

Oxidative degradation of Metolcarb by electro Fenton process

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Research Article

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Abstract

This study presents the degradation and the mineralization of Metolcarb or 3-methylphenyl methylcarbamate by electro Fenton process with volume cathode. This pesticide was treated using this cathode which is filled with graphite carbon granules. The solutions of Metolcarb were electrolyzed in an reactor of 1.4 liter which shows the performance and the efficiency of the process. Indeed, the effects of different parameters such as the initial concentration of Metolcarb and the intensity of applied current on the degradation kinetics of Metolcarb have been discussed as a function of time. The found results proved that the insecticide removal followed a pseudo first order. The competitive kinetics analysis of Metolcarb during its electrochemical treatment was carried out by using benzoic acid as a reference compound. The absolute rate constant for the oxidation of Metolcarb by hydroxyl radicals consequently is equal to $3.59 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. The mineralization of Metolcarb in terms of total organic carbon was monitored during its electrolysis by the electro Fenton process. The organic carbon is then equivalent to the total carbon determined in reaction analysis. Carbon chains can therefore be formed. The various intermediates which are produced into the electrochemical processing of Metolcarb were determined by the mass spectrometry LC/MS. The biodegradation of Metolcarb has also been investigated in active clay.

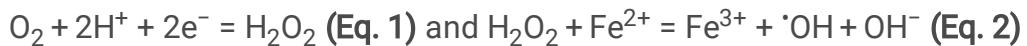
1 Introduction

The environment is the set of natural components of the earth, such as water, air and atmosphere and all of the various phenomena and interactions. The natural conditions of the environment are susceptible to act on the complex living system which is the product of successive variations during an evolution. Water for the environment is used to target specific outcomes for living beings by providing the right amount of water at the right time for their growth. Indeed, quantifying the soil-environment impacts during the management of agricultural land and water resources and supporting sustainable agricultural management is particularly important [1–3]. For a best agricultural productivity, there are several techniques which are especially effective environmentally [4, 5]. Pesticides have been developed and utilized to enhance agricultural yields [6, 7] and to protect plants from pests [8] and the harmful organisms [9] in general. Pesticides are groups of chemical substances that are a subject of some chemical processes of degradation [10]. They are extensively used as insecticides [11], herbicides [12], acaricides [13] or of other biological effects [14].

These products are derived from several chemical families for pests control as carbamates (carbaryl), organophosphorus compounds (parathion) and organochlorine compounds (aldrin) [15–17]. Indeed, carbamates pesticides have become increasingly important in recent years.

Metolcarb or 3-methylphenyl methylcarbamate is widely used in fruits and vegetables such as rice, citrus and onion for its high effectiveness [18]. It is one of the main products of many commercially available carbamate insecticides and acaricides [19]. An efficient process for the degradation of a pesticide requires that the medium be adapted to it for following the evolution characteristics of the substance.

Advanced Oxidation Processes (AOPs) are widely-used techniques in the treatment of organic compounds due to their significant advantages [20–22]. Different research works have shown that the electro Fenton process has an essential effect on the treatment of solutions of pesticides from several chemical classifications [23–25]. In this context, the electro Fenton process is an advanced oxidation process that based on hydroxyl radical production from the Hydrogen peroxide H₂O₂ decomposition in the presence of ferrous ions Fe²⁺ in acidic medium as Fenton's reaction. The addition of the electrochemically produced Fe²⁺ ions to the continuously generated H₂O₂ gives a strong oxidant ·OH (Equations 1 and 2).



In this process, the hydroxyl radical ·OH is an active species and highly reactive and non selective oxidant for organic compounds as pesticides. The degradation of Metolcarb by electro Fenton process volume cathode has been investigated in terms of various experimental conditions. Indeed, chemical transformations in this study using electric current were carried out in an electrochemical reactor.

2 Experimental Materials And Methods

2.1 Chemicals

Metolcarb (C₉H₁₁NO₂, 5-methylphenyl methylcarbamate, (purity 99%) was purchased from Sigma Aldrich. Sodium sulphate Na₂SO₄ and Iron (II) sulphate pentahydrate FeSO₄.7H₂O used as inert supporting electrolyte and catalyst respectively, were from Acros Organics. Benzoic acid was obtained from Merck. Acetic acid was purchased from Acros Organics, and used without further purification. Acetonitrile (HPLC grade) was supplied by Fisher Scientific. The initial pH of solutions was regularized to 3 using analytical grade sulfuric acid H₂SO₄ from Acros. All solutions were prepared with ultra-pure water 18.2 MΩ cm (PURELAB).

2.2 HPLC and LC-MS analysis

Metolcarb degradation and its by-products were observed by High Performance Liquid Chromatography (HPLC) with Diode Array Detection (DAD) and Ultra-High Pressure Liquid Chromatography using an Acquity UHPLC - Waters. For these interpretations, we also used a triple quadrupole mass spectrometer with an electron spray ionization interface and a heated nebulizer, in the positive mode, respectively. Acquity UPLC – Waters BEH C18 1.7–2.1 μm × 100 mm and Reversed phase Symmetry 5-μm, 4.6 × 250 mm columns were applied in UHPLC-MS/MS and HPLC experiments, respectively. Five and fifty microliters of Metolcarb samples were injected. The chromatographic separation was achieved by columns as described above, using a mobile phase of 40% water and 60% acetonitrile in HPLC/DAD, at isocratic conditions, with a flow rate of 1 mL min⁻¹. In UHPLC-MS/MS experiments, the mixture was 90% of water and 10% of acetonitrile with flow rates of 50 L h⁻¹ and 750 L h⁻¹. HPLC detections were investigated at 205 nm.

2.3 Ion Chromatography (IC)

The identification of carboxylic acids and inorganic ions detected during electrolysis was released by DIONEX DX120 Ion Chromatography equipped with a conductivity detector. We used an anion-exchange column Ion Pac AS 19 (4×250 mm) as the stationary phase. A solution of KOH (10–45 mM up to 35 min) in water was the mobile phase.

2.4 Total Organic Carbon (TOC) analysis

A Shimadzu TOC - V_{CPH} analyzer was used to measure TOC of electrolyzed samples of Metolcarb. The detector of TOC system was a Non-Dispersive Infra-Red detector (NDIR). For total carbon (TC) and inorganic carbon (IC), adjustment of analyzer was determined with respectively sodium hydrogen carbonate and potassium hydrogen phthalate standards (Kyoto-Japan, Nacalai Tesque). The variation between TC and IC analysis gives TOC of the pesticide solution sample.

2.5 Biochemical Oxygen Demand (BOD₅)

In order to calculate the quantity of biodegradable organic matter contained in a solution of Metolcarb treated by Electro fenton process, we used Biochemical Oxygen Demand for five days, or BOD₅. In this study, activated sludge was collected from a local wastewater treatment plant in Rennes. Minerals were doped in solution medium to reach the following initial composition, Na₂HPO₄ (6.8 g L⁻¹), MgSO₄.7H₂O (22.5 g L⁻¹), CaCl₂ (27.5 g L⁻¹), KH₂PO₄ (2.8 g L⁻¹), NH₄Cl (2.00 g L⁻¹) and FeCl₃ (0.15 g L⁻¹). The initial pH was adjusted to 7.

2.6 Electrochemical reactor

Degradation and mineralization of Metolcarb (0.1 mM) by electro Fenton process was achieved in an open electrochemical reactor (PRIAM electrolyser) with volumic cathode to treat 1.4 L of pesticide solution. Carbon graphite granules are contained in a cassette (14.2 cm × 10.9 cm). H₂O₂ is produced in the volumic cathode. Two anodes are placed on the other side of the cathode which is set vertically to the reactor center and thus perpendicular to the flow of pesticide solution in the electrolyzer. Anode is a rectangular grid of titanium coated with ruthenium dioxide (DSA). DC power supply G INSTEK, model GPS – 303000 works in galvanostatic mode to control current intensity at a value of 3A. Ionic strength was maintained constant by adding Na₂SO₄ (0.05 M). For the circulation of the solution to be analyzed, we used a peristaltic pump (flow rate of 460 L h⁻¹).

3 Results And Discussion

3.1 Effect of experimental conditions on Metolcarb degradation

3.1.1 Initial concentration of pesticide

The evolution in function of time of a chemical reaction can be influenced by kinetic factors such as the concentration of a chemical product. So a kinetic factor allows to reach during time a determined state of progress of reaction, such as the case of electrolysis of pesticide by an advanced oxidation process.

The treatment of Metolcarb solutions of two different concentrations 10^{-4} M and 3×10^{-4} M by electro Fenton process is studied in acid medium, in presence of sodium sulphate (Na_2SO_4) like a carrier electrolyte, at current intensity of 500 mA, at $\text{pH} = 3$, for 90 min and at room temperature.

Figure 1 shows result curves, $[\text{Mcb}] = f(t)$ during electrochemical treatment of insecticide Metolcarb. It is noted that by increasing the initial concentration of the pollutant to be treated, the rate of its degradation decreases under the experimental conditions previously described. In consequence, the concentration as a kinetic factor is modified the duration of evolution of the electrolysis reaction of Metolcarb by the electro Fenton process.

3.1.2 Intensity of applied current

The intensity of electric current has an effect in general on the concentration of an aqueous electrolytic solution and therefore on its electrolysis in function of time. In fact, intensity of applied current influences on the dissociation of the organic matter during its electrochemical treatment.

The degradation of Metolcarb by electro Fenton process and in acidic solution was investigated by HPLC. By chromatography, Metolcarb appeared at a retention time of 4.4 min. To examine the effect of current intensity on the rate of electrolytic decomposition of this pesticide, we monitored its concentrations at the following applied current intensities, 100 mA, 500 mA and 800 mA and for 90 min. The experimental results are given in Fig. 2.

Concentration - time curves of Metolcarb pesticide present the changes of its concentrations at the three current intensities with its different degradation rates (Fig. 3).

By exploiting the obtained curves, we note that the augmentation of applied current intensity from 100 mA to 800 mA leads to faster degradation kinetics. These results cause almost total degradation of Metolcarb after electrolysis duration of 60 min at 100 mA, 25 min at 500 mA and 15 min at 800 mA. Thus, it proves an improvement in the efficiency of the electrochemical treatment. Graphical representations of Fig. 3 showed that the degradation of Metolcarb by electro Fenton process followed pseudo first order reaction kinetics.

3.2 Absolute rate constant of Metolcarb degradation by hydroxyl radicals

The hydroxyl radical $\cdot\text{OH}$ is a very powerful oxidant, it is the species having the highest oxidizing power after the fluorine. This hydroxyl radical has the possibility to attack organic and inorganic substrates. Their reaction with Metolcarb pesticide as an organic matter is an important step in the oxidative degradation. The rate constant of this reaction can be determined by the competitive kinetics method by

competing the constant substrate to be determined with a reference compound which kinetic constant is known [26–28]. The following equation shows the rate expression of Metolcarb with hydroxyl radicals (Eq. (1)).

$$d[\text{Metolcarb}]/dt = k_{\text{app}} \times [\text{Metolcarb}] = k_{\text{abs}} \times [\text{HO}^{\cdot}] \times [\text{Metolcarb}] \quad (1)$$

In Eq. (1), k_{app} is the apparent rate constant of Metolcarb degradation by hydroxyl radicals and k_{abs} is the absolute rate constant. The absolute kinetic constant of the electrolysis reaction of Metolcarb (Mcb) is determined by the competitive kinetics with benzoic acid (BA), which its absolute rate constant with hydroxyl radicals is known, $k_{\text{abs}} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [29]. Figure 4 presents the graphical representation of the straight line $\ln ([\text{Mcb}]_0 / [\text{Mcb}]_t)$ in function of $\ln ([\text{BA}]_0 / [\text{BA}]_t)$.

According to these results, it is found that the value of the absolute kinetic constant k_{abs} of the reaction of hydroxyl radicals with Metolcarb is equal to $3.59 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value indicates that the magnitude of the kinetic constants generally obtained for the reactions between the aromatic compounds and the hydroxyl radicals belongs to a high range and that the interactions of this pesticide reaction are rapid.

3.3 Mineralization of Metolcarb

Organic matter can be distinguished from mineral matter, so carbon plays a central role. For that, the chemical molecule can pass through decomposition steps under defined experimental conditions.

To characterize and follow the evolution of the mineralization of insecticide Metolcarb by electro Fenton process in aqueous and acidic medium, we are studied the progression of the total organic carbon (TOC) during its electrolysis reaction. Indeed, at different current intensities, we are measured the TOC values of the pesticide solutions and for 90 min. Figure 5 presents the evolution of TOC values in function of time for the electrolyzed pollutant.

These results are highlighted the efficiency of this electrochemical process to reach an advanced stage of Metolcarb mineralization. The obtained curves show progressive diminution in values of TOC versus time from 100 mA to 800 mA and for 90 min. Figure 5 proves that in the first 30 min, TOC removal is faster at 800 mA than at 500 mA and at 100 mA. The obtained TOC values during 3 hours of Metolcarb electrolysis are given in Fig. 6.

It can be seen from this figure that after 3 hours the rate of the mineralization of Metolcarb has been improved. Thus, at 100 mA the percentage of the decomposition of Metolcarb by electro Fenton is changed gradually from 26.39–36.21% and at 800 mA from 53.78–58.84%. Organic matter such as the case of Metolcarb pesticide is consisting of different pure bodies. Then, its chemical composition provides the proportions of its decomposition by measuring parameters such as TOC and COD.

3.4 By-products of Metolcarb degradation

3.4.1 Identification of aromatic intermediates

It is notable, in advance, to highlight and detect organic compounds such as carbon molecules as intermediates of reaction media. In general, electrolytic reactions are important for the degradation of pesticides. In experimental conditions that are described above, LC–MS analysis were used to determine the aromatic by-products of Metolcarb during its electrolysis by electro Fenton process. Indeed, hydroxyl radicals are reacted with insecticide carbamate evidently, and then various by-products are formed in solution. Table 1 presents the obtained compounds and its m/z reports.

Table 1 Molecular compounds of intermediates formed during electrolysis of Metolcarb by electro Fenton process.

t_R (min)	m/z	Intermediate	Chemical structure
0.76	129	cyclohexa-2,5-diene-1,2,4-triol	
0.77	157	5-methylbenzene-1,2,3,4-tetraol	
3.05	180	3-hydroxy-5-methyl phenyl methylene-carbamate	
3.07	163.06	5-methyl phenyl methylenecarbamate	
107.9		m-cresol	
91.1		Hydroxymethyl acetate	
3.29	160.7	Benzene-1,2,3,4,5-pentaol	
3.51	111.3	Hydroquinone	
3.9	-	Benzoquinone	
4.14	166	Metolcarb	

The fragmentation of organic compounds is observed when these molecules are subjected to internal and external energies. Peaks of the fragmentation make it therefore possible to identify the different molecular structures of the matter. Under our experimental conditions, benzoquinone was determined by HPLC analysis. The other cyclic and aromatic compounds are formed during the electrochemical treatment of Metolcarb ($t_R = 4.14$ min) by the electro Fenton process and are identified by LC-MS. Other by products and components of the reaction medium of pesticide electrolysis could be characterized by another chromatographic method.

3.4.2 Determination of carboxylic acids

In general, carboxylic acids are abundantly found in nature under several forms. Acids that derive from chemical reactions such as reduction and oxidation of pesticides can be detected and can also express the degradation of the insecticide. Indeed, several studies were concerned the detection of different acids during the mineralization of pesticides in aqueous solutions [30–32]. In this study, we have tried to investigate the formation of carboxylic acids throughout the electrolysis of Metolcarb by electro Fenton process (Fig. 7).

At the experimental and interactional level, the electrolysis medium of Metolcarb by electro Fenton process being oxidizing, the functional groups alcohols are oxidized to aldehydes, themselves converted to carboxylic acids. In the case of this carbamate and according to results presented in Table 1, hydroxymethyl acetate was identified by LC / MS chromatography. We think that this carbonyl compound is converted to a carboxylic acid. As it is seen in Fig. 7, acetic acid is detected by Ion Chromatography (IC) during 90 min of the electrochemical treatment of Metolcarb. This acid was started to form at the beginning of the reaction. This curve shows that its evolution was fairly rapid and it was reached its maximum at 30 min.

3.4.3 Detection of nitrate ions

Compounds that are given by the decomposition of hydrocarbons carrying functional aldehyde, alcohol or carbamate groups can be ions such as nitrate ions [33]. NO_3^- ions are powerful eutrophics and they can be resulted in situations of interactions in aqueous media. In this part, we are noted the formation of nitrate ions during the electrolysis of Metolcarb by electro Fenton. These anions were detected by Ion chromatography (IC). The curve of Fig. 8 is attributed to the evolution of nitrate ions in this reaction versus time.

The detection of these ions experimentally as it is observed in Fig. 8 indicated that the nitrogen atom of the structure of Metolcarb can be converted to nitrate ions during the oxidation of this carbamate by electro Fenton. Thus, at the first 30 min the quantity of the detected ions is superior than at 60 min and at 75 min. The organic products, the carboxylic acid and the nitrate ions which are detected by different chromatographic methods make it possible to present the mechanism of mineralization of Metolcarb.

3.5 Metolcarb degradation mechanism

In order to develop the monitoring of the degradation and mineralization of Metolcarb as an organic compound, we are analyzed the interaction between the generated hydroxyl radicals and this pesticide during its electrolysis by the advanced oxidation process electro Fenton. The diverse transformations and reaction steps are highlighted and allow to characterize the oxidation of Metolcarb in acidic aqueous medium. Thus, these observations were revealed breaking and changing of chemical bonds as well as addition and formation of functional groups under the influence of experimental effects. In Fig. 9, we are proposed the mechanism of electrochemical degradation of Metolcarb.

The pathways of this mechanism are based on the determination of the above described aliphatic and aromatic by-products of Metolcarb. In pathway 1, the decomposition of Metolcarb by electrolysis gives the formation of 5-methylphenyl methylene carbamate by its deprotonation. This insecticide can be oxidized by the hydroxyl radicals to an unstable radical as noted in pathway 2, which is converted after other reactions to an intermediate and there to 5-methylphenol. Indeed, the addition of the hydroxyl groups to the benzene ring is seen in various processing steps of this pesticide. The mechanism continues from 5-methylbenzene-1,2,3,4-tetraol to lead successively to the formation of hydroquinone and then benzoquinone. On the other hand, the generation of carboxylic acids is the result of the oxidative opening of the aromatic ring. The electrolysis of an organic acid under the effect of the electric current allows it to be transformed into a carboxylate ion being unstable and it provides the carbon dioxide by its decarboxylation. Therefore, we note that Metolcarb can decompose electrolytically to various elements, while its biodegradation will be investigated.

3.6 Biodegradation of electrolyzed Metolcarb solution

The degree of decomposition of an organic substance and the time required for its decomposition and its sensitivity to the reaction medium can express its biodegradability.

BOD₅ of a pesticide is used to determine the ability of this chemical product to react with the active clay used as an environmental medium of significant ecological character. However, the measurement of oxygen consumption is a suitable measure to assess its biodegradation.

Generally we follow the biodegradation of Metolcarb by testing the evolution of the solution during this study. clay is a locally abundant material, very diverse and treated before its utilization in this research part. Thus the solution of Metolcarb electrolyzed by the electro Fenton process is mixed with the reagents described in 2.5. This experimental technique allows to the measurements of the Biological Oxygen Demand (BOD₅) of Metolcarb which having certain physico chemical properties while having others. The biodegradation of Metolcarb is investigated after its electrochemical treatment at current intensities 100 mA and 800 mA and during 3 hours. The results of the measurements in this paragraph correspond to the determination of the ratios of the Chemical oxygen demand and the Biological Oxygen Demand. Then, the found COD / BOD₅ ratios indicate the biodegradability of Metolcarb using the same experimental method. These ratios are 1.4 and 0.2 at current intensities 100 mA and 800 mA respectively. It is then noted that the two ratios are less than 5. We deduce that the Metolcarb is biodegradable after its two electrolyses by electro Fenton process. Indeed, by increasing the electric current, the COD / BOD₅ ratio decreases and Metolcarb is more biodegradable.

4 Conclusion

The treatment of aqueous solutions of Metolcarb or 3-methylphenyl methylcarbamate was firstly carried out by electro Fenton process using a volume cathode. Furthermore, the electrolysis of Metolcarb (10^{-4} M) at different current intensities showed that the electro Fenton process was an efficient process for its

degradation and mineralization at a short reaction time. Mineralization or decomposition of the organic part of Metolcarb and the analysis of the mineral part of the reaction medium were also studied. We have concluded that after 3 hours of electrolysis, the total organic carbon (TOC) of Metolcarb was reduced continuously. Therefore more than 55% of organic carbon in this pesticide has been mineralized at 800 mA. While after 7 hours and 30 minutes, the mineralization of Metolcarb was total. The kinetics of a reaction is obviously concerned the rates of the reaction. According to the found results, the absolute rate constant of Metolcarb using benzoic acid in its electrolysis is thus equal to $3.59 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}$. This constant corresponds to the high value of the rate of the catalytic oxidation of Metolcarb. Several intermediate products were detected by LC/MS during its treatment by electro Fenton process. In this study we also identified acetic acid following the electrolysis of Metolcarb as a function of time. This step involves that this chemical intermediate is produced during the transformation of this compound to another product. Nitrate ions NO_3^- as anions are formed in term of a reaction procedure based on the electrochemical analysis of Metolcarb. Indeed, the degradation mechanism of Metolcarb was a method to define the sequence of steps and elementary reactions by which an electrochemical change takes place. Therefore, because of its characteristics and efficiency, the biodegradation of Metolcarb has been evaluated by measuring COD / BOD_5 ratio. This method has shown that Metolcarb is biodegradable.

Declarations

Data availability All data generated or analysed during this study are included in this published article and are however available from the authors upon reasonable request.

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Figures

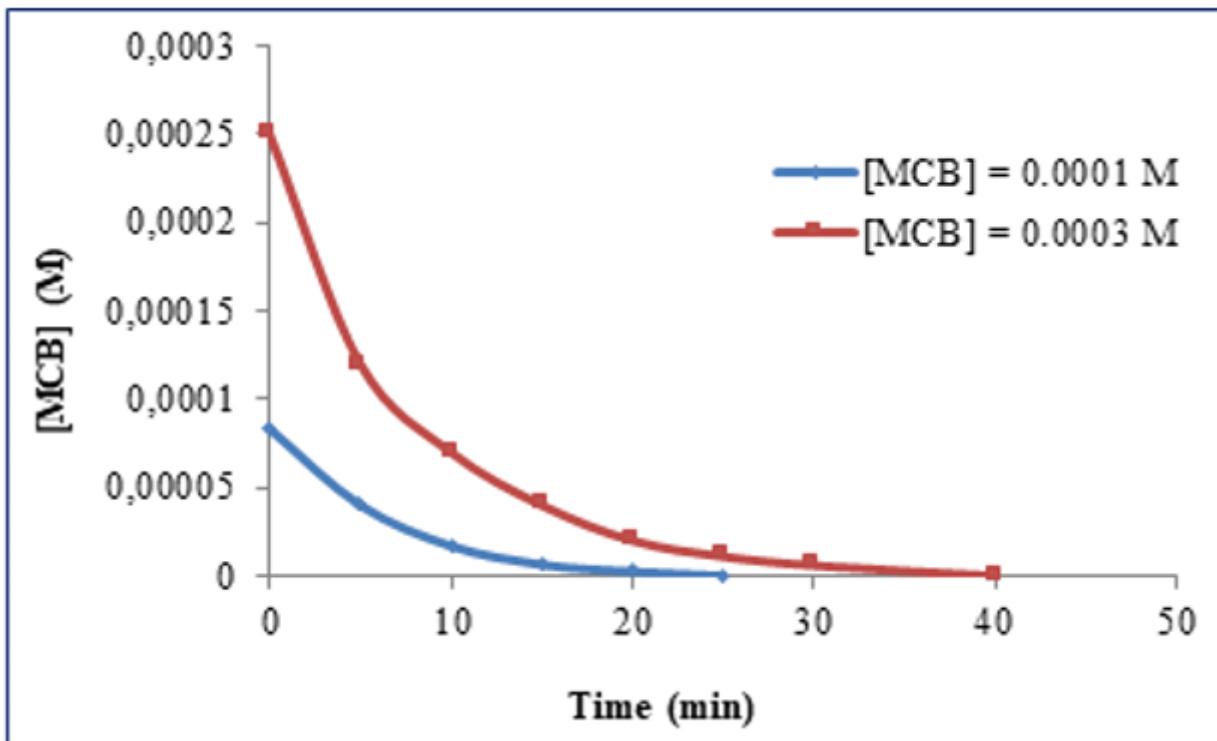


Figure 1

Degradation of Metolcarb solutions by electro Fenton process, at two different concentrations and at a current intensity $I = 500$ mA.

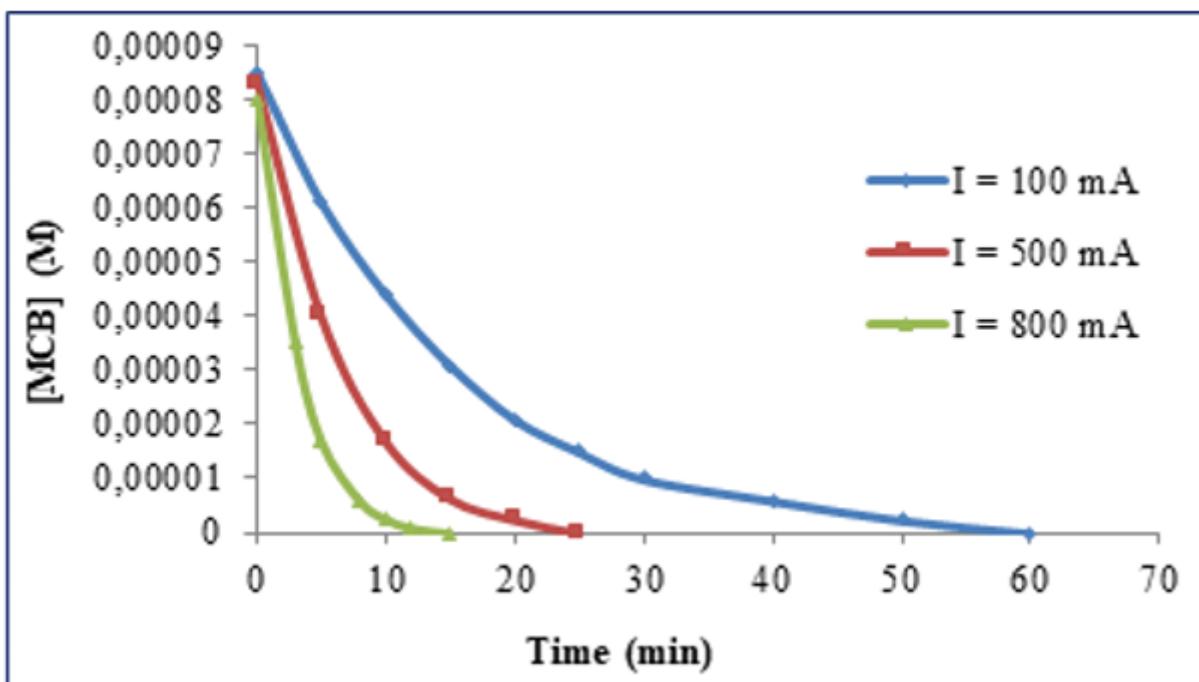


Figure 2

Degradation kinetics of Metolcarb (10^{-4} M) at different current intensities, $[Fe^{2+}] = 5 \times 10^{-4}$ M.

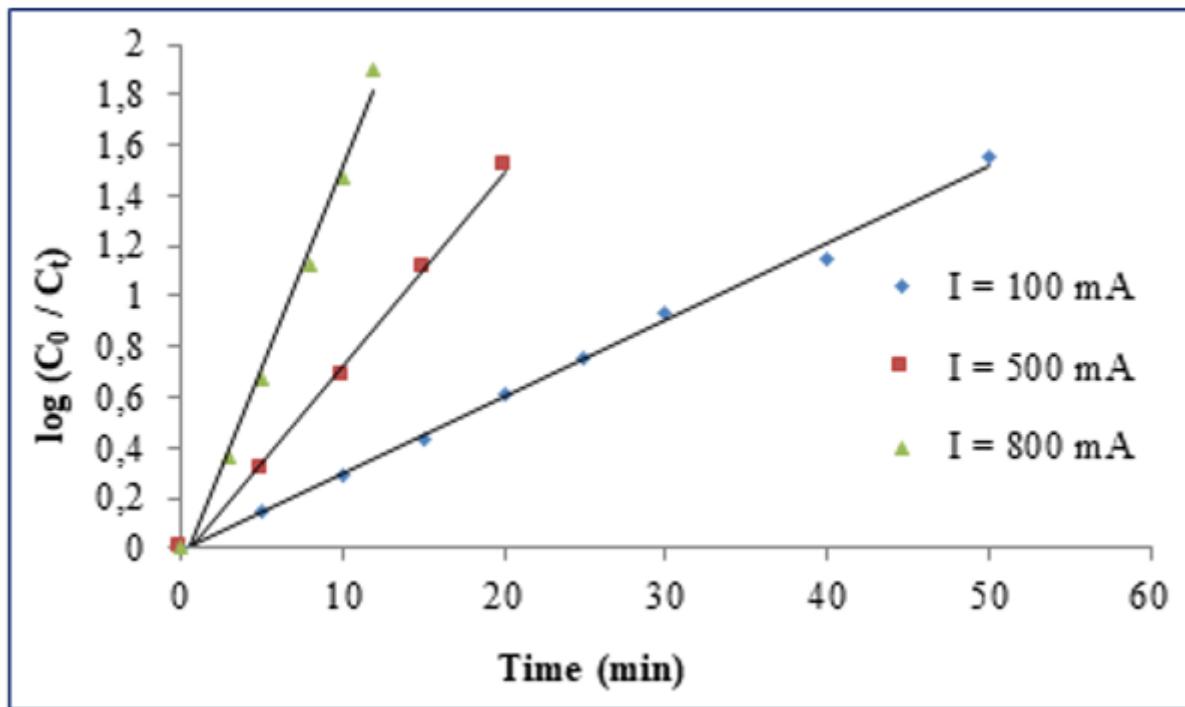


Figure 3

Kinetic observations of Metolcarb degradation by electro Fenton process at current intensities: 100 mA, 500 mA and 800 mA.

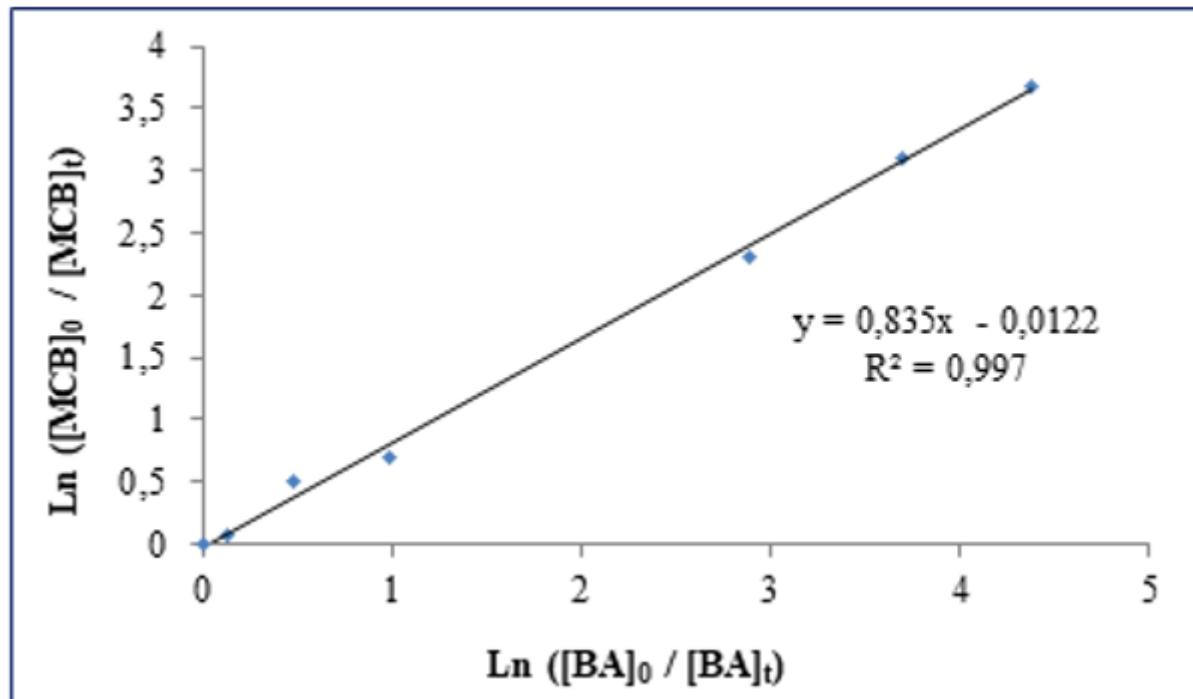


Figure 4

Indication of the absolute constant of oxidation of Metolcarb (10^{-4} M) by hydroxyl radicals $\cdot\text{OH}$, $[\text{BA}] = 10^{-4}$ M.

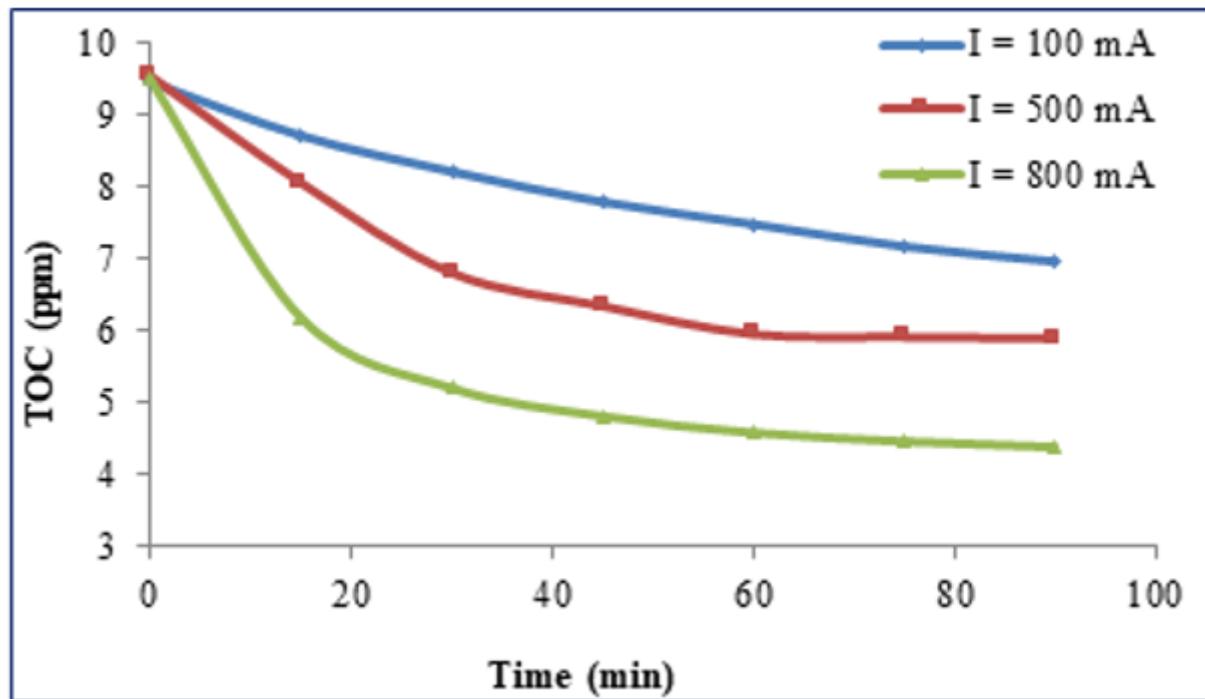


Figure 5

Evolution of TOC during mineralization of Metolcarb (10^{-4} M) by electro Fenton process and at 100 mA, 500 mA and 800 mA.

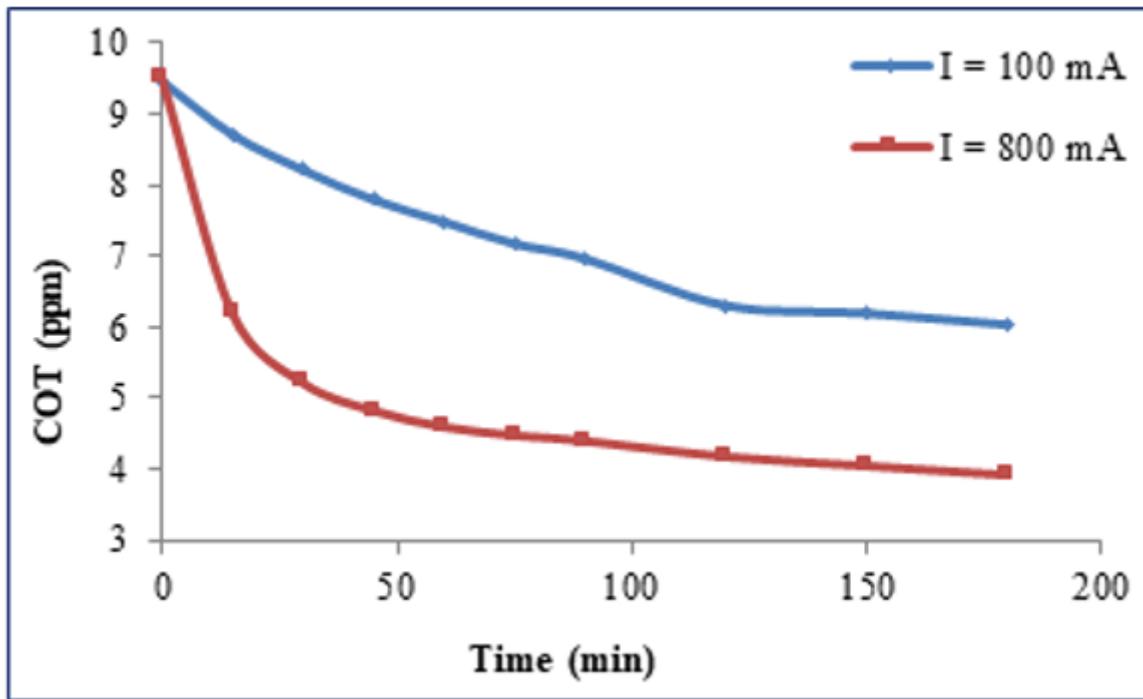


Figure 6

Metolcarb mineralization during 3 hours of electrolysis by electro Fenton process at 100 mA and 800 mA.

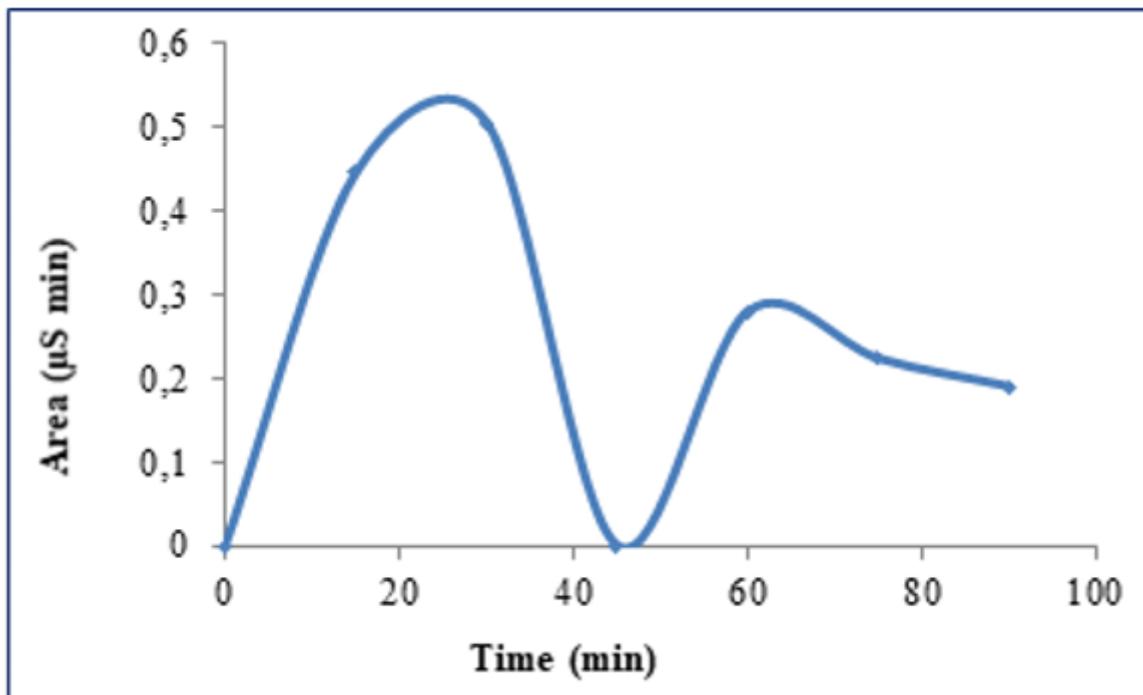


Figure 7

Evolution of acetic acid during the mineralization of Metolcarb by electro Fenton process.

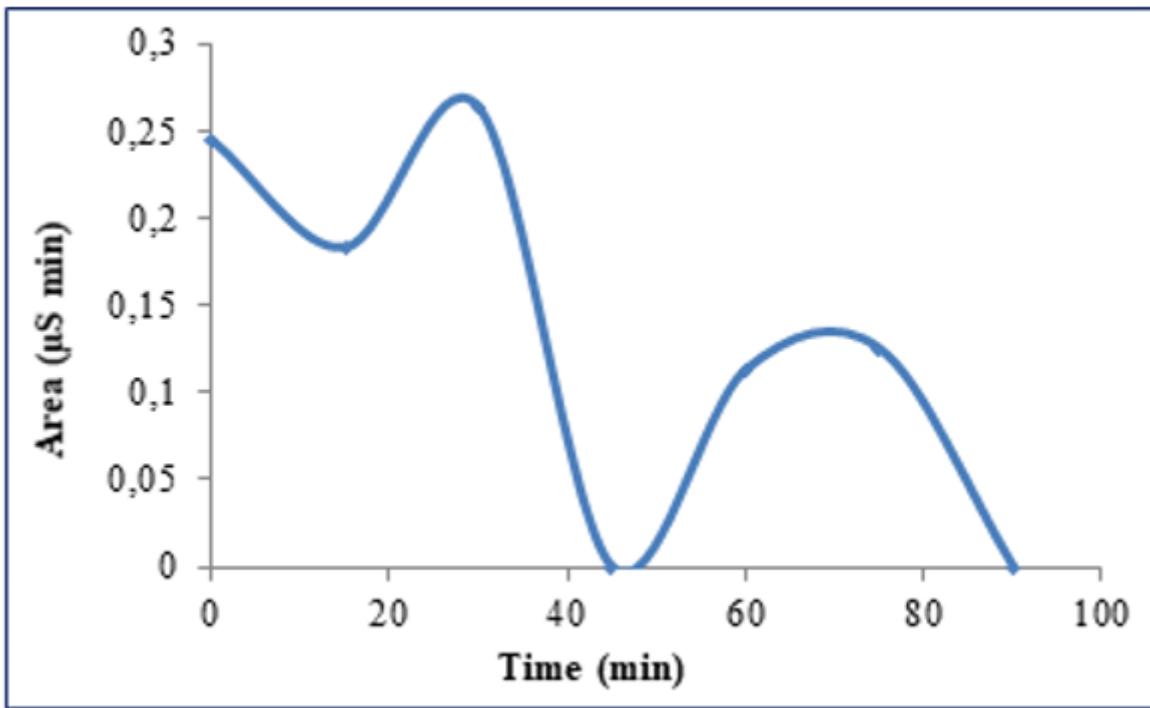


Figure 8

Nitrate ions evolution throughout electrolysis of Metolcarb by electro Fenton process.

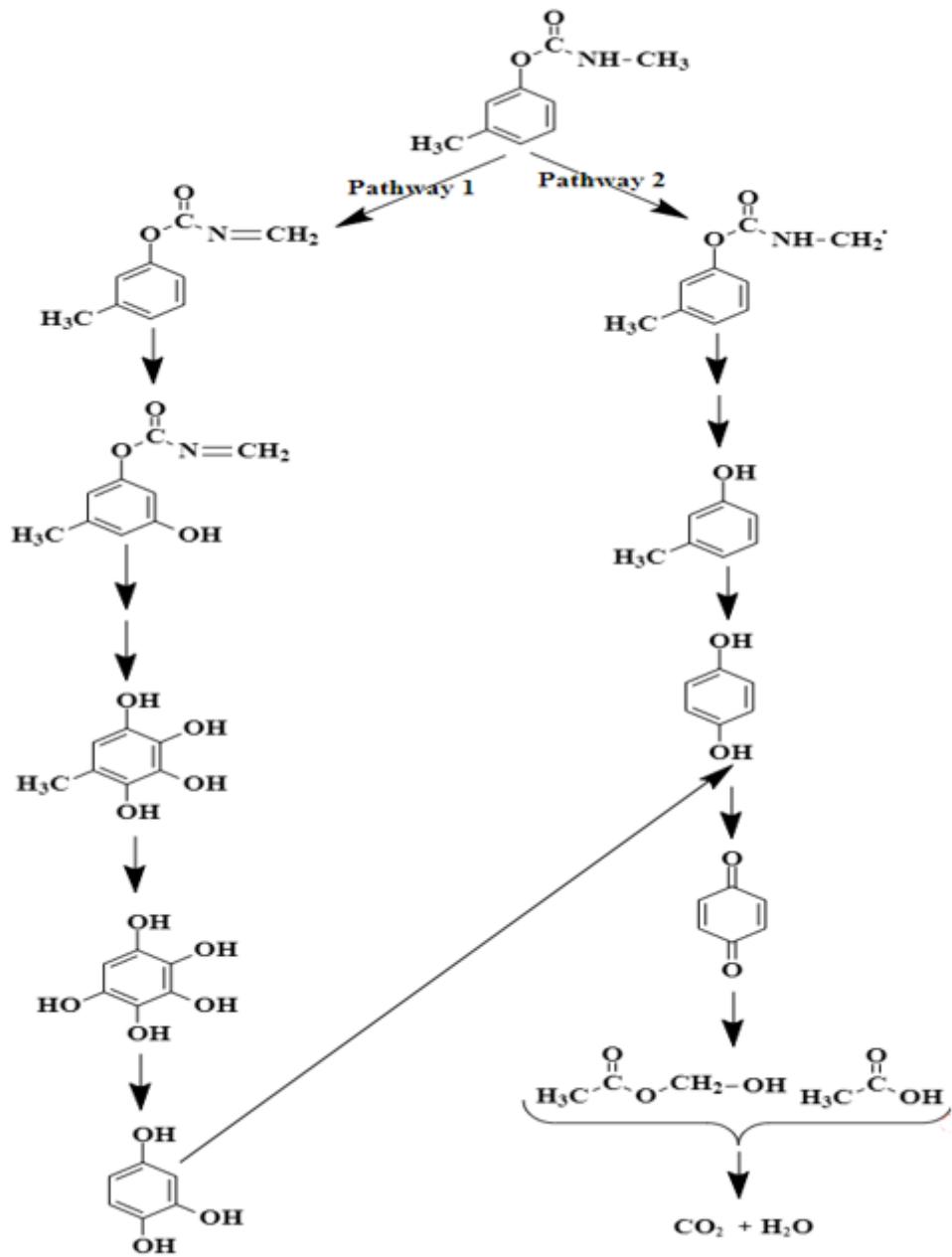


Figure 9

Mechanism of degradation of Metolcarb in acidic aqueous medium and by electro Fenton process.