

# The Effect of Wavelength and pH on the Direct Photolysis of Chlorophenols by Ultraviolet Excilamps

Galina Matafonova, Natalya Philippova, and Valeriy Batoev

**Abstract**—The effect of wavelength and pH on the direct photolysis of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) in aqueous solution was studied by UV XeBr (282 nm) and KrCl (222 nm) excilamps. The highest pseudo-first order rate constants and quantum yields were found for molecular form of 4-CP (at pH 2 and 5.7) and anionic forms of 2-CP and 2,4-DCP (at pH 11) when irradiated by XeBr excilamp.

The maximum removal efficiency of molecular 2-CP and 2,4-DCP with the lowest UV dose of absorbed energy was observed using KrCl excilamp. On the contrary, the XeBr excilamp needed the lowest dose ( $\sim 2 \text{ J}\cdot\text{cm}^{-2}$ ) for complete degradation of molecular 4-CP and anionic 2-CP. The highest removal efficiency of anionic 4-CP (65%) was achieved when using KrCl excilamp.

**Index Terms**—Aqueous solution, chlorophenols, direct photolysis, degradation, excilamp, UV dose.

## I. INTRODUCTION

Chlorophenols (CPs) are well-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 a synthesis of diaminoanthraquinone 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. Ultraviolet (UV) radiation is widely applied in advanced oxidation

technologies of CPs removal from water and wastewater [3]. Low- and medium-pressure mercury lamps have been traditionally used as UV sources. Currently, one of the most promising UV sources for water treatment are modern mercury-free excimer and exciplex lamps, which emit UV radiation in a narrow emission band [5], [6]. In our previous work [7] 2-CP, 4-CP and 2,4-DCP were degraded at initial pH values of their aqueous solutions by direct UV photolysis using XeBr excilamp. Recently, the kinetics of 4-CP photolysis at initial pH value by KrCl excilamp was studied [8]. It was shown that the KrCl excilamp can facilitate higher 4-CP removal efficiencies than the enzyme (soybean peroxidase) [9].

The aim of this study was to study the effect of wavelength and pH on the direct photolysis of 2-CP, 4-CP and 2,4-DCP in aqueous solution using XeBr and KrCl excilamps.

## II. MATERIALS AND METHODS

### A. Reagents

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

### B. Materials

Two barrier-discharge excilamps (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<sup>3</sup> of chlorophenol solution at initial concentration of 20 mg·L<sup>-1</sup> and pH of 5.4–5.7. The initial pH of 2 and 11 were preliminarily adjusted by H<sub>2</sub>SO<sub>4</sub> ( $4.6 \times 10^{-3}$  M) and NaOH ( $2.5 \times 10^{-4}$  M). Before irradiation the upper part of the reactor, which was an open system, was placed directly under an UV output window of excilamp. The solutions were irradiated at room temperature  $23 \pm 2$  °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 [10]. The UV intensities of XeBr and KrCl excilamps delivered to the solution were 6.6 and 2.3 mW·cm<sup>-2</sup>, respectively.

Manuscript received December 29, 2010.

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#### D. Analytical methods

The residual 2- and 4-CP concentrations were determined by colorimetric method using a reaction with 4-aminoantipyrene [11], [12]. 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  $\mu\text{L}\cdot\text{min}^{-1}$ . The UV absorbance spectra were recorded using an Agilent 3843 UV-VIS spectrophotometer. The pH was measured using an I-16 ion meter.

### III. RESULTS AND DISCUSSION

#### A. Comparison of Photolysis Rates and Quantum Yields

Fig. 1 shows the photolysis profiles as residual and initial concentration ratio [chlorophenol]/[chlorophenol]<sub>0</sub> versus treatment time. The profiles reasonably fit a pseudo-first order law, as in previous studies [3], [7], [13], [14]. The calculated first order rate constants and half-lives are presented in Table II. The highest photolysis rates and lowest half-lives were found with the XeBr excilamp (282 nm) at pH 11 for 2-CP and 2,4-DCP and at pH 2 and 5.7 for 4-CP (Fig. 1).

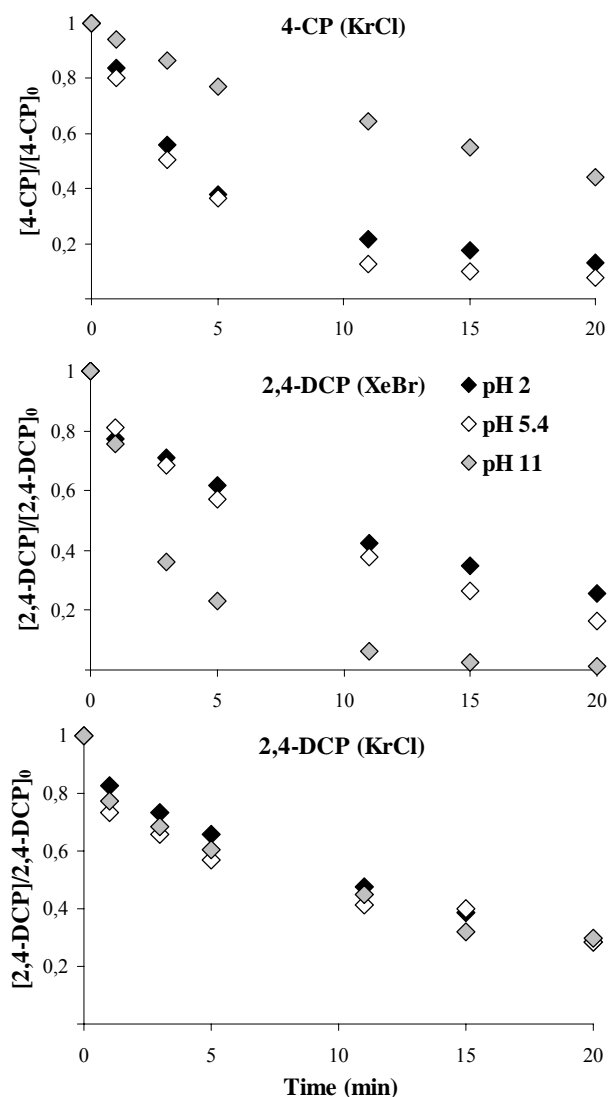
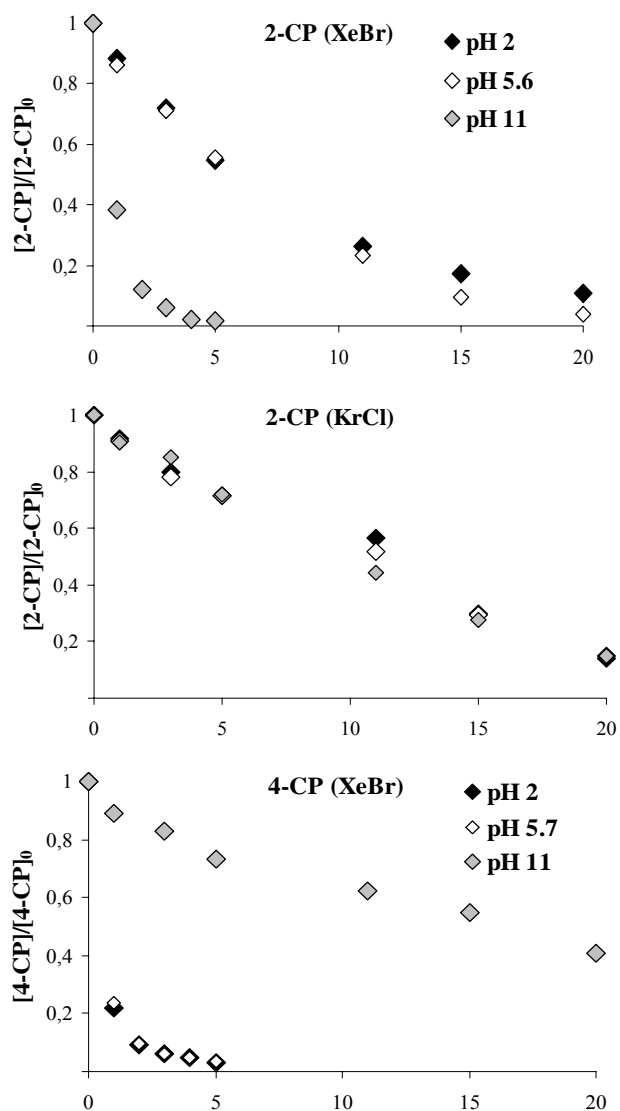


Fig. 1 Evolution of normalized chlorophenol concentration as a function of treatment time and pH during direct photolysis by XeBr and KrCl excilamps.

TABLE I  
SPECTRAL CHARACTERISTICS OF CHLOROPHENOLS

Chlorophenol	$\lambda_{\text{max}}$ , nm	pH <sub>initial</sub>	Form	$\epsilon_{\lambda_{\text{max}}}$ , $\text{M}^{-1}\cdot\text{cm}^{-1}$
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 are present mainly in the molecular form at  $\text{pH} < \text{pK}_a$  (8.1–9.4 for compounds studied) and in the dissociated form (anions) at  $\text{pH} > \text{pK}_a$  [15]. Furthermore, the dissociated forms are considered to be more reactive than the molecular forms [13]. The bathochromic shift of absorbance maximum bands in the medium- and long-wave UV spectral range is observed at pH 11, indicating the presence of anionic forms (Table I). The results propose that the radiation at 282 nm might be absorbed effectively by the low-energy electronically excited states of 2-CP and 2,4-DCP anions and

4-CP molecules, resulting in a scission of C-Cl, O-H and C-C bonds.

In order to compare these 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 [16], [17]:

$$\phi = \frac{k}{2.303 I_{\lambda} \epsilon_{\lambda} l} \quad (1)$$

where  $k$  ( $\text{min}^{-1}$ ) is the pseudo-first order rate constant,  $\phi$  is the quantum yield,  $I_{\lambda}$  ( $\text{Einstein}^{-1} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ ) is the radiation intensity at wavelength  $\lambda$ ,  $\epsilon_{\lambda}$  ( $\text{cm}^{-1} \cdot \text{M}^{-1}$ ) is the molar absorption coefficient at wavelength  $\lambda$ , and  $l$  (cm) is the cell path length.

This equation is applicable for the excilamps used as their emission half-widths does not exceed 1 nm.

TABLE II

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

Chlorophenol	pH <sub>0</sub>	$\lambda$ , nm	$\epsilon_{\lambda}$ , $\text{M}^{-1} \cdot \text{cm}^{-1}$	$k$ , $\text{min}^{-1}$	$t_{1/2}$ , min	$\phi$
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	0.174
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	0.015
	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	0.026
	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  $\phi$  values for 2-CP anions and 4-CP molecules at 282 nm ( $\phi_{282}$ ) were significantly higher than those found for 2-CP molecules and 4-CP anions. The  $\phi_{282}$  for 2,4-DCP anions was also higher than that for its molecules. These values correspond with literature data for 2-CP photolysis at 296 nm ( $\phi = 0.03$ – $0.04$  for molecules and  $0.20$ – $0.30$  for anions) [13], [18], [19] and for 2,4-DCP photolysis ( $\phi = 0.01$ – $0.02$  for molecules and  $0.10$  for anions) [20], [21].

As in [18], 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 shown in Table II, the  $\phi_{282}$  for 4-CP molecules was comparable with the literature value. Nevertheless,  $\phi_{222}$  was one order of magnitude lower than  $\phi_{282}$ , and comparable with  $\phi$  (0.017), found earlier for 4-CP molecules photolysis by a high-pressure mercury lamp, emitting in the broad spectrum of 238–579 nm with maximum emission bands at 254, 313 and 366 nm [22].

The lowest quantum yields 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 [23]. Therefore, when excited with a light at 282 nm, the Cl atom is easily detached

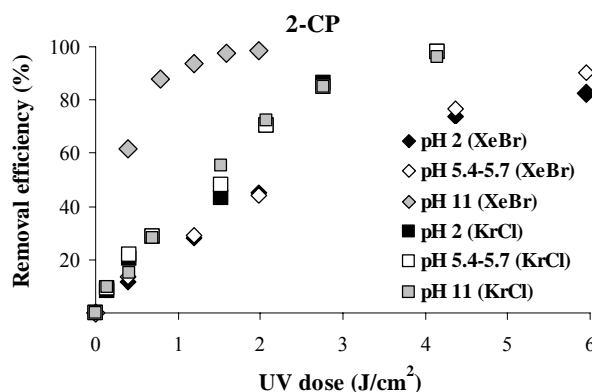
from the 4-CP aromatic ring, forming hydroquinone and *p*-benzoquinone and causing yellow coloring of the solution. This was also confirmed by GC/MS analysis in our previous work [7]. The decreased rates of photolysis of 2-CP and 2,4-DCP in the molecular form, compared to 4-CP molecules, may be explained 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 [13].

The direct photolysis of anionic 2-CP and molecular 4-CP using KrCl excilamp (222 nm) achieved lower quantum yields 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. This suggests that the electronic transitions from the high energy electronically excited states did not lead directly to the bonds scission, but to another process such as non-radiative energy dissipation.

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

### B. Comparison of UV doses

In Fig. 2 the removal efficiency of CPs is plotted versus fluence or UV dose ( $\text{J} \cdot \text{cm}^{-2}$ ). It can be seen that the maximum removal efficiency of molecular 2-CP and 2,4-DCP (at pH 5.4–5.6 and 2) with the lowest UV dose ( $4.1 \text{ J} \cdot \text{cm}^{-2}$ ) was achieved using KrCl excilamp. This finding is in agreement with the previously-reported results on the direct photolysis of molecular 4-CP at higher initial concentrations without stirring [24]. In contrast, from these experimental data, the XeBr excilamp needed the lowest dose ( $\sim 2 \text{ J} \cdot \text{cm}^{-2}$ ) for complete degradation of molecular 4-CP (at pH 2 and 5.7). The same result was obtained for photolysis of 2-CP in the anionic form (at pH 11), whereas the energy requirements to degrade the anionic 2,4-DCP were similar for both lamps. The highest removal efficiency of anionic 4-CP (65%) with the dose of  $\sim 4 \text{ J} \cdot \text{cm}^{-2}$  was achieved when using KrCl excilamp.



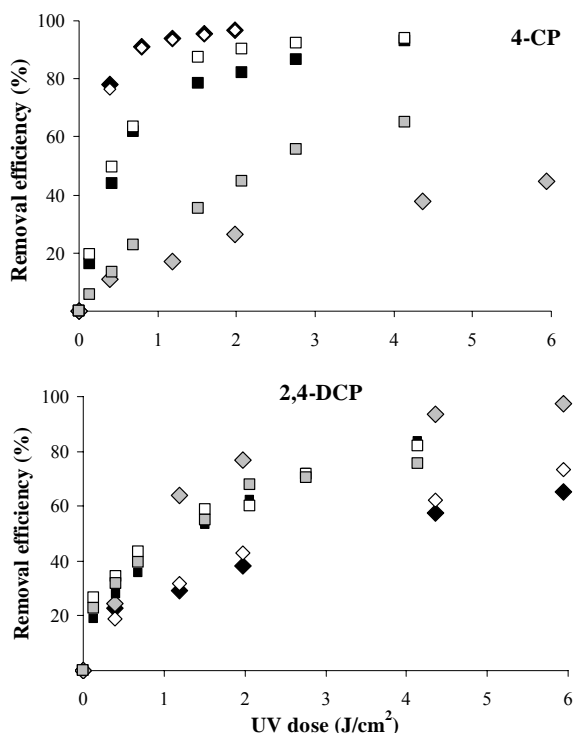


Fig. 2 Removal efficiency of chlorophenols as a function of UV dose and pH during direct photolysis by XeBr and KrCl excilamps.

#### IV. CONCLUSION

The present study demonstrates the high potential of modern UV excilamps for removal of chlorophenols from aqueous solution by direct photolysis. The degradation of these compounds using excilamps in advanced oxidation processes needs to be studied in future work.

#### ACKNOWLEDGMENT

The authors thank Dr. Erzhenia Pavlova and Taras Kolodin for technical support in HPLC analysis.

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