



Electrochemical oxidation of carbendazim on boron-doped diamond anode

H. Bouya¹, M. Errami¹, R. Salghi^{1,*}, B. Gözmen², M. Messali³

¹Equipe de Génie de l'Environnement et de Biotechnologie, ENSA, Université Ibn Zohr, BP 1136, Agadir, Morocco

²Department of Chemistry, Arts and Sciences Faculty, Mersin University, 33343 Mersin, Turkey

³Chemistry Department, Faculty of Science, Taibah University, 30002, Al-Madinah Al-Mounawwara, Saudi Arabia

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*Corresponding Author. E-mail: r.salghi@uiz.ac.ma; Tel: (+212661145512)

Abstract

Biological and physical-chemical factors may play a role in the degradation to variable extent. Therefore, but our study focused on revealing the influence of operating factors on the reaction of electro-oxidation of pesticide by boron-doped diamond anode (BDD) electrode, The influence current density, sodium chloride concentration and pesticide concentrations were critically examined. Further the pesticide investigated in our work named carbendazim. The toxicity of the examined pesticide is well known; however, little information is available regarding his natural degradation process. The degradation processes as current density were followed by high-performance liquid chromatography (HPLC) technique. The results of these influences are expressed in terms of the Chemical Oxygen Demand (COD removal). In this manuscript we report that, the highest electro degradation activity was achieved in the presence of NaCl (0.1g/l), 80 mA/cm², 30 ppm carbendazim concentration and temperature of 25 °C.

Keywords: Pesticide, electrooxidation, BDD, carbendazim

1. Introduction

Pesticides are widely used for the control of weeds, diseases, and pests of cultivated plants all over the world, mainly since after the Second World War. At present, around 2.5 million tons of pesticides are used annually and the number of registered active substances is higher than 500 [1]. However, as pesticides are toxic substances that may have undesirable effects, their use has to be regulated.

Risk assessment of pesticides requires information on the toxicological and ecotoxicological properties of these compounds as well as their levels in food and environmental compartments. Therefore, reliable analytical methods are needed to carry out the monitoring of pesticide residues in those matrices. Consumer concerns on food safety and society awareness of chemical contaminants in the environment have increased in the past few years.

As a consequence, more restrictions in the use of chemical products have been imposed at national and international levels. carbendazim is a systemic fungicide widely used to control broad range of fungal diseases in agriculture and forestry. Two closely related fungicides, benomyl [methyl 1-(butylcarbamoyl)benzimidazol-2-ylcaxbamate] and thiophanate-methyl [dimethyl 4,4'-(o-phenylene)bis(3-thioallophanate)] can be readily degraded into carbendazim, not only when applied to crops but also in contact with water or under moist soil [2,3]. Whereas benomyl and thiophanate-methyl may breakdown shortly after application, the produced carbendazim remains for a longer time. Therefore, their total residues are usually determined in the form of carbendazim, and a single maximum residue limit (MRL) has been recommended for this group of fungicides [4].

The electrochemical method for the oxidation of organic pollutants for waste water treatment has attracted a great deal of attention recently, mainly due to the development of new effective anode material [5]. In fact it has been found that the oxidation of organics take place always with simultaneous oxygen evolution, this has allow to search new anode material with high oxygen evolution overpotential in order to favor the reaction of organics oxidation over the side reaction of oxygen evolution[6,9-18].

In recent studies Salghi and co-workers studied the electrooxidation of various groups pesticides bupirimate [10-17]; methidathion [17-21], cypermethrin [14], endosulfan [20], difenconazole [19], in brine solution using BDD and SnO₂ anodes. The authors studied the electrooxidation of various organic compound by Iniesta and co-workers, organic substrates [22]; 4-chlorophenol [23]; 1, 2-dichloroethane [24].

Carbendazim is fungicide that is used in a number of crops to help control the growth of unwanted fungus and mold. If left untreated, mold, fungus, pests and insects on crops can damage the safety and quality of our food supply. Carbendazim formulation is commercially available in the LASKOR 50 WG (50% Carbendazim) (Figure 1).

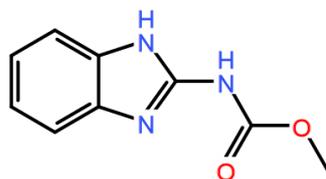


Figure 1. Chemical structure of carbendazim

2. Materials and methods

2.1. 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 cm³) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of BDD electrode with effective surface area of 1 cm², whereas the cathode was a platinum electrode, and the gap between electrodes was 0.5 cm. A saturated calomel electrode was used as a reference. Galvanostatic electrolysis was carried out with a volume of 75 cm³ aqueous solution of 30 mgL⁻¹ de carbendazim. The range of applied current was 40–80 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 [18]. 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.

2.2. Extraction procedure

2.2.1. Extraction step

In the case of carbendazim weigh (1 ± 0.1) ml into 50 mL the centrifuge tube. This centrifuge tube contain of 4 g ± 0,2 g of magnesium sulfate anhydrous, 1 g ± 0.05 g of sodium chloride, 1 g ± 0.05 g of trisodium citrate dihydrate and 0.5 g ± 0.03 g of disodium hydrogencitrate sesquihydrate. Close the tube and immediately shake vigorously for 1 min and centrifuge for 5 min at > 3000 g. An aliquot of 6 mL of the acetonitrile phase obtained in first extraction is transferred into the centrifuge tube already containing 150 mg PSA and 900 mg of magnesium sulphate (PSA SPE Cleanup Tube 1). Close the tube; shake vigorously for 30 s and centrifuge (for 5 min at > 3000 g). For 1mL of extract 150 mg magnesium sulfate and 25 mg PSA are necessary.

2.3. Instrumentation

Liquid chromatography (LC) coupled to mass spectrometry (MS/MS) is the preferred approach for analysing these kind of compounds of low volatility or thermal lability. LC-MS/MS is very effective in separating analytes, while MS allows their identification and/or confirmation at trace levels. In the last few years, LC-MS has been widely used for analysis of pesticide residues in fruits and vegetables [25-26]. More recently, the coupling LC with tandem mass spectrometry detection (MS-MS) is gradually becoming important for pesticide residue analysis [27-28]. Monitoring of secondary fragmentation products provides greater discrimination from matrix interferences than the use of primary fragmentation products that is single-stage MS operation mode. In fact, this technique enables analysis of pesticides at trace levels in the presence of many interfering compounds. The controlled MS fragmentation is an essential tool for obtaining confidence in pesticide identification. The chromatographic system consisted of Applied Biosystems HPLC equipment (model API3200) including an HPLC ternary pump, a Waters LC analytical column (model Column Restek UHPLC Column), length 100 mm, inside diameter 2.1 mm, particle size 1.9 µm, pore size 140 Å, mobile phase A: Ammonium formate solution in water, c = 5 mmolL⁻¹, mobile phase B: Ammonium formate solution in methanol 5 mmolL⁻¹. Column temperature 40°C. The sample is manually diluted with mobile phase A before being injected.

3. Results and discussion

3.1. Effect of the NaCl Concentration

Variation of NaCl concentration were applied to investigate the removal of carbendazim under the following conditions: 80 mAcm⁻² of current density, temperature of 25°C, pH =6.7, initial concentration 30 mgL⁻¹, the time of electrolysis is 120 min. Figure 2 represent the effect of different NaCl concentrations on the degradation rate of carbendazim and the corresponding COD elimination [10, 12-13]. A general trend was observed: an increase of the carbendazim degradation rate and COD removal with decreasing the electrolyte concentration up

to 0.1gL^{-1} using DDB electrode. Further increasing the NaCl concentration up to this value leads to not change in the rate of carbendazim degradation and COD removal [24-27].

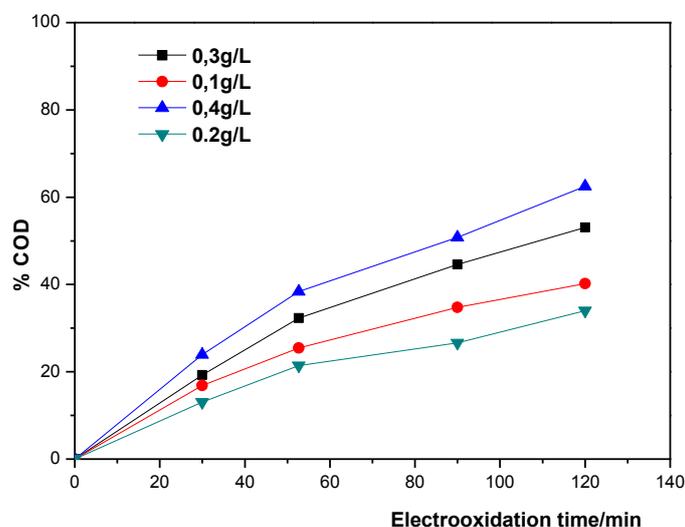


Figure 2. Effect of NaCl concentration on the % COD (30 mg.L^{-1} carbendazim solution, 80 mA.cm^{-2} , $\text{pH}=6.7$, and $T=25^\circ\text{C}$).

The decay of COD concentration exhibits an exponential behavior with all the applied current indicating a first-order reaction kinetics for the oxidation reaction[17-18]. Working in galvanostatic condition, the concentration of OH^- or Cl^- can be approximated in a steady state and therefore, the oxidation rate expression can be written as follows:

$$\frac{d[\text{COD}]}{dt} = K[\text{OH}^\cdot][\text{COD}] = K_{\text{app}}[\text{COD}]$$

This can be integrated to give the following expression:

$$\ln\left(\frac{\text{COD}_0}{\text{COD}_t}\right) = K_{\text{app}}t$$

Where COD_0 and COD_t are the COD of the solution at the beginning and at time t respectively, and k_{app} is the apparent observed pseudo first-order rate constant. Apparent rate constants determined by plotting the $\ln(\text{COD}_0/\text{COD}_t)$ against time at different applied current (**Table 1**). Figure 3 illustrate the apparent kinetic constants for oxidation of carbendazim at different concentration of NaCl as a function of the electrolysis time [18-19]. The apparent kinetic constants constant of carbendazim (k) varies from $82 \times 10^{-4}\text{ min}^{-1}$ for 0.1gL^{-1} , $63 \times 10^{-4}\text{ min}^{-1}$ for 0.2 gL^{-1} and $42 \times 10^{-4}\text{ min}^{-1}$ for 0.3 gL^{-1} , 35×10^{-4} for 0.4 gL^{-1} of NaCl.

3.2. Effect of current density

As shown in Figures (4-5) carbendazim COD removal increase with increasing the applied current density up to 80 mAcm^{-2} by using DDB electrode. Further increase of the current density was followed by gradual decrease in carbendazim COD removal due to increase in temperature [14-19]. In other words, the rate of degradation of carbendazim increases with increase in current density by maintains a moderate temperature. Different current densities were applied to investigate the optimum current density for degradation of carbendazim. Optimum current density is 80 mAcm^{-2} , at which the maximum removal of carbendazim is observed. The treatment processes were carried out for 120 min under the temperature of 25°C , $\text{pH}=6.7$ and using DDB electrode, initial concentration 30 mgL^{-1} and the concentration of NaCl is 0.1gL^{-1} [15].

The electro-degradation was carried out at current density of 80 mA cm^{-2} . At this value there is a great possibility of electro-generation of Cl_2 in solution. As current density is increased, hypochlorite production also increases. However cell temperature increases with increasing current density. All these observations were depicted in figure 4.

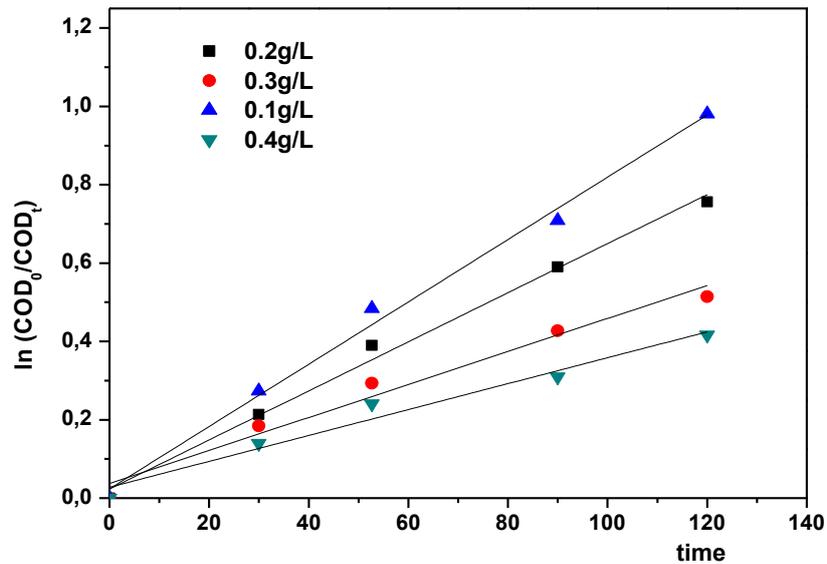


Figure 3. Pseudo first-order plot oxidation of carbendazim 30 mgL^{-1} in 0.1 gL^{-1} NaCl at 25°C under different current inputs.

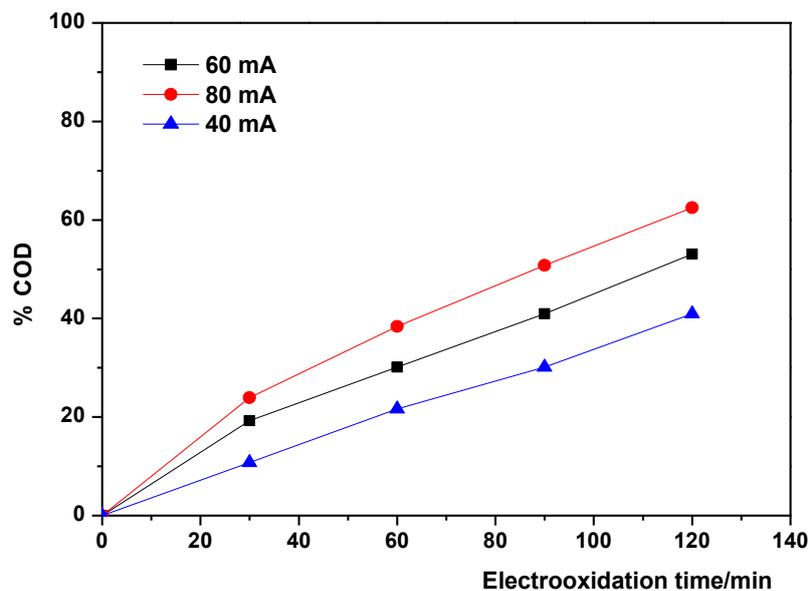


Figure 4. Effect of applied current on the COD% (30 mg.L^{-1} carbendazim solution, $\text{pH}=6.7$, and $T=25^\circ\text{C}$)

The COD of carbendazim was observed to fall with pseudo first-order kinetics (fig.5), on all the surface studied. This is related to the dependence of the rate of oxidation on the rate of formation of the oxidising species at the electrode surface, the pseudo first-order constant of carbendazim (k) varies from $44 \times 10^{-4} \text{ min}^{-1}$ (40 mA) to $82 \times 10^{-4} \text{ min}^{-1}$ (80 mA). From these results it was calculated that the best applied current is 80 mA.

3.3. Effect of concentration

Different standard solutions of carbendazim with concentration from $15\text{--}45 \text{ mgL}^{-1}$ were prepared to measurement the degradation in different conditions. The effect of carbendazim concentration on the rate of COD removal using DDB electrode was investigated. This investigation was carried out under the optimum operating conditions mentioned above [15, 17-18].

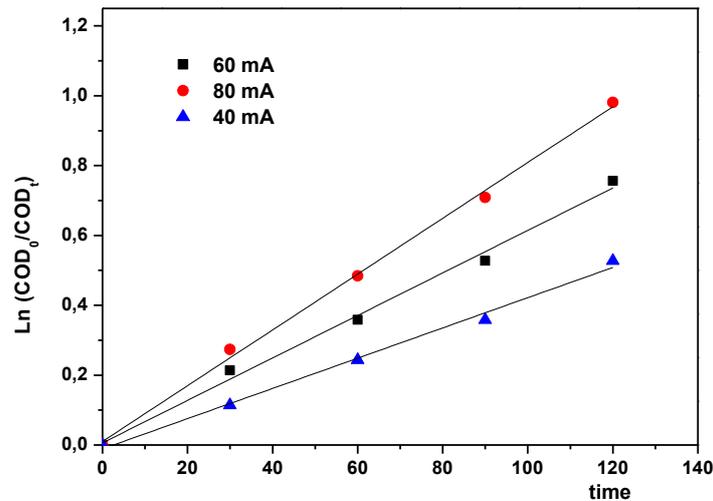


Figure 5. Pseudo first-order plot oxidation of carbendazim 25°C, 0.1g.L⁻¹NaCl at 80 mA/cm², pH=6.7 for different concentration.

Figures (6-8) show the effect of different initial carbendazim concentrations on the rate of remaining concentration (mg.L⁻¹) and COD removal. The removal of the carbendazim and COD can be achieved in the presence of initial carbendazim load up to 45 mg.L⁻¹. However, increasing the carbendazim concentration above this level resulted in a decrease in the electrooxidation rate of degradation. The removal efficiency of the carbendazim by using DDB electrode at 45 mg.L⁻¹ was the optimum concentration for the initial load concentration of carbendazim. These experiments were carried out under the operating conditions of current density is 80 mA.cm⁻², pH=6.7 and using DDB electrode, temperature 25°C and the concentration of NaCl 1g.L⁻¹. The time of electrolysis was 120 min using DDB electrode.

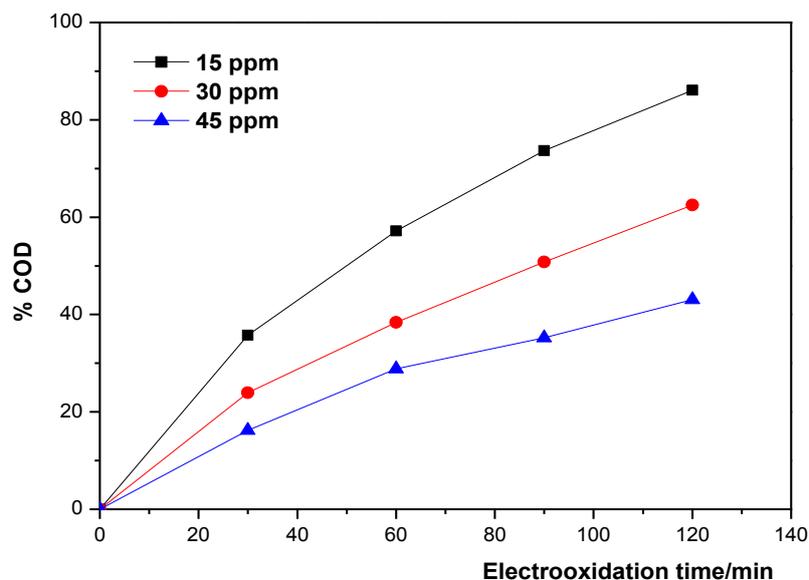


Figure 6. Effect of initial concentration of carbendazim on the COD% (80 mA/cm², pH=6.7, and T=25°C)

The pseudo first-order constant of carbendazim (k) varies from $44 \times 10^{-4} \text{ min}^{-1}$ (40 mA) to $82 \times 10^{-4} \text{ min}^{-1}$ (80 mA). This is exemplified in Figure 7 where the pseudo first-order plot is presented. From these results it was calculated that the best applied current is 80 mA.

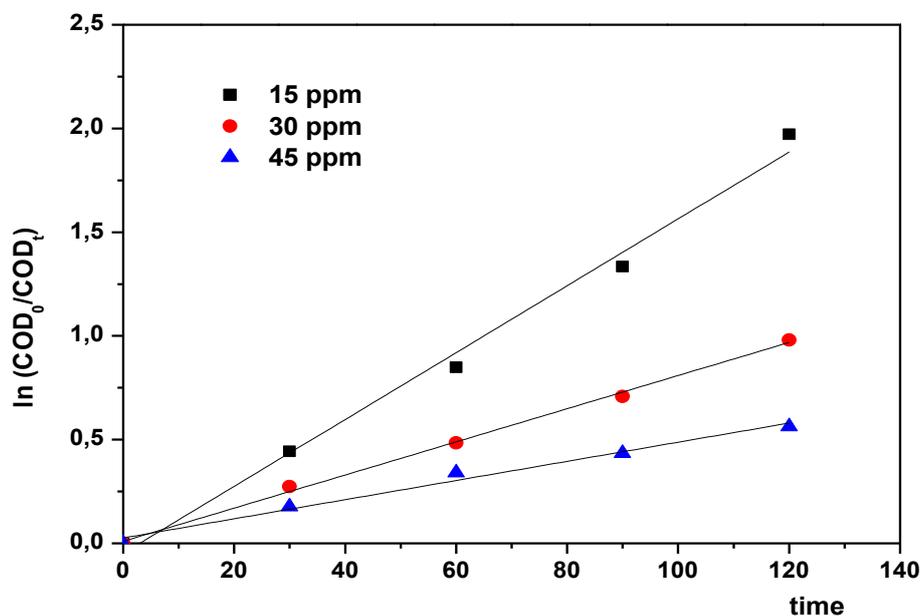


Figure 7. Pseudo first-order plot oxidation of carbendazim 30 mgL^{-1} in 0.1 gL^{-1} NaCl at 25°C under different current inputs.

As a reason to confirm the degradation of carbendazim we have uses another technical to follow the kinetic in order to approve that our results are similar relative of COD analysis (figure 8).

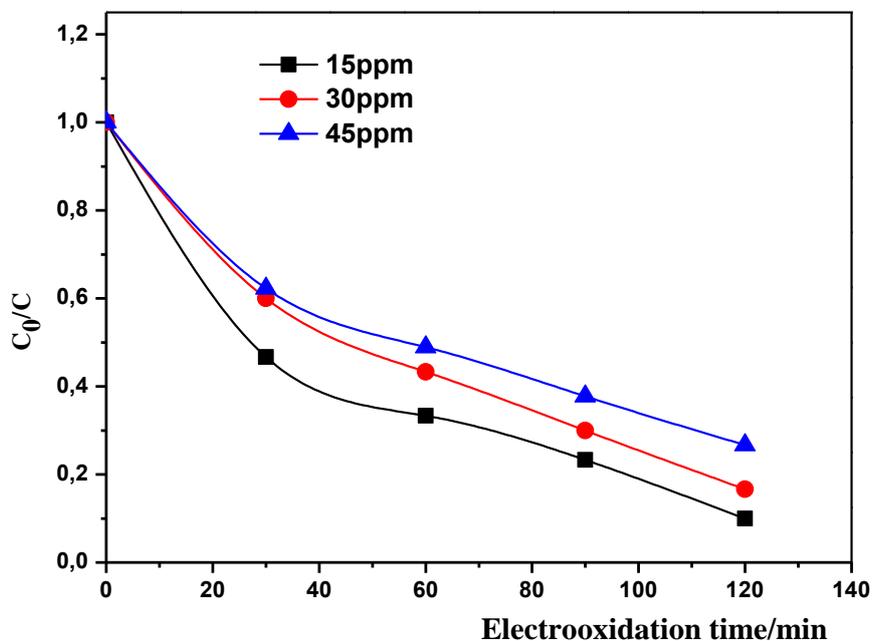


Figure 8. Influence of carbendazim concentration during DBB anodic oxidation (Operating conditions: electrolyte = 0.1 gL^{-1} NaCl, current density = 80 mAcm^{-2} , $T = 25^\circ\text{C}$, and $\text{pH}=6.7$).

The results of studying the possibility of using DDB electrode in the treatment of carbendazim and COD removal were presented in Table 1.

Table 1. Values of COD percentage and rate constant of carbendazim, for each type of operating condition.

Type of operating condition	Operating quantity used	Rate constant K(min ⁻¹)	COD Removal (%)
NaCl Concentration (gL ⁻¹)	0.1 gL ⁻¹	82x10 ⁻⁴	62.5
	0.2 gL ⁻¹	63 x10 ⁻⁴	53
	0.3 gL ⁻¹	42 x10 ⁻⁴	40
	0.4 gL ⁻¹	35 x10 ⁻⁴	34
Concentration of Carbendazim (ppm)	15 ppm	164 x10 ⁻⁴	86
	30 ppm	82 x10 ⁻⁴	62.5
	45 ppm	47 x10 ⁻⁴	43
Current intensity (mA/cm ²)	80 mA/cm ²	82 x10 ⁻⁴	62.5
	60 mA/cm ²	63 x10 ⁻⁴	53
	40 mA/cm ²	44 x10 ⁻⁴	41

The effect of different operating conditions such as: current density, initial concentration carbendazim and NaCl concentration were studied. From the results of this study, the optimum operating conditions for that electrode to degradation carbendazim pesticide were determined. At these conditions, the electrode is more efficient at the optimum results for the removal of COD.

Conclusion

The main conclusions of this work can be summarized in the following points:

- BDD-anodic oxidation can be used successfully to remove almost all the COD of synthetic wastewaters polluted with carbendazim.
- For 0.1 gL⁻¹NaCl and 0.2 gL⁻¹NaCl the achieved reduction were 62.5% and 53% respectively. For 0.3 gL⁻¹NaCl and 0.4 gL⁻¹were 40% and 34% respectively.
- The COD of carbendazim was observed to fall with pseudo first-order kinetics, on all the surface studied.
- The applied current increases the rate of electrochemical oxidation process.

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