

Photocatalytic ozonation of 4-chloro-2-methylphenoxyacetic acid and its reaction intermediate 4-chloro-2-methyl phenol

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Abstract:

Aqueous 4-chloro-2-methylphenoxyacetic acid (MCPA) has been treated by the systems UVA/TiO₂/N₂, O₃, TiO₂/O₃, UVA/O₃, UVA/TiO₂/O₂, and UVA/TiO₂/O₃. Under the conditions investigated (T = 20 °C, pH = 4.5, Q_{gas} = 30 L/h, V = 1 L, C_{O₃} = 5 ppm, C_{MCPA} = 5 ppm, C_{TiO₂} = 0.5 g/L), MCPA is removed in less than 30 min. Photocatalytic ozonation is the most efficient process both in terms of MCPA removal rate (100% conversion in less than 15 min) and mineralization extent (60% after 3 h and 25 °C). 4-Chloro-2-methyl phenol (CMP) is detected in those systems combining TiO₂ and UVA radiation. The presence of ozone involves the complete depletion of CMP following its generation. The direct rate constant between CMP and ozone corroborates the high reactivity observed ($7.2 \pm 0.3 \times 10^4 \text{ (M s)}^{-1}$, $4.4 \pm 0.2 \times 10^5 \text{ (M s)}^{-1}$, and $2.9 \pm 0.7 \times 10^6 \text{ (M s)}^{-1}$ at pHs 4, 7 and 10, respectively). Identified intermediates detected in the UVA/TiO₂/O₃ applied to MCPA correspond to oxygenated species derived from the parent compound after loss of some substitution groups. No significant toxicity of intermediates is observed in BOD₅, *Daphnia parvula*, and *Culex pipiens* larvae tests.

Keywords: MCPA; Photocatalytic ozonation; 4-Chloro-2-methyl phenol; Kinetics; Herbicides

1. Introduction

4-Chloro-2-methylphenoxyacetic acid (MCPA) is a widely used herbicide of the chlorophenoxy type family. Phenoxy herbicides act by simulating the action of natural hormones to produce uncoordinated plant growth. Their action is selective as they are toxic to dicotyledonous plants. The acid is the parent compound, but a number of formulations in use contain the more water-soluble amine salts or the ester derivatives, which are readily dissolved in an organic solvent. Regulatory agencies in their evaluations of these two constituents have found MCPA unlikely to be human carcinogen; however, a number of epidemiologic studies have found positive associations between exposure to chlorophenoxy compounds and an increased risk of some lymphohematopoietic cancers, primarily non-Hodgkins lymphoma, but also Hodgkin's disease, soft-tissue sarcoma, and to a lesser extent, leukemia [1].

MCPA can be easily degraded in aqueous solution by means of TiO_2 mediated photocatalysis in the presence of UVA or visible light [2], [3]. MCPA photocatalysis leads to the complete removal of the parent compound in a relatively short period of time; however, the herbicide is not completely mineralized and some intermediates accumulate in the reaction media [4]. 4-Chloro-2-methyl phenol (CMP) is the main intermediate that accumulates in the MCPA photocatalytic process. CMP is generated from MCPA by direct photolysis and $\cdot\text{OH}/\text{h}^+$ reaction (higher CMP yield). CMP is more toxic than the parent compound [5]. Accordingly, water treatment technologies dealing with MCPA removal should take into consideration the evolution of this byproduct. The accumulation of CMP in the Degussa P-25 mediated photocatalysis has been previously experienced [6].

In the present study, the photocatalytic ozonation of MCPA is investigated and compared to other systems such as single ozonation, photolytic ozonation, catalytic ozonation and photocatalysis. Use of ozone in photocatalytic processes shows some advantages if

compared to the system in the absence of ozone, namely the presence of an additional oxidant (O_3) reacting with organic molecules by direct or indirect ($\cdot OH$) pathways, additional generation of free radicals by ozone photolytic scission, potential catalytic ozone decomposition by the TiO_2 surface, etc. [7].

Photocatalytic ozonation has normally been applied by using UV-C radiation, few works have applied cheap black light lamps (UVA radiation), [8], [9]. Additionally, the number of studies focused on the photocatalytic ozonation of pesticides is also limited. Some works can be listed. Rajeswari and Kanmani [10] combined UVA radiation and ozone in the presence of titanium dioxide and carbaryl as model pollutant. Under their experimental conditions, 76.5% of total organic carbon (TOC) removal and increase of the five-day biological oxygen demand–chemical oxygen demand ratio (BOD_5/COD) were reported. Farré and co-workers [11], [12] conducted a preliminary chemical treatment of pentachlorophenol, isoproturon, diuron, alachlor and atrazine pesticides in aqueous solutions analyzing the toxicity of the effluent after the treatment. Beduk and collaborators [13] carried out the photocatalytic ozonation in the presence of UV-C radiation of the organophosphorus pesticides malathion and parathion. Cernigoj and coworkers [14], [15] also studied the photocatalytic ozonation of thiacloprid and neonicotinoid insecticides.

In this work the influence of pH, photocatalyst and MCPA initial concentration has been assessed in the UVA/ TiO_2/O_3 system. Additionally, the response of CMP toward the studied technologies has also been investigated. Toxicity tests have completed the work.

2. Experimental

2.1. Photoreactor and procedure

A 1 L capacity perfectly mixed borosilicate glass photoreactor was used in all the experiments. The reactor was placed in the middle of a 31 cm external diameter pipe (54 cm height). The internal wall of the pipe was covered by aluminum foil to increase the photons reflection toward the reaction media. Four black light lamps (41 cm length) were evenly distributed and attached to the pipe. The lamps (LAMP15TBL HQPOWER™ manufactured by Velleman®) had a nominal power of 15 W mainly emitting within the range 350–400 nm, the maximum being located at 365 nm. Actinometry experiments in the presence of ferryoalate led to a value of 6.86×10^{-5} Einstein/min/L when 4 lamps were used.

Previously to the photodegradation experiments, the mixture water + photocatalyst was stirred for 60 min in the dark to achieve the MCPA adsorption equilibrium on the photocatalyst surface. Oxygen or a mixture oxygen–ozone was continuously bubbled into the water bulk by means of a diffuser placed at the reactor bottom. The gas flow rate was kept constant at 30 L/h in all the experiments. Photocatalysts were maintained in suspension by magnetic stirring. Prior to the analysis, the solid was removed from samples by filtration through Millex-HA filters (Millipore, 0.45 μm).

Ozone was produced from pure oxygen by using a Sander Laboratory Ozone Generator. Dissolved ozone in solution was determined by the indigo method, the analysis is based on the decoloration of the 5,5,7-indigotrisulfonate [16]. Ozone in the gas phase was monitored by means of an Anseros Ozomat ozone analyser. The analysis was based on the absorbance at 254 nm. All experiments were conducted at the natural pH of the solutions, with no addition of buffering substances.

2.2. Materials

Pure MCPA from Aldrich (>99%) was used in different experiments, the rest of chemicals were purchased from Sigma-Aldrich and used as received (acetaminophen >99%, CMP 97%, phosphoric acid 85%). Organic solvents were HPLC grade obtained from Panreac. Commercial TiO₂ Degussa P25 photocatalyst (70% anatase and 30% rutile) was used with an average particle size of 30 nm and BET surface area of 50 m²/g. Water purified by a Milli-Q water system (Millipore) was used in the preparation of solutions and suspensions.

2.3. Analysis

MCPA and CMP were analyzed by high-performance liquid chromatography (Agilent 1100). The column used was a Kromasil 100 5C18. The mobile phase acetonitrile/water/phosphoric acid 85% (40:54:6) was pumped at a flow rate of 1 mL/min. Detection was conducted at 230 nm. In the case of acetaminophen, the reference compound in rate constant determination experiments, the mobile phase was changed to acetonitrile/water/phosphoric acid (18:76.5:8.5), and detection was conducted at 244 nm. Byproducts were tentatively identified by HPLC coupled to mass spectrometry. The detector was a quadrupole-time-of-flight mass spectrometer (Agilent Technologies 6520, Accurate-Mass Q-TOF LC/MS) equipped with a dual ESI electrospray interface. The analytical operating conditions were as follows: capillary 3500 V; nebulizer, 30 psi; gas flow, 5 L/min; gas temperature 300 °C; skimmer voltage, 65 V; octapole rf, 750 V; fragmentor, 100 V. The mass spectra were processed by means of the Agilent Mass Hunter Qualitative Analysis B.04.00 software.

In order to assess the degree of mineralization, total organic carbon was determined by a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solution. The pH of the

reaction media was measured by means of a Radiometer Copenhagen pH-meter. pH adjustment was carried out by addition of NaOH or perchloric acid. Biological oxygen demand after five days determination was conducted by the respirometry method, based on the absorption of the CO₂ generated in the microbial metabolism by solid NaOH.

2.4. Ecotoxicity bioassays with *Daphnia parvula* and *Culex pipiens* larvae

The acute toxicity tests using *Daphnia parvula* were conducted using US EPA standard operating procedures [17]. This procedure was extrapolated to carry out similar trials with mosquito *Culex pipiens* larvae. A culture for *D. parvula* or *C. pipiens* larvae was received from installations of Extremadura's University, where organisms were naturally cultured in artificial ponds.

20 young *D. parvula* or 15 s-instar *C. pipiens* larvae were placed in 100 mL of test solution using a disposable plastic transfer pipette, and were subjected to 16:8 light:dark photoperiods at room temperature. Survival numbers were recorded and monitored at 6, 24 and 48 h for *D. parvula*; 24, 46, 72 and 96 h for *C. pipiens*. Organisms were not fed during the experiments. In ecotoxicity tests, commercial MCPA (MCPA 60% from KENOGARD®) or CMP solutions were prepared in mineral water (10.7 mg/L HCO₃⁻, 5.3 mg/L SO₄²⁻, 19.0 mg/L, Cl⁻, 2.7 mg/L, Ca²⁺ 2.7 mg/L Mg²⁺, 14.7 mg/L, Na⁺, and 14.3 mg/L SiO₂). pH was adjusted to 7 ± 0.1. Three blank tests, without MCPA or CMP addition, were considered per each run.

Initially trials were carried out at various parent compound initial concentrations in order to determine the concentration which causes the 50% mortality (LC50). Organisms were exposed to nine concentrations (1000, 500, 250, 125, 62.5, 31.2, 15.6, 7.8, and 3.9 mg/L of MCPA; or 10, 5, 2.5, 1.25, 0.62, 0.31, 0.15, 0.08 and 0.04 mg/L for CMP). After this preliminary study, samples from photocatalytic ozonation experiments at different stages

of oxidation extent (0, 25, 50, 75, 100% of initial MCPA removal) were taken. An additional sample was also considered when TOC removal reached the steady state level.

3. Results and discussion

3.1. Preliminary experiments: Technologies comparison

3.1.1. 4-Chloro-2-methylphenoxyacetic acid oxidation

Some preliminary experiments were initially carried out to compare the performance of individual systems derived from the UVA/TiO₂/O₃ technology. **Fig. 1** shows the results obtained in terms of MCPA normalized degradation and TOC conversion when an aqueous solution of the herbicide was treated by means of UVA/TiO₂/N₂, O₃, TiO₂/O₃, UVA/O₃, UVA/TiO₂/O₂, and UVA/TiO₂/O₃.

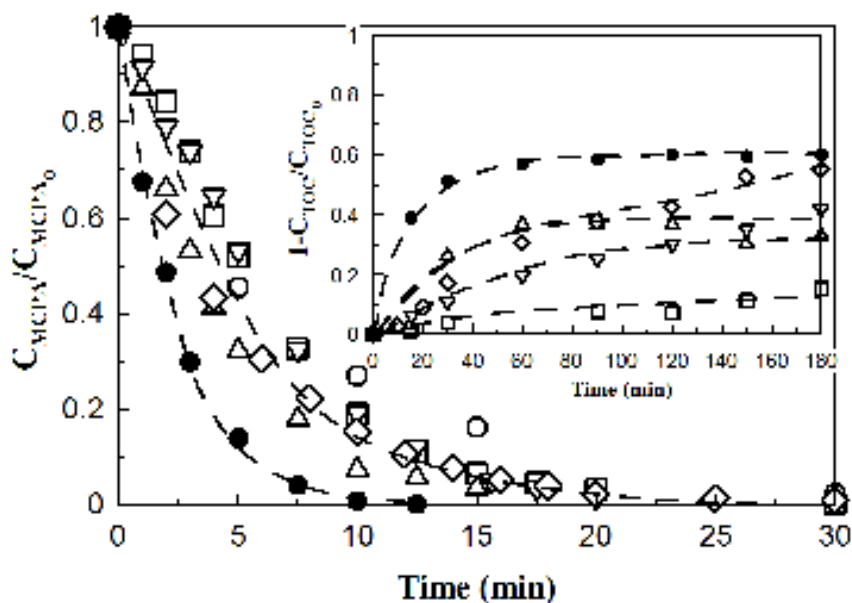


Fig. 1. Removal of MCPA and TOC conversion by different systems. Experimental conditions: $T = 298 \text{ K}$, $\text{pH} = 4.5$, $Q_{\text{gas}} = 30 \text{ L/h}$, $V = 1 \text{ L}$, $C_{\text{O}_3} = 5 \text{ ppm}$, $C_{\text{MCPA}} = 5 \text{ ppm}$, $C_{\text{TiO}_2} = 0.5 \text{ g/L}$. \circ , UVA/TiO₂/N₂; \square , O₃; \triangle , TiO₂/O₃; ∇ , UVA/O₃; \diamond , UVA/TiO₂/O₂; \bullet , UVA/TiO₂/O₃.

From **Fig. 1** it can be observed that, under the operating conditions investigated, MCPA (5 ppm) quickly disappears in less than 20–25 min regardless of the oxidizing system used. Roughly, all the technologies used present a similar efficiency with the exception, perhaps, of the photocatalytic ozonation, capable of reducing the time to completely oxidize MCPA to 12–14 min. However, different patterns were experienced when TOC conversion was monitored. In this latter case, single MCPA ozonation only achieved a scarce 15% in TOC conversion after 180 min of treatment. The combination of ozone with either TiO_2 or UVA light increased the final TOC removal to values close to 30–35%. TiO_2 can act as a catalyst in ozonolysis reactions by accelerating the ozone decomposition into radical species. Alternatively, oxidation reactions can take place on the solid surface decreasing the activation energy of the ozonolysis [18], [19], [20], [21]. The positive effect of the pair ozone-UVA may be attributed to the photoactivity of ozonation intermediates that would accumulate in the absence of the radiation.

The photocatalysis in the presence of ozone (UVA/ TiO_2/O_3) or oxygen (UVA/ TiO_2/O_2) led to a TOC conversion in the proximity of 60%, however this high value was reached by the UVA/ TiO_2/O_3 system in just 60 min, compared to >180 min required by the UVA/ TiO_2/O_2 system. Roughly 40% of the initial TOC content remains in solution after 3 h of treatment. As occurring in most oxidation processes, accumulation of low weight oxygenated species (carboxylic acids, aldehydes, ketones, etc.) form the recalcitrant TOC remaining in solution.

The synergistic effect experienced when using the UVA/ TiO_2/O_3 system is the result of a higher inhibition of electron–hole recombination, the catalytic effect of TiO_2 in the presence of ozone, and the high photoactivity of ozone intermediates.

CMP was only detected in those systems combining UVA radiation and titanium dioxide (no matter the presence or absence of ozone). As stated previously, CMP is generated from direct photolysis or $\cdot\text{OH}$ attack to MCPA, suggesting that the systems O_3 and/or O_3/TiO_2 proceed through a mechanism different from hydroxyl radical formation (i.e. direct ozone attack). In this sense, Benoit-Guyod and co-workers [22] report two distinct ozonolysis pathways in the presence and absence of UV radiation: ring-hydroxylation and cleavage by molecular ozone in the dark, and side-chain oxidation by hydroxyl radicals under irradiation. Alternatively, CMP could have been generated and instantaneously removed, as a consequence CMP presence could not be detected.

Since CMP is the main intermediate detected in the MCPA photocatalytic ozonation (the most efficient system), the response of this compound to the oxidizing agents used in this work was also assessed.

3.1.2. 4-Chloro-2-methyl phenol oxidation

Fig. 2 shows the normalized CMP removal after application of different oxidizing systems. From this figure the fact that the UVA/ TiO_2/O_2 process is the less effective technology is inferred, hence, the accumulation of this compound in the MCPA photocatalysis system is corroborated. However, when ozone is used, CMP is completely eliminated in less than 10 min regardless of the simultaneous application of UVA radiation or UVA + TiO_2 . Similarly to MCPA degradation, in terms of TOC conversion, Degussa P-25 did show some catalytic effect in the ozonation process if compared to the single ozone application.

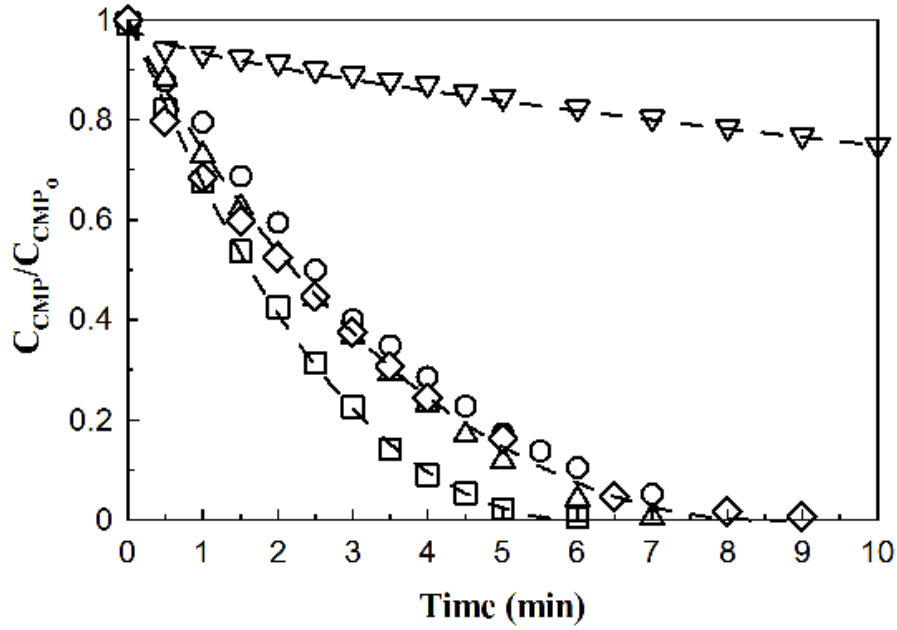


Fig. 2. Removal of 4-chloro-2-methyl phenol by different systems. Experimental conditions: $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 5.0$, $Q_{\text{gas}} = 30\text{ L h}^{-1}$, $V = 1\text{ L}$, $C_{\text{O}_3} = 5\text{ ppm}$, $C_{\text{CMP}} = 5\text{ ppm}$, $C_{\text{TiO}_2} = 0.5\text{ g L}^{-1}$. ○, O₃; □, TiO₂/O₃; Δ, UVA/O₃; ▽, UVA/TiO₂/O₂; ◇, UVA/TiO₂/O₃

The potential of ozone to oxidize CMP was corroborated by calculating the second order rate constant corresponding to the direct reaction between molecular ozone and CMP. Accordingly, three series of ozonation experiments in a homogeneous and semicontinuous mode, in the presence of 0.01 M of tert-butanol (radical scavenger), were completed. The method consists in the continuous pumping of an ozone saturated solution to a tank containing CMP and a reference compound whose ozonation rate constant is previously known [21].

The mass balance equations describing the system are:

$$\left. \begin{aligned} V \frac{d(C_T)}{dt} + C_T \frac{d(V)}{dt} &= -z_T V k_{\text{O}_3, C_T} C_{\text{O}_3} C_T \\ V \frac{d(C_R)}{dt} + C_R \frac{d(V)}{dt} &= -z_R V k_{\text{O}_3, C_R} C_{\text{O}_3} C_R \\ \frac{d(V)}{dt} &= Q \end{aligned} \right\} \quad (1)$$

In the above equations, Q , is the ozone saturated solution flow-rate, V is the reaction volume, C is concentration, z , the stoichiometric coefficient, and the subscripts “T” and “R” refer to target and reference compounds, respectively. To eliminate the unknown C_{O_3} concentration, if the reference and target compound mass balances are divided, after integration it follows:

$$\ln \frac{VC_T}{VC_T|_{t=0}} = \frac{z_T}{z_R} \frac{k_{O_3, C_T}}{k_{O_3, C_R}} \ln \frac{VC_R}{VC_R|_{t=0}} \quad (2)$$

A plot of the left-hand side of Eq. 2 versus $\ln \frac{VC_R}{VC_R|_{t=0}}$ should lead to a straight line of

slope $\frac{z_T}{z_R} \frac{k_{O_3, C_T}}{k_{O_3, C_R}}$. By assuming a stoichiometric coefficient of one mol of ozone per mol

of organic and acetaminophen as the reference compound [14], the rate constants of CMP- O_3 at pHs 4, 7 and 10 were $7.2 \pm 0.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, $4.4 \pm 0.2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, and $2.9 \pm 0.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, respectively (results not shown).

These values corroborate the high reactivity of ozone and CMP experimentally observed in this study. Also, the variation of the rate constant with pH indicates the higher reactivity of the anionic form of CMP if compared to the neutral or protonated forms. The pK_a value from the neutral to the anionic form of CMP is 9.7 while no data is available on the pK_a value for the protonation, in any case protonation of phenols usually shows pK_a values in the proximity of 6.

In order to compare the direct ozonolysis of CMP versus the reaction with hydroxyl radicals, the second order rate constant of the latter was calculated by means of the hydrogen peroxide photolysis in the presence of CMP. Thus by using the method reported by Beltrán and co-workers [15], the calculated values of $k_{HO^\bullet, MCPA}$ and $k_{HO^\bullet, CMP}$ were 4.3

$\times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Typical HO^\bullet concentrations in advanced oxidation systems range in the interval 10^{-13} - 10^{-14} M suggesting that the following inequality applies $k_{\text{HO}^\bullet, \text{MCPA}}C_{\text{HO}^\bullet} \ll k_{\text{O}_3, \text{MCPA}}C_{\text{O}_3}$.

3.2. The system UVA/TiO₂/O₃. Operating variables effect

Given the higher efficiency in TOC removal of the MCPA photocatalytic ozonation if compared to the rest of technologies studied, the former system was investigated in more detail. Accordingly, the influence of some operating variables was investigated, namely TiO₂ concentration, MCPA initial concentration and pH.

3.2.1. Catalyst concentration

TiO₂ concentration was tested in the range 0.01 to 1.5 g/L. **Fig. 3** shows the results obtained. As a rule of thumb, no significant differences were found in terms of MCPA degradation rate regardless of the amount of catalyst used. The experiment conducted with 1.0 g/L of TiO₂ seems to proceed slightly faster than the rest, indicating the existence of an optimum in photocatalyst concentration, typical of photocatalytic processes, however differences are not statistically significant.

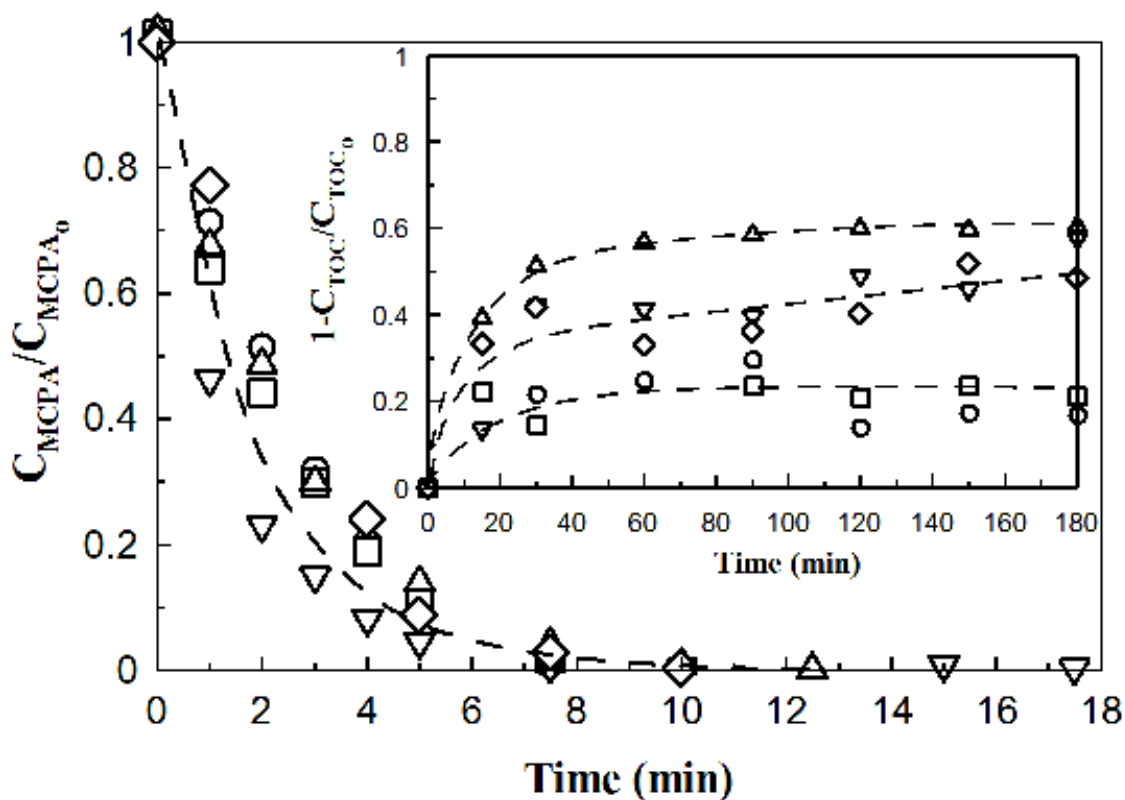


Fig. 3. Removal of MCPA and TOC conversion in the UVA/TiO₂/O₃ system. Experimental conditions: T = 25 °C, pH = 4.5, Q_{gas} = 30 L h⁻¹, V = 1 L, C_{O₃} = 5 ppm, C_{MCPA} = 5 ppm, C_{TiO₂} (g L⁻¹): ○, 0.01; □, 0.1; △, 0.5; ▽, 1.0; ◇, 1.5.

Differences in TOC conversion are more significant. Hence, TOC elimination is substantially lower in experiments conducted with the lowest TiO₂ amount, achieving removal degrees in the proximity of 20% when 0.01 and 0.1 g/L of catalyst were used. TOC elimination percentage increased to 50–60% in the rest of experiments. TiO₂ positive effect is undoubtedly related to its capacity to catalyze the ozonolysis process and its crucial role in the photocatalysis due to the formation of electron–hole pairs.

The evolution of CMP is depicted in **Fig. 4**. As inferred from this figure, the evolution of this intermediate is highly influenced by TiO₂ concentration. Broadly speaking, TiO₂ concentration exerts a positive influence in CMP generation. The presence of high amounts of TiO₂ promotes the photocatalytic process in detriment of the direct ozonation.

This effect involves the formation of CMP which is apparently associated to the TiO₂/UVA system. In all cases, the simultaneous application of ozone leads to a Gaussian profile of CMP concentration, being this compound removed from the reaction media in roughly 10 min.

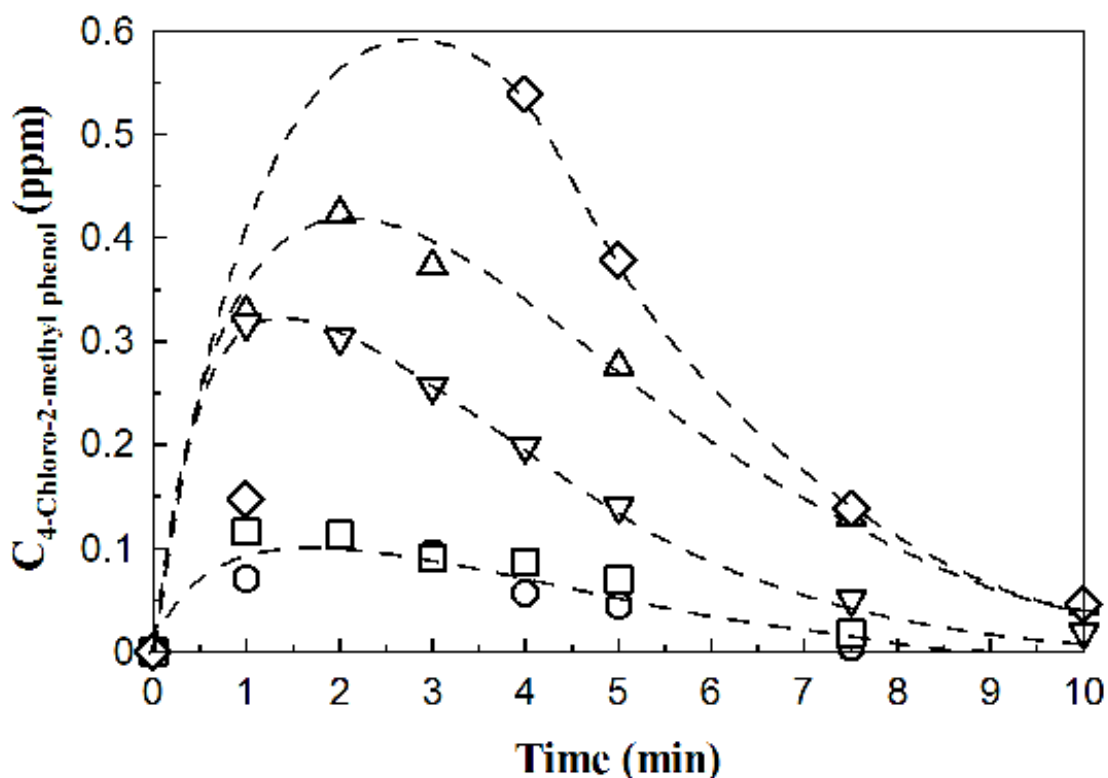


Fig. 4. Evolution of 4-chloro-2-methyl phenol in the UVA/TiO₂/O₃ system applied to MCPA. Experimental conditions: T = 25 °C, pH = 4.5, Q_{gas} = 30 L h⁻¹, V = 1 L, C_{O₃} = 5 ppm, C_{MCPA} = 5 ppm, C_{TiO₂} (g L⁻¹): ○, 0.01; □, 0.1; △, 0.5; ▽, 1.0; ◇, 1.5.

3.2.2. MCPA concentration

MCPA initial concentration was tested within the range 1.5–50 ppm. **Fig. 5** shows the results obtained in terms of MCPA removal and TOC conversion. As expected, decay profiles are steep in those runs with low initial MCPA concentration. The slope is less pronounced in the run carried out with 50 ppm of MCPA. However, in terms of MCPA removal rate the trend is the opposite, thus, the higher the initial MCPA concentration the

higher its elimination rate. An experiment was conducted at 35 °C showing the positive effect of this parameter, particularly in terms of mineralization extent after 180 min. Thus, TOC profiles indicate a lower conversion (35–40%) in the experiment completed with the lowest MCPA concentration than in the rest of runs. Conversion values of 50–60% are experienced when MCPA initial concentration is above 5 ppm. This experimental fact suggests a partial autocatalytic behavior in terms of TOC removal. The maximum TOC conversion (90%) was achieved at the highest temperature tested. Temperature likely accelerates the reactions of organic radicals substantiating the hypothesis of the autocatalytic pathway in terms of mineralization.

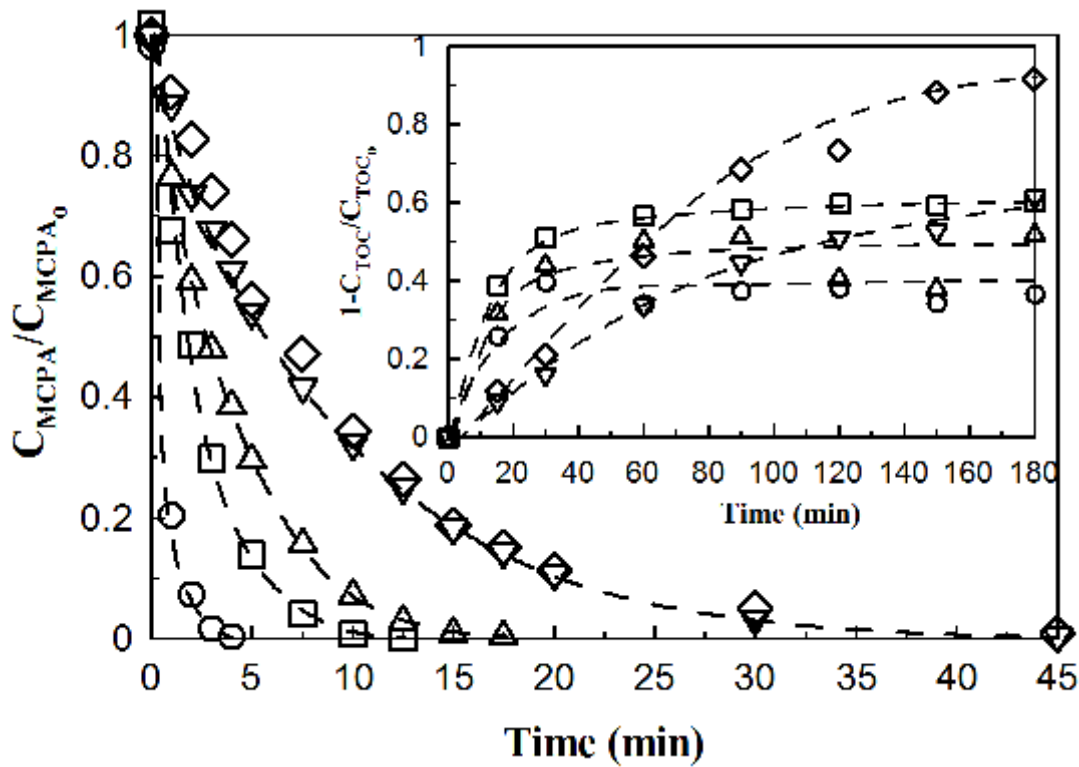


Fig. 5. Removal of MCPA and TOC conversion in the UVA/TiO₂/O₃ system. Experimental conditions: T = 25 °C, pH = 4.5, Q_{gas} = 30 L h⁻¹, V = 1 L, C_{O₃} = 5 ppm, C_{TiO₂} = 0.5 g L⁻¹, C_{MCPA} (ppm): ○, 1.5; □, 5; △, 11; ▽, 50; ◇, 50 (35 °C).

Fig. 6 illustrates the evolution of CMP. As expected, the higher the initial MCPA concentration, the higher the amount of CMP generated. Also, temperature exerted a significant effect in CMP generation.

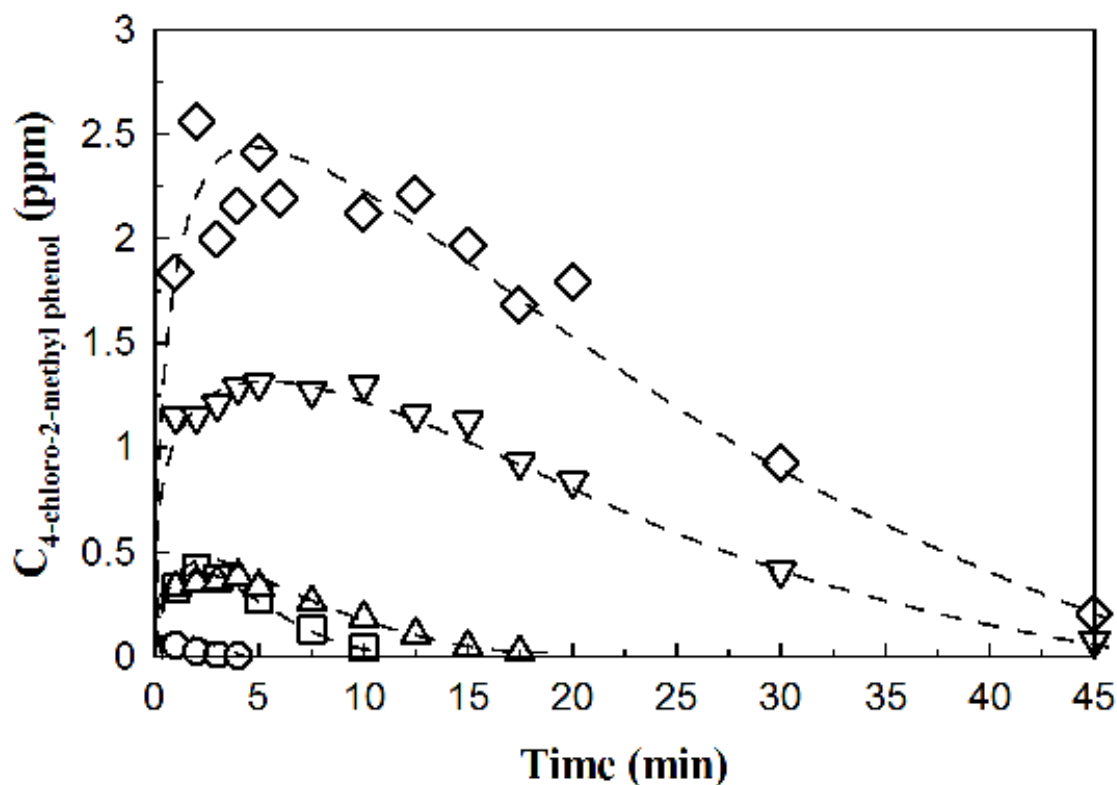


Fig. 6. Evolution of 4-chloro-2-methyl phenol in the UVA/TiO₂/O₃ system applied to MCPA. Experimental conditions: T = 20 °C, pH = 4.5, Q_{gas} = 30 L h⁻¹, V = 1 L, C_{O₃} = 5 ppm, C_{TiO₂} = 0.5 g L⁻¹, C_{MCPA} (ppm): ○, 1.5; □, 5; △, 11; ▽, 50; ◇, 50 (35 °C).

3.2.3. pH influence

Finally, pH was tested under acidic (pH 2), natural (pH 5), neutral (pH 7) and basic (pH 12) conditions (results not shown). pH did not appreciably affect MCPA removal rate, however CMP profiles were severely influenced by this parameter. Thus, when pH was initially varied by NaOH or HClO₄ addition, the amount of CMP generated was drastically reduced, with no significant CMP formation/detection at pHs 7 and 12. Similarly, variations in the initial pH also reduced the final TOC conversion after 180

min from 60% (no pH variation) to 20% (pHs 7 and 2). The worst results were obtained at pH 12 with no observable TOC reduction.

3.3. Detected intermediates and toxicity

Different samples of the MCPA photocatalytic ozonation were analyzed by mass spectrometry. Some positively identified intermediates are shown in **Table 1**.

Table 1. Transformation products tentatively identified in MCPA photocatalytic ozonation at low conversion values.

Mass	Proposed formula	Ion m/z	Proposed structures
114	C ₄ H ₂ O ₄	112.9769	a) 3-hydroxy-2,5-Furandione b) 2,3-Dioxosuccinaldehyde
142	C ₇ H ₇ ClO	140.9989	4-chloro-2-methyl phenol
200	C ₉ H ₉ ClO ₃	198.9978	MCPA
160	C ₇ H ₉ ClO ₂	158.9245	a) 4-chloro-6-methyl-3,5-cyclohexadiene-1,2-diol b) 5-Chloro-2-cyclohexene-1-carboxylic acid
196	C ₈ H ₄ O ₆	194.9704	2,5-dicarboxy-1,4-benzoquinone
158	C ₇ H ₇ ClO ₂	156.9920	a) 4-Chloro-2-(hydroxymethyl)phenol b) 5-Chloro-3-methylbenzene-1,2-diol c) 3-Chloro-2,5-cyclohexadiene-1-carboxylic acid
196	C ₆ H ₉ ClO ₅	195.0118	a) (2E)-2-Chloro-2,3-dideoxyhex-2-enonic acid b) dimethyl 2-chloro-3-hydroxybutanedioate
126	C ₆ H ₆ O ₃	125.1081	4-Hydroxycatechol
124	C ₇ H ₈ O ₂	123.9865	Methyl hydroquinone

Identified intermediates are mainly oxygenated species derived from the parent compound after losing some of the substitution groups. In some cases, the ring may have been opened leading to aliphatic oxygenated chains as it is the case of 2,3-dioxosuccinaldehyde. Not many works have dealt with subproducts in the photocatalytic ozonation of MCPA. Zertal and collaborators [4] report the formation of 4-chloro-2-methylphenol, methylhydroquinone and 5-chloro-2-hydroxy-3-methylphenylacetic acid in photocatalytic experiments in the presence of TiO₂. The first two substances were also identified in this work. Topalov and co-workers [25] propose the formation of 4-chloro-

2-methylphenol in a similar process, further oxidation of this species would easily lead to the formation of 4-chloro-2-(hydroxymethyl)phenol or 5-chloro-3-methylbenzene-1,2-diol tentatively detected in this research. Benoit Guyod and co-authors [22] claim the formation of 4-chloro-2-methylphenyl formate, 4-chloro-salicylaldehyde, 4-chlorosalicylic acid and 5-chloro-3-methylbenzene-1,2-diol monomethyl ether in the photolytic ozonation of MCPA. None of them were found in the samples analyzed in this work.

Toxicity of the intermediates generated during the photocatalytic ozonation of MCPA was assessed by measuring the BOD₅ of the reacted solutions after 10 and 180 min of reaction. Nutrients were added to water samples according to the recipe given in the literature [26], [27], [28]. As seen in **Fig. 7**, neither MCPA nor the intermediates showed any appreciable toxic effect toward the activated sludge used in the BOD analysis, even when a high MCPA initial concentration was applied.

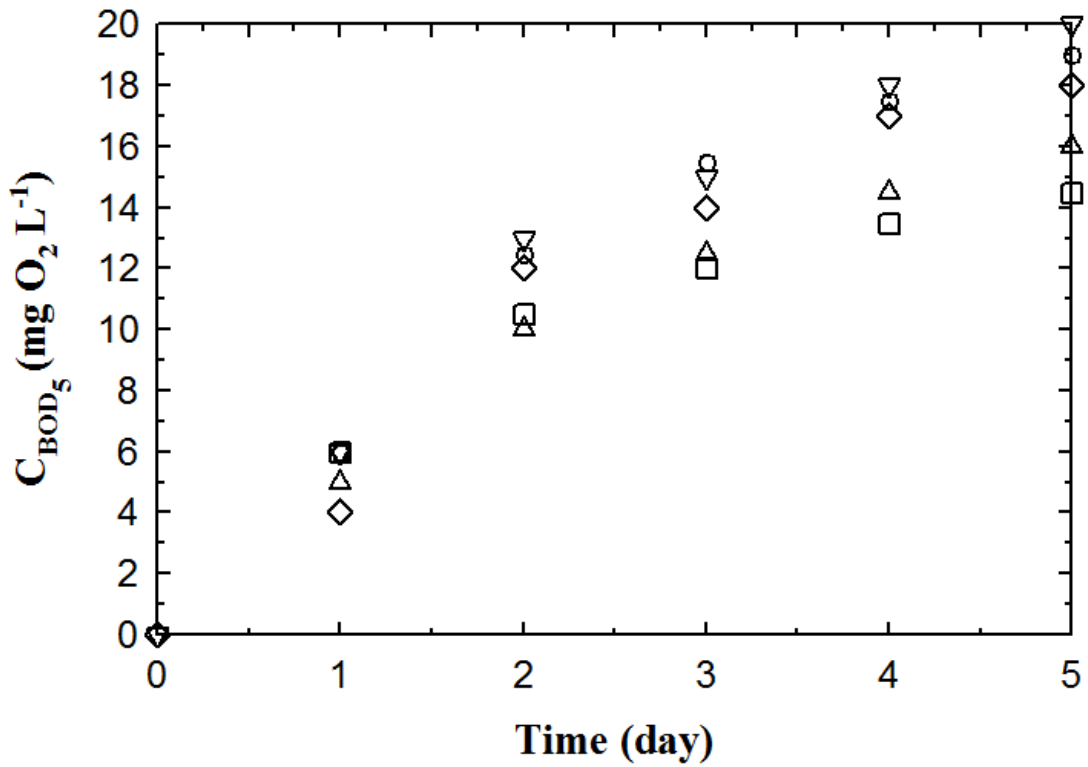


Fig. 7. Evolution of BOD₅ after UVA/TiO₂/O₃ applied to MCPA. Experimental conditions: T = 20 °C, pH = 4.5, Q_{gas} = 30 L h⁻¹, V = 1 L, C_{O₃} = 5 ppm, C_{TiO₂} = 0.5 g L⁻¹. ○, Control run; □, 1.0 ppm of initial MCPA, time reaction = 0 min; Δ, 5.0 ppm of initial MCPA, time reaction = 0 min; ∇, 5.0 ppm of initial MCPA, time reaction = 10 min; ◇, 5.0 ppm of initial MCPA, time reaction = 180 min.

Additional toxicity tests were carried out by using two species, *D. parvula* and larvae of *C. pipiens* (common mosquito).

For comparison purposes, some preliminary ecotoxicity assays were completed with the parent compounds MCPA (commercial) and CMP at different concentrations. These tests are shown in **Fig. 8**. Survival percentage was corrected to account for natural mortality in control runs by means of the expressions [29]:

$$\% \text{ Corrected mortality} = \frac{\% \text{MWC} - \% \text{CM}}{100 - \% \text{CM}} \quad (3)$$

$$\% \text{ Corrected survival} = 100 - \% \text{Corrected mortality} \quad (4)$$

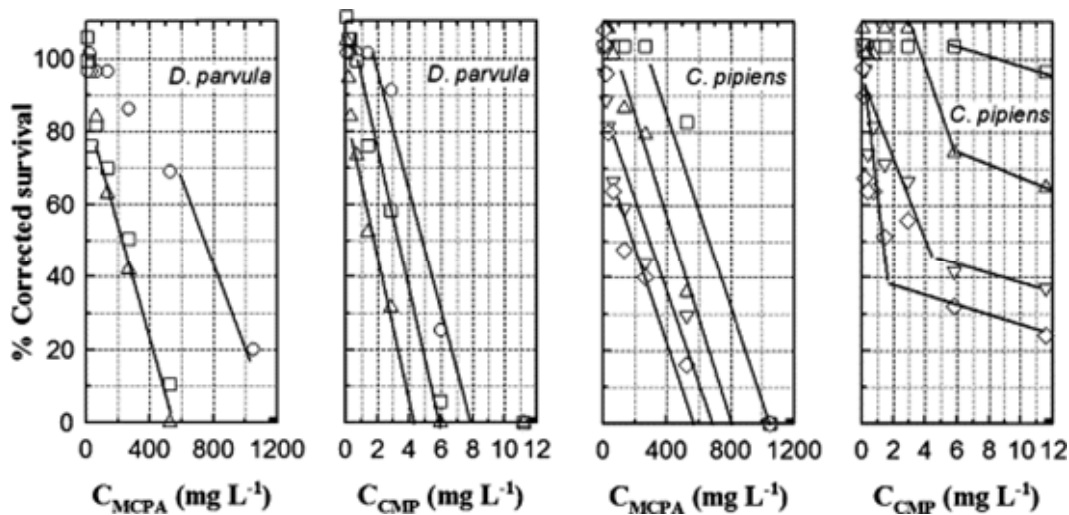


Fig. 8. Percentage of survival of *D. parvula* and *C. pipiens* larvae in different solutions of MCPA or CMP. Time of exposure (h): \circ , 6.0; \square , 24; \triangle , 48; ∇ , 72; \diamond , 96.

In Eq. (3), MWC and CM stand for mortality without correction and control mortality (mortality in blank runs), respectively.

Fig. 8 reveals that the intermediate CMP is more toxic than the parent compound MCPA. *D. parvula* LC50 values corresponding to MCPA at 6, 24, and 48 h are approximately 717, 266 and 230 mg/L, in accordance with the data provided by the supplier (LC50 to *D. magna* at 48 h > 190 mg/L) while *D. parvula* LC50 values corresponding to CMP at 6, 24, and 48 h are roughly 9.0, 6.5 and 1.5 mg/L. These differences in toxicity were also experienced when *C. pipiens* were used. In this latter case, MCPA and CMP showed values of 206 and 150 mg/L (MCPA) and 1.5 and 0.5 mg/L (CMP) after 72 and 96 h of larvae exposure, respectively.

The goal to be achieved is the application of the photocatalytic ozonation to remove MCPA without generating an effluent more toxic than the initial herbicide solution. Accordingly, a number of samples were withdrawn from the reactor at different oxidation times and the toxicity analyzed. **Fig. 9** illustrates the results obtained.

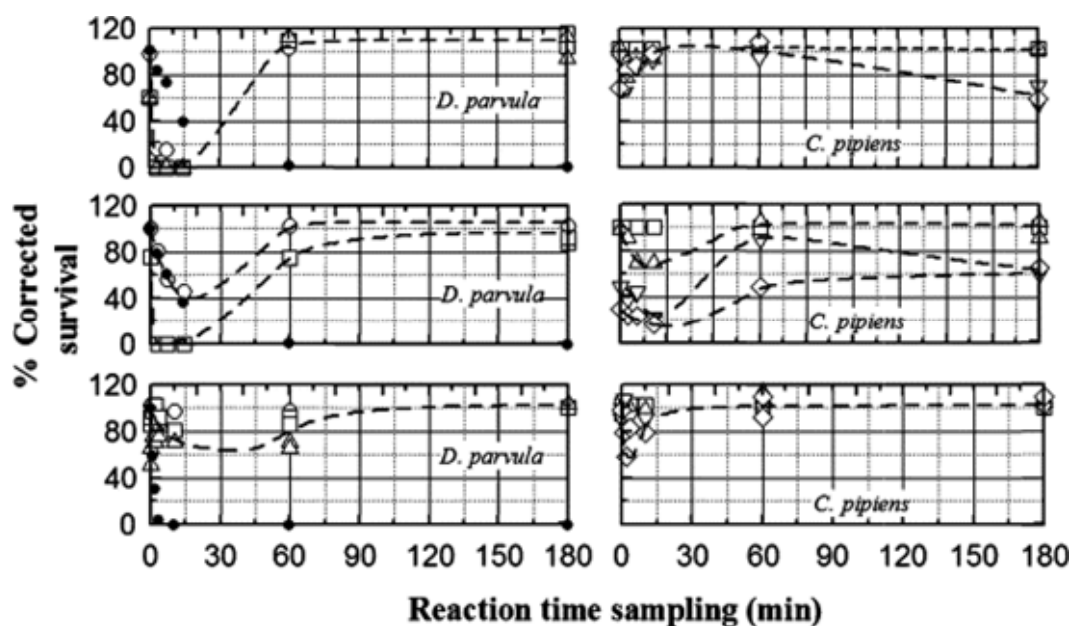


Fig. 9. Percentage of survival of *D. parvula* and *C. pipiens* larvae in solutions of photocatalytic ozonated MCPA at different reaction periods. Initial MCPA concentration: top figure = 100 mg/L; middle figure = 50 mg/L; bottom figure = 5 mg/L. Time of exposure (h): \circ , 6.0; \square , 24; \triangle , 48; ∇ , 72; \diamond , 96. (solid circles = remaining MCPA percentage).

In the case of *D. parvula*, a clear relationship between toxicity and MCPA abatement is inferred. For instance, when analyzing the experiment completed with an initial MCPA of 100 mg/L, the oxidized solution goes through a period when mortality increases to values of 100% regardless of the exposure time. Once MCPA is completely eliminated, the solution becomes non-toxic. Similar results were obtained when 50 mg/L of MCPA were oxidized. The most diluted MCPA concentration barely showed a small increase in toxicity in the first 30 min of photocatalytic ozonation. Thereafter, *D. parvula* survival increased to values close to 100%.

In the case of *C. pipiens*, patterns are similar to those obtained when *D. parvula* was used. The experiment conducted with 5 mg/L does not present appreciable toxicity after 5–10 min of treatment (100% MCPA conversion). When high MCPA concentrations were used, mortality significantly reduced to values close to zero when MCPA was removed from

solution (60 min), however, 72 and 96 h samples slightly reduced the survival percentage when the ozonation process was extended to 180 min. Increasing the reaction period to 180 min involves the generation of low weight carboxylic acids and release of free chlorine. Likely the accumulation of these species affects the survival of the larvae.

In any case, as a rule of thumb, after the oxidation, all samples showed toxicity values lower than the initial non-treated MCPA solution.

4. Conclusions

- MCPA is easily degraded by single ozonation or any combination of light, ozone and TiO₂.
- The photocatalytic ozonation leads to a significant mineralization of the initial TOC content at acceptable rates.
- TOC removal in TiO₂/O₃/UVA is significantly increased when working at 35 °C instead of 25 °C.
- The main intermediate generated in the photocatalytic ozonation of MCPA is 4-chloro-2-methyl phenol which is steadily removed from the media due to its high reactivity with ozone.
- TiO₂ concentration does not affect MCPA removal rate. TOC conversion is dependent on the amount of solid used. An optimum at 0.5 g/L was found under the experimental conditions investigated.
- End products accumulated after the photocatalytic ozonation present toxicity values toward *D. parvula* and *C. pipiens* larvae below the values obtained for the un-treated MCPA solutions.

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