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## Detoxification of Bupirimate Pesticide in Aqueous Solutions by Electrochemical Oxidation.

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### ABSTRACT

The commercial bupirimate pesticide (5-butyl-2-(ethylamino)-6-methyl-4-pyrimidinyl dimethyl sulfamate) is widely used for crop production and fruit tree treatment, but this disposal cause serious environmental problems. This work presents an electrochemical oxidative removal of this pesticide by an electrolysis system on a boron-doped diamond (BDD) anode and platinum cathode. A number of experiments were run and the results are presented. The achieved reductions were 74% and 52% for 2% NaCl and 3% NaCl respectively. The chemical oxygen demand (COD) of bupirimate solution was observed to fall with pseudo first-order kinetics. As a conclusion, electrochemical oxidation could be used as a pretreatment stage for detoxification of toxic wastes with bupirimate.

**keywords:** Bupirimate; boron doped diamond electrode; electrochemical oxidation.

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### INTRODUCTION

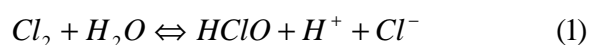
The disposal of pesticide-containing waste is a problem of worldwide concern, with almost every stage of pesticide use involving the formation of wastes [1], which can contain substances that

are strictly controlled by regulatory bodies. The presence of large stocks of pesticides that are unusable, either due to the fact that they are banned or have exceeded their self life, is of great concern – especially in developing countries [2]. For the disposal and degradation of pesticide waste have recently been well reviewed by Felsot & al. [1,3]. Various methods for pesticide treatment methods are available, according to the World Health Organisation, including high temperature incineration, chemical treatment or removal to specially engineered landfill sites [1]. Amongst the possible methods of treatment of pesticides, ozonation [4], oxidation with Fenton's reagent [5], photodegradation [6] and photocatalysis with  $\text{TiO}_2$  have been investigated for a wide variety of pesticides [7]. Since the 1990s, electrochemical methods have been widely studied for the removal of organic substances and a number of reviews are available in the literature [8-9-10].

The advantages of electrochemical treatment are various and well documented: the catalyst/electrode is immobilised (thus reducing the need to separate the catalyst from the reaction mixture), the variables (i.e. current and potential) are easily controlled and facilitate automation of a process and the cost of the equipment is generally not that high [10]. In addition, electrochemical processes are easily adapted for use in flow systems [10], a fact that is considered important for the feasibility of pesticide treatment systems [1].

The electrochemical oxidation of modal substrates has been investigated at several anodic materials, generally metal oxides like  $\text{IrO}_2$ ,  $\text{PbO}_2$ ,  $\text{SnO}_2$  and  $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_5$  [11-12]. These electrodes may be either inefficient in treating wastewaters or chemically unstable especially in an acidic medium. Recently, Boron-Doped Diamond (BDD) electrodes, which are the boundaries of the new electrode materials technology, have been used for oxidation of organics. In fact, the wide potential window and the high anodic stability of the BDD films allow their applications in various fields like electroanalysis, synthesis of powerful oxidants and wastewaters treatment. BDD anode surfaces allow to producing large quantities of hydroxyl radicals from water electrolysis [13-14]. The BDD surface does not interact with these radicals and as a consequence, these radicals can only couple to form oxygen or oxidize the organic matter present in the waste. This anodic material has shown high performance levels for the conversion and/or the combustion of different compounds such as phenol, carboxylic acids, 4-chlorophenol, 3-methylpyridine, benzoic acid, 2-naphtol, polyacrylates, 4-chlorophenoxyacetic acid, amaranth dyestuff, chlorophenols, nitrophenols and polyhydroxybenzenes by electrochemical oxidation [15-16].

The recent use of a BDD thin film anode in anodic oxidation has shown that its  $\text{O}_2$  overvoltage is much higher than that of conventional anodes such as  $\text{PbO}_2$ , doped  $\text{SnO}_2$ ,  $\text{IrO}_2$  and Pt, then producing larger amounts of adsorbed  $\text{OH}^*$  by reaction (1) giving a more rapid destruction of pollutants [17,18]. Anodic oxidation with BDD then seems a suitable procedure to mineralize organics [27-28-29], as found for  $\text{HClO}_4$  aqueous solutions containing carboxylic acids such as acetic, malic, formic and oxalic [15], 4-chlorophenol [19], phenol [20], benzoic acid [21], bupirimate [27], and methidation [28-29] as well as for malic acid at pH 2.7 and ethylenediaminetetra acetic acid at pH 9.2 [16].



Bupirimate (5-butyl-2-(ethylamino)-6-methyl-4-pyrimidinyl dimethylsulfamate) (Fig.1) is an effective pyrimidine fungicide in controlling roses and apple. To our knowledge, the study of the electrochemical oxidation of this pesticide has not been presented in the literature. Thus, the current paper presents the study the electrochemical treatment system for bupirimate in aqueous solution using a BDD electrode.

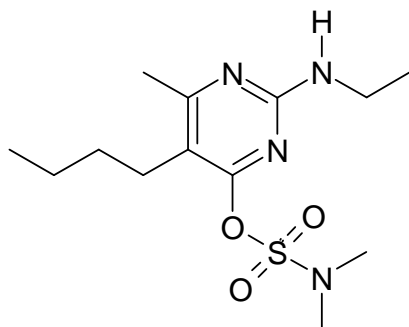


Figure. 1 Structural formula of bupirimate pesticide.

## MATERIALS AND METHODS

### 2.1. Materials and reagents

Electrochemical measurements were accomplished by using a PGP 201 Potentiostat/Galvanostat with a Tacussel Standard CEC/TH thermo-regulated glass cell and Volta-Master 1 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 cm<sup>3</sup> aqueous solution of bupirimate 1.4 mg/L during 120 minutes. The range of applied current density was 20 to 60 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. To characterize the toxicity removal, the global parameter, the chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [14]. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

The commercial formulation NIMROD 25 EC (25% Bupirimate) was purchased from AAKO distributed by SAOAS. The chemical sodium chloride used was of analytical-reagent grade and was obtained from Sigma-Aldrich (St. Louis, MO, USA).

### 2.2. Extraction

The method used for the extraction of bupirimate was adapted from Charles and Raymond [22]. For each 2 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 sodium chloride (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 analysed by gas chromatography.

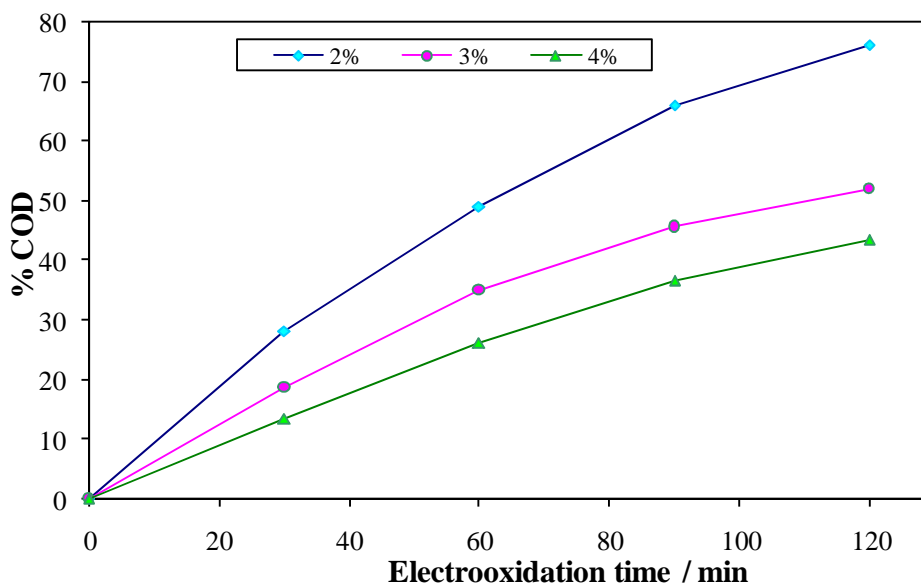
### 2.3 GC analysis

Analysis of the bupirimate pesticide was carried out with a Hewlett–Packard 6890 gas chromatograph equipped with an ECD Detector, on-column 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.

## RESULTS AND DISCUSSION

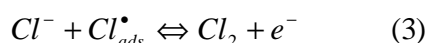
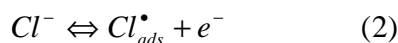
### 3.1. Effect of chloride concentration

The Figure 2 shown effect of chloride ions concentration on the destruction of bupirimate solution, carried out at 60 mA/cm<sup>2</sup>. As shown in this Figure, the utilization of electrolysis to detoxify bupirimate pesticide has the ability to reduce considerably the chemical oxygen demand (COD).

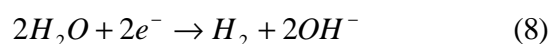
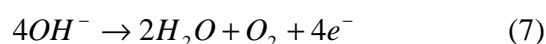
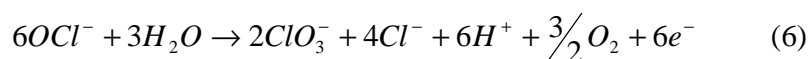
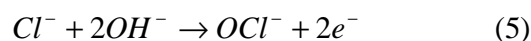


**Fig. 2 Direct electrooxidation at BDD anode: effect of NaCl concentration on the % COD**  
(230 mg.L<sup>-1</sup> Bupirimate solution, 60 mA.cm<sup>-2</sup>, pH=6.2, and T=25°C).

The achieved reduction was 74% and 54% for 2% NaCl and 3% NaCl respectively, while for 4% NaCl was 43%. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of bupirimate on the electrode or indirect via some mediators like chlorinated species or other radicals [23-24]. Since, some oxidant compounds that are produced during oxidation of water (like O<sub>2</sub>, O<sub>3</sub> or hydroxyl radical OH<sup>•</sup>) or oxidation of chlorine ions following equation (2) to (4):



Several main reactions are believed to occur during the oxidation of bupirimate in the presence of NaCl, probably reactions in basic solutions, (equations 5 to 7) take place at the anode, where as reaction (equation 8) takes place at the cathode.



The presence of a weak concentration of chloride ions allows to inhibit the water discharge into oxygen, and to favorise hydroxyl or chloride and oxchloride radicals, which are very powerful oxidants. It can be explain why until 2% of NaCl concentration the COD removal increases with NaCl concentration. Increasing the chloride concentration more than 3% cause a “potentiostatic buffering” by the chlorine redox system and consequently a decrease of the anode potential. Another possibility is the presence of competitive reactions, in particular oxygen and chloride evolution due to recombination of radicals that becomes bigger with the increasing NaCl concentration. The balance of all these phenomena results that there is an optimum of NaCl concentration which is 2% mass of NaCl for the degradation of bupirimate.

Figure 3 shows the change of pH in bupirimate solution during the electrolysis. The pH in all cases became strong basic. It is obvious that the continuous addition of high levels of organic matter in the electrolytic cell, resulted in the increase of pH. The electrolysis was more effective in terms of %COD reduction when the pH was in the basic range. The pH solution also changed during the electrolysis process.

The pH increased from the initial value of 6.2 to below 10.4 can be observed in first minutes is due to the formation of radicals  $OH^\bullet$  after 10 minutes of electrolyse the bupirimate was being electrochemically oxidized, the pH of solution approached 8.2 when the COD reduction was 74% after 2h of electrolysis. The increase in pH was caused by the formation of basic substances from the bupirimate degradation.

In NaCl electrolyte used, the concentration of bupirimate was observed to fall with pseudo first-order kinetics (Figure4), This is related to the dependence of the rate of formation of the oxidising species at the electrode surface. The pseudo first-order constant of bupirimate removal (k) varies from approximately the  $109 \times 10^{-4} \text{ min}^{-1}$  (2% NaCl) to  $49 \times 10^{-4} \text{ min}^{-1}$  (4% NaCl).

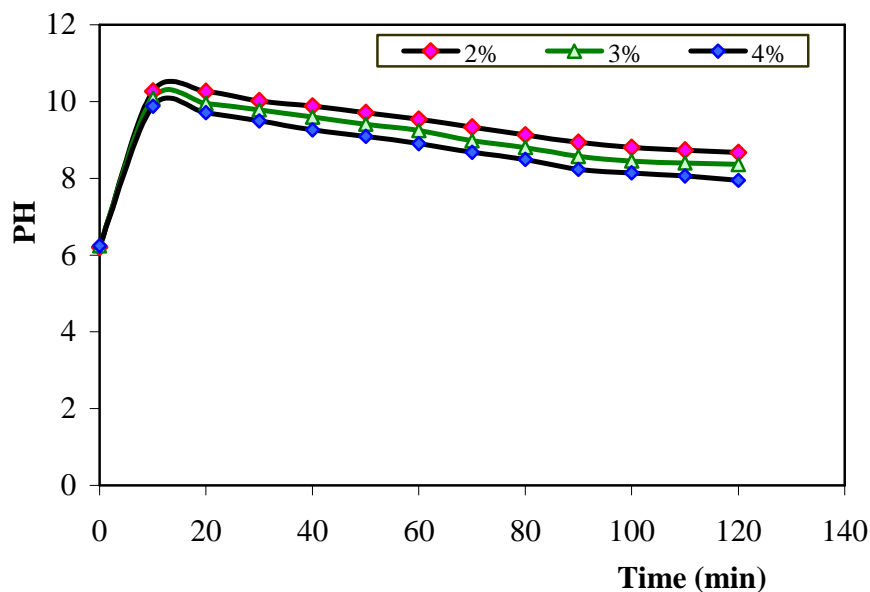


Fig. 3 pH reduction of bupirimate 230 mg/L for 120 min of electrolysis at 60 mA/cm<sup>2</sup> and 25 °C, volume of treated solution: 75 cm<sup>3</sup>

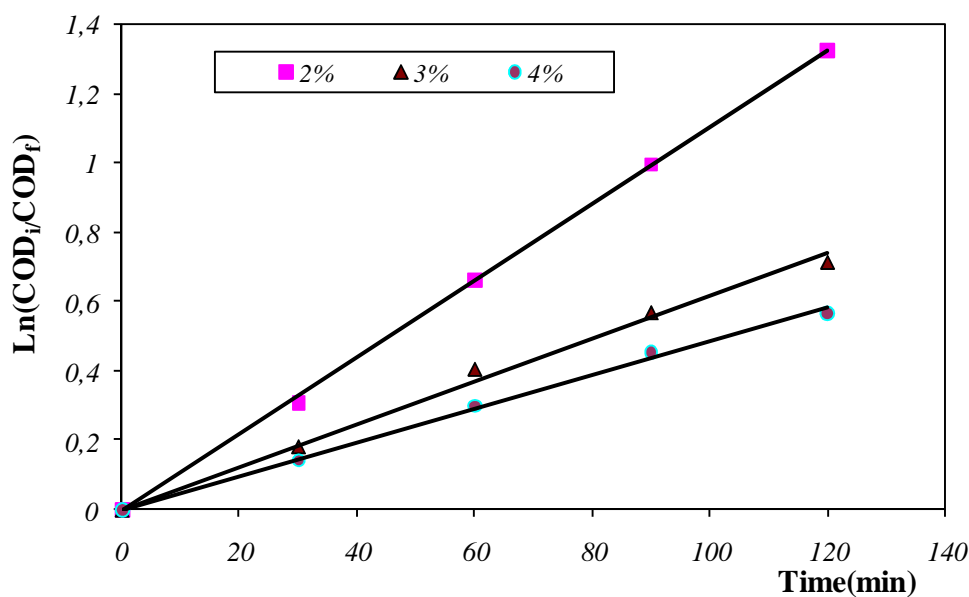


Fig. 4 Pseudo first-order plot for oxidation of 230 mg/L Bupirimate at 60 mA and 25 °C.

### 3.2. Effect of applied current

Applied current is an important factor affecting the electrolysis kinetics and process economics. The effect of applied current on the electrochemical process was demonstrated in several studies [24-25]. In Figure 5 the % COD reduction for the bupirimate is presented under different current inputs (NaCl 2%). These studies concluded that applied current increases the rate of electrochemical oxidation process. The % COD of bupirimate was observed to fall with pseudo first-order kinetics on all the surface studied (Figure 6). This is related to the dependence of the rate of oxidation of formation of the oxidising species at the electrode surface. The pseudo first-

order constant of bupirimate ( $k$ ) varies from  $30 \times 10^{-4} \text{ min}^{-1}$  (20 mA) to  $109 \times 10^{-4} \text{ min}^{-1}$  (60 mA). From these results it was calculated that the best applied current is 60 mA.

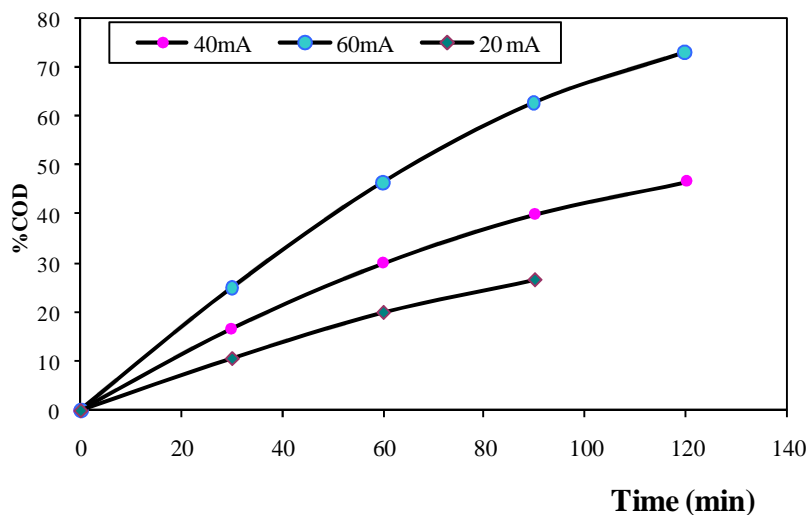


Fig. 5 % COD reduction for Bupirimate 230 mg/L under different current inputs (chlorides=2%) and 25°C.

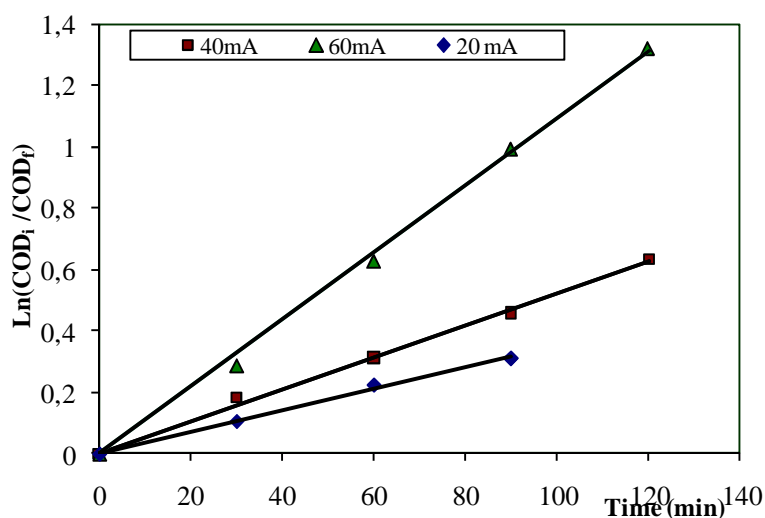


Fig. 6 Pseudo first-order plot oxidation of Bupirimate 230 mg/L in 2% NaCl at 25°C under different current inputs (COD at a given time,  $t$  during electrolysis).

### 3.3. Effect of temperature

Figure 7 illustrates the % COD reduction of bupirimate at different temperature under 60 mA current input. It is observed that for 25°C and 65 °C the achieved reduction was 74% and 33 % respectively.

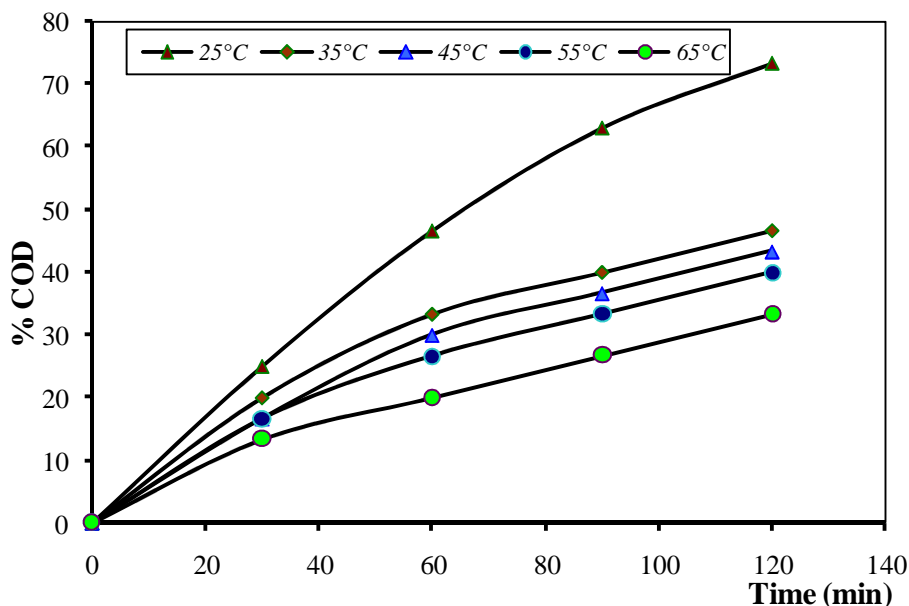


Fig. 7 % COD reduction for of Bupirimate 230 mg/L in 2% NaCl at 25°C at different temperatures.

The COD of bupirimate was observed to fall with pseudo first-order kinetics (Fig. 8). The pseudo first-order constant of bupirimate (k) varies from  $109 \times 10^{-4} \text{ min}^{-1}$  (25 °C) to  $35 \times 10^{-4} \text{ min}^{-1}$  (65 °C).

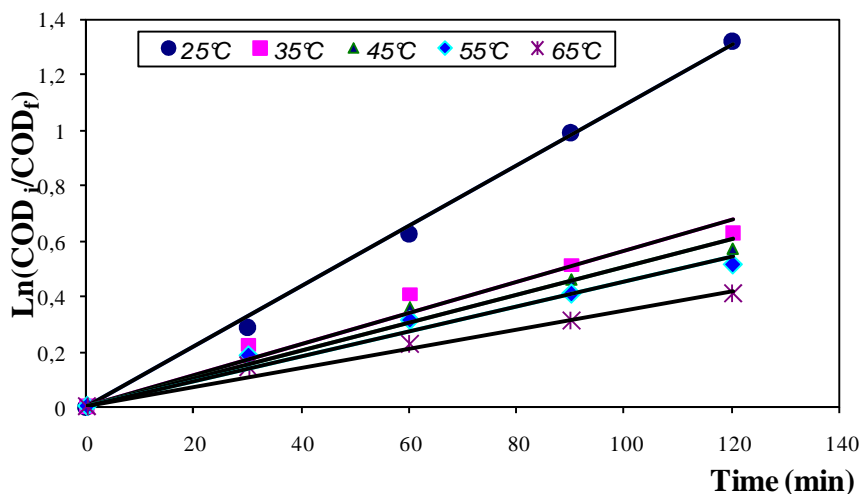


Fig.8 Pseudo first-order plot oxidation of Bupirimate 230 mg/L in 2% NaCl at 60 mA under different temperatures (COD at a given time, t during electrolysis).

The effect of temperature on the rates of constant was modelled using the Arrhenius plots, are shown in (Fig. 9). The apparent activation energies were determined by:

$$K = A \exp(-E_a/RT) \quad (9)$$



Where  $K$  is rate constant,  $A$  is constant,  $E_a$  is the activation energy,  $T$  is the temperature (K) and  $R$  is the gas law constant. The obtained activation energy equal at  $-20.95$  kJ/mol indicate that the electrochemical degradation is complex.

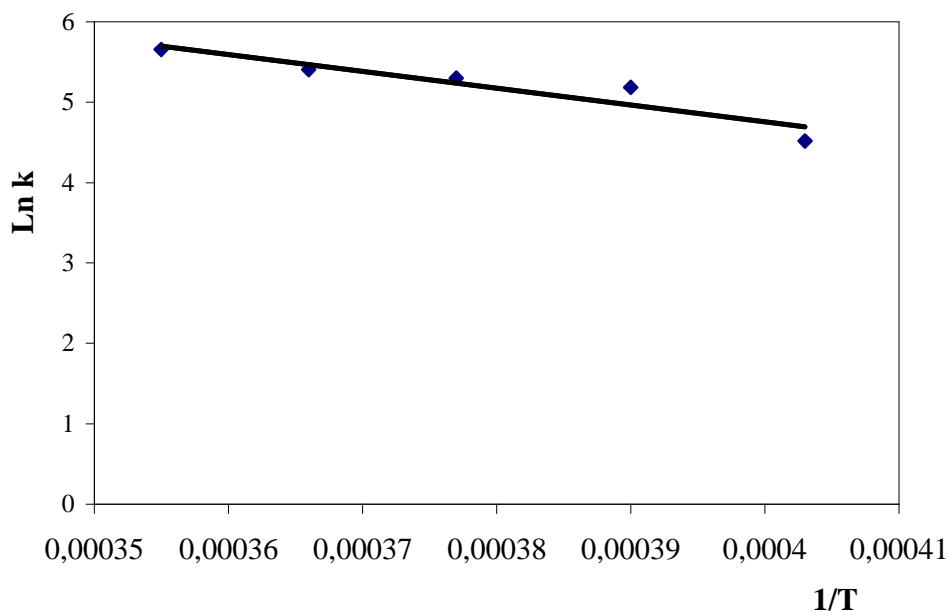


Fig.9 Arrhenius plote oxidation of Bupirimate 230 mg/L in 2% NaCl at 60 mA under different temperatures.

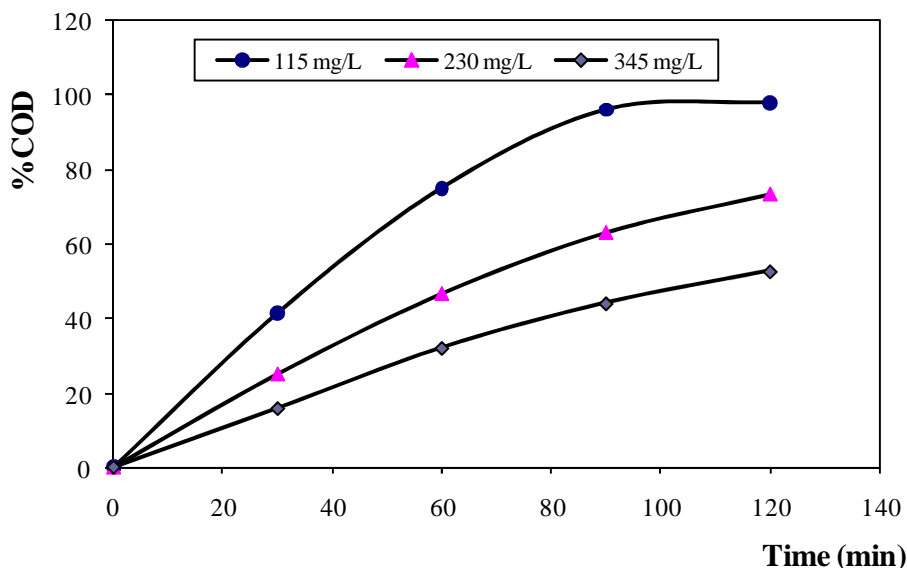


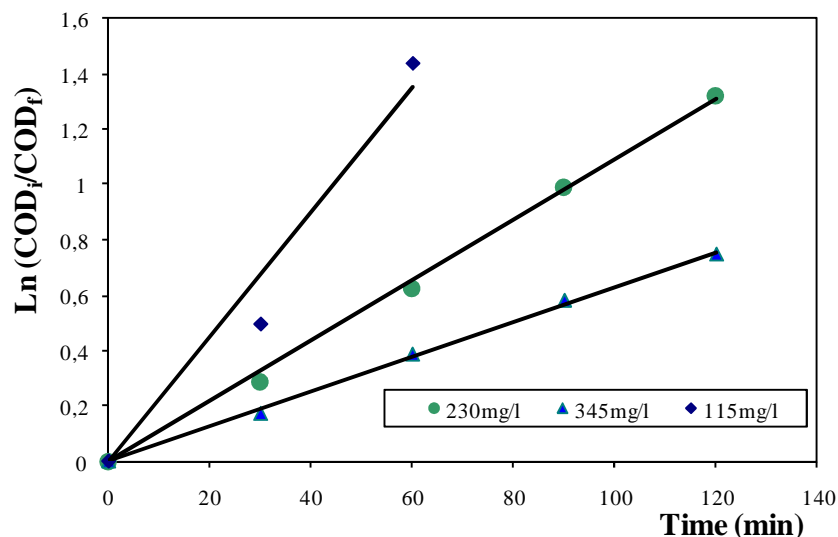
Fig.10 % COD reduction for of different concentration Bupirimate in 2% NaCl at 25°C and 60 mA.

### 3.4. Effect of pesticide concentration and current efficiency

The % COD reduction was studied at three different concentration of bupirimate (115, 230 and 345 mg/L) under the previous optimum conditions. As shown in the Figure 10, in the presence of 115 mg/L bupirimate the oxidation is complete after 1h. The increased rate of organic degradation is due to the diminution of bupirimate concentration and formation of chlorine gas at

anode and hypochlorite after reaction with  $\text{OH}^-$  at the cathode. The degradation of different concentration of pesticide was observed with pseudo first-order kinetics (Fig. 11).

The pseudo first-order kinetics constant of bupirimate removal ( $k$ ) varies from approximately  $244 \times 10^{-4} \text{ min}^{-1}$  for 0.115 mg/L to  $62 \times 10^{-4} \text{ min}^{-1}$  for 345 mg/L.



**Fig. 11** Pseudo first-order plot for oxidation of different concentration of pesticide in 2% NaCl at 60 mA and 25°C (COD at a given time,  $t$  during electrolysis).

The instantaneous current efficiency (ICE) for the anodic oxidation of bupirimate has been calculated from the values of COD using the relation [26].

$$ICE = 4FV_r \frac{(COD)_t - (COD)_{t+\Delta t}}{I_a \times A \times \Delta t} \quad (10)$$

Where  $(COD)_t$  and  $(COD)_{t+\Delta t}$  are the chemical oxygen demands at times  $t$  and  $t + \Delta t$  (in mol  $\text{O}_2/\text{L}$ ) respectively.  $I_a$  is the applied current density ( $\text{A}/\text{cm}^2$ ),  $F$  is the Faraday constant ( $96487 \text{ C}/\text{mol}$ ),  $A$  is the anodic surface ( $\text{cm}^2$ ) and  $V_r$  is the electrolyte volume (L).

The Figure 12 shown effect of instantaneous current efficiency (ICE) on the destruction of bupirimate solution, carried out at  $60 \text{ mA}/\text{cm}^2$ . The ICE decrease exponentially with the time. It is worth noting that the observed ICE decrease is due to the mass-transfer limitation and not due to the reduction of the anodic activity. Also under these conditions bupirimate is completely eliminated, these results were confirmed by bupirimate UV-spectra (Figure 13). As can be seen in this Figure, after 60 min of treatment, the UV-spectrum changed greatly and had a weak absorbance at 310 nm and 240 nm. It is confirmed that the cleavage of dimethylsulfamate and pyrimidinyl atom respectively was destroyed most completely at 90 min.

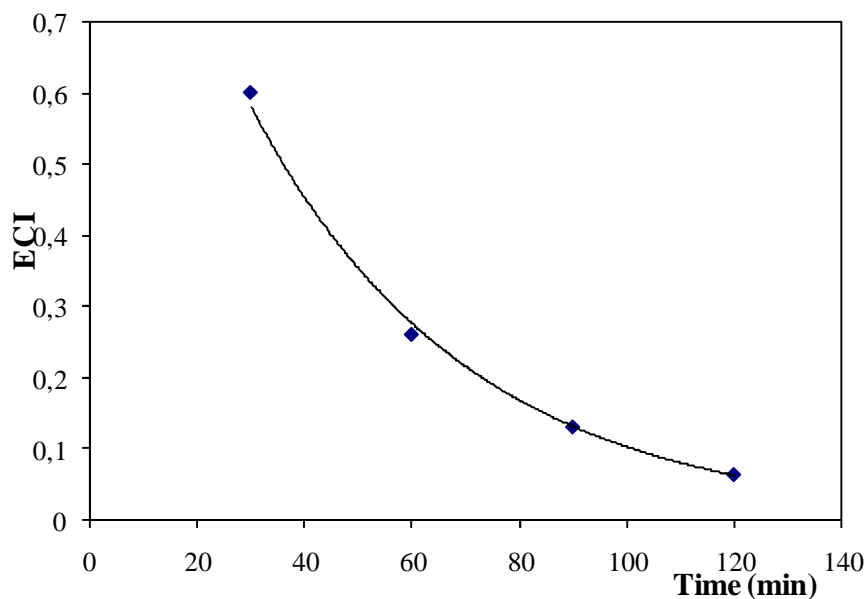


Fig. 12 ICE for Bupirimate 230 mg/L in 2% NaCl at 25°C and volume of electrolysis 75 cm<sup>3</sup> in function time.

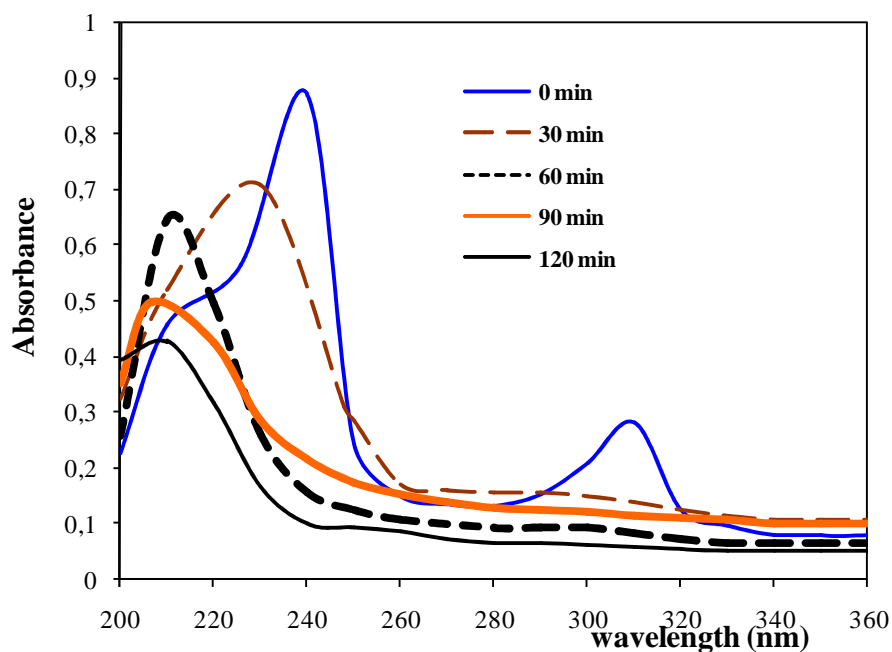
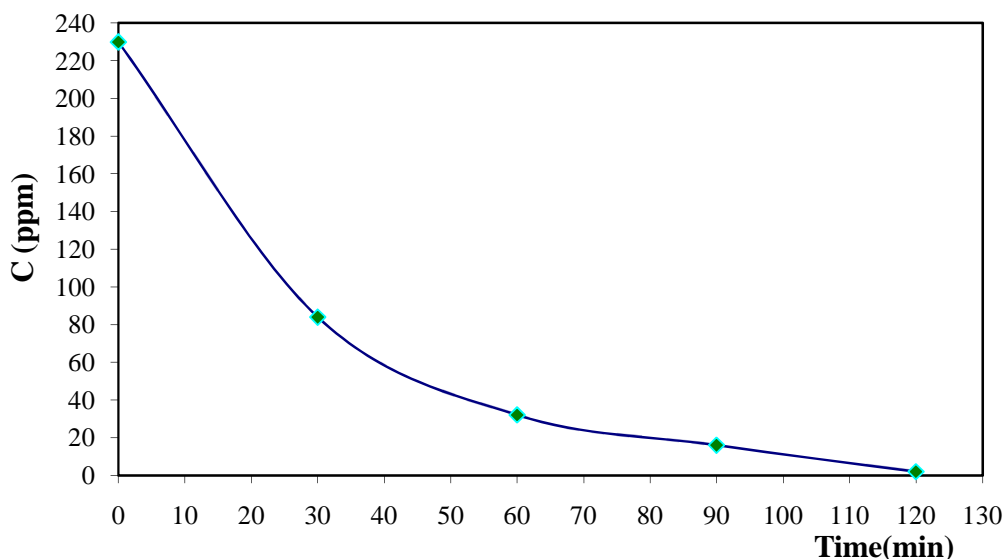


Fig.13 UV spectra for the electrooxidation assays performed at the BDD anode (Operating conditions: Bupirimate initial concentration = 230 mg/L, current density = 60mAcm<sup>-2</sup>, pH = 6.2, electrolyte = 2% NaCl).

The concentration of bupirimate was measured using GC and the variations of bupirimate concentration with electrolysis time for the two anodes are shown in figure 14.

The kinetic curve was characterized by rapid and steady decrease in the concentration of pesticides during the electrolysis. These results show that the reduction percentage of bupirimate found by gas chromatography is the same as analyzed by the COD.



**Fig. 14** Electrolysis time dependence of bupirimate concentration for anode BDD, Bupirimate initial concentration = 230 mg/L, current density =  $60\text{mAcm}^{-2}$ , pH = 6.2, electrolyte = 2% NaCl.

### CONCLUSION

This work is a first attempt to investigate the degradation of bupirimate in electrochemical treatment with  $\text{SnO}_2$ . Electrochemical oxidation is a method that has been utilized to date for the treatment of several types of wastes. This article provides new results on the electrochemical degradation of bupirimate and led to the following conclusion:

- The application of electrolysis in pesticide has the ability reduce the COD. For 2% mass NaCl and 3% mass NaCl the achieved reduction was 74% and 52% respectively. For 4% NaCl was 43%.
- In all cases, the pH of electrolysis was significantly reduced after 90 min.
- The COD of bupirimate was observed to fall with pseudo first-order kinetics, on all the surface studied.
- The applied current increases the rate of electrochemical oxidation process.
- The effect of temperature shown that for 25 °C and 65 °C the achieved reduction was 74% and 33 % respectively.
- The activation energy indicates that the electrochemical degradation is complex.
- The ICE decrease exponentially with the time. Diminution of ICE is due to the Mass-transfer limitation and not due to the reduction of the anodic activity .that is shown by UV-spectra of bupirimate at different times of electrolysis.

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