The phototransformation of 4-chloro-2-methylphenoxyacetic acid under KrCl and XeBr excilamps irradiation in water

Olga N. Tchaikovskaya [a,b,*], Elena A. Karetnikova [c], Irina V. Sokolova [a,b], Georgy V. Mayer [a], Dmitry A. Shvornev [d]

[a] Laboratory of Photophysics and Photochemistry of Molecules, Department of Physics, Tomsk State University, 36, Lenine Ave, Tomsk 634050, Russia
[b] Department of Photonics, Siberian Physical Technical Institute at Tomsk State University, 1, Novosobornaya Sq., Tomsk 634050, Russia
[c] Laboratory of Ecological Biotechnology, Institute of Water and Ecological Problems of the Far Eastern Branch of Russian Academy of Sciences, 65, Kim-Yu-Chen St., Khabarovsk 680000, Russia
[d] Khabarovsk Referent Centre, Federal Service for Veterinary and Phytosanatory Surveillance, 65, K. Marks St., Khabarovsk 680000, Russia

ARTICLE INFO

ABSTRACT

The effect of UV radiation of a KrCl and a XeBr on the photodegradation of 4-chloro-2-methylphenoxyacetic acid (MCPA) was studied. The main photoproducts were identified by gas chromatograph/mass spectrometry (GC/MS). The variation of chlorine-ion and active chlorine in MCPA aqueous solution exposed to excilamp radiation was also defined by analytical methods. Irradiation of MCPA solution with a KrCl excilamp emitting mainly at 222 nm yield 2-methylhydroquinone and lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid as the main photoproducts. Irradiation of MCPA solution with a XeBr excilamp emitting mainly at 283 nm yield 2-methylhydroquinone as the main photoproduct. Biological processes are not suitable for MCPA removal due to low or total absence of biodegradability of this class of pollutants. Estimation of biodegradability of phototreated MCPA solution was carried out according to ratios of biological oxygen demand (BOD_5) to chemical oxygen demand (COD). The biodegradability of MCPA solutions increased after irradiation.

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1. Introduction

Phenoxyacetic acid derivatives are widely used soluble herbicides. MCPA (4-chloro-2-methylphenoxyacetic acid) is commonly used for soil treatment in agriculture [1]. As the result chlorine-containing organic products are formed in natural waters and influence remediate processes. According to world ecological statistics many pesticides are included in to the so-called "disgusting dozen" group of ecotoxicants. Depending on the total herbicide concentration, dampness, oxygen regime and organic soil compounds, the time of the semi-decomposition of MCPA may take from several weeks to a few months and may cause the formation of pollutants of secondary toxicity in the environment [2]. The decrease of dampness, oxygen concentration and temperature lead to the inhibition of MCPA decomposition in soil [3,4]. It is known that in the ecosystems processes of transformation and utilization of organic compounds take place under certain physical, chemical and biological factors. Microorganisms play the major role among these factors as they directly contribute to the degradation of pollutants of different composition and origin [3]. Microbial degradation as an important removal force of many organic toxicants is used in coupling systems for wastewater treatment. Usually these systems are based on physico-chemical oxidizing processes and biodegradation.

Modern environment protection technologies of sewage water treatment necessarily include photoreactors with UV sources [4]. According to literature reports on pesticide photodegradation [5] direct photolysis of organic toxicants was reviewed under typical high and middle pressure conditions of mercury lamps. The MCPA transformation as a result of direct photolysis and photocatalytic processes under these UV-sources were investigated [6–8]. Although detailed structures of basic MCPA photoproducts were shown, unfortunately the effect of radiation wavelength on their formation mechanism was not established [7]. It is known that phototransformation of some pollutants can lead to the formation of more soluble and more toxic products than parent compounds [9,10]. The employment of the artificial UV irradiation may lead to the secondary pollution with extremely toxic substances. Data on MCPA photoproduct toxicity and stability to further microbial degradation are not fully reported. The European Scientific

* Corresponding author at: Siberian Physical Technical Institute at Tomsk State University, 1, Novosobornaya Sq., Tomsk 634050, Russia. Tel.: +7 3822 533426; fax: +7 3822 533034.
E-mail address: tchon@phys.tsu.ru (O.N. Tchaikovskaya).

Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 2001) has proposed a draft on the environmental risk assessment of medical and chemical products. To need to take into account not only herbicide, but also their phototransformation products is recommended. Although the hydrolytic and photolytic cleavage of chlorine containing pesticides and drugs widely used, the main degradation products toward aquatic organisms were toxic at the expense of the formation of a radical intermediates [11,12].

Therefore nowadays studies of the effectiveness of modern UV sources are still very important. The irradiation of these sources is absorbed by the high-lying electronically excited states of the organic molecules and may lead to the influence of radiation wavelength on optimal canals of the molecule phototransformation. Such sources are a KrCl and a XeBr excilamps [13]. Besides the results of MCPA phototransformation in water under the excilamps it is actually interesting to determine the effect of photoproduct toxicity on sequential biological treatment. Biological processes do not always appear relevant for the removal of chlorinated photoproducts due to low biodegradability of this class of pollutants.

The aim of the work was to determine the content and structure of MCPA phototransformation and chlorine-ion and active chlorine concentrations in MCPA water solution exposed to a KrCl and a XeBr excilamps, and also to estimate biodegradability of phototreated MCPA solutions.

2. Materials and methods

2.1. Phototreatment conditions

4-Chloro-2-methylphenoxyacetic acid (95%) was supplied by Aldrich. Distilled water was used to prepare MCPA solutions. The initial concentration of MCPA was 2×10^{-3} M.

As sources of UV radiation for photochemical transformation, we used a pulsed U-type barrier discharge excilamps with working KrCl (the wavelength of irradiation: $\lambda_{rad} \sim 222$ nm) and XeBr ($\lambda_{rad} \sim 283$ nm) molecules. The parameters were $\Delta\lambda = 5$–10 nm, peak output power $W_{peak} = 18$ mW cm^{-2}, $f = 200$ kHz, and pulse duration 1 μs. The incident light intensity at 283 nm was evaluated at 3×10^{15} photons s^{-1} cm^{-2} by potassium ferrioxalate actinometry.

2.2. Chemical analyses

Concentrations of chloride ion, active chlorine and quinones were maintained with standard procedures [14]. Chloride ion was determined by titration with Hg(NO$_3$)$_2$ [14] in the presence of diphenylcarbazon; active chlorine measurements were carried out in burette with methyl orange; a Thermo Evolution 600 (Varian, United States) spectrophotometer with benzolsulfonic acid at 320 nm was applied to analyze the concentration of quinones.

Irradiated and non-irradiated MCPA solutions were extracted with diethyl ether after acidification to pH 2. The extraction was repeated twice. The extracts were mixed and evaporated to volume 1.0 ml. The extracted solutions ware analyzed with an ULTRA TRACE DSQ gas chromatograph with a MS detector (Thermo Electron Chromatography and Mass Spectrometry Division, United States). Determination conditions were as follows: column—Trace TR-5MS; temperature—100 °C (5 min); heating at a rate of 10 °C min^{-1} to 180 °C (5 min); heating at a rate of 100 °C min^{-1} to 300 °C (1 min); carrier gas—helium.

Also the separation of photoproducts in the ether extract was carried by thin layer chromatography (TLC). The analyses were performed on a silica gel plates (Sorbifol, Russia). Following solvent system was used—toluene:1,4-dioxane:acetic acid (90:20:4).
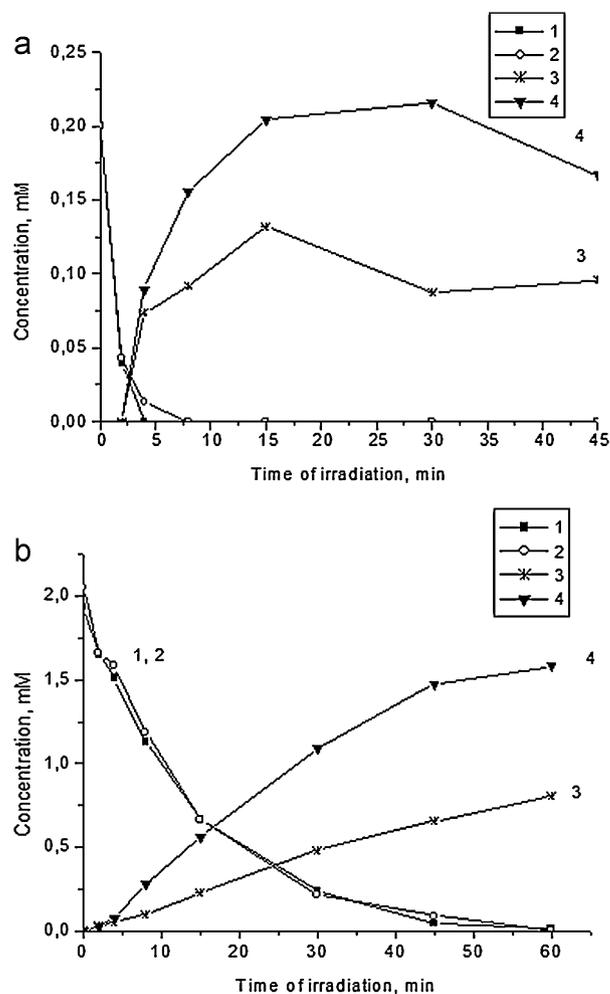

Fig. 1. Kinetics of MCPA disappearance and formation of 4-methylhydroquinone in an air-saturated solution irradiated a KrCl and a XeBr excilamps: initial concentration 2×10^{-4} M (a) and 2×10^{-3} M.

Aromatic aldehydes were visualized as a orange spots after being sprayed and 2,4-dinitrophenylhydrazine (0.1%) in 2 M HCl.

2.3. Assessment of biodegradability

The ratio of biological oxygen demand (BOD$_5$) to chemical oxygen demand (COD) is widely used for assessment of biodegradability of wastewaters [15,16]. This ratio was also applied to estimate biodegradability of phototreated MCPA solutions. The activated sludge (AS) was used as inocula for this procedure. The sample of AS was collected at the sewage treatment facilities of the Tomsk Petrochemical Enterprise (Siberia, Russia). After sampling the sludge was being shaken for 8 h and then liquid phase was separated by filtration (membrane filter with pore size 1.2 nm, Vladipor, Russia). Separation of bacteria from AS liquid fraction was carried out by filtration through the membrane (pore size 0.2 nm) and washing with sterile NaCl solution (0.5%) to remove organic compounds from AS. Microorganisms were washed away from the membrane filter with a sterile NaCl solution to be further used in experiments. BOD$_5$ and COD calculations were performed according to standard methods (dilution method) for water and wastewater examination [17].

For investigation of sequential photo- and biodegradation of MCPA (2×10^{-3} M) 50 ml phototreated and non-phototreated (as a control) solutions were placed in conical flasks (250 ml). Liquid fraction of AS (prepared by filtration through 1.2 nm pore
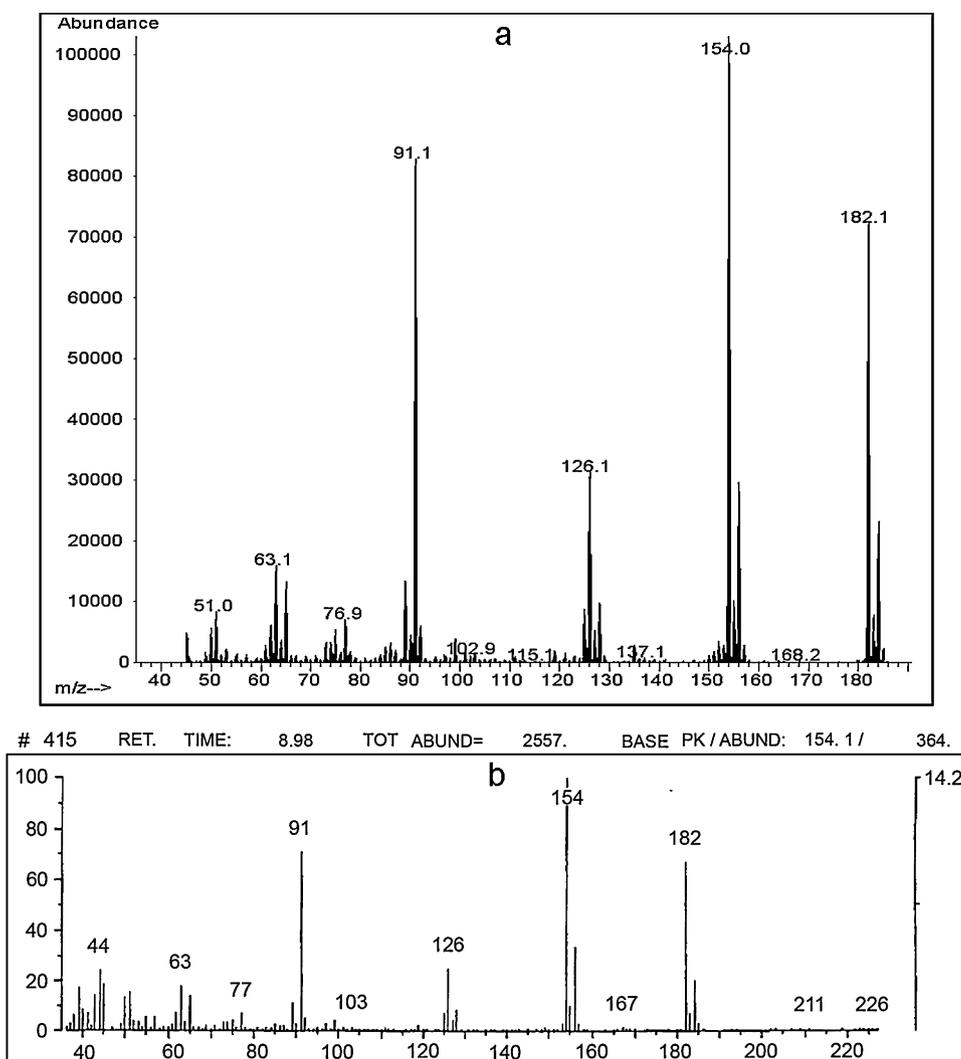
Fig. 2. Mass spectrum of the photoproduct (with MW 182) in MCPA solution after 30 min of KrCl excilamps irradiation (a) and lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid obtained by Prof. A. Zertal (b).

size membrane) was added (50 ml) to each sample of MCPA solutions.

3. Results and discussion

3.1. Efficiency of energy absorption by MCPA solutions treated with excilamps

The selection of excilamp irradiation wavelength is based on the fact that $\lambda_{rad} \sim 222$ nm is absorbed by the high-lying electronically excited states of MCPA. It is possible to make a transfer from these states to photodissociative states which take place in the photocleavage of O–H, O–C and C–Cl bonds. It causes the increase of photolysis efficiency of organic molecules [18,19]. The effect of UV radiation of a XeBr excilamp at $\lambda_{rad} \sim 283$ nm activates the direct population of photodissociative states which contribute to the effectiveness of the reaction of the photobreak of C–Cl bond [18,20]. The operating parameters of lighting sources are listed in Table 1. From UV–vis spectrum of MCPA in aqueous solution two absorption maxima are located at 278 nm and 226 nm [18]. The radiation energy (66%) of a KrCl excilamp was concentrated at 222 nm. The remaining energy was radiated at 196, 235, 240 and 257.8 nm. The radiation energy (66%) of a XeBr excilamp was concentrated at 283 nm. The remaining energy was radiated at 224, 315 and 360 nm.

The incident light intensity at 222 nm was at 2×10^{15} photons s^{-1} cm^{-2}. The intensity values exclude the possibility of multiphoton processes and photoionization in the studied systems.

3.2. GC/MS analysis of phototreated MCPA solutions with concentration 2×10^{-4} M

Earlier 2-methylhydroquinone, 2-methylcathehol, 2-methyl-phenol, 2-methylresorcinol, 2,6-dimethylhydroquinone were

Table 1
The accumulated energy in MCPA solutions during KrCl and XeBr excilamps treatment.

Solution	Time of phototreatment (min)	Output energy (J/cm³)	
		KrCl	XeBr
	15	1.30	0.09
1×10^{-4} M MCPA	30	2.61	0.18
	60	5.20	0.36
2×10^{-4} M MCPA	15	1.44	0.17
	8	0.63	0.63
2×10^{-3} M MCPA	15	1.19	1.17
	30	2.38	2.35
	60	4.64	4.57
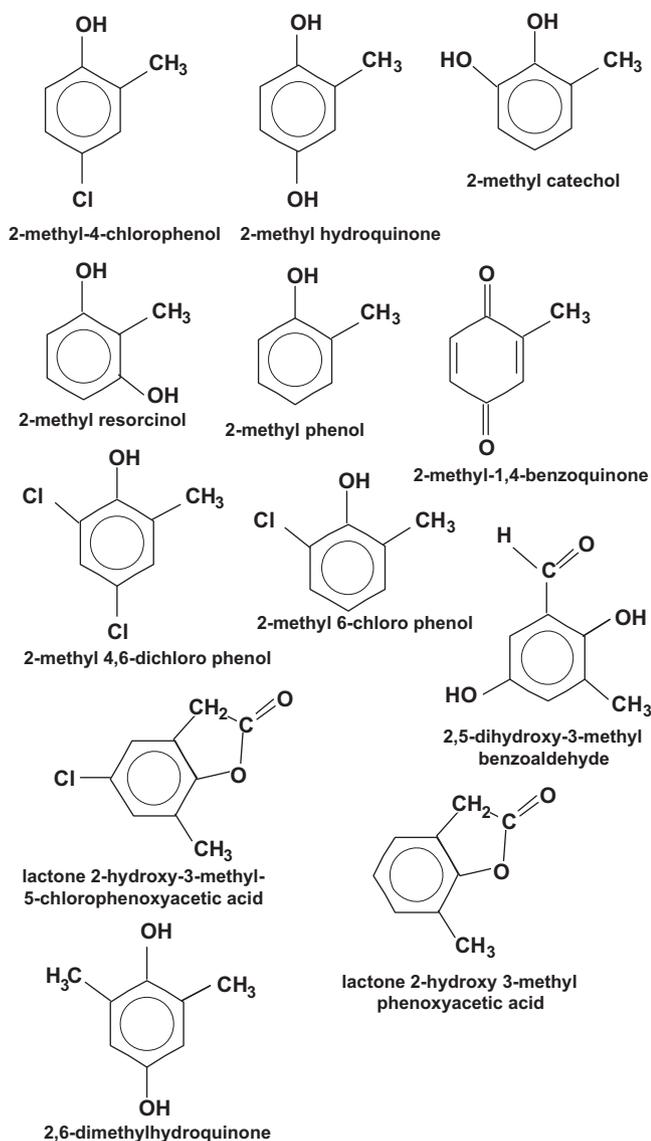
Fig. 3. The structure of MCPA transformation products.

Fig. 4. Mass spectrum of the photoproduct (with MW 148) in MCPA solution after 30 min of XeBr excilamp irradiation.

identified in MCPA solution (2×10^{-4} M) [20]. In present work, according to HPLC data, during 2–4 min UV radiating of KrCl or XeBr excilamps MCPA was completely transformed. Kinetics presented in Fig. 1a show that MCPA is rapidly degraded. After 30 min of irradiation photoproducts mentioned above were also fixed in solution. But only 2-methylhydroquinone was one of dominating products among these compounds. The others were the minor. Another main product after UV pre-irradiation also registered in solution and for this photoproduct $m/z = 152$ may be corresponds to molecular ion and molecular weight for this compound is also 152. Additionally three photoproducts at $m/z = 182$, 148 and 158 also corresponded to molecular ions were detected in lower concentrations (see Fig. 2a). The Cl atom in the structure of a photoproduct appears only in molecules with MW = 182 and 158. The structure of identified photoproducts is shown in Fig. 3.

Previously Zertal et al. [7] reported that after high pressure mercury lamp irradiation of a MCPA molecular form at pH 1.5 both 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid and corresponding lactone (MW = 182) were detected on the HPLC chromatogram and identified by MS and ^{1}H NMR. The main photoproduct resulting from the irradiation of an anionic form of MCPA at pH 5.9 was 4-hydroxy-2-methylphenoxyacetic acid (see Fig. 2b). In
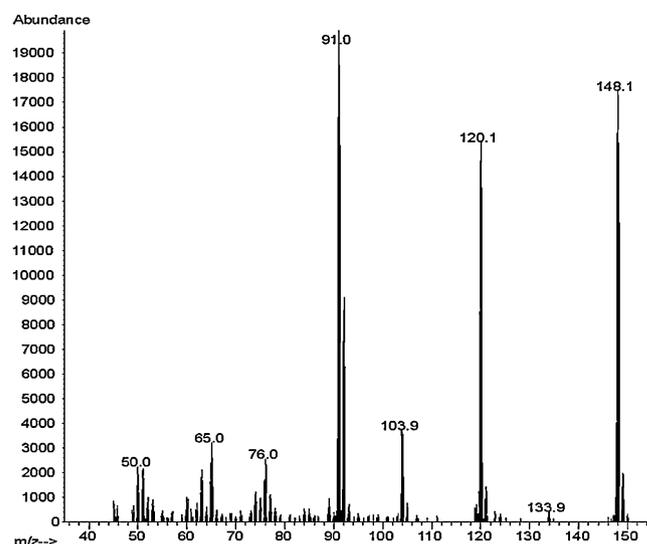
comparison our mass spectrum shows that photoproduct with molecular ion 182 presents lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid (see Fig. 2). The dehalogenated lactone structure of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid was suggested from mass spectrum of the photoproduct with molecular ion 148. Loss of a particle with a mass of 28 a.m.u. confirms the presence of C=O group in molecule (see Fig. 4). Group of peaks at $m/z = 148$ and 150 allows to exclude the presence of Cl as A + 2 element in molecule [21]. This fact may prove that the photobreak of C–Cl bond during the direct photolysis may originate both in MCPA and its photoproducts.

According to mass spectrum the compound ($m/z = 152$) is a substituted salicylaldehyde. As mentioned above peak at $m/z = 152$ could be corresponded with molecular ion and groups of peaks at $m/z = 152$ and 154 shows the absence of A + 2 element (like Cl) in molecular structure. The number of C atoms N in this photoproduct was determined with using the following formula [21]:

$$N = \frac{100\,I_{m+1}}{1.1\,I_m},$$

where I_m is signal intensity of molecular ion m (% relative abundance), I_{m+1} is signal intensity of ions with mass $m + 1$ (% relative abundance).

In our case $m/z = 152$ and $m + 1/z = 153$, according this formula $N = 160{,}000 \times 100/1.1 \times 1{,}800{,}000 = 8$. The molecular weight of compound is 152 and the rest of MW (56 a.m.u.) accounted on H and O atoms. We can propose the presence of three O atoms and as a result we had obtained the formula of photoproduct is $C_8O_3H_8$.

Number of double bonds R in molecule was calculated with following formula [21]:

$$R = \frac{x - y}{2} + \frac{z}{2},$$

where x is number of C atoms, y is number of H atoms, and z is number of N atoms.

For this compound amount of double bonds is 4. Presence of [M-29] peak in mass spectrum apparently corresponds to aldehyde group. So this photoproduct with molecular formula $C_8O_3H_8$ may be identified as 2,5-dihydroxy-3-methyl-benzoaldehyde. After the photochemical treatment the presence of aldehyde in solution was confirmed by TLC. As a result, the presence of aldehyde was detected in the chromatogram with $K_f = 0.63$. The possible way of obtaining this compound includes the
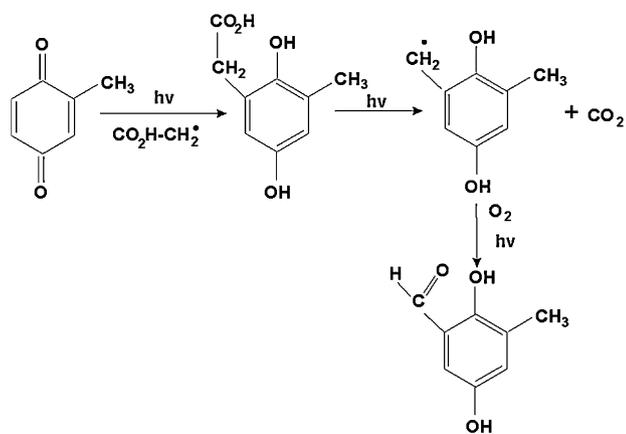
Fig. 5. Proposed pathway for the formation of 2,5-dihydroxy-3-methyl benzaldehyde.

Table 2
Variation of concentration of chlorine-ion and active chlorine in MCPA solutions ($C = 2 \times 10^{-3}$ M) after UV treatment of KlCl and XeBr light.

Irradiation time (min)	Chlorine-ion (mg/l)		Active chlorine (mg/l)	
	XeBr	KrCl	XeBr	KrCl
15	36 ± 3.2	22 ± 2.0	0.4	0.6
30	56 ± 5.0	34 ± 3.1	1.4	0.8
60	68 ± 6.1	46 ± 4.1	2.0	1.3

2-methyl-1,4-benzoquinone reduction before the formation of 2.5-dihydroxy-3-methylphenoxyacetic acid (see Fig. 5). Then decarboxylation of the last one exactly forms 2,5-dihydroxy-3-methylbenzoaldehyde. But because of the lack of the analytical standard of 2,5-dihydroxy-3-methylbenzoaldehyde it is impossible to confirm the presence of this compound in the solution by typical GC/MS parameters (retention time and mass-spectrum). However, the detailed study of the formation mechanism of the product is the goal of our further research. But in any case this photoproduct is dehalogenated.

Also the concentration of 2-methyl-4,6-dichlorophenol was not depend on the UV sources. Dichlorinated derivative in the photo-transformation of MCPA is connected with the presence of active Cl^- ion in solutions. This dichlorinated product was indicated early during the photolysis of 10^{-4} M MCPA without mixing [20] after the exposure of a XeBr excilamp. Concentration of quinonic compounds after 30 min of phototreatment was $1.5–1.6 \times 10^{-5}$ M for both types of excilamps.

3.3. GC/MS analysis of phototreated MCPA solutions with concentration 2×10^{-3} M

MCPA also readily photodegraded under a KrCl or a XeBr photolysis in higher concentration. According to HPLC data irradiation for 30 min after excilamps irradiation resulted in 90% MCPA transformation in stirring. The disappearance of MCPA in irradiated solution reported in Fig. 1b. 2-Methylhydroquinone is formed when MCPA is irradiated with a XeCl excilamp.

The composition of the main products was similar and not dependent on the irradiation wavelength. After the exposure to UV light 2-methylphenol, 2-methyl-4-chlorophenol, 2-methyl-6-chlorophenol and lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid were recorded in the solution by GC/MS analysis. The direct photolysis under KrCl irradiation produces to 2-methyl-4-chlorophenol as the main photoproduct. According to GC/MC data after 15 min irradiation at 283 nm 2-methyl-1,4-benzoquinone was additionally found in MCPA solution.

Moreover the increase of active chlorine and the Cl ion quantity in the irradiated MCPA solutions show that there is an effective reaction of C–Cl bond photocleavage which proves the increase in chloride ion concentration in the solution. The Cl^- evolution is consistent with the MCPA degradation. In comparison with a KrCl, using a XeBr excilamp radiation may accelerate this process (Table 2). After 60 min of a XeBr excilamp irradiation chloride ion concentration in the solution was maximal and approximately equal to the total amount of its mass fraction in MCPA. This fact confirms the tentative mechanism of direct photolysis of MCPA at $\lambda_{rad} \sim 283$ nm which passes exactly through C–Cl photocleavage. But after the prolonged exposure the formation of dichlorinated products can occur and the effectiveness of further biodegradation of MCPA may reduce. Therefore to combine techniques of UV radiation and biological treatment the time of pre-irradiation treatment must be optimally chosen. Photometric method data also reveal the presence of quinonic derivatives which concentration was high (3×10^{-4} M) after the UV irradiation for 60 min. The experimental data demonstrate that the total concentration of quinonic compounds does not depend on the wavelength of the UV sources. However, according to [7], the disappearance of MCPA was more efficient in the presence of quinonic products formed as intermediates.

According to GC/MS data after 15 min MCPA irradiation 2-methyl-4-chlorophenol, 2-methylhydroquinone, 2-methylphenol, 2-methyl-1,4-benzoquinone, lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid were found in the solutions. After 30 or 60 min of irradiation by XeBr and KrCl excilamps, respectively 3-methyl-2,5-dihydroxybenzoaldehyde appeared in the solutions and its concentration depended on the irradiation wavelength (Table 3). As the result of MCPA photolysis not only 2-methyl-4-chlorophenol but also 2-methyl-6-chlorophenol was formed. The formation mechanism of 2-methyl-4-chlorophenol is connected with direct photobreak of the ether bond in the process of photocatalytic reaction [7,8], and the quinone influence on the MCPA oxidation [7], and also with the formation of unstable MCPA peroxide, and its phototransformation into 2-methyl-4-chlorophenol and 2-methyl-4-chlorophenoxyformaldehyde [8]. The formation of 2-methyl-6-chlorophenol might be the result of 2-methyl-4-chlorophenol photoisomerization. After the long irradiation of 2×10^{-3} M MCPA solution with both excilamps 2,6-dichloro-3-methylphenol ($R_t = 9.02$ min) and 4,6-dichloro-2-methylphenol ($R_t = 11.28$ min) were found only in traces and these derivatives were not the main photoproducts.

After 15 min of irradiation the concentration of MCPA was reduced by 85–90% and during 15–60 min period a significant part of energy was spent not only on MCPA degradation, but also on the transformation of photoproducts. The ratio between peak areas of photoproducts after 15 min treatment with different excilamps shows that XeBr was more effective in terms of photoproduct formation (Table 3). Analysis of the dynamics of main photoproduct concentrations (as a ratio between peaks areas at different time) shows that under KrCl excilamp irradiation the concentration of products continued to increase with the increase of the irradiation time, except for 2-methyl-6-chlorophenol. The concentration of 2-methylhydroquinone increased markedly (Table 3). Dominant photoproducts after 60 min irradiation were 2-methyl-4-chlorophenol, lactone of 2-hydro-3-methyl-5-chlorophenoxyacetic acid and 2-methylhydroquinone. In comparison under XeBr excilamp irradiation between 15 and 60 min the concentration of photoproducts decreased with the exception of 2-methylhydroquinone which was the dominant product together with lactone of 2-hydro-3-methyl-5-chlorophenoxyacetic acid. This fact indicates that the dechlorination process of initial photoproducts is effective at $\lambda_{rad} \sim 283$ nm. Therefore, the results of MCPA photolysis at

Table 3
Dynamic of photoproducts (C_t/C_{15}) in air-saturated solution of MCPA irradiated at 222 and 283 nm.

No.	Photoproduct	R_t, min	C_{15} XeBr/C_{15} KrCl	Irradiation time, min					
				KrCl			XeBr		
				15	30	60	15	30	60
1	2-Methyl-1,4-benzoquinone	4.0	11.7	1	2.5	6.7	1	1.2	0.6
2	2-Methylphenol	4.4	4.4	1	2.3	6.7	1	1.7	1.6
3	2-Methyl-6-chlorophenol	8.4	0.6	1	1.5	0.2	1	1.1	0
4	2-Methyl-4-chlorophenol	9.3	1.2	1	1.9	7.7	1	1.1	0.5
5	2-Methylhydroquinone	10.6	2.5	1	2.1	3.6	1	1.9	2.8
6	2,5-Dihydroxy-3-methylbenzoaldehyde	12.8	–	–	–	1	–	1	1.6
7	Lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid	13.3	6.8	1	3.6	10	1	1.2	0.6

$\lambda_{rad} \sim 283$ nm are of great interest as they indicate the possibility to decrease the concentration of chlorinated initial photoproducts and accumulation of 2-methylhydroquinone and 2,5-dihydroxy-3-methylbenzoldehyde. The photodecomposition of MCPA in water under the XeBr excilamp light leads to rapid formation of dechlorinated photoproducts. C–Cl bond cleavage is an enhancement mechanism for photodegradation.

3.4. The effect of MCPA phototransformation on the sequential biological treatment

A coupling process based on photochemical and biological treatment of wastewater is one of possibilities to increase the efficiency of degradation of some organic pollutants. But in this case it is necessary to estimate the biodegradability of UV treatment solutions of toxicants. The value of COD after the phototreatment during 60 min did not change significantly and was $515 + 56$ and $595 + 65$ mgO L^{-1} for non-phototreated and phototreated solutions, respectively.

From the point of view of coupling wastewater treatment, it is very important that pre-irradiation increase the biodegradability of wastewater, i.e. increase the ratio BOD5/COD before the activated sludge process. According our experimental data the ratio of BOD$_5$ to COD for non-phototreated 2×10^{-3} M MCPA solution was 0.13. The UV pretreatment increased this value to 0.4. The BOD$_5$/COD value of 0.4 is considered to be a threshold of biodegradability of organic compounds, and several authors consider it as the boundary of biodegradability [15,16].

GC/MS analysis shows that in a batch culture with AS as inocula traces of MCPA and non-halogenated photoproducts disappeared from media after 14 days of biodegradation. Sequential photo-biotreatment with a XeBr excilamp caused complete degradation not only of MCPA but also of 2-methyl-4-chlorophenol. After the KrCl light pretreatment traces of 2-methyl-4-chlorophenol in solutions were observed. Biodegradation of non-irradiated solution of MCPA led to decreasing in its concentration by 80–87%.

4. Conclusion

Thus, application of excilamps significantly improved the efficiency of MCPA phototransformation in aqueous solutions. The dechlorination processes also highly depend on the irradiation wavelength. MCPA underwent rapid photodehalogenation under UV irradiation of a XeBr excilamp although the output energy was lower then in case of a KrCl source. 2-Methylhydroquinone is the main photoproduct. Also the direct MCPA photolysis under exposure to a KrCl excilamp led to the formation of the lactone of 2-hydroxy-3-methyl-5-chlorophenoxyacetic acid which was the major product.

Estimation of biodegradability solutions based on determining of the ratio BOD$_5$ to COD shown increasing of biodegradability of MCPA solutions after excilamps photo-pretreatment. There is the fact that products of MCPA photolysis are biodegradable. In the context of the integration of phototransformation process and a biological treatment, the evolution of global parameters, like BOD and COD may be helpful.

The results show that using of excilams provides the effective phototransformation of MCPA and coupling of photo- and bioprocesses allows removing from water residuals of initial pollutant and photoproducts.

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