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Nihal Oturan, Mehmet A. Oturan. Degradation of three pesticides used in viticulture by electrogenerated Fenton's reagent. Agronomy for Sustainable Development, 2005, 25 (2), pp.267-270. hal-00886267

HAL Id: hal-00886267
https://hal.science/hal-00886267

Submitted on 11 May 2020

Agron. Sustain. Dev. 25 (2005) 267–270
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DOI: 10.1051/agro:2005005

Research article

Degradation of three pesticides used in viticulture by electrogenerated Fenton's reagent

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(Accepted 1 March 2004)

Abstract – The degradation of three pesticides: Mistel GD (Cymoxanil + Mancozeb + additives), Cuprofix CZ (Cymoxanil + Zineb + $CuSO_4$ + additives) and Lannate 20L (Metomyl + ethanol + other additives) (Fig. 1), used in viticulture and marketed by various companies, was studied by the Electro-Fenton process. The Fenton's reagent, generated in situ by electrochemistry in a catalytic way, leads to the production of hydroxyl radicals which are very powerful oxidizing agents. These radicals react with organic pollutants and thus lead to their degradation. Each pesticide contains many active ingredients and additives. The treated solutions were followed by HPLC (High Performance Liquid Chromatography) analysis. The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the mineralization efficiency. The degradation efficiency was measured for the pesticides under examination using electrogenerated Fenton's reagent. The effects of catalyst nature and concentration on the degradation and the mineralization rates were studied.

Electro-Fenton / Fenton's reagent / hydroxyl radicals / pesticide / mineralization

1. INTRODUCTION

An increasing number of studies have been recently published dealing with the degradation of toxic, non-biodegradable and refractory organic pollutants in water using indirect electro-oxidation methods such as the Electro-Fenton process (Aaron and Oturan, 2001; Boye et al., 2002; Brillas et al., 1995, 2002; Gozmen et al., 2003; Guivarch et al., 2003; Harrington et al., 1999; Oturan, 2000; Oturan et al., 1999, 2000, 2001; Pons de Leon and Pletcher, 1995). This process is based on the electrogeneration of hydroxyl radicals $^{\bullet}OH$, which is a non-selective, very powerful oxidizing agent. In such treatment, hydroxyl radicals are continuously supplied to the contaminated solution from in situ electrochemically generated Fenton's reagent ($H_2O_2 + Fe^{2+}$). Catalytic iron(III) salt is initially introduced to the solution and H_2O_2 is generated at the cathode by two-electron reduction of oxygen gas from compressed air:

$$O_2\,(g) + 2H^+ + 2e^- \longrightarrow H_2O_2 \qquad (1)$$

At the reduction potential of oxygen gas, the ferric ion, which is dominantly presented under $Fe(OH)^{2+}$ form in acidic medium (pH = 3), is simultaneously reduced to ferrous ion:

$$Fe(OH)^{2+} + e^- \longrightarrow Fe^{2+} + OH^- \qquad (2)$$

H_2O_2 and Fe^{2+} formed at the cathode surface migrate into the bulk of the solution and the homogeneous Fenton reaction takes place:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(OH)^{2+} + {}^{\bullet}\mathbf{OH} \qquad (3)$$

The ferrous ions needed for reaction 3 are supplied in a catalytical way by reaction 2. Thus reaction 3 continuously supplies hydroxyl radicals to the treated solution. In the case of a Pt anode, the main anodic reaction is water oxidation (Comninellis et al., 1993; Tahar and Savall, 1998):

$$H_2O \longrightarrow {}^{\bullet}\mathbf{OH}_{ads} + H^+ + e^- \qquad (4)$$

Organic pollutants present in the solution can be efficiently degraded by reaction with $^{\bullet}OH$ radicals in solution (reaction 3) and/or at the surface of a Pt anode (reaction 4) yielding hydroxylated (reaction 5) or dehydrogenated (reaction 6) intermediates. Initial rate constants are about 10^8–10^{10} $M^{-1}\,s^{-1}$ for addition reactions and 10^6–10^8 $M^{-1}\,s^{-1}$ for hydrogen atom abstraction reactions (Buxton et al., 1988). By addition of molecular oxygen these intermediates yield peroxyl radicals, which in turn initiate chain reactions of oxidative degradation, leading finally to CO_2, H_2O and inorganic ions (Oturan, 2000).

$$R + {}^{\bullet}OH \longrightarrow ROH^{\bullet} \qquad (5)$$

$$RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O \qquad (6)$$

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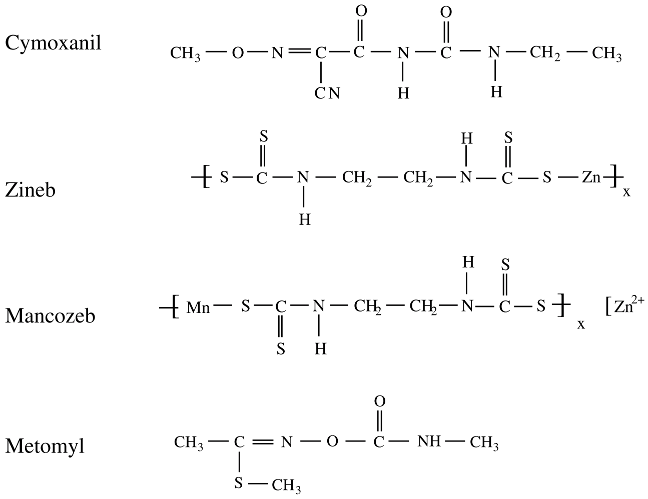

Figure 1. Developed chemical formula of active ingredients of pesticides under study.

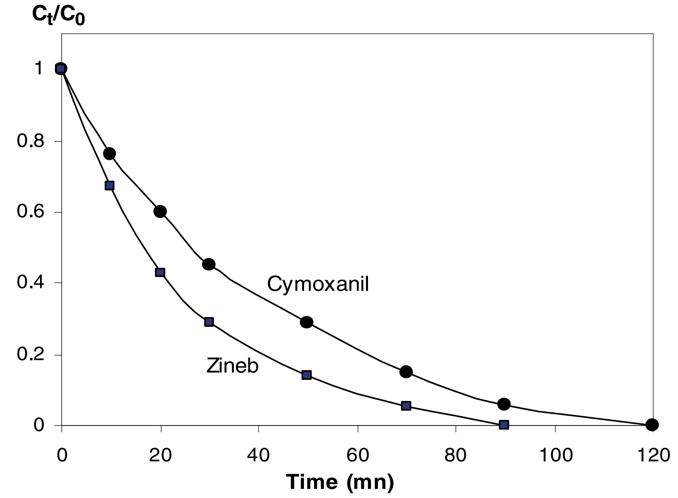

Figure 2. Time-course of Cymoxanil (C_0= 1.7 × 10^{-4} mol·L^{-1}) and Zineb (C_0= 0.7 × 10^{-4} mol·L^{-1}) in Cuprofix CZ during degradation by the Electro-Fenton process (I = 100 mA, pH = 3) at room temperature without addition of a catalyst. Cu^{2+} ions present as $CuSO_4$ in Cuprofix CZ solution at a concentration of 4.25 g Cu/L ($[Cu^{2+}]$ = 0.125 mol·L^{-1}) act as a catalyst.

We have already applied the Electro-Fenton process successfully to the total mineralization of different organic pollutants (Gozmen et al., 2003; Guivarch et al., 2003; Oturan et al., 1999, 2000, 2001). In this study we applied this process to degrading three pesticides used in viticulture. The evolution of each initial active molecule and its aromatic derivatives was followed by high performance liquid chromatography (HPLC) analysis. The effect of different catalysts on the degradation rate was studied. The decay of organic matter in the solution is followed by chemical oxygen demand (COD) measurements during Electro-Fenton processing. The COD values permitted the evaluation of the mineralization efficiency versus electrical charge passed for two different catalysts.

2. MATERIELS AND METHODS

The pesticides Mistel GD (Cymoxanil + Mancozeb + additives), Cuprofix CZ (Cymoxanil + Zineb + $CuSO_4$ + additives) and Lannate 20L (Metomyl + ethanol + other additives) were obtained from ITV (Centre Technique Interprofessionnel de la Vigne et du Vin). Mistel GD and Cuprofix CZ were solid (powder), Lannate 20L was liquid. Standard reagents (Fig. 1): Cymoxanil $C_7H_{10}N_4O_3$ (1-(2-cyano-2-methoxyimunoacetyl)-3-ethylurea), Zineb $(C_4H_6N_2S_4Zn)_x$ ([1,2 ethanediylbis [carbamodithioato]-(2-)] zinc), Mancozeb $(C_4H_6MnN_2S_4)_x(Zn)_y$ ([[1,2 ethanediylbis [carbamodithioato]]-(2-)] manganese mixture with [[1,2 ethanediylbis [carbamodithioato]]-(2-)] zinc) and Metomyl $C_5H_{10}N_2O_2S$ (S-methyl–[(methylcarbomyl) oxy] thioacetimidate) were purchased from Riedel-deHaën. Aqueous solutions were prepared with ultrapure water from the Millipore simplicity system.

Electrochemical treatments were carried out with an EG&G Princeton Applied Research 273A Potentiostat/Galvanostat. Electrolyses were performed in a non-divided electrochemical cell equipped with a Pt anode and a carbon felt cathode (Carbone-Lorrain). The volume of the electrochemical cell was 150 cm^3. Compressed air was bubbled through the solution prior to electrolysis. Samples were degraded under current-controlled electrolysis conditions (I = 60–300 mA). The pH of solutions was maintained in the range of 3–4 by addition of sulfuric acid. Electro-Fenton treatment was carried out in the presence of a ferric or cupric salt as catalyst. Predetermined amounts of aliquots were withdrawn at certain time intervals or at certain coulombic charges passed. These aliquots were followed by HPLC or COD analyses.

The evolution of parent molecules and their derivatives formed during processing was followed by a Merck Lachrom HPLC-DAD liquid chromatograph, fitted with a Purospher RP-18, 5-µm, 4.6 × 250 mm column (Merck). Detection was conducted at λ = 240 nm for Mistel GD and Cuprofix CZ and λ = 230 nm for Lannate 20L. The mobile phase was a mixture of acetonitrile and water with a flow rate of 0.7 mL/min in both cases. A gradient program (CH_3CN %: 0, 30, 30, 0 v/v at respectively 0, 15, 25 and 30 min) was applied in the case of Mistel GD and Cuprofix CZ. Chromatograms of Lannate 20L were performed in isocratic mode with a mobile phase composition as follows: H_2O/CH_3CN: 80/20 v/v.

The mineralization of pesticide solutions was monitored by the decay of their COD (Chemical Oxygen Demand) removal values using the AFNOR NFT-90-101 method (AFNOR, 1990).

3. RESULTS AND DISCUSSION

3.1. Degradation kinetics

Degradation of pesticide solutions was carried out in aqueous solution in current-controlled electrolysis conditions by application of a constant current of 100 mA. The disappearance of active species was followed by reverse phase liquid chromatography where they exhibited well-defined peaks. The evolution of active ingredient concentrations of Cuprofix CZ (Cymoxanil + Zineb + $CuSO_4$) with electrolysis time during the treatment is presented in Figure 2. The particularity of this trial is that it was carried out without any addition of a catalyst. The $CuSO_4$ (4.25 g/L) present in the Cuprofix CZ formulation acts as a catalyst. An important advantage of using Cu^{2+} ions as a substitute for Fe^{3+} ions in the Electro-Fenton process lies in easy electrochemical recuperation of this ion after treatment and reuse of it for the next trials.

The degradation of active molecules exhibits an exponential decrease with electrolysis time according to a pseudo-first-order kinetic. The disappearance of both Cymoxanil and Zineb was very fast, with a significant degradation rate for Cymoxanil. For example, the complete destruction of Zineb (C_0 = 0.07 mM) and Cymoxanil (C_0 = 0.17 mM) needed, respectively, 90 and 120 minutes. It should be noted that organic additives present in the Cuprofix CZ matrix also consume the $^{\bullet}OH$ radicals and decrease the degradation rate of active molecules.

Figure 3 shows the evolution of Cymoxanil and Mancozeb normalized concentrations (C_t/C_0) in Mistel GD with electrolysis time. The total disappearance of Cymoxanil took place at 90 minutes, in a shorter time than that of Cuprofix CZ, in spite of a more significant initial concentration (C_0 = 0.22 mM), which indicates that the matrix of Mistel GD is less reactive with the $^{\bullet}OH$ radicals than that of Cuprofix CZ. On the other hand, the degradation rates of Cymoxanil and Mancozeb were slightly better when electrolysis was performed in the presence of Cu^{2+} ions as a catalyst instead of Fe^{3+} ions. Similar results can be observed in the literature (Gozmen et al., 2003; Walling and Kato, 1971; Walling and Goosen, 1973).

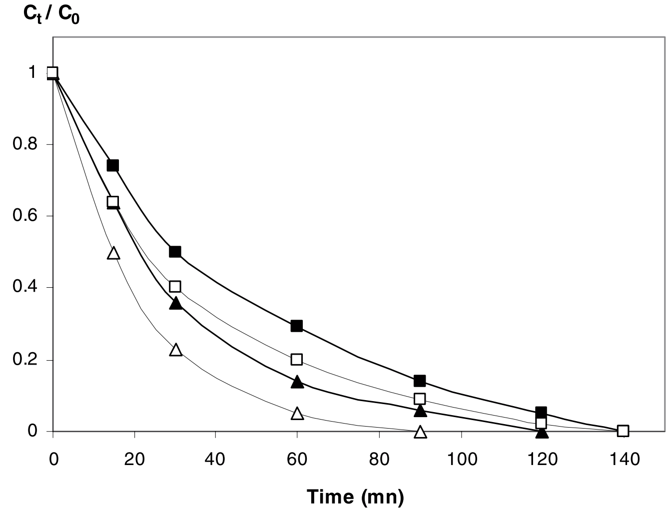

Figure 3. Effect of the catalyst on the degradation kinetics of Cymoxanil (C_0= 2.2 × 10^{-4} mol·L^{-1}, ▲: Fe^{3+}, △: Cu^{2+}) and Mancozeb (C_0= 4.2 × 10^{-4} mol·L^{-1}, ■: Fe^{3+}, ❑: Cu^{2+}) in aqueous Mistel GD solution during Electro-Fenton processing (I = 100 mA, pH = 3, [catalyst]: 10^{-3} mol·L^{-1}) at room temperature. Degradation kinetics are faster in the presence of Cu^{2+} as a catalyst.

Lannate 20L exhibited similar degradation behavior. In all cases, the kinetic curves are characterized by a relatively rapid and regular decrease in the active molecule concentration during electrolysis.

3.2. Mineralization efficiency

Mineralization of the treated pesticide solutions during Electro-Fenton treatment was followed by measuring the chemical oxygen demand (COD) values to evaluate the organic carbon content of these solutions. Electrolysis was performed at I = 300 mA for 5.5 h (6000 coulombs) for the Mistel GD solution. In the case of Cuprofix CZ and Lannate 20L, electrolyses were achieved at 10 000 coulombs by applying a current of 350 mA (electrolysis time = 8 h). Figure 4 shows the mineralization kinetics in terms of COD for Mistel GD (Cymoxanil + Mancozeb + additives) and Lannate 20L (Metomyl + ethanol + additives) in function of coulombic charge passed during electrolysis. A similar trend was observed for Cuprofix CZ.

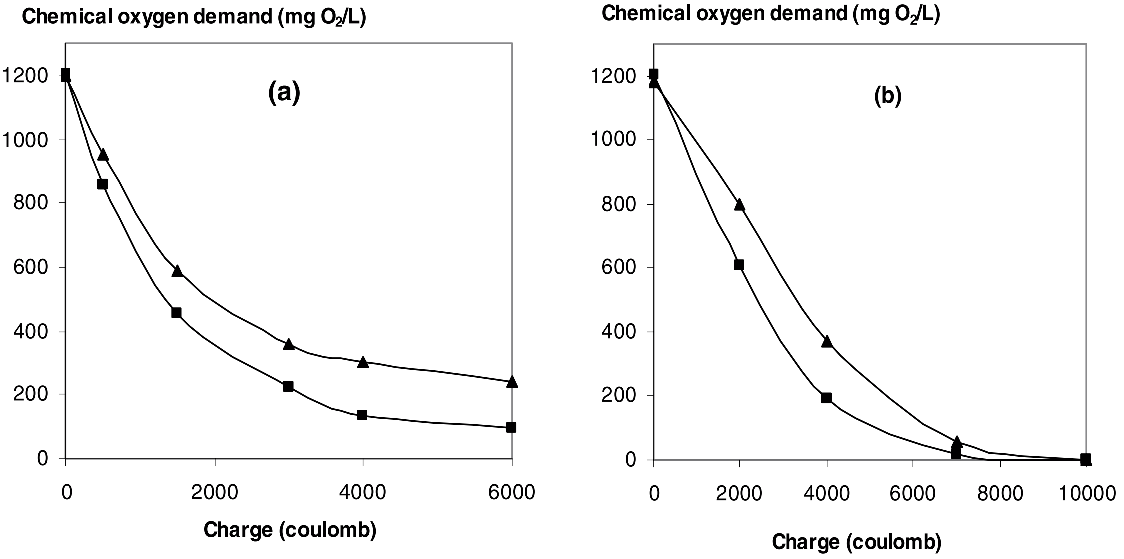

Figure 4. Chemical oxygen demand (COD) removal with electrical charge consumed during constant current electrolysis (I = 300 mA) for Mistel GD (a) and Lannate 20L (b) in the presence of Fe^{3+} (■, 1 mM) and Cu^{2+} (▲, 1 mM) as catalysts. For the same initial concentration, mineralization efficiency is better when Fe^{3+} is used as a catalyst.

These results indicate a fast COD decay and consequently, a high oxidative ability of the Electro-Fenton process, since the solution COD is rapidly reduced by 92% and 80%, respectively, in the presence of Fe^{3+} and Cu^{2+} as catalysts at 6000 coulombs for Mistel GD (Fig. 4a). HPLC analyses indicate that the parent active molecules and all aromatic intermediates were degraded after 1 hour of treatment. This degradation leads to aliphatic compounds formed by ring opening reactions due to the oxidative reaction of hydroxyl radicals on aromatics (Boye et al., 2002; Oturan, 2000; Oturan et al., 2000, 2001). Because the medium is strongly oxidant, aliphatic compounds are oxidized to corresponding acids, oxalic acid being the final intermediate before mineralization.

In the case of Lannate 20 L, electrolyses were conducted until complete mineralization of the aqueous solution (Fig. 4b). As can be seen in Figure 4, in all cases the most efficient mineralization was obtained when Fe^{3+} ions were utilized as a catalyst contrary to degradation kinetic behavior. This behavior can be explained by the decrease in Cu^{2+} concentration during electrolysis. Cu^{2+} ions are probably reduced by organic radicals formed by reactions 5 and 6 to metallic Cu which is deposited on the cathode.

The rapid and continuous COD removal during the first three hours of Electro-Fenton treatment can be explained by the high mineralization rate of the organic compounds with unsaturated bonds with the great amounts of hydroxyl radicals supplied by reactions 3 and 4. The mineralization rate becomes much slower over longer times because oxalic acid forms stable complexes with ferric iron, which reacts very weakly with hydroxyl radicals (Boye et al., 2002; Oturan et al., 2000).

4. CONCLUSION

We showed that the Electro-Fenton process is efficient for degradation of the three pesticides under examination: Mistel GD, Cuprofix CZ and Lannate 20 L. The complete degradation of active ingredients was observed in less than 120 minutes in all cases. Not only the active ingredients, but also the additives of the formulations were quickly mineralized. Chemical oxygen demand measurements indicated an efficient abatement of organic carbon in all cases.

As we observed in the case of the Cuprofix CZ, when the initial pesticide contains a metal ion which belongs to a redox couple such as Cu^{2+}/Cu^{+}, Co^{3+}/Co^{2+} or Ag^{2+}/Ag^{+}, the Elecro-Fenton process does not require the addition of a catalyst. The use of Cu^{2+} as a catalyst has the advantage of being able to recover it by electrolysis after treatment for reuse. However, the mineralization yields were found to be better when Fe^{3+} was used as a catalyst. The hydroxyl radicals being a non-selective oxidizing agent, the Electro-Fenton process can be generalized for the treatment of wastewater polluted by any organic pollutants or phytosanitary products.

Acknowledgements: The authors thank ITV-France and Christophe Alliot to provide the pesticide formulations.

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