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Electrochemical Detoxification of Obsolete Pesticides Stocks

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1. Introduction

The disposal of pesticides can cause serious problems due to the chemical nature of the active ingredients in pesticide formulation and due to the large quantities of the unwanted products. These products undergo physical and chemical alterations either due to extended storage, beyond the recommended expiry date, or storage under improper conditions (high humidity and temperature). Commercial synthetic chemical pesticides are utilized in all countries and as a consequence reach even remote regions. Wherever pesticides are used, unusable or unwanted pesticides and empty pesticides containers have to be properly and safely managed. In many countries, large quantities of pesticides have been accumulated since they have lost their desirable characteristics. Although these products are not suitable for use, they still contain toxic compounds. Many surplus pesticides, still within their expiry limits, may become useless, when their future use is prohibited due to toxicological or environmental concerns. Food and Agricultural Organization of the United Nations (FAO) estimated that between 400.000 and 500.000 tones of obsolete pesticides are stocked in developing countries (FAO, 2001).

The biological degradation of pesticides is generally difficult due to their high content in toxic matter (Felsot, 1996; Zaleska & Hupka, 1999). An ideal treatment method for pesticide surplus should be non-selective, should achieve rapid and complete mineralization, and should be suitable for small-scale wastes (Krueger et al., 1984; Bourke et al., 1991). Today the main disposal method of obsolete pesticide stock is incineration, an impractical and expensive procedure. High-temperature incineration in dedicated hazardous waste incinerators is the currently recommended method for obsolete pesticide treatment. However, sophisticated incinerators do not exist in developing countries (FAO, 2000).

Various innovative technologies have been proposed for the disposal of obsolete pesticides. These technologies include photocatalytic oxidation (Pignatello & Sun, 1995; Chen et al., 1998), ultrasonic radiation (Kotronarou et al.,1997). The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with very low active ingredient content, rather than highly concentrated obsolete pesticide stocks.

Electrochemical methods have been successfully applied in the purification of domestic sewage (Della Monica et al., 1980), olive oil wastewaters (Israilides et al., 1996), textile wastes (Vlyssides et al., 1999) etc.

The electrochemical reactions, which take place during the electrolysis of a chloride-containing solution (brine solution), are complicated and not entirely known. The electrochemical oxidation of aqueous solutions which contain organic matter, by the use of Ti/Pt anode, proceeds in two steps (Comninellis et al., 1992). The first step is the anodic discharge of the water, forming hydroxyl radicals which are absorbed on the active sites of the electrode surface M [ ].

$$H_2O + M[\,] \rightarrow M[OH^-] + H^+ + e \quad (1)$$

After this the absorbed hydroxyl radical oxidizes the organic matter.

$$R + M[OH^-] \rightarrow RO + M[\,] + H^+ + e^- \quad (2)$$

where RO represents the oxidized organic matter which can be produced continuously by the hydroxyl radicals which are also continuously formed, since the anodic discharge of the water goes on. The radicals $OH^{\cdot}$, O. and $HClO^{\cdot}$ have a very short life-time due to their high oxidation potential and are either decomposed to other oxidants (such as Cl_2, O_2, ClO_2, O_3, and H_2O_2) or oxidize organic compounds (i.e. direct oxidation). The primary (Cl_2, O_2) and secondary (ClO_2, O_3, and H_2O_2) oxidants that are produced from the destruction of radicals have quite a long life-time and are diffused into the area away from the electrode, thus continuing the oxidation process (indirect oxidation). Effective pollutant degradation is based on the direct electrochemical process (that takes place in a closed area around the electrode) because the secondary oxidants are not able to convert totally all the organic species into water and carbon dioxide.

In the last few years, interest in direct and indirect electrochemical oxidations of organic pollutants increased significantly. In the direct anodic oxidation, adsorbed OH• radicals are produced from water oxidation at an anode made from Pt, PbO_2, doped SnO_2 (Comninellis & Pulgarin, 1993; Comninellis, 1994) or boron-doped diamond (BDD) (Weiss et al., 2007; Hachami et al., 2008):

$$H_2O \rightarrow OH^{\cdot}_{ads} + H^+ + e^- \quad (3)$$

This radical is the main mineralizing agent of organics, causing their conversion to CO_2, water and inorganic ions.

Recently, electrooxidation has received great attention due to the use of non-active boron-doped diamond (BDD) thin film electrodes, which possess high O_2-overvoltage that favors the production of great quantity of reactive BDD ($OH^{\cdot}$) with ability to completely mineralize organics, as reported for several aromatics (Marselli et al.,2003; Flox et al., 2009) and carboxylic acids (Weiss et al., 2007). The recent use of BDD thin-film as new anode material has shown that it possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and extremely wide potential windows in aqueous medium (Panizza & Cerisola,2005). In comparison with conventional anodes such as Pt, PbO_2, doped PbO_2, doped SnO_2 and

IrO_2, the BDD anode has much greater O_2-overvoltage allowing the generation of greater amount of OH. from reaction (4) or (5) and hence, a quicker oxidation of aromatics and pesticides in acid and neutral media:

$$BDD(H_2O) \rightarrow BDD(HO^{\cdot}) + H^{+} + e^{-} \quad (4)$$

in basic media (pH ≥ 10):

$$BDD(OH^{-}) \rightarrow BDD(HO^{\cdot}) + e^{-} \quad (5)$$

In this paper we report on a comparative study on the electrochemical oxidation and the degradation process in supporting electrolytes NaCl of a solution containing high concentration of Bupirimate and methidathion, respectively a systemic fungicide widely and insecticide used in agriculture fields. Two electrodes were selected for this investigation: BDD electrode and a metal oxide anode SnO_2.

2. Materials and methods

2.1 Chemicals

Bupirimate, a substituted pyrimidine (a sulphamate ester of ethirimol, 5-butyl-2-ethylamino-6-methyIpyrimidin-4-yl-dimethylsulphamate), is a local systemic fungicide that is effective in controlling mildew in roses and apples. Bupirimate formulation is commercially available in the NIMROD 25 EC (25% Bupirimate) (Figure 1). It was Purchased from AAKO (Morocco). All chemicals used in the experiments were of analytical pure grade and used without further purification. The concentration of bupirimate in wastewater for these experiments was 230 mg/L with a corresponding COD value of 1440 mgO_2/L.

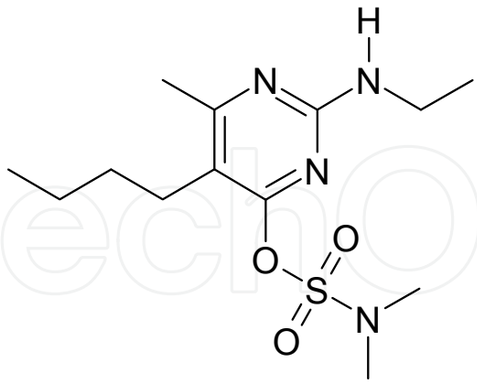


Fig. 1. Chemical structure of bupirimate.

Methidathion [O,O-dimethylS-(5-methoxy-1,3,4-Thiadiazoliny-l-3-methyl) dithiophosphate] (Figure 2) is a widely used organophosphorous insecticide, The commercial formulation Methidaxide (40 % methidation) was purchased from Bayer. The concentration of methidathion in wastewater for these experiments was 1.4 mM with a corresponding COD value of 2400 mgO_2/L. The sodium chloride used was of analytical-reagent grade and was obtained from Aldrich (Spain).

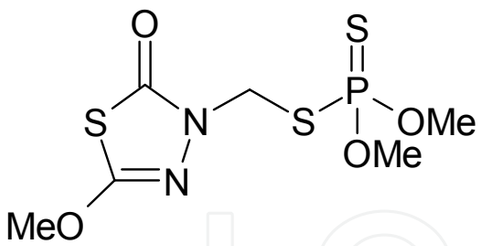


Fig. 2. Structural formula of methidathion

2.2 Electrolytic system

Electrochemical measurements were performed using a computer controlled by Potentiostat/Galvanostat model PGP 201 associated to "Volta-Master1" software. A conventional three electrodes cell (100 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 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 mL aqueous solution of pesticide during 120 minutes. The range of applied current density was 20 to 60 $mAcm^{-2}$ and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. In all cases, sodium chloride (NaCl) was added to the electrolytic cell at different concentrations.

Comparative degradation of bupirimate was studied by electrolyzing 75 mL of solutions containing 230 mg/L of initial pollutant and 2% NaCl of pH 6.2. In all trials, a constant current density of 60 $mAcm^{-2}$ was applied.

2.3 Analytical procedures

The UV–Vis spectra of bupirimate were recorded in 200–400 nm range using a UV–Vis spectrophotometer (UV-1700 Pharmaspec, Shimadzou) with a spectrometric quartz cell (1 cm path length). The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method.

The method used for the extraction of bupirimate was adapted from Charles and Raymond (Charles & Raymond, 1991). 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 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 analysed by gas chromatography.

2.4 Gas chromatography analysis

Analysis of the bupirimate 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 programme 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.

3. Results and discussion

3.1 Electrooxidation of bupirimate

3.1.1 Effect of the NaCl concentration

Figures 3-a and 3-b show the effect of the electrolyte concentration on the % COD for both BDD and SnO_2 respectively. 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 bupirimate 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 oxycloride radicals' formation. 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.

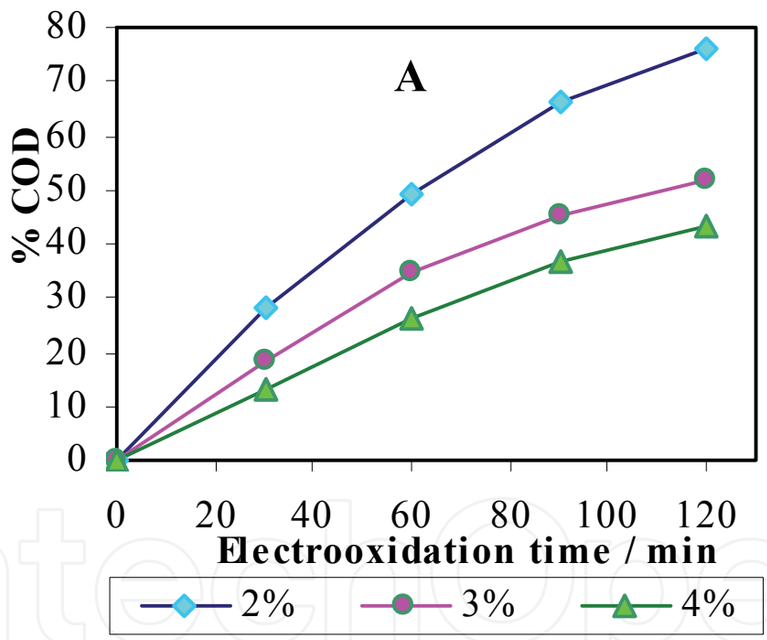


Fig. 3. a. Direct electrooxidation at BDD anode: effect of NaCl concentration on the %COD (230 mg.L^{-1} Bupirimate solution, 120 min, (60 mA.cm^{-2}, pH=6.2, and T=25 °C).

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 Bupirimate.

Kinetic studies were carried out to determine the COD reduction efficiency for both electrodes at different concentration of NaCl. For this purpose, the removal rate of COD was assumed to obey a first order kinetic as follows (Laviron ,1972).

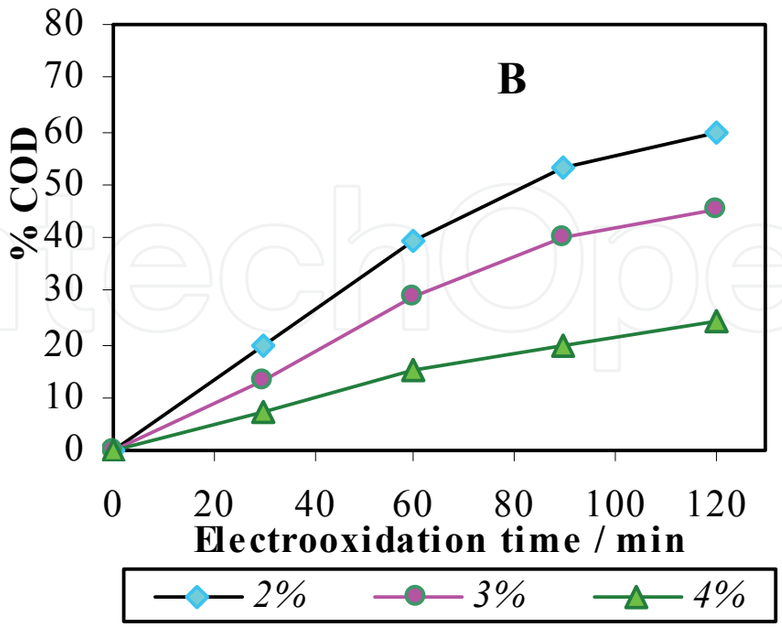


Fig. 3. b. Direct electrooxidation at SnO2 anode: effect of NaCl concentration on the %COD (230 mg.L-1 Bupirimate solution, 120 min, (60 mA.cm−2, pH=6.2, and T=25 °C).

$$d[COD]/dt = -K[COD] \quad (6)$$

The values of rate constant for different NaCl concentration are summarized in table 1. The rate constant, K was calculated for all mass of supporting electrolyte. At each mass of NaCl, COD reduction was estimated at different time intervals and using Eq. (4), rate constant K was calculated at each time interval and averaged. The effect of supporting electrolyte on rate constant increased with decreasing concentration of NaCl and the higher reaction rate constant (109x10-4 min^{-1}) was obtained at 2% of NaCl supporting electrolyte. This indicates that the bupirimate molecules were easily attacked by hydroxyl radicals at lower concentration of NaCl. These results are in agreement with previously reported results (Hachami et al., 2010; Hachami et al., 2008).

Elect rode	NaCl concentration, %	Rate constant, K (min^{-1})	% COD
BDD	2	$109x10^{-4}$	74
	3	$61x10^{-4}$	53
	4	$49x10^{-4}$	44
SnO_2	2	$85x10^{-4}$	60
	3	$57x10^{-4}$	45
	4	$35x10^{-4}$	24

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

3.1.2 Effect of the applied current density

The effect of applied current density on the electrochemical process was reported in several studies (Hachami et al., 2008; Radha et al., 2009). It is an important factor affecting the electrolysis kinetics. Degradation assays of 230 mg/L bupirimate solutions were performed using the BDD and SnO_2 electrodes at different current densities (Figures 4-a, 4-b and Table 2). Overall, COD removal efficiency increased with increasing applied current density. As illustration, when the current is increased from 20 $mAcm^{-2}$ to 60 $mAcm^{-2}$ %COD removal increased from 26 % to 74 % for BDD and from 24 % to 60 % for SnO_2.

Electrode	Current intensity ($mA.cm^{-2}$)	Rate constant, K (min^{-1})	%COD
BDD	20	$109x10^{-4}$	74
	40	$52x10^{-4}$	47
	60	$35x10^{-4}$	26
SnO_2	20	$80x10^{-4}$	60
	40	$75x10^{-4}$	58
	60	$28x10^{-4}$	24

Table 2. Effect of current intensity: values of rate constant and %COD.

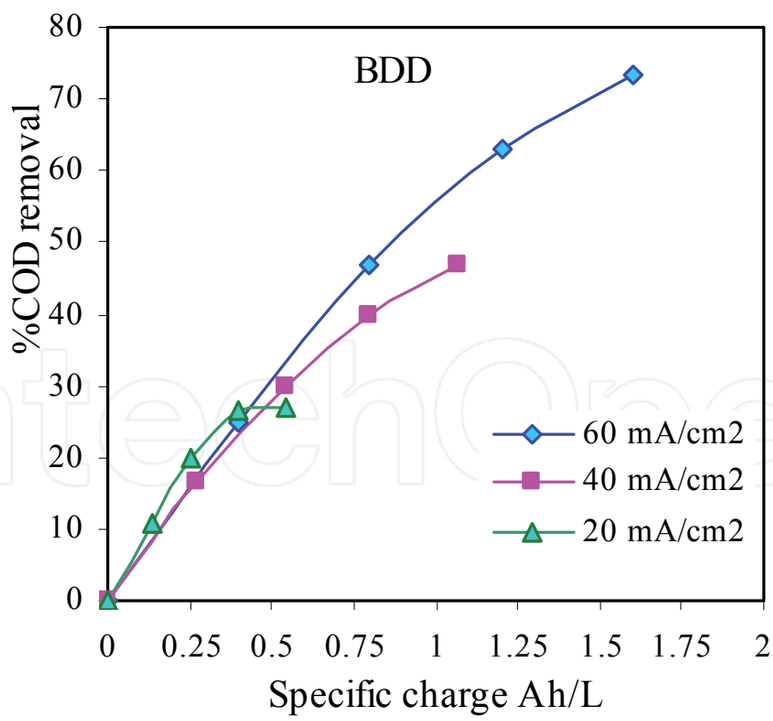


Fig. 4. a. Variation of %COD as a function of the specific charge passed during electrolysis of bupirimate performed with BDD and at several current densities (20, 40 and 60 $mAcm^{-2}$). Initial bupirimate concentration = 230 mg/L, pH = 6.2, T = 25 °C, electrolyte = 2 % NaCl.

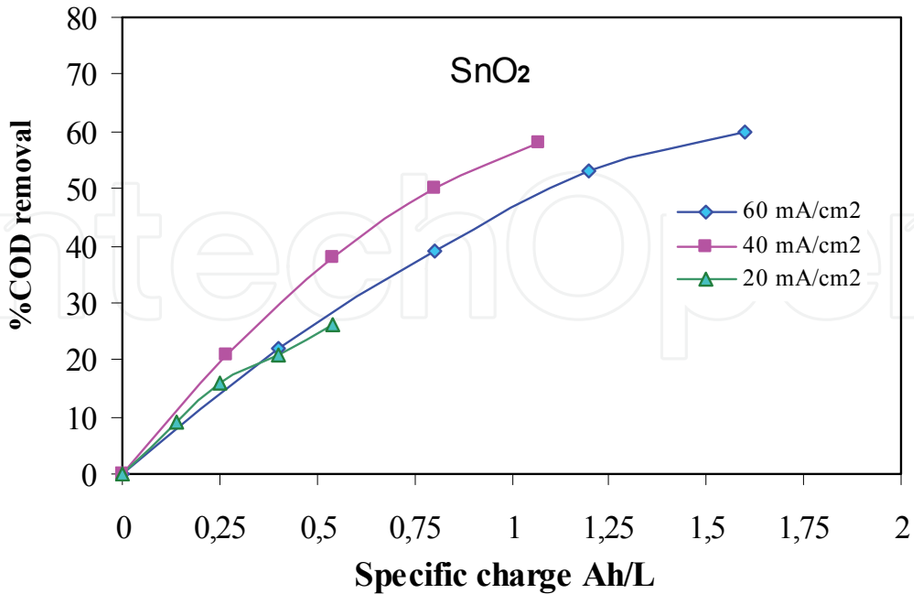


Fig. 4. b. Variation of COD removal as a function of the specific charge passed during electrolysis of bupirimate performed with SnO2 and at several current densities (20, 40 and 60 $mAcm^{-2}$). Initial bupirimate concentration = 230 mg/L, pH = 6.2, T = 25 °C, electrolyte = 2 % NaCl.

3.1.3 Effect of initial concentrations of bupirimate on the degradation efficiency

To investigate the electrooxidation efficiency on high concentration of bupirimate, the experiments of electrochemical degradation of 115, 230 and 345 mg/L bupirimate solutions were carried out with a selecting current density and NaCl concentration. As shown in Figures 5-a and 5-b, complete bupirimate removal can be achieved on 115 mg/L concentration of bupirimate for BDD anode as the electrolysis time was extended. The trends of normalized COD are moderately overlapped and same electrolysis-times are required to achieve the best values of COD abatement for two anodes BDD and SnO2. 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 Panizza and Cerisola (Panizza & Cerisola, 2007, 2008).

The electrolysis time for complete removal of bupirimate was proportional to the concentration of bupirimate. In conclusion, the BDD anode performs well for electrochemical degradation of high concentration of bupirimate solution with appropriate current density and NaCl concentration as supporting electrolyte.

3.1.4 Effect of pH at the BDD anode

The effect of initial pH on the degradation of bupirimate solutions was investigated. The pH of the effluent was adjusted using H_2SO_4 and NaOH (initial pH was 6.2). Experiments were carried out in four different pH (11, 8, 5 and 2.5) at a constant current density of 60 $mAcm^{-2}$ using the boron doped diamond electrode as the anode. The initial concentration of bupirimate was 230 mg/L (Figure 6). The decrease of the pH 11 to 2.5 leads to a decrease of

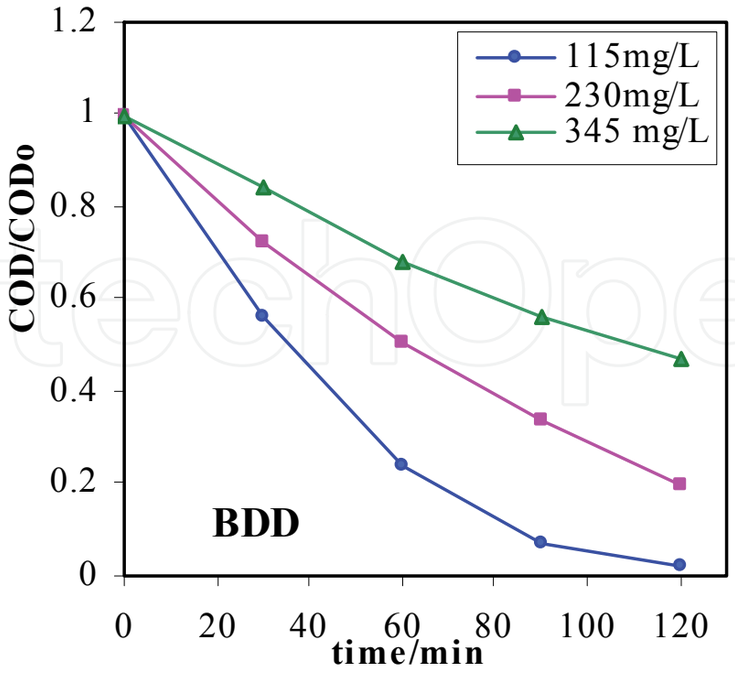


Fig. 5. a. Influence of bupirimate initial concentration on the normalized COD during BDD-anodic oxidation. Operating conditions: electrolyte = 2 % NaCl, current density = 60 $mAcm^{-2}$, T = 25 °C.

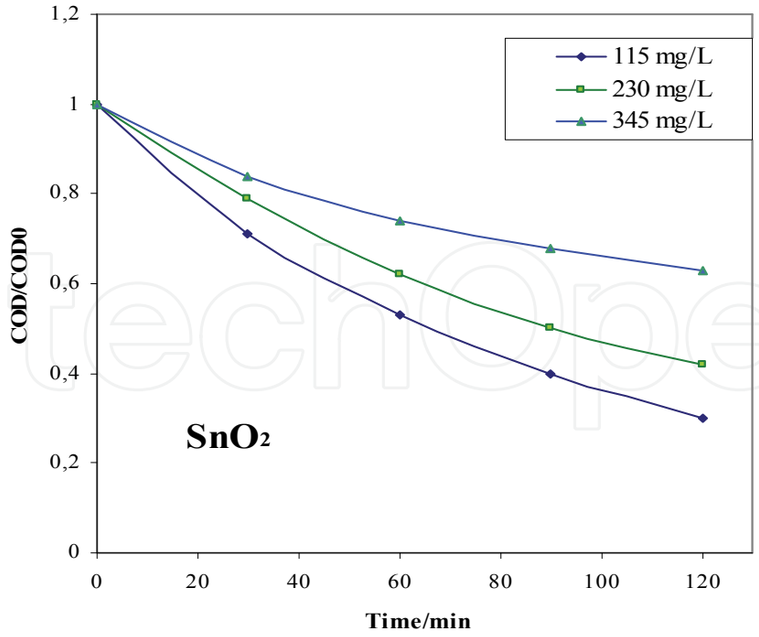


Fig. 5. b. Influence of bupirimate initial concentration on the normalized COD during SnO_2 anodic oxidation of bupirimate. Operating conditions: electrolyte = 2 % NaCl, current density = 60 $mAcm^{-2}$, T=25°C.

the absorbance of the peaks located at 240 nm and 310 nm. At pH=5, the peak located at 310 nm disappeared. This result indicates that the reaction rate is less in basic condition, which indicates that the OH- is unstable in basic condition. Decrease in pH increases the hydroxyl radicals, which favours the rate of oxidation (Yavuz & Savas, 2008).

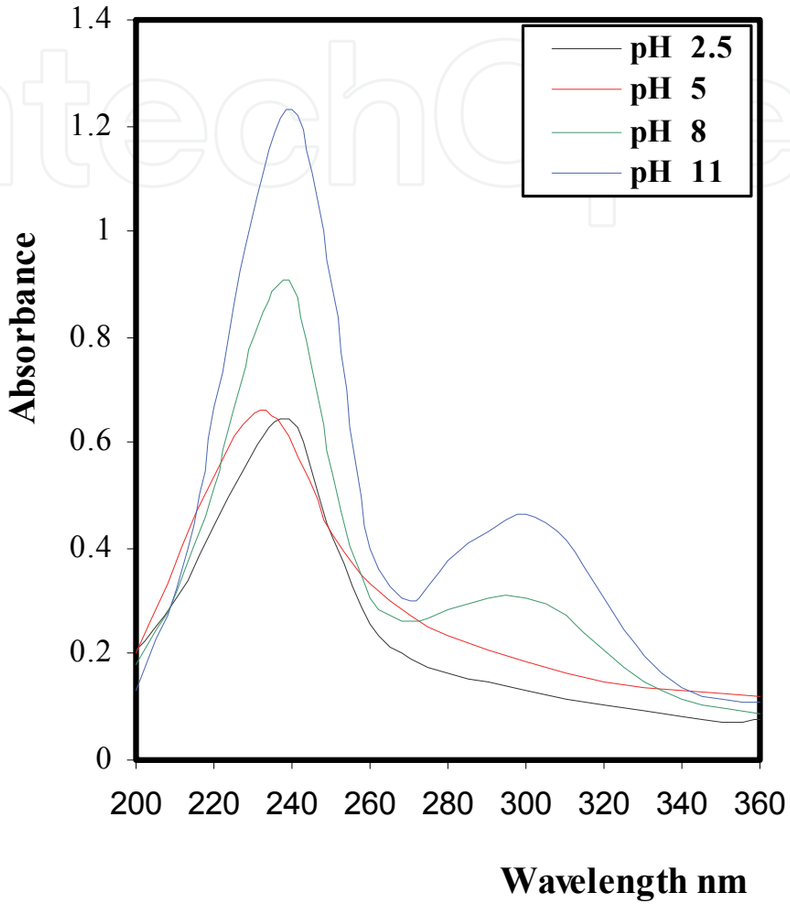


Fig. 6. Effect of initial pH on the variations of UV spectra for 2 h of the electrooxidation assays performed at a BDD anode. Bupirimate initial concentration = 230 mg/L, current density = 60mAcm^{-2}, electrolyte = 2 % NaCl.

3.1.5 Comparative study of electrochemical degradation efficiency on BDD and SnO_2 electrodes

The comparative study of electrochemical degradation of bupirimate was also performed on BDD and SnO_2 electrodes. The absorption spectral changes during galvanostatic electrolysis in aqueous solution are shown in figures 7-a and 7-b. It can be observed that the absorption spectrum of bupirimate is characterized by a band in the UV region with its maxima located at 240 nm and by a band in region located at 310 nm. The absorbance peak at 240 nm can be attributed to the sulfamate, while the absorbance at 310 nm is probably due to the presence of amine group in the pyrimidine pesticide. For BDD electrode, the absorption of the band located at 310 nm decreased sharply with the time and disappeared after 120 min (Figure 7-a). The same observation could be made for SnO_2 electrode but with slower arte.

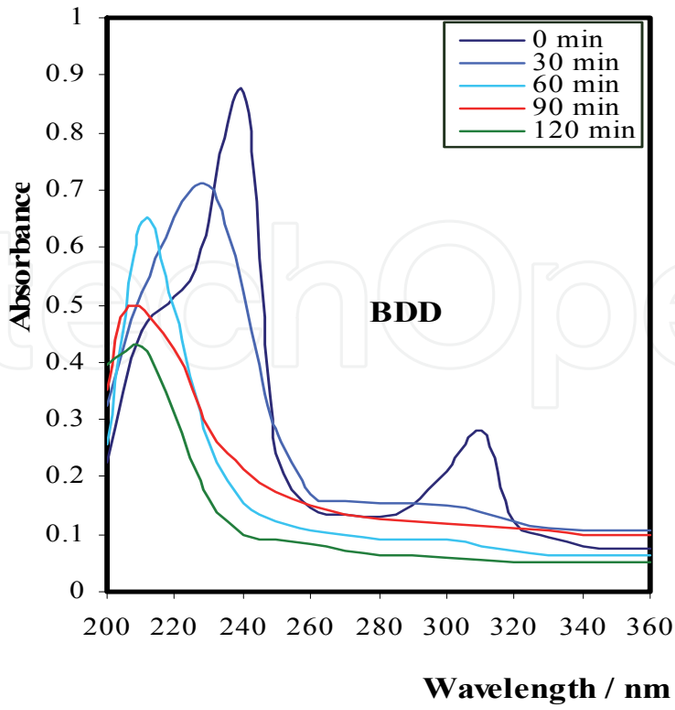


Fig. 7. a. UV spectra for the electrooxidation assays performed at the BDD anode. Bupirimate initial concentration = 230 mg/L, current density = 60 $mAcm^{-2}$, pH = 6.2, electrolyte = 2 % NaCl.

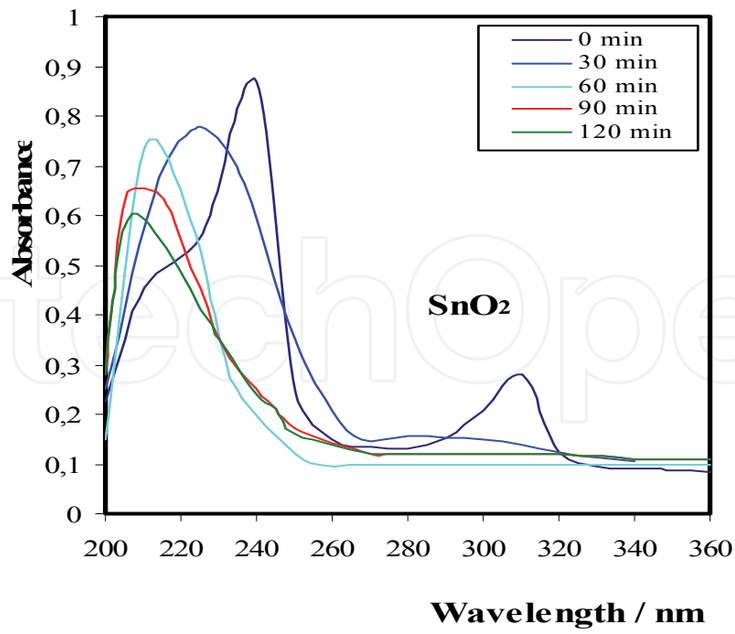


Fig. 7. b. UV spectra for the electrodegradation assays performed at the SnO_2 anode. Bupirimate initial concentration = 230 mg/L, current density = 60 $mAcm^{-2}$, pH = 6.2, electrolyte = 2 % NaCl.

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 8. At the same electrolysis time, the rate of electrodegradation of bupirimate is different for both anodes. The reaction rate is fast on the BDD anode, while the reaction rate is relatively slow on the SnO_2 anode. Table 3 indicates that different electrodes exhibit different performance in the rate of electrochemical degradation of pesticide. These results show that the % of abatement bupirimate found by GC is the same as analyzed by COD.

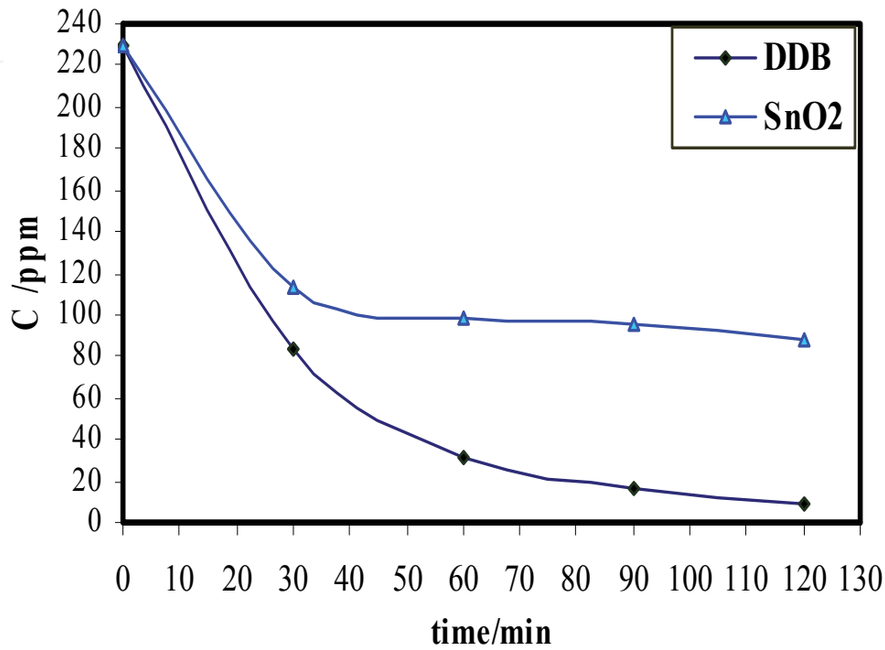


Fig. 8. Electrolysis time dependence of bupirimate concentration for two anodes (BDD, SnO_2). Bupirimate initial concentration = 230 mg/L, current density = 60 $mAcm^{-2}$, pH = 6.2, electrolyte = 2 % NaCl.

Anodes	Rate constant, K (min^{-1})	%COD
BDD	288.10^{-3}	74
SnO_2	80.10^{-3}	59

Table 3. Apparent rate constants of bupirimate removal fitted by a first order model and %COD for BDD and SnO_2 anodes.

3.1.6 Conclusion

The electrochemical degradation of high concentration bupirimate in sodium chloride-mediated wastewater at a BDD electrode was investigated in comparison with SnO_2 electrode. In 2 % of NaCl, the electrochemical degradation efficiency of bupirimate on BDD electrode was much greater than that on SnO_2 with a COD removal of 74 % on BDD anode and 59 % on SnO_2 anode. The different experimental conditions tested using the BDD anode allow us to conclude that the increases of the pH of the solutions, from acidic solution (pH = 2.5) to basic solution (pH = 11), slightly decreases the rate of absorbance of the peaks

located at 240 nm and 310 nm. When comparing the performances of both anode materials, at 60 $mAcm^{-2}$, the degradation efficiency is much higher for the BDD anode than that of SnO_2 anode. This means that the rate of mineralization is higher for the BDD anode. However, at 20 and 40 $mAcm^{-2}$, identical values are obtained for both anodes, with a COD removal of 26 and 58 %, respectively. Furthermore, the increase in initial bupirimate concentration from 230 mg/L to 345 mg/L increases the absolute removal of COD. These results lead to the conclusion that the BDD electrode is the most efficient compared to SnO_2.

3.2 Electrooxidation of methidathion

3.2.1 Electrooxidation of methidathion by anodic boron doped diamond electrode

3.2.1.1 Effect of chloride concentration

We observed that the application of electrolysis in this pesticide have the ability to reduce considerably the COD. For example, for 2 % mass NaCl and 3 % NaCl the achieved reduction was 85 % and 72 % respectively, while for 4 % NaCl was 56 %.

The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of methidathion on the electrode or indirect via some mediators like chlorinated species or other radicals (Tatapudi & Fenton, 1994; Lin et al.,1998).

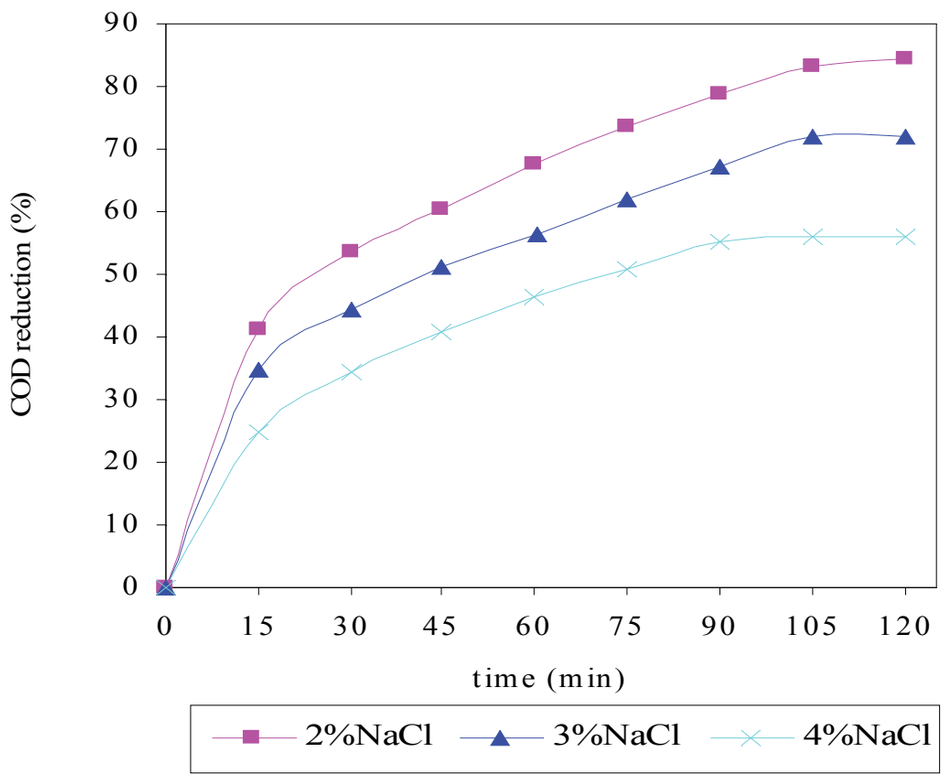


Fig. 9. The chemical oxygen demand (COD) reduction (in %) for methidathion 1.4 mM solution for 120 min of electrolysis at 60 mA and 25 °C.

Since some oxidant compounds that are produced during oxidation of water (like O2, O3 or hydroxyl radical) or oxidation of chlorine ions following Eq (7) to (9):

$$Cl^- \Leftrightarrow Cl^{\cdot}_{ads} + e^- \quad (7)$$

$$Cl^- + Cl^{\cdot}_{ads} \Leftrightarrow Cl_2 + e^- \quad (8)$$

$$Cl_2 + H_2O \Leftrightarrow HClO + H^+ + Cl^- \quad (9)$$

As cited in reference (Bonfatti et al., 2000), at pH higher than 4.5 the complete dismutation of Cl_2 into HClO and Cl^- is occurred. An explanation of the mediating role of chloride ions has been proposed by Bonfatti et al (Bonfatti et al., 2000). The presence of a weak concentration of chloride ions allows to inhibit the water discharge into oxygen, and to favorise hydroxyl or chloride and oxycloride 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 methidathion. Figure 10 illustrates that the pH during the electrolysis is significantly reduced.

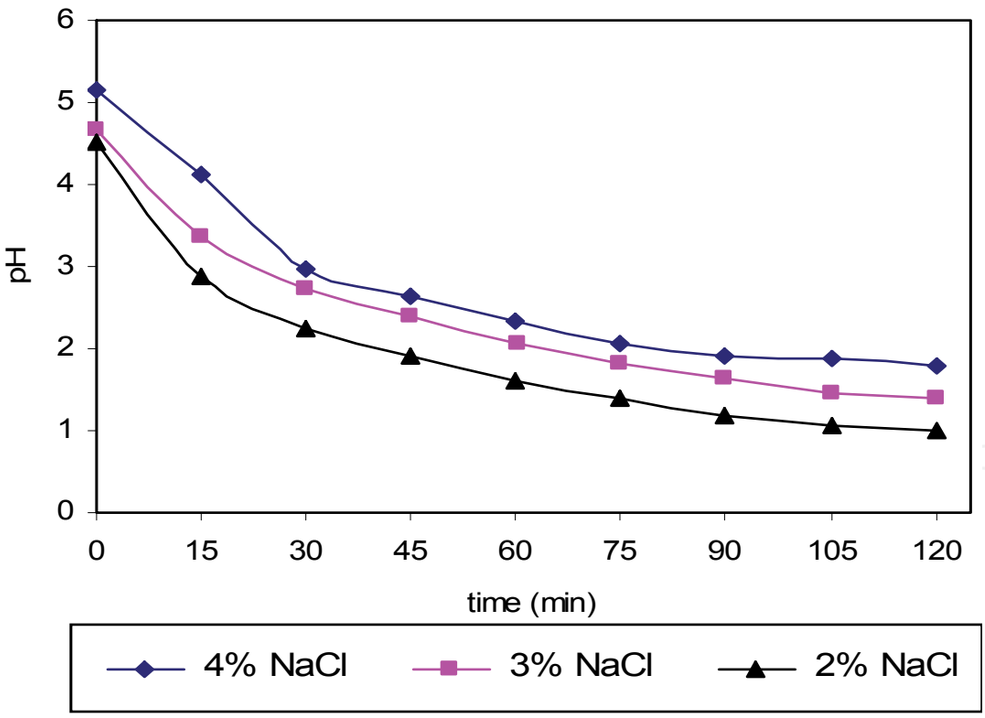


Fig. 10. pH reduction for methidation 1.4 mM solution for 120 min of electrolysis at 60mA and 25 °C.

Finally the pH in all cases became strong acidic. It is obvious that the continuous addition of high levels of organic matter in the electrolytic cell, resulted in the drop of pH. The electrolysis was more effective in terms of %COD reduction when the pH was in the acid

range. This drop of the pH, during pesticides degradation, was also reported by Bonfatti et al that while the mineralization goes to completion and the solution pH get more and more acidic.

3.2.1.2 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. In Figure 11 the % COD reduction for the methidathion is presented under different current inputs (chlorides = 2 %).

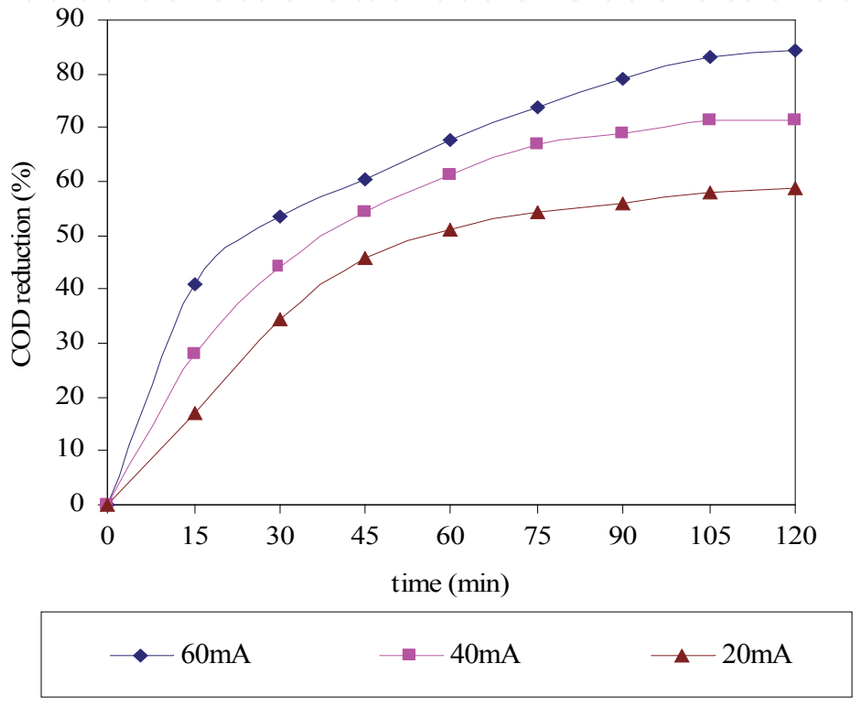


Fig. 11. % COD reduction for methidathion 1.4 mM under different current inputs (chlorides= 2%) and 25°C

These studies concluded that applied current increases the rate of electrochemical oxidation process. The COD of methidathion was observed to fall with pseudo first-order kinetics, 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 methidathion (k) varies from 0.0073 s^{-1} (20 mA) to 0.0146 s^{-1} (60 mA). This is exemplified in Figure 12 where the pseudo first-order plot is presented. From these results it was calculated that the best applied current is 60 mA.

3.2.1.3 Effect of temperature

In Figure 13 the % COD reduction for methidathion at different temperatures under current input 60 mA is presented. It is observed that for 25 °C and 65 °C the achieved reduction was 85 % and 66 % respectively. The COD of methidathion was observed to fall with pseudo first-order kinetics Figure 14. The pseudo firstorder constant of methidathion (k) varies from 0.0131 s^{-1} (25 °C) to 0.0077 s^{-1} (65 °C).

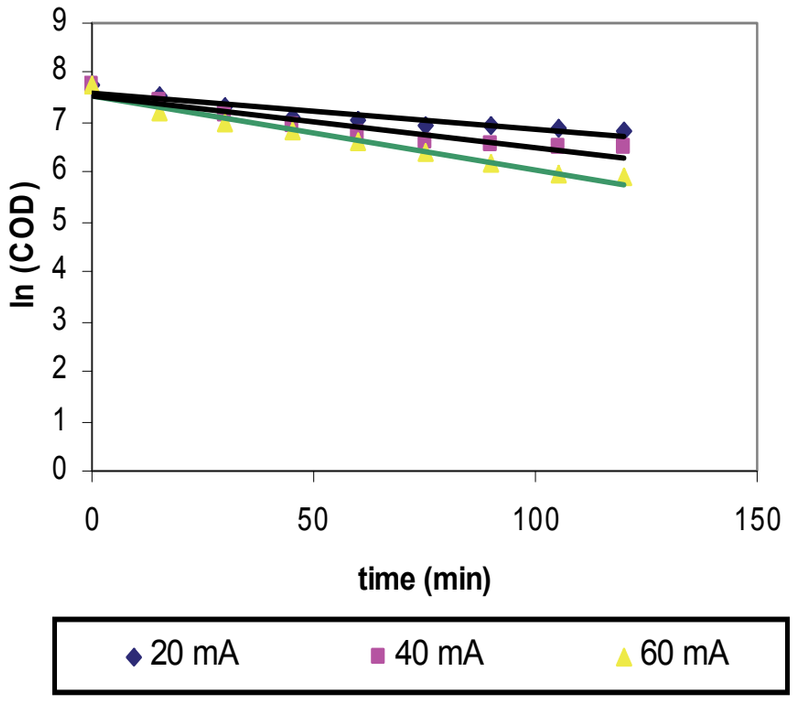


Fig. 12. Pseudo first-order plot oxidation of methidation 1.4 mM in 2% NaCl at 25°C under different current inputs (COD at a given time, t,during electrolysis).

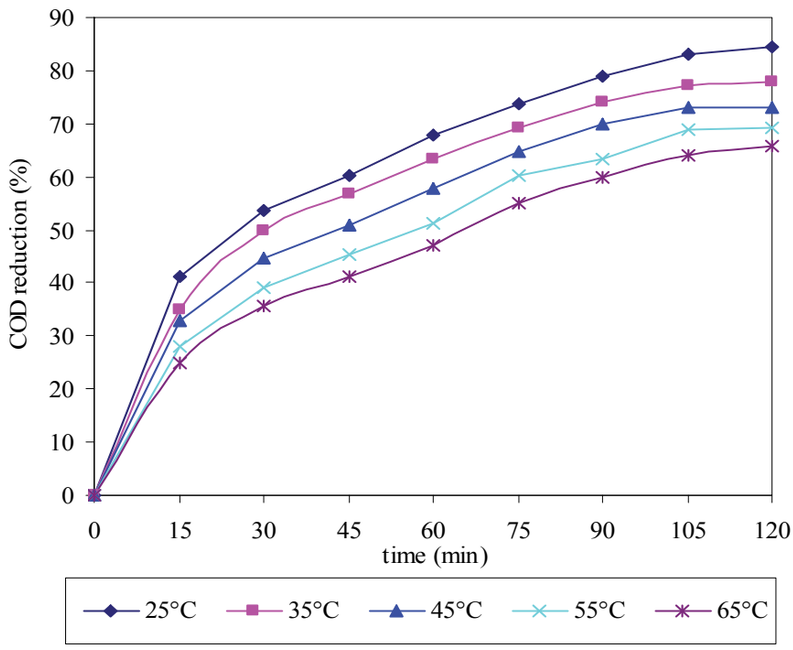


Fig. 13. COD reduction (in %) for methidathion 1.4 mM solution in 2 % NaCl at 25 °C at different temperatures.

The effect of temperature on the rates of constant was modelled using the Arrhenius plots, are shown in Figure 15. The apparent activation energies were determined by

$$K = A.\exp(-E_a / RT) \tag{10}$$

where K is rate constant, A is constant, Ea is the activation energy, T is the temperature (K) and R is the gas law constant.

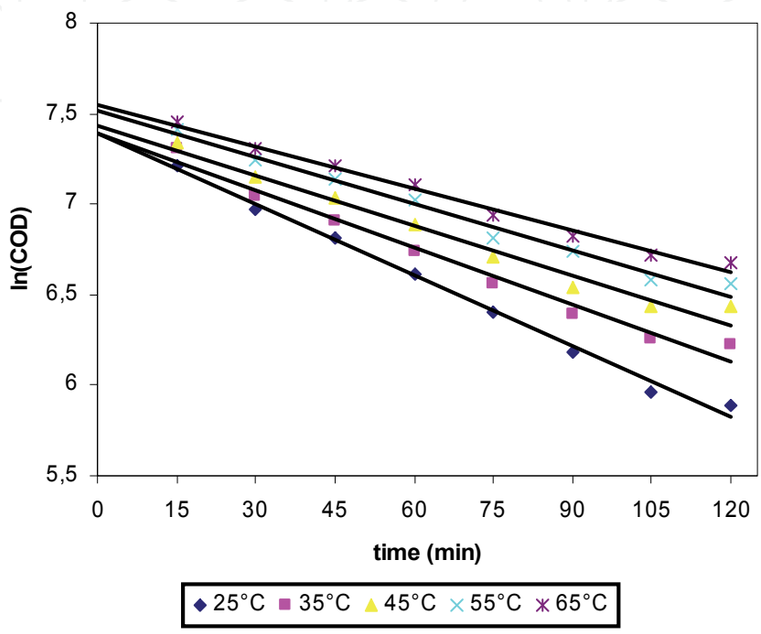


Fig. 14. Pseudo first-order plot oxidation of methidation 1.4 mM in 2% NaCl at 60 mA under different temperatures (COD at a given time, t,during electrolysis).

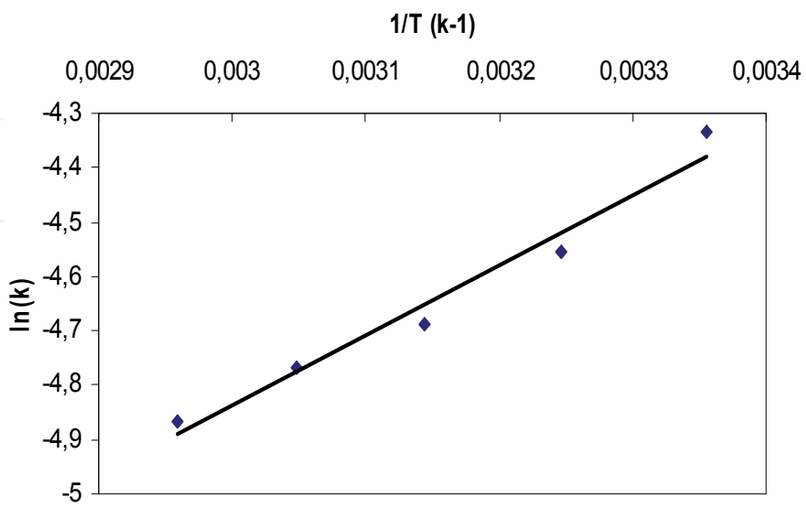


Fig. 15. Arrhenius plote of methidation 1.4 mM in 2% NaCl at 60 mA at various temperatures.

The obtained activation energy (-10.75 kj) indicate that the electrochemical degradation is complex.

3.2.2 Electrooxidation of methidathion by anodic SnO_2 electrode

3.2.2.1 Effect of applied current

In Figure 16 the COD for the methidathion is presented under different current inputs (chlorides = 2%). These studies concluded that the rise of applied current increases the rate of electrochemical oxidation process. In fact the COD abatement is faster as the applied current 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 applied current 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 applied current.

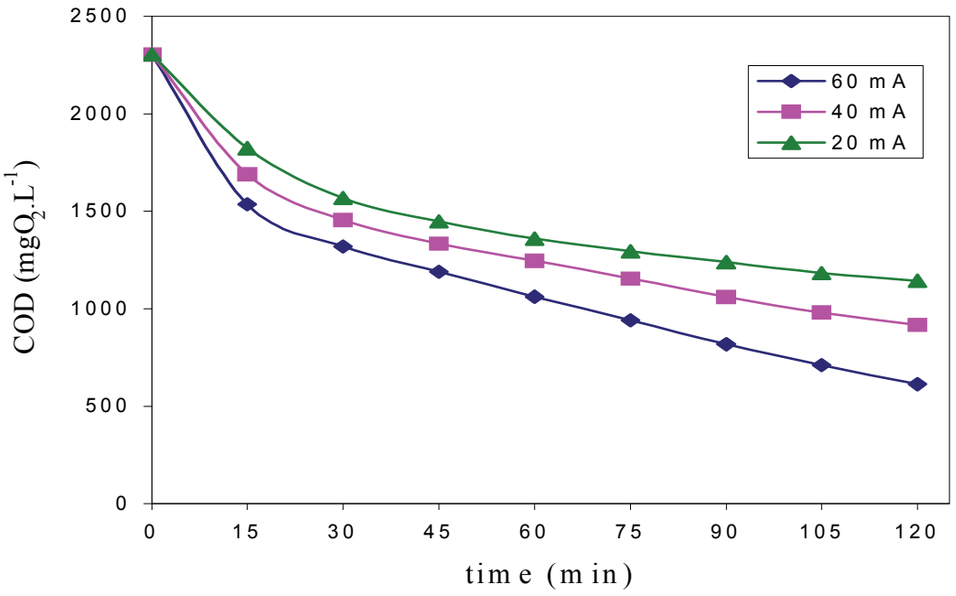


Fig. 16. % COD reduction for methidathion 1.4 mM under different current inputs (chlorides= 2%). 25°C and volume of treated solution: 75 cm^3

An important factor in the electrochemical treatment of organic containing effluents is the energy necessary to achieve the desired results. For an electrochemical reactor under galvanostatic conditions, the electrolysis energy is given by the equation (11):

$$E = \int_t U(t)\, I\, dt \tag{11}$$

The cell voltage U(t) is given by the following sum of terms:

$$U = U^0 + \eta_A + \eta_C + \sum RI \tag{12}$$

where, U_0 is the potential at nil current, η_A and η_B are respectively the anodic and cathodic overvoltages and Ω(RI) represent the ohmic drop through the solution of resistance R. The cell voltage was directly measured during electrolyses.
The energy consumption after 50 % reduction of COD of aqueous methidation solution is summarized in Table 4.

	COD input (mg)	Time of electrolysis (min)	Energy consumption (kWh/g COD).
20 mA	2304	115	$6.12\ 10^{-4}$
40 mA	2304	75	$9.61\ 10^{-4}$
60 mA	2304	48	$9.72\ 10^{-4}$

Table 4. Energy consumption after 50 % reduction of COD.

As can be seen, an increase in applied current caused the decrease of the time of electrolysis under 50% percent COD reduction while the energy consumption value increased. At lower current, the voltage is insufficient to mediate side reactions. Therefore, the energy is utilized for the degradation reaction only. However, under high current, the side reactions of oxygen evolution are more dominant.
The COD of methidathion was observed to fall with pseudo first-order kinetics, on the entire 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 methidathion (k) varies from 0.0043 s^{-1} (20 mA) to 0.0086 s^{-1} (60 mA). This is exemplified in Fig. 17 where the pseudo first-order plot is presented. These results show that the rate constant depends on the applied current.

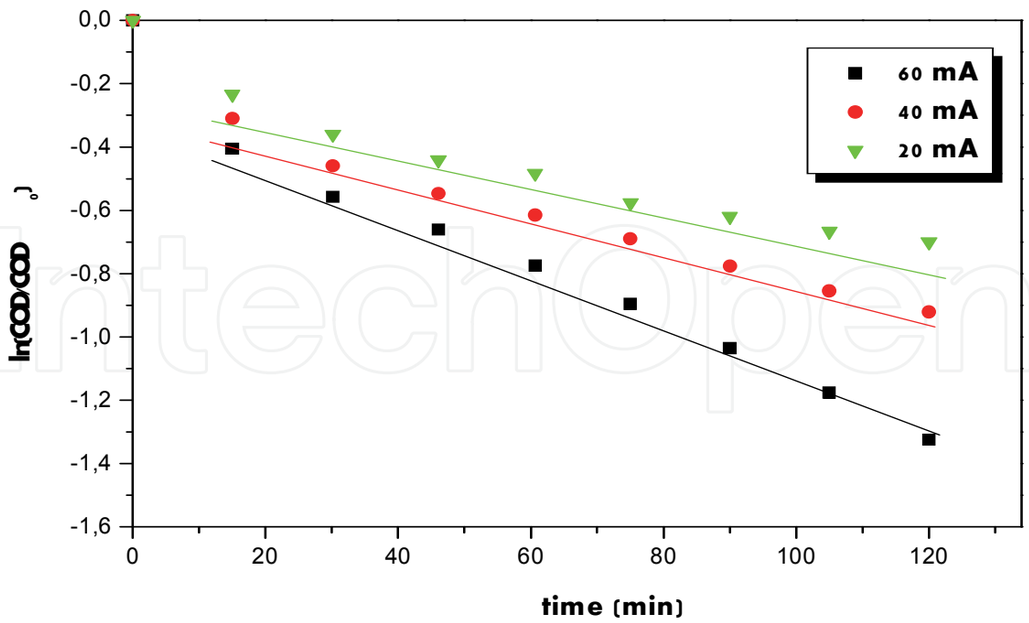


Fig. 17. Pseudo first-order plot oxidation of methidation 1.4 mM in 2% NaCl at 25°C and volume of treated solution: 75 cm3 under different current inputs (COD_t and COD_0 at t=0 and at a given time, t, during electrolysis).

3.2.2.2 Effect of temperature

To determine the effect of temperature on the % COD reduction for methidathion, experiments were carried under current input 60 mA for which reduction for methidathion is more important. Figure 18 shows the % COD reduction for methidathion at different temperatures. It was observed that, the % COD reduction decrease with temperature, for 25°C and 65°C the achieved reduction was 75 % and 50 % respectively.

The COD of methidathion was observed to fall with pseudo first-order kinetics. The pseudo first-order constant of methidathion (kI) varies from 0.0085 s^{-1} at 25 °C to 0.0038 s^{-1} at 65 °C (Fig. 19).

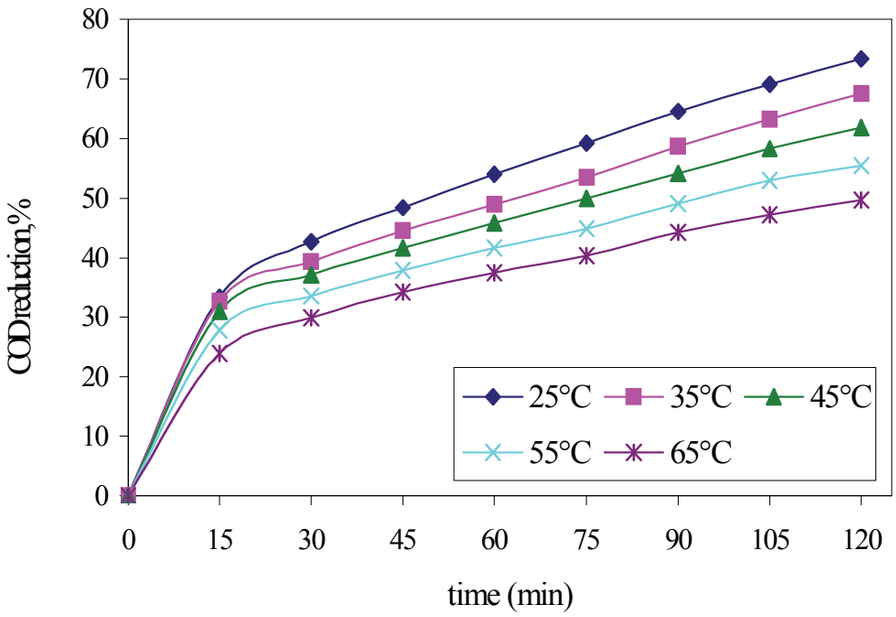


Fig. 18. % COD reduction for methidathion 1.4 mM in 2% NaCl at 25°C and volume of treated solution: 75 cm^3 at different temperatures.

The values of the rate constant (k) at different temperatures are listed in Table 5.

T (K)	k_I (s^{-1})
298	0.0085
308	0.0068
318	0.0056
328	0.0046
338	0.0038

Table 5. k_I as a function of temperature.

The linear least square fit of all the data points provided by the experiments at different temperatures leads to the Arrhenius parameters (activation energy and preexponentiel factor):

$$k_I(T) = (9.80 \pm 0.30)x10^{-6} \exp(2016 \pm 10 / T)\ s^{-1}$$

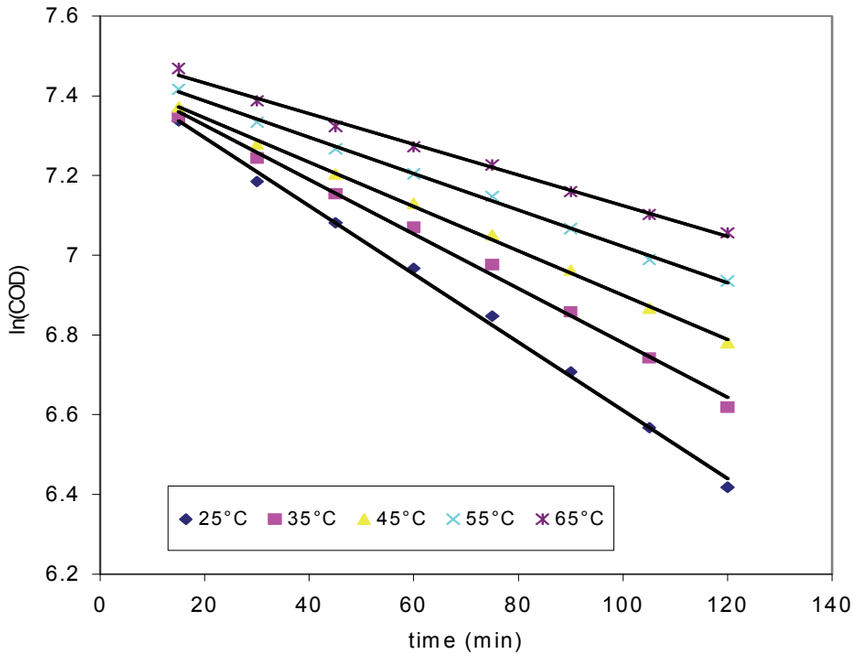


Fig. 19. Pseudo first-order plot oxidation of methidation 1.4 mM in 2% NaCl at 60 mA and volume of treated solution: 75 cm^3 under different temperatures (COD at a given time, t, during electrolysis).

As can be seen the rate constant k_I exhibits a negative temperature coefficient which confirms that the electrochemical degradation proceed via a complex mechanism.

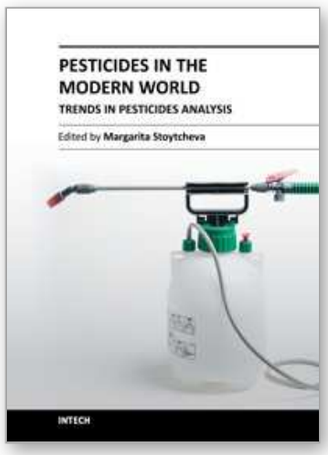
3.2.3 Conclusion

The application of electrolysis in pesticide has the ability reduce the COD. For 2 % NaCl the achieved COD removal was 85 % and 75 % for BDD and SnO_2 respectively. In all cases, the pH of electrolysis was significantly reduced after 45 min for both electrodes. The COD of methidathion was observed to fall with pseudo first-order kinetics, on the entire surface studied. The applied current increases the rate of electrochemical oxidation process.
The effect of temperature shows that for 25 °C and 65 °C by BDD achieved was 85 % and 66 % respectively. The rate constant k_I obtained exhibits a negative temperature coefficient which confirms that the electrochemical degradation proceeds via a complex mechanism.
The COD of methidathion was observed to fall with pseudo first-order kinetics, on the totally surface studied.
The applied current increases the rate of electrochemical oxidation process.
The activation energy indicates that the process of electrochemical degradation is a complex one.

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Pesticides in the Modern World - Trends in Pesticides Analysis
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The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

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