

Photo-Fenton Treatment of 1,3-dichloro-2-Propanol Aqueous Solutions using UV Radiation and H_2O_2 – A Kinetic Study

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Abstract—The photochemical and photo-Fenton oxidation of 1,3-dichloro-2-propanol was performed in a batch reactor, at room temperature, using UV radiation, H_2O_2 as oxidant, and Fenton's reagent. The effect of the oxidative agent's initial concentration was investigated as well as the effect of the initial concentration of Fe(II) by following the target compound degradation, the total organic carbon removal and the chloride ion production. Also, from the kinetic analysis conducted and proposed reaction scheme it was deduced that the addition of Fe(II) significantly increases the production and the further oxidation of the chlorinated intermediates.

Keywords—1,3-dichloro-2-propanol, hydrogen peroxide, photo-Fenton, UV.

I. INTRODUCTION

DRINKING water is vital for supporting life on earth and as such, we should do everything within our power to safeguard its quality. Despite the fact that the greatest part of earth is covered by water, only a small percentage of this water is appropriate for drinking. According to WHO estimations, one quarter of the world's population lacks hygienic drinking water. Unfortunately, our daily routine as well as the production of various goods results in the discharge of many organic compounds in the aquatic environment. Among them, dichloropropanols constitute an important class of water pollutants because of their toxicity to living organisms and bioaccumulation. In particular, 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 [1] 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 [2]. Although little information is available on

the photodegradation of 1,3-DCP [3,4], considerable attention has been paid to its biodegradation [1] and on toxicity studies [5]- [6].

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/O_3 , $\text{UV/H}_2\text{O}_2$), photocatalysis (TiO_2/UV , photo-Fenton reagent), and chemical oxidation processes (O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$). The light driven AOPs involve the production of hydroxyl radicals, which react almost non-selectively with the organic pollutants at very high rates. 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.

Among AOP processes, Fenton reaction has been widely studied because it is an important source of hydroxyl radicals, generated from the reaction between hydrogen peroxide and ferrous ions in acid medium. The efficiency of the Fenton reaction depends on the sample characteristics, pH, iron concentration, H_2O_2 dosage and the reaction time [7]. The oxidation of organic compounds in the Fenton's reaction is likely to occur in several steps: (i) generation of $\bullet\text{OH}$ radicals and their oxidative reaction with organic compounds; (ii) direct action of H_2O_2 toward the pollutant; (iii) $\bullet\text{OH}$ scavenging due to Fe^{2+} ions and H_2O_2 ; (iv) reaction of Fe^{3+} with H_2O_2 leading to regeneration of Fe^{2+} ions and formation of hydroperoxyl radicals ($\text{HO}_2\bullet$); and (v) reduction of Fe^{3+} to Fe^{2+} by $\text{HO}_2\bullet$ [8].

The objective of this study was to investigate the feasibility of treating highly concentrated 1,3-dichloro-2-propanol aqueous solutions by the $\text{UV/H}_2\text{O}_2$ process in a batch reactor. Experiments were conducted under two different initial hydrogen peroxide concentrations. Also, the effect of photo-Fenton's system on the photo-oxidation of 1,3-DCP was investigated. Finally, a kinetic study based on a proposed reaction scheme was performed in order to evaluate the efficiency of these processes by calculating the rate constants.

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II. MATERIALS AND METHODS

The photochemical oxidation of 1,3-DCP was investigated with a photoreactor (Heraeus Noblelight UV-RS-3) that consists of a low-pressure Hg lamp of 15W, which produces ultraviolet light of 253.4 nm, immersed in the center of a glass cylindrical vessel 1000 mL volume. 1,3-DCP was dissolved in water. Immediately after adding the hydrogen peroxide and/or the catalyst, 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. Because of the photonic activation, the system did not require heating and was operating at 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 0.024M. H₂O₂ solution, 28% w/w, was used as a source of hydroxyl radicals. Iron(II) sulfate heptahydrate was used as the source of ferric ions. Only deionized water was used.

The evolution of the 1,3-DCP degradation 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 program used for sample analysis was the following: the oven was set at 50°C for 1.50 min, then the temperature increases at a rate of 50°C/min up to 150°C and remains stable for 1min, then the temperature increases at a rate of 10°C/min up to 200°C, and with 20°C/min up to 240°C, total duration 11.50min.

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 4mm) was used for the qualitative and quantitative determination of chloride ion, chloroacetic, formic and acetic acid. The chromatograms obtained were analyzed by means of a personal computer and the appropriate software (Peaknet 6, Version 6.4).

III. RESULTS AND DISCUSSION

A. Photochemical Oxidation

Ultraviolet photolysis combined with hydrogen peroxide (UV/H₂O₂) is one of the most appropriate AOP technologies for removing toxic organics from water because it may occur in nature itself. This process involves the production of reactive OH• that are ultimately capable of mineralizing organic contaminants. This oxidation may occur via one of three general pathways: hydrogen abstraction, electron transfer and radical addition [9].

Experiments with two different initial hydrogen peroxide concentrations were carried out for studying the photochemical oxidation of 1,3-DCP in aqueous solutions, whereas the initial 1,3-DCP concentration was held constant at 0.024M. All experiments were conducted under UV

irradiation. Reactor samples were collected at specific time intervals (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 120, 150, 180 min).

In Fig. 1, the effect on the conversion of 1,3-DCP and TOC, as well as on chloride ion production is depicted for initial hydrogen peroxide concentration 0.163 M (Fig. 1 (a)) corresponding to the stoichiometric concentration required for total conversion of 1,3-dichloro-2-propanol to carbon dioxide and for 0.081 M (Fig. 1 (b)) corresponding to the half of the stoichiometric concentration:

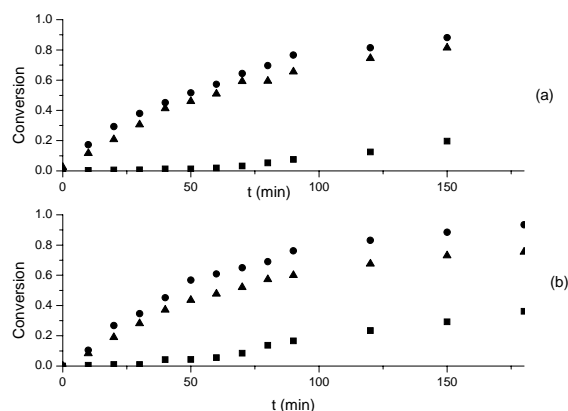
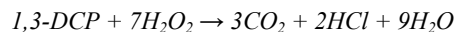


Fig. 1 TOC removal (■), 1,3-DCP conversion (●) and chloride ion production (▲) for initial 1,3-DCP concentration 0.024M 3000mg/L and for initial hydrogen peroxide concentration 0.081M (a) and 0.163 M (b) under UV irradiation

As it can be seen from Fig. 1 the reaction progress leads to practically the same 1,3-DCP conversion (88%) after 150 min reaction time and to a total organic carbon removal of 20% for [H₂O₂] 0.081 M and of 36% for [H₂O₂] 0.163 M, while the chloride ion production reaches 81% and 75% respectively. It must be noted that although 1,3-DCP efficiently degraded, the total organic carbon concentration decreases with a lower rate. The production of the chloride ions was indicative of the degree of dechlorination of the chlorinated intermediates formed in the course of the reaction.

B. Photo-Fenton Process

The feasibility of treating 1,3-DCP aqueous solutions under the synergistic effect of the photo-Fenton reaction and of hydrogen peroxide as an extra oxidative agent was investigated. The initial concentration of 1,3-DCP was 0.024 M, the amount of Fe(II) added was 20, 40, 80 mg/L. The TOC removal, the 1,3-DCP conversion and the chloride ion production are presented in Fig. 2 and 3 for hydrogen peroxide initial concentrations 0.081 and 0.163 M respectively.

From Fig. 2 and 3 it is clear that for an initial concentration of Fe(II) of 20 mg/L the results obtained for the dechlorination degree of the reactor solution are significantly lower than for the other two concentrations. Also, for [Fe(II)]₀=80mg/L and for [H₂O₂]₀=0.081M, the lowest TOC conversion is observed. Bearing into consideration that the use

of greater amounts of iron in solution has a negative effect in terms of practicability, since it implies the need of an additional treatment step for the subsequent removal of iron hydroxide, it is to the benefit of the process to retain the addition of ferrous ions to as low levels as possible. Therefore, the best results for the experimental conditions investigated in this work for the photo-Fenton process are obtained for $[\text{Fe(II)}]_0 = 40 \text{ mg/L}$.

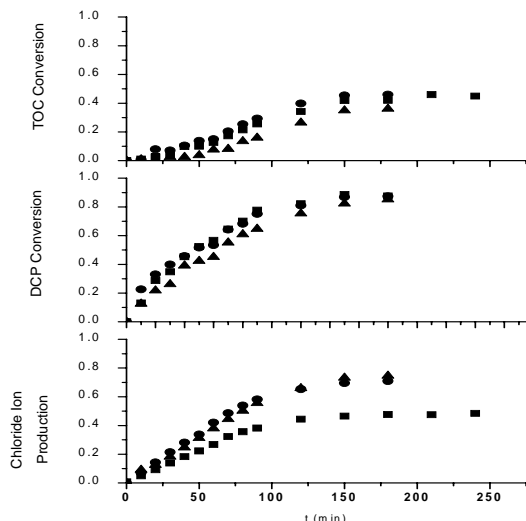


Fig. 2 TOC removal, 1,3-DCP conversion and chloride ion production for initial 1,3-DCP concentration 0.024M, for initial hydrogen peroxide concentration 0.081M under UV irradiation and for initial $[\text{Fe}^{2+}]$ concentrations 20 mg/L (■), 40 mg/L (●) and 80 mg/L (▲)

Comparing the two processes investigated in this work, it is established that the addition of ferrous ions promoted significantly the mineralization that took place during the reaction. Namely, whereas the TOC conversion for the UV/ H_2O_2 process was 20 and 36% for 0.081M and 0.163M respectively, in the photo-Fenton process and under the different initial $[\text{Fe(II)}]$ investigated the TOC removal was above 36 and 53 % for 0.081M and 0.163M respectively. On the other hand, the differences between the two processes in terms of 1,3-DCP conversion and chloride ion production are not significant (with an exception for 20mg/L $[\text{Fe(II)}]_0$).

C. Kinetic Models

Based on the data acquired by the experiments performed in this study a kinetic analysis of the UV/ H_2O_2 process as well as for the photo-Fenton oxidation of 1,3-DCP was conducted. The reaction mechanism was developed using the concentrations of 1,3-DCP, the production of the organic acids arising as intermediates and the TOC measurements. The experimental results led to the following observations: a) 1,3-DCP degradation follows pseudo-first order kinetics, b) the organic acids concentration initially rise and then decrease or remain approximately stable and c) TOC measurements indicate the mineralization taking place during the reaction. According to these observations several series of parallel

reactions were assumed and two of them indicating the best fitting on the experimental data are presented here.

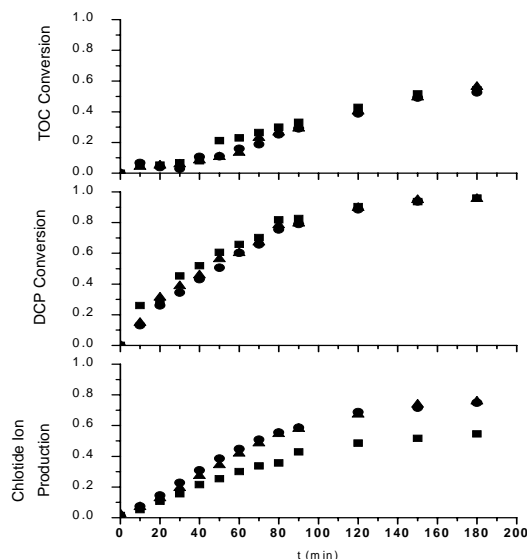
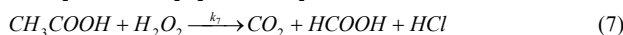
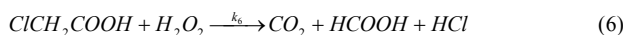
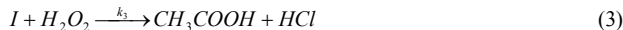
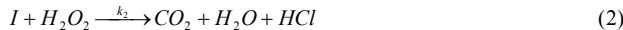


Fig. 3 TOC removal, 1,3-DCP conversion and chloride ion production for initial 1,3-DCP concentration 0.024 M, for initial hydrogen peroxide concentration 0.163M under UV irradiation and for initial $[\text{Fe}^{2+}]$ concentrations 20 mg/L (■), 40 mg/L (●) and 80 mg/L (▲)

These reaction models involve the following steps:



Where, k_i are the reaction kinetic constants ($\text{mol L}^{-1} \text{s}^{-1}$) and I represents the total chlorinated organic intermediates except from chloroacetic acid, that is separately determined quantitatively. Several reaction schemes were investigated prior to establishing the ones with the best fit presented thoroughly in this work. The most important observations that should be made is that: (a) reaction schemes leading to the direct CO_2 production from 1,3-DCP did not converge and (b) formic acid is resistant to oxidation and does not degrade to CO_2 (data not shown). Model 1 comprises of reactions (1)-(5). In Model 2 [reactions (1)-(7)] it is assumed that the oxidation proceeds further to the formation of formic acid and CO_2 from chloroacetic and acetic acid. A system of differential equations has been postulated based on mass balance calculations for each model. The unknown k_i parameters have been estimated by fitting the model to the experimental data (using MathCAD version 12 by Mathsoft) by means of a nonlinear regression analysis (a fixed-step Runge-Kutta method). The objective function, the sum of squares of the

differences between the experimental and the calculated values of concentrations, was minimized by the nonlinear Levenberg – Marquardt algorithm in order to determine the reaction rate coefficients. Finally the solution obtained was tested and compared to the experimental results. In Fig. 4 is presented an example of the comparison between calculated and experimental data. The estimated k_i parameters are reported in Tables I, II.

In Table I, for the photo-Fenton process for $[\text{Fe(II)}]_0 = 20 \text{ mg/L}$ and for both $[\text{H}_2\text{O}_2]_0$, it is shown that chloroacetic and acetic acid are not oxidized any further and their concentrations tend to stabilize in the reactor solution (Model 1). Increasing the initial $[\text{H}_2\text{O}_2]$ a significant increase is noted in the value of k_2 , corresponding to an enhancement in the oxidation of the chlorinated intermediate I to CO_2 .

From Table II it can be seen that the 1,3-DCP oxidation during the $\text{UV}/\text{H}_2\text{O}_2$ process is best described by Model 2 and more specifically increasing the initial hydrogen peroxide concentration, the oxidation proceeds to the production of organic acids that arise as intermediates with higher rate

TABLE I
ESTIMATED KINETIC PARAMETERS FOR MODEL 1

	k_1 , $\cdot 10^{-4}$	k_2 , $\cdot 10^{-4}$	k_3 , $\cdot 10^{-4}$	k_4 , $\cdot 10^{-4}$	k_5 , $\cdot 10^{-4}$
20mg/L Fe(II), [H ₂ O ₂] ₀ = 0.081M	2.35	1.592	0.329	0.348	0.270
20mg/L Fe(II), [H ₂ O ₂] ₀ = 0.163 M	2.875	2.451	0.249	0.588	0.520

$\text{ki mol L}^{-1} \text{ s}^{-1}$

constants (k_2 , k_3 , k_4 , k_5), whereas their oxidation to CO_2 is limited (k_6 , k_7). Therefore the TOC removal remains at low levels.

For a constant $[\text{H}_2\text{O}_2]_0 = 0.163 \text{ M}$, the addition of Fe(II) ions does not affect the oxidation of 1,3-DCP to the chlorinated

intermediate I (k_1). On the other hand, the Fe(II) ions addition promotes the oxidation towards the production of organic acids. More specifically, the rate constant k_2 exhibits a five-fold increase, corresponding to higher TOC removal. Also, the reaction rate for the production of organic acids increases by a factor of 2.

The behavior of the photo-Fenton system in terms of the kinetic models and of the calculated rate constants is complex. This can be attributed to the fact that the ferrous ion and H_2O_2 not only react to form hydroxyl radicals, but are also scavengers of hydroxyl radicals. Therefore, the ratio of Fe(II) to H_2O_2 affects the rates of hydroxyl radical production and scavenging [10].

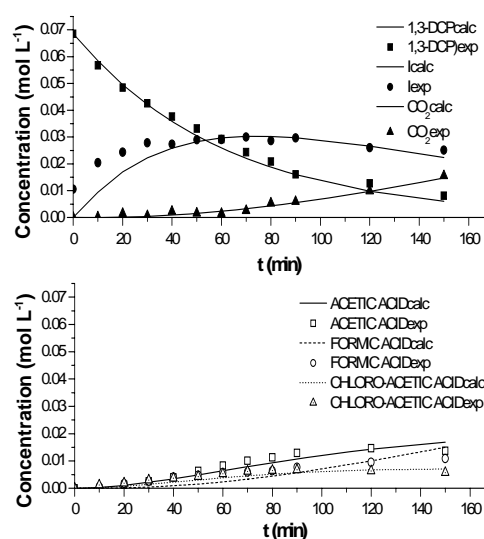


Fig. 4 A comparison of calculated concentrations (Model 2) with experimental data under $\text{H}_2\text{O}_2/\text{UV}$ process. $\{[\text{H}_2\text{O}_2]_0 = 0.081 \text{ M}\}$

TABLE II
ESTIMATED KINETIC PARAMETERS FOR MODEL 2

	k_1 , $\cdot 10^{-4}$	k_2 , $\cdot 10^{-4}$	k_3 , $\cdot 10^{-4}$	k_4 , $\cdot 10^{-4}$	k_5 , $\cdot 10^{-4}$	k_6 , $\cdot 10^{-4}$	k_7 , $\cdot 10^{-4}$
H ₂ O ₂ /UV [H ₂ O ₂] ₀ = 0.081M	2.696	0.054	0.978	0.066	0.719	2.328	0.629
H ₂ O ₂ /UV [H ₂ O ₂] ₀ = 0.163M	2.598	1.475	1.931	0.968	1.632	0.410	0.420
40mg/L Fe(II) [H ₂ O ₂] ₀ = 0.163M	2.447	5.872	3.106	1.987	2.975	0.097	0.850
80 mg/L Fe(II) [H ₂ O ₂] ₀ = 0.163M	2.626	4.933	2.836	1.554	2.415	0.086	0.936

$\text{ki mol L}^{-1} \text{ s}^{-1}$

IV. CONCLUSION

The addition of Fe(II) was found to significantly promote the degradation process in comparison to the UV/H₂O₂ process. Increasing the initial H₂O₂ concentration does not affect the degradation of 1,3-DCP to the chlorinated intermediate I, but significantly increases the rate constants corresponding to the production of CO₂ and organic acids from I. Finally, it should be noted that formic acid produced during the oxidation remains resistant to further degradation, posing an obstacle to the total mineralization of 1,3-DCP.

REFERENCES

- [1] M. D. Nikolaki, and C. J. Philippopoulos, "Photochemical degradation of 1,3-dichloro-2-propanol aqueous solutions", *J. Haz. Mat.*, vol. 146(3), July 2007, pp. 674-679.
- [2] M. D. Nikolaki, D. Malamis, S. G. Pouloupoulos and C. J. Philippopoulos, "Photocatalytical degradation of 1,3-dichloro-2-propanol aqueous solutions by using an immobilized TiO₂ photoreactor", *J. Haz. Mat.*, vol. 137(2), September 2006, pp. 1189-1196.
- [3] F. Bastos, J. Bessa, C. Pacheco, P. De Marco, P. M. L. Castro, M. Silva, R. Ferreira Jorge, "Enrichment of microbial cultures able to degrade 1,3-dichloro-2-propanol: A comparison between batch and continuous methods", *Biodegrad.*, 13, 2002, pp. 211-220.
- [4] Wai-cheung Chung, Kwan-ying Hui, Sze-chung Cheng, "Sensitive method for the determination of 1,3-dichloropropan-2-ol and 3-chloropropane-1,2-diol in soy sauce by capillary gas chromatography with mass spectrometric detection", *J. Chromatogr. A* 952, 2002, pp. 185-192.
- [5] N. L'Huillier, M.K. Pratten, R.H. Clothier, "The relative embryotoxicity of 1,3-dichloro-2-propanol on primary chick embryonic cells", *Tox. in Vit.*, 16, 2002, pp. 433-442.
- [6] A. H. Hammond, M. J. Garle, J. R. Fry, "Toxicity of dichloropropanols in rat hepatocyte cultures", *Environ. Toxicol. Pharmacol. I*, 1996, pp. 39-43.
- [7] I. Schwingel de Oliveira, L. Viana, C. Verona, V. L. Vargas Fallavena, C. M. Nunes Azevedo, M. al Pires, "Alkydic resin wastewaters treatment by fenton and photo-Fenton processes", *J. Haz. Mat.*, vol. 146, 2007, pp. 564-568.
- [8] L. Mater, E. V. C. Rosa, J. Berto, A.X.R. Correa, P.R. Schwingel, C.M. Radetski, "A simple methodology to evaluate influence of H₂O₂ and Fe²⁺ concentrations on the mineralization and biodegradability of organic compounds in water and soil contaminated with crude petroleum", *J. Haz. Mat.*, vol.149, 2007, pp.379-386.
- [9] R. Alnaizy, A. Akgerman, "Advanced oxidation of phenolic compounds", *Adv. Environ. Res.*, vol. 4, 2000, pp. 233-244.
- [10] S. Parsons, *Advanced Oxidation Processes for Water and Wastewater Treatment*. UK, IWA Publishing, 2004, ch. 5.