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Photochemical degradation of 1,3-dichloro-2-propanol aqueous solutions

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Abstract

The photochemical oxidation of 1,3-dichloro-2-propanol (1,3-DCP) was studied by following the target compound degradation, the total carbon removal rate by a total organic carbon (TOC) analyzer and by identifying the oxidation products by gas chromatography–mass spectrometry (GC–MS). The reaction was performed in a batch recycle reactor, at room temperature, using UV radiation provided by a low pressure 12 W Hg lamp and H_2O_2 as oxidant. Chloride ions, formic, acetic and chloroacetic acid were measured by ion chromatography. Apart from the chloride ions and the organic acids, the presence of 1,3-dichloro-2-propanone and chloroacetyl chloride was also detected and a possible pathway is proposed for the degradation of the parent compound. Complete degradation of 1,3-dichloro-2-propanol was achieved and the TOC removal reached as much as 80% at the end of the reaction time. The effect of the initial concentration of hydrogen peroxide was investigated and it was established that higher concentrations of H_2O_2 slow down the reaction rate. Finally, the effect of the initial concentration of 1,3-DCP was investigated.
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1. Introduction

Dichloropropanols constitute an important class of water pollutants because of their toxicity to living organisms and bioaccumulation. They are used in industries such as hard resin production, chlorination of water or fabrication of paper. 1,3-DCP is carcinogenic, mutagenic and genotoxic, having a high risk factor for human and animal toxicity with regards to the environment. All formulations which contain more than 0.1% of DCP have to be labeled as toxic and carcinogenic according to EU directive 91/155/EEC [1]. The toxicity and persistence of halocarbons in the biological environment is attributed to the stability of the C−Cl bond.

Advanced Oxidation Processes (AOPs) have been demonstrated to be very effective in the effort to eliminate hazardous compounds, particularly as a means of water remediation. AOPs make use of different reacting systems, including photochemical degradation processes (UV/O_3, UV/H_2O_2), photocatalysis (TiO$_2$, photo-Fenton reagent) and chemical oxidation processes (O_3, O_3/H_2O_2, H_2O_2/Fe^{2+}). The most efficient of those used in recent years involve the use of UV irradiation. In general,

the term "AOPs" is used to describe the oxidation mechanism that depends on the production of very active species like hydroxyl radicals, which react almost non-selectively with the organic pollutants at very high rates, while addition of H_2O_2, commonly used as the source of these radicals since it decomposes to $^{\bullet}OH$ under ultraviolet irradiation, has been reported to accelerate the decomposition of organic compounds [2]. Moreover, the UV/H_2O_2 combination is one of the most appropriate AOP technologies for removing toxic organics from water because it may occur in nature itself and it follows one of three general pathways: (1) hydrogen abstraction, (2) electron transfer and (3) radical addition [3].

There are various studies in the related literature concerning the oxidation of chlorinated compounds using UV/H_2O_2 [3–10], the photo-Fenton process [11–14] or photocatalysis [15,16]. Chemical treatment of wastewaters by AOPs can result in the complete mineralization of the pollutants to carbon dioxide, water, inorganic compounds or, at least, in their transformation to harmless end products. On the other hand, partial decomposition of non-biodegradable organic contaminants may lead to biodegradable intermediates.

Little information is available on the photodegradation of 1,3-DCP, while a paper has been published by Nikolaki et al. [17] on the photocatalytical degradation of 1,3-DCP in a

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UV/H$_2$O$_2$/TiO$_2$ system. On the other hand, considerable attention has been paid to its biodegradation. Bastos et al. [18] compared two reactor systems, suspension batch and immobilized continuous, according to the degradation of 1,3-DCP. Degradation rates were lower when single species were used, reaching 45 mg l^{-1} d^{-1}, as compared to 74 mg l^{-1} d^{-1} of the consortia enriched on the batch method. Also, a lot of work has been done on toxicity studies. L'Huillier et al. [19] studied the relative embryotoxicity of 1,3-dichloro-2-propanol on primary chick embryonic cells and suggested that it had an inhibitory effect on embryo development. Hammond et al. [20] showed that 1,3-DCP was toxic to 24 h cultures of rat hepatocytes.

In the work considered here, the liquid containing the organic substrate was fed to a cylindrical batch recycle reactor. Experiments were performed at various initial 1,3-DCP and H$_2$O$_2$ concentrations to investigate the effects of their initial concentration on the oxidation rates. The contribution of this paper is to investigate the feasibility of treating 1,3-DCP contaminated water with UV/H$_2$O$_2$. We performed direct UV photolysis, and UV photolysis combined with H$_2$O$_2$ oxidation of 1,3-DCP solutions. Also, we performed experiments at various initial 1,3-DCP and H$_2$O$_2$ concentrations to estimate the influence of the active ingredient and the oxidative agent concentration on the reaction course. An attempt has been made to identify the oxidation products and to propose a possible pathway for the degradation.

2. Materials and methods

The photochemical oxidation of 1,3-DCP was investigated. The photoreactor consists of a low pressure Hg lamp of 12 W, which produces ultraviolet light of 254.7 nm, placed in the center of a glass cylindrical vessel with 19.5 cm height and 20 ml effective volume. 1,3-DCP was dissolved in water and the solution was recirculated with a pump. Pump supply was fixed at 50 ml/min. Immediately after adding the hydrogen peroxide, the light was turned on. During the reaction, the solution was maintained in suspension by magnetic stirring. The solution pH was measured during the experiment for observing the progress of the reaction by a PTW-pH90 pH-meter.

All reagents were used as received without any further purification. Fresh 1,3-DCP solutions were used. The initial concentration of each 1,3-DCP solution was 0.012 M. H$_2$O$_2$ solution, 28% (w/w), was used as a source of hydroxyl radicals. Only deionised water was used.

The evolution of the oxidation was attended via gas chromatography–mass spectroscopy analysis (Hewlett Packard GC 6890–MS 5973, column HP1-MS) for determining 1,3-DCP concentration and for the detection of the oxidation intermediates. The concentrations of total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) were measured with a total organic carbon analyzer (TOC-V 108 CSH, Shimadzu). A DX600 Ion Chromatographer Dionex (column: IonPac AS9-HC 4 mm) was used for the qualitative and quantitative determination of chloride ions, formic and acetic acid. Each experiment lasted 150 min.

3. Results and discussion

3.1. Base run

In the base run experiment, a solution of 1,3-DCP with a concentration of 0.012 M was prepared and it was oxidized with 0.081 M hydrogen peroxide under ultraviolet irradiation. Reactor samples were collected at specific time intervals (0, 5, 15, 30, 60, 90, 120 and 150 min).

The total organic carbon concentration decrease, the 1,3-DCP decrease and the production of acetic acid, formic, chloroacetic acid and chloride ions are depicted in Fig. 1.

It is obvious from Fig. 1 that the reaction progress leads to the complete degradation of 1,3-DCP and to a total organic carbon concentration decrease, while the chloride ion production increases and organic acids are produced. It must be noted that although 1,3-DCP is totally destroyed after the first hour of the reaction, the total organic carbon concentration decreases with a lower rate and at the end of the reaction reaches a total conversion of 65%. The production of the chloride ions was indicative of the mineralization of 1,3-DCP that took place gradually during the reaction. Approximately, 85% of the maximum chloride ion concentration that could be produced was detected at the end of the reaction, therefore, showing the degree of dechlorination of the chlorinated intermediates formed in the course of the reaction. From the diagram we can also observe that formic, acetic and chloroacetic acid arise as oxidation intermediates in the course of the reaction.

The difference between the parent compound and the TOC conversions can be attributed either to the insuffiency of free radicals produced in the reaction system under the investigated oxidation conditions or to the fact that more stable intermediates are formed during the degradation of the parent compound, such
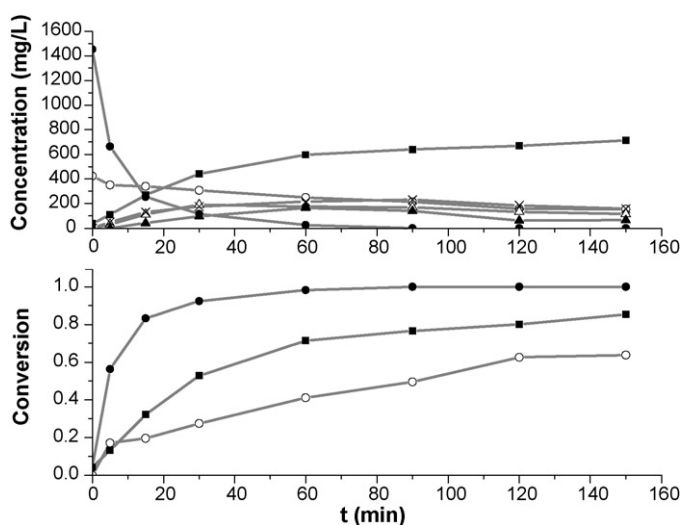

Fig. 1. 1,3-DCP, TOC concentration decrease, chloride ion concentration increase, acetic, formic, chloroacetic acid production and 1,3-DCP conversion, TOC removal and chloride ion production. For initial 1,3-DCP concentration 0.012 and 0.081 M hydrogen peroxide, under UV irradiation. (1,3-DCP (●), TOC (○), chloride ions (■) formic acid (△), acetic acid (▲) and chloroacetic acid (×)).

as of formic and acetic acid, which are small and stable organic acids [21].

3.2. Influence of hydrogen peroxide concentration

Experiments with different initial hydrogen peroxide concentrations were carried out for studying the photochemical oxidation of 1,3-DCP in water solutions, whereas the initial 1,3-DCP concentration was held constant at 0.012 M. All experiments were conducted under UV irradiation.

In Fig. 2, the effect on the conversion of 1,3-DCP and TOC is depicted for various φ, where φ is defined as the ratio of hydrogen peroxide initial concentration to the stoichiometric hydrogen peroxide concentration required for total conversion of 1,3-dichloro-2-propanol to carbon dioxide according to Eq. (1):

$$1,3\text{-DCP} + 7H_2O_2 \rightarrow 3CO_2 + 2HCl + 9H_2O \quad (1)$$
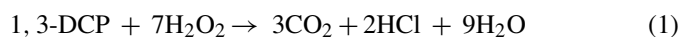
Consequently, $\varphi = 0$ means no hydrogen peroxide is present (photolysis of 1,3-DCP), whereas $\varphi = 1$ corresponds to the stoichiometric concentration of H_2O_2. The quantities of hydrogen peroxide 0, 0.008, 0.041, 0.081, 0.163, 0.244 and 0.407 M correspond to $\varphi = 0$, 1/10, 1/2, 1, 2, 3 and 5, respectively, and were selected in order to cover the range from complete lack to excess of oxidative agent. Reactor samples
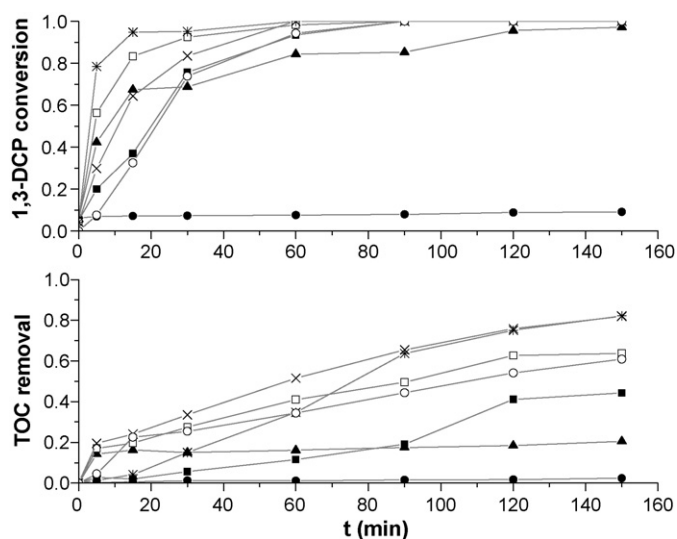

Fig. 2. 1,3-DCP conversion and TOC conversion for initial 1,3-DCP concentration 11.63 mmol/l, under UV irradiation, and for different hydrogen peroxide concentrations: ($\varphi = 0$ (●), $\varphi = 1/10$ (▲) $\varphi = 1/2$ (■) $\varphi = 1$ (□), $\varphi = 2$ (×), $\varphi = 3$ (*), $\varphi = 5$ (○).

were collected at specific time intervals (0, 5, 15, 30, 60, 90, 120 and 150 min). Figs. 2 and 3 exhibit the behavior of the reaction for ranging hydrogen peroxide concentrations.
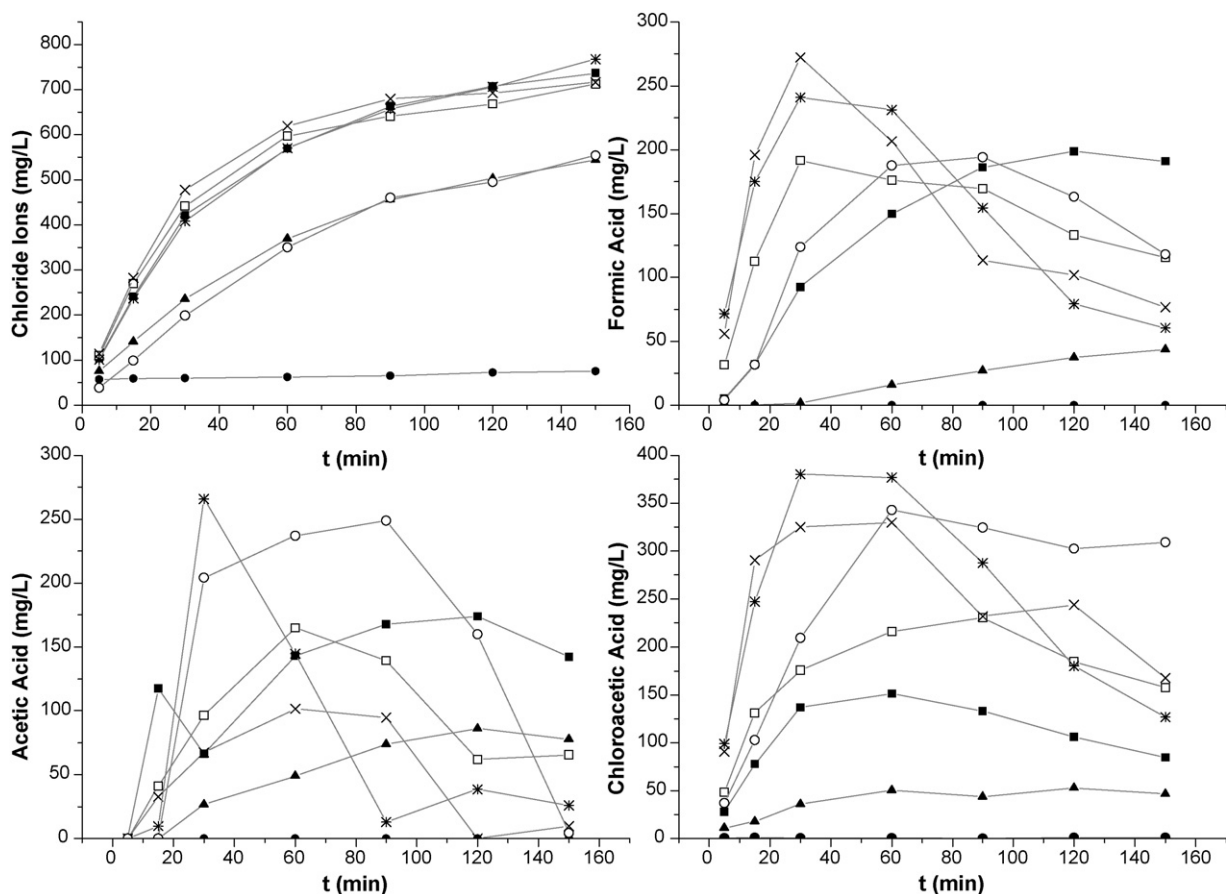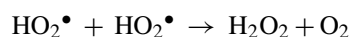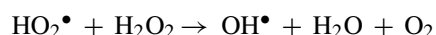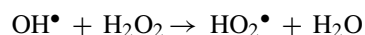

Fig. 3. Chloride ion production, formic, acetic and chloroacetic acid production for initial 1,3-DCP concentration 11.63 mmol/l under UV irradiation, and for different hydrogen peroxide concentrations. ($\varphi = 0$ (●), $\varphi = 1/10$ (▲), $\varphi = 1/2$ (■), $\varphi = 1$ (□), $\varphi = 2$ (×), $\varphi = 3$ (*), $\varphi = 5$ (○).

In photolysis (without H_2O_2), 1,3-DCP conversion reached 10% within 150 min and for stoichiometric analogies above $\varphi = 1/10$, 1,3-DCP is totally converted after the first hour of the reaction. Fig. 2 also presents the removal of the organic pollutants resulting from different hydrogen peroxide concentrations. For the case of direct photolysis, the TOC removal is negligible (2%), while for $\varphi = 1/10$ and 1/2, it does not exceed 20 and 45%, respectively. Higher yields are achieved for $\varphi = 1, 2, 3$ and 5. The maximum final TOC conversion are accomplished for $\varphi = 2$ and 3 corresponding to about 80%, while it must be noted that the final conversion is the same for $\varphi = 1$ and 5 rising slightly above 60%.

In UV direct photolysis, the contaminant to be destroyed absorbs the incident radiation and undergoes degradation starting from its excited state [2]. Since, the parent compound does not absorb radiation in the UV region emitted by the lamp, the small 1,3-DCP and TOC conversions observed could be attributed to the generation of hydroxyl radicals by photolysis of the aqueous medium. Also, UV irradiation alone would attack and decompose some organic molecules by bond cleavage and free radical generation, but usually at very slow rates [8]. It must also be noted that when the concentration of the oxidative agent is increased to $\varphi = 5$, the final conversion is decreased. This is attributed to the fact that high H_2O_2 concentration scavenges the radicals, making the process less effective [2]. This can be seen by the following reactions:

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$$

$$HO_2^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O + O_2$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$$

From Fig. 3, it can be seen that at the end of the reaction for complete lack of oxidative agent the chloride ion concentration is very low, that is 10% of the maximum possible, while for mild oxidative conditions ($\varphi = 1/10$), the ion production rises to 65%. For $\varphi = 1/2, 1$ and 2, the system follows a similar behavior, which can be attributed to the fact that the hydroxyl radicals extract chloride atoms from the chlorinated organic compounds, thus, achieving a constant chloride ion production rate for the first 30 min of treatment. After the first hour the chloride ion concentration tends to stabilize around a final value of about 80%. This is probably due to the formation of more resistant chlorinated intermediates and prevents the complete detachment of chloride ions from the organic molecules. For $\varphi = 5$ it must be noted that the chloride ion production yield is the same as for $\varphi = 1/10$, whereas for $\varphi = 3$ it is slightly higher. This fact is also due to radical scavenging by H_2O_2, as described above.

From Fig. 2 it can also be observed that for $\varphi = 0$ no acids are detected, while for $\varphi = 1/10$ the acids are produced in small quantities. For $\varphi = 1/2$, formic and acetic acid are produced during the decomposition of 1,3-DCP, but due to the insufficiency of oxidative agent, their concentration in the solution tends to stabilization as the reaction proceeds, whereas chloroacetic acid presents a peak at $t = 60$ min and then its concentration decreases. For all the other stoichiometric analogies, the organic acids concentration rise, reach a maximum and then gradually fall.

It is, therefore, deduced that TOC removal depends strongly on H_2O_2 concentration, while the 1,3-DCP decomposition does not exhibit strong dependence on the quantity of oxidative agent.

3.3. Influence of 1,3-DCP initial concentration

In order to investigate whether the initial 1,3-DCP concentration influences the 1,3-DCP conversion and the total organic carbon removal rate, experiments were conducted with the following initial 1,3-DCP concentrations: 0.012, 0.008, 0.004 and 0.002 M, while the stoichiometric analogy was held constant. The 1,3-DCP conversion, the TOC removal, the chloride ion production, formic, acetic and chloroacetic acid are depicted comparatively for the aforementioned initial concentrations in Figs. 4 and 5.

The experiments showed that for different initial 1,3-DCP concentrations, the target compound disappears completely at the end of the reaction indicating that the initial concentration does not influence the degradation of 1,3-DCP. In Fig. 4, the TOC conversion is also plotted for different 1,3-DCP initial concentrations. It must be noted that the highest final TOC conversion is observed for 0.002 M (70%), followed by 0.012 M (64%). The lowest TOC conversion is found for initial concentration 0.008 M (50%).

From Fig. 5, the gradual production of chloride ions is established as they arise in the reactor solution by the oxidation of 1,3-DCP and its chlorinated intermediates for different initial 1,3-DCP concentrations. It is observed that the initial production rate is particularly high, especially for the 0.012 and 0.008 M, and as the reaction progresses, the rate drops converging to a maximum constant value. The final chloride ion concentration provides a characteristic image of the oxidation of the chlorinated organic pollutants. At the end of the reaction, it must be noted that for 1,3-DCP initial concentrations 0.008 and 0.004 M all chloride ions initially attached to the 1,3-DCP molecule have
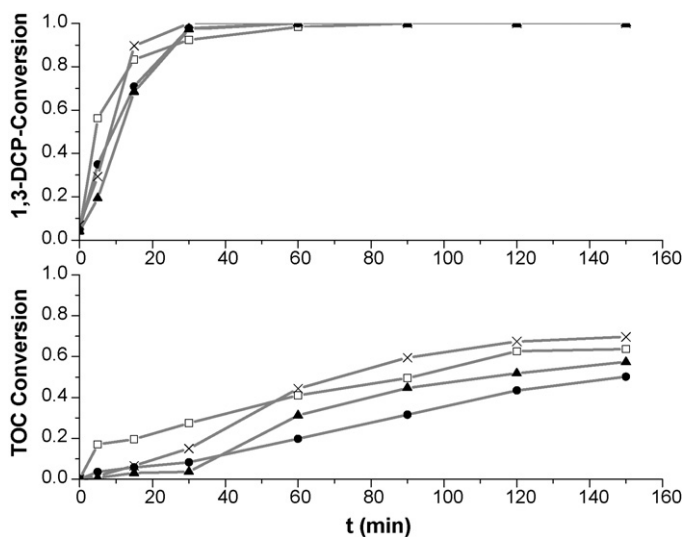

Fig. 4. 1,3-DCP conversion and TOC conversion for different initial 1,3-DCP concentrations and for a constant stoichiometric analogy $\varphi = 1$. (0.012 M ($\square$), 0.008 M ($\bullet$), 0.004 M ($\blacktriangle$) and 0.002 M ($\times$)).
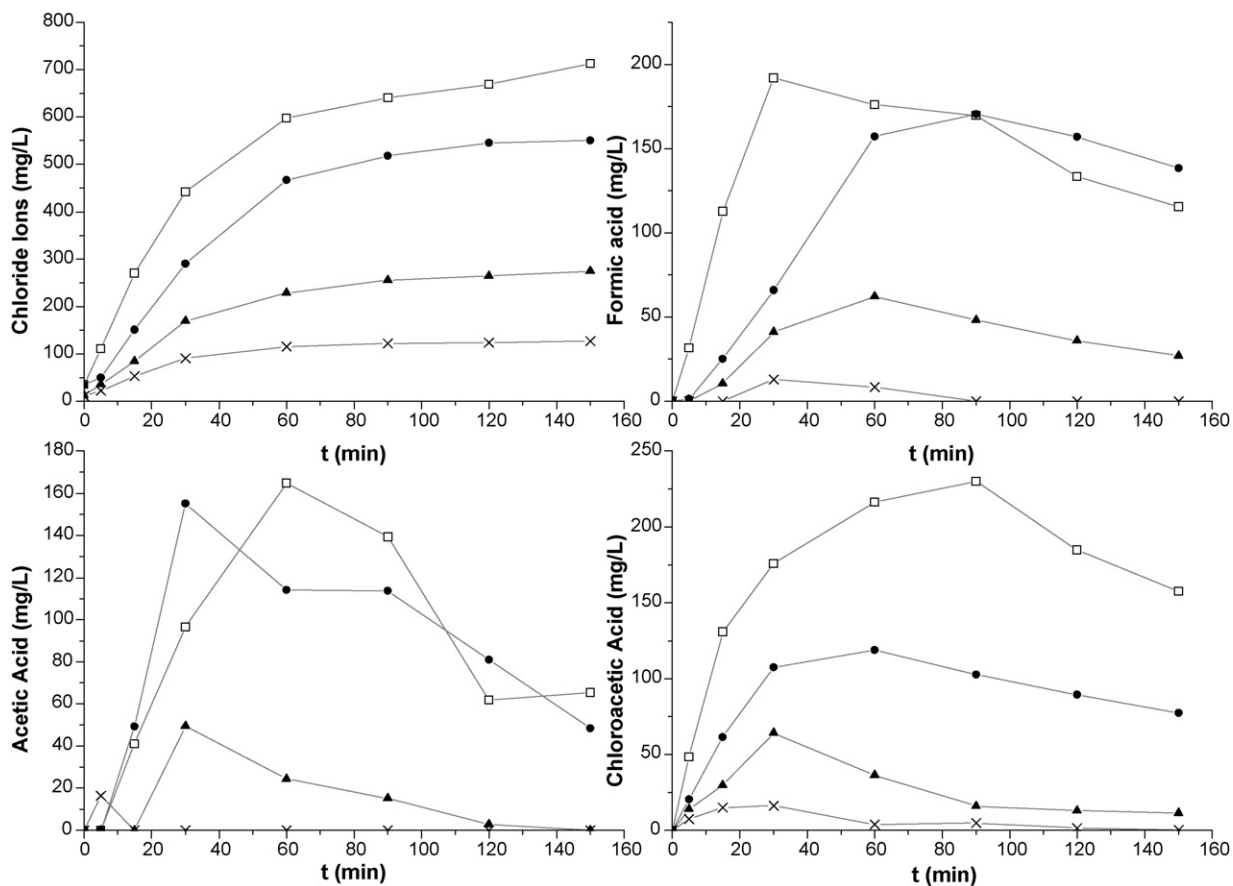
Fig. 5. Chloride ion production, formic, acetic and chloroacetic acid conversion for different initial 1,3-DCP concentrations and for a constant stoichiometric analogy $\varphi = 1$. (0.012 M (□), 0.008 M (●), 0.004 M (▲) and 0.002 M (×)).

been released in the reactor solution indicating that 1,3-DCP, as well as all the chlorinated intermediates have been dechlorinated. Also for 0.012 and 0.002 M the chloride ion yield accounts for 85% of the maximum possible.

Formic, acetic and chloroacetic acid are produced as intermediates during the oxidation of 1,3-DCP. From Fig. 5 it is observed that organic acids exhibit a similar behavior for different initial 1,3-DCP concentrations. Their concentrations rise, reach a maximum and then gradually fall, as they are decomposed. For small initial concentrations, 0.004 and 0.002 M, chloroacetic and acetic acid have been totally converted before the end of the reaction. Also, it must be noted that the chloroacetic and acetic acid production rates decrease for decreasing 1,3-DCP initial concentrations.

3.4. Intermediates

The intermediates detected during the photochemical oxidation of 1,3-DCP in the reactor system by the means of GC–MS analysis are the following: 1,3-dichloro-2-propanone, chloroacetyl chloride, chloroacetic acid, acetic acid and formic acid. Apart from the organic acids, for the rest of the intermediates only qualitative analysis has been conducted.

Based on the intermediates detected, a possible pathway for the oxidation of 1,3-dichloro-2-propanol is the follow-

ing: Primarily, the 1,3-dichloro-2-propanol molecule forms 1,3-dichloro-2-propanone under oxidative conditions. Consequently, chloroacetyl chloride and chloroacetic acid are formed. As a next step, chloroacetyl chloride is also converted to chloroacetic acid by the substitution of the chloride ion by a hydroxyl ion. Then, chloroacetic acid degrades to formic acid and formic acid decomposes to carbon dioxide.

3.5. Optimum value of the hydrogen peroxide concentration

It is obvious that for stoichiometric analogies above $\varphi = 1/10$ complete disappearance of the parent compound is achieved. On the other hand, due to the formation of intermediates, the total degradation of the target compound does not correspond to the total mineralization to carbon dioxide and water. Therefore, in order to deduce safe conclusions in terms of optimum oxidant agent concentration, the TOC concentration has to be taken into consideration, as well as the chloride ion final production, so as to ensure that the amount of chlorinated intermediates present in the final solution is as low as possible for the given process. The experimental data for different initial hydrogen peroxide concentrations show that the cases of $\varphi = 2$ and 3 combine the maximum TOC final conversion with a respectably high ion production. It must also be noted that increasing the H_2O_2 concentration enhanced the oxidation process up to a certain point

at which H_2O_2 started to inhibit the degradation, acting as a free radical scavenger itself.

4. Conclusions

In this work, the photochemical oxidation of 1,3-dichloro-2-propanol was studied in a H_2O_2/UV system. According to the results, the effect of the initial concentration of hydrogen peroxide was investigated and it was established that higher concentrations of H_2O_2 slow down the reaction, because H_2O_2 acts as scavenger of highly reactive OH^* to form oxygen and perhydroxyl radicals. TOC removal depends strongly on H_2O_2 concentration, while the 1,3-DCP decomposition does not exhibit strong dependence on the quantity of oxidative agent. 1,3-dichloro-2-propanone, chloroacetyl chloride, chloroacetic acid anhydride, acetic acid and formic acid were detected as intermediates by the means of GC–MS analysis and a possible pathway for the oxidation of 1,3-dichloro-2-propanol is proposed. The initial concentration of the target compound was found not influence the degradation of 1,3-DCP. The optimum hydrogen peroxide concentration was found to be $\varphi = 2$ and 3 combining the maximum TOC final conversion with a respectably high ion production and indicating a high mineralization degree.

Acknowledgements

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