Degradation and Mineralization of Pesticide Isoprocarb by Electro Fenton Process

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ABSTRACT

Electro Fenton with volumic cathode consisting of granules of carbon graphite was applied to degrade the insecticide Isoprocarb in aqueous solutions. The effects of various factors including current intensity and pesticide initial concentration were investigated in order to obtain the best experimental conditions for its degradation and mineralization. Kinetic studies determined that the insecticide removal followed a pseudo first order. The absolute rate constant for the oxidation of Isoprocarb by hydroxyl radicals were determined as 3.32×10^9 L mol⁻¹s⁻¹ by competitive kinetics method taking benzoic acid as reference compound. In this work, we have also studied the mineralization of aqueous solutions of this insecticide in term of total organic carbon (TOC). After 3 hours of electrolysis, and at I = 800 mA, more than 40 % of the organic carbon presented in the solution is mineralized. Various aromatic by-products, principally formed by oxidation of the pesticide, accompanied by hydroxylation of the aromatic cycle, have been identified. Thus, the oxidative opening of the aromatic ring leads to the formation of carboxylic acids and nitrate ions. The biodegradability of Isoprocarb is estimated by the measurement of its Biochemical Oxygen Demand (BOD₅).

Keywords: Isoprocarb, electro Fenton, mineralization, hydroxyl radicals, oxidation.

INTRODUCTION

Pollution by organic pollutants, and especially by pesticides, is mainly perceived through their presence in different environmental compartments such as water [1] or in foodstuffs [2]. The reduction of their impact on aquatic environments requires monitoring of their behavior during their chemical or physical treatments. Isoprocarb or 2-isopropyl phenyl-N-methylcarbamate is considered as one of the most important carbamate pesticides [3,4]. This insecticide is used in the fight against a wide variety of defoliators that attack many fruit and vegetable crops by inhibiting acetyl cholinesterase [5]. Isoprocarb is used against various types of pests in the treatment of tropical and subtropical plants such as rice and cotton [6]. There are different methods developed for the destruction of organic pollutants in water. These technologies include Advanced Oxidation Processes (AOPs), which can use chemical [7], photochemical [8] or electro-chemical [9] methods. Recently, the application of the electro Fenton technology with iron heterogeneous catalysts has noticed by different research

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groups [10,11]. It is based on the action of very reactive hydroxyl radicals, which is electrochemically generated in situ. In this process, molecular oxygen O₂ reduced on the cathode continuously to generate hydrogen peroxide H_2O_2 (Eq. (1)). Thus, the addition of ferrous iron (Fe²⁺) catalyst, produces a powerful oxidant 'OH (Eq. (2)) [12,13].

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$$
(1)
$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$
(2)

During the treatment of the pollutant solutions by this method, it is possible to use different cathodes such as: sheet of mercury [14], modified graphite [15], carbon felt [16], or oxygen diffusion cathode [17]. In addition to pesticides [18-21], electro Fenton process has been efficiently applied to the treatment of other pollutants, including phenols [22,23], synthetic dyes [24-26], drugs [27,28] and wastewaters [29,30]. In the present work, we studied the degradation of Isoprocarb by electro Fenton process in volumic electrochemical reactor of 1.4 L, using the carbon graphite cathode.

EXPERIMENT

Chemicals

Isoprocarb (C₁₁H₁₅NO₂, 2-isopropyl phenyl-N-methylcarbamate, purity 99%) was purchased from Sigma-Aldrich. Sodium sulphate Na₂SO₄ (purity 99%) and Iron (II) sulphate pentahydrate FeSO₄.7H₂O (purity 99%) used as inert supporting electrolyte and catalyst respectively, were obtained from Across Organics. Benzoic acid was from Merck. Oxalic and acetic acids were purchased from Pro LABO and Across Organics respectively, and used without further purification. Acetonitrile (purity 99.9%) (HPLC grade) were supplied by Fisher Scientific. The initial pH of solutions was adjusted to 3 using analytical grade sulfuric acid H₂SO₄ (purity 95%) from Across. All solutions were prepared by utilizing ultra-pure water 18.2 M Ω cm (PURELAB).

Electrochemical reactor

The degradation of Isoprocarb (0.1 mM) by electro Fenton process was realized in an open electrochemical reactor with volumic cathode treating 1.4 Liter (PRIAM electrolyser). H_2O_2 is produced in volumic cathode, which consisting of carbon graphite granules contained in a cassette (14.2 cm × 10.9 cm). Two anodes are placed on either side of the cathode which is placed vertically to the reactor center and therefore perpendicular to the flow of the solution in the electrolyzer. The anode is a rectangular grid of titanium coated with ruthenium dioxide (DSA). DC power supply G INSTEK, model GPS - 303000 operates in galvanostatic mode to control the current intensity at a value of 3 A. The ionic strength was maintained constant by adding Na₂SO₄ (0.05 M). A peristaltic pump (flow rate of 460 L h⁻¹) is used for the circulation of the electrolytic solution.

HPLC and LC-MS analysis

Isoprocarb degradation and its by-products were followed by High Performance Liquid Chromatography (HPLC) with Diode Array Detection (DAD) and Ultra High Pressure Liquid Chromatography using an Acquity UHPLC - Waters. For these analyzes, 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 μ m × 100 mm and Reversed phase Symmetry 5- μ m, 4.6 × 250 mm columns were applied in UHPLC-MS/MS and HPLC experiments, respectively. Five and fifty microliters of pesticide samples were injected. The chromatographic separation was achieved by columns *as* described above, using a mobile phase of 50% water and 50% 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 carried out at 210 nm.

Ion Chromatography (IC)

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

Total Organic Carbon (TOC) analysis

A Shimadzu TOC - V_{CPH} analyzer was used to determine the TOC of the electrolyzed samples of Isoprocarb. The detector of the TOC system was a Non-Dispersive Infra-Red detector (NDIR). For total carbon (TC) and inorganic carbon (IC), adjustment of analyzer was achieved 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 sample.

Biochemical Oxygen Demand (BOD5)

In order to measure the amount of biodegradable organic matter contained in a solution of electrochemically treated Isoprocarb, we used Biochemical Oxygen Demand for five days, or BOD₅. Activated Sludge utilized in this study was collected from a local wastewater treatment plant in Rennes. Minerals were doped in the medium as highly concentrated solutions to attain the following initial composition (g L⁻¹): CaCl₂ (27.5), MgSO₄.7H₂O (22.5), Na₂HPO₄ (6.8), KH₂PO₄ (2.8), FeCl₃ (0.15) and NH₄Cl (2.00). The initial pH was adjusted to 7.

RESULT AND DISCUSSION

Influence of experimental conditions on Isoprocarb degradation Initial concentration of insecticide

In order to study the effect of concentration of the pesticide on the degradation process, electrochemical treatment is carried out on Isoprocarb solutions of two different concentrations 0.1 mM and 0.53 mM in acid medium, at pH = 3, at a current intensity of 500 mA, for 90 minutes and at room temperature. This study was realized in presence of a carrier electrolyte Na₂SO₄ (50 mM). Figure 1 gives the following result curves.

These curves show that the degradation time of Isopracarb increases with increasing of initial concentration of the organic pollutant. In these experiments, the intensity of current is kept constant at 500 mA, which involves the same rate of production of H_2O_2 for the reduction of oxygen. Increasing the concentration of Isoprocarb makes the number of

pesticide molecules in the solution more important for the same number of hydroxyl radicals, which leads to a decrease in the rate of degradation.



Figure 1. Degradation of Isoprocarb by electro Fenton process at different concentrations and at a current intensity I = 500 mA.

Intensity of applied current

For determine the efficiency of the electro Fenton process under different values of an experimental parameter, such as the applied current intensity, the insecticide degradation rate was investigated. Different solutions of equal concentrations of this pollutant (0.1 mM) were electrolyzed at different current intensities ranging from 100 to 800 mA. Figure 2 shows the monitoring of the concentration of Isoprocarb.



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

The plot of log (C_0/C_t) versus time (Figure 3) indicates a linear variation suggesting pseudo-first order kinetics with apparent rate constants more important for an imposed current of 800 mA. By increasing the intensity of the current applied between the cathode and the anode, it is noted that the kinetics of degradation are higher. This augmentation leads to the

improvement of the rate of hydroxyl radical formation and consequently the rate of degradation of the insecticide. 800 mA is the optimum current with the used electrolyser. Apparent kinetic constants are calculated by linear regressions of the pseudo-first order kinetic model with correlation coefficients superior than or equal to 0.99. These constants are 0.05, 0.07 and 0.1 min⁻¹ for the respective current intensities 100, 500 and 800 mA.



Figure 3. Kinetic analysis of the degradation reaction of Isoprocarb (0.1 mM) by the electro Fenton process at current intensities: 100, 500 and 800 mA, $[Na_2SO_4] = 50$ mM, $[Fe^{2+}] = 0.5$ mM.

Absolute rate constant of Isoprocarb by hydroxyl radicals

Under other experimental conditions, the rate of the hydroxyl radicals ('OH) production is electrochemically controlled and can be considered to be practically constant. As it is a very reactive species, not accumulative in the reaction medium and has a very short life (of the order of a few nanoseconds) [31]. Therefore, the hydroxylation reaction of the carbamate insecticide can be assimilated to first-order pseudo kinetics.

 $Isp + OH \longrightarrow Oxidation products$

Tracing of the curve Ln ([Isp]₀ / [Isp]_t) versus time of electrolysis allows to determine the apparent rate constant of the oxidation reaction of Isoprocarb by hydroxyl radicals. The Isp absolute rate constant can be evaluated by the reaction of benzoic acid (BA) with 'OH as a standard, and by investigating the competitive kinetic of BA and Isp under standard experimental conditions. The absolute rate constant of benzoic acid with hydroxyl radicals is well known, $k_{abs} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [32]. The absolute kinetic constant is thus deduced from the curve Ln ([Isp]₀ / [Isp]_t) in function of Ln ([AB]₀ / [AB]_t). An equimolar mixture (0.1 mM) of Isoprocarb and benzoic acid is electrolyzed by the electro Fenton process and the evolution of their concentrations is measured by HPLC at $\lambda = 210$ nm. The obtained results are shown in Figure 4. A $3.32 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is the value of the absolute kinetic constant of the reaction of hydroxyl radicals on Isoprocarb. This value is in orders of magnitude of kinetic constants obtained for reactions between aromatic compounds and hydroxyl radicals [33,34].



Figure 4. Determination of absolute constant of Isoprocarb oxidation by 'OH, $[Na_2SO_4] = 50 \text{ mM}$, $[Fe^{3+}] = 0.5 \text{ mM}$, pH = 3, [Isp] = 0.1 mM, [BA] = 0.1 mM.

Mineralization of Isoprocarb

Mineralization is the decomposition of organic matter by various processes such as the advanced oxidation process. This is an important decomposition for the liberation of substances in organic form to a mineral form. Analysis of Total Organic Carbon (TOC) is carried out during the electrolysis of Isoprocarb at different current intensities. This measure allows to highlight the effectiveness of mineralization by the electro Fenton process.



Figure 5. Isoprocarb mineralization (0.1 mM) during electro Fenton process in terms of TOC at current intensities of 100, 500 and 800 mA, $[Fe^{2+}] = 0.5$ mM.

Electrolysis of initial solutions of the insecticide is accompanied by a progressive decrease in TOC measurement versus time, thus the progression of the mineralization. Figure 5 shows the evolution of TOC values in function of time for the electrolysed insecticide. TOC value of the treated Isoprocarb solution decreases regularly and with faster kinetics at the beginning of electrolysis. According to these results, we notice that the applied current at 800 mA is the best value for partial mineralization under the experimental conditions. Percentages of mineralization are 20%, 25% and 31% at current intensities of 100, 500 and 800 mA respectively, for an electrolysis time of about 90 minutes. Thus, by increasing treatment time, the percentage of Isoprocarb mineralization is superior during 3 hours.

It is interesting to note that at a current value I = 800 mA and during 3 hours of electrolysis, the percentage of mineralization of Isoprocarb exceeded 40%. Thus, the degradation of isoprocarb leads to intermediate aromatic compounds which are mineralized.

Table 1. Molecular structures of cyclic intermediates generated during the electrolysis

 Isoprocarb.

t_{R} (min)	m/z	Intermediate	Chemical structure
3.13	167	Hydroxyphenyl N-methylcarbamate	$\mathbf{H}_{3}\mathbf{C}-\mathbf{H}\mathbf{N}-\mathbf{C}-\mathbf{O}$
			ОН
3.9	-	Benzoquinone	o=
4.2	210	Hydroxy-2-isopropylphenyl N-methyl carbamate	$H_{3}C-HN-C-O$ CH_{3} $CH_{CH_{3}}$
	111	Dihydroxyphenyl	ОН
4.44	180	2-Isopropylphenyl carbamate	
	137.9	2-Isopropylphenol	OH CH CH ₃ CH ₃
4.91	194	Isoprocarb	$ \begin{array}{c} & & \\ & & $
	95	Phenol	СН3

Analysis of Isoprocarb insecticide degradation products Determination of aromatic intermediates

Organic compounds degraded by the electro Fenton process can contribute to water and soil pollution and pose real environmental problems. Therefore, the identification and

monitoring of these reaction intermediates of oxidative degradation are necessary. In this part, we have tried to identify the aromatic products generated during the electrolysis of Isoprocarb by electro Fenton process. A solution of Isoprocarb (0.53 mM) is electrolyzed at a constant current intensity of 500 mA. We carried out the identification of by-products of Isoprocarb oxidation reaction by hydroxyl radicals using coupling LC-MS.

Molecular structures of detected organic products are summarized in Table 1. The degradation of Isoprocarb is accompanied by the appearance of oxidation products, at the first minutes of treatment. The identification of benzo- quinone ($t_R = 3.9$) is performed by HPLC. The other aromatic intermediates appear at retention times t_R of 3.13, 4.2, 4.44 and 4.91 min. The appearance and disappearance of these intermediates during the electrolysis of Isoprocarb by electro Fenton process are shown in Figure 6.

The analysis of this figure proves that the degradation compounds of Isoprocarb begin to form at the beginning of the electrolysis. They reach their maximum concentration almost between 30 and 40 min without the similar kinetics.



Figure 6. Evolution of aromatic intermediates of Isoprocarb (0.53 mM) during oxidation by electro Fenton process, $[Fe^{2+}] = 0.5$ mM, pH = 3.

Identification of carboxylic acids

The successive oxidation of the aromatic molecules leads to its rupture. The compounds involving the nucleus fragmentation are saturated hydrocarbons and unsaturated with carboxyl, aldehyde, ketone or alcohol functional groups [35]. In consequence, we tried in this study to identify qualitatively and quantitatively the carboxylic acids that are formed during the mineralization of Isoprocarb. Thus, the solutions of Isoprocarb treated at 800 mA were analyzed by ion chromatography using a column (Ion Pac AS 19) (4 μ m, 25 cm). Carboxylic acids detected during the degradation of Isoprocarb are Acetic acid (t_R = 5.8 min) and oxalic acid (t_R = 19.8 min). Acetic acid and oxalic acid that were identified during the mineralization of Isoprocarb are shown in Figure 7. As it shows this figure, acetic acid and oxalic acid are formed since the beginning of Isoprocarb electrolysis, they reach their maximum of concentrations approximately between 45 and 90 min with a kinetics not similar. It is obvious that the concentration of oxalic acid is low compared to the other acid.



Figure 7. Evolution of carboxylic acids during the mineralization of Isoprocarb by electro Fenton process, pH = 3, [Na₂SO₄] = 0.5 mM, I = 800 mA.

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Evolution of nitrate ions

The process of mineralization of pesticides involves also the conversion of organic matter into inorganic ions because of the presence of heteroatoms in the starting molecule such as nitrogen in the case of Isoprocarb. On the other hand, the organic molecules containing nitrogen are mineralized with the formation of NH_4^+ and or NO_3^- [36]. Thus, the detection of nitrate ions during electro Fenton treatment is determined by ion chromatography (Figure 8). After 45 minutes of electrolysis, the concentration of nitrate ions reaches a value of 0.88 mg L⁻¹. The total quantity of nitrogen at the end of the mineralization is equal to 0.8 mg L⁻¹. It represents almost 20% of the theoretical total nitrogen. Therefore, the nitrogen atom of the molecule of Isoprocarb is susceptible to be converted to NO_3^- .



Figure 8. Evolution of nitrate ions during electro Fenton treatment of aqueous solutions of Isoprocarb at I = 800 mA, $[Fe^{2+}] = 0.5$ mM, pH = 3.

Isoprocarb degradation pathway

The identification of aromatic intermediates, carboxylic acids and mineral compounds formed during the mineralization reaction, and its evolution versus time during treatment of aqueous solutions, allows us to propose a mechanism of mineralization of Isoprocarb by electro Fenton process. A plausible reaction mechanism in agreement with the detected intermediates has been proposed in Figure 9.

Two hypotheses are suggested by attacking hydroxyl radicals in the presence of O_2 on Isoprocarb. In the first case (pathway 1), the mineralization began with the formation of hydroxyisoprocarb. Additional reactions of these intermediates with 'OH led to the formation of benzoquinone. And then, the decarboxylation of carboxylic acids takes place to eliminate carbon dioxide. In the second case (pathway 2), oxidation by addition to the benzene molecule leads to the formation of the radical Isoprocarb Ar' which then reacts with molecular oxygen to produce Ar (O_2)'. The other steps of oxidation resulted in the formation of 2-isopropylphenol and then phenol. The next step involves an oxidative opening of the aromatic cycle with the generation of carboxylic acids.

Biodegradation of electrolyzed pesticide solution

Degradation of organic matter by micro-organisms defines biodegradation. So, a material is said to be biodegradable when it can undergo biodegradation. Thus, the determination of the biodegradation capacity of a molecule requires well-defined measurements. In this study, the degradation and mineralization of Isoprocarb (0.1 mM) were studied by the electro Fenton process at different current intensities. To evaluate the biodegradability of Isoprocarb solution, the measurement of its Biochemical Oxygen Demand (BOD₅) was realized after 3 hours of treatment by electro Fenton process and at applied current of 800 mA. The measured reports COD/BOD₅ of treated pesticide solution by the electrochemical process is equal to 3.2. This experimental value shows that Isoprocarb insecticide could be considered as biodegradable.



Figure 9. Mechanism of Isoprocarb mineralization in aqueous solution, in presence of oxygen by hydroxyl radicals generated by electro Fenton process.

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CONCLUSION

The obtained results during this study show that the kinetics of the degradation of Isoprocarb insecticide by electro Fenton process is pseudo first order. Absolute rate constant of the reaction of hydroxyl radicals on Isoprocarb carbamate measured by the method of competitive kinetics is high and it equal to 3.32×10^9 M⁻¹ s⁻¹. This value of rate constant indicates that the carbamate insecticide is highly reactive with hydroxyl radicals. Also, the degradation and the mineralization of Isoprocarb depended on experimental conditions. Indeed, the augmentation of initial concentration of insecticide decreases kinetics of the degradation. While, increasing the electrolysis current causes an increase of the degradation rate. In addition, the study of the mineralization of the insecticide has shown that TOC decreases regularly depending on the time, and that the progress of mineralization exceeds 40% for Isoprocarb, for treatment duration of 3 hours. Also, we have identified several aromatic by products, carboxylic acids and miral ion issued from the oxidation of Isoprocarb and then the proposition of mechanism of Isoprocarb mineralization. The determination of biodegradation factor BOD₅ proves that Isoprocarb is biodegradable.

CONFLICT OF INTEREST

authors declare there is no any conflict of interest.

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