A Comparative Study of Chlorophenols Photolysis Using XeBr and KrCl Excilamps

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***Abstract*—The direct photolysis of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) in aqueous solution at different initial pH values using UV XeBr (282 nm) and KrCl (222 nm) excilamps has been studied. The highest photolysis rates and quantum yields were found for 4-CP molecules, 2-CP and 2,4-DCP anions when irradiated by XeBr excilamp.**

The maximum removal efficacy of 2-CP and 2,4-DCP molecules with the lowest UV doses of absorbed energy was achieved using KrCl excilamp, whereas the lower doses for photolysis of 2-CP and 2,4-DCP anions were required for XeBr excilamp. The contrary dependence was found for 4-CP molecules and anions.

***Index Terms*—Aqueous solution, chlorophenols, direct photolysis, ultraviolet excilamp.**

I. INTRODUCTION

Chlorophenols (CPs) are known hazardous chemicals included by the U.S. EPA in the list of 126 Priority Pollutants [1]. CPs are currently used for a wide range of domestic, agricultural and industrial purposes [2], [3]. For example, *2-chlorophenol (2-CP)* is used in the production of azodyes and vulcanization accelerators. *4-chlorophenol (4-CP)* is a raw material for diaminoanthraquinon synthesis and is used as a refining solvent, a disinfectant, a denaturant and an antifungal agent. The principal use of *2,4-dichlorophenol (2,4-DCP)* is as an intermediate in the manufacture of 2,4-D and other herbicides. Once released into the aquatic ecosystem, CPs may cause severe environmental contamination problems because of their toxicity to organisms, potential carcinogenic and mutagenic activity, and low threshold levels causing odor and taste in water up to 0.1 ppb [4]. Due to the ubiquitous presence of CPs in the aquatic environment and their toxic properties, understanding the mechanisms of photochemical degradation of these compounds is critically important. The UV radiation is widely applied in advanced oxidation technologies of CPs removal from water and wastewater [3]. The low- and medium-pressure mercury lamps have been traditionally used as UV sources. Nowadays, one of the most promising UV sources for water treatment are modern mercury-free excimer and exciplex lamps, emitting UV radiation in a narrow emission band [5], [6]. Earlier, the efficacy of photolysis of phenol, 4-CP, 4-bromophenol [7] and methylated phenols in aqueous solution [8] was shown using KrCl (222 nm), XeBr (282 nm) and XeCl (308 nm) excilamps. It was found, that the degradation of 2,4-D occurs more efficiently in the case of KrCl and XeBr excilamps in comparison with XeCl excilamp and mercury lamp [9]. More recently, the kinetics of 4-CP photolysis at initial pH value by KrCl excilamp was studied [10]. It was shown that the KrCl excilamp can facilitate higher 4-CP removal efficacies than the enzyme (soybean peroxidase) [11].

The present study compares the efficacy of direct photolysis of 2-CP, 4-CP and 2,4-DCP in aqueous solution under different pH values using XeBr and KrCl excilamps.

II. MATERIALS AND METHODS

A. Reagents

2- and 4-chlorophenol, 2,4-dichlorophenol (purity >98%) were purchased from Merck. 4-aminoantipyrene and potassium ferricyanide (purity 99%) were obtained from Sigma-Aldrich.

B. Materials

Two barrier-discharge excilamps (purchased from Institute of High Current Electronics SB RAS, Russia) were used as UV sources in the photolysis experiments. These were XeBr and KrCl excilamps, emitting mainly at 282 and 222 nm, respectively [5], [6].

C. UV Treatment Procedure

All photolysis experiments were run in a magnetically stirred glass reactor (diameter 5 cm, height 3.2 cm) containing 20 cm^3 of chlorophenol solution at initial concentration of 20 $mg \cdot L^{-1}$ and initial pH of 5.4–5.7. The initial pH values of 2 and 11 were preliminary adjusted by H_2SO_4 (4.6×10^{-3} M) and NaOH (2.5×10^{-4} M). Before irradiation the upper air-opened part of reactor was placed directly under an UV output window of excilamp. The solutions were irradiated at room temperature 23±2 °C under static conditions. The UV intensity of excilamps was measured with a H8025-222 photodetector (Hamamatsu Photonics KK) and was tested using an electrochemical actinometer, as described in [12]. The UV intensities of XeBr and KrCl excilamps delivered to the solution were 6.6 and 2.3 $mW \cdot cm^{-2}$, respectively.

D. Analytical methods

The residual 2- and 4-CP concentrations were determined by colorimetric method using a reaction with

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4-aminoantipyrene [13], [14]. The 2,4-DCP concentration was measured by HPLC employing a Milichrom A-02 chromatograph with UV detector and ProntoSIL-120-5-C18 AQ (2 mm × 75 mm) column. The mobile phase was a mixture of acetonitrile and water (1:1 v/v) with a flow rate of 150 μL·min^{-1}. The UV absorbance spectra were recorded using a spectrophotometer Agilent 3843 UV-VIS. The pH was measured using an ion meter I-16.

III. RESULTS AND DISCUSSION

A. Comparison of Photolysis Rates and Quantum Yields

Fig. 1 shows the CPs photolysis profiles as residual and initial concentration ratio [chlorophenol]/[chlorophenol]$_0$ versus treatment time. They reasonably fit a pseudo-first order law, as in previous studies [3], [15], [16]. The calculated first order rate constants and half-lives are shown in Table II. The highest photolysis rates and lowest half-lives were found for 2-CP and 2,4-DCP photolysis by XeBr excilamp (282 nm) at pH 11. The same was observed for 4-CP at pH 2 and initial pH (5.7).

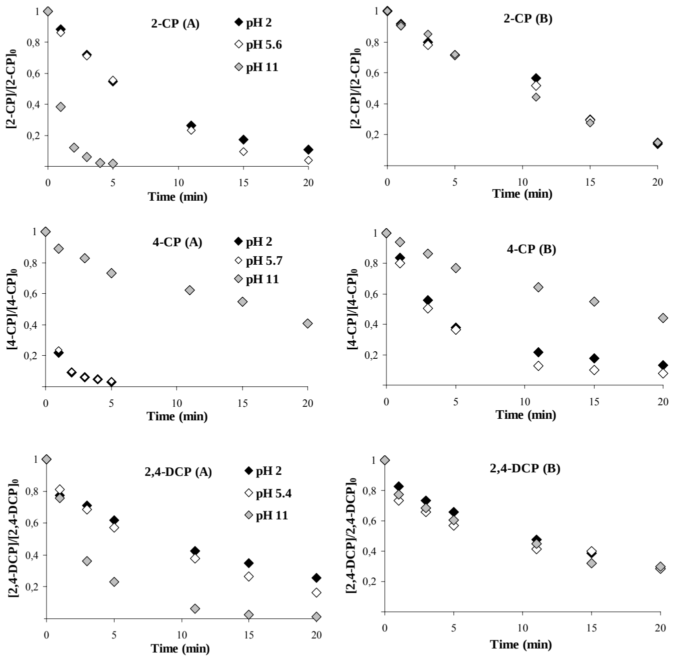


Fig. 1 Evolution of normalized chlorophenols concentration as function of treatment time at different initial pH values using XeBr excilamp (A) and KrCl excilamp (B).

TABLE I
SPECTRAL CHARACTERISTICS OF CHLOROPHENOLS

Chlorophenol	λ_{max}, nm	pH$_{initial}$	Form	$\varepsilon_{\lambda max}$, M^{-1}·см$^{-1}$
2-CP	223	2 and 5.6	Molecular	3788
	274	2 and 5.6	Molecular	1958
	237	11	Anionic	8242
	293	11	Anionic	3733
4-CP	225	2 and 5.7	Molecular	8599
	280	2 and 5.7	Molecular	1609
	244	11	Anionic	12056
	298	11	Anionic	2599
2,4-DCP	225	2 and 5.4	Molecular	6099
	284	2 and 5.4	Molecular	2062
	245	11	Anionic	9726
	305	11	Anionic	3654

It is known, that CPs are weak acids and partially dissociate in aqueous media. CPs present mainly in the molecular form at pH < pK$_a$ (8.1–9.4 for compounds studied) and in the dissociated form (anions) at pH > pK$_a$ [17]. Furthermore, the dissociated forms are considered to be more reactive than molecular ones [15]. As shown in Table I, the bathochromic shift of absorbance maximum bands in the medium- and long-wave UV spectral range is observed at pH 11 that indicates the anionic forms formation. We propose that the radiation at 282 nm might be absorbed effectively by low-energy electronically excited states of 4-CP molecules and 2-CP and 2,4-DCP anions, resulting in cleavage of the C-Cl, O-H and C-C bonds.

In order to compare our results with the literature data, the quantum yields of degradation were calculated from spectroscopic measurements of the absorption bands. Quantum yield of first-order degradation with monochromatic radiation for the direct photolysis can be calculated using the following equation [18], [19]:

$$\varphi = \frac{k}{2.303 I_\lambda \varepsilon_\lambda l} \tag{1}$$

where k (min^{-1}) is the pseudo-first order rate constant, φ is the quantum yield, I_λ (Einstein^{-1}·L^{-1}·min^{-1}) is the radiation intensity at wavelength λ, ε_λ (cm^{-1}·M^{-1}) is the molar absorption coefficient at wavelength λ, and l (cm) is the cell path length.
This equation is applicable for the excilamps used, as their emission half width does not exceed 1 nm.

TABLE II
THE PSEUDO-FIRST ORDER RATE CONSTANTS k, HALF-LIVES $t_{1/2}$ AND QUANTUM YIELDS φ OF CHLOROPHENOLS PHOTOLYSIS BY XeBr (282 nm) AND KrCl (222 nm) EXCILAMPS.

Chlorophenol	pH$_{initial}$	λ, nm	ε_λ, M^{-1}·см$^{-1}$	k, min^{-1}	t$_{1/2}$, min	φ
2-CP	2	222	4288	$8.5 \cdot 10^{-2}$	8.1	0.034
	5.6	222	4253	$8.5 \cdot 10^{-2}$	8.2	0.034
	11	222	4860	$8.7 \cdot 10^{-2}$	7.9	0.031
	2	282	1519	$1.1 \cdot 10^{-1}$	6.1	0.036
	5.6	282	1498	$1.5 \cdot 10^{-1}$	4.5	0.049
	11	282	2440	$9.0 \cdot 10^{-1}$	0.8	0174
4-CP	2	222	7662	$1.5 \cdot 10^{-1}$	4.6	0.034
	5.7	222	8185	$1.9 \cdot 10^{-1}$	3.6	0.041
	11	222	4739	$4.0 \cdot 10^{-2}$	17.0	0.015
	2	282	1436	$8.0 \cdot 10^{-1}$	0.9	0.264
	5.7	282	1545	$7.9 \cdot 10^{-1}$	0.9	0.241
	11	282	1458	$4.3 \cdot 10^{-2}$	16.1	0.014
2,4-DCP	2	222	6575	$6.6 \cdot 10^{-2}$	10.4	0.017
	5.4	222	6293	$6.8 \cdot 10^{-2}$	10.2	0.019
	11	222	4677	$6.9 \cdot 10^{-2}$	10.0	0.026
	2	282	2091	$6.7 \cdot 10^{-2}$	10.4	0.015
	5.4	282	1979	$9.1 \cdot 10^{-2}$	7.6	0.022
	11	282	1114	$1.8 \cdot 10^{-1}$	3.8	0.077

In Table II the φ values for 2-CP anions and 4-CP molecules at 282 nm (φ_{282}) were significantly higher than those found for 2-CP molecules and 4-CP anions. The φ_{282} for 2,4-DCP anions was also higher than that for its molecules. This is in good agreement with literature data on the 2-CP photolysis at 296 nm (φ = 0.03–0.04 for molecules and 0.20–0.30 for anions) [15], [20], [21], also on the 2,4-DCP photolysis (φ = 0.01–0.02 for molecules and 0.10 for anions) [22], [23].

As in [20], the average quantum yield of 4-CP photolysis is 0.25 in the pH range from 1 to 13 when irradiated at a wavelength of 254 or 296 nm (medium- and high-pressure mercury lamps). As can be seen from Table II, the φ_{282} for 4-CP molecules was comparable with the higher mentioned value, whereas φ_{222} was one order of magnitude lower and comparable with φ (0.017), found earlier for 4-CP molecules photolysis by high-pressure mercury lamp, emitting in the broad spectrum of 238–579 nm with maximum emission bands at 254, 313 and 366 nm [24].

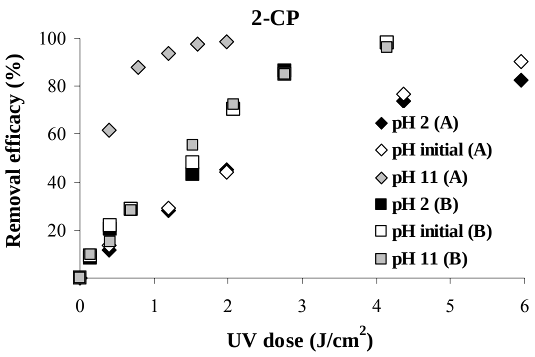
The lowest φ values were found for 4-CP anions degradation. The wavelength of 282 nm is very close to the long-wave maximum absorbance band of 4-CP molecules (280 nm), caused by the electronic transition $S_0 \rightarrow S_2$ ($\pi\sigma^*$), partially localized at C-Cl bond [25]. Therefore, when excited with a light at 282 nm, the Cl atom should be easily detached from the 4-CP aromatic ring with a formation of hydroquinone and *p*-benzoquinone as two main intermediates causing yellow-coloring of solution. This was also confirmed by GC/MS analysis in our previous work [16]. The decreased rates of photolysis of 2-CP and 2,4-DCP molecules in comparison with 4-CP molecules may be explained by the intermolecular hydrogen bonding between the *ortho*-positioned Cl atom and a hydrogen from the hydroxyl group. Additionally, hydrogen bonds may be formed internally between Cl and OH as well as externally between 4-CP molecule and water [15].

The direct photolysis of 2-CP anions and 4-CP molecules using KrCl excilamp (222 nm) achieved lower quantum yield than that using XeBr excilamp (282 nm). Although the radiation at 222 nm is in the range of short-wave maximum absorbance bands, there were relatively low quantum yields and photolysis rates, suggesting that the electronic transitions from high energy electronically excited did not lead directly to the bonds opening, but to another processes, e.g., nonradiative energy dissipation.

Thus, under the experimental conditions used, the rates of photolysis by XeBr and KrCl excilamps were found to be increased in the order: 2,4-DCP < 2-CP < 4-CP for molecules (pH 2 and 5.4–5.7) and 4-CP < 2,4-DCP < 2-CP for anions (pH 11). The maximum photolysis rates (and shorter treatment times to totally degrade a compound) were observed for 4-CP molecules and 2-CP and 2,4-DCP anions using XeBr excilamp (282 nm).

B. Comparison of UV doses

In Fig. 2 the removal efficacy of CPs are plotted versus fluence or UV dose (J·cm^{-2}). It can be seen, that the maximum removal efficacy of 2-CP and 2,4-DCP molecules (at pH 5.4–5.6 and 2) with the lowest required doses was achieved when using KrCl excilamp. This finding is in agreement with previously reported data on the direct photolysis of 4-CP molecules at initial pH value and higher initial concentrations without stirring [26]. By contrast, from our experimental data, the XeBr excilamp required lower doses for complete degradation of 4-CP molecules (at pH 2 and 5.7). The same result was obtained for degradation of 2-CP and 2,4-DCP anions (pH 11).



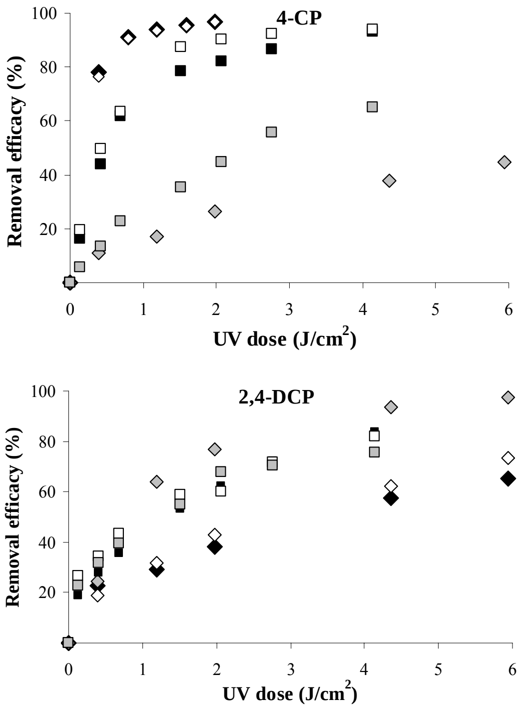


Fig. 2 Chlorophenols removal efficacy as function of UV dose at different pH values using XeBr excilamp (A) and KrCl excilamp (B).

IV. CONCLUSION

The present study demonstrates the high potential of modern UV excilamps for removal of chlorophenols from aqueous media by direct photolysis. The degradation of these compounds using excilamps in advanced oxidation processes is proposed to be carried out in further investigations.

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