. The methoxyl group content of the PCOLs is in the range of 0.38–0.47 OCH_3/C_9, except for PCOL-4 (0.79 OCH_3/C_9), appreciably lower than that of kraft lignin, 0.77 OCH_3/C_9. The observed loss of methoxyl content most likely occurred in the C_D stage, although a small part of it could conceivably occurred in the kraft pulping. Among the POCL fractions, PCOL-1 has the lowest COOH content but the highest OH content. This is in agreement with the fact that the solubility of PCOL-1 in water is the lowest among the PCOL fractions.

3.3. ArF* (193 nm) excimer photolysis of polychlorinated oxylignin (PCOL) fractions

3.3.1. Decolorization of polychlorinated oxylignin (PCOL) fractions

The PCOL fractions contain not only organically bound chlorine (OCl), but also chromophoric structures, which are responsible for the color of the effluent. In the ArF* (193 nm) excimer irradiation of O_2-saturated PCOL-2 solution with 2% H_2O_2 per POCL-2 at 20 °C, the degradation of the chromophoric structures was monitored by measuring their Co–Pt color unit. The decolorization proceeded faster in alkaline solution (pH 10.5) than in neutral solution (pH 7) (Fig. 2). Moreover, an addition of H_2O_2 to the O_2-saturated PCOL-2 solution at pH 10.5 increased the decolorization appreciable

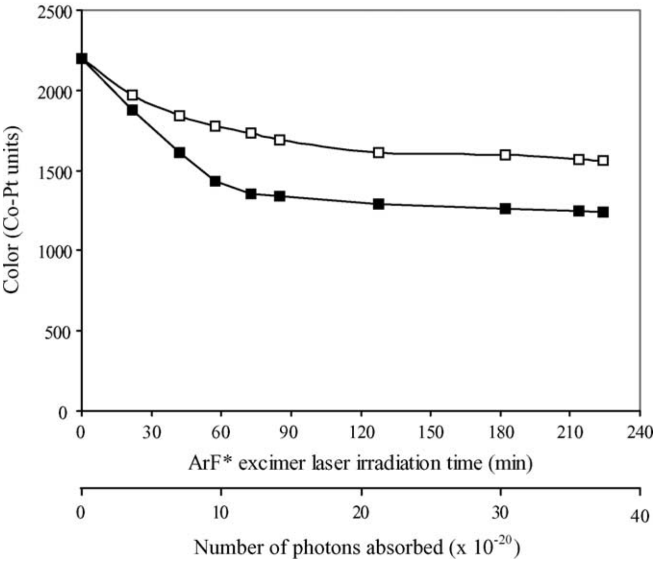

Fig. 2. The effect of pH on the decolorization of PCOL-2 in O_2-saturated solution at 20 °C by ArF* (193 nm) excimer laser photolysis. -□-□- at pH 7; -■-■- at pH 10.5.

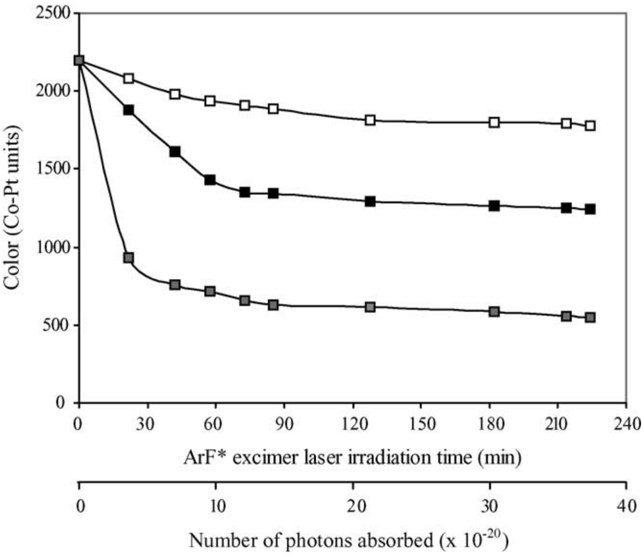

Fig. 3. Effect of the concentration of hydrogen peroxide on the decolorization of PCOL-2 at pH 10.5 in O_2-saturated solution at 20 °C by ArF^* (193 nm) excimer laser photolysis. -□-□- without addition of H_2O_2; -■-■- with addition of 2% H_2O_2 per POCL-2; ▨ with addition of 8% H_2O_2 per POCL-2.

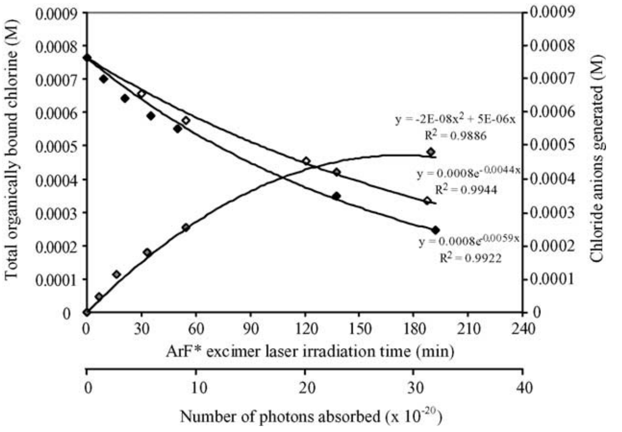

Fig. 4. Effect of pH on the dechlorination of POCL-1 in O_2-saturated solution at 20 °C with addition of 2% hydrogen peroxide per POCL-1 by ArF^* (193 nm) excimer laser photolysis. -◇-◇- at pH 7; -◆-◆- at pH 10.5; ◈ generation of chloride ions at pH 10.5.

(Fig. 3). The reduction of color increased with increasing concentration of H_2O_2. The color removal was inappreciable in the absence of H_2O_2, the color reduction of only approximately 160 units at the 60 min irradiation of ArF^* excimer laser radiation. With the additions of 2% and 8% H_2O_2 per PCOL-2, the color reduction increased to approximately 720 and 1490 units at the irradiation time of 60 min, respectively.

The degradation of chromophores occurred on the ArF^* (193 nm photon) excimer laser irradiation in two distinct phases. In the first phase (initial 60 min), the color of the PCOL-2 decreased rapidly and then leveled off. This indicates that the bulk of the chromophores were degraded in the first phase. The generation of organic acids by the photo-oxidation of PCOL-2 preparation could slow down the reaction rate for the removal of chromophoric structures in second phase, since pH of the reaction mixture could decrease with increasing formation of carboxylic acid groups. The pH of reaction mixture decreased from the initial 10.5–8.6 at the end of the irradiation. In addition, the decrease in pH would result in slowing down the oxidative degradations promoted by base, i.e., decrease in ionization of the phenolic groups. Moreover, the degradation of the chromophoric structures would lead to decrease in the chromophoric structures susceptible to the degradation by the ArF^* excimer laser-H_2O_2 photolysis.

3.3.2. *Kinetics of dechlorination of polychlorinated oxylignin (PCOL) fractions*

3.3.2.1. Effect of pH. Initially, PCOL-1 was irradiated with ArF^* (193 nm) laser radiation at pH 7 and 10.5 with 2% H_2O_2 in O_2-saturated solution at 20 °C to verify the correctness of the optimum conditions determined by the results of model compound experiments [1,2]. The dechlorination reactions of the PCOLs were first order reactions; first order with respect to the total organically bound chlorine (TOCl), first order overall, as evidenced by a linear relationship between $-\ln[\mathrm{TOCl}]_t/[\mathrm{TOCl}]_0$ and excimer laser radiation irradiation time t. As in the model compound experiments [2], the dechlorination rate of PCOL-1 was indeed appreciably faster at pH 10.5 than at pH 7, the rate constant of $0.983 \times 10^{-4}\,\mathrm{s}^{-1}$ versus $0.733 \times 10^{-4}\,\mathrm{s}^{-1}$ (Table 3, Fig. 4). At pH 10.5, the rate for the formation of chloride anions (Cl^-) was a slightly slower than the dechlorination rate, the rate constant of $0.933 \times 10^{-4}\,\mathrm{s}^{-1}$ versus $0.983 \times 10^{-4}\,\mathrm{s}^{-1}$.

3.3.2.2. Effect of hydrogen peroxide. The PCOL-2 was then irradiated with ArF^* (193 nm) excimer laser radiation at pH

Table 3
Dechlorination reaction rate constants of polychlorinated oxylignin (PCOL) fractions in O_2-saturated solution at 20 °C by ArF^* (193 nm) laser photolysis

Fraction	pH	Oxidant per substrate	κ (s^{-1})	Coefficient of determination (R^2)
PCOL-1	7.0	2% H_2O_2	0.733×10^{-4}	0.9944
	10.5	2% H_2O_2	0.983×10^{-4}	0.9922
	10.5	2% H_2O_2	0.933×10^{-4}[a]	0.9677
PCOL-2	10.5	None	0.833×10^{-4}	0.9915
	10.5	2% H_2O_2	1.083×10^{-4}	0.9904
PCOL-4	10.5	2% H_2O_2	0.8×10^{-4}	0.9897

Initial concentration: 450 mg substrate/l.

[a] Rate constant for the formation of chloride ions.

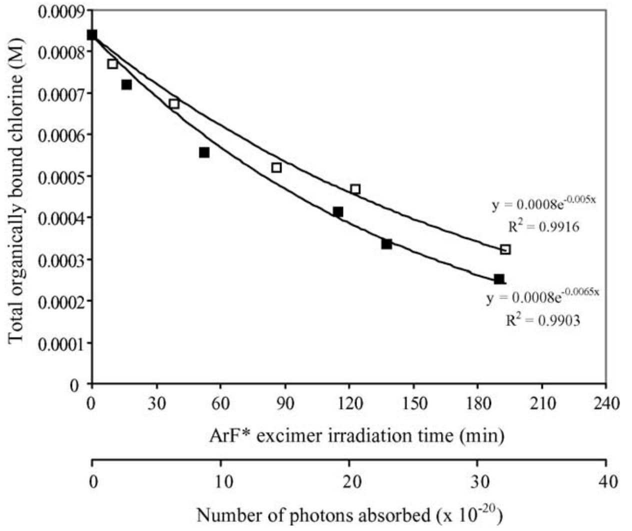

Fig. 5. The effect of hydrogen peroxide on the dechlorination of POCL-2 at pH 10.5 in O_2-saturated solution at 20 °C by ArF* (193 nm) excimer laser photolysis. -□-□- ArF* (193 nm) excimer laser photolysis only; -■-■- with addition of 2% H_2O_2 per POCL-2.

10.5 in O_2-saturated solution with and without addition of 2% H_2O_2 per PCOL-2 by weight at 20 °C. The addition of 2% H_2O_2 per substrate appreciably accelerated the dechlorination rate, the rate constant increased from 0.833×10^{-4} to $1.083 \times 10^{-4}\ s^{-1}$ (Table 3, Fig. 5). However, the effect of H_2O_2 on the dechlorination rate was not discernable in the initial stage of the laser photolysis up to 30 min corresponding to 5×10^{20} 193 nm photons absorbed. In the later stage, H_2O_2 promoted appreciably the dechlorination of PCOL-2.

In alkaline solution, H_2O_2 undergoes photolysis under the reaction condition to produce hydroxyl radials ($HO^\bullet$), which in turn abstract hydrogen atoms from H_2O_2 to produce hydroperoxyl radicals ($HOO^\bullet$) [19]. Thus, the resulting active oxygen radical species, such as hydroxyl and hydroperoxyl ($HO^\bullet$ and $HOO^\bullet$) radicals, promote the dechlorination reaction. First of all, the hydroxyl radicals ($HO^\bullet$) extracted an electron from phenoxide anions to produce phenoxyl radicals that in turn gave *ortho* and *para* (C-2, C-4, C-6) radical species via mesomerism. Coupling of hydroxyl radicals ($HO^\bullet$) with these radical species could result in removal of chloride anion (Cl^-) with concomitant formation of the corresponding quinones if these positions were substituted by chlorine.

3.3.2.3. *Effect of relative molecular mass.*

The alkaline solutions of PCOL-1, PCOL-2 and PCOL-4 at pH 10.5 were subjected to ArF* (193 nm) excimer laser photolysis with 2% H_2O_2 per PCOL in O_2-saturated solution at 20 °C. The PCOL-3 was not available because of the shortage of the preparation. The decrease in the total organically bound chlorine (TOCl) of the reaction mixture was monitored by quantitative analysis. Chloroform, chlorinated acetic acid and other volatile materials that might have been formed in the excimer laser photolysis were not determined. In general, the total organically bound chlorine (TOCl) in the substrates decreased with the corresponding generation of chloride anions (Cl^-) (Table 4) as in the case of the ArF* excimer laser photolysis of PCOL-1 (Fig. 4).

The dechlorination rates of the different fractions, PCOL-1, PCOL-2 and PCOL-4, were compared in order to elucidate the effect of relative molecular mass (M_r). The PCOL-1, PCOL-2 and PCOL-4 had the M_r of 6500, 6000 and 3500, respectively. The dechlorination rate of PCOL-2 was the fastest, followed by that of PCOL-1, and that of PCOL-4 was the slowest, rate constants of 1.083, 0.983 and $0.8 \times 10^{-4}\ s^{-1}$, respectively (Table 3; Fig. 6). Thus, The dechlorination rate constants of PCOLs decreased with decreasing the relative molecular mass (M_r), but with increasing organically bound chlorine (OCl) content/C_9-unit. The dechlorination rates of the PCOL fractions were found to be, in general, slower than the rates found for the model compounds under the same reaction conditions. For example, to achieve 50% dechlorination in the PCOL fractions, approximately 120 min irradiation of ArF* (193 nm) eximer laser radiation was required. In contrast, less than 30 min irradiation of ArF* (193 nm) eximer laser radiation was required to obtain the same degree of dechlorination in the model compounds under the same reaction conditions [1,2]. The chlorine anions (Cl^-) generated at the 30 min irradiation of ArF* excimer laser radiation and the quantum yield for the generation of chloride anions from the PCOL fractions were summarized in Table 4. It is evident

Table 4
Quantum yields for generation of chloride ions from polychlorinated oxylignin fractions at 30 min irradiation of ArF* (193 nm) excimer laser radiation in O_2-saturated solution at 20 °C

Fractions	pH	Oxidant	$[TOCl]_0$ (mol l^{-1})	$[TOCl]_{30}$ (mol%)	Chloride ions generated		Quantum yield (Φ)
					mol%[a]	mol l^{-1}	
PCOL-1	7.0	2% H_2O_2	0.000764	87.63	12.37[a]	0.0000945	≈0.02
	10.5	2% H_2O_2	0.000764	83.78	16.22[a]	0.0001239	≈0.027
	10.5	2% H_2O_2	0.000764	N/A	15.46[b]	0.0001181	≈0.026
PCOL-2	10.5	None	0.000839	86.07	13.93[a]	0.0001169	≈0.025
	10.5	2% H_2O_2	0.000839	82.28	17.72[a]	0.0001487	≈0.031
PCOL-4	10.5	2% H_2O_2	0.001029	86.59	13.41[a]	0.000138	≈0.029

Initial concentration: 450 mg substrate/l. N/A = not applicable.

[a] Calculated from $\{100 - [TOCl]_{30}\}$ in mol%.

[b] Determined directly the chloride ions generated in the reaction mixture.

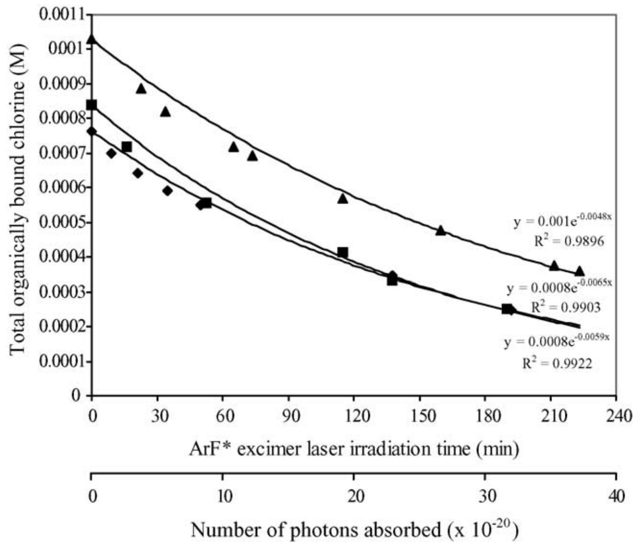

Fig. 6. The dechlorination of PCOL-1, PCOL-2 and PCOL-4 at pH 10.5 in O_2-saturated solution at 20 °C with 2% hydrogen peroxide per substrate by ArF* (193 nm) excimer laser photolysis. –▲–▲– PCOL-1; -■-■- PCOL-2; –◆–◆– POCL-4.

that the quantum yields for the chloride anion (Cl^-) formation from the PCOL fractions were much smaller than the values observed for model compounds [1,2]. This could be attributed to the organically bound chlorine (OCl) content, the complex chemical structure as well as the chemical environment of organically bound chlorine in the PCOL fractions.

3.3.3. *Degradation of polychlorinated oxylignin (PCOL) fractions*

The degradation of PCOLs by ArF* (193 nm) laser photolysis was preliminarily studied by monitoring change in the intensity of the peak corresponding to lignin fragments having the relative molecular mass (M_r) of 6000 in the POCL-2 solutions with concentrations of 900 and 450 mg/l. The degradation of PCOC-2 with concentration of 450 mg/l was negligible at pH 10.5 in N_2-saturated solution at 20 °C up to 600 min irradiation of ArF* (193 nm) laser radiation (Fig. 7). However, approximately 18, 26 and 29% of the M_r 6000 fragments underwent degradation, producing fragments with M_r of 1500 at pH 10.5 in O_2-saturated solution with 2% H_2O_2 per substrate at 20 °C on 240, 360 and 600 min irradiation of ArF* (193 nm) laser radiation, respectively. Although the degradation rate increased with increasing concentration of substrate, the rate for the solution with concentration of 900 mg/l was faster than that with concentration of 450 mg/l only by approximately 1.1–1.2 hold, 80% versus 71.4% at the 600 min irradiation. In addition, when the concentration of H_2O_2 was increased from 2% to 8% per POCL-2, then the percentage of M_r 6000 fragments undergoing degradation were increased to approximately 53, 62 and 71%, respectively. Evidently, the results indicate that the ArF* excimer laser photolysis alone does not bring about appreciable degradation of the high molecular mass fractions. However, addition of a small amount of oxidants, such as 2% H_2O_2 in O_2-saturated solution, the ArF* (193 nm) excimer laser photolysis resulted in appreciable degradation of the PCOL-2.

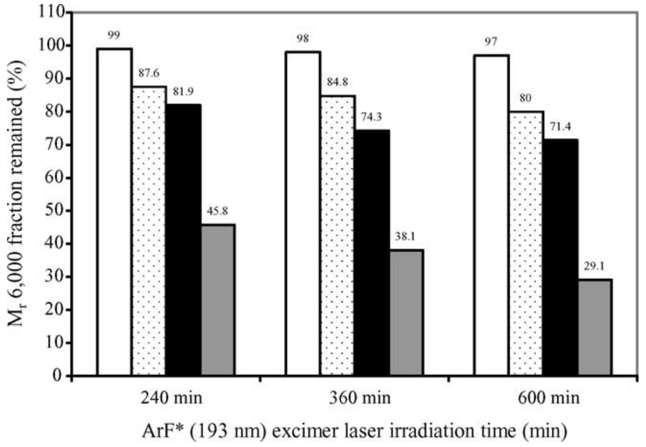

Fig. 7. Degradation of PCOL-2 at pH 10.5 and 20 °C under following conditions. (☐) concentration: 450 mg/l in N_2-saturated solution, (▨) concentration: 900 mg/l with 2% hydrogen peroxide in O_2-saturated solution, (■) concentration: 450 mg/l with 2% hydrogen peroxide in O_2-saturated solution, (▩) Concentration: 450 mg/l with 8% hydrogen peroxide in O_2-saturated solution.

On irradiation of ArF* (193 nm) excimer laser radiation up to 600 min, the PCOL-2 readily underwent oxidative photodegradation at pH 10.5 with 6% H_2O_2 per substrate in O_2-saturated solution at 20 °C. The fragments with relative molecular mass (M_r) of 6000 was degraded into fragments with M_r of 1500, the peak of which is rather sharp and symmetric. The M_r 6000 peak decreased with the corresponding increasing in the new M_r 1500 peak, as the ArF* excimer laser photolysis proceeded (Fig. 8).

In the cases of PCOL-1, PCOL-3 and PCOL-4, the profile for the change in the molecular distribution pattern is different

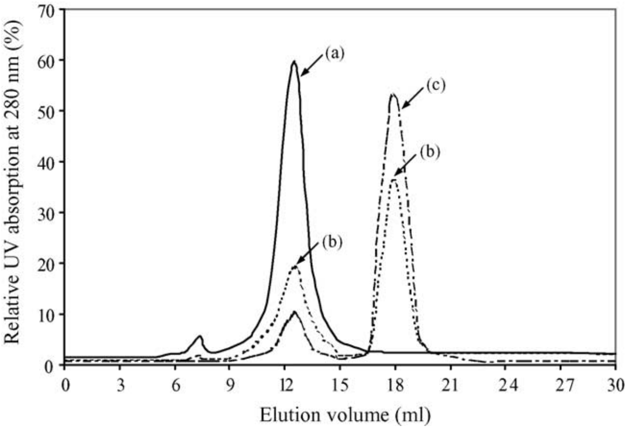

Fig. 8. Degradation of PCOL-2 by ArF* (193 nm) excimer laser photolysis at pH 10.5 with 8% hydrogen peroxide per substrate in O_2-saturated solution. Concentration of PCOL-2: 450 mg/l. — (a) before irradiation [M_r 6000 (largest); M_r 1500 (none)]; - - - - - (b) irradiation time of 360 min [M_r 6000 (smaller) and M_r 1,500 (larger); – – – – – (c) irradiation time of 600 min [M_r 6000 (smallest) and M_r 1500 (larger)]. Calibration: $\log M_r = -0.1242 \times [\text{elution volume (ml)}] + 5.3317$.

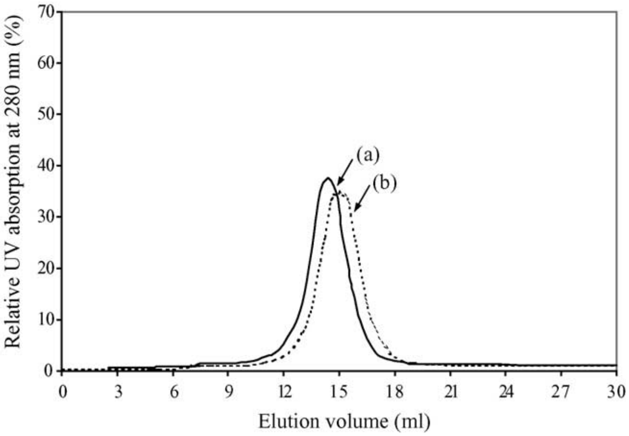

Fig. 9. Degradation of PCOL-1 by ArF* (193 nm) excimer laser photolysis at pH 10.5 with 8% hydrogen peroxide per substrate in O_2-saturated solution. Concentration of PCOL-1: 450 mg/l. — (a) before irradiation (M_r 6500); - - - - - (b) irradiation time of 360 min (M_r 7,000). Calibration: $\log M_r = -0.1242 \times$ [elution volume (ml)] + 5.3317.

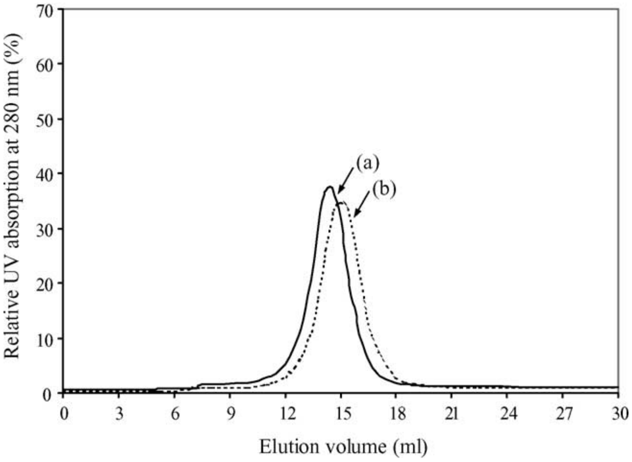

Fig. 11. Degradation of PCOL-4 by ArF* (193 nm) excimer laser photolysis at pH 10.5 with 8% hydrogen peroxide per substrate in O_2-saturated solution. Concentration of PCOL-4: 450 mg/l. — (a) before irradiation (M_r 3500); - - - - - (b) irradiation time of 360 min (M_r 3000) Calibration: $\log M_r = -0.1242 \times$ [elution volume (ml)] + 5.3317.

from that of PCOL-2 under the same reaction conditions. At 360 min irradiation of ArF* (193 nm) excimer laser radiation, the M_r 6500 peak in the PCOL-1 was disappeared completely with appearance of the fragments with M_r of 7000 (Fig. 9), probably caused by recombination among the resulting degraded radical fragments. In contrast, the M_r 5500 and 3500 peaks in the PCOL-3 and PCOL-4 were completely degraded into the fragment with M_r of 4000 and M_r of 3000, respectively (Figs. 10 and 11). Thus, the photochemical degradation pattern of PCOL-1 is different from those of PCOL-2, PCOL-3 and PCOL-4. The difference in the degradation behavior among PCOL-1, PCOL-2 PCOL-3 and PCOL-4 could be caused by differences in skeletal feature of their chemical structures. Conceivably, PCOL-2 should have been containing uniform units that should be susceptible to oxidative cleavage by ArF* (193 nm) excimer laser photolysis to produce POCL fragments with M_r of approximately 1500 from the initial. M_r 6000 fragments. In contrast the PCOL-3 and PCOL-4 probably contain peripheral units with M_r of approximately 1500 and 500 respectively, which should be susceptible to elimination with oxidative cleavage on ArF* (193 nm) excimer laser photolysis, producing the fragments with M_r of approximately 4000 and 3000, respectively. Conceivably, the skeletal feature for chemical structure of PCOL-1 should be similar to that of PCOL-2. However, the units that should be susceptible to oxidative cleavage in PCOL-1 should be readily to produce radical fragments by the photolysis, which should immediately undergo radical recombination to produce the fragments with M_r of approximately 7000, but not that of PCOL-2.

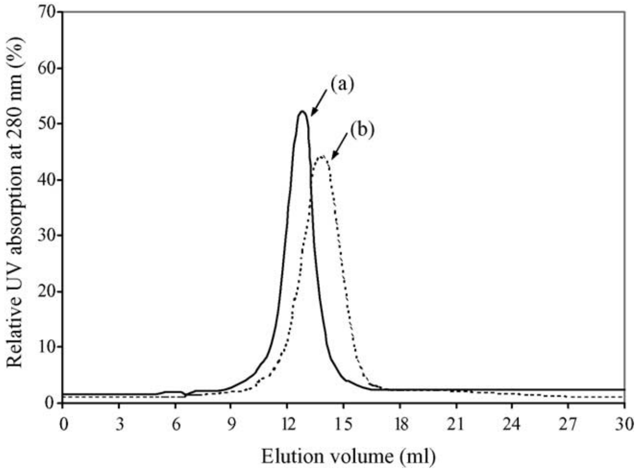

Fig. 10. Degradation of PCOL-3 by ArF* (193 nm) excimer laser photolysis at pH 10.5 with 8% hydrogen peroxide per substrate in O_2-saturated solution. Concentration of PCOL-3: 450 mg/l. — (a) before irradiation (M_r 5500); - - - - - (b) irradiation time of 360 min (M_r 4000). Calibration: $\log M_r = -0.1242 \times$ [elution volume (ml)] + 5.3317.

4. Conclusions

Ultrafiltration technique is very effective in the fractionation of E-1 effluent into polychlorinated oxylignin (PCOL) fractions PCOL-1, PCOL-2, PCOL-3 and PCOL-4 with relative molecular mass (M_r) of 6500, 6000, 5500 and 3500, respectively. The chemical Compositions of the PCOL fractions indicate that the use of 15.2% chlorine dioxide substitution in the chlorine bleaching stage results in an appreciable decrease in the total organically bound chlorine content in the E-1 effluent.

The irradiation of ArF* (193 nm) excimer laser radiation in O_2-saturated solution alone is effective in the dechlorination of POCL fractions, but not in the decolorization. However, addition of oxidants in O_2-saturated solution, such as H_2O_2, is necessary to improve both degradation and decolorization of PCOLs by ArF* excimer laser photolysis. The PCOLs undergo effectively decolorization and dechlorination at pH 10.5 in the presence of H_2O_2 in O_2-saturated solution at 20 °C by ArF* excimer laser photolysis. Both the decolorization and dechlorination of PCOLs are dependent of pH and concentration of H_2O_2. The rates of decolorization and dechlorination increase with increasing pH and initial concentration of H_2O_2. At pH 10.5 and 8% H_2O_2 per substrate to the initial reaction mixture, approximately 70% of chromophoric structures were degraded at 60 min irradiation of ArF* laser radiation, then leveled off.

The kinetics for the dechlorination of PCOLs shows that the dechlorination reactions follow the first rate order with respect to total organically bound chlorine. The declorination rates increase with increasing pH and concentration of H_2O_2 per substrate. The quantum yields (Φ) for the generation of chloride ions from PCOLs were appreciably lower than the values for monomeric chlorophenols.

The degradation of PCOLs by ArF* excimer laser photolysis is more effective in the presence of oxidatants, such as H_2O_2. Addition of H_2O_2 in the range 2–8% per substrate resulted in enhancing the degradation, suggesting that the active oxygen radical species generated by the photolysis, such as hydroxyl and hydroperoxyl radials ($HO^\bullet$, $HOO^\bullet$), are playing an important role in the oxidative degradation. After 360 min irradiation of ArF* (193 nm) laser radiation, approximately 62% of POCL-2 was degraded into degraded into fragments with relative molecular mass (M_r) of approximately 1500 at pH 10.5 with 8% H_2O_2 per substrate in O_2-saturated solution at 20 °C. Similarly, PCOL-3 and PCOL-4 were degraded to degraded fragments with M_r of approximately 4000 and 3000, respectively. In contrast, the fragments M_r 6500 of PCOL-1 was increased fragments with M_r of approximately 7000, indicating the occurrence of condensation among the degraded fragments. The degree of degradation increases with increasing irradiation time of ArF* (193 nm) excimer laser.

Acknowledgements

This project is supported by the USDA competitive research grant under cooperative agreement Nos. 88-33521-4084 and 90-37291-5723, for which the authors are thankful. The authors are also grateful to Westvaco Corporation for supplying the E-1 effluent for this study.

References

[1] T.-y. Xie, Dechlorination and Decolorization of Organics in Bleaching Plant E-1 Effluent by Photochemical Processes, Ph.D. Thesis, North Carolina State University, Raleigh, North Carolina, USA, 1994.
[2] T.-y. Xie, C.-L. Chen, J.S. Gratzl, J. Photochem. Photobiol. A: Chem. (2005), doi:10.1016/j.photochem.2004.10.021.
[3] G. Lente, J.H. Espenson, New J. Chem. 28 (2004) 847–852.
[4] K. Shimada, Mokuzai Gakkaishi 28 (1982) 378–382.
[5] F. Archibald, L. Roy-Arcand, Water Res. 31 (1997) 85–94.
[6] S. Hara, Kami Pa Gikyoshi 57 (2003) 1018–1023.
[7] G.M. Normandeau, Pulp Paper Can. 104 (2003) 32–36.
[8] S. Raghuveer, IPPTA 14 (2002) 17–20.
[9] M. Bjoerklund, U. Germgard, P. Jour, A. Forsstroem, Appita J. 56 (2003) 200–205.
[10] K. Lindström, F. Österberg, Holzforschung 38 (1984) 201–212.
[11] NCASI. NCASI Technical Bulletin No. 253, 1971.
[12] C.-L. Chen, E.A. Capanema, H.S. Gracz, Agric. Food Chem. 51 (2003) 1932–1941.
[13] Tappi. T244 om-93, in Tappi Test Methods, Tappi Press, Atlanta, GA, USA, 1994.
[14] C.-L. Chen, in: C. Dence, S. Lin (Eds.), Methods in Lignin Chemistry, Springer-Verlag, Berlin/Heidelberg, 1992, pp. 465–472 (Chapter 7.6).
[15] C.-L. Chen, in: C. Dence, S. Lin (Eds.), Methods in Lignin Chemistry, Springer-Verlag, Berlin/Heidelberg, 1992, pp. 409–522 (Chapter 7.1).
[16] D.J. Bennett, C.W. Dence, F.-L. Kung, P. Luner, M. Ota, Tappi 54 (12) (1971) 2019–2026.
[17] R. Wang. Chemical Modification of Kraft Lignin and Resulting Surface-Active Properties, Ph.D. Thesis, North Carolina State University, Raleigh, North Carolina, USA, 1993.
[18] R. Wang, C.-L. Chen, J.S. Gratzl, Holzforschung 58 (2004) 622–630, 631–639.
[19] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671–698.