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

Part 1. Dechlorination of chlorophenols identified in E-1 effluent

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Abstract

Among the chlorophenols identified in the bleaching plant E-1 effluent, 4,5-chloroguaiacol (**2**), 3,4,5,6-tetrachloroguaiacol (**3**), 2,4,6-trichlorophenol (**4**) and 2,3,4,5-chlorophenol (**5**) were selected as model compounds for dechlorination at pH 7 and 10.5 in nitrogen- and oxygen-saturated aqueous solutions at 20 °C by ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses. The ArF* (193 nm) excimer laser photolysis was more effective than the KrF* (248 nm) excimer laser photolysis in dechlorinating **2**–**5**. The dechlorinations of **2**–**5** were determined to be first order reactions; first order with respect to total organically bound chlorine of substrate, first order overall. The efficiency of dechlorination was found to depend on the initial pH of reaction mixture, substituent pattern of **2**–**5**, and the wavelength of excimer laser radiation. The dechlorination rates of chlorinated guaiacols **2** and **3** were faster than the chlorinated phenols **4** and **5** under the same reaction condition while rate of **3** was faster than that of **2**. Furthermore, the dechlorination rate of a substrate increased with increasing initial pH. The dechlorination rates of chlorophenols investigated were almost the same in N_2- and O_2-saturated solutions. However, when 2% H_2O_2 per substrate was added to the initial reaction mixture of **5** in the ArF* (193 nm) excimer laser photolysis, the dechlorination rate increased considerably. Quantum yields (Φ) for the generation of chloride ions were determined for the ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses of **2**–**5** in both N_2- and O_2-saturated solutions. In general, the quantum yields in O_2-saturated solutions were slightly higher than the corresponding values in N_2-saturated solutions and was increased appreciably with addition of 2% H_2O_2.

Keywords: Pulp bleaching plant E-1 effluent; Advanced oxidation processes; ArF* and KrF* eximer laser photolyses; 193 and 248 nm photons; Dechlorination; Oxygen; Hydrogen peroxide; Kinetics

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1. Introduction

Very recently, Wang et al. characterized the E-1 effluent from bleaching of Loblolly kraft pulp with C_DEPDD sequence [1]. Color of the effluent was 13,000 Co–Pt units indicating that it contains considerable color carriers. The total solid of the effluent was 5.2 g l^{-1}, of which 3.2 and 2.0 g l^{-1} were organic and inorganic materials, respectively. The total chlorine content of the effluent was 912 mg l^{-1}, of which 667 and 268 mg l^{-1} were chloride (Cl^-) and organically bound chlorine (OCl), respectively. Approximately 5% of the OCl were present in the ether-extractable fraction. Thus, the majority of OCl was present in the high relative molecular-mass fraction that consisted of toxic ether-insoluble polychlorinated oxylignins [2,3]. The chlorophenols identified in the E-1 effluent included 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, 4-chloroguaiacol, 4,5-dichloroguaiacol, 3,4,5-trichloroguaiacol, 4,5,6-tri-chloroguaiacol and 3,4,5,6-tetrachloroguaiacol. Among the chlorophenols identified, 2,3,4,5-tetrachlorophenol and 4,5-dichloroguaiacol were the ma-

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jor components, while 4-chlorophenol and 4-chloroguaiacol were detected only in trace amount.

In the past two decades, considerable efforts have been made in adopting environmentally benign bleaching processes. However, the appreciable reduction in the discharge of potentially toxic chloro-organics is expected to be a long-term mission. Thus, it is important to develop viable industrial processes to decompose the potentially hazardous chloro-organics before the bleaching effluents are discharged into the environment. The limited ability of the conventional biological treatment systems to effectively decolorize and degrade the high molecular-mass chloro-organics has directed our attention to look for alternative waste water treatment technologies by photo-oxidative processes, known as, advanced oxidative processes (AOPs) [4]. Numerous investigations on the effectiveness of AOPs such as O_3/UV, H_2O_2/UV, TiO_2/UV for the wastewater treatment have been carried out. Potentials of photo-oxidative processes to degrade the high and low relative molecular-mass substances have been confirmed [1,5–7]. Furthermore, Thomas et al. investigated the dechlorination of 4-chlorophenol (**1**; see Fig. 1 for structure) by ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses, which were carried out in N_2- and O_2-saturated aqueous solutions [8,9]. At the higher starting substrate concentration (1.1×10^{-2} M), the average initial quantum yields (Φ) for the disappearance of **1** ($\Phi \approx 0.30$) and for the generation of chloride ions ($\Phi \approx 0.25$) were approximately the same for both the ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses. However, when the number of photons absorbed (n) became greater than approximately 3×10^{20}, more chloride ions (higher Φ) were generated by the former than by the latter. Oligomers were the major products for both excimer laser photolyses, but the quantity of oligomers generated was greater using the ArF* (193 nm) laser photolysis. With the KrF* (248 nm) excimer laser photolysis, an appreciable amount of hydroquninone was generated, whereas hydroqunone was not detected with the ArF* (193 nm) laser photolysis. In addition, an appreciable amount of 4-chlorocatechol was generated during the direct photolysis of **1** with either ArF* (193 nm) or KrF* (248 nm) excimer laser radiation. This is a new result for the photolysis of **1** at wavelength longer than 193 nm in the absence of added H_2O_2. At the lower starting substrate concentration (4.5×10^{-4} M), the average initial quantum yields for the disappearance of **1** ($\Phi \approx 0.55$) and for the generation of chloride ions ($\Phi \approx 0.45$) were much greater using the 193 nm radiation than 248 nm radiation ($\Phi \approx 0.20$ and 0.10, respectively). At the ArF* (193 nm) laser photolysis, oligomers were still the major products generated, but the fraction of oligomeric products generated was less than the fraction at the higher initial substrate concentration. This is the consistent with the fact that on ArF* (193 nm) laser photolysis of **1**, hydroqunone was generated in appreciable amount at lower substrate concentration, but did be not detected at higher substrate concentration. Grabowski observed that chloro- and bromophenols underwent carbon–halogen bond cleavage with hydroxyl group replacing the halogen atom in alkaline solution by irradiating with 313 nm radiation [10]. Omura and Matsuura found that the major pathway for dehalogenation of *p*-substituted halogenophenols in alkaline solution using 253.7 nm radiation was also carbon–halogen bond cleavage [11]. Crosby and Wong [12] and Yasuhara et al. [13] independently observed that **1** decomposed slowly with UV irradiation at 300–450 nm and $\lambda > 250$ nm, respectively. Boule et al. studied the direct potolysis at 254 and 296 nm of **1** in aqueous solution and determined the quantum yield (Φ) of approximately 0.40 for the disappearance of substrate. They found that this quantum yield was independent of (a) pH in the range of 1–13, (b) substrate concentration in the range of 1×10^{-2} to 2×10^{-4} M, (c) wavelength of radiation (254 and 296 nm) and finally (d) presence or absence of dissolved molecular oxygen. They also reported the quantum yield (Φ) of approximately 0.20 for the generation of chloride ions [14–16]. Jacob et al. used an Xe excimer emission lamp (172 nm) developed by Eliasson et al. [17] to study the oxidative degradation of **1** in aqueous solution at substrate concentration of 5×10^{-4} M in vacuum UV (VUV) region of the spectrum. They found at this short wavelength that the dominant pathway for the oxidation of **1** was its reaction with hydroxyl radicals ($HO^\bullet$) derived from the photolysis of water. The quantum yield (Φ) for the disappearance of substrate was determined to be 0.0068 [18]. Comparison of these results [10–18] with these of Thomas et al. [8,9] indicates the advantage of using an excimer laser radiation for the photolytic dechlorination of **1** with or without addition of oxidants such as hydrogen peroxide, but without addition of photocatalyst or additives.

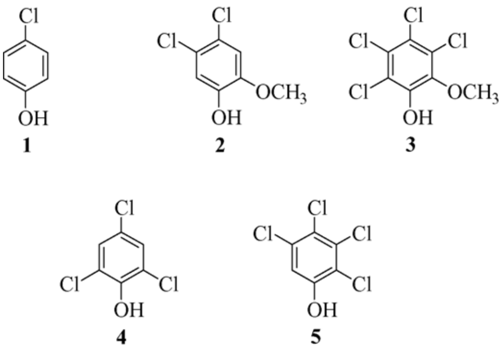

Fig. 1. Chlorophenols selected as model compounds.

Among the chlorophenols identified in the E-1 bleaching effluent, 4,5-chloroguaiacol (**2**), 3,4,5,6-tetrachloroguaiacol (**3**), 2,4,6-trichlorophenol (**4**) and 2,3,4,5-chlorophenol (**5**) were selected as model compound (see Fig. 1 for structure). These compounds have been identified as major constituents of chlorophenols in the E-1 effluent [1]. In addition, compound **4** is believed to be one of the main precursors for the formation of polychlorinated dibenzo-*p*-dioxin (PCDDs) and dibenzofurans (PCDFs) [19]. The compound is one of the major products formed in chlorination of residual lignin in pulp through side chain elimination of α-OH type lignin substructure [20]. Compounds **3** and **5** are among the most toxic compounds in the bleaching effluent [2]. There are very few data on the direct photolysis of chlorophenols **2**–**5** using deeper UV-radiation in monochromic form such as ArF* (193 nm) and KrF* (248 nm) eximer laser radiation applied in this investigation.

The objectives of the present investigation is to elucidate the optimum reaction conditions for the dechlorination of chlorophenols by ArF* (193 nm) and KrF* (248 nm) eximer laser photolyses. This will eventually lead to pave the way to developing an advanced oxidative processes technology for the dechlorination of toxic polychlorinated oxylignins (PCOLs) by the excimer laser photolyses.

2. Experimental

2.1. Model compounds

2,4,6-Trichlorophenol and 2,3,4,5-tetrachlorophenol were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI, USA, while 4,5-dichloroguaiacol and tetrachloroguaiacol from Helix Biotech. Corp., Toronto, Ont., Canada. These compounds were recrystallized from chloroform–petroleum ether.

2.2. ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses

The 193 nm radiation of an ArF* excimer laser (Lumonics Series TE-860-3, Lumonics Inc. Ontario, Canada) and the 248 nm radiation of a KrF* excimer laser (Lambda Phsyik LPX 300, Lambda Phsyik, Göttingen, Germany) were directed through the sample by using an appropriate 2 in. diameter, 45° flat 95% reflector (Acton Research Corp., Acton, MA, USA). The irradiations were carried out in a glass reactor having a 5 mm thick quartz window (Suprasil) and a side arm with a septum for sampling. The laser photolyses of chlorinated phenols were carried out under both oxygen and nitrogen saturated conditions with the starting solution having an initial substrate concentration of 2 mM. The reactor was filled with 200 ml of starting solution. 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 substrate concentration and Cl^- content.

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

The total chlorine content ($OCl + Cl^-$) of a reaction mixture was determined by the Schöniger combustion method [1,21,22] in combination with ion chromatograph, Dionrx 2010i (Dionrx Corp. Sunnyvale, CA, USA) equipped with an anion separator column AS-4 to analyze and quantify the Cl^- formed. The amount of inorganic chloride (Cl^-) in a reaction mixture was determined by the ion chromatograph, Dionrx 2010i. The OCl in a reaction mixture was then determined by subtracting the amount of inorganic chloride from the total chlorine content. The instrument was calibrated by using a standard solution of NaCl. For the AS-4 anion separator column, an eluent concentration of 2.2 mM Na_2CO_3/0.75 mM $NaHCO_3$ and a reagent concentration of 20–25 mN H_2SO_4 was used. Experimental error was ±2%.

2.4. Experimental errors

All experiment was conducted at least in triplicate. The experimental errors were then determined in term of accuracy, i.e., the average deviation (A.D.) 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: $\text{A.D.} = \text{a.d.}/n^{1/2}$.

3. Results and discussion

3.1. Factors affecting dechlorination of chlorinated phenols by laser photolysis

In the laser photolysis, 200 ml of 2 mM of chlorinated phenols radiation in N_2- or O_2-saturated aqueous solutions were irradiated with either ArF* (193 nm) or KrF* (248 nm) excimer laser up to 2 h individually with and without addition of a small amount of H_2O_2. The reactions were mostly carried out at an initial pH 10.5. The dechlorination was monitored by the quantitative analysis of chloride ion (Cl^-) formed during the laser photolysis. The factors affecting the dechlorination reaction are discussed below.

3.1.1. Effect of initial pH on dechlorination

The effect of initial pH in reaction mixture on dechlorination rate was studied with 4,5-dichloroguaiacol (**2**) using as a model. The formation rate of chloride anions (Cl^-) was determined in the AF* (193 nm) laser photolysis of **2** in N_2-saturated aqueous solutions with concentration of 2 mM at pH 7 and 10.5 on irradiation of 193 nm photons for 90 min (Fig. 2). A plot of $-\ln [\text{TOCl}]_t/[\text{TOCl}]_0$ as function of ArF* (193 nm) excimer laser irradiation time (t) gives a liner correlation, indicating that the dechlorination of **2** followed a first order law; first order with respect total organically bound chlorine (TOCl), first order overall. The dechlorination rate constant (κ) of **2** increased by approximately four-fold when the initial pH was increased from 7 to 10.5 ($1.55 \times 10^{-4}\ s^{-1}$ versus $6.45 \times 10^{-4}\ s^{-1}$; Table 1). Thus, the dechlorination of chlorophenols is a pH dependent reaction. The faster dechlorination rate at higher pH is attributable to the ionization of phenolic hydroxyl group. The mesomeric effect of the negative charged phenoxide anion results in higher electron density at carbons *ortho* and *para* to the phenoxide anion. Conse-

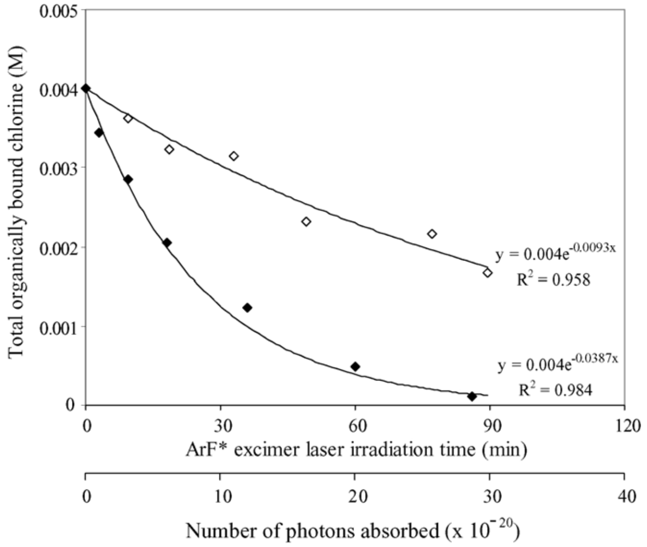

Fig. 2. Effect of initial pH on the dechlorination of 4,5-dichloroguaiacol (**2**) on the ArF* (193 nm) excimer laser photolysis at initial pH of 7 and 10.5, and at 20 °C in N_2-saturated solution. (◇) pH 7; (◆) pH 10.5.

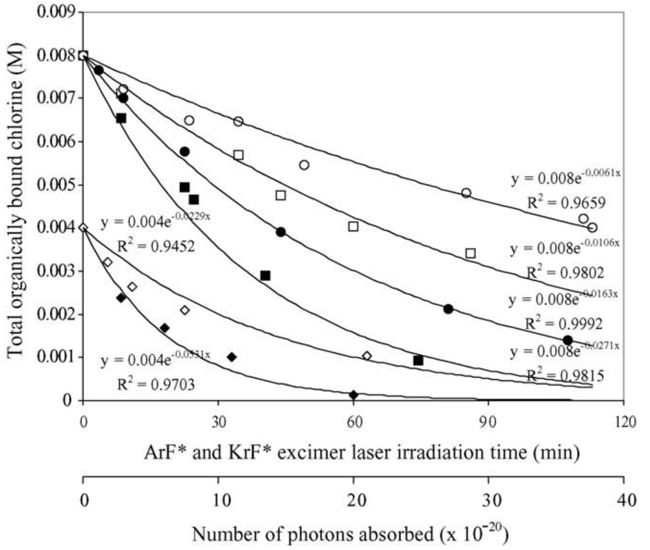

Fig. 3. Dechlorination of 4,5-dichloroguaiacol (**2**), 3,4,5,6-tetrachloroguaiacol (**3**) and 2,3,4,5-tetrachlorophenol (**5**) at pH 10.5 in O_2-saturated solution and 20 °C on the ArF* (193nm) and KrF* (248) excimer laser photolyses. (◆) **2** on ArF* excimer laser photolysis; (◇) **2** on KrF* excimer laser photolysis; (■) **3** on ArF* excimer laser photolysis; (□) **3** on KrF* excimer laser photolysis; (●) **5** on ArF* excimer laser photolysis; (○) **5** on KrF* excimer laser photolysis.

quently, phenoxide anions with chlorine substituents at these positions readily undergo heterolytic cleavage on absorbing the photons to give a carbene intermediate and chloride anion (Cl^-) on the photolysis. Alternatively, phenolic hydroxyl groups form hydrogen bond with water at low pH (<pK_a of the compound), which requires energy of about 5 Kcal/mol to be broken. As a result, the efficiency of photons on removing organically bound chlorine decreases. On the basis of this result, the dechlorination of **2**–**5** was carried out at the initial pH of 10.5.

3.1.2. *Effect of substituents on the reactivity of chlorinated phenols towards laser photolysis*

The dechlorination rates of chlorinated guaiacols (**2** and **3**) and chlorinated phenols (**4** and **5**) were different on both ArF* (193 nm) and KrF* (248 nm) photolyses (Figs. 3–6 and Table 1), in which the chlorinated guaiacols had faster dechlorination rates than the chlorinated phenols at pH 10.5 in both N_2- and O_2-saturated solutions. In the N_2-saturated solution, 4,5-dichloro-guaiacol (**2**) has the fastest dechlorination rate on irradiation of 193 nm photons, and 2,3,4,5-tetrachlorophenol (**5**) the slowest, with first order rate constant of $6.45 \times 10^{-4}\,s^{-1}$ versus $2.67 \times 10^{-4}\,s^{-1}$ (Table 1). Conceivably, the easiness in dechlorinating these chlorophenolics depends on the electronegativity and resonance effects of substituents. The faster dechlorination rates of the chloroguaiacols could be attributable to the presence of the methoxyl group *ortho* to the phenolic hydroxyl group in the

Table 1
Dechlorination reaction rate constants of chlorophenols **2**–**5** on ArF* (193 nm) and KrF* (248 nm) excimer laser irradiation[a,b,c]

Chlorophenols	N_2-/O_2-saturated Solution	Wavelength (nm)	k (s^{-1})	Coefficient of determination (R^2)
4,5-Dichloroguaiacol (**2**)	N_2	193	6.45×10^{-4}	0.9812
	N_2[d]	193[d]	1.55×10^{-4}	0.9428
	O_2	193	8.85×10^{-4}	0.9590
	O_2	248	3.82×10^{-4}	0.9194
3,4,5,6-Tetrachloroguaiacol (**3**)	N_2	193	4.25×10^{-4}	0.9925
	O_2	193	4.52×10^{-4}	0.9765
	O_2	248	1.77×10^{-4}	0.9674
2,4,6-Trichlorophenol (**4**)	N_2	193	3.10×10^{-4}	0.9957
2,3,4,5-Tetrachlorophenol (**5**)	N_2	193	2.67×10^{-4}	0.9966
	O_2	193	2.72×10^{-4}	0.9991
	O_2 + 2% H_2O_2	193	4.42×10^{-4}	0.9959
	N_2	248	1.13×10^{-4}	0.9854
	O_2	248	1.03×10^{-4}	0.9052

[a] Initial pH: 10.5.
[b] Initial concentration of starting substrate: 2 mM.
[c] Temperature: 20 °C.
[d] Initial pH: 7.0.

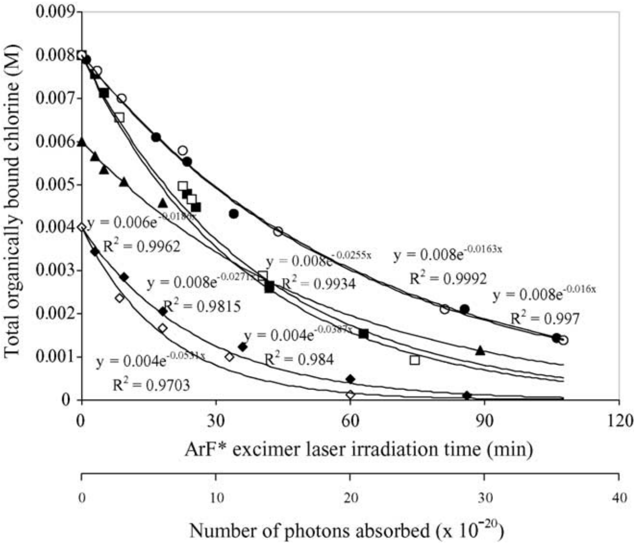

Fig. 4. Dechlorination of chlorophenols **2**–**5** at pH 10.5 in N_2- and O_2-saturated solutions at 20 °C on the ArF* (193 nm) excimer laser photolysis. (♦) **2** in N_2-saturated solution; (◊) **2** in O_2-saturated solution; (■) **3** in N_2-saturated solution; (□) **3** in O_2-saturated solution; (▲) **4** in N_2-saturated solution; (●) **5** in N_2-saturated solution; (○) **5** in O_2-saturated solution.

chloroguaiacols. The methoxyl group would contribute to stabilizing the delocalized phenoxyl radical species that are formed by single-electron-abstraction from the corresponding phenoxide anion species. As an electron-donating group, it would also contribute to increase in the nucleophilicity of aromatic ring. As a result, the electron density at the positions *para* and *ortho* (C-3 and C-5) to the methoxyl group would be increased, and the aromatic ring would be thus activated at these positions by lowering the electron binding energy level. In contrast to **5**, **3** has an activated positions not only at the positions *para* and *ortho* to the phenolic OH group, but also at the positions *para* and *ortho* to the OCH_3 group.

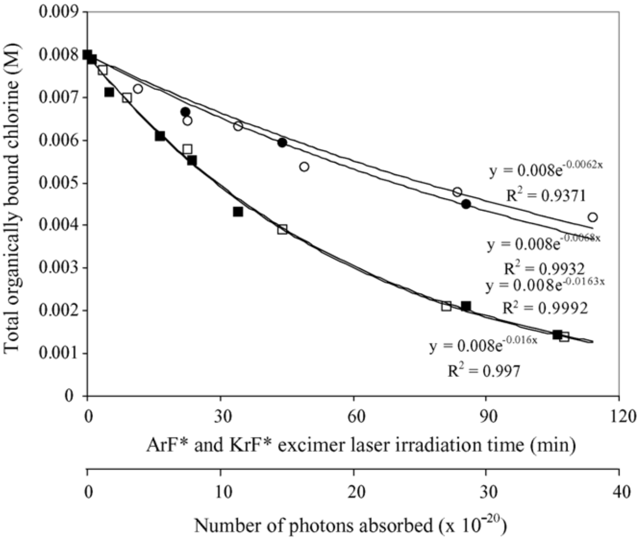

Fig. 5. Dechlorination of 2,3,4,5-tetrachlorophenol (**5**) at pH 10.5 in N_2- and O_2-saturated solution at 20 °C on the ArF* (193nm) and KrF* (248) excimer laser photolyses. (■) On ArF* excimer laser photolysis in the N_2-saturated; (□) on KrF* excimer laser photolysis in the O_2-saturated; (●) on ArF* excimer laser photolysis in the N_2-saturated; (○) on KrF* excimer laser photolysis in the O_2-saturated.

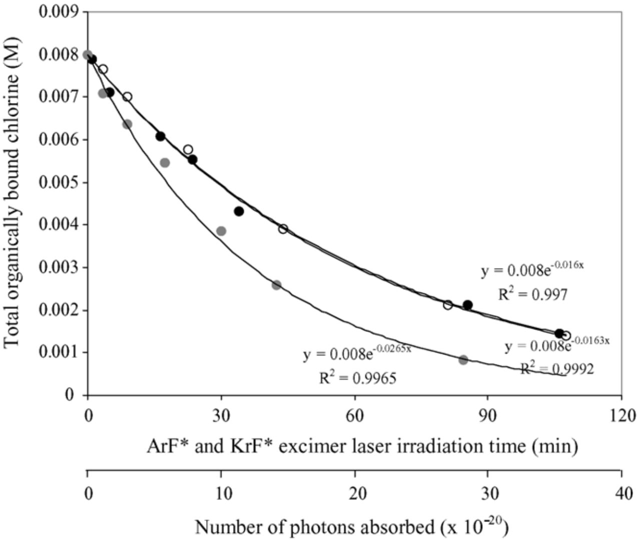

Fig. 6. Effect of hydrogen peroxide on the dechlorination of 2,3,4,5-tetrachlorophenol (**5**) at pH 10.5 in N_2-saturated solution, and with and without addition of 2% hydrogen peroxide per substrate in O_2-saturated solution at 20 °C on the ArF* (193nm) excimer laser photolysis. (●) **5** in N_2-saturated solution; (○) in O_2-saturated solution; (●) with addition of 2% hydrogen peroxide per substrate in O_2-saturated solution.

3.1.3. *Effect of photon source on dechlorination*

The dechlorination of 4,5-dichloroguaiacol (**2**), 3,4,5,6-tetrachloroguaiacol (**3**) and 2,3,5,6-tetrachlorophenol (**5**) proceeded at different rates on the laser photolysis with different photon sources, i.e., ArF* (193 nm) and KrF* (248 nm) laser radiation, in the O_2-saturated solution (Fig. 3). Based on the consumption of the same number of photons, dechlorination of these compounds was faster with the irradiation of 193 nm photons than with that of 248 nm photons. In addition, more organically bound chlorine (OCl) was converted to inorganic chloride (Cl^-) in the former than the latter (Table 2). This could be attributable to the fact that 193 nm photon has higher energy than 248 nm photon according to the Planck's equation $E = h\nu = hc/\lambda$. In addition to the excitation of ground state molecules to the excited S_1 state and the crossing of the S_1state to the T_1 state, the reaction rate of photo-oxidative degradation processes depends on the energy required to bring about homolytic cleavage of a given chemical bond.

The dechlorination could proceed via two pathways that are dependent on the energy of photons irradiated, i.e., radical and substitution pathways. In the radical mechanism, C–Cl bond undergoes homolytic cleavage by photo-dissociation through absorbing an appropriate photon source. In aqueous solution, the radical species produced by the photo-dissociation could recombine before they could escape from the solvent cage. Since the 193 nm photons have higher energy than 248 nm photons, they generate radical species

Table 2
Quantum yield for generation of chloride ions at 30 min of ArF* (193 nm) and KrF* (248 nm) excimer laser radiation irradiation under N_2- and O_2-saturated solutions[a,b,c,d]

Chlorophenols	N_2-/O_2-saturated solution	Wave-length (nm)	$[TOCl]_0$ (M)	$[TOCl]_{30}$ (M)	Chloride ions (Cl^-) generated (M)[e]	Quantum yield (Φ)
4-Chlorophenol (**1**)[f]	N_2	193	0.002	0.00055	0.00145	≈0.31
	O_2	193	0.002	0.00046	0.00154	≈0.33
4,5-Dichloroguaiacol (**2**)	N_2	193	0.004	0.00125	0.00275	≈0.59
	O_2	193	0.004	0.00081	0.00319	≈0.68
	O_2	248	0.004	0.00201	0.00199	≈0.43
3,4,5,6-Tetrachloroguaiacol (**3**)	N_2	193	0.008	0.00372	0.00428	≈0.92
	O_2	193	0.008	0.00355	0.00445	≈0.96
	O_2	248	0.008	0.00582	0.00218	≈0.47
2,4,6-Trichlorophenol (**4**)	N_2	193	0.006	0.00343	0.00257	≈0.55
2,3,4,5-Tetrachlorophenol (**5**)	N_2	193	0.008	0.00495	0.00305	≈0.66
	O_2	193	0.008	0.00491	0.00309	≈0.66
	$O_2 + 2\%\ H_2O_2$	193	0.008	0.00361	0.00439	≈0.94
	N_2	248	0.008	0.00652	0.00148	≈0.32
	O_2	248	0.008	0.00664	0.00136	≈0.29

[a] Initial pH: 10.5.

[b] Reaction temperature: 20 °C.

[c] Initial concentration of substrate: 2 mM.

[d] ArF* (193 nm) and KrF* (248 nm) excimer laser radiation irradiation of 30 min corresponds to absorption of 10×10^{20} 193 nm and 248 nm photons, respectively.

[e] Chloride ions generated (M) = $[TOCl]_0 - [TOCl]_{30}$.

[f] Adopted from [8,9].

with higher energy level and electron configuration that has higher energy to force their way out of the solvent cage before they undergo recombination. As expected, 193 nm photons brought about greater photo-dissociation of organically bound carbon–chlorine bond and higher quantum yield (Φ) for generation of chloride anions (Cl^-) than 248 nm photons in the O_2-saturated solution (Table 2). In the substitution mechanism, chlorine is substituted by hydroxyl radical ($HO^\bullet$). The hydroxyl radicals are generated by the photo-dissociation of water (HO–H), the solvent. Higher energy photons (193 nm) thus enhance photo-dechlorination reactions by enhancing photo-dissociation of both C–Cl and HO–H bonds.

The UV-spectra of the chlorinated phenols **2**–**5** showed that they have higher molar absorption coefficient in the region of 190–210 nm (at 193 nm, $\varepsilon = 3–3.3 \times 10^4$) than in the region of 250–260 nm (at 248 nm, $\varepsilon = 5–8 \times 10^3$) [23]. In the photochemical process, only the photons absorbed by the molecule will bring about the chemical reaction. When the wavelength of the photon source used is in the higher absorbency region of a substrate, the substrate will absorb the photon energy more efficiently to bring about chemical reactions.

3.1.4. Effect of oxidant on dechlorination

The relative dechlorination rates of the model compounds varied when the solutions were irradiated in the presence of oxidants. Approximately 90, 75 and 60 mol% of organically bound chlorine (OCl) in 4,5-dichloroguaiacol (**2**), 3,4,5,6-tetrachloroguaiacol (**3**) and tetrachlorophenol (**5**) were converted into inorganic chloride ions (Cl^-) from in both N_2- and O_2-saturated solutions (2 mM) at pH 10.5 by ArF* (193 nm) excimer laser photolysis for 60 min at 20 °C, respectively (Fig. 4). In addition to ArF* (193 nm) photolysis, dechlorination of **5** was also carried out by KrF* (248 nm) phtotolysis (Fig. 5). Only approximately 35 mol% organically bound chlorine (OCl) in **5** were converted into inorganic chloride ions (Cl^-) in both N_2- and O_2-saturated solutions by the KrF* (248 nm) photolysis for 60 min, which was much lower than that by the ArF* (193 nm) photolysis. The laser irradiation time of 60 min at 20 °C corresponded to the absorption of 20×10^{20} photons. No appreciable increase in the dechlorination rate of **3** and **5** was found when the ArF* (193 nm) photolysis was conducted in the O_2-saturated solution instead of in the N_2-saturated solution. At this time, no explanation can be offered for this finding. Further studies for the photochemical reaction mechanisms in the presence and absence of oxygen are required. However, the dechlorination rate for **2** increased appreciably, from 6.45×10^{-4} to $8.85 \times 10^{-4}\ s^{-1}$ when the ArF* (193 nm) photolysis was conducted in the O_2-saturated solution instead of in the N_2-saturated solution (Fig. 4 and Table 1). The possible pathway for the reactions of molecular oxygen with chlorinated phenols will be discussed in Section 3.4.

When 2% H_2O_2 per substrate was added to the O_2-saturated solution of **5** at pH 10.5, the dechlorination rate was appreciably increased from 2.72×10^{-4} to $4.42 \times 10^{-4}\ s^{-1}$ in the O_2-saturated solution (Figs. 6 and Table 1). In aqueous solution, H_2O_2 undergoes photolysis on absorbing appropriate photons, producing hydroxyl radicals ($HO^\bullet$). The photolysis rate of H_2O_2 (Eq. (1)) in aqueous solution was found to be pH dependent and increases with increasing pH [24,25]. Since the pK_a of H_2O_2 is 11.62, only approximately 7.8% of the H_2O_2 are dissociated at the initial stage of the reaction. Hydrogen peroxide is known to decompose by photo-induced dismutation reactions, Eqs. (2)–(4) [4].

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet} \quad (1)$$

$$H_2O_2 + HOO^- \xrightarrow{h\nu} H_2O + O_2 + HO^{\bullet} + e^- \quad (2)$$

$$HOO^- \xrightarrow{h\nu} {}^{\bullet}O^- + HO^{\bullet} \quad (3)$$

$$H_2O_2 + HO^{\bullet} \rightarrow HOO^{\bullet} + H_2O \quad (4)$$

Thus, the reactive oxygen radical species, such as hydroxyl and hydroperoxyl ($HO^{\bullet}$ and $HOO^{\bullet}$) radicals, were involved in promoting the dechlorination reaction. The hydroxyl radicals could first extract an electron from phenoxide anions to form phenoxyl radicals that would in turn form *ortho* and *para* (C-2, C-4, C-6) radical species via mesomerism. Coupling of these radical species with hydroxyl radicals ($HO^{\bullet}$) could result in removal of chloride anion (Cl^-) with concomitant formation of the corresponding quinones if these positions were substituted by chlorine. In the case of chloroguaiacols, coupling at C-2 with hydroxyl radicals ($HO^{\bullet}$) would result in ring cleavage to give the corresponding methyl ester. Hydroperoxyl radicals ($HOO^{\bullet}$) could be bifunctional: (1) inserting peroxyl bridge into aromatic ring resulting in ring cleavage and/or formation of enone structures, and (2) generating hydrogen atom ($H^{\bullet}$) by losing one oxygen molecule, which recombines with the aromatic radical species ($R^{\bullet}$). Both possibilities could prevent the recombination between $Cl^{\bullet}$ and $R^{\bullet}$.

3.2. *Kinetics of laser photolysis of model compounds*

No matter which pathway the reaction follows, the kinetic of the dechlorination of chlorophenols **1**–**5** by either ArF* or KrF* excimer laser photolysis can be expressed as follows:

$$\mathrm{TOCl} \xrightarrow{k} x\mathrm{Cl}^- + (\mathrm{TOCl} - x\mathrm{Cl}) \quad (5)$$

$$\frac{\mathrm{d}[\mathrm{TOCl}]}{\mathrm{d}t} = -k[\mathrm{TOCl}] \quad (6)$$

$$\ln[\mathrm{TOCl}] = -kt \quad (7)$$

where TOCl is the initial total organically bound chlorine (TOCl) content of a substrate in the system, (TOCl − xCl) is the total organically bound chlorine content in the dechlorinated substrate at the irradiation time of t, and $x\mathrm{Cl}^-$ is the amount of chloride anions generated at the irradiation time of t. It can be assumed that dechlorination of the substrate occurs on absorbing the appropriate photon-energy. Consequently, the dechlorination reaction must follow first order reaction law, first order with respect to the TOCl of substrate, first order overall. This was verified by plotting $-\ln[\mathrm{TOCl}]_t/[\mathrm{TOCl}]_0$ versus irradiation time (t). All the compounds investigated gave a linear relationship between $-\ln[\mathrm{TOCl}]_t/[\mathrm{TOCl}]_0$ and excimer laser radiation irradiation time t whether they were irradiated with ArF* or KrF* eximer laser radiation under either N_2 or O_2-saturated solution with the coefficient of determination (R^2) larger than 0.90 (Table 1). The first order rate constants k thus calculated from the plots are dependent on the number and type of chlorine substituents on the aromatic ring. It can be observed that the chlorophenols with guaiacol structure have greater dechlorination rate constants than the chlorophenols with phenol structure. Within a same system, the one with more chlorine substituent has a smaller dechlorination rate constant.

3.3. *Quantum yield of chloride ion formation*

Not every photon absorbed is effective in bringing about dechlorination. The efficiency of a photochemical process is defined by the quantum yield of the product. Quantum yield (Φ) is used to estimate the efficiency of the photon energy absorbed. In the dechlorination reaction, quantum yield (Φ) of dechlorination is the mole number of chloride anions (Cl^-) generated when the substrate absorbs one mole of photons. If the quantum yield (Φ) of a product is finite and invariant with the changes in experimental conditions, then it is likely that the product is formed in a primary rate determining process. Since the conversion of organically bound chlorine (OCl) to inorganic chloride ion (Cl^-) versus number of photons irradiated is not a straight line (Figs. 2, 4, and 6), the quantum yield (Φ) for chloride ion generated is not linear. At the irradiation times of 30, 60, 90, and 120 min, the number of both 193 and 248 nm photons absorbed are 10, 20, 30 and 40×10^{20}, respectively. Thus, the dechlorination is conceivably a complex reaction. It depends on the structure of the compounds and the chemical environment of the C–Cl bond. The quantum yields (Φ) for generation of chloride ions (Cl^-) at the ArF* and KrF* laser radiation irradiation time of 30 min are summarized in Table 2. At the same initial concentration (2 mM), the quantum yield (Φ) of substrates increases with increasing initial total organically bound chlorine $[\mathrm{TOCl}]_0$ of the substrates investigated (Table 2). This implies that the quantum yield (Φ) increases with number of chlorine substituents in benzene ring. However, 3,4.5,6-tetrachloroguaiacol (**3**) has higher quantum yield (Φ) than that of 2,3,4,5-tetrachlorophenol (**5**) although they have the same amount of $[\mathrm{TOCl}]_0$. Conceivably, this is caused by the fact that the former has a methoxyl group *ortho* to phenolic hydroxyl group and *ortho* and *para* to chlorine substiuents at C-3 and C-5. In addition, the quantum yields are slightly higher in O_2-saturated solution than in N_2-saturated solution under the same reaction condition, except for **5**, which are almost the same. This indicates that presence of oxygen in the reaction system does not affect dechlorinating the substrate appreciably. When H_2O_2 (2% on amount of substrate) was added to the 2 mM solution of **5**, in O_2-saturated solution, the quantum yield (Φ) increased from ≈0.66 to ≈0.94, indicating involvement of radical chain reactions. Hydrogen peroxide undergoes excimer laser photolysis to produce reactive oxygen radical species such as hydroxyl and hydroper-

Table 3
Dechlorination reaction rate constants for 4,5dichloroguaiacol (**2**), dechlorination of 2,4,6-trichlorophenols (**4**), and 2,3,4,5-phenol (**5**) by UV-photolysis with 254 nm photons with and without added oxidants, and with addition of hydrogen peroxide and ozone[a,b,c]

Chlorophenols	N_2-/O_2-saturated solution	Oxidants	k (s^{-1})	Coefficient of determination (R^2)
4,5-Dichloroguaiacol (**2**)	N_2	None	1.8×10^{-4}	0.9967
	O_2	None	1.5×10^{-4}	0.9987
	N_2	2% H_2O_2[d]	1.65×10^{-4}	0.9981
2,4,6-Trichlorophenol (**4**)	N_2	None	0.6×10^{-4}	0.9953
	O_2	None	0.92×10^{-4}	0.956
	N_2	100% H_2O_2[d]	0.45×10^{-4}	0.9806
2,3,4,5-Tetrachlorophenol (**5**)	N_2	None	0.42×10^{-4}	0.9444
	O_2	None	0.23×10^{-4}	0.9823
	N_2	2% H_2O_2	0.45×10^{-4}	0.9665

Ozone stream of with ozone concentration of 4.5% with flow rate of 50 ml/min, corresponding to ozone charge of 0.1 mmol/min.

[a] Data adopted from [7].

[b] Low pressure mercury lamp emits 254 nm photons over 90% of its radiation is used.

[c] Substrate solution: 400 ml with concentration of 0.5 mM in 0.1 M NaOH, corresponding to 0.2 mmol substrate.

[d] Hydrogen peroxide charge on substrate in weight.

oxyl radicals ($HO^\bullet$ and $HOO^\bullet$), by which the substrate undergoes oxidative dechlorination as discussed in the previous section.

3.4. Comparison of the dechlorinating some of the chlorophenols by ArF (193 nm) and KrF* (248 nm) excimer laser photolyses and by UV-photolysis with 254 nm radiation*

Very recently, Wang et al. investigated the dechlorination of 4,5-dichloroguiacol (**2**), 2,4,6-trichlorophenol (**4**) and 2,3,4-5-tretrachlorophenol (**5**) with UV-photolysis using 254 nm radiation that was emitted from a low pressure mercury lamp over 90% of its radiation [7]. The rate constants for declorination of **2**, **4** and **5** in the N_2-saturated alkaline solution in the UV-photolysis using 254 nm radiation are 1.8×10^{-4}, 0.6×10^{-4} and $0.42 \times 10^{-4}\,s^{-1}$, respectively (Table 3). Similarly, the corresponding rate constants of these compounds in the O_2-saturated alkaline solution under the same condition are 1.5×10^{-4}, 0.92×10^{-4} and $0.23 \times 10^{-4}\,s^{-1}$, respectively (Table 3). For the ArF* (193 nm) excimer laser photolysis, the declorination rate constants of **2**, **4**, and **5** in the N_2-saturated alkaline solution are 6.45×10^{-4}, 3.10×10^{-4} and $2.67 \times 10^{-4}\,s^{-1}$, respectively, while the corresponding rate constants for **2** and **5** in O_2-saturated alkaline solution are 8.85×10^{-4}, and $2.72 \times 10^{-4}\,s^{-1}$, respectively (Table 1). In addition, the rate constant of **5** in the UV-photolysis using 254 nm radiation in N_2-saturated alkaline solution with addition of 2% hydrogen peroxide per substrate is $0.45 \times 10^{-4}\,s^{-1}$. In comparison, the rate constant of **5** in the ArF* (193 nm) excimer laser photolysis is $2.72 \times 10^{-4}\,s^{-1}$ in O_2-saturated alkaline solution with addition of 2% hydrogen peroxide per substrate. Thus, the results indicate that the ArF* (193 nm) and KrF* (248 nm) excimer laser photolyses are in general more effective in dechlorinating chlorophenols than the UV-photolysis using 254 nm radiation.

4. Conclusions

ArF* (193 nm) excimer and Kr* (248 nm) excimer laser proteolyses of 4,5-chloroguaiacol (**2**), 3,4,5,6-tetrachloroguaiacol (**3**), 2,4,6-trichlorophenol (**4**) and 2,3,4,5-chlorophenol (**5**) were carried out in the aqueous solution at pH 7 and 10.5 in N_2- and O_2-saturated solutions at 20 °C. The dechlorination reaction is, in general, a first order reaction; first order with respect to the total organically bound chlorine of substrate, first order overall. The efficiency of dechlorination was found to be depending on substituents, initial pH of the reaction mixture and wavelength of excimer laser radiation. The optimum condition was found to be initial pH of 10.5 in O_2-saturated solution at 20 °C by ArF* (193 nm) excimer laser photolysis.

The dechlorination rate of chlorinated guaiacols were faster than the corresponding chlorinated phenols because of an additional methoxyl group substituted *ortho* to phenolic hydroxyl group. In contrast, the dechlorination rate of 3,4,5,6-tetrachloroguaiacol (**3**) was faster than that of 4,5-chloroguaiacol (**2**). Both methoxyl and chlorine substituents are electron-donating group, contributing to stabilize the delocalized phenyl radical species formed by single-electron-transferring oxidation upon the irradiation of exciter laser radiation. Furthermore, the dechlorination rate of a substrate increased with increasing pH, because the dissociation of phenolic hydroxyl groups produce the corresponding phenoxide anion species at alkaline pH, which readily undergo single-electron-transferring oxidation more than the corresponding undissociated phenolic hydroxyl groups. In addition, the ArF* (193 nm) excimer laser photolysis is more effective than the KrF* (248 nm) excimer laser photolysis in dechlorinating the chlorinated phenols. The chlorophenols absorb more readily the 193 nm photons than the 248 nm photons. The dechlorination rates of chlorophenols investigated are almost the same under N_2- and O_2-saturated solutions. However, when 2% H_2O_2 per substrate was added to the initial O_2-saturated solution of **5**, the dechlorination rate increased considerably. Furthermore, the efficiency for dechlorinating **2**, **4** and **5** by the UV-photolysis using 254 nm radiation was compared with those by the ArF* (193 nm) exciter and KrF* (248 nm) exciter laser photolyses. The results showed that the latter two were more effective than the former in dechlorinating chlorophenols both in N_2- and O_2-saturated alkaline solutions.

On the basis of these results, the optimum reaction conditions for dechlorination of the toxic ether-insoluble high relative mass polychlorinated oxylignins are determined. The polychlorinated oxylignins should be dechlorinated by irradiation with ArF* (193 nm) excimer laser photolysis at pH 10.5 in O_2-saturated solution at 20 °C with addition of 2% H_2O_2 per polychlorinated oxylignins or more.

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