

Degradation and Mineralization Study of Promecarb by Electro Fenton Process

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Abstract: Organic substances as pesticides, especially aromatic compounds are a major environmental concern. In the present work, solutions of Promecarb or 3-isopropyl-5-methylphenyl-N-methylcarbamate of pH = 3 have been degraded by electro Fenton process, using a volumic electrochemical reactor filled with carbon graphite. Effects of nature of material of cathode, initial concentration of insecticide and applied current on the kinetics of oxidative degradation and mineralization efficiency have been investigated. Kinetic analysis showed that the oxidation of Promecarb by hydroxyl radicals follows a reaction kinetic of pseudo first order. The absolute rate constant for Promecarb oxidation by hydroxyl radicals was determined as $10.88 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ by competitive kinetics method and benzoic acid was used as reference compound. Mineralization of this pesticide by hydroxyl radicals consists in its transformation to mineral products. The evolution of the mineralization during Promecarb treatment by electro Fenton process was followed by analysis of Total Organic Carbon TOC. Thus, after 3 hours of electrolysis and at $I = 800 \text{ mA}$, more than 50% of the organic carbon present in the solution is mineralized. Several degradation products were formed during its electro Fenton treatment. These intermediates were identified using High Performance Liquid Chromatography HPLC, Ionic Chromatography IC and Liquid Chromatography - Mass Spectrometry LC-MS. Based on identification of aromatic intermediates and carboxylic acids, a plausible Promecarb mineralization pathway is proposed. Also, we realized the measurement of the Biochemical Oxygen Demand BOD_5 of insecticide solution after treatment by electro Fenton process, to evaluate its biodegradability.

Keywords: Promecarb, Electro Fenton, Hydroxyl Radicals, Oxidation, Mineralization

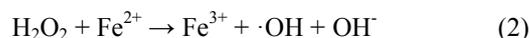
1. Introduction

Use of pesticides [1] has received extensive attention nationally and internationally. Study of pesticides degradation with an objective of reducing the risk of environmental pollution is essential. In the 1950s, synthetic carbamate pesticides were introduced into field applications [2]. It is mentioned that the carbamates were derivatized with natural products as physostigmine and nereistoxin. This type of synthetic pesticides was associated with high toxicity [3]. Promecarb or 3-isopropyl-5-methyl-N-methylcarbamate phenyl is an insecticide belonging to a large family of pesticides [4] derived from the N-methylcarbamic acid. This insecticide has a mechanism of action involving inhibition of cholinesterase enzyme [5]. It is used for the treatment of

fruits like citrus and potatoes [6].

Various treatment processes of pesticides have been used as physical treatments, chemical treatments and biological treatments [7, 8]. Advanced oxidation processes (AOPs) may be used for decontamination of water containing these compounds [9, 10]. These chemical processes have proven their capacity to remove persistent organic substances [11]. They are oxidized by generation of highly oxidant radicals in situ such as hydroxyl radicals ($E_0 = 2.8 \text{ V}$) [12]. Fenton and electro Fenton techniques have been applied by investigators around the world [13-17]. Thus, basic principle of electro Fenton process is the reaction between the continuous electro generation of hydrogen peroxide H_2O_2 and reduction of

oxygen O_2 on the cathode (Eq. (1)) and the added ferrous iron (Fe^{2+}) as catalyst. It produces powerful oxidant $\cdot OH$ (Eq. (2)) [18, 19].



Electro Fenton process offers the advantage of avoiding the continuous addition of H_2O_2 , which is an unstable and potentially harmful compound. Many studies have reported the oxidation of pesticides by electro Fenton process using different cathodes, such as carbon-felt [20-23] and in cylindrical cells of few milliliters [24, 25].

In this research work, we studied the performance of carbon graphite cathode for the degradation of Promecarb by electro Fenton process in volumic electrochemical reactor of 1.4 L. We have investigated therefore its partial transformation and the byproducts.

2. Materials and Methods

2.1. Chemicals

Promecarb ($C_{12}H_{17}NO_2$, 3-isopropyl-5-methyl-N-methylcarbamate, purity 99%) was purchased from Sigma-Aldrich. Iron (II) sulphate pentahydrate $FeSO_4 \cdot 7H_2O$ (purity 99%) and sodium sulphate Na_2SO_4 (purity 99%) used as catalyst and inert supporting electrolyte were from Acros Organics. Benzoic acid was obtained from Merck. Oxalic and acetic acids were obtained from Pro Labo and Acros Organics respectively. Acetonitrile (purity 99.9%) (HPLC grade) was from Fisher Scientific. The initial pH of solutions was adjusted to 3 using analytical grade sulfuric acid H_2SO_4 (purity 95%) from Acros. All solutions were prepared using ultra-pure water 18.2 M Ω cm (Purelab).

2.2. Electrochemical Reactor

Degradation of Promecarb by electro Fenton process was conducted in an open electrochemical reactor with volumic cathode (Priam electrolyser) treating 1.4 Liter of solution. This cathode producing H_2O_2 is a volumic electrode consisting of carbon graphite granules contained in a cassette (14.2 cm \times 10.9 cm). Anode is a rectangular grid of titanium coated with ruthenium dioxide (DSA). Cathode and anode were connected to a DC power supply G Instek, model GPS - 303000 operating in galvanostatic mode to control the current intensity at a value of 3A. Ionic strength was maintained constant by the addition of Na_2SO_4 (0.05 M). Electrolytic solution was in circulation with help of a peristaltic pump (flow rate of 460 L h^{-1}). The initial insecticides carbamates concentration was 0.1 mM.

2.3. HPLC and LC – MS Analyzes

Decomposition of Promecarb and its by products were monitored by High Performance Liquid Chromatography HPLC equipped with a diode array detector and Ultra High Pressure Liquid Chromatography using an Acquity UHPLC -

Waters and a triple quadrupole mass spectrometer with an electron spray ionization interface and a heated nebulizer. Reversed phase Symmetry 5 μm , 4.6 \times 250 mm and Acquity UPLC - Waters BEH C18, 1.7 - 2.1 μm \times 100 mm columns were used in HPLC and UHPLC - MS/MS respectively. Fifty and five microliters of the samples were injected. Columns were eluted with a mixture of water - acetonitrile at 40 / 60 and 90 / 10 with flow rates of 1 in HPLC/DAD and 50 L h^{-1} and 750 L h^{-1} in UHPLC - MS/MS. HPLC detections were performed at 210.2 nm.

2.4. Ion Chromatography (IC)

Generated carboxylic acids and inorganic ions were identified by Dionex Dx120 Ion Chromatography equipped with a conductivity detector, using an anion exchange column Ion Pac AS 19 (4 \times 250 mm) as the stationary phase, and a solution of KOH (10 - 45 mM up to 35 min) in water as the mobile phase. The flow rate was set at 1 mL min^{-1} .

2.5. Total Organic Carbon TOC Analysis

TOC of initial and electrolyzed samples of Promecarb was determined with a Shimadzu TOC - V_{CPH} analyzer. Organic carbon compounds were combusted and converted to CO_2 , which was detected and measured by a Non Dispersive Infra Red detector (NDIR). Calibration of the analyzer was achieved with potassium hydrogen phthalate and sodium hydrogen carbonate standards (from Nacalai Tesque, Kyoto - Japan) for total carbon (TC) and inorganic carbon (IC) respectively. Difference between TC and IC analysis gives TOC data of the sample.

2.6. Biochemical Oxygen Demand BOD₅

Activated Sludge used in this study was collected from a local wastewater treatment plant in Rennes. It was washed several times by successive centrifugation. Culture medium was prepared in duplicate in serum bottles of 250 mL containing 100 mL of Promecarb solution pretreated by electro Fenton process for 90 min. Minerals were added in aqueous medium as highly concentrated solutions to reach the following initial composition (g L^{-1}): $MgSO_4 \cdot 7H_2O$ (22.5), $CaCl_2$ (27.5), $FeCl_3$ (0.15), NH_4Cl (2.00), Na_2HPO_4 (6.8), KH_2PO_4 (2.8) and the initial pH was adjusted to 7. Activated sludge was mixed in order to have initial concentration of 1 g L^{-1} of dry matter. Cultures were agitated at room temperature and 5 mL of samples were taken regularly for BOD₅ measurements.

3. Results and discussion

3.1. Effect of Operational System Parameters on Promecarb Degradation Efficiency

Electro Fenton process involves a number of experimental parameters. Thus, optimization governs the efficiency of degradation. These parameters were found electrochemical factors as material fills in the cathode and applied current and

kinetic factors as initial concentration of the pesticide.

3.1.1. Nature of Material Fills in Cathode: Glassy Carbon and Carbon Graphite

We followed the degradation of Promecarb by electro Fenton process during 90 minutes of electrolysis and at 800 mA, using two different materials fill in cathode: glassy carbon and carbon graphite. The found results are shown in Figure 1.

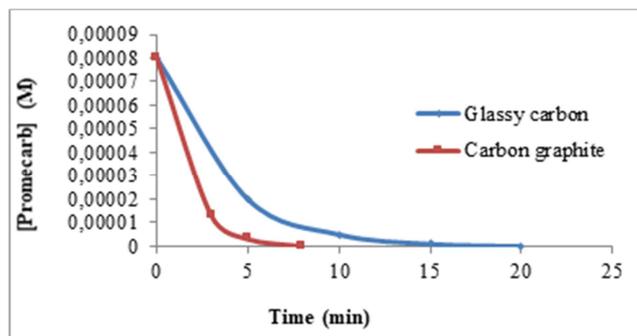


Figure 1. Kinetics of Promecarb degradation by electro Fenton process and on cathodes of glassy carbon and carbon graphite, $[Promecarb]_0 = 0.1 \text{ mM}$, $I = 800 \text{ mA}$ and $[Fe^{2+}] = 0.5 \text{ mM}$.

Variation of the insecticide concentration in function of time shows that the degradation of Promecarb by electro Fenton process and on cathodes of glassy carbon and carbon graphite is fast. We note that degradation of Promecarb is faster when using carbon graphite as material of cathode. Thus, glassy carbon instead of carbon graphite slows the rate of pesticide degradation. Complete degradation (over 99%) of Promecarb by this electrochemical process at a current intensity $I = 800 \text{ mA}$ requires 8 and 20 minutes using respectively cathodes of glassy carbon and carbon graphite. This electrochemical reaction of promecarb more rapid in presence of carbon graphite is due to the increase of formation rate of hydroxyl radicals during electrolysis. In the following, we will develop the electrochemical treatment of promecarb on a cathode filled with carbon graphite.

3.1.2. Initial Concentration of Promecarb

Electrochemical analysis of Promecarb solutions is carried out on two different concentrations 0.1 mM and 0.53 mM in acid medium of $\text{pH} = 3$, at a current intensity of 500 mA, during 90 minutes and at room temperature, to study the effect of pesticide concentration on the degradation process. This study was realized in the presence of a supporting electrolyte Na_2SO_4 (50 mM).

Figure 2 includes the observed results. These curves show that the degradation time of Promecarb increases from 20 to 90 minutes with increasing of initial concentrations of the organic compound from 0.1 to 0.39 mM. In these experiments and at current intensity of 500 mA, rates of the production of hydrogen peroxide and of the oxygen reduction were in fact high. Then, augmentation of Promecarb concentration increases the number of pesticide molecules in the solution for the same number of hydroxyl radicals, which leads to decrease the degradation rate of Promecarb.

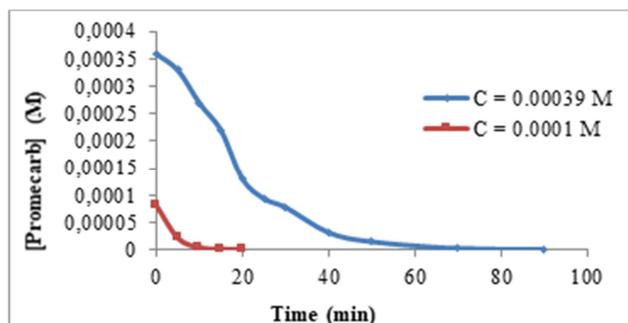


Figure 2. Promecarb deterioration by electro Fenton process at different concentrations and at a current intensity $I = 500 \text{ mA}$.

3.1.3. Applied Current

Electric current is the rate of flow of electric charge through an aqueous medium to electrolyze solutions of pesticide Promecarb. Then it is necessary to determine intensity of optimal current during analysis of this insecticide by electro Fenton process. Different solutions at equal concentrations of Promecarb (0.1 mM) were electrolyzed at different current intensities ranging from 100 to 1000 mA. Figure 3 shows curves of Promecarb concentrations versus time and straight lines corresponding to concentrations ratios versus time too.

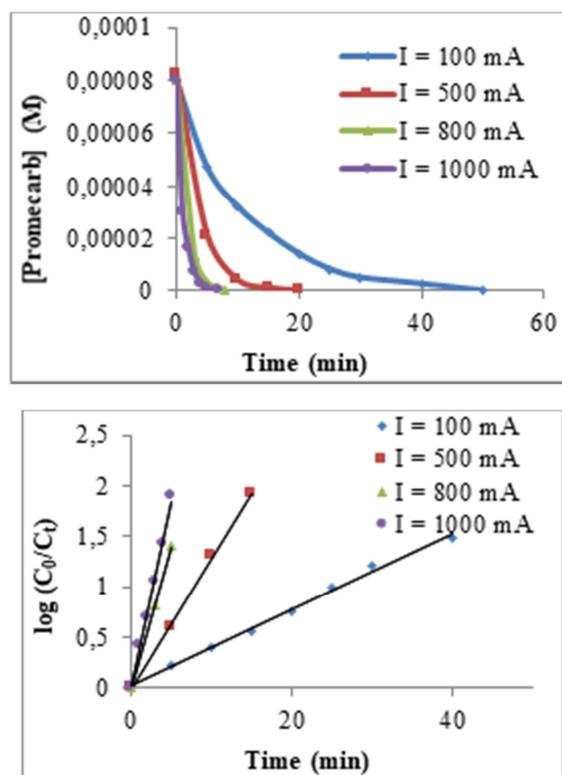


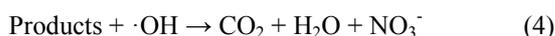
Figure 3. Effect of applied current intensity on Promecarb degradation kinetics (0.1 mM), $[Fe^{2+}] = 0.5 \text{ mM}$.

In general, this graphical representation allows to summarize evolution of experimental data. The obtained curves show that augmentation of applied current intensity leads to faster degradation kinetics. Indeed, an electric current from 100 to 1000 mA, provides the enlargement of Promecarb removal rate after 90 minutes of electrolysis,

indicating an improvement in efficiency of treatment. These results are confirmed by values of apparent rate constants k_{app} : 0.84, 0.64, 0.3 and 0.085 min^{-1} at respective current intensities 1000, 800, 500 and 100 mA.

3.2. Mineralization of Promecarb in Aqueous Solution

Hydroxyl radical is a strong oxidizing species and is able to mineralize any organics compounds [26]. Therefore $\cdot\text{OH}$ generated by electro Fenton process reacts with Promecarb and produce a number of reaction intermediates. These intermediates follow other reactions Eq. (3) and (4) allowing formation of CO_2 and inorganic ions.



In order to investigate the mineralization behavior of Promecarb, several experiments were performed at different current values with 0.5 mM of Fe^{2+} . Mineralization progress of aqueous Promecarb solutions during 90 minutes of electrolysis was monitored in terms of TOC abatement efficiency during the electrochemical analysis. The obtained TOC values are shown in Figure 4. TOC decay rate was increased by raising the applied current from 100 to 1000 mA.

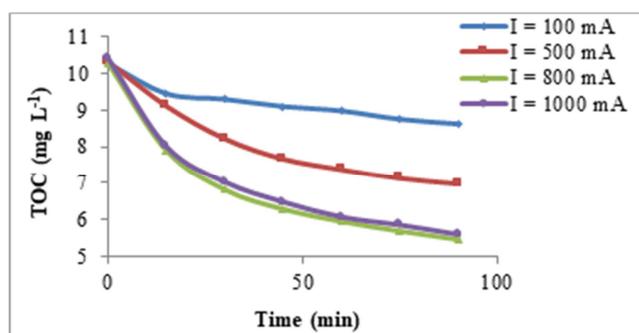


Figure 4. Mineralization kinetics of Promecarb in acidic media at several current intensities $I = 100, 500, 800$ and 1000 mA by electro Fenton process: $C_0 = 0.1$ mM, $[\text{Na}_2\text{SO}_4] = 50$ mM and $[\text{Fe}^{2+}] = 0.5$ mM.

TOC is an important parameter to define some reaction behaviors. Continuous decrease of TOC is attributed to the oxidation of Promecarb with $\cdot\text{OH}$. Figure 4 shows that there is a fast TOC removal at current values from 500 to 1000 mA. According to these results, 1000 mA was determined as the limit current value in the given conditions. After 90 min of electrolysis, more than 46% of organic carbon present in initial Promecarb solution was mineralized. Thus, mineralization rate has rapidly decreased and reached to a steady state value especially in the case of 800 and 1000 mA. On the other hand, the found TOC values during 3 hours of electrolysis and at applied current $I = 800$ mA are given with time. About this figure, we had noted that these values decreased sharply during the first 2 hours. After this time, TOC values slowly decreased and reached a steady state value at the end of the electrolysis. In this case, Promecarb mineralization percentage was more than 52% versus 3 hours of treatment by electro Fenton process.

3.3. Absolute Rate Constant of Promecarb with Hydroxyl Radicals

Under our experimental conditions in which an aqueous solution is saturated with oxygen, $I_{app} = \text{constant} = 100$ mA, rate of production of hydroxyl radicals was controlled electrochemically. Reaction rate of the oxidation of Promecarb is related to its high affinity towards $\cdot\text{OH}$. To confirm this affinity, the absolute rate constant k_{abs} of the first order reaction between Promecarb and hydroxyl radicals was determined by competitive kinetics method [27] using benzoic acid as standard competitor. We note that the absolute constant of benzoic acid is $k_{abs}(\text{BA}) = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Hydroxyl radical is a very reactive species so it doesn't accumulate easily in solution and its concentration takes a steady value during treatment. Therefore, the next equation can be written:

$$K_{abs}(\text{Promecarb}) = k_{abs}(\text{BA}) \times k_{app}(\text{Promecarb}) / k_{app}(\text{BA}) \quad (5)$$

This part of the study was carried out with equal concentrations of 0.1 mM of Promecarb and BA at 100 mA and during 90 min of electrolysis. It allows to highlight the composition of possible reaction intermediates. The straight line of Figure 5 has the equation $y = 2,5312x + 0,3424$, $R^2 = 0,9928$. The absolute rate constant of Promecarb k_{abs} during electrochemical treatment gives a high value of $10.88 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 5).

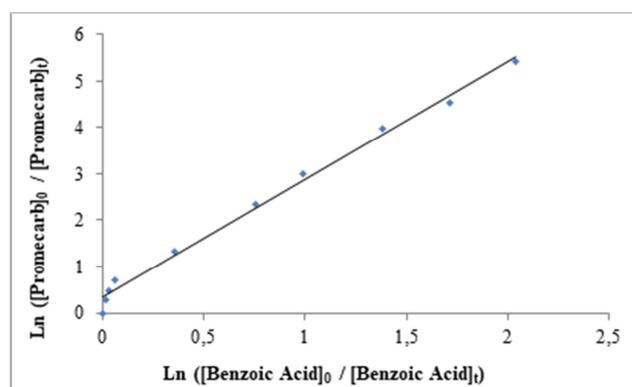


Figure 5. Determination of absolute rate constant of Promecarb with hydroxyl radicals, $[\text{PCB}]_0 = 0.1$ mM, $[\text{BA}]_0 = 0.1$ mM and $[\text{Fe}^{2+}] = 0.5$ mM.

The value of this constant is in accordance with k_{abs} values for hydroxylation reactions of aromatic compounds with hydroxyl radicals [28, 29].

3.4. Chromatographic Analysis of Promecarb

3.4.1. Identification of Aromatic Intermediates

A solution of Promecarb is electrolyzed at a constant current intensity of 500 mA. Analytical study of aqueous solution of Promecarb treated by electro Fenton process had shown the formation of several intermediates products. HPLC/DAD and LC/MS/MS analysis were used to determine the aromatic by products of Promecarb during oxidation. The identified products were presented in Table 1.

Table 1. Aromatic by products of Promecarb using LC/MS/MS and HPLC/DAD analysis.

t_R (min)	m/z	Intermediate	Chemical structure
3.79	241	Dihydroxy-3-isopropyl-5-methylphenyl- N-methylcarbamate	
3.85	208	Promecarb	
109	-	m-cresol	
3.9	-	Benzoquinone	
4.72	222	4-hydroxy-3-isopropyl-5-methylphenyl-methylene carbamate	
95	-	Phenol	
5.52	151	3-isopropyl-5-methylphenol	

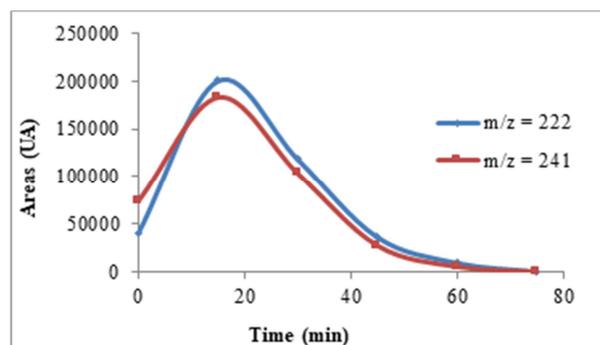
Degradation of Promecarb is accompanied simultaneously by the appearance of oxidation products from the first minutes of treatment. The identification of benzoquinone ($t_R = 3.9$) is carried out by HPLC by comparison with the retention time of the standard chemical compound, then t_R is the time from injection to detection. Different aromatic intermediates had appeared at these retention times: 3.79; 3.85; 3.9; 4.72 and 5.52 min. The evolution of some aromatic compounds during the electrolysis of Promecarb by electro Fenton process is given in Figure 6.

As it is shown in Figure 6, the aromatic intermediates of Promecarb were completely degraded after 80 min. They reach their maximum of concentration between 20 and 25 min with almost similar kinetics. Concentrations of these compounds were quickly decreased to zero. However, other by products were formed in small amounts.

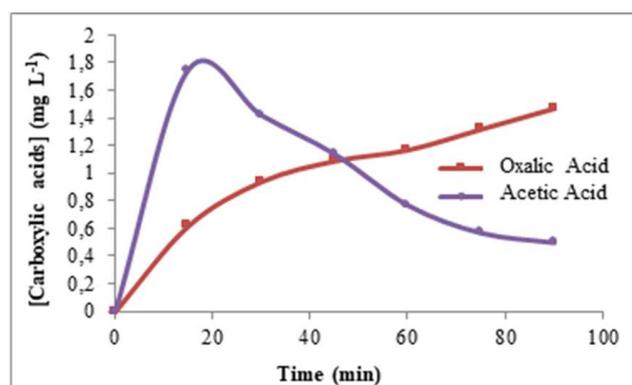
3.4.2. Evolution of Carboxylic Acids Derived from Electrolysis of Promecarb

Successive oxidation of aromatic molecules weakens chemical bonds. Addition of hydroxyl groups transformed them to other compounds as quinone form, and leads to oxidative degradation. Compounds emanating from the nucleus fragmenting are saturated and unsaturated hydrocarbons bearing carboxyl functional groups, aldehyde, ketone or alcohol [30, 31]. Therefore, we have tried in this study to identify qualitatively and quantitatively the carboxylic acids formed during the mineralization of Promecarb. Thus,

solutions of this insecticide treated at applied current $I = 800$ mA were analyzed by Ion Chromatography.

**Figure 6.** Evolution of some aromatic intermediates of Promecarb by LC/MS.

Carboxylic acids detected during the electrolysis of Promecarb have been quantified in mgL^{-1} . Acetic acid and oxalic acid that have been identified during the pesticide mineralization are shown in Figure 7. Their respective retention times are 5.8 and 19.8 min. These acids began to form almost simultaneously.

**Figure 7.** Evolution of carboxylic acids during mineralization of Promecarb by electro Fenton process.

From this figure, it appears that acetic and oxalic acids are not completely degraded after 90 min of treatment of Promecarb. This low degradation rate of the two acids is due primarily to their high stability in the presence of ferrous ions (Fe^{2+}) and secondly to their low reactivity with HO^{\cdot} radicals [32]. These results indicate that there are other species of the organic carbon present and have not yet been identified.

3.4.3. Detection of Nitrate Ions

Pesticide mineralization process involves the conversion of organic matter to carbon dioxide and inorganic ions from the presence of heteroatoms in starting molecule, such as nitrogen in Promecarb molecule. Furthermore, previous work [33, 34] have shown that the organic molecules containing nitrogen are mineralized with formation of NO_3^- . This reaction was verified in this work for the mineralization of Promecarb. Thus, the release of nitrate ions during the treatment of this molecule by electro Fenton process is determined by Ion Chromatography (Figure 8).

Attack of hydroxyl radicals on nitrogen atom is one way or another facilitated by amide group and leads to a high efficiency for the formation of nitrate ions. In addition to the release of nitrogen group in initial molecule of Promecarb, the formation of nitrate ions may also attribute to the oxidation of undetected ammonium ions. Under our experimental conditions, the concentration of nitrogen under nitrate form is reached steady state after 90 min of treatment and more than 58% of the initial nitrogen is converted.

3.4.4. Degradation Pathway of Promecarb

Identification of aromatic by products of degradation and analysis of released acids and nitrate ions, allows us to propose the mineralization mechanism of Promecarb. Two pathways were in accordance with the detected intermediates from electrolysis of the pesticide by electro Fenton process.

In this mechanism, two hypotheses are suggested in Figure 9 by attack of hydroxyl radicals on Promecarb with the presence of dioxygen O_2 :

In the first case (pathway 1): addition of a radical on aromatic ring leading to compound (2). Successive oxidations reactions allow to the hydroxylation of aromatic ring so the detection of compound (3), followed by the formation of intermediates (4) and (5) in the next steps. Furthermore, its conversion by known reactions to short chain carboxylic acids is also possible. This way of mineralization of Promecarb represented one of pathways of degradation of this insecticide carbamate by electro Fenton process. Then, Propham is a known carbamate pesticide was studied by electro Fenton and published elsewhere [35].

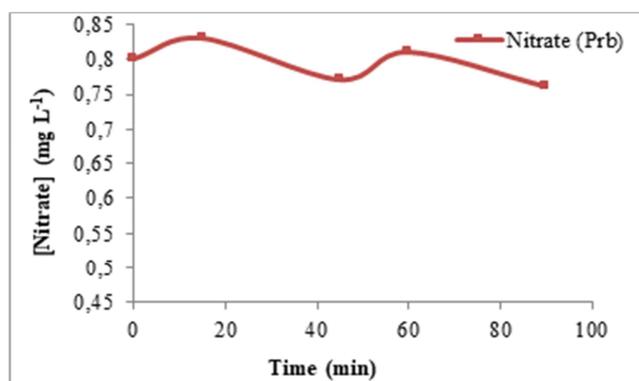


Figure 8. Detection of nitrate ions during treatment of Promecarb solutions by electro Fenton at 800 mA.

In the second case (pathway 2): oxidation and addition reaction on benzene ring leads to the formation of Promecarb radical which also reacts with molecular oxygen to produce $Ar(O_2)$. Oxidation of the latter had given then compounds (6) and (7). The next step involves an oxidative opening of the aromatic ring with the generation of carboxylic acids and nitrate ions. The proposed mechanism for degradation and mineralization of Promecarb has been added to results of other studies for carbamate pesticides degradation by advanced oxidation processes and in particular by electro Fenton process [36].

The main effect of rejection of degradable organic material

in the natural environment is the O_2 consumption that results. Estimation of biochemical oxygen demand therefore due to evaluate this phenomenon and to determine its effects. Almost all organic effluents, despite their different characteristics have biodegradability including reports of Chemical Oxygen Demand COD and Biochemical Oxygen Demand BOD_5 less than 3 on average [37, 38]. In this study, we realized the measurement of BOD_5 of Promecarb solution after treatment by electro Fenton process at two different applied current 800 mA and 1000 mA, to analyze its biodegradability. Two ratios COD/ BOD_5 of treated insecticide solutions by electrochemical process are the same for both applied currents and are equal to 0.6. In conclusion, Promecarb could be considered as biodegradable, and may follow up a biochemical treatment by activated sludge.

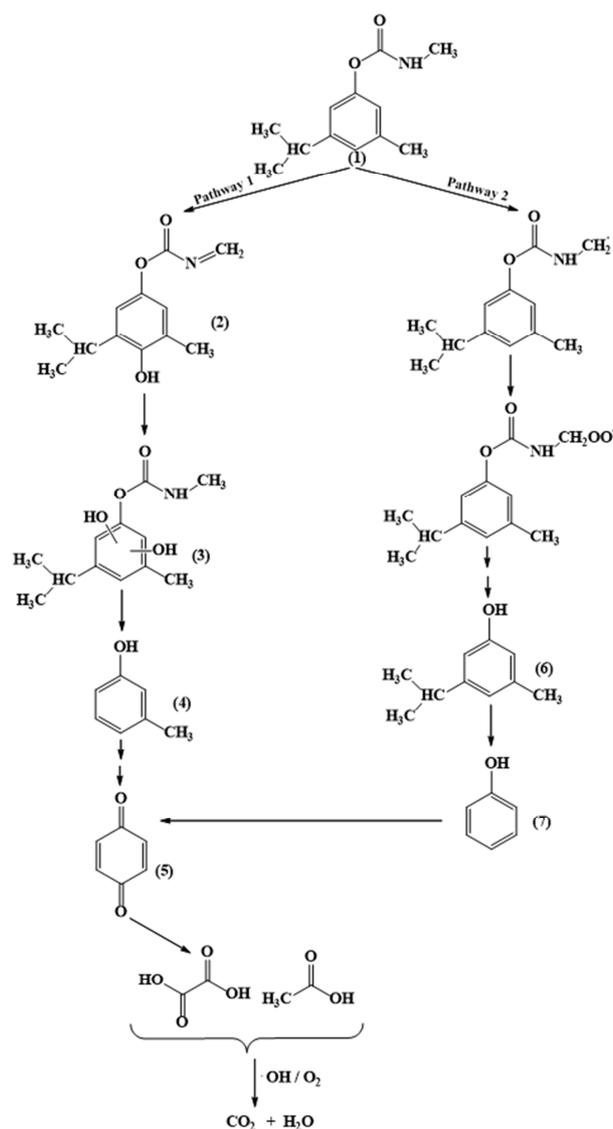


Figure 9. Mechanism of mineralization of Promecarb by electro Fenton process. 3.5. Biodegradation of Promecarb.

4. Conclusion

Mineralization of Promecarb (0.1 mM) is performed by

action of hydroxyl radicals formed by Fenton reaction from hydrogen peroxide electrochemically generated. Indeed, H₂O₂ production has been carried out in situ by production in an open electrochemical reactor from the reduction of molecular oxygen on volumic cathode consists of carbone graphite grains. The study of the insecticide solutions by electro Fenton process shows that the organic carbon abatement rate measured in terms of TOC increases with increasing of reaction time. Mineralization rate of Promecarb exceeded 50% at applied current intensity I = 800 mA, and during 3 hours of electrolysis. Then, kinetics of pesticide degradation is largely influenced by experimental parameters. An increase of current intensity causes an augmentation of speed of degradation up to a limit value of 1000 mA under conditions of operation of the electrolyser (flow, air bubbling...). It corresponds to a maximum production of hydrogen peroxide and hydroxide radicals. On the other hand, a higher initial concentration of the pesticide decreases the degradation kinetics because excess of organic molecules traps hydroxyl radicals. The absolute kinetic constant of $10.88 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is very high and shows a big reactivity of this insecticide in presence of hydroxyl radicals. Several aromatic by products of degradation of Promecarb were identified. They are derived mainly from oxidation of the N-terminal group of this carbamate followed by hydroxylation of aromatic ring with ultimately release of organic acids. Also, nitrate ions were quantified during its treatment by electro Fenton process. Total mineralization of Promecarb would require continuously other hours and to give its potential biodegradability. We had showed too that the ratio of biodegradability of treated promecarb solution is 0.6, which proved that this pesticide is biodegradable.

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