



## Electrooxidation of cypermethrin pesticide: A Comparative Study of SnO<sub>2</sub> and Boron Doped Diamond Anodes

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### ABSTRACT

Conventional wastewater treatment techniques are inefficient to manage large quantities of refractory organics discharged by specialty chemical industries. The aim of this work was to investigate the approaches to reduce the negative impacts of cypermethrin on the environment. Specifically, two approaches to electrooxidize cypermethrin are compared. The first approach was based on the use of SnO<sub>2</sub> anode. This electrode is a commercial grid of 1cm<sup>2</sup> of SnO<sub>2</sub>. The second approach was based on the use of Boron Doped Diamond (BDD) anode. The influence of several operating parameters, such as applied current density, initial cypermethrin insecticide concentration, temperature, and supporting electrolyte, was investigated. GC and chemical oxygen demand measurements were conducted to study the reaction kinetics of pesticide mineralization. The results showed that the rate of the electrooxidation increases with increasing current density and decreasing NaCl. The overall results indicated that BDD electrode exhibited the best performance.

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

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### INTRODUCTION

Pesticides are used in agriculture and they have an important role, but the prevention of their negative effects requires a systematic control of their content remaining in agricultural products, food, soil and water. More than 600 kinds of agrochemicals are used around the world [1]. Pesticides have been determined in different kinds of samples such as soil [2], liver samples of birds [3], agrochemicals [4,5] and water samples [6,7]. In previous works, the electrochemical incineration of cypermethrin as a model organic substrate has been studied, at different anode materials [8-10] and in presence of chloride as incineration mediator [11].

Various innovative technologies have been proposed for the disposal of obsolete pesticides.

These technologies include photocatalytic oxidation [12, 13], ultrasonic radiation [14], bioremediation and thermal desorption [15].

Electrochemistry is another alternative that has attracted considerable research attention [8-11]. Toxic organics can be effectively oxidised by electrochemical reaction [16-18]. With unique features such as simplicity and robustness in structure and operation, the EC process has the potential to be developed as a cost-effective technology for the treatment of aromatic pollutants, particularly for low volume applications.

In anodic oxidation [19–28], organic pollutants are directly destroyed by reaction with adsorbed hydroxyl radical formed at the anode surface from water oxidation:

The recent use of a boron-doped diamond (BDD) thin film anode [8–10] in anodic oxidation has shown that its  $O_2$  overvoltage is much higher than that of conventional anodes such as  $PbO_2$ , doped  $SnO_2$ ,  $IrO_2$  and Pt, then producing larger amounts of adsorbed  $OH^\bullet$  by reaction

(1), giving a more rapid destruction of pollutants.



Cypermethrin is a synthetic chemical similar to the pyrethrins in pyrethrum extract (which comes from the chrysanthemum plant). Pyrethroids, including cypermethrin were designed to be effective longer than pyrethrins [28]. Cypermethrine (Cyano(3-phenoxy phenyl) methyl 3-(2,2-dichloro ethenyl)-2,2-dimethyl cyclopropane carboxylate) is a widely used petroide pesticide for crop production and fruit tree treatment. It is a very toxic substance for all organisms and graded to the first toxicity category according to the Environmental Protection Agency (US) [29-31]. This paper discusses the treatment of cypermethrin by an electrochemical method, in laboratory scale plant using an  $SnO_2$  electrode as anode.

## EXPERIMENTAL SECTION

### Chemicals

Cypermethrin is a pyrethroid insecticide. is a local systemic insecticide that is effective for control of cutworms (*H.armigera*) in the tomato crop and pepper in area of Agadir (Morocco). Cypermethrin formulation is commercially available in the AZTEC 25 EC ( 250 g/L Cypermethrin) (Figure 1).

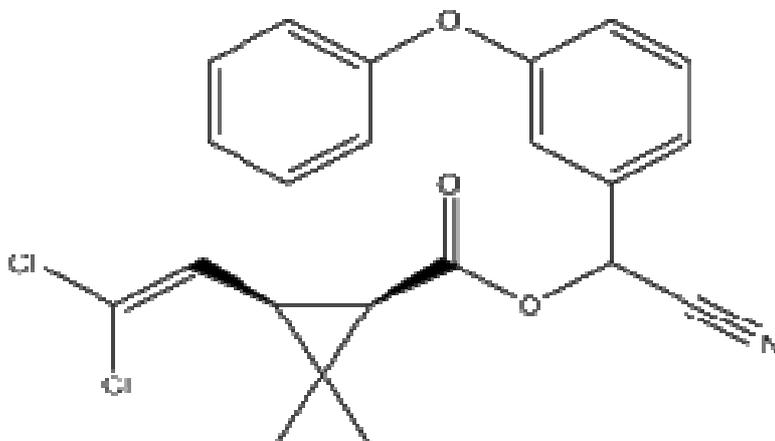


Figure 1. Chemical structure of Cypermethrin.

It was purchased from EZZOUHOUR (Morocco). 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 electrodes cell ( $100\text{ cm}^3$ ) thermoregulated glass cell was used (Tacussel Standard CEC/TH).

The anode was a square plate of BDD electrode or  $SnO_2$  with effective surface area of  $1\text{ cm}^2$ , whereas the cathode was a platinum electrode, and the gap between electrodes was 5 mm. A saturated calomel electrode (SCE) was used as a reference.

Galvanostatic electrolysis was carried out with a volume of 75 cm<sup>3</sup> aqueous solution of 50 mg/L. The range of applied current density was 40 to 80 mA/cm<sup>2</sup> 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.

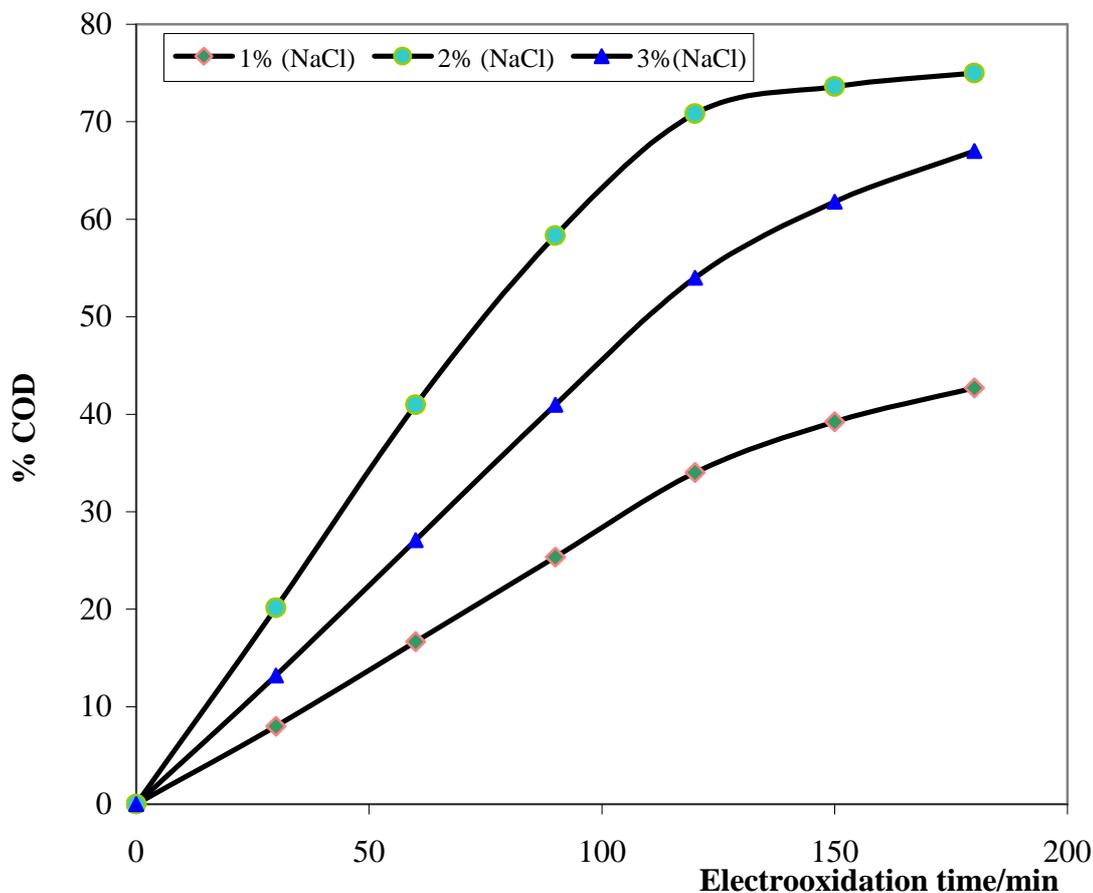
The chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [33]. The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

#### *Analytical procedures*

The method used for the extraction of cypermethrin was adapted from Charles and Raymond [34]. For each 5 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 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.

#### *Gas Chromatography analysis*

Analysis of the cypermethrin pesticide was carried out with a Hewlett–Packard 6890 gas chromatograph equipped with an ECD Detector, on-colum injection port, and HP-5 column (5% diphenyl copolymer/95% dimethylpolysiloxane) (25 m × 0.32 mm ID, 0.52 μm film thickness). The temperature program applied in GC/ECD was as follows: 80–250°C at 15°C/min, 80°C (1.00 min). The injection volume was 1 μl. The temperature of the detector was 300°C.



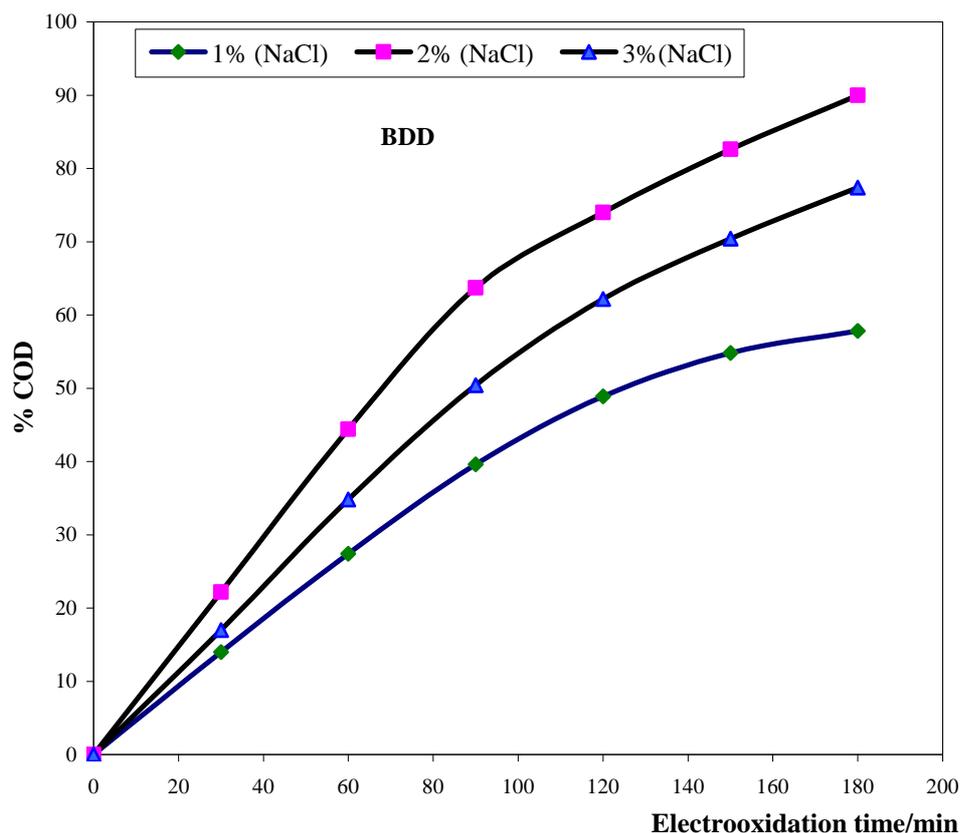


Figure 2 a) Direct electrooxidation at BDD anode: effect of NaCl concentration on the %COD (50 mg.L<sup>-1</sup> cypermethrin solution, 80mA.cm<sup>-2</sup>, pH=5.4, and T=25°C) b) Direct electrooxidation at SnO<sub>2</sub> anode: effect of NaCl concentration on the %COD (50 mg.L<sup>-1</sup> cypermethrin solution, 80mA.cm<sup>-2</sup>, pH = 5.4, and T = 25°C).

## RESULTS AND DISCUSSION

### *Effect of the NaCl concentration*

Electrolytes of NaCl of the following salts: 1%, 2%, and 3% were studied by BDD and SnO<sub>2</sub> electrode. As appears in Fig. 2, the NaCl were the most effective conductive electrolyte for the electrocatalytic degradation of the investigated cypermethrin and COD removal while 1% (NaCl) and 1% (NaCl) electrolytes show poor results.

As shown in this graph, the % COD increases with the increase of electrooxidation time but decreases with the amount of NaCl in the solution. This indicates that at low concentration of NaCl, the cypermethrin removal ratios increased with time. The presence of a low concentration of chloride ions (2% of NaCl) allows inhibiting the water discharge into oxygen, and promotes hydroxyl, chloride, and oxchloride radicals formation [8]. The increase of the NaCl concentration (>3%) could cause a “potentiostatic buffering” by the chlorine redox system and, consequently, a decrease of the anode potential. It is also possible that the presence of competitive reactions, in particular oxygen and chloride evolution due to recombination of radicals that becomes bigger with the increasing of NaCl concentration. The balance of all of these phenomena results in an optimum of NaCl concentration, which is 2% mass of NaCl for the degradation of cypermethrin insecticide.

Further increase, above this limit, causes an inversion of the trend. Possibly, when the chloride concentration becomes sufficiently high, a decrease of the anode potential takes place, due to the potentiostatic buffering by the chlorine evolution reaction. The balance of all of these phenomena results in an optimum of NaCl concentration, which is 2% mass of NaCl for the degradation of cypermethrin. The achieved reduction was 92% and 74% for 2% NaCl and 3% NaCl respectively, while for 1% NaCl was 57%. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of cypermethrin on the electrode or indirect via some mediators like chlorinated species or other radicals [8-10].

The effect of supporting electrolyte on rate constant increased with decreasing concentration of NaCl and the higher reaction rate constant ( $109 \times 10^{-4} \text{ min}^{-1}$ ) was obtained at 2% of NaCl supporting electrolyte. This indicates that the

cypermethrin molecules were easily attacked by hydroxyl radicals at lower concentration of NaCl. These results are in agreement with previously reported results [9].

**Table 1. Effect of NaCl concentration on the values of the rate constant and the % COD.**

Electrode	Dosages of NaCl	Rate constant, K (min <sup>-1</sup> )	COD removal (%)
<b>BDD</b>	1%	39.10 <sup>-4</sup>	57%
	2%	185.10 <sup>-4</sup>	92%
	3%	109.10 <sup>-4</sup>	77%
<b>SnO<sub>2</sub></b>	1%	42.10 <sup>-4</sup>	67%
	2%	103.10 <sup>-4</sup>	75%
	3%	72.10 <sup>-4</sup>	42%

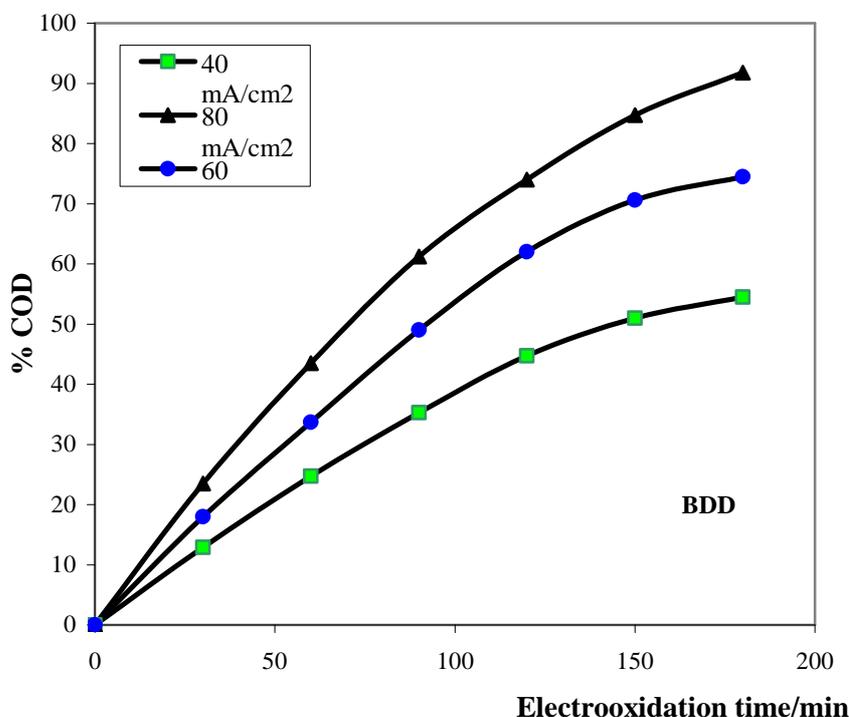
#### *Effect of the applied current density*

The effect of current density on the electrochemical process was reported in several studies [8, -12]. 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). Degradation assays of 50 mg/L cypermethrin solutions were performed using the BDD and SnO<sub>2</sub> electrodes at different current densities (Figures 3-a, 3-b and Table 2).

**Table 1. Effect of applied current concentration on the values of the rate constant and the % COD**

Electrode	Current intensity (mA.cm <sup>-2</sup> )	Rate constant, K (min <sup>-1</sup> )	COD removal (%)
<b>BDD</b>	40	49.10 <sup>-4</sup>	54%
	60	86.10 <sup>-4</sup>	74%
	80	185.10 <sup>-4</sup>	92%
<b>SnO<sub>2</sub></b>	40	37.10 <sup>-4</sup>	44%
	60	56.10 <sup>-4</sup>	53%
	80	103.10 <sup>-4</sup>	76%

Overall, COD removal efficiency increased with increasing applied current density. As illustration, when the current is increased from 40 mAcm<sup>-2</sup> to 80 mAcm<sup>-2</sup> %COD removal increased from 54% to 92% for BDD and from 44% to 76% for SnO<sub>2</sub>.



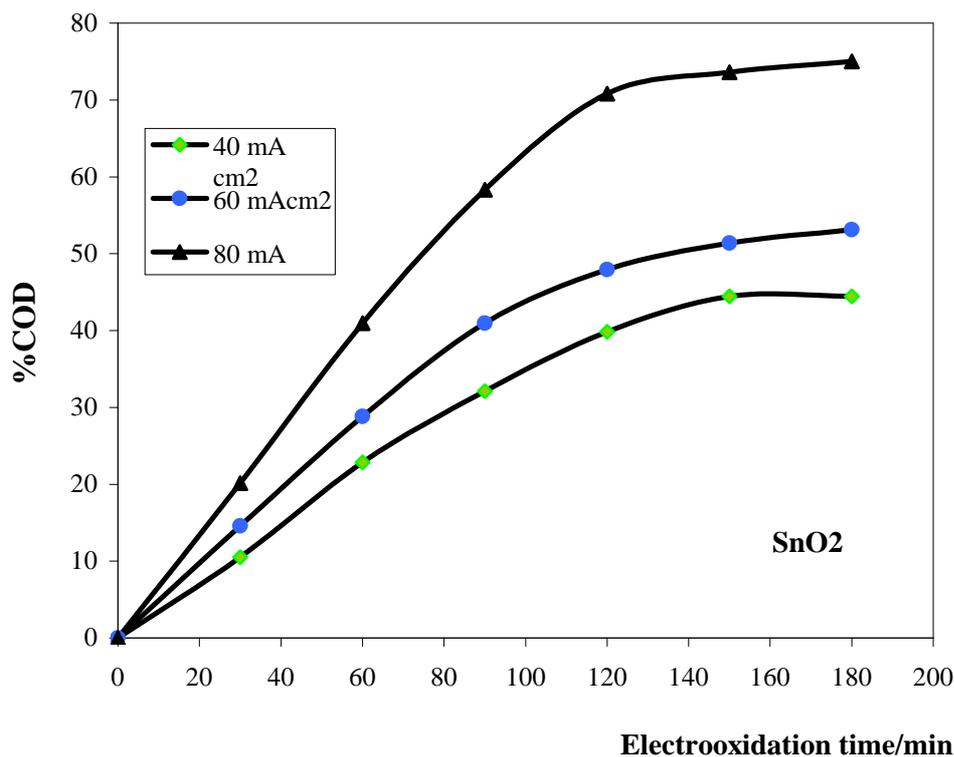


Figure 3 a) Direct electrooxidation at BDD anode: effect of applied current on the %COD (50 mg.L<sup>-1</sup> cypermethrin solution, 80mA.cm<sup>-2</sup>, pH=5.4, and T=25°C) b) Direct electrooxidation at SnO<sub>2</sub> anode: effect of applied current on the %COD (50 mg.L<sup>-1</sup> cypermethrin solution, 80mA.cm<sup>-2</sup>, pH = 5.4, and T = 25°C).

#### *Effect of initial concentrations of cypermethrin on the degradation efficiency*

To investigate the electrooxidation efficiency on high concentration of cypermethrin, the experiments of electrochemical degradation of 25, 50 and 75 mg/L cypermethrin solutions were carried out with a selecting current density and NaCl concentration. Figure 4 shows the effect of the initial concentration of cypermethrin (25, 50 and 75mgL<sup>-1</sup>) on the Concentration removal during electrolysis at pH 5.4, temperature of 25°C and using a current density of 80 mAcm<sup>-2</sup>. Overall cypermethrin oxidation was achieved in all cases but the time for the complete Concentration pesticide removal increased with initial cypermethrin concentration due to the presence of a greater amount of pesticide in the medium [10].

The trends of normalized concentration are moderately overlapped and same electrolysis-times are required to achieve the best values of concentration abatement for two anodes BDD and SnO<sub>2</sub>. This indicates that the oxidation rate and process efficiency are directly proportional to organic matter concentration. This outcome is in agreement with the data reported by salghi *et al.*, [10, 11]. The electrolysis time for complete removal of cypermethrin was proportional to the concentration of that pesticide. In conclusion, the BDD anode performs well for electrochemical degradation of high concentration of pesticide solution with appropriate current density and NaCl concentration as supporting electrolyte.

The concentration of cypermethrin was measured using GC and the variations of cypermethrin concentration with electrolysis time for the two anodes are shown in figure 4. At the same electrolysis time, the rate of electrodegradation of cypermethrin is different for both anodes. The reaction rate is fast on the BDD anode, while the reaction rate is relatively slow on the SnO<sub>2</sub> anode. Table 3 indicates that different electrodes exhibit different performance in the rate of electrochemical degradation of pesticide.

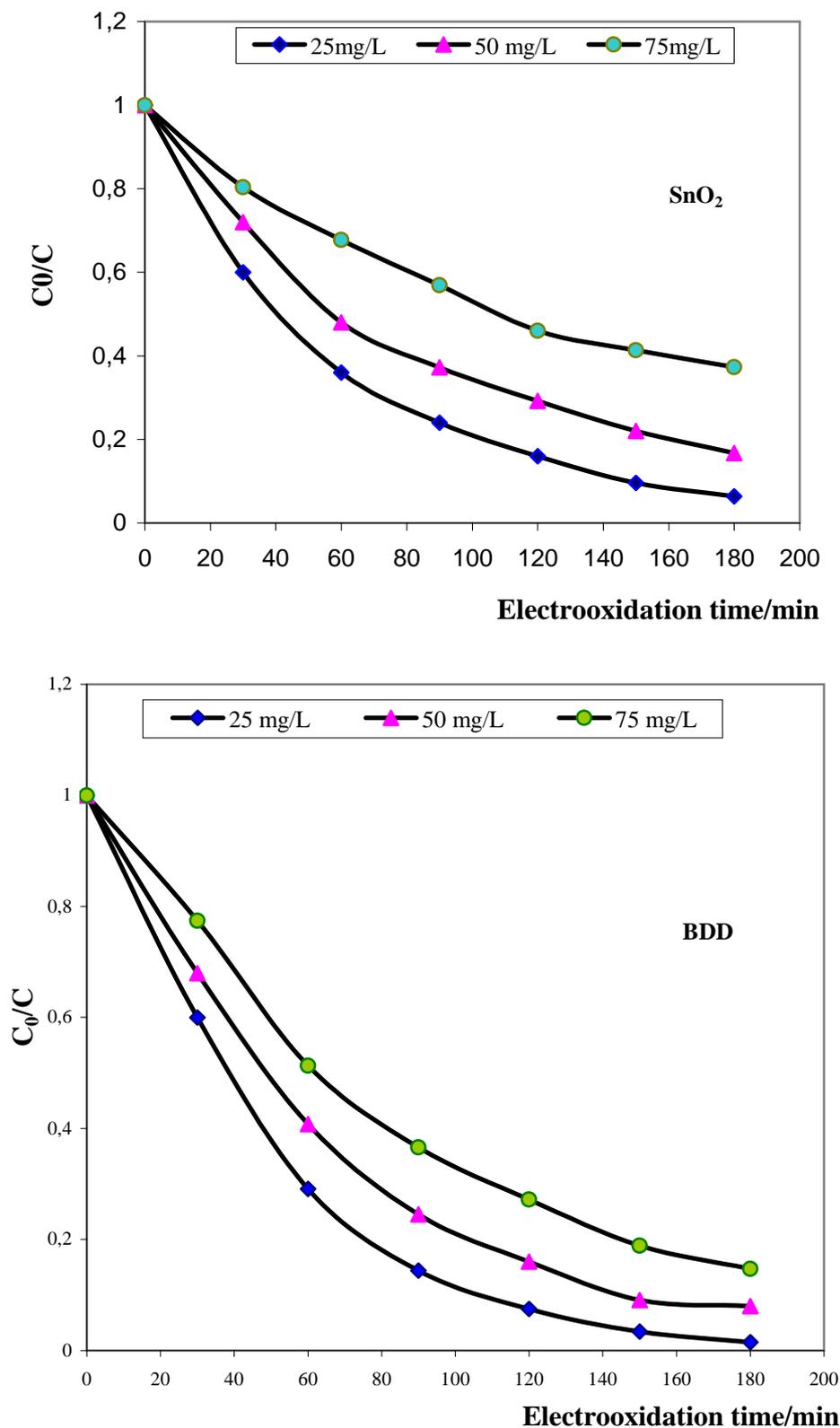


Figure 4. a) Influence of cypermethrin initial concentration on the normalized Concentration during BDD-anodic oxidation (Operating conditions: electrolyte = 2% NaCl, current density =  $80\text{mAcm}^{-2}$ ,  $T = 25^\circ\text{C}$ ). b) Influence of cypermethrin initial concentration on the normalized Concentration during  $\text{SnO}_2$  anodic oxidation of cypermethrin (Operating conditions: electrolyte = 2% NaCl, current density =  $80\text{mAcm}^{-2}$ ,  $T=25^\circ\text{C}$ )

Table 3: Apparent rate constants of cypermethrin removal fitted by a first order model for different anodes

Electrode	Concentration of pesticide (mg/L)	Rate constant, K (min <sup>-1</sup> )
BDD	25	201.10 <sup>-4</sup>
	50	185.10 <sup>-4</sup>
	75	77.10 <sup>-4</sup>
SnO <sub>2</sub>	25	178.10 <sup>-4</sup>
	50	103.10 <sup>-4</sup>
	75	66.10 <sup>-4</sup>

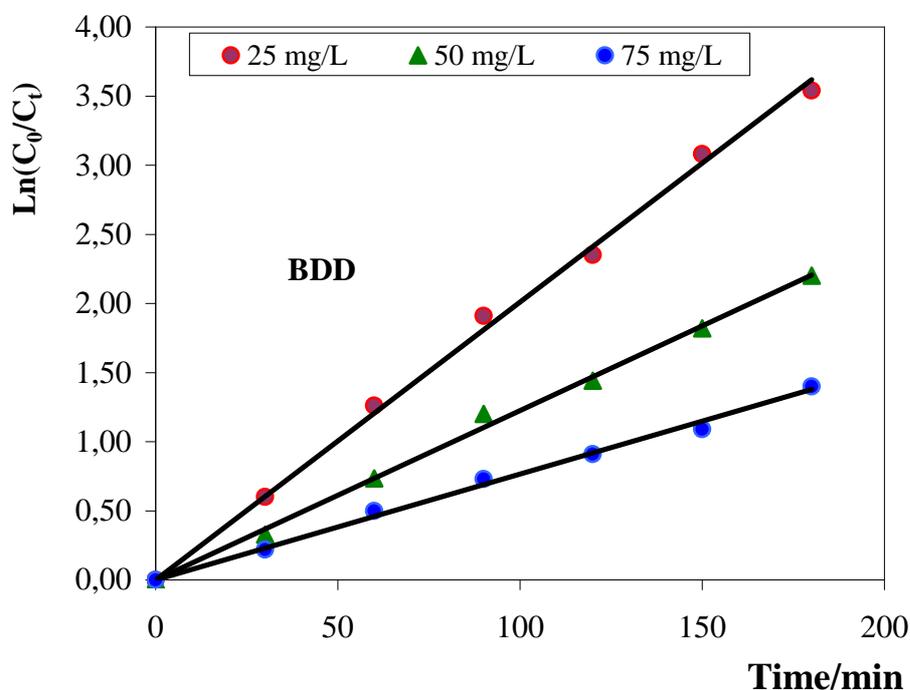
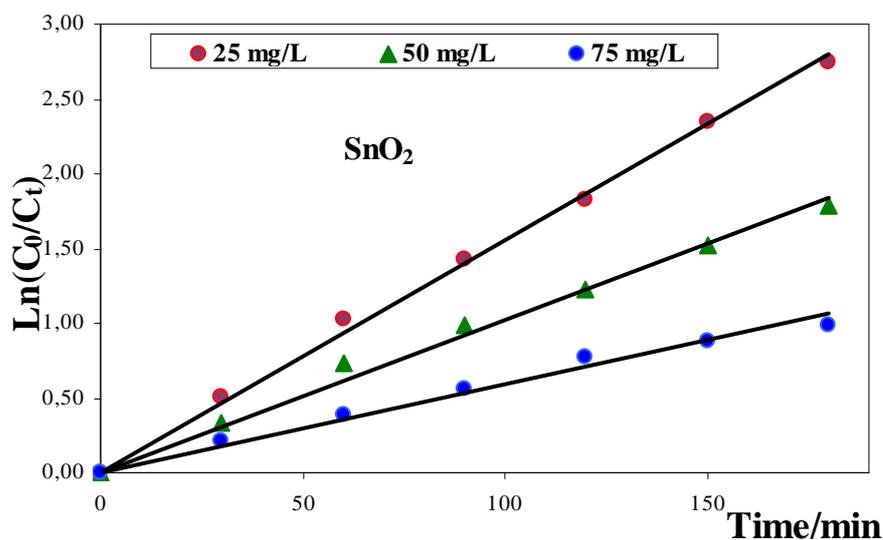


Figure 5. a) Linear regression for Influence of cypermethrin initial concentration on the normalized concentration during BDD-anodic oxidation (Operating conditions: electrolyte = 2% NaCl, current density = 80mAcm<sup>-2</sup>, T = 25°C). b) Influence of cypermethrin initial concentration on the normalized Concentration during SnO<sub>2</sub> anodic oxidation of cypermethrin (Operating conditions: electrolyte = 2% NaCl, current density = 80mAcm<sup>-2</sup>, T=25°C)

## CONCLUSION

The electrochemical degradation of high concentration cypermethrin in sodium chloride-mediated wastewater at a BDD electrode was investigated in comparison with SnO<sub>2</sub> anode.

This work is a first attempt to investigate the degradation of cypermethrin insecticide in electrochemical treatment with direct electrooxidation. In 2% of NaCl, the electrochemical degradation efficiency of cypermethrin on BDD electrode was much greater than that on SnO<sub>2</sub> with a COD removal of 92% on BDD anode and 76% on SnO<sub>2</sub> anode. When comparing the performances of both anode materials, at 80 mAcm<sup>-2</sup>, the degradation efficiency is much higher for the BDD anode than that of SnO<sub>2</sub> anode. This means that the rate of mineralization is higher for the BDD anode. However, at 40 and 60 mAcm<sup>-2</sup>, identical values are obtained for both anodes.

Furthermore, the increase in initial cypermethrin concentration from 50 mg/L to 75 mg/L increases the absolute removal of pesticide concentration. These results lead to the conclusion that the BDD electrode is the most efficient compared to SnO<sub>2</sub>.

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