Oxidation of the Pesticide Dicofol at Boron-Doped Diamond Electrode

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1. Introduction

The contamination of the environment by toxic substances is linked both to industrialization and to agriculture. Toxic substances find their way into ecosystems from discharges and leaks of industrial products, consumer wastes and urban sewage, from farming and forestry runoff, and from accidental spills. Organochlorine pesticides (OP), such as dicofol, cypermethrin and hexachlorocyclohexane (HCH), are potentially toxic, highly persistent and resistant to biodegradation and it readily accumulates in human body tissues, causing a variety of health hazards [1]. Due to the long residence time of these substances in the environment, there is a great interest in examining the pollution they cause. Various technologies and processes, such as hydrogen peroxide, extraction, UV, ultrasonic radiation and biodegradation have been proposed for dicofol treatment. The major disadvantage of these technologies is that they are not suitable for the higher concentrations of unwanted pesticides.

Recently, the electrochemical oxidation has become one of the most promising techniques for the treatment of wastewaters, which is environmentally compatible with the cleanest oxidant, electron, easy to control and without secondary pollution [2]. This technology has been applied in the purification of domestic sewage [3,4] tannery waste liquors [5] landfill leachate [6] olive oil wastewaters [7, 8]. Boron-doped diamond (BDD) electrodes have received much interest due to their high resistance to fouling by chemisorbed metals or other impurities, high mechanical strength, very low catalytic activity for oxygen evolution, high chemical attack, high mechanical strength and high stability under anodic polarization [9-12]. These properties have allowed the BDD electrodes to be used in a wide variety of electrochemical applications [13-15]. Recently, Salghi and co works [13, 16-17, 22-24] demonstrated that the pesticides difenoconazol, bupirimate can be electrochemically removed from aqueous solutions using BDD anodes. They found that current density influence is remarkably clear on the BDD electrodes.

The objective of this work is to study the electrochemical oxidation of aqueous wastes containing dicofol using boron doped diamond thin-film electrodes, and to determine the influence of the waste characteristics and the main operation parameters (temperature and current density) on the process.

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ABSTRACT

The electrochemical oxidation of dicofol pesticide was performed using a boron doped diamond (BDD) electrode, commercially available at Adamant Technologies. Tests were performed with model solutions of dicofol, with concentrations ranging from 25 to 75 ppm for the BDD electrode, using different concentration of NaCl as the electrolyte, in a batch cell, at different current densities (30, 50 and 70 mAcm$^{-2}$). GS/MS and Chemical Oxygen Demand (COD) tests were conducted for all samples. The results have shown a very good degradation of dicofol pesticide, with COD removals between 53 and 89% and % removals for concentration varying from 77 to 97%, in 3 hours experiments. General Current Efficiency and Mineralization Current Efficiency, determined for BDD electrode, show a good degradation for 70mAcm$^{-2}$ but a very less at 30 mAcm$^{-2}$. The best obtained conditions for COD removal on the BDD anode to degrade dicofol solutions include operating at 70 mA cm$^{-2}$ and 25 °C. The high efficiency of this technology can be explained in terms of the direct electrooxidation at the BDD surface and the oxidation carried out by hydroxyl radicals (OH$^\cdot$) and other electrogenerated oxidants (Cl$^-$, CI$O^-$).

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2. Materials and methods

2.1. Chemicals

Dicofol, is a non-systemic organochlorine acaricide that is extensively used on a wide variety of fruit trees, vegetables, ornamental and field crops [18, 19]. It has a moderate acute oral toxicity and a relatively high degree of acute dermal toxicity as being a nerve poison. Dicofol is identified chemically as 2,2,2-trichloro-1,1-bis(4chlorophenyl)ethanol (Figure 1).

![Chemical structure of dicofol](image)

Figure 1: Chemical structure of dicofol

2.2. 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 0.5 cm. A saturated calomel electrode was used as a reference Galvanostatic electrolysis was carried out with a volume of 75 cm^3 aqueous solution of 50 mg L⁻¹ de dicofol. The range of applied current was 30 – 70 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 and operating conditions: T= (25±3)°C; i=70 mA. cm⁻².

2.3. Liquid-liquid and solid-phase extraction procedure

The method used for the extraction of dicofol was adapted from Charles and Raymond [21]. For each 1 ml of the sample, 100 mL of acetonitrile 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 acetonitrile were partitioned with saturated aqueous NaCl (30 mL) and dichloromethane (70 mL) in a separating funnel. The extraction was repeated with another 70 mL 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 acetonitrile/hexane (1: 9) mixture (10 mL). In the clean-up step, 1mL of the extract was collected and evaporated on a rotatory evaporator at 40°C and the residues were dissolved in an acetonitrile/hexane (1: 9) mixture (10 mL). The pesticide residues were eluted with acetonitrile/diethyl ether (6: 4) (4 mL). All samples were extracted separately and analysed by gas chromatography.

2.4. Chromatographic conditions

Analysis of dicofol was carried out with a Hewlett-Packard 6890 gas chromatograph (PaloAlto, CA, USA) equipped with an ECD Detector, split/split less injection port, and HP-5 column (5 % diphenyl copolymer/95 % dimethylpolysiloxane) (25 m x 0.32 mm ID, ID, 0.52 µm film thickness); and temperature programming from 80° to 250°C (15°C/min); injector temperature 250°C and detector temperature 300°C. carrier gas (helium) flow rate, 2.6 mL/min; makeup gas (nitrogen) flow rate, 60 mL/min; injection volume, 1 µL; and splitless time, 0.1min.

3. Results and discussion

3.1. Effect of the NaCl concentration

Figure 2 shows the influence of the chloride ions present in fractional conversion of dicofol at acide pH and 70mAcm⁻². A considerable increase in degradation at shorter times was observed when chloride ions were present. Final current efficiencies for COD in the 0.5g/L and presence of 1.5g/L NaCl were 53 and 90%, respectively. However, more information can be obtained from the analysis of the experiments in the absence of chloride anions.

![Evolution of concentration dicofol during galvanostatic electrolyses of wastes polluted with 25 mg.L⁻¹ of dicofol pesticide under effect of NaCl concentration.](image)

Figure 2: Evolution of concentration dicofol during galvanostatic electrolyses of wastes polluted with 25 mg.L⁻¹ of dicofol pesticide under effect of NaCl concentration. Operating conditions: T= (25±3)°C; i=70 mA. cm⁻².

3.2. Liquid-liquid and solid-phase extraction procedure

The method used for the extraction of dicofol was adapted from Charles and Raymond [21]. For each 1 ml of the sample, 100 mL of acetonitrile 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 acetonitrile were partitioned with saturated aqueous NaCl (30 mL) and dichloromethane (70 mL) in a separating funnel. The extraction was repeated with another 70 mL 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 acetonitrile/hexane (1: 9) mixture (10 mL). The pesticide residues were eluted with acetonitrile/diethyl ether (6: 4) (4 mL). All samples were extracted separately and analysed by gas chromatography.

![Pseudo first-order plot oxidation of 50 mg/L Dicofol in concentration of NaCl at at T= (25±3)°C; iapp=70 mA.cm⁻².](image)

Figure 3: Pseudo first-order plot oxidation of 50 mg/L Dicofol in concentration of NaCl at at T= (25±3)°C; iapp=70 mA.cm⁻². (COD at a given time, t during electrolysis)
The Ln ([COD]_t/ [COD]_0) vs. time plot appears to be linear (Fig 3), which means that the process is kinetic under mass transport control. Thus, we can obtain the mass transport coefficient from the slope of the linear plot. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of pesticide on the electrode or indirect via some mediators like chlorinated species or other radicals [12-14]. The effect of supporting electrolyte NaCl on rate constant increased with decreasing concentration of NaCl and the higher reaction rate constant (1.36 x 10^2 min^-1) was obtained at 1.5g/L of NaCl supporting electrolyte. This indicates that the dicofol molecules were easily attacked by hydroxyl radicals at lower concentration of NaCl. These results are in agreement with previously reported results [14].

3.2. Effect of current density

The role of current density has been followed, testing values smaller that the previously considered as the optimum. The influence of the current density on the COD removal during the electrochemical oxidation of dicofol at the anode is shown in Fig. 4.

As expected, the COD abatement is faster as the current density is greater, but the results are a logical consequence of the major quantity of charge passing in solution. On the other hand, the application of the highest current density can be suggested in order to obtain the complete abatement of the organic content in the smallest time; obviously, the efficiency of the oxygen evolution reaction is larger at higher current densities [13, 17, 22-24].

Figure 4: Influence of current density on the decay of concentration pesticide during electrooxidation of 50 mg L^-1 dicofol. Conditions: NaCl (1.5 g L^-1), and T = 25 °C.

After 2h time of electrolysis, the COD percent removal increased from 44% to 90% when the current density increased from 30 to 70 mA.cm^-2. This behavior indicates that in these experimental conditions, the oxidation of dicofol is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]

This was confirmed by the fact that the COD (mg/L of O_2) decreased with the current density. The decay of COD concentration exhibits an exponential behavior with all the applied current indicating first-order reaction kinetics for the oxidation reaction. Working in galvanostatic condition, the concentration of \( \cdot \)OH can be approximated in a steady state and therefore, the oxidation rate expression can be written as follows [13, 17, and 22]:

\[ \frac{d[COD]}{dt} = K[OH] [COD] = K_{app}[COD] \]

This can be integrated to give the following expression:

\[ \text{Ln}\left(\frac{\text{COD}_0}{\text{COD}_t}\right) = K_{app} t \]

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 pseudo first-order rate constant. Apparent rate constants determined by plotting the Ln (COD_0/COD_t) against time at different applied current (Figure Table 1).

Figure 5: Pseudo first-order plot oxidation of 50 mg/L Dicofol on BDD anode under different current density. Conditions: NaCl (1.5g/L), and T = 25 °C.

The instantaneous current efficiency (ICE) can be defined as the art of the current directly used for the oxidation of the organic compounds [13, 17, and 24]. ICE during electrolysis can be performed from the decrease of COD by means of the following relation: where F is the Faraday constant (96,487 C.mol^-1), V is the volume of the solution (L), COD_t and COD_{t+Δt} are the chemical oxygen demands at times t and t+Δt (gO_2 L^-1), respectively, and I is the current (A).

Figure 6: ICE during the electrochemical oxidation of dicofol (C_0= 50 mg.L^-1) on the BDD anode. NaCl (1.5g/L) and T=25°C.
The instantaneous current efficiency (ICE) can be defined as the art of the current directly used for the oxidation of the organic compounds [13, 17, and 24]. ICE during electrolysis can be performed from the decrease of COD by means of the following relation: where \( F \) is the Faraday constant (96,487 C.mol\(^{-1}\)), \( V \) is the volume of the solution (L), COD\(_t\) and COD\(_{t+\Delta t}\) are the chemical oxygen demands at times \( t \) and \( t+\Delta t \) (gO\(_2\) L\(^{-1}\)), respectively, and \( I \) is the current (A).

**Table 1:** Effect of the current intensity on the values of the rate constant and the %COD.

<table>
<thead>
<tr>
<th>Current intensity (mA.cm(^{-2}))</th>
<th>Rate constant, ( K ) (min(^{-1}))</th>
<th>%ICE</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>((6.20 \pm 1.2) \times 10^{-3})</td>
<td>14.3</td>
</tr>
<tr>
<td>50</td>
<td>((8.70 \pm 0.8) \times 10^{-3})</td>
<td>8.12</td>
</tr>
<tr>
<td>70</td>
<td>((13.7 \pm 1.4) \times 10^{-3})</td>
<td>5.2</td>
</tr>
</tbody>
</table>

The ICE decrease exponentially with the specific charge. It is worth noting that the observed 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 70 mA.cm\(^{-2}\) by using BDD electrode. Further increase of the current density was followed by gradual decrease in dicofol degradation and COD removal due to increase in the mass-transfer limitation.

### 3.3. Effect of concentration of pesticide

The initial concentration of pesticide is always an important parameter in wastewater agriculture treatment. Fig. 7 shows the effect of the initial concentration of dicofol. Experiments on the electrochemical destruction of dicofol pesticide were carried during electrolysis at pH 6.7, temperature of 25 °C and using a current density of 70mA.cm\(^{-2}\). The effect of several concentration of pesticide was investigated. The experimental data was curving fitted (Fig. 7).

\[
C = C_0 \exp(-bt)
\]

For low concentrations (\( C_0 = 25 \) and 50 mg.L\(^{-1}\)), the Concentration decreased to zero after about 3 h, meaning complete degradation of dicofol. However, for higher concentrations, the total degradation requires longer time of electrolysis as shown in the trend of the curve (\( C_0 = 75 \)mg.L\(^{-1}\)) in Fig. 7. kapp values (Table 3) calculated from the straight lines, considering a second-order reaction (Fig. 7), decreased when the initial concentration of dicofol increased. However, overall mass transfer rates increased with the increase of the initial COD (in Table 3, we showed the initial overall mass transfer rate) [13, 17], which explains the fact that the degradation rate was found increasing with the increase of the initial concentration.

**Table 2:** Effect of the concentration pesticide on the values of the rate constant and the Concentration removal %

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Rate constant, Kapp (s(^{-1}))</th>
<th>Concentration removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>((1.12 \pm 0.81) \times 10^{-4})</td>
<td>77%</td>
</tr>
<tr>
<td>50</td>
<td>((1.61 \pm 0.96) \times 10^{-4})</td>
<td>86%</td>
</tr>
<tr>
<td>25</td>
<td>((3.32 \pm 0.75.4) \times 10^{-4})</td>
<td>99%</td>
</tr>
</tbody>
</table>

### 3.4. Effect of initial 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 [24 –26]. The effect of solution initial pH on the electrooxidation of pesticide has been previously investigated by many works [14, 22, and 25]. Some authors reported that the oxidation process is more favorable in acidic media [14]. In contrast, others indicated that the efficiency of the process was increased in alkaline media [22 -26]. According to this literature, it can be concluded that the effect of pH strongly depends on the nature of the investigated pesticide and of the supporting electrolyte. Therefore, the effect of pH on the degradation rate of dicofol was studied at large pH range from acidic to basic. The solutions of dicofol (50 mg L\(^{-1}\)) were electrolyzed at pH values of 2, 6.9, and 12 (Fig. 8).

**Figure 7:** Influence of the initial concentration pesticide during electrolysis on the BDD anode. \( I_{app} = 70 \text{ mA cm}^{-2} \), \( \text{pH} = 6.7 \), \( \text{NaCl} = (1.5 \text{ g L}^{-1}) \) and \( T = 25^\circ \text{C} \).

**Figure 8:** Influence of pH on the destruction of dicofol. Conditions: \( T=25^\circ \text{C} \), \( 1.5 \text{ g/L(NaCl)} \), initial concentration of pesticide 50 mg/L, set current densities70mA/cm\(^2\), working electrodes BDD, counter-electrode Pt.
Actually, pH values below 3 are known to favor chemical oxidation pathways involving hydrogen peroxide (e.g. Fenton reactant [4]). It might be guessed that a certain role in this context is also played by the higher concentration of sulfates present in the anolyte after sulfuric acid addition. The higher the sulfate concentration, the more favored the persulfate formation and the consequent HO₂ generation by persulfate hydrolysis.

### Table 3: Effect of the solution pH on the values of the rate constant and the Concentration removal %.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Rate constant, Kapp (s⁻¹)</th>
<th>Concentration removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(3.38 ± 0.81) × 10⁻⁴</td>
<td>98%</td>
</tr>
<tr>
<td>6</td>
<td>(2.19 ± 0.96) × 10⁻⁴</td>
<td>87%</td>
</tr>
<tr>
<td>9</td>
<td>(1.58 ± 0.75) × 10⁻⁴</td>
<td>63%</td>
</tr>
<tr>
<td>12</td>
<td>(1.01 ± 0.75) × 10⁻⁴</td>
<td>51%</td>
</tr>
</tbody>
</table>

As can be seen from this figure, the pH of the medium slightly affects the degradation kinetics of SC and this indicates that the degradation of dicofol caramate can be performed at pH value 2 without significant increased in oxidation efficiency of the system (table 3). For this reason, the electrochemical oxidation is a viable treatment for electrooxidation of pesticides where adjustment of the effluent’s pH are recommended.

### 4. Conclusions

The electro-degradation of dicofol has been investigated under galvanostatic conditions using BDD anode at various current densities, supporting electrolytes, solution pH and in a wide range of pesticide concentrations. The experimental results showed that:
- The best results were obtained when electrolyses were carried out at high densities, 70 mA cm⁻², and in the presence of supporting electrolyte NaCl (1.5 g L⁻¹) with T=25°C.
- The removal rate of COD increases with applied current density until 70 mA cm⁻² 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 basic solution (pH = 12) to neutral solution (pH = 7), 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 dicofol pesticide.

### References