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Research Article

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Electrochemical degradation of imazalil and pyrimethanil by anodic oxidation on boron-doped diamond

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ABSTRACT

The electrochemical oxidation of mixture pesticides imazilil and pyrimethanil pesticides has been studied on boron-doped diamond (BDD) electrodes on acid medium by bulk electrolysis. The influences of current density, conductive electrolyte, pH, and concentration of pesticide were investigated. GC and chemical oxygen demand measurements were conducted to study the reaction kinetics of pesticides mineralization. The best obtained conditions for COD removal on the BDD anode to degrade imazalil and pyrimethanil solutions include operating at 50 mA cm^{-2} and 25 ± 3 °C. 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 ($OH^{\bullet}$) and other electrogenerated oxidants (Cl^-, ClO^-).

Keywords: Electrochemical oxidation , Pesticide, Direct electrooxidation, Boron-doped diamond , fungicide.

INTRODUCTION

The rapid increase of population and intensive agriculture in our planet has resulted in large quantities of organic and inorganic wastes being discharged into environnement, thus giving rise to serious environmental problems and deterioration of the agro ecosystems. In general, different technologies developed for the elimination of refractory organic micropollutants from drinking and wastewaters include chemical oxidation methods, which are successfully applied in drinking water purification plants.

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.

These technologies include photocatalytic oxidation [**1,2**], ultrasonic radiation [**3**], bioremediation and thermal desorption [**4**]. The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with a very low active ingredient content, rather than highly concentrated obsolete pesticides stocks.

Among these technologies, electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents. In recent years, electrochemical methods are drawing attention and starting to substitute traditional processes due to the advantages such as high efficiency, ease of operation, and environmental compatibility [**5-11**].

In anodic oxidation, organic pollutants are directly destroyed by reaction with hydroxyl radical (HO•) formed at the anode surface from water oxidation [8, 9]:

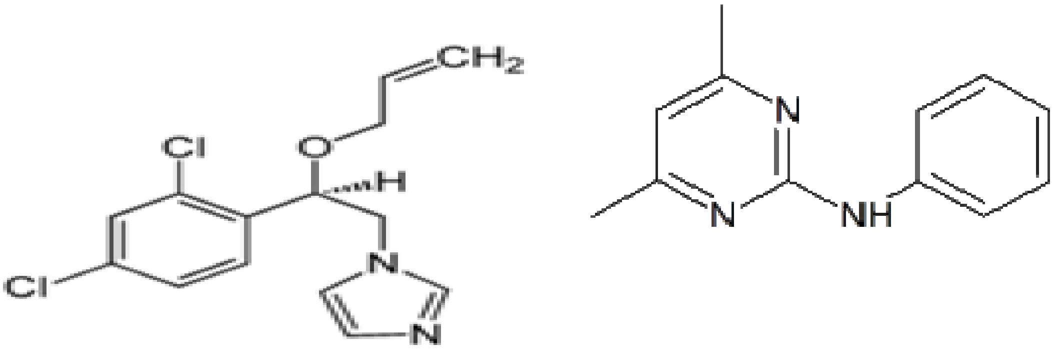
$$H_2O \longrightarrow OH^{\cdot} + H^+ + e$$

Several anode materials such as Pt [12–14], SnO_2 [6, 8], PbO_2 [15–17] and BDD [6, 7, 10, 11] have been used for pesticides removal. The new anode material (BDD) possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous medium [18, 19].

Recently, Salghi et al. [8–12] demonstrated that the pesticides methedation, cypermethrin, endosulfane, deltamethrine and bupirimate can be electrochemically removed from aqueous solutions using BDD anode. 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 bupirimate and buprofezin mineralization was reached with the application of 60 mA cm^{-2}.

Imazalil and pyrimethanil is two pesticides of the most widely used fungicide pesticides in agriculture (Fig. 1). Imazalil and pyrimethanil formulation is commercially available in the Philabuster 400 SC.

Philabuster combines the active ingredients imazalil sulfate and pyrimethanil, two fungicides with different modes of action, into a single product to facilitate adoption of resistance management strategies in postharvest disease control. Pyrimethanil is an anilinopyrimidine fungicide (Figure 1) that interferes with the secretion of enzymes necessary for infection by several postharvest pathogens, while imazalil sulfate is an imidazole fungicide (Figure 1) that inhibits sterol synthesis thus affecting cell wall permeability. Pyrimethanil does not exhibit cross-resistance to sterol-inhibiting or benzimidazole fungicides. Use PHILABUSTER fungicide for the control of the following postharvest diseases caused by *Penicillium italicum* (blue mold), *Penicillium digitatum* (green mold), *Colletotrichum gloeosporioides* (anthracnose) and *Phomopsis citri & Diaporthe citri* (stem-end rot) on citrus fruits. Use of PHILABUSTER should be integrated into an overall disease management program within each packinghouse. Provides curative and preventative activity - treat fruit within the same day of picking. For suppression of sporulation, use the highest labeled rate.



Imazalil **Pyrimethanil**

Figure 1. Chemical structure of Pyrimethanil and Imazilil

This paper presents the study of a prospective electrochemical treatment system for imazalil and pyrimethanil using a commercial BDD electrode. The effect of using different supporting electrolytes (NaCl, Na_2CO_3, and Na_2SO_4), varying the pH, effect of concentration of mixte pesticide, and current density (10–50 mA.cm^{-2}) upon the rate of two pesticide and chemical oxygen demand (COD) removal are investigated.

EXPERIMENTAL SECTION

Materials

Pyrimethanil is an anilinopyrimidine, 4,6-dimethyl-N-phenyl-2-pyrimidinamine. Imazalil sulfate: 1-[2-(2,4-dichlorophenyl)-2-(2-propenyloxy)ethyl]-1H- imidazole sulfate. The molecular structure of two pesticides is shown in Fig. 1. 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).

Electrolytic system

Electrochemical measurements were performed using a computer controlled by Potentiostat/Galvanostat model PGZ 100 associated to ‘‘Volta-Master 4’’ software.

A conventional three-electrode cell (100 cm^3) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of BDD electrode with effective surface area of 1 cm^2, whereas the cathode was a platinum electrode, and the gap between electrodes was 1 cm. A saturated calomel electrode was used as a reference. The range of applied current was 10–50 $mA.cm^{-2}$ and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests were performed at (25 ± 3) °C in magnetically stirred and aerated solutions. In all cases, sodium chloride was added to the electrolytic cell, at different concentrations. The COD is measured according to the standard methods for examination of water and wastewater [**20**]. The COD values were determined by the open reflux, with 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 two pesticides was adapted from Charles and Raymond [21]. For each 5 mL of the sample, 100 mL of acetone was added and the mixture was stirred for 2 h. The extraction was carried out respectively with 100 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 dichloromethane fraction was collected and the separation process with (70 mL) dichloromethane were combined and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure at 40 °C and the residues were dissolved in an acetone–hexane (1:9) mixture (10 mL). Samples were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Effect of supporting electrolytes

Electrolytes of 0.1 g. L^{-1} of the following salts: NaCl, Na_2CO_3, and Na_2SO_4 were studied by Boron Doped Diamond anode. As appears in Fig. 2, the NaCl were the most effective conductive electrolyte for the electrocatalytic degradation of the investigated mixture pesticides and COD removal while Na_2SO_4 and Na_2CO_3 electrolytes show poor results. The operating conditions of the treatment process were: applied current of 50 mA cm^{-2}, pH (6.32 ± 0.2), temperature of 25 °C, initial concentration of two pesticides 40 mg L^{-1}, and the distance between the two electrodes was 0.5 cm.

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation pesticides at different supporting electrolytes. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [8]. Figure 3 represents the kinetic studies of the different supporting electrolyte in a (0.1 g L^{-1}) NaCl, (0.1 g L^{-1}) Na_2CO_3, (0.1 g L^{-1}) Na_2SO_4 solution in the presence of mixture pesticides Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil.

It was disclosed above that in the Na_2CO_3 medium BDD was more suitable for electrochemical incineration of organics than Na_2SO_4.

In the presence of NaCl, due to the different electrochemical behaviors of active chlorines formation on different materials, this complex effect would make the degradation performance even completely inverted. It was reported that the COD removal was much higher on BDD than that on SnO_2 for the treatment of wastewater containing bupirimate in the presence of NaCl [6]. In the present work, the degradation of mixture pesticide Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil was investigated in three systems of mixture supporting electrolyte: (0.1 g L^{-1} Na_2CO_3 + 0.1 g L^{-1} NaCl), (0.1 g L^{-1} Na_2CO_3 + 0.1 g L^{-1} Na_2SO_4) and (0.1 g L^{-1} Na_2SO_4 + 0.1 g L^{-1} NaCl).

As shown in Fig. 4 and Fig 5, the presence of mixture electrolyte 0.1 g L^{-1} Na_2CO_3 + 0.1 g L^{-1} NaCl promoted the best electrooxidation of pesticide at BDD electrode. These results could also be confirmed by the kinetic studies of the different supporting electrolyte systems. As shown in Table 1, after 2 h treatment, the COD removal on BDD in the absence of NaCl was about 52 %, but in the presence of NaCl, it significantly increased to 87 %. It was also observed that at BDD anode, the electrooxidation on 0.1 g L^{-1} Na_2CO_3 + 0.1 g L^{-1} NaCl performed much better than that on 0.1 g L^{-1} Na_2CO_3 + 0.1 g L^{-1} Na_2SO_4 and 0.1 g L^{-1} Na_2SO_4 + 0.1 g L^{-1} NaCl electrolytes. As discussed before, the degradation of fungicides in the presence of NaCl would be the co-action of direct oxidation and NaCl indirect oxidation. Presumably, the heterogeneous oxidation (i.e., direct oxidation on the electrode surface) presented the same performance in two media since other conditions except NaCl addition were similar and there was the same Na_2SO_4 and Na_2CO_3 presence in both electrolyte media.

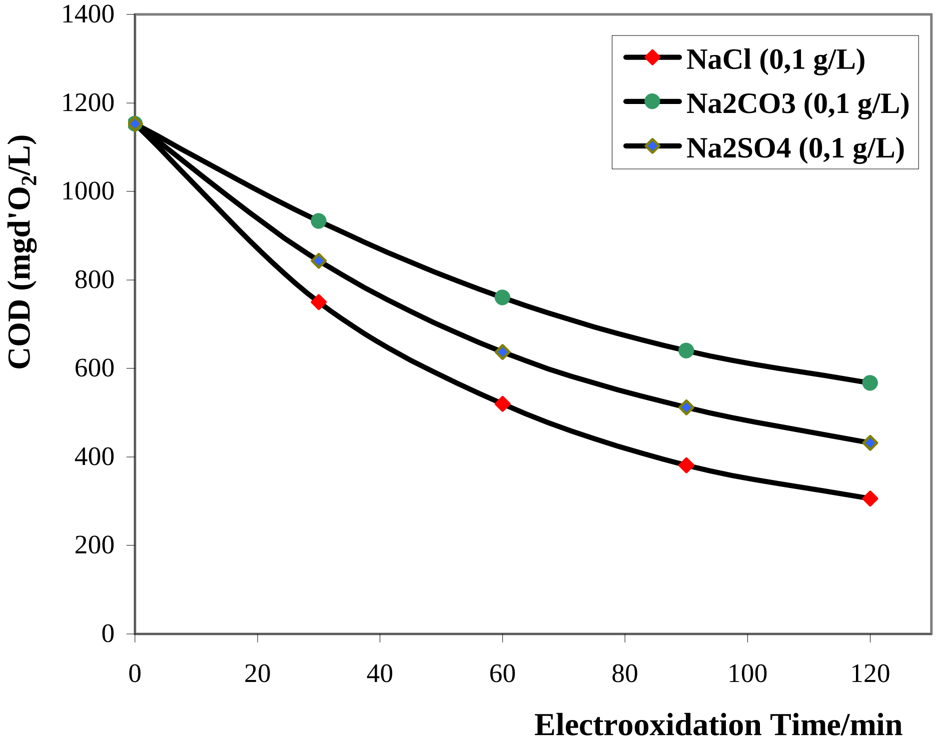


Figure 2. Influence of supporting electrolytes on the decay of COD during electrooxidation of 40 (mg L^{-1}) Imazalil + (40 mg L^{-1}) Pyrimethanil on BDD anode. Conditions: applied current 50 mA cm^{-2}, T = 25 °C.

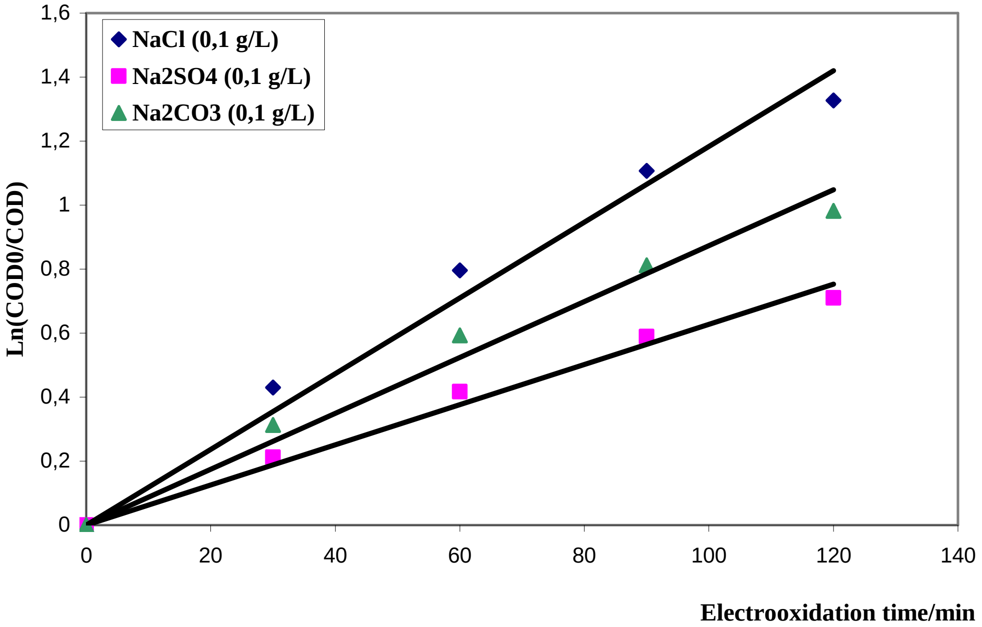


Figure 3. Pseudo first-order plot oxidation of Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil in different electrolytes at 50 mA cm^{-2}.

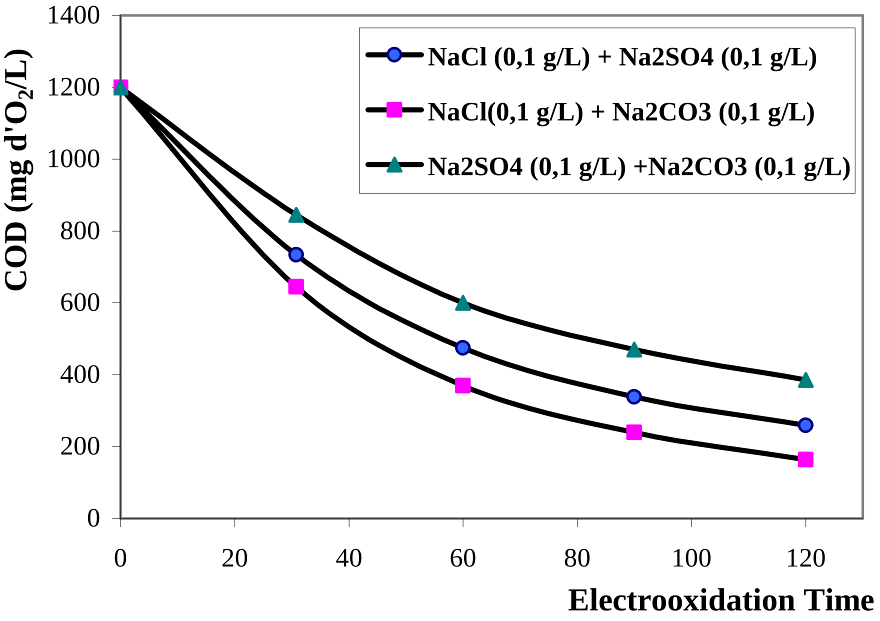


Figure 4. Influence of supporting electrolytes on the decay of COD during electrooxidation of Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil on BDD anode. Conditions: applied current 50 mA cm^{-2}, pH = 6.3, T = 25 °C.

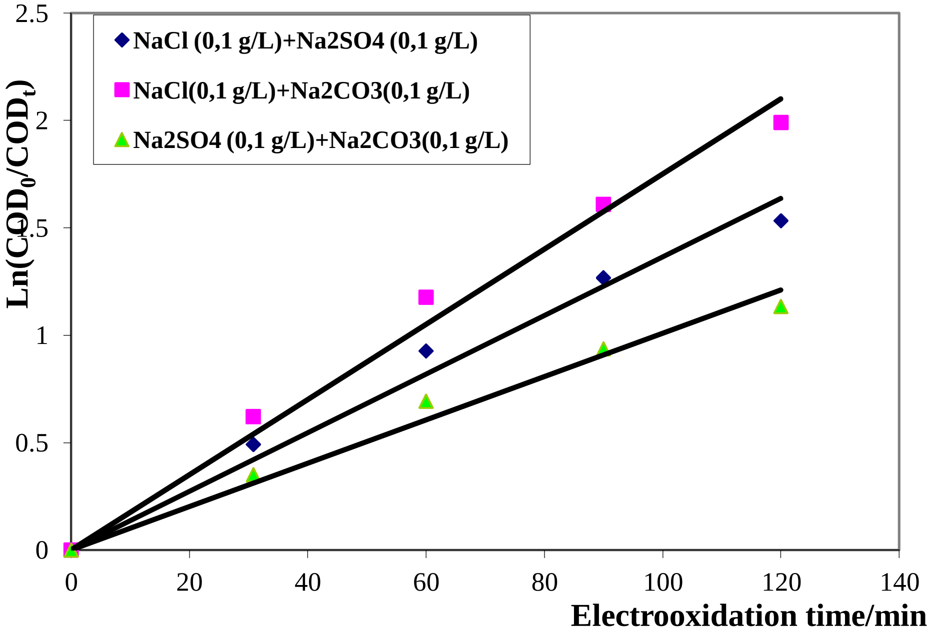


Figure 5. Pseudo first-order plot oxidation of Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil in different electrolytes at 50 mA cm^{-2}.

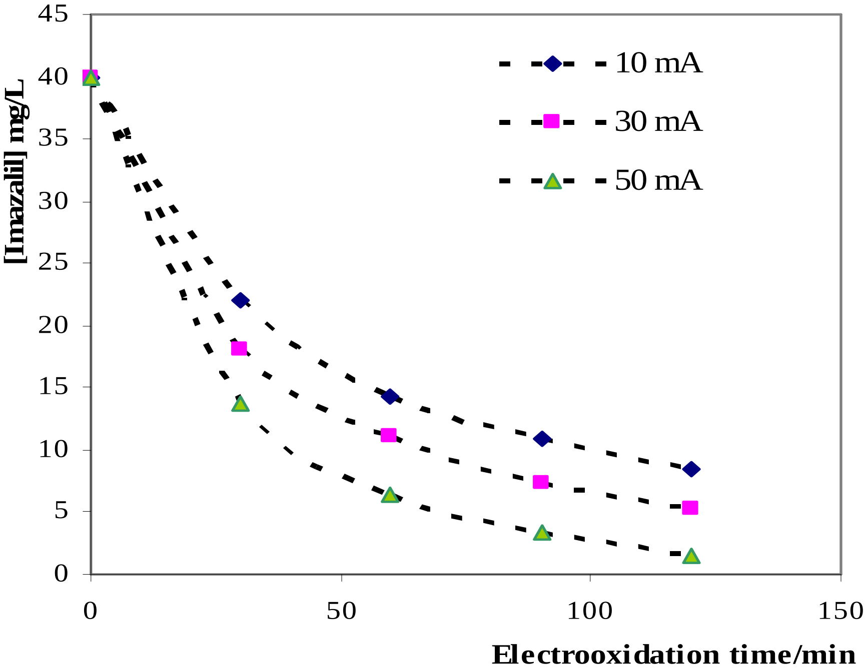
Table 1 Kinetic rate constants of Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil removal fitted by a first order model and %COD for BDD anode under diferent electrolytes.

Supporting electrolytes	Rate constant, K (min^{-1})	% COD
NaCl (0.1 g/L)	(1.184 ± 0.13)×10^{-2}	74%
Na_2SO_4 (0.1 g/L)	(0.87 ± 0.09)×10^{-2}	63%
Na_2CO_3 (0.1 g/L)	(0.63 ± 0.073)×10^{-2}	52%
Na_2CO_3 (0.1 g/L) + NaCl(0.1 g/L)	(1.75 ± 0.42)×10^{-2}	87%
Na_2CO_3 (0.1 g/L) + Na_2SO_4 (0.1 g/L)	(1.01 ± 0.24)×10^{-2}	67%
NaCl (0.1 g/L) + Na_2SO_4(0.1 g/L)	(1.36 ± 0.16)×10^{-2}	78%

Effect of applied current

The effect of current density on the electrochemical process was reported in several studies [**6, 7, 8**]. It is an important factor affecting the electrolysis kinetics. Two reaction zones of an anode can be distinguished:

electrochemical reaction zone (i.e., anodic surface and diffusion layer) where direct oxidation by electron transfer and/or OH occurs, and chemical reaction zone (i.e., bulk liquid) where compounds are oxidized by electrogenerated oxidant species (i.e., indirect oxidation).



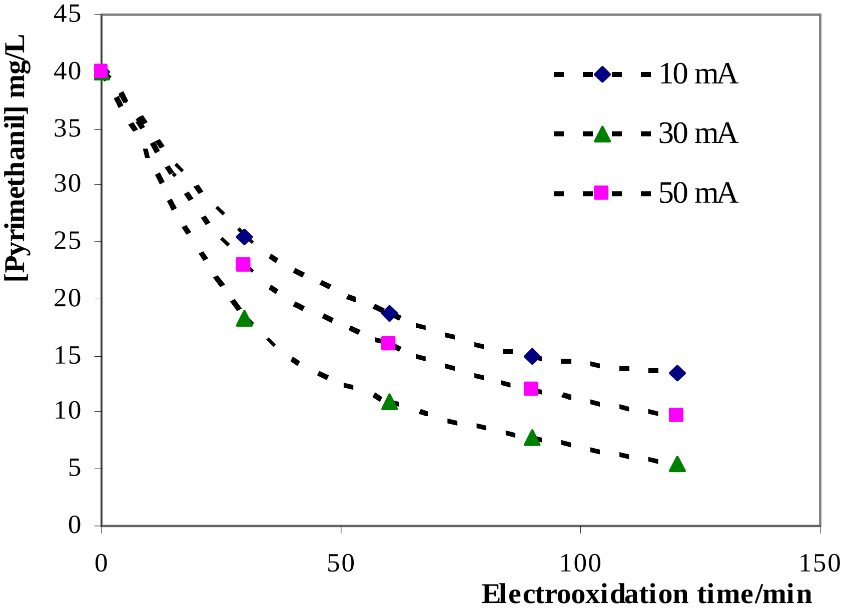


Figure 6. Influence of the applied current on the decay of concentration pesticide during electrooxidation of Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil on BDD anode. Conditions: Na_2CO_3 (0.1 g L^{-1}) + NaCl (0.1 g L^{-1}), T = 25 °C.

The influence of the current density on the COD removal during the electrochemical oxidation of mixture pesticide Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil at the BDD anode is shown in Fig. 6.

Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil degradation rise with increasing the applied current density up to 50 mA by using BDD electrode. The apparent rate constants of imazalil (k) varies from 2.82×10^{-2} min^{-1} (50 mA) to

1.19 10^{-2} min^{-1} (10 mA), four Pyrimethanil (k) varies from 2.14× 10^{-2} min^{-1} (50 mA) to 0.89 10^{-2} min^{-1}(10 mA) results it was calculated that the best applied current is 50 mA.

Effect of the concentration

The initial concentration of pesticide is always an important parameter in wastewater treatment. To investigate the electrooxidation efficiency on high concentration of Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil, the experiments of electrochemical degradation of COD0 = 900, 1400 and 1800 mg of O_2/L solutions were carried out with a selecting current density and Na_2CO_3 (0.1 g/L) + NaCl(0.1 g/L). Influence of the initial COD on the trends of COD during electrolysis as shown in Figures 7.

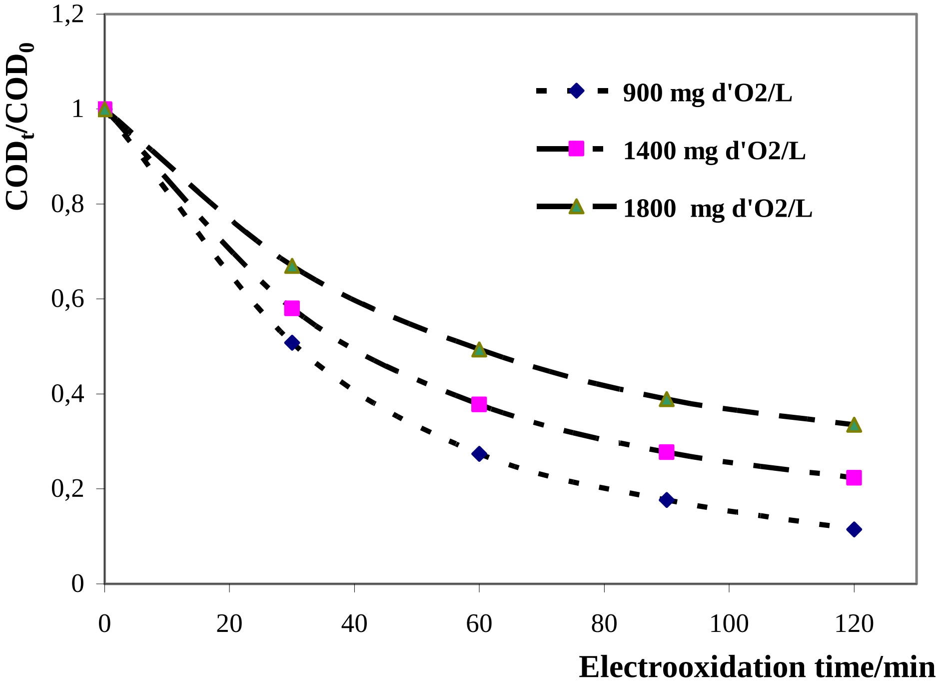


Figure 7 Influence of the initial COD on the trends of COD during electrolysis on the BDD anode. iap = 50mA; pH=6.3, Na_2CO_3 (0.1 g/L) + NaCl(0.1 g/L) and T=25°C.

For low concentrations (COD0 = 900 and 1400 mgL-1), the COD decreased to 41 and 370 mgL^{-1} after about 2h. However, for higher concentrations, the total degradation requires longer time of electrolysis as shown in the trend of the curve (COD0 = $1800mgL^{-1}$) in kap values (Table 2) calculated from the straight lines, considering a first-order reaction, decreased when the initial concentration of mixture Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil increased.

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. [6,7,8], Panizza Cerisola [22, 23]. The electrolysis time for complete removal of mixture Imazalil and Pyrimethanil was proportional to the concentration of pesticide.

Table 2 Effect of the initial mixture Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil concentration on the values of the rate constant and the %COD.

COD_0 (mg L^{-1})	900	1400	1800
COD removal (%)	95%	70%	40%
K ap ×10^{-2} (min^{-1})	(2.3 ± 0.12)	(1.02 ± 0.2)	(0.41 ± 0.085)

CONCLUSION

This work studied the efficiency of an electrochemical oxidation system for the treatment of fungicides. Electrochemical oxidation is a method that has never been applied for the treatment of this type of wastes. This work is a first attempt to investigate the degradation of mixture fungicide Imazalil and Pyrimethanil in electrochemical treatment with BDD. The electrochemical degradation of mixture Imazalil (40 mg L^{-1}) + (40 mg L^{-1}) Pyrimethanil has been investigated using BDD anode under all conditions tested involving, applied current density from 10 to 50 mA, type of electrolyte, and initial concentration of pesticide. The experimental results allowed us to draw the following conclusions:

- The best results were obtained when electrolyses were carried out at high densities, 50 mA, and in the presence of mixture supporting electrolyte NaCl (0.1g/L) with Na_2CO_3 (0.1g/L).
- The removal rate of COD increases with applied current density until 50 mA 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 theinitiale concentration of pesticide in the solutions, from 900 mg of O_2/L to 1800 mg of O_2/L, slightly decreases the rate of electrooxidation of pesticides.

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