



Electrochemical degradation of difenoconazole on BDD electrodes

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ABSTRACT

The electrochemical oxidation of fungicide difenoconazole (*Cis-trans-3-chloro-4-[4-methyl-2-(1H-1,2,4-triazol-1-ylmethyl)-1,3-dioxlan-2-yl]phenyl 4-chlorophenylether*), one kind of triazole fungicides is potentially dangerous and biorefractory, was studied by galvanostatic electrolysis using boron-doped diamond (BDD) as anode. The influence of several operating parameters, such as applied current density, initial difenoconazole concentration, temperature, supporting electrolyte, and initial pH value, was investigated. GC and chemical oxygen demand measurements were conducted to study the reaction kinetics of pesticide mineralization. The experimental results showed that the electrochemical process was suitable for almost completely removing COD, due to the production of hydroxyl radicals on the diamond surface. In particular, the COD removal follows a pseudo first-order kinetics and the apparent rate constant increased with current density and supporting electrolyte NaCl, while it is almost unaffected by temperature, and pH. Under optimal experimental conditions of temperature ($T=25\text{ }^{\circ}\text{C}$) and current density (i.e. 80 mA/cm^2), 73% of COD was removed in 3 h electrolysis.

Keywords: Electrochemical oxidation, boron-doped diamond, Triazole pesticide, fungicides, Reaction kinetics.

INTRODUCTION

The intensive use of pesticides in agriculture and the improper storage or disposal of obsolete pesticides are a source of contamination of soil, ground water, rivers, lakes, rainwater and air. Various innovative technologies have been proposed for the removal of pesticides from water. Among these technologies, the electrochemical processes constitute the emergent methods for the degradation of pesticides. This environmentally friendly technique is based on the generation of adsorbed hydroxyl radical (OH^{\bullet}) at the surface of a high O_2 -overvoltage anode such as boron-doped diamond (BDD) from oxidation of water in acid and neutral media [1-3].

In anodic oxidation, organic pollutants are directly destroyed by reaction with hydroxyl radical (HO^{\bullet}) formed at the anode surface from water oxidation [4-6]:



Several anode materials such as Pt [7-11], SnO_2 [12,15], PbO_2 [16,17] and BDD [18-21] have been used for pesticides removal. Recently, boron-doped diamond (BDD) thin film coating on a p-Silicon substrate becomes a

new electrode material, which has attracted much attention. BDD electrode has the advantages of wide potential window, low background current, stable dimension and mechanical properties, exhibiting high chemical inertness and extended lifetime. In such electrodes, the part which brings about the anodic oxidation is the oxidized surface of the electrode. The kinetics of the adsorption of an organic substance on a surface is closely related to the chemical nature and properties of the surface on which it is adsorbed [22,23].

Recently, Errami *et al.* [15, 18, 19, 24] demonstrated that the pesticides methidation, cypermethrin, endosulfan, buprofezin and bupirimate can be electrochemically removed from aqueous solutions using SnO₂ and BDD anodes. They found that current density influence is remarkably clear on the BDD electrodes where it was evident that the most efficient current density toward a complete buprofezine mineralization was reached with the application of 80 mA.cm⁻² [24].

Difenoconazole (Cis-trans-3-chloro-4-[4-methyl-2-(1H-1,2,4-triazol-1-ylmethyl)-1,3-dioxolan-2-yl]phenyl 4-chloro phenyl ether) belonging to the triazole group of pesticides, As a kind of systemic sterol demethylation inhibitor (DMI), difenoconazole has a good ability to interfere with the mycelial growth and inhibit the spore germination of pathogens that ultimately results in inhibiting fungal growth. Difenoconazole is extensively used in a wide range of crops in many countries for its good control of various fungal diseases [25, 26]. This paper presents the study of a prospective electrochemical treatment system for difenoconazole using a commercial BDD electrode. The effect of using different concentration supporting electrolytes NaCl, varying the pH, effect of concentration of pesticide, and current density (40–80 mA.cm⁻²) upon the rate of difeconazole and chemical oxygen demand (COD) removal are investigated.

EXPERIMENTAL SECTION

Chemicals

Difenoconazole is a triazole fungicide. is a local systemic fungicide that is effective for control of various fungal diseases. Has a good ability to interfere with the mycelial growth and inhibit the spore germination of pathogens that ultimately results in inhibiting fungal growth. Difenoconazole formulation is commercially available in the SCORE (250 g/L difenoconazole) (Figure 1). It was purchased from syngenta crop science. All chemicals used in the experiments were of analytical pure grade and used without further purification. The sodium chloride used was of analytical-reagent grade and was obtained from Aldrich (Spain).

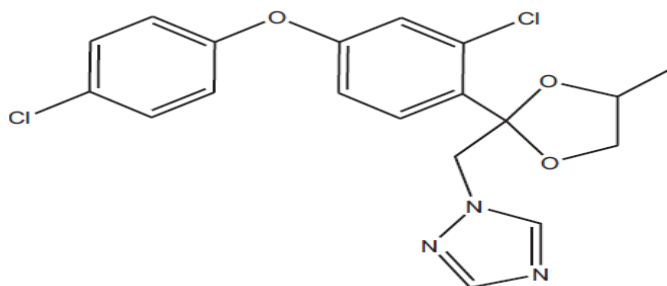


Figure 1. Chemical structure of difenoconazole.

Electrolytic system

Electrochemical measurements were performed using a computer controlled by Potentiostat/Galvanostat model PGZ 100 associated to "Volta-Master 4" software. A system of three electrodes has been used: a saturated calomel electrode (SCE) reference electrode, a platinum auxiliary electrode and boron-doped diamond (BDD) as a working electrode. Galvanostatic electrolysis was carried out with a volume of 75 cm³ aqueous solution of difenoconazole 125 mg/L during 180 minutes. The range of applied current density was 40 to 80 mA/cm² and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests have been performed at different temperature in magnetically stirred and aerated solutions. In all cases sodium chloride was added to the electrolytic cell, at different concentrations.

The chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [27]. The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

Analytical procedures

The method used for the extraction of difenoconazole was adapted from Charles and Raymond [28]. For each 1 ml of the sample, 100 mL of acetone was added and the mixture was stirred for 2 hours. The extraction was carried out respectively with 100 ml and 50 ml of acetone. After filtration, the residues in acetone were partitioned with saturated aqueous NaCl (30 mL) and dichloromethane (70 mL) in a separating funnel. The extraction was repeated with another 70mL of dichloromethane and the combined extracts were dried over anhydrous sodium sulphate. The dichloromethane fraction was collected and evaporated on a rotatory evaporator at 40°C and the residues were dissolved in an acetone/hexane (1 : 9) mixture (10 mL). In the clean-up step, 1mL of the extract was passed through a florisil column previously conditioned with 5mL of acetone/diethyl ether (6 : 4) and 5mL of diethyl ether. The pesticide residues were eluted with acetone/diethyl ether (6 : 4) (4 mL). All samples were extracted separately and analysed by gas chromatography.

Gas Chromatography analysis

Analysis of the difenoconazole pesticide was carried out with a Hewlett-Packard model 6890 (Palo Alto, CA, USA) equipped with a split/splitless injection port, autosampler, a micro electron-capture detector (μ ECD) and HP-5 column (5% diphenyl copolymer/95% dimethylpolysiloxane) (25m length, 0.32mm internal diameter and 0.52 mm film thickness). The chromatographic conditions were as follows: detector temperature, 300°C; injector temperature, 250°C; temperature programming from 80°C to 250°C ($15^\circ\text{C min}^{-1}$), carrier gas (helium) flow rate, 2.6mLmin^{-1} ; makeup gas (nitrogen) flow rate, 60mLmin^{-1} ; injection volume, 1 μl ; and splitless time, 0.1 min.

RESULTS AND DISCUSSION

Effect of the NaCl concentration

The Figure 2 shown effect of chloride ions concentration on the degradation of difenoconazole solution, carried out at $80\text{ mA}\cdot\text{cm}^{-2}$. As shown in Figure.2, the utilization of electrolysis to detoxify difenoconazole pesticide has the ability to reduce considerably the chemical oxygen demand (COD).

The achieved reduction was 73% for $1.5\text{ g}\cdot\text{L}^{-1}$ NaCl, while for $0.5\text{ g}\cdot\text{L}^{-1}$ NaCl was 55%. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of difenoconazole on the electrode or indirect via some mediators like chlorinated species or other radicals [18, 19, 23].

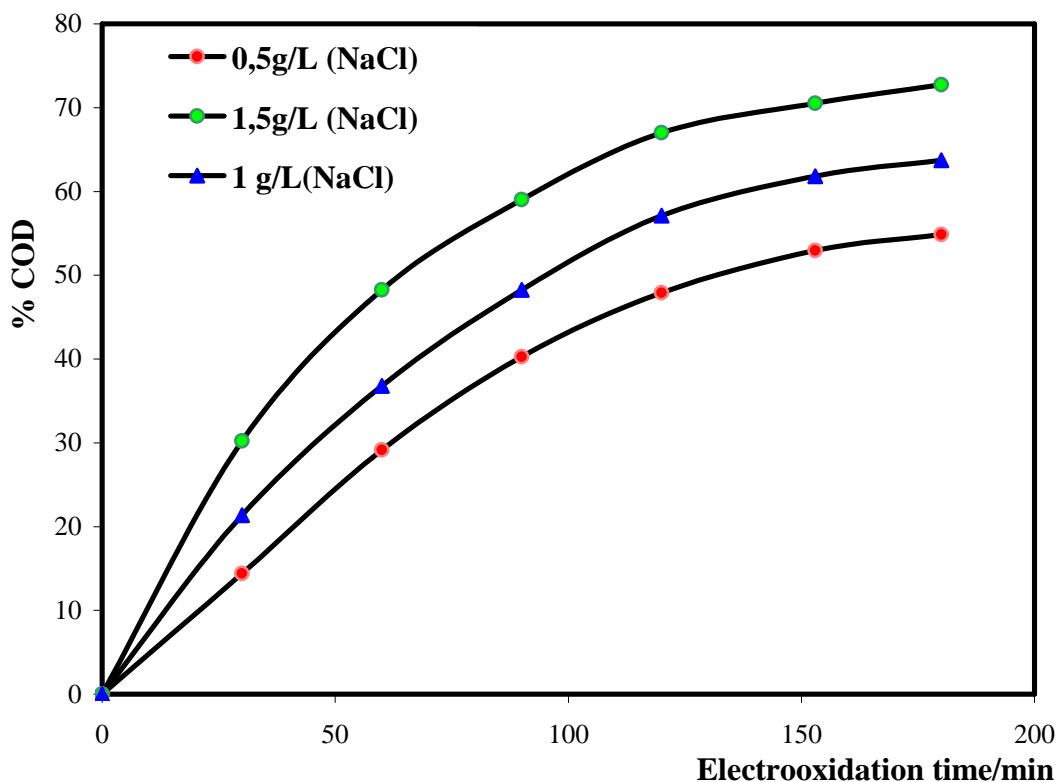


Figure 2. Effect of %NaCl concentration on the trends of % COD during the electrochemical oxidation of difenoconazole ($C_0=125\text{ mg}\cdot\text{L}^{-1}$) using a 1 cm^2 BDD anode, and $T=25^\circ\text{C}$.

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation difenoconazole at different supporting electrolytes. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [19]. Figure 3 represents the kinetic studies of the different concentration of supporting electrolyte in the presence of 125 mg. L⁻¹ of difenoconazole fungicide.

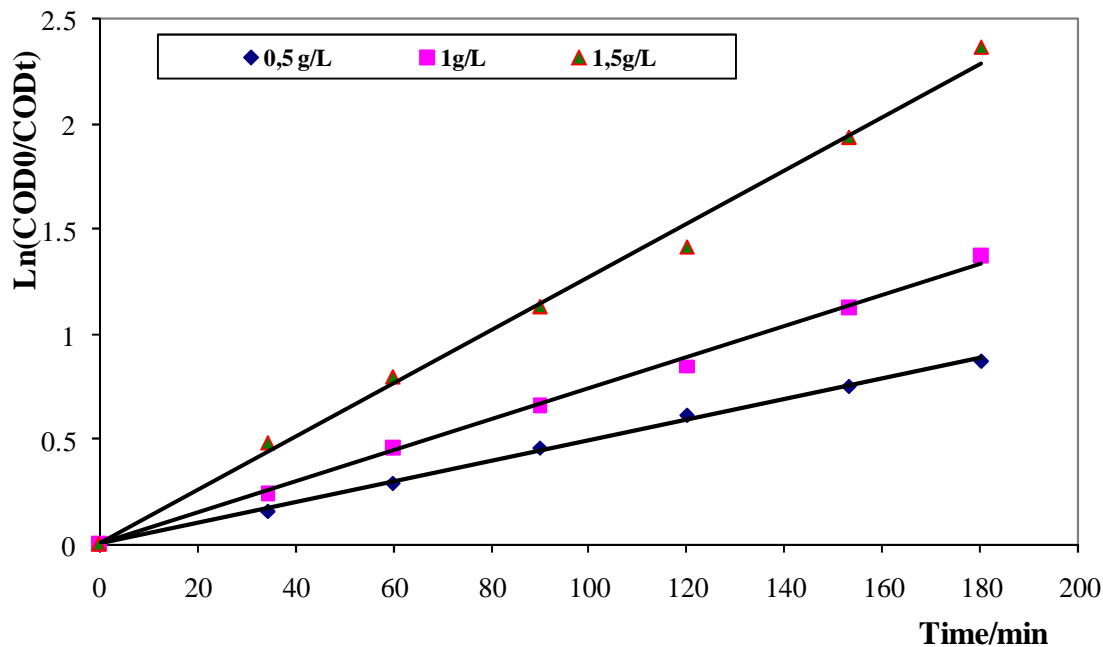


Figure 3. Pseudo first-order plot oxidation of difenoconazole 125 mg. L⁻¹ in different electrolytes at 80 mA cm⁻²

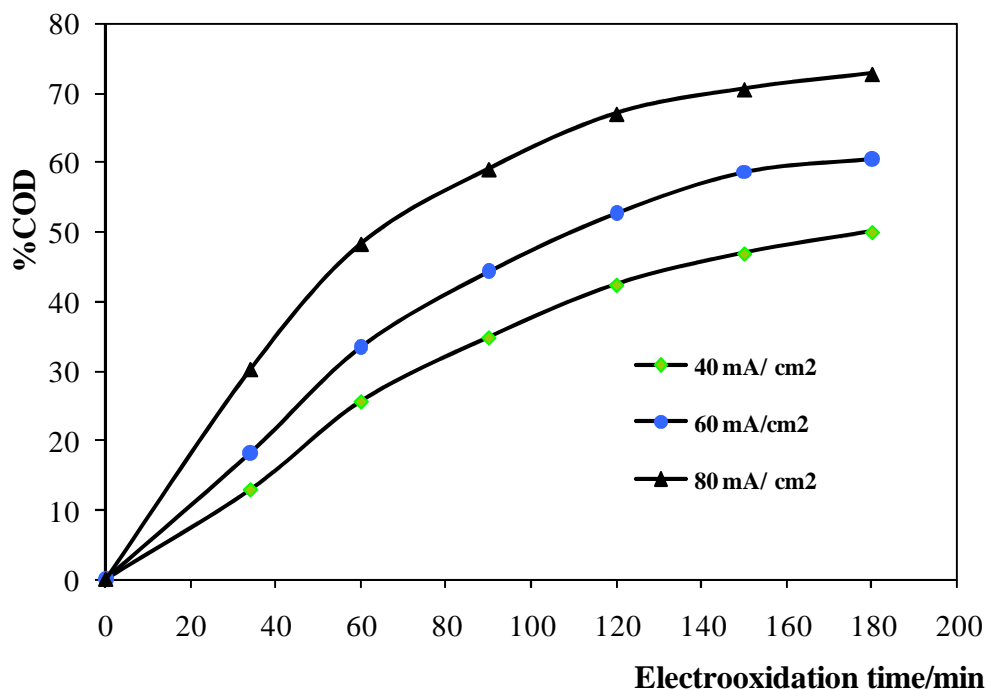


Figure 4. Influence of the applied current density on the trends of %COD during the electrooxidation of difenoconazole ($C_0=125 \text{ mg.L}^{-1}$) using a 1 cm² BDD anode, and T=25°C.

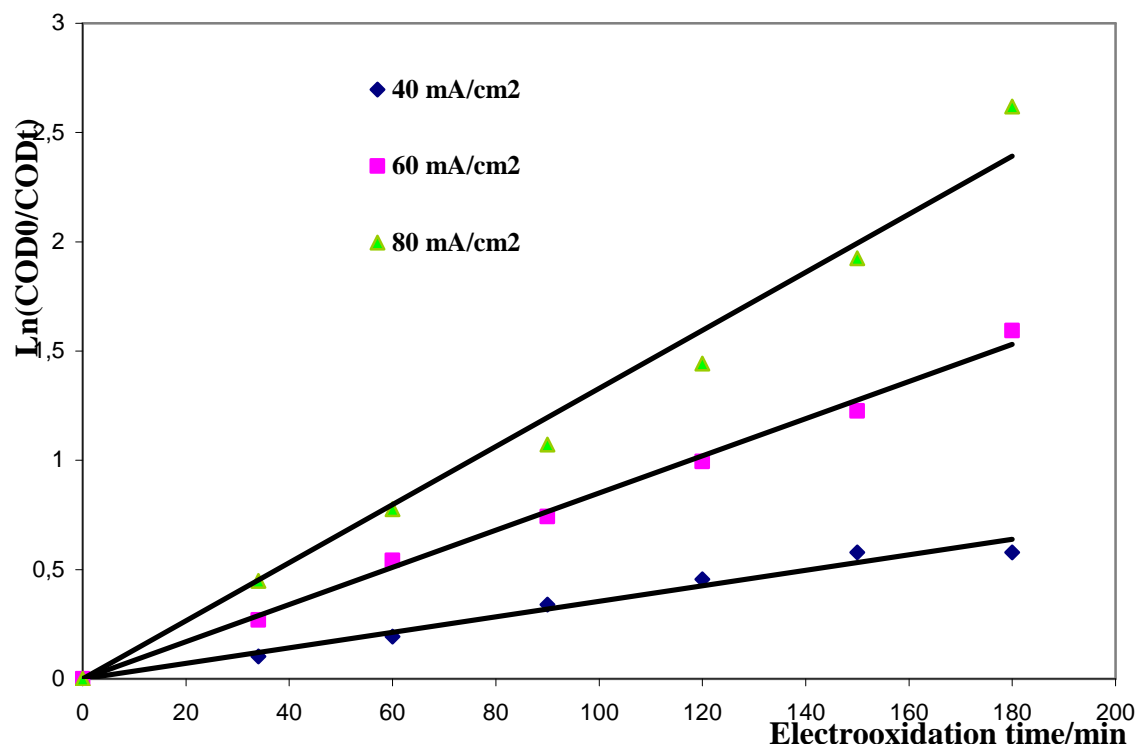
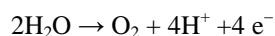


Figure.5. Pseudo first-order plot oxidation of difenoconazole 125 mg. L⁻¹ under different density current applied.

Effect of applied current density

Applied current density is an important factor affecting the electrolysis kinetics and process economics. The effect of applied current density on the electrochemical process was demonstrated in several studies [19,23]. These studies concluded that applied current increases the rate of electrochemical oxidation process and the increase is linear with the applied current density. The influence of the current density on the COD removal during the electrochemical oxidation of difenoconazole at the BDD anode is shown in Fig. 4.

After 3h time of electrolysis, the COD percent removal increased from 46% to 73% when the current density increased from 40 to 80 mA.cm⁻². This behavior indicates that in these experimental conditions, the oxidation of difenoconazole is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:



The % COD of difenoconazole was observed to fall with pseudo first-order kinetics on all the surface studied (Figure 5). This is related to the dependence of the rate of oxidation of formation of the oxidizing species at the electrode surface. The pseudo first-order constant of difenoconazole (*k*) varies from 35×10⁻⁴ min⁻¹ (40 mA.cm⁻²) to 133×10⁻⁴ min⁻¹ (80 mA.cm⁻²). From these results it was calculated that the best applied current is 80 mA.cm⁻².

The instantaneous current efficiency (ICE) can be defined as the part of the current directly used for the oxidation of the organic compounds. ICE during electrolysis can be performed from the decrease of COD by means of the following relation:

$$ICE = FV \frac{COD_t - COD_{t+\Delta t}}{8I\Delta t}$$

where *F* is the Faraday constant (96,487 C.mol⁻¹), *V* is the volume of the solution (L), COD_{*t*} and COD_{*t*+Δ*t*} are the chemical oxygen demands at times *t* and *t*+Δ*t* (gO₂ L⁻¹), respectively, and *I* is the current (A).

The ICE decrease exponentially with the specific charge. It is worth noting that the observed. That decrease of ICE is due to the mass-transfer limitation and not due to the reduction of the anodic activity. As shown in Fig.6. ICE increase with decreasing the applied current density up to 40 mA.cm⁻² by using BDD electrode. Further increase of the current density was followed by gradual decrease in difenoconazole degradation and COD removal due to increase in the mass-transfer limitation.

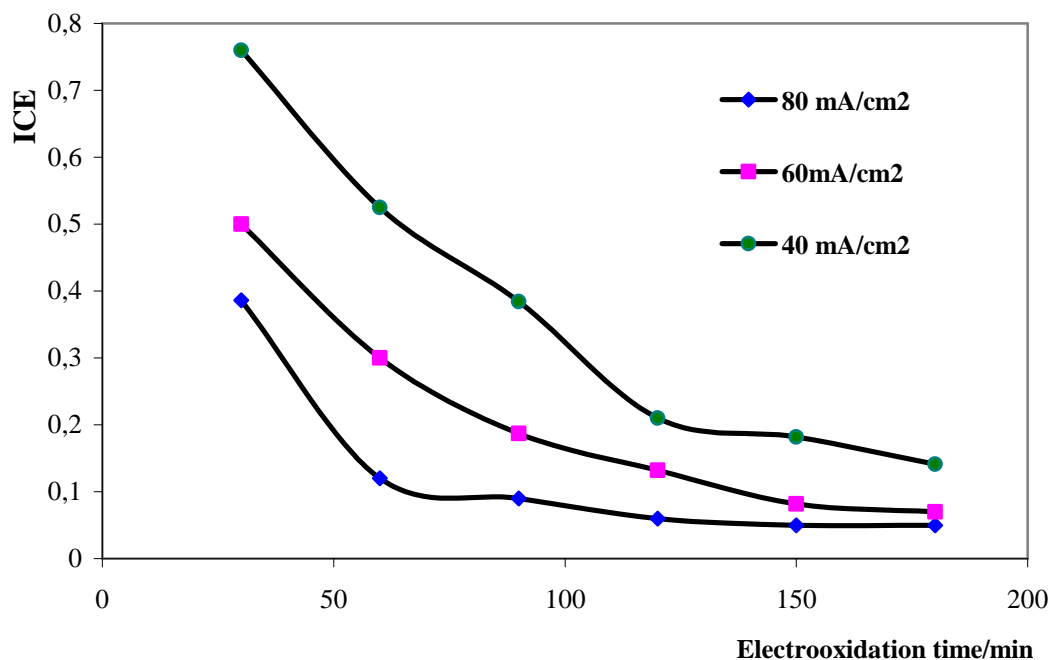


Figure 6. ICE during the electrochemical oxidation of difenoconazole ($C_0 = 125 \text{ mg.L}^{-1}$) on the BDD anode. NaCl (1.5g/L) and $T = 25^\circ\text{C}$.

Effect of concentrations of pesticide

The initial concentration of pollutants is always an important parameter in wastewater treatment. Fig. 8 shows the effect of different initial difenoconazole concentrations on the rate of fungicide degradation and corresponding Concentration removal during electrolysis at temperature of 25 °C, NaCl (1.5g/L) and using a current density 80 mA.cm⁻².

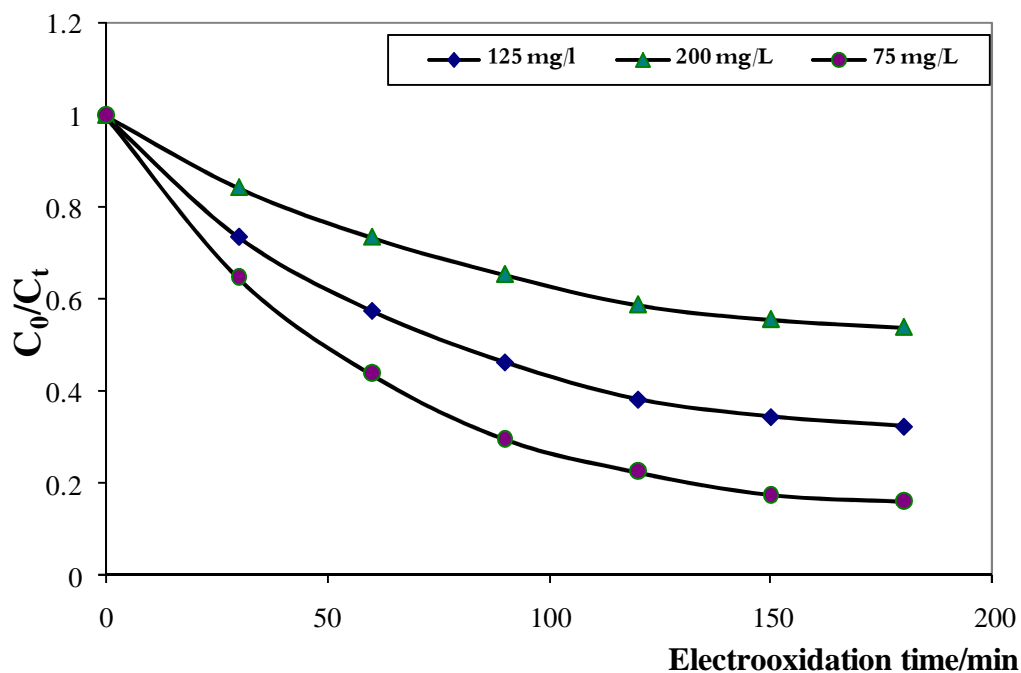


Figure 7. Influence of the concentration pesticide on the decay of concentration pesticide during electrooxidation of difenoconazole on BDD anode. Conditions: NaCl (1.5 g L⁻¹), current density 80 mA.cm⁻², and $T = 25^\circ\text{C}$

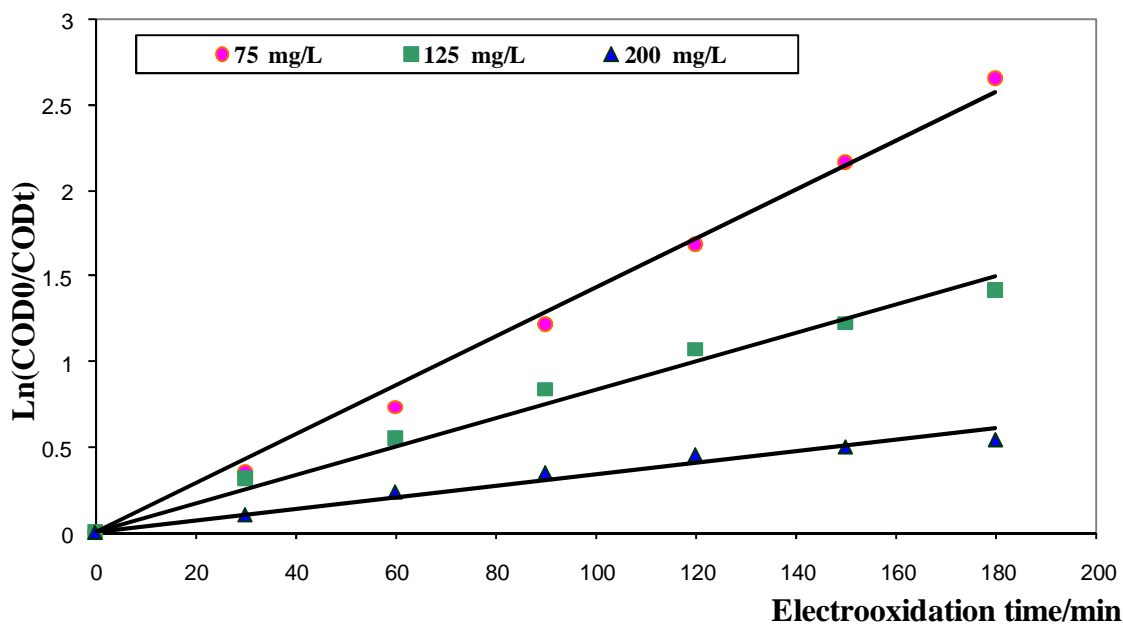


Figure 8. Linear regression for concentration removal with time during the electrochemical oxidation of difenoconazole on the BDD anode for different concentrations. NaCl ($1.5 \text{ g}\cdot\text{L}^{-1}$), $i = 80 \text{ mA cm}^{-2}$, and $T = 25 \text{ }^\circ\text{C}$.

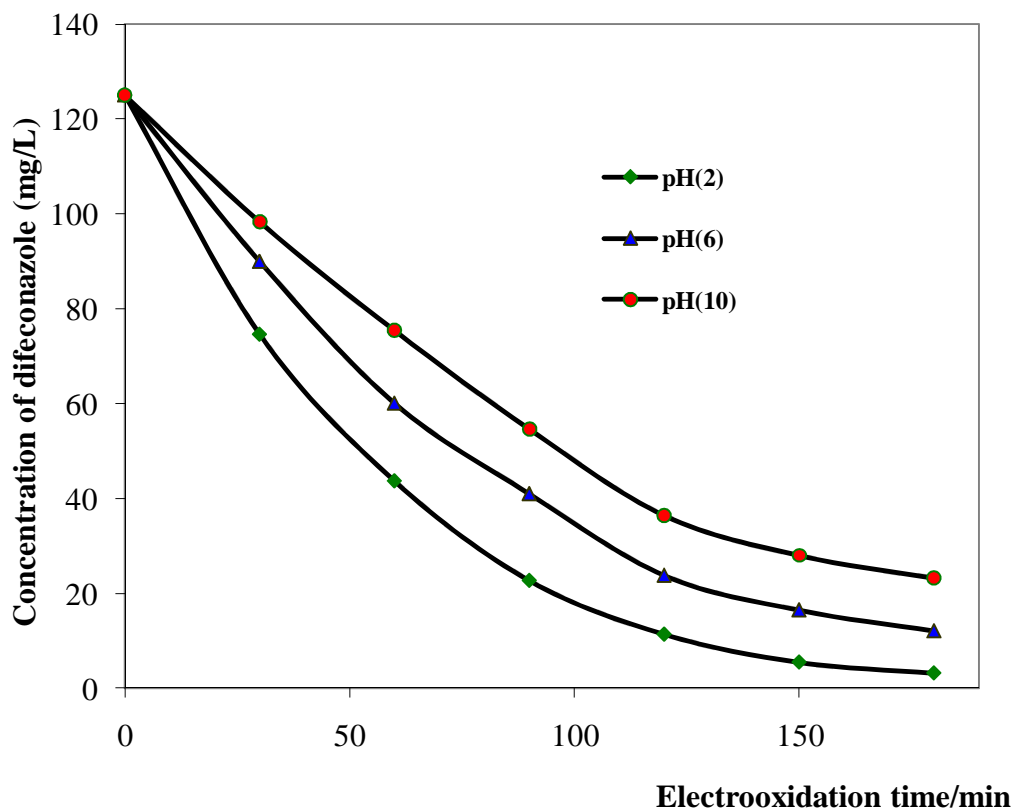


Figure 9. Influence of pH on the decay of concentration pesticide during electrooxidation of 125 mg L^{-1} difenoconazole on BDD anode. Conditions: NaCl (1.5 g L^{-1}), applied current = 80 mA cm^{-2} and $T = 25 \text{ }^\circ\text{C}$.

For low concentrations ($C_0 = 75 \text{ mg/L}$ and 125 mg/L), the concentration of difenoconazole decreased to 2.6 and 12 mg L^{-1} after about 3 h. However, for higher concentrations, the total degradation requires longer time of electrolysis as shown in the trend of the curve ($C_0 = 200 \text{ mg L}^{-1}$) in k values calculated from the straight lines, considering a

first-order reaction, decreased when the initial concentration of difenoconazole increased. The pseudo first-order constant of fungicide k varies from $143 \times 10^{-4} \text{ min}^{-1}$ (75mg/L) to $34 \times 10^{-4} \text{ min}^{-1}$ (200 mg/L).

This indicates that the oxidation rate and process efficiency are directly proportional to pesticide concentration. This outcome is in agreement with the data reported by Salghi *et al.* [18,19,23]. The electrolysis time for complete removal of difenoconazole was proportional to the concentration of organic matter.

Effect of pH

Solution pH is an important factor for wastewater treatment. In anodic oxidation, there are many reports on the influence of solution pH, but the results are diverse and even contradictory due to different organic structures and electrode materials [22, 19].

Some authors reported that the oxidation process is more favorable in acidic media [8]. In contrast, others indicated that the efficiency of the process was increased in alkaline media [9]. According to this literature, it can be concluded that the effect of pH strongly depends on the nature of the investigated organics and of the supporting electrolyte. Therefore, the effect of pH on the degradation rate of difenoconazole fungicide was studied at large pH range from acidic to basic. Aqueous solutions of difenoconazole (125 mg.L^{-1}) were electrolyzed at pH values of 2, 6, and 10 (Fig. 9). As can be seen from this figure, the pH of the medium slightly affects the degradation kinetics of pesticide and this indicates that the degradation of difenoconazole can be performed at pH value 2 without significant increased in oxidation efficiency of the system. For this reason, the electrochemical oxidation is a viable treatment for electrooxidation of pesticides where adjustment of the effluent's pH are recommended.

CONCLUSION

Electrochemical oxidation using a BDD anode has been successfully applied to treat aqueous solutions containing difenoconazole. The experimental results showed that:

- The process was under mass transport control within the range studied, regardless of the experimental conditions, due to the extraordinary high activity of hydroxyl radicals from the water discharge and the removal of COD was well described by a pseudo first-order kinetic.
- The removal rate of COD increases with applied current density due to the increase of the mass transport caused by oxygen evolution reaction, but decreases for higher values due to the improvement of this reaction.
- The different experimental conditions tested using the BDD anode allow us to conclude that the increases of the pH of the solutions, from acidic solution (pH = 2) to neutral solution (pH = 7), and (pH=10) slightly decreases the rate of electrooxidation.

This preliminary study suggests that anodic oxidation with BDD electrode constitutes an excellent method for the treatment of effluents contaminated with difenoconazole pesticide.

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