# Kinetic and mechanistic investigations of mesotrione degradation in aqueous medium by Fenton process

Nasr Bensalah [a,b,*], Ahmed Khodary [b], Ahmed Abdel-Wahab [b]

[a] Department of Chemistry, Faculty of Sciences of Gabes, University of Gabes, Cite Erriadh, Zrig 6072, Gabes, Tunisia
[b] Department of Chemical Engineering, Texas A&M University at Qatar, Education City, PO Box 23874, Doha, Qatar

## ARTICLE INFO

## ABSTRACT

In this work, chemical oxidation of mesotrione herbicide by Fenton process in acidic medium (pH 3.5) was investigated. Total disappearance of mesotrione and up to 95% removal of total organic carbon (TOC) were achieved by Fenton's reagent under optimized initial concentrations of hydrogen peroxide ($H_2O_2$) and ferrous iron ($Fe^{2+}$) at pH 3.5. The time-dependent degradation profiles of mesotrione were satisfactorily fitted by first-order kinetics. Competition kinetic model was used to evaluate a rate constant of $8.8(\pm0.2) \times 10^9\,M^{-1}\,s^{-1}$ for the reaction of mesotrione with hydroxyl radicals. Aromatic and aliphatic intermediates of mesotrione oxidation were identified and quantified by high performance liquid chromatography (HPLC). It seems that the degradation of mesotrione by Fenton process begins with the rupture of mesotrione molecule into two moieties: cyclohexane-1,3-dione derivative and 2-nitro-4-methylsulfonylbenzoic acid. Hydroxylation and release of sulfonyl and/or nitro groups from 2-nitro-4-methylsulfonylbenzoic acid lead to the formation of polyhydroxylated benzoic acid derivatives which undergo an oxidative opening of benzene ring into carboxylic acids that end to be transformed into carbon dioxide.

## 1. Introduction

Herbicides are widely used in agriculture and management of grasslands in the landscape. Almost all herbicides in use today are considered organic herbicides in that they contain carbon as a primary molecular component. Herbicides have been detected in surface and ground water [1–6], despite their rapid microbial and photo-induced decomposition. However, concerns about the potential impacts of pesticides on human health have arisen because the extensive use of these substances leads to their presence, together with their metabolites, in surface wastewaters from agricultural activities and in drinking waters. Herbicides may pose an environmental threat because they are designed to have a specific physiological effect on humans or animals since some of them are known to be xenobiotic, mutagenic, carcinogenic or teratogenic [7–10]. Their elimination from wastewater effluents is now the subject of considerable concern of environmental remediation and has attracted many researchers in recent years [9,10]. Because herbicides are toxic to many organisms, conventional biological remediation processes are not suitable to completely remove herbicides from contaminated water [11–14], and therefore more effective treatment methods are required. Partial removal of herbicides during wastewater treatment processes has led to the detection of these compounds in a variety of surface water and groundwater throughout the world [1,2,14].

Advanced oxidation processes (AOPs) are alternative to traditional treatment and have recently received considerable attention for herbicides removal [15–19]. In the last decade, these processes have been shown to be effective for the destruction of refractory pollutants [20,21]. They are based on the generation of highly reactive and oxidizing hydroxyl radicals ($HO^\bullet$). Fenton's reagent, $H_2O_2/UV$, $O_3/UV$, $TiO_2/air/UV$ are the main types of AOPs that have been suggested. Various combinations of them are employed for complete mineralization of pollutants. Fenton process is a promising and easy to manipulate advanced oxidation technology in which a mixture of hydrogen peroxide ($H_2O_2$) and ferrous iron ($Fe^{2+}$) salts is added directly to the wastewater. This mixture promotes the formation of $HO^\bullet$ radicals by catalytic decomposition of $H_2O_2$ in acidic medium (pH in the range 3–4) as shown by the reactions sequence (1–5):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \qquad (2)$$

$$Fe(OOH)^{2+} \rightarrow HO_2^\bullet + Fe^{2+} \qquad (3)$$

* Corresponding author at: Department of Chemistry, Faculty of Sciences of Gabes, University of Gabes, Cite Erriadh, Zrig 6072, Gabes, Tunisia. Tel.: +216 75392600; fax: +216 75392421.
E-mail addresses: nasr.bensalah@issatgb.rnu.tn, nassrother@yahoo.fr (N. Bensalah).

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \qquad (4)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (5)$$

In addition to the oxidation mediated by HO$^\bullet$ radicals, ferric ions generated during the first stage can promote the removal of pollutants by coagulation. Fenton's reagent is used for many years in the municipal and industrial water and wastewater treatment industry [22]. Fenton oxidation is also applied in soil and groundwater treatment for the removal of persistent contaminants [22–24]. Free oxidizing radicals react non-selectively with organic contaminants in oxidation/reduction reactions sequences to form environmental friendly and biodegradable compounds [25,26]. Industrial applications Fenton process involved several stages including (i) pH adjustment, (ii) oxidation/reduction reactions, (iii) neutralization and coagulation, and precipitation. The main operation parameters of this process are $H_2O_2$ and $Fe^{2+}$ doses, organic content and pH.

The goal of this work is to investigate the degradation of mesotrione (benzoylcyclohexanedione herbicide) in aqueous solutions by Fenton's reagent in order to support the development of Fenton process as practical treatment method to remove triketone herbicides from water. The triketone herbicides represent the newest class of herbicides that have been introduced onto the market today. Mesotrione was the first of these herbicides used in agriculture to replace atrazine and within short time became one of the most popular herbicides used by farmers to control broadleaf weed in maize [27–29]. However, it may affect microbial activity and can exhibit moderate retention capacity in soil and so can be leached to surface water [29]. Additionally, in our best of knowledge there is no information in the literature concerning its removal from water and especially its degradation pathways by AOPs are poorly known [30–35]. The influence of $H_2O_2$ and $Fe^{2+}$ doses under acidic conditions on mesotrione and TOC removals was studied. Aromatic and aliphatic byproducts of mesotrione oxidation by Fenton's reagent were identified and quantified by high performance liquid chromatography (HPLC) analyses. Based on HPLC results a simple mechanism of mesotrione oxidation by Fenton's reagent was proposed.

## 2. Experimental

### 2.1. Chemicals

Mesotrione herbicide (2-[4-methylsulfonyl-2-nitrobenzoyl]-1,3-cyclohexanedione), 2,4-dihydroxybenzoic acid (DHBA), 2-nitrobenzoic acid (NBA), 4-chlorobenzoic acid (CBA) and benzoic acid (BA) and were purchased from Sigma–Aldrich in analytical grade form (purity >99%). 2-nitro-4-methylsulfonylbenzoic acid (NMSBA), 4-methylsulfonylbenzoic acid (MSBA) were obtained from Wuhan CheMax Chemical Industrial Co., Ltd., China. Carboxylic acids (>99%) were of analytical grade and purchased from Fluka. Hydrogen peroxide was a 30% (w/w) solution (ACS reagent, Sigma–Aldrich). The other chemicals such as sulfuric acid, sodium hydroxide, ferrous sulfate heptahydrate, are of analytical grade and purchased from Sigma–Aldrich or Fluka.

### 2.2. Analytical procedures

The carbon concentration was monitored using Shimadzu TOC-5050 analyzer. The degradation of mesotrione herbicide was followed by liquid chromatography. Aromatics were monitored by HPLC using a Nucleosil C18 column (mobile phase 74% water–25% methanol–1% acetic acid; flow rate, 0.70 mL min$^{-1}$). In this case, the UV detector was set to 270 nm to give linear calibration curves with a detection limit higher than 0.2 μM for all aromatic compounds. Carboxylic acids were monitored with a detection limit higher than 0.1 μM by HPLC using a Supelcogel H column (mobile phase, 0.15% phosphoric acid solution; flow rate, 0.15 mL min$^{-1}$). The UV detector was set at 210 nm. All calibration curves were linear with correlation values ($R^2$) higher than 0.97. $H_2O_2$ was measured according to Eisenberg [36].

### 2.3. Fenton process

Fenton oxidation assays were carried out in lab-scale thermostated mixed batch reactors. The experimental setup consists of a multistirrer device (Ikamag RO 5 power, IKA-WERKE GmbH & Co. KG, Staufen, Alemania) with fifteen mixing sites coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain). Pyrex flasks (250 cm$^3$) hermetically sealed and equipped with magnetic stirrers were used as reactors. They were submerged in the thermostatic bath. Stock solution of 2 mM mesotrione was prepared in deionized water from the Millipore system (resistivity 18.2 MΩ cm and TOC ≤ 5 ppb). Aqueous solutions of mesotrione were prepared at appropriate concentration by diluting the stock solution in deionized water. In each assay, the reactors were filled with 100 cm$^3$ of mesotrione aqueous solution. Then, an appropriate amount of $Fe^{2+}$ in the range from 0 to 4 mM was added (as FeSO$_4$·7H$_2$O) and the pH was adjusted to 3.5 ± 0.1 with sodium hydroxide or sulphuric acid. According to literature [37,38], this pH is in the optimum range of pH (3–4) to promote the formation of HO$^\bullet$ radicals in Fenton process, which has been verified by performing several experiments for pH ranges from 3 to 6, and it was found that 95–100% TOC removal was obtained in the pH range of 3–4. In all cases, the reaction was started by adding appropriate dose of $H_2O_2$ (30%) to obtain concentrations of 2–20 mM $H_2O_2$ in solution. Preliminary experiments were carried out to determine the time needed to meet the steady state conditions (no changes in mesotrione and TOC removals and total disappearance of $H_2O_2$). From these experiments a reaction time of 4 h was selected (a period of time necessary for total disappearance of $H_2O_2$ obtained in equilibrium experiments). During kinetic experiments, samples were taken at desired reaction times. For each taken sample 0.1 g of sodium sulphite was immediately added to quench $H_2O_2$ and stop Fenton reaction and then was filtered through 0.45 μm cartridge. Concentrations of TOC, mesotrione, oxidation by-products and $H_2O_2$ were measured. Several set of experiments (in duplicate) were carried out at fixed pH of 3.5 to determine the range of $H_2O_2$ and $Fe^{2+}$ needed to obtain optimum results.
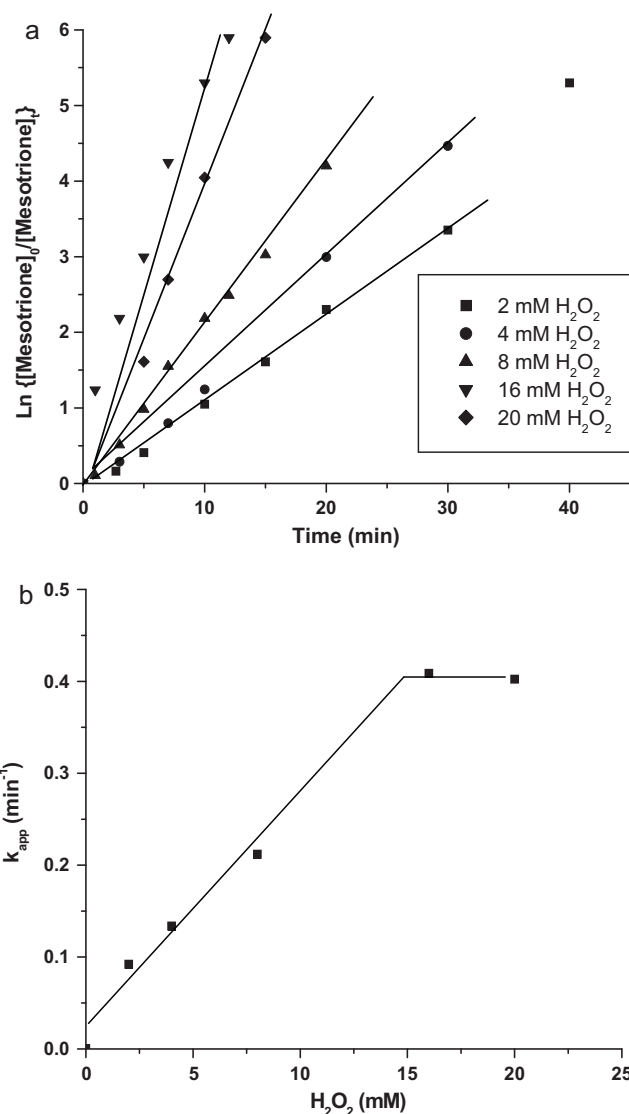
## 3. Results and discussion

Fig. 1 presents the changes of mesotrione and TOC concentrations as function of time during Fenton treatment of aqueous solution containing 0.2 mM mesotrione and 1 mM $Fe^{2+}$ at pH 3.5 using different $H_2O_2$ initial concentrations. Total disappearance of mesotrione was obtained for all $H_2O_2$ concentrations used in range 2–20 mM $H_2O_2$. The increase of $H_2O_2$ initial concentration from 2 to 16 mM decreases time needed to reach almost total disappearance of mesotrione from 40 min to 15 min but $H_2O_2$ initial concentration greater than 16 mM has lower influence on this time. Also, Fig. 1b shows that the increase of $H_2O_2$ initial concentration enhances efficiency of TOC removal. Indeed, increasing of $H_2O_2$ initial concentration from 2 mM to 16 mM increases TOC removal from 57% to 96% after 60 min Fenton treatment. When 20 mM $H_2O_2$ was added to 0.2 mM mesotrione aqueous solution Fenton process achieves total TOC removal within 60 min treatment. It is then evident that an initial concentration of $H_2O_2$ higher than 16 mM does not increase enough kinetics or efficiency of $Fe^{2+}/H_2O_2$ treatment in terms of mesotrione disappearance and TOC removal. Accordingly,
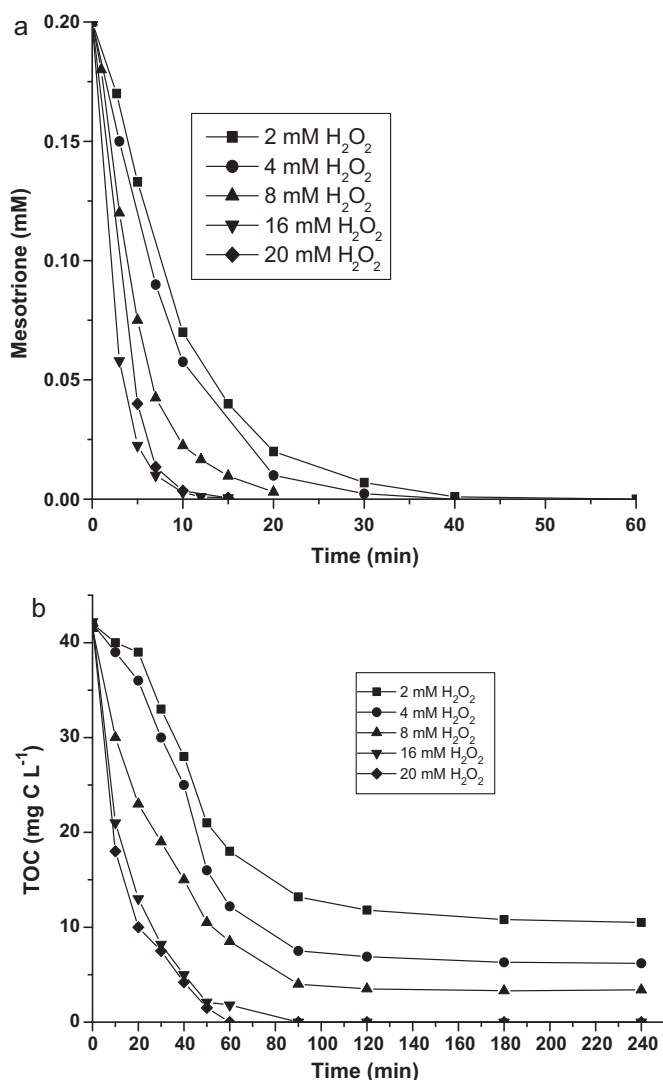
**Fig. 1.** Influence of $H_2O_2$ initial concentration on changes with time of (a) mesotrione concentration, and (b) TOC during Fenton treatment of aqueous solution containing 0.2 mM mesotrione and 1 mM $Fe^{2+}$ at pH 3.5.



**Fig. 2.** (a) Kinetics analysis of mesotrione degradation during Fenton treatment, (b) variation of apparent pseudo-first order rate constant $k_{app}$ vs. $H_2O_2$ initial concentration. Experimental conditions: 0.2 mM mesotrione, 1 mM $Fe^{2+}$, pH 3.5, different $H_2O_2$ concentrations.

$H_2O_2$ concentration of 16 mM is optimal for a complete disappearance of mesotrione in 15 min and total TOC removal in 90 min Fenton treatment of aqueous solutions containing 0.2 mM mesotrione and 1 mM $Fe^{2+}$ at pH 3.5. For low $H_2O_2$ initial concentrations, HO• radicals generated from the catalytic decomposition of $H_2O_2$ (reaction (1)) cannot totally degrade mesotrione and remove high amount of TOC. As $H_2O_2$ initial concentration increases, HO• radical increases and hence the rates of mesotrione disappearance and TOC removal are increased. For higher $H_2O_2$ initial concentrations, although theoretically more HO• radicals can be produced (reactions (1–5)), the rate and percentage of TOC removal remain almost the same. This can be explained by the competition between the reaction of hydroxyl radicals with organics and scavenging them by $H_2O_2$ in excess (reactions (6 and 7)) which does not provide an increase in HO• radicals [39]. The scavenging effect of $H_2O_2$ reduces the efficiency of the treatment through the consumption of HO• radicals leading to the formation of $HO_2$• radicals (reaction (7)). $HO_2$• radicals have lower oxidation potential than HO• radicals, and then their contribution in the removal of TOC is lower than that of HO• radicals. Also when the concentration of $H_2O_2$ becomes sufficiently high, the secondary reaction of $H_2O_2$ auto-decomposition into $O_2$ and $H_2O$ (reaction (8)) is thermodynamically shifted to the right and then a significant amount of $H_2O_2$ is consumed by this reaction.

$$HO^\bullet + OrganicPollutant \leftrightharpoons Products \quad (6)$$

$$HO^\bullet + H_2O_2 \leftrightharpoons HO_2^\bullet + H_2O \quad (7)$$

$$2 H_2O_2 \leftrightharpoons O_2 + 2H_2O \quad (8)$$

Kinetic analysis was performed in order to identify mesotrione degradation kinetics and to evaluate the rate constant of mesotrione with hydroxyl radicals. The plots of mesotrione concentration vs. time indicate in a first approach, that degradation of mesotrione can be described by a pseudo-first-order kinetics as given by Eq. (9).

$$-\frac{d[M]}{dt} = k_{app}[M] \quad (9)$$

where $[M]$ is the concentration of mesotrione at instant $t$, $k_{app}$ is the apparent mesotrione degradation rate constant, and $t$ is the time.

According to this assumption, the rate equation can be integrated (Eq. (10)) with the boundary conditions $[M] = [M]_0$ for $t = 0$
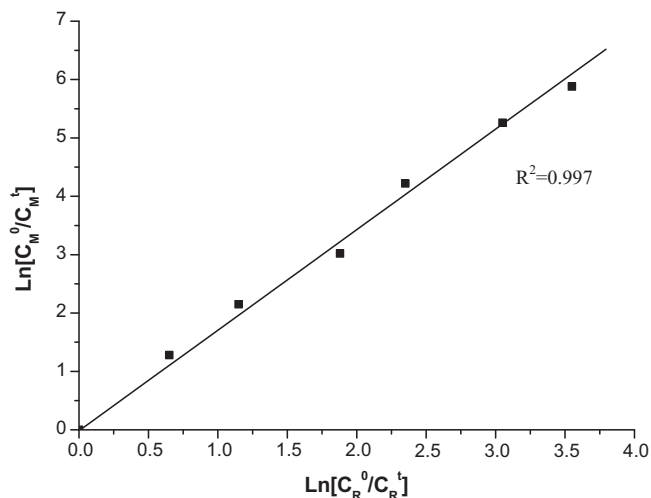
**Fig. 3.** Competitive kinetic model for the determination of rate constant of mesotrione reaction with hydroxyl radicals using 4-chlorobenzoic acid a s reference compound. Experimental conditions: 0.2 mM mesotrione, 0.2 mM 4-chlorobenzoic acid, 16 mM $H_2O_2$, 1 mM $Fe^{2+}$, pH 3.5.
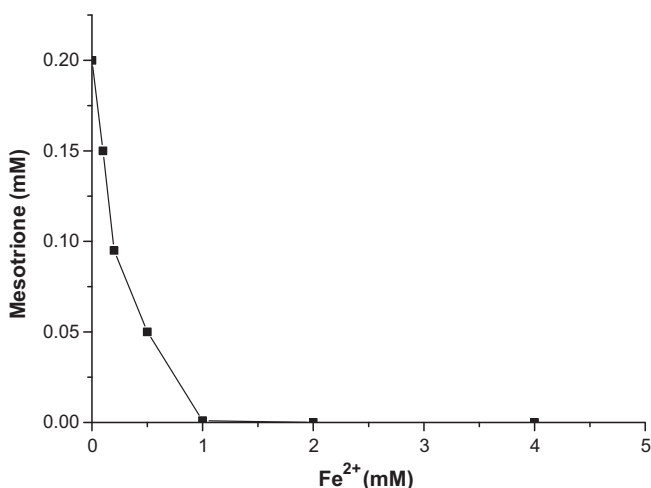


**Fig. 4.** Influence of $Fe^{2+}$ dose on the evolution with time of mesotrione concentration during Fenton treatment. Experimental conditions: 0.2 mM mesotrione, 16 mM $H_2O_2$, pH 3.5, reaction-time 4 h.

and $[M] = [M]_t$ for $t = t$, leading to Eq. (11):

$$\int_{[M]_0}^{[M]_t} \frac{d[M]}{[M]} = \int_0^t k_{app} dt. \tag{10}$$

$$\ln\left(\frac{[M]_{t=0}}{[M]_{t=t}}\right) = k_{app} \cdot t \tag{11}$$

The plots of $\ln([M]_{t=0}/[M]_{t=t})$ vs. time ($t$) at different $H_2O_2$ concentrations are presented in Fig. 2a. The plots are straight lines pass by the original point with correlation coefficients ($R^2$) higher than 0.97. The linearity of $\ln([M]_{t=0}/[M]_{t=t}) = f(t)$ curves confirms that the mesotrione degradation rate is a pseudo-first-order reaction. In accordance with Eq. (11), each line has a slope equal to $k_{app}$ which is the apparent mesotrione degradation rate constant. All $k_{app}$ values were calculated for a same initial concentration of mesotrione (0.2 mM) and at various initial concentrations of $H_2O_2$. Fig. 2b represents the variation of $k_{app}$ with $H_2O_2$ concentration. The profile of obtained $k_{app}$ values vs. $H_2O_2$ dose suggests that mesotrione degradation rate by Fenton oxidation increases linearly with the increase of $H_2O_2$ concentration up to 16 mM then it reaches a plateau at 0.4 min$^{-1}$. Once the apparent pseudo-first-order rate constant for
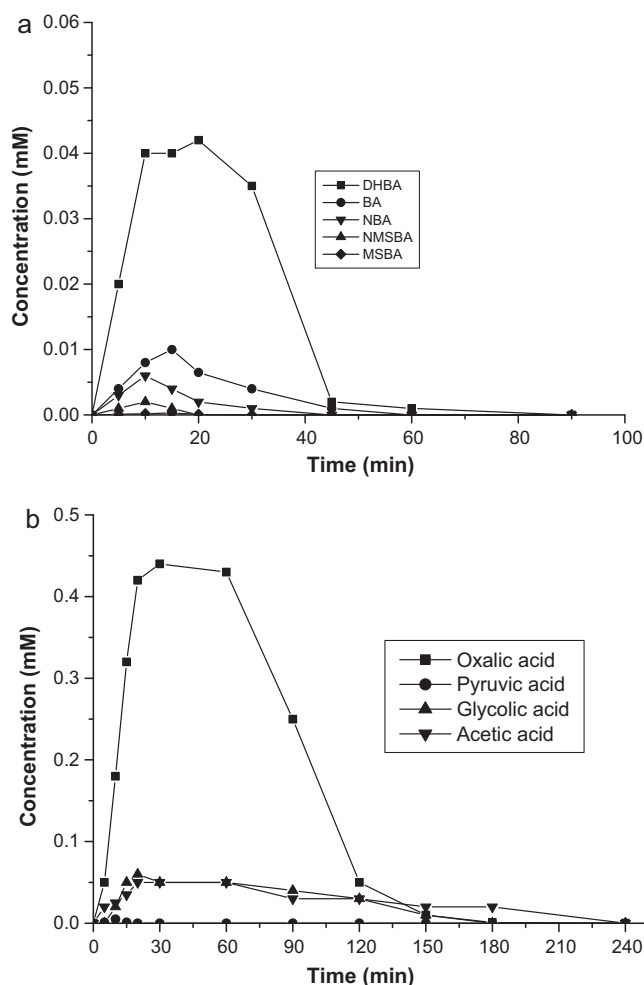


**Fig. 5.** Changes with time of (a) of aromatic intermediates, and (b) carboxylic acids concentrations during mesotrione oxidation by Fenton's reagent. Experiment conditions: 2 mM mesotrione, 20 mM $H_2O_2$, 2 mM $Fe^{2+}$, pH 3.5.

the Fenton process have been determined, the rate constant for the reaction of mesotrione with $HO^\bullet$ radicals can be evaluated. This evaluation is performed by means of a competition kinetic model, which has been previously used by several authors [40–42]. This model consists of the simultaneous Fenton's reaction of a mixture of two organic compounds: one of them is the reference compound R, whose $HO^\bullet$ rate constant is previously known [41]; the second compound constitutes the target compound (mesotrione) M. Reactions between hydroxyl radicals and both mesotrione and the reference compound are considered to follow second order kinetics. Taking into account these considerations, the reaction rate between $HO^\bullet$ radicals and the target compound M (mesotrione) in the mixture can be given by Eq. (12):

$$-\frac{d[M]}{dt} = k_{M-HO^\bullet}[HO^\bullet][M] \tag{12}$$

While this rate equation for the reference compound R, in that mixture is expressed by Eq. (13):

$$-\frac{d[R]}{dt} = k_{R-HO^\bullet}[HO^\bullet][R] \tag{13}$$

where $k_{M-HO^\bullet}$ and $k_{R-HO^\bullet}$ are the rate constants for the reaction of $HO^\bullet$ radicals with M and R, respectively. By dividing both equations and integrating between $t = 0$ and $t = t$, Eq. (14) is obtained:

$$\ln\left(\frac{[M]_{t=0}}{[M]_{t=t}}\right) = \frac{k_{M-HO^\bullet}}{k_{R-HO^\bullet}} \ln\left(\frac{[R]_{t=0}}{[R]_{t=t}}\right) \tag{14}$$
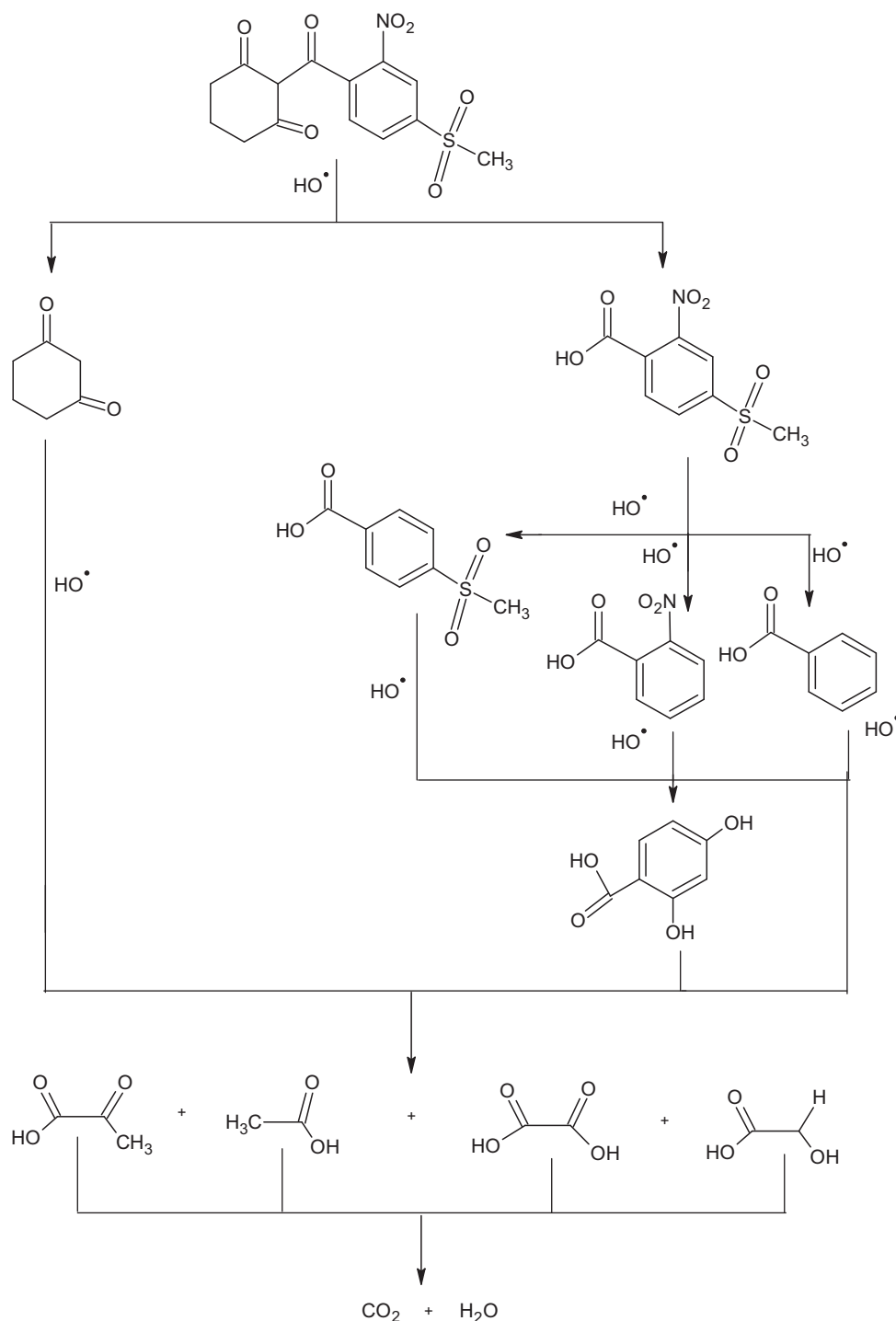
**Fig. 6.** Simple mechanistic scheme for mesotrione degradation by Fenton oxidation.

According to this equation, the plot of $\ln([M]_{t=0}/[M]_{t=t})$ against $\ln([R]_{t=0}/[R]_{t=t})$ must be a straight line with a slope equal to the ratio of rate constants; and as $k_{R-HO\bullet}$ is known, $k_{M-HO\bullet}$ can then be determined. In this work, 4-chlorobenzoic acid was used as a reference compound R, with a previously known [43] rate constant for its oxidation by HO• radicals of $k_{R-HO\bullet} = 5 \times 10^9 \, M^{-1} \, s^{-1}$. The plot of $\ln([M]_{t=0}/[M]_{t=t})$ as function of $\ln([R]_{t=0}/[R]_{t=t})$ during Fenton process (16 mM $H_2O_2$, 1 mM $Fe^{2+}$ at pH 3.5) of a mixture of mesotrione (0.2 mM) and CBA (0.2 mM) given in Fig. 3 is straight line with a slop equal to 1.76. Following this procedure, a value of $8.8(\pm 0.2) \times 10^9 \, M^{-1} \, s^{-1}$ was obtained for the rate constant for the

reaction of mesotrione with HO• radicals. This rate constant is in same range than those mentioned in the literature for phenyl-urea herbicides [18].

In the second set of experiments $Fe^{2+}$ dose was varied from 0 to 4 mM, while pH value, mesotrione concentration, and $H_2O_2$ concentration were fixed at 3.5, 0.2 mM, and 16 mM, respectively. The experimental data in Fig. 4 show the changes in residual mesotrione concentration with $Fe^{2+}$ dose after 4 h Fenton treatment. It was found that the residual concentration of mesotrione decreases with increasing $Fe^{2+}$ initial concentration to reach total disappearance of mesotrione at $Fe^{2+}$ concentration equal to or higher than 1 mM.

Hence, $Fe^{2+}$ concentration of 1 mM is selected to be optimal for total mesotrione removal by Fenton process. This catalytic amount of $Fe^{2+}$ is extremely favorable to avoid the problem of sludge formation and prevent further treatment stages.

To elucidate the mechanism of degradation of mesotrione by Fenton process, HPLC was used to identify and quantify the main intermediates of mesotrione degradation. Identification of oxidation byproducts was realized by comparison of retention times with commercially available standards and with intermediates reported by Alferness and Wiebe [35] during biotransformation of mesotrione in soil. Fig. 5 presents the evolution with time of aromatic and aliphatic intermediates during the treatment of aqueous solution containing 2 mM mesotrione by Fenton oxidation of mesotrione by 20 mM $H_2O_2$ and 2 mM $Fe^{2+}$ and at pH 3.5. With these reagents doses a slow degradation is supposed to be occurred which confers a high possibility to detect major oxidation intermediates in concentrations higher than their detection limits by HPLC. Fig. 5a shows that 2,4-dihydroxybenzoic (DHBA), 2-nitrobenzoic (NBA) and benzoic acids are main aromatic intermediates identified during the oxidation of mesotrione by Fenton process. Also traces of 2-nitro-4-methylsulfonylbenzoic acid (NMSBA) and 4-methylsulfonylbenzoic acid (MSBA) were also detected. Oxalic, acetic, glycolic acid and pyruvic acids are the detectable aliphatic intermediates of mesotrione oxidation by Fenton oxidation (see Fig. 5b). The concentration of each intermediate shows a rapid increase at the beginning of the treatment to reach a maximum value during the first half-hour and then it gradually decreases to end with a total disappearance at the end of the treatment.

According to TOC and chromatography analyses, a simple mechanistic scheme can be proposed. The main sequential steps of mesotrione degradation by Fenton process are given in Fig. 6. Mesotrione degradation mechanism starts with $HO^\bullet$ radicals attack on the carbonyl group to form cyclohexanone derivatives such as cyclohexane-1,3-dione and 2-nitro-4-methylsulfonylbenzoic acid which is converted rapidly to benzoic, 2-nitrobenzoic and 4-methylsulfonylbenzoic acids by the release of sulfonyl and/or nitro groups. These intermediates could be easily transformed into polyhydroxybenzoic acids mainly 2,4-DHBA by hydroxylation. Polyhydroxylated benzoic acids and cyclohexanone derivatives undergo oxidative opening of benzene rings into aliphatic carboxylic acids such as oxalic, glycolic acetic and pyruvic acids. Carboxylic acids are slowly transformed into $CO_2$, $H_2O$ and other inorganic ions in the final stages of Fenton process.

## 4. Conclusion

Fenton process was successfully used for complete disappearance of mesotrione herbicide from water within 15 min and total TOC removal during 90 min under optimized $H_2O_2$ and $Fe^{2+}$ doses and at pH 3.5. Kinetic investigation indicated that mesotrione degradation follows a pseudo-first order kinetic at fixed $H_2O_2$ concentration. A rate constant of $8.8(\pm 0.2) \times 10^9\,M^{-1}\,s^{-1}$ was determined for the reaction between mesotrione and $HO^\bullet$ radicals through a competition kinetic model using CBA as a reference compound. Chromatography analyses have shown that the mechanism of mesotrione oxidation starts by the rupture of mesotrione molecule into two moieties: cyclohexane-1,3-dione derivative and 2-nitro-4-methylsulfonylbenzoic acid through $HO^\bullet$ radicals attack on the aliphatic ketone group. Successive oxidation steps lead to the formation of polyhydroxylated benzoic acid derivatives by hydroxylation and release of sulfonyl and/or nitro groups. The polyhydroxylated benzoic acid derivatives undergo a rapid oxidative opening of benzene rings to form aliphatic carboxylic acid which are finally mineralized into $CO_2$, $H_2O$. According to the results obtained in this study, it can be concluded that Fenton oxidation

process can be a viable technology for the removal of triketone herbicides from water.

## References

[1] J.P. Duguet, Occurrence of pesticides in natural waters and removal during drinking water treatment processes, Water Supply 12 (1994) 111–115.
[2] W. Hua, E.R. Bennett, R.J. Letcher, Ozone treatment and the depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada, Water Res. 40 (2006) 2259–2266.
[3] N. Stamatis, I. Konstantinou, D. Hela, Pesticide inputs from the sewage treatment plant of Agrinio to River Acheloos, western Greece: occurrence and removal, Water Sci. Technol. 62 (2010) 1098–1105.
[4] O. Griffini, M.L. Bao, C. Barbieri, D. Burrini, F. Pantani, Occurrence of pesticides in the Arno river and in potable water—a survey of the period 1992–1995, Bull. Environ. Contam. Toxicol. 59 (1997) 202–209.
[5] M.L. Hladik, E.J. Bouwer, A.L. Roberts, Neutral degradates of chloroacetamide herbicides: occurrence in drinking water and removal during conventional water treatment, Water Res. 42 (2008) 4905–4914.
[6] I.K. Konstantinou, D.G. Hela, T.A. Albanis, The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I: review on occurrence and levels, Environ. Pollut. 141 (2006) 555–570.
[7] B.D. Giudice, A. Massoudieh, X. Huang, T.M. Young, A stochastic simulation procedure for selecting herbicides with minimum environmental impact, Environ. Sci. Technol. 42 (2008) 354–360.
[8] S. Giacomazzi, N. Cochet, Environmental impact of diuron transformation: a review, Chemosphere 56 (2004) 1021–1032.
[9] R. Castorina, A. Bradman, L. Fenster, D.B. Barr, R. Bravo, M.G. Vedar, M.E. Harnly, T.E. Mckone, E.A. Eisen, B. Eskenazi, Comparison of current-use pesticide and other toxicant urinary metabolite levels among pregnant women in the CHAMACOS cohort and NHANES, Environ. Health Perspect. 118 (2010) 856–863.
[10] O. Oluwole, R.A. Cheke, Health and environmental impacts of pesticide use practices: a case study of farmers in Ekiti State, Nigeria, Int. J. Agric. Sustain. 7 (2009) 153–163.
[11] N. Glæsner, J. Bælum, B.W. Strobel, C.S. Jacobsen, Atrazine is not readily mineralized in 24 temperate soils regardless of pre-exposure to triazine herbicides, Environ. Pollut. 158 (2010) 3670–3674.
[12] T. Cai, L. Qian, S. Cai, L. Chen, Biodegradation of benazolin-ethyl by strain methyloversatilis sp.cd-1 isolated from activated sludge, Current Microbiol. 62 (2011) 570–577.
[13] M. Gennari, C. Abbate, A. Baglieri, M. Negre, Fate and degradation of triasulfuron in soil and water under laboratory conditions, J. Environ. Sci. Health B 43 (2008) 498–505.
[14] H. Jiang, C. Adams, Treatability of chloro-s-triazines by conventional drinking water treatment technologies, Water Res. 40 (8) (2006) 1657–1667.
[15] R. Pourata, A.R. Khataee, S. Aber, N. Daneshvar, Removal of the herbicide Bentazon from contaminated water in the presence of synthesized nanocrystalline $TiO_2$ powders under irradiation of UV-C light, Desalination 249 (2009) 301–307.
[16] G. Kaichouh, N. Oturan, M.A. Oturan, A. Elhourch, K. Elkacemi, Mineralization of herbicides imazapyr and imazaquin in aqueous medium by Fenton, photo-Fenton and electro-Fenton processes, Environ. Technol. 29 (2008) 489–496.
[17] G.F. Ijpelaar, R.T. Meijers, R. Hopman, J.C. Kruitof, Oxidation of herbicides in groundwater by the Fenton process: a realistic alternative for $O_3/H_2O_2$ treatment, Ozone Sci. Eng. 22 (2000) 607–616.
[18] F.J. Benitez, F.J. Real, J.L. Acero, C. Garcia, Kinetics of the transformation of phenyl-urea herbicides during ozonation of natural waters: rate constants and model predictions, Water Res. 41 (2007) 4073–4084.
[19] M.Y. Shih, S.C. Fanga, J.L. Gaw, Degradation of carbofuran in aqueous solution by ultrasound and Fenton processes: effect of system parameters and kinetic study, J. Hazard. Mater. 178 (2010) 320–325.
[20] C. Comninellis, A. Kapalka, S. Malato, S.A. Parsons, I. Poulios, D. Mantzavinos, Advanced oxidation processes for water treatment: advances and trends for R&D, J. Chem. Technol. Biotechnol. 83 (2008) 769–776.
[21] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.
[22] J.J. Pignatello, E. Oliveros, A. Mackay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (1) (2006) 1–84.
[23] R. Baciocchi, M.R. Boni, L. D'Aprile, Hydrogen peroxide lifetime as an indicator of the efficiency of 3-chlorophenol Fenton's and Fenton-like oxidation in soils, J. Hazard. Mater. B96 (2003) 305–329.
[24] M.A. Fontecha-Camara, M.A. Alvarez-Merino, F. Carrasco-Marin, M.V. Lopez-Ramon, C. Moreno-Castilla, Heterogeneous and homogeneous Fenton processes using activated carbon for the removal of the herbicide amitrole from water, Appl. Catal. B: Environ. 101 (2011) 425–430.
[25] C. Walling, R.A. Johnson, Fenton's reagent, V. Hydroxylation and side chain cleavage of aromatics, J. Am. Chem. Soc. 97 (1975) 363–367.
[26] J.A. Zimbron, K.F. Reardon, Hydroxyl free radical reactivity toward aqueous chlorinated phenols, Water Res. 39 (2005) 865–869.
[27] M.D. Meyer, J.K. Pataky, M.M. Williams II, Genetic factors influencing adverse effects of mesotrione and nicosulfuron on sweet corn yield, Agronomy J. 102 (2010) 1138–1144.

[28] R.E. Nurse, A.S. Hamill, C.J. Swanton, F.J. Tardif, P.H. Sikkema, Weed control and yield response to mesotrione in maize (Zea mays), Crop Prot. 29 (2010) 652–657.

[29] J. Rouchaud, O. Neus, H. Eelen, R. Bulcke, Mobility and adsorption of the triketone herbicide mesotrione in the soil of corn crops, Toxicol. Environ. Chem. 79 (2001) 211–222.

[30] I. Batisson, O. Crouzet, P. Besse-Hoggan, M. Sancelme, J.F. Mangot, C. Mallet, J. Bohatier, Simulated solar light irradiation of mesotrione in natural waters, Environ. Sci. Technol. 40 (2006) 3842–3847.

[31] J.S. Dyson, S. Beulke, C.D. Brown, M.C.G. Lane, Adsorption and degradation of the weak acid mesotrione in soil and environmental fate implications, J. Environ. Quality 31 (2002) 613–618.

[32] S. Durand, P. Amato, M. Sancelme, A.M. Delort, B. Combourieu, P. Besse-Hoggan, First isolation and characterization of a bacterial strain that biotransforms the herbicide mesotrione, Lett. Appl. Microbiol. 43 (2006) 222–228.

[33] S. Durand, B. Legeret, A.S. Martin, M. Sancelme, A.M. Delort, P. Besse-Hoggan, B. Combourieu, Biotransformation of the triketone herbicide mesotrione by a Bacillus strain. Metabolite profiling using liquid chromatography/electrospray ionization quadrupole-time of flight mass spectrometry, Rapid Commun. Mass Spectrom. 20 (2006) 2603–2613.

[34] S. Durand, M. Sancelme, P. Besse-Hoggan, B. Combourieu, Biodegradation pathway of mesotrione: complementarities of NMR, LC-NMR and LC–MS for qualitative and quantitative metabolic profiling, Chemosphere 81 (2010) 372–380.

[35] P. Alferness, L. Wiebe, Determination of mesotrione residues and metabolites in crops, soil, and water by liquid chromatography with fluorescence detection, J. Agric. Food Chem. 50 (2002) 3926–3934.

[36] G.M. Eisenberg, Colorimetric determination of hydrogen peroxide, Ind. Eng. Chem. Anal. Ed. 15 (1943) 327–328.

[37] Y.W. Kang, K.Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res. 34 (2000) 2786–2790.

[38] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. B98 (2003) 33–50.

[39] A. Bedoui, M.F. Ahmadi, N. Bensalah, A. Gadri, Comparative study of eriochrome black T treatment by BDD-anodic oxidation and Fenton process, Chem. Eng. J. 146 (1) (2009) 98–104.

[40] W.R. Haag, D.C.C. Yao, Rate constants for reaction of hydroxyl radicals with several drinking water contaminants, Environ. Sci. Technol. 26 (1992) 1005–1013.

[41] F.J. Benitez, J.L. Acero, F.J. Real, J. Garcia, Kinetics of photodegradation and ozonation of pentachlorophenol, Chemosphere 51 (2003) 651–662.

[42] M.J. Farre, S. Brosillon, X. Domenech, J. Peral, Evaluation of the intermediates generated during the degradation of Diuron and Linuron herbicides by the photo-Fenton reaction, J. Photochem. Photobiol. A: Chem. 189 (2007) 364–373.

[43] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($OH^\bullet/O^-$) in aqueous solutions, J. Phys. Chem. 17 (1988) 513–886.