

Photocatalytical degradation of 1,3-dichloro-2-propanol aqueous solutions by using an immobilized TiO₂ photoreactor

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Abstract

The photocatalytic oxidation of 1,3-dichloro-2-propanol (1,3-DCP) was studied by following the target compound degradation, the total organic carbon removal rate and by identifying the oxidation products. The reaction was performed in a batch recycle reactor, at room temperature, using UV radiation, H₂O₂ as oxidant, and immobilized TiO₂ as catalyst. 1,3-Dichloro-2-propanone, chloroacetyl-chloride, chloroacetic acid, formic and acetic acid were detected as reaction intermediates and a possible pathway for the oxidation of 1,3-dichloro-2-propanol is proposed. The effect of the oxidative agent's initial concentration was investigated and it was established that higher concentrations of H₂O₂ slow down the reaction rate. The investigation of the effect of the 1,3-DCP initial concentration showed no influence on the degradation process. The carbon and chloride ion mass balance calculations confirmed the fact that chlorinated intermediates are formed and that they degrade with a lower rate than 1,3-DCP.

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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 and fabrication of paper [1]. 1,3-Dichloro-2-propanol (1,3-DCP) is formed in the reaction of epichlorohydrin with chloride ions and belongs to the family of halohydrins that are used widely as reagents in chemical manufacture. Moreover, 1,3-DCP is carcinogenic, mutagenic and genotoxic, having a high risk factor for human and animal toxicity with regards to the environment [2] and according to EU directive 91/155/EEC, all formulations which contain more than 0.1% of DCP have to be labeled as toxic and carcinogenic [3].

Although little information is available on the photodegradation of 1,3-DCP, considerable attention has been paid to its biodegradation. Bastos et al. [2] compared two reactor systems, suspension batch and immobilized continuous, and concluded that degradation rates reached 45 mg L⁻¹ day⁻¹, as compared to

74 mg L⁻¹ day⁻¹ of the batch method. Also a lot of work has been done on toxicity studies. L'Huillier et al. [1] 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 and Hammond et al. [5] showed that 1,3-DCP was toxic to 24 h cultures of rat hepatocytes.

Advanced oxidation processes are at present considered to have considerable potential in degrading chlorinated organic compounds. AOPs make use of different reacting systems, including photochemical degradation processes (UV/O₃, UV/H₂O₂), photocatalysis (TiO₂/UV, photo-Fenton reagent), and chemical oxidation processes (O₃, O₃/H₂O₂, H₂O₂/Fe²⁺). 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.

Photocatalytic degradation of water organic pollutants appears to be the method of choice, in particular when using TiO₂. TiO₂ is currently considered as the most promising photocatalyst because of its absence of toxicity, reasonable photocatalytic activity, relatively low cost, and high stability toward photocor-

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Nomenclature

C_{acetic} carbon concentration contained by acetic acid (mg/L)

C_{DCP} carbon concentration contained by 1,3-DCP (mg/L)

C_{formic} carbon concentration contained by formic acid (mg/L)

Chloride ion production the ratio of the chloride ions concentration measured in the sample to the maximum chloride ion concentration that could be released in the reactor sample

C_{inter} carbon concentration contained in organic intermediates except organic acids (mg/L)

Cl_{DCP} chloride ion concentration contained by 1,3-DCP (mg/L)

Cl_{free} chloride ion concentration measured in the reactor sample (mg/L)

Cl_{inter} chloride ion concentration contained in organic intermediates (mg/L)

1,3-DCP 1,3-dichloro-2-propanol

1,3-DCP conversion the ratio defined as the difference of the initial 1,3-DCP concentration minus the concentration at a given time to the initial concentration

TOC total organic carbon (mg/L)

TOC conversion the ratio defined as the difference of the initial TOC concentration minus the concentration at a given time to the initial concentration

Greek letter

ϕ the ratio of hydrogen peroxide initial concentration to the necessary hydrogen peroxide concentration for total conversion of 1,3-dichloro-2-propanol to carbon dioxide according to Eq. (1)

ca. 6% of the solar spectrum [9]. Wang et al. [10] report that in the case of TiO_2 the major advantages of photocatalytic processes are the following: (i) complete oxidation of organic pollutants in a few hours; (ii) highly active catalyst adaptable to specially designed reactor system; (iii) oxidation of pollutant in ppb range.

The pH of the aqueous solution is one of the important environmental parameters that significantly influences the physico-chemical properties of semiconductors, including the charge on particle, the aggregation numbers of particles, and the position of the conduction and valence bands. Higher pH can provide hydroxyl ions to react with positively charged holes on the catalyst surface to form hydroxyl radicals [11].

In the work considered here, TiO_2 catalyst was supported on the surface of a cylindrical reactor, across which the liquid containing the organic substrate was fed. Experiments were performed under UV light at 254.7 nm provided by a 12 W low-pressure Hg lamp at various initial 1,3-DCP and H_2O_2 concentrations in order to investigate the effects of their initial concentration on the oxidation rates. The contribution of this paper is to present photocatalytic oxidation data for 1,3-dichloro-2-propanol, to identify the oxidation products, to propose a possible pathway for the photocatalytic degradation of the substrate, to estimate the influence of the active ingredient and the oxidative agent concentration on the reaction course. Finally carbon and chloride ion mass balance calculations were made in order to confirm the oxidation course of the intermediates.

2. Materials and methods

The photocatalytic oxidation of 1,3-DCP was investigated with the apparatus shown in Fig. 1. The photoreactor consists of a low-pressure Hg lamp of 12 W, which emits mainly (85–90%) ultraviolet light at 254.7 nm and 7–10% at 184.9 nm. The lamp is 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. After a series of experiments for different recycling solution feed, it was established that pump supply does not affect process results. 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-pH 90 pH-

rosion. According to Rideh et al. [6] the primary mechanism of photodegradation is the generation of hydroxyl radicals obtained by the reaction of holes with surface hydroxyls or water and their attachment to organic compounds. Hydroxyl radicals are very reactive neutral species; they react rapidly and non-selectively with organic compounds and are the common oxidizing agent [6]. However, there are reports in the literature [7] about free radical formation in water by TiO_2 emphasizing on the fact that depending upon the exact conditions, the holes, OH^\bullet radicals, O_2^- , H_2O_2 and O_2 itself can all play important roles in the photocatalytic reaction mechanisms.

Particularly heterogeneous photocatalysis is an alternative economical and harmless technology of AOP for removal of organic impurities. During the process illuminated semiconductor absorbs light and generates active species. A distinct advantage of photocatalysis lies in its ability to utilize solar energy in the production of active species [8]. TiO_2 has a large bandgap energy, and as a consequence is able to absorb ultraviolet light (typically <380 nm), which represents a small fraction,

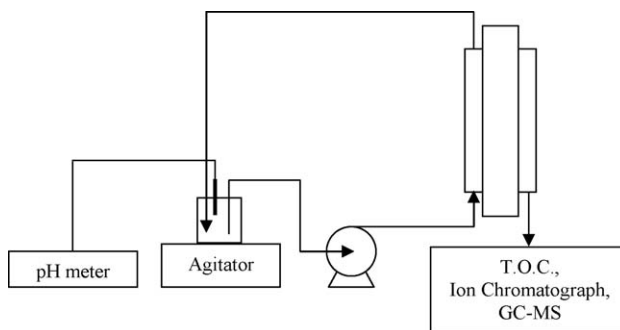


Fig. 1. Experimental apparatus.

meter. Due to the low output of the lamp (12 W) the system did not require heating or refrigeration. Moreover the reactor temperature was monitored during lamp operation and was found to have a ± 1 °C fluctuation from room temperature.

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. H₂O₂ solution, 28% (w/w), was used as a source of hydroxyl radicals. Only deionised water was used.

The catalyst is immobilized in the internal surface of the cylindrical tube. The method used for the immobilization [12] is the following: a borosilicate glass cylindrical vessel was used as support substrate after etching with NaOH solutions. It was thoroughly cleaned before immobilization with detergent solutions, different organic solvents, hydrochloric acid, and ultrapure water. The immobilization technique employed was based on titania powder (Degussa P25). The TiO₂ powder was suspended with a concentration $\rho = 5$ g/L in a methanol–water mixture 95%/5% adjusted at pH 3 with HNO₃. The suspension was sonicated for 30 min. The titania suspension was spread by pipetting on the heated borosilicate glass (100 °C) and dried (30 min) in an oven at 100 °C. As the crystal structures of the TiO₂ coating depend on the sintering, the coated glass was sintered for 3 h at 450 °C. After the catalyst immobilization procedure, the TiO₂ surface macroscopically appeared to be homogeneous.

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 chromatograms obtained were analyzed via a personal computer and the appropriate software (HP Chemstation). 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 ion, formic and acetic acid. The chromatograms obtained were analyzed by means of a personal computer and the appropriate software (Peaknet 6, Version 6.4). Each experiment lasted 150 min.

3. Results and discussion

3.1. Base run

Preliminary experiments were conducted in an identical reactor without using immobilized titanium dioxide as catalyst and in complete lack of hydrogen peroxide in order to study the contribution of direct photolysis. The results showed that TOC removal after 150 min was below 2% and, therefore, removal due to photolysis was considered negligible in the rest of the experiments.

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 and in the presence of immobilized titanium dioxide. Reactor samples

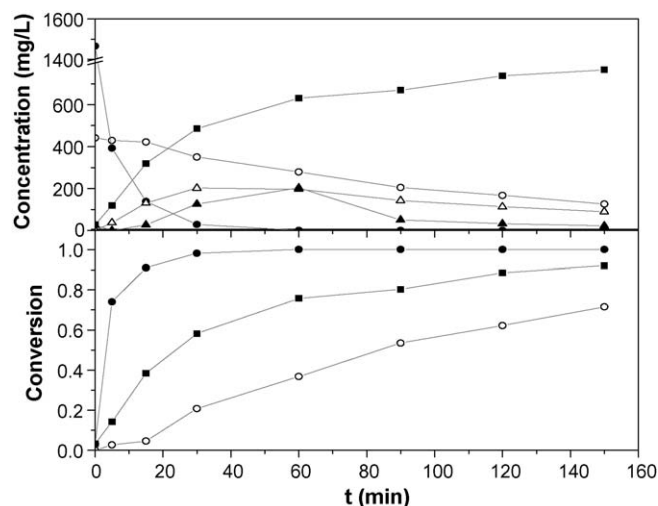


Fig. 2. 1,3-DCP, TOC concentration decrease, chloride ion concentration increase, acetic and formic acid production, TOC removal and chloride ion production. For initial 1,3-DCP concentration 0.012 M, 0.081 M hydrogen peroxide, in the presence of TiO₂ and under UV irradiation (1,3-DCP, ●; TOC, ○; chloride ions, ■; formic acid, △; acetic acid, ▲).

were collected at specific time intervals (0, 5, 15, 30, 60, 90, 120, 150 min).

The total organic carbon concentration decrease, the 1,3-DCP decrease and the production of acetic acid, formic acid and chloride ions are depicted in Fig. 2.

It is obvious from Fig. 2 that the reaction progress leads to the complete disappearance of 1,3-DCP and to a total organic carbon concentration decrease, while the chloride ion production increases and formic and acetic acid 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 70%. The production of the chloride ions was indicative of the mineralization of 1,3-DCP that took place gradually during the reaction. Approximately 90% 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 and acetic acid, which arise as intermediates, exhibit similar behaviors. Formic acid has a higher production rate than acetic acid, its concentration reaches a maximum at $t = 30$ min and then drops smoothly as it is converted to carbon dioxide. On the other hand, acetic acid reaches a maximum at $t = 60$ min, then its concentration drops with a higher decomposition rate and at the end of the reaction most of it has been converted to carbon dioxide.

3.2. Influence of hydrogen peroxide concentration

Experiments with different initial hydrogen peroxide concentrations were carried out for studying the photocatalytic 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.

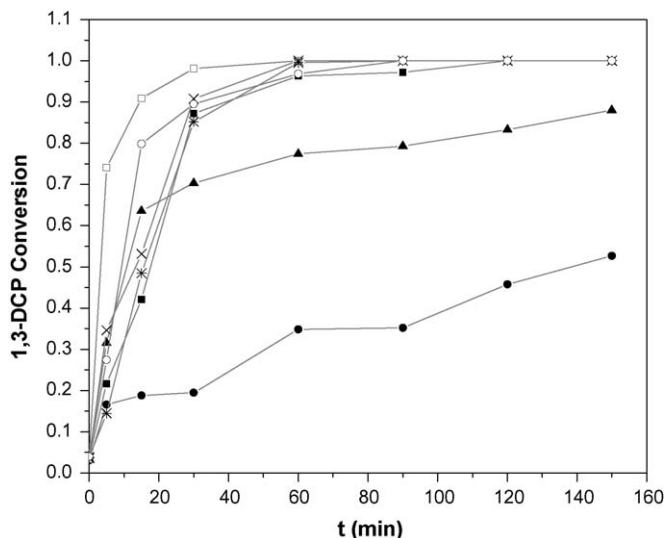
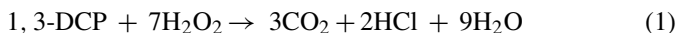


Fig. 3. 1,3-DCP conversion. For initial 1,3-DCP concentration 0.012 M, in the presence of TiO_2 and under UV irradiation, and for different hydrogen peroxide concentrations ($\varphi=0$, ●; $\varphi=1/10$, ▲; $\varphi=1/2$, ■; $\varphi=1$, □; $\varphi=2$, ×; $\varphi=3$, *; $\varphi=5$, ○).

tion and in the presence of immobilized titanium dioxide as catalyst.

In Fig. 3, the effect on the conversion of 1,3-DCP 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):



Consequently, $\varphi=0$ means no hydrogen peroxide is present (photocatalysis 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, 0.407 M correspond to $\varphi=0$, 1/10, 1/2, 1, 2, 3, 5, respectively, and were selected in order to cover the range from complete lack to excess of oxidative agent.

In photocatalysis (without H_2O_2), 1,3-DCP conversion reached 50% within 150 min and for mild oxidative conditions ($\varphi=1/2$) conversion rose to almost 90%. For stoichiometric analogies above $\varphi=1$, 1,3-DCP is totally converted after the first hour of the reaction. The highest initial conversion rate is observed for $\varphi=1$, whereas between conversions for $\varphi=2, 3, 5$ very small differences are noted.

Fig. 4 exhibits the behavior of TOC removal versus time for the different hydrogen peroxide stoichiometric analogies. For $\varphi=0, 1/10$ only a very small amount of TOC has been converted to carbon dioxide at the end of the reaction, 7 and 20% respectively. Similar results are obtained for $\varphi=1/2$, with the removal reaching almost 50%. For $\varphi=1$ and 5 the behavior of the system is similar and the final removal exceeds 70%. The maximum TOC removal is accomplished for $\varphi=3$, where as much as 95% of the initial concentration is converted to carbon dioxide at the end of the reaction, followed by $\varphi=2$ with a final TOC removal of 88%. This fact indicates that higher concen-

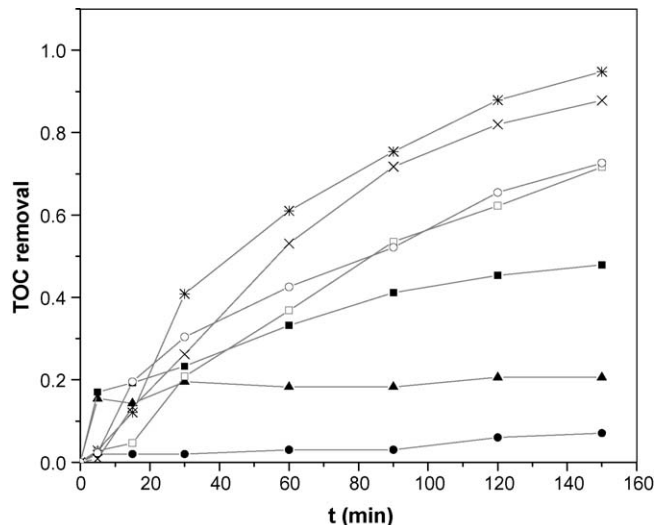


Fig. 4. TOC removal. For initial 1,3-DCP concentration 0.012 M, in the presence of TiO_2 and under UV irradiation, and for different hydrogen peroxide concentrations ($\varphi=0$, ●; $\varphi=1/10$, ▲; $\varphi=1/2$, ■; $\varphi=1$, □; $\varphi=2$, ×; $\varphi=3$, *; $\varphi=5$, ○).

trations of H_2O_2 slow down the reaction, because H_2O_2 acts as scavenger of highly reactive OH^\bullet to form oxygen and perhydroxyl radicals [13].

In Fig. 5 the chloride ion production has been plotted versus time for the different stoichiometric analogies. It is obvious that as the reaction proceeds, the chloride ion production increases. For $\varphi=0$, the chloride ion production is extremely low (8%), whereas for $\varphi=1/10$ the percentage rises to almost 50% of the maximum chloride ion concentration that can be produced from 1,3-DCP. All the other stoichiometric analogies exhibit similar behaviors: the production rises with a decreasing rate and tends towards a constant value at the end of the reaction, ranging from 80 to 90%.

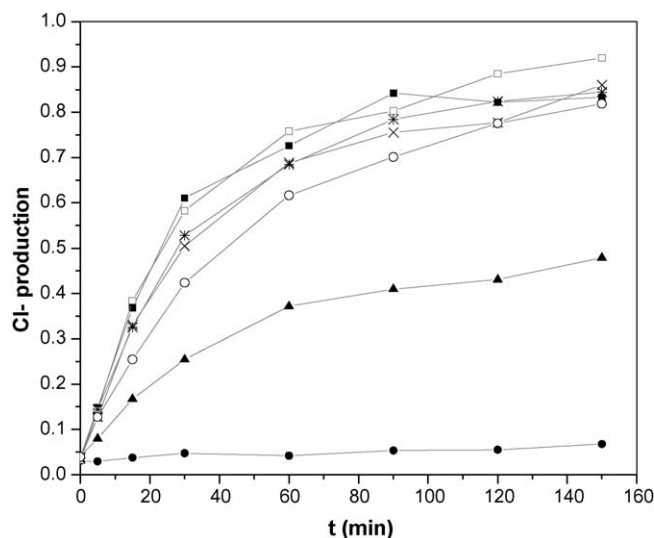


Fig. 5. Chloride ion production. For initial 1,3-DCP concentration 0.012 M, in the presence of TiO_2 and under UV irradiation, and for different hydrogen peroxide concentrations ($\varphi=0$, ●; $\varphi=1/10$, ▲; $\varphi=1/2$, ■; $\varphi=1$, □; $\varphi=2$, ×; $\varphi=3$, *; $\varphi=5$, ○).

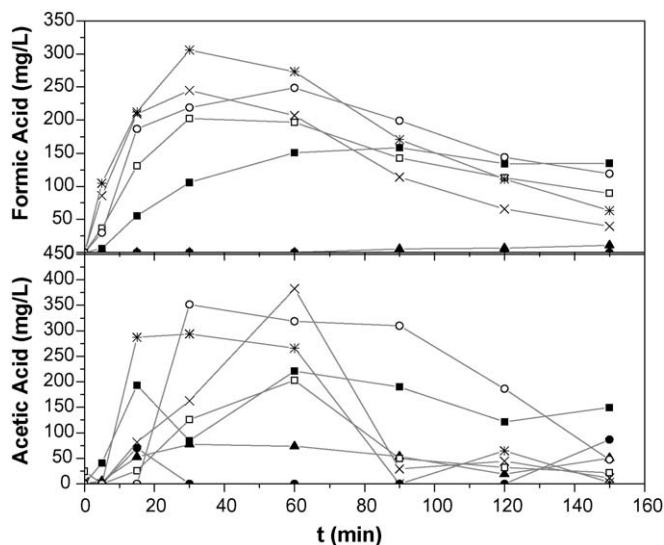


Fig. 6. Formic and acetic acid production. For initial 1,3-DCP concentration 0.012 M, in the presence of TiO_2 and under UV irradiation, and for different hydrogen peroxide concentrations ($\varphi=0$, ●; $\varphi=1/10$, ▲; $\varphi=1/2$, ■; $\varphi=1$, □; $\varphi=2$, ×; $\varphi=3$, *; $\varphi=5$, ○).

From Fig. 6 we observe that for $\varphi=0$ no acids are detected, while for $\varphi=1/10$ only a very small concentration of acetic acid is measured. 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 towards stabilization as the reaction proceeds. For the other analogies, the formic acid concentration follows a similar behavior: it rises with approximately the same rate, reaches a maximum and then gradually falls, as formic acid is apparently decomposed to carbon dioxide. On the other hand, the behavior of the acetic acid concentration is complicated, exhibiting two local maximums. This can be attributed to parallel reactions taking place in the reactor system.

It is, therefore, deduced that TOC removal depends strongly on H_2O_2 concentration, while the 1,3-DCP degradation does not exhibit strong dependence on the quantity of oxidative agent. No significant difference is observed for $\varphi=1, 2, 3, 5$ regarding the chloride ion, formic and acetic acid production.

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, 0.002 M, while the stoichiometric analogy was held constant.

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.

The TOC removal, the chloride ion production and formic and acetic acid production are depicted comparatively for the aforementioned initial concentrations, in Figs. 7–9, respectively. The data in these figures demonstrate that for different initial 1,3-

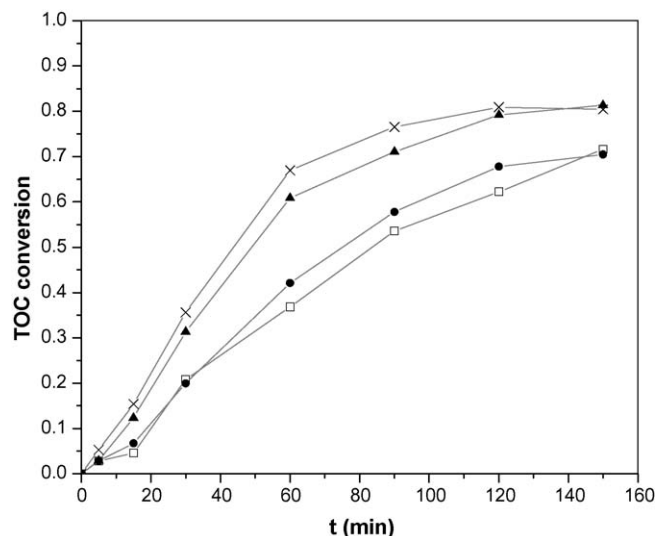


Fig. 7. TOC conversion in the presence of TiO_2 and under UV irradiation for different initial 1,3-DCP concentrations and for a constant stoichiometric analogy $\varphi=1$ (0.012 M, □; 0.008 M, ●; 0.004 M, ▲; 0.002 M, ×).

DCP concentrations, the reaction progress led to total organic carbon concentration decrease, while the chloride ions, formic and acetic acid concentrations increased.

In Fig. 7 is plotted the TOC conversion for different 1,3-DCP initial concentrations. It must be noted that for 0.002, 0.004 M the final conversion achieved reaches 80% against 70% for 0.008 and 0.012 M. This difference in the final conversion percentages can be attributed to the fast formation of intermediates, which compete for active centers onto Ti-surface, are adsorbed and block photoreactive sites, thus having an inhibiting effect on the degradation rate. Another parameter that may act as a limiting factor in TOC conversion is the recombination of the photogenerated electron/hole pairs on the catalyst surface.

Fig. 8 shows the gradual production of chloride ions, as they arise in the reactor solution by the oxidation of 1,3-DCP

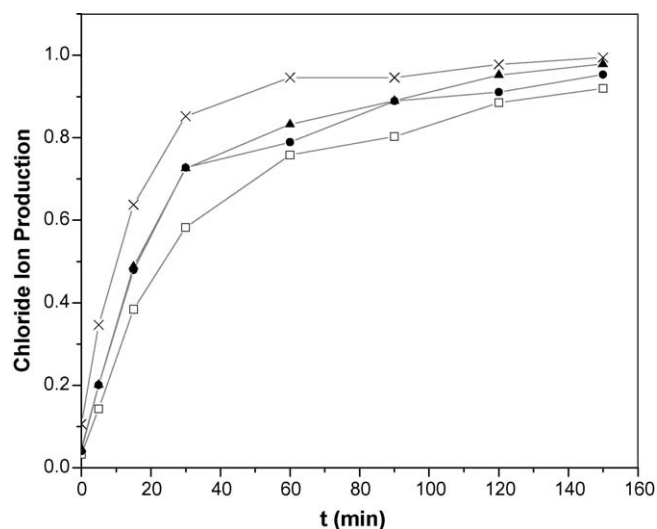


Fig. 8. Chloride ion production in the presence of TiO_2 and under UV irradiation for different initial 1,3-DCP concentrations and for a constant stoichiometric analogy $\varphi=1$ (0.012 M, □; 0.008 M, ●; 0.004 M, ▲; 0.002 M, ×).

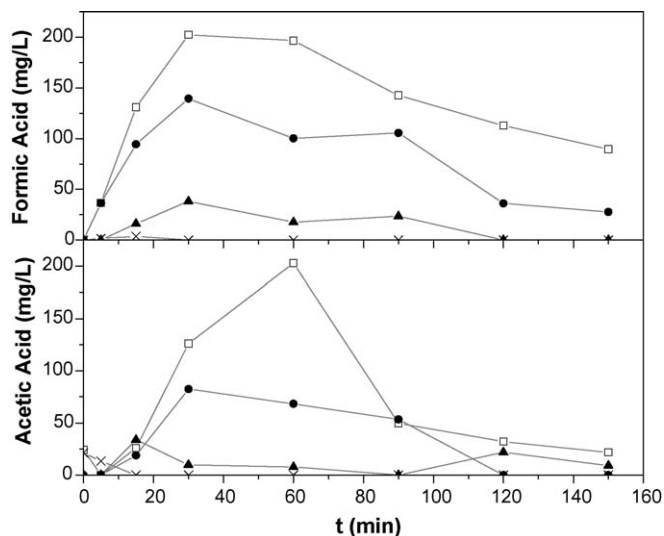


Fig. 9. Formic and acetic acid production concentrations in the presence of TiO_2 and under UV irradiation for different initial 1,3-DCP concentrations and for a constant stoichiometric analogy $\varphi = 1$ (0.012 M, \square ; 0.008 M, \bullet ; 0.004 M, \blacktriangle ; 0.002 M, \times).

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 initial concentrations of 0.012 and 0.004 M, and as the reaction proceeds 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. The lower the initial 1,3-DCP concentration is, the larger the percentage of the chloride ions produced. At the end of the reaction for 0.002 M it must be noted that all chloride ions initially attached to the 1,3-DCP molecule have been released in the reactor solution indicating that 1,3-DCP, as well as all the chlorinated intermediates have been dechlorinated. Also for 0.008 and 0.004 M the chloride ion yield accounts for 95% of the maximum possible.

The lower chloride ion production rates for higher 1,3-DCP initial concentrations can be attributed to the fact that chloride ions compete with organic species for active reaction sites on the catalyst surface.

As it has been mentioned before, formic and acetic acid are produced as intermediates during the oxidation of 1,3-DCP. From Fig. 9 it is observed that both acids exhibit a similar behavior for different initial 1,3-DCP concentrations. The concentration of formic acid rises, reaches a maximum at $t = 30$ min and then gradually falls, as it is decomposed to carbon dioxide. For small initial concentrations, 0.004 and 0.002 M, formic acid has been totally converted to carbon dioxide at the end of the reaction. Also, it must be noted that the formic acid production rate decreases for decreasing 1,3-DCP initial concentrations. The production of acetic acid is related to the initial concentration of the organic substrate. The maximum in its concentration is detected earlier in the course of the reaction for smaller initial 1,3-DCP initial concentrations and then the concentration drops as the reaction proceeds.

3.4. Intermediates—pathway

The intermediates detected during the photocatalytic 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 formic and acetic acid, 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 following: 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. Mass balance

In water purification processes is important not only the degradation of the parent compound, but also its complete degradation to inorganic ingredients, such as carbon dioxide and inorganic compounds. As far as halocarbons are concerned, their toxicity and persistence in the biological environment is attributed to the stability of the C–Cl bond. Moreover, when organochlorine compounds undergo oxidation, they may produce other organochlorine compounds that may be more toxic than the parent compound itself [4].

Therefore, the oxidation data has been processed in terms of carbon and chloride ion mass balance, in order to examine the mineralization grade of 1,3-dichloro-2-propanol during the photocatalytic process. The results presented here arise from the data of the base run (0.012 M 1,3-DCP, $\varphi = 1$).

In Fig. 10 for 1,3-DCP initial concentration of 0.012 M and for the stoichiometric analogy $\varphi = 1$ have been plotted the total organic carbon concentration (TOC), the concen-

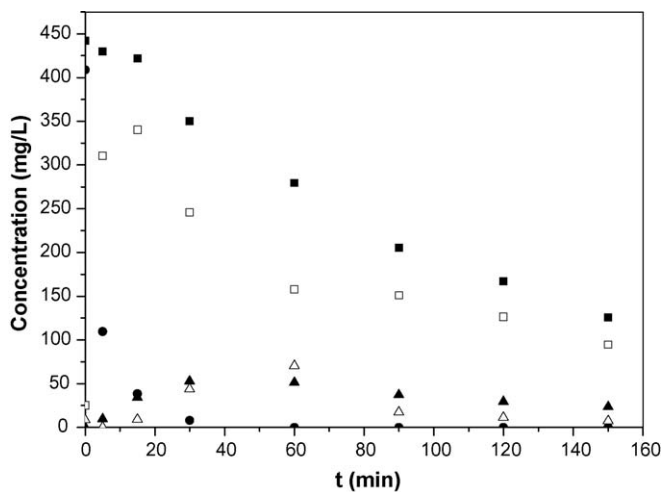


Fig. 10. TOC, C_{DCP} , C_{inter} , C_{formic} , C_{acetic} concentrations in the presence of TiO_2 and under UV irradiation for a constant stoichiometric analogy $\varphi = 1$ (TOC, \blacksquare ; C_{DCP} , \bullet ; C_{inter} , \square ; C_{formic} , \blacktriangle ; C_{acetic} , \triangle).

tration of the carbon bound on 1,3-DCP (C_{DCP}), on formic (C_{formic}) and on acetic acid (C_{acetic}), as well as the concentration of the carbon bound on the oxidation intermediates (C_{inter}), that has been calculated as the difference $C_{\text{inter}} = \text{TOC} - C_{\text{DCP}} - C_{\text{acetic}} - C_{\text{formic}}$.

From Fig. 10 it can be deduced that the concentration of carbon attached to 1,3-DCP decreases rapidly, while the TOC concentration exhibits a far smoother decrease with time. As the reaction proceeds, a part of the carbon bound initially on 1,3-DCP is transformed to carbon dioxide and organic acids, while another part of it remains bound on the organic intermediates. It must be noted that the intermediates are formed mainly during the first steps of the oxidation and that they also undergo degradation themselves, apparently towards carbon dioxide and organic acids. Therefore, although 1,3-DCP completely disappears at the end of the reaction, complete mineralization has not occurred.

Since it has been established that organic intermediates persist in the final reactor solution, an additional check has been performed in order to confirm whether the intermediates are chlorinated or not. Therefore the mass chloride ion balance has also been calculated as follows: Cl_{DCP} represents the chloride ions attached to the 1,3-DCP molecule, Cl_{free} are the chloride ions measured in the reactor solution, Cl_{inter} is the chloride ion concentration that is attributed to the intermediates, since it is neither no longer bound on 1,3-DCP nor exists in the form of chloride ions in the solution.

Fig. 11 shows that during the degradation of 1,3-DCP some chloride ions are gradually released in the solution, while a considerable amount initially bound on 1,3-DCP remain bound on the intermediates, before also ending up in the reactor solution. Therefore, it is confirmed that the intermediates produced during the photocatalytic degradation are chlorinated. Finally from the slope of the intermediates' carbon and chloride ion concentration it is deduced that the intermediates degrade with a lower rate than 1,3-DCP.

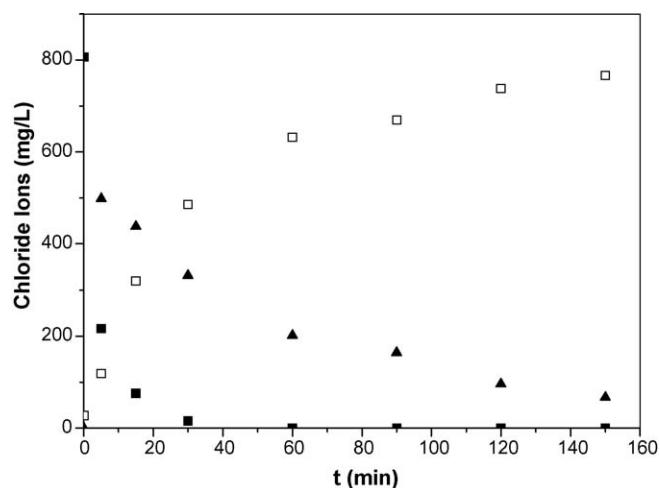


Fig. 11. $\text{Cl}_{1,3\text{-DCP}}$, Cl_{free} , Cl_{inter} concentrations in the presence of TiO_2 and under UV irradiation for a constant stoichiometric analogy $\varphi = 1$ (Cl_{DCP} , ■; Cl_{free} , □; Cl_{inter} , ▲).

3.6. 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 case of $\varphi = 3$ combines 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 photocatalytic oxidation of 1,3-dichloro-2-propanol was studied in a $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ system. From the experimental results the following conclusions can be drawn:

- The effect of the initial hydrogen peroxide concentration was investigated and it was established that higher concentrations of H_2O_2 slow down the reaction rate, because H_2O_2 acts as scavenger of highly reactive OH^\bullet to form oxygen and perhydroxyl radicals.
- TOC removal depends strongly on H_2O_2 concentration, while the 1,3-DCP degradation does not exhibit strong dependence on the quantity of oxidative agent.
- 1,3-Dichloro-2-propanone, chloroacetyl-chloride, chloroacetic acid, 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 to influence its degradation, while it was observed that the higher the initial concentration, the lower the chloride ion production rate due to the fact that chloride ions compete with organic species for active reaction sites on the catalyst surface.
- The optimum hydrogen peroxide concentration was found to be $\varphi = 3$ combining the maximum TOC final conversion with a respectably high ion production and indicating a high mineralization degree.
- The carbon and chloride ion mass balance calculations confirmed the fact that chlorinated intermediates are formed and that they degrade with a lower rate than 1,3-DCP.

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