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Electrochemical Degradation of Cypermethrin Pesticide on a SnO_2 Anode

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This paper presents the study of the electrochemical oxidation of the pesticide cypermethrine at a SnO_2. In this work, the effect of using different supporting electrolytes (NaCl, NaOH, Na_2CO_3, H_2SO_4 and Na_2SO_4) during the galvanostatic electrolysis of cypermethrine was investigated. It was observed that the removal of cypermethrine and chemical oxygen demand (COD) was only achieved at appreciable rates when NaCl was used as the supporting electrolyte, due to the oxidising species formed in this electrolyte. Variation of the NaCl concentration demonstrated that, although only low concentrations of NaCl are necessary to result in the complete removal of cypermethrine in solution. The achieved reductions of % COD were 75% for 2% NaCl. Examination of the applied current density indicates that the efficiency of COD removal reaches a maximum at 80 $mA.cm^{-2}$. in this work presents, the effect of temperature and pesticide concentration of cypermethrine are investigated. The high efficiency of this technology can be explained in terms of the direct electro-oxidation at the SnO_2 surface and the oxidation carried out by hydroxyl radicals ($OH^{\cdot}$) and other electro-generated oxidants (ClO^-).

Keywords: Electrochemical treatment, Pesticide Cypermethrine , Insecticide, Electrooxidation, Cyclic voltammetry; Galvanostatic electrolysis.

1. INTRODUCTION

The rapid increase of population and intensive agriculture in our planet has resulted in large quantities of organic and inorganic wastes being discharged into environment, thus giving rise to serious environmental problems and deterioration of the agroecosystems. This process may also cause a risk in the human health. The potential problems in environment caused by pesticides, heavy metals, fertilizers, agricultural residues, wastewater, sewage sludge, solid wastes, atmospheric fallout and transgenic organisms. The results are an increase in toxic elements in air, soil and water resources. Once heavy metals enter the environment, they are very difficult to remove. Since the area of the world is limited opening new fields for agriculture is not possible in order to meet the requirement of increasing population. Pesticides come first among the inputs used to increase product amount to be obtained from unit of area.

Commercial synthetic chemical pesticides are utilized in all countries and as a consequence reach even the remotest regions. Wherever pesticides are used, unusable or unwanted pesticides and empty pesticides containers have to be managed and disposed safely. Food and Agricultural Organization of the United Nations (FAO) estimated that more than 500000 tonnes of obsolete pesticides are stored worldwide [1]. Various innovative technologies have been proposed for the disposal of obsolete pesticides. These technologies include photocatalytic oxidation [2,3], ultrasonic radiation [4], bioremediation and thermal desorption [5]. The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with a very low active ingredient content, rather than highly concentrated obsolete pesticides stocks.

Electrochemical techniques have been proposed for the treatment of wastewater containing bio refractory and toxic organic pollutants. According to this process electro-conversion and electro-combustion reactions transform the non-biodegradable organic species, dissolved in aqueous solutions, respectively, to biodegradable organic compounds or final inorganic ones, like CO_2 and H_2O [6-7]. The advantages of electrochemical treatment are various and well documented: the catalyst/electrode is immobilized (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 [8]. In addition, electrochemical processes are easily adapted for use in flow systems [8], a fact that is considered important for the feasibility of pesticide treatment systems [9]. In recent studies Salghi and co-workers studied the electrooxidation of bupirimate and methidathion in brine solution using Boron Doped Diamond Anodes (BDD) and SnO_2 anodes [10-14]. Vlyssides et al studied the electrooxidation of various organophosphorous pesticides such as methylparation [15,16]; Phosalone, Azinphos-methyl, Methidathion [17]; Demeton-S-methyl, Metamidophos, Fenthion and Diazion [18].

Cypermethrin is a synthetic chemical similar to the pyrethrins in pyrethrum extract (whichcomes from the chrysanthemum plant). Pyrethroids, including cypermethrin were designed to be effective longer than pyrethrins [19]. Cypermethrine (Cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate) is a widely used pertroide 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) [20-22]. This paper discusses the treatment of cypermethrin by an electrochemical method, in laboratory scale plant using an SnO_2 electrode as anode.

2. MATERIALS AND METHODS

2.1. 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).

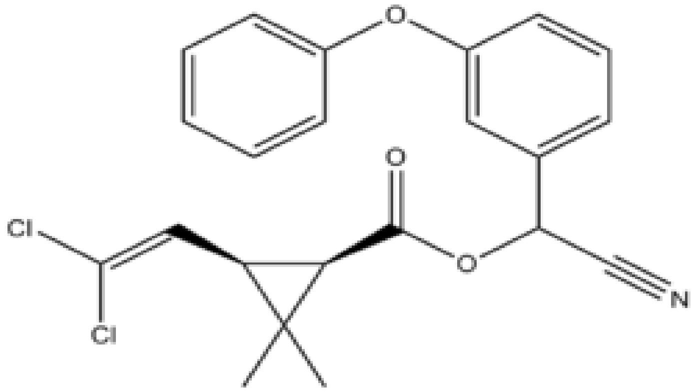

Figure 1. Chemical structure of Cypermethrin.

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).

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 electrodes cell (100 cm^3) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of SnO_2 electrode with effective surface area of 1 cm^2, whereas the cathode was a platinum electrode, and the gap between electrodes was 1cm. A saturated calomel electrode (SCE) was used as a reference.

Galvanostatic electrolysis was carried out with a volume of 75 cm^3 aqueous solution of 50 mg/L. The range of applied current density was 40 to 80 mA/cm^2 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 [24]. 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.

2.3 Analytical procedures

The method used for the extraction of cypermethrin was adapted from Charles and Raymond [23]. 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.

2.4. 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 300ºC.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry – effect of electrolyte

Prior to each electrolysis, cyclic voltammetry investigations were performed in order to characterise the electrodes used. Cyclic voltammetry is a useful technique for probing the processes that occur at the electrode/solution interface [25]. The current variation that results when the electrode potential is varied can provide valuable insight into the reactions that occur at the electrode surface. It is widely accepted that cyclic voltammetry offers the most sensitive in situ characterisation of oxide materials [26]. In the case of the oxides used in this study, the voltammetric experiment is performed in the potential region where no permanent modification of the oxide surface occurs (-1–1.5 V versus RHE). However, in order for the oxidation of cypermethrin pesticide to occur at oxide electrodes, potentials that enter the region of the oxygen evolution reaction (OER), i.e. >1.4V, must be applied [27]. Figure 2 represents the cyclic voltammograms of the five different supporting electrolyte in a 2% NaCl, 2% NaOH, 2% Na_2CO_3, 2% H_2SO_4 and 2% Na_2SO_4 solution in the presence of 50 mgL^{-1} of cypermethrin pesticide.

In 2% NaCl it can be observed that cypermethrin promotes has a significant increase in charge or current associated with the oxygen evolution reaction for the SnO_2 electrode. However, the auther supporting electrolyte response presents a considerable decrease in charge when cypermethrin is added. These results would indicate that the interaction of the pesticide molecule with the electrode surface using 2% NaCl is distinct to that of the other supporting electrolyte.

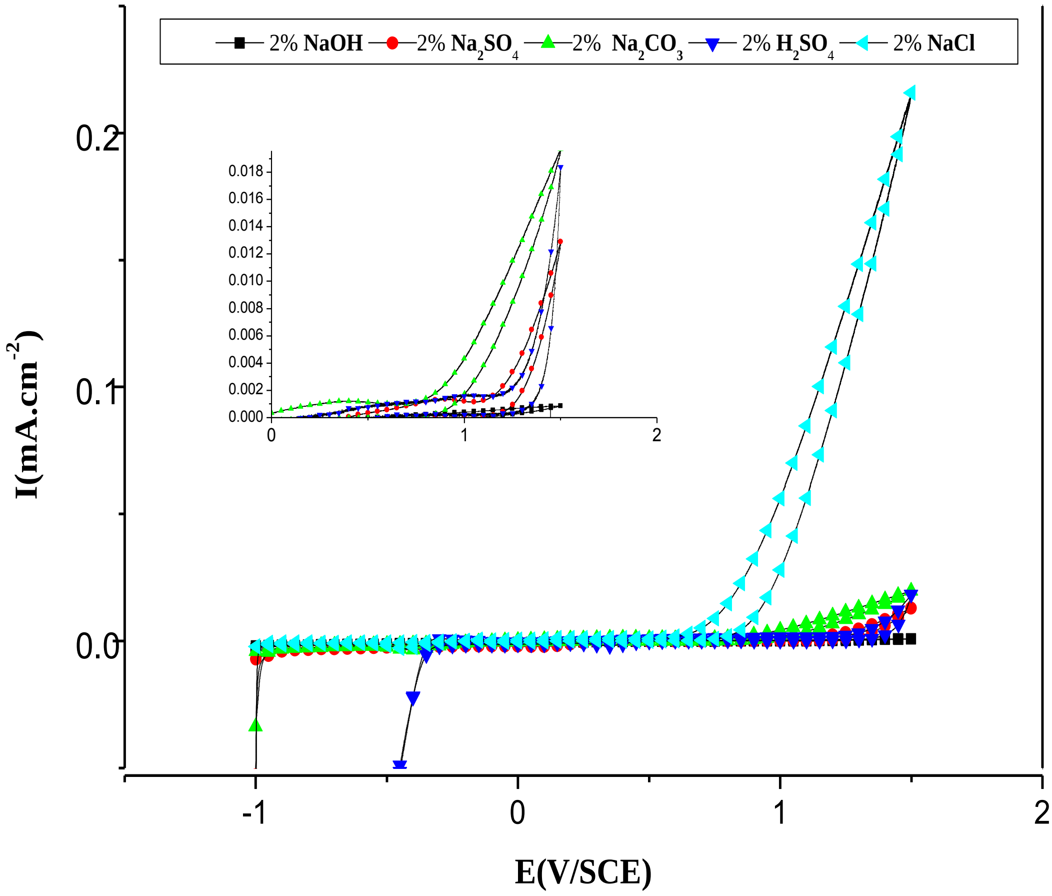

Figure 2. Voltammetric profiles of the SnO_2 electrode in different supporting electrolyte of cypermethrin 50 mg.L^{-1}. Auxiliary electrode: platinum; reference electrode: SCE; scan rate: 10 mVs^{-1}.

3.2. Effect of the NaCl concentration

The investigation of the mediator concentration effect has been performed in the range 1-3% for NaCl. The Figure 3 shown effect of chloride ions concentration on the degradation of cypermethrin solution, carried out at 80 mA/cm^2. As shown in this Figure, the utilization of electrolysis to detoxify cypermethrin pesticide has the ability to reduce considerably the chemical oxygen demand (COD). The electrochemical degradation of the organic substrate is achieved at reasonable rates only in the presence of the mediator and is higher at 2% NaCl concentrations.

Further increase, above this limit, causes and 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 75% and 64% for 2% NaCl and 3% NaCl respectively, while for 1% NaCl was 43%. 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 [10-14].

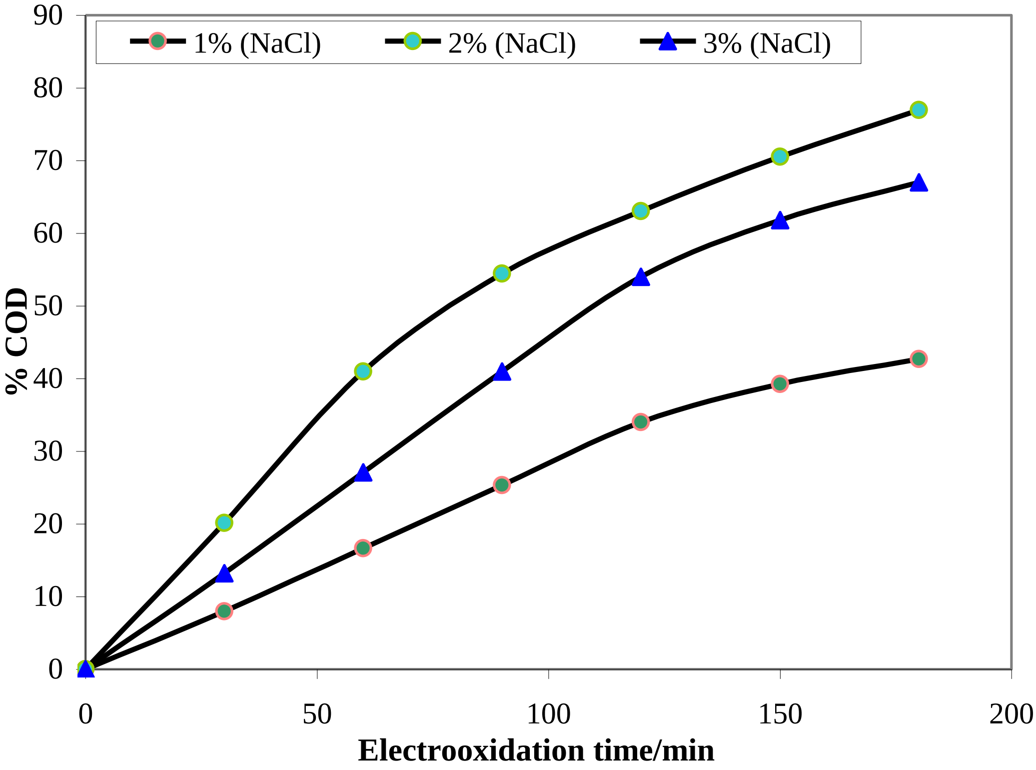

Figure 3. Direct electrooxidation at SnO_2 anode: effect of NaCl concentration on the %COD (50 mg.L^{-1} cypermethrin solution, 80 mA.cm^{-2}, pH=5.4, and T=25°C).

The concentration of cypermethrin was measured using GC and the variations of pesticide concentration with electrooxidation time for the SnO_2 anode are shown in figure 4. At the same electrolysis time, the rate of electrodegradation of bupirimate is different for both anodes. The reaction rate is fast for 2% NaCl, while the reaction rate is relatively slow on the 3% NaCl and 1% NaCl.

The results obtained in the present work also indicate that degradation of Cypermethrin is greatly influenced by concentration of supporting electrolyte NaCl in solution.

Figure 5 illustrates the apparent kinetic constants for oxidation of Cypermethrin at different concentration of NaCl as a function of the electrolysis time. The apparent kinetic constants constant of Cypermethrin (k) varies from 42×10^{-4} min^{-1} for 1%NaCl, 103×10^{-4} min^{-1} 2% NaCl and 72×10^{-4} min^{-1} 3% NaCl.

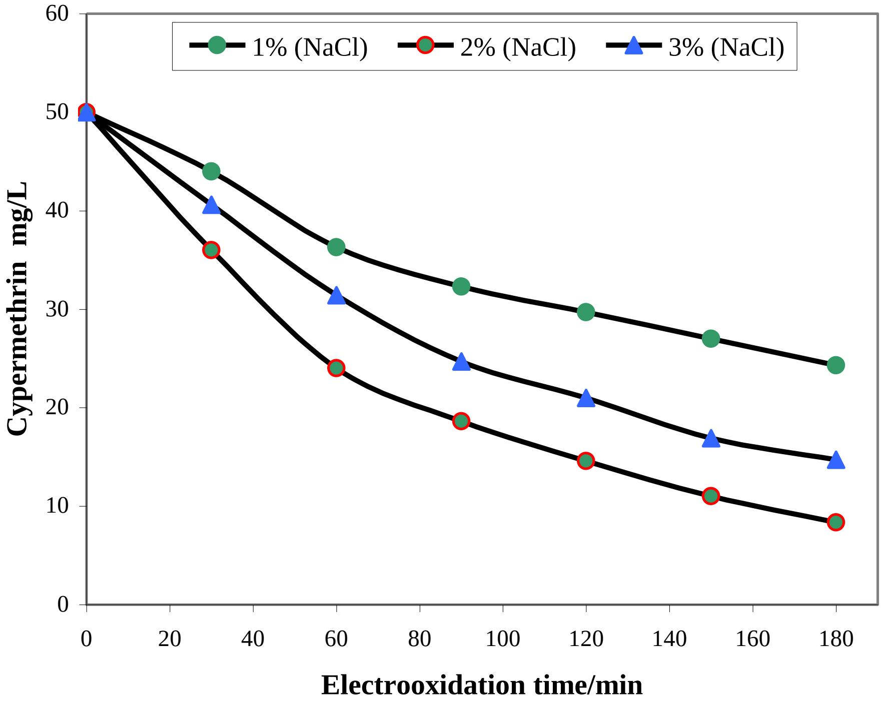

Figure 4. Evolution of concentration cypermethrin during the galvanostatic electrolyses of wastes polluted with 50 mg L^{-1} of cypermethrin pesticide under effect of NaCl concentration. Operating conditions: T=25°C; pH 5.4; i=80 mA. cm^{-2}.

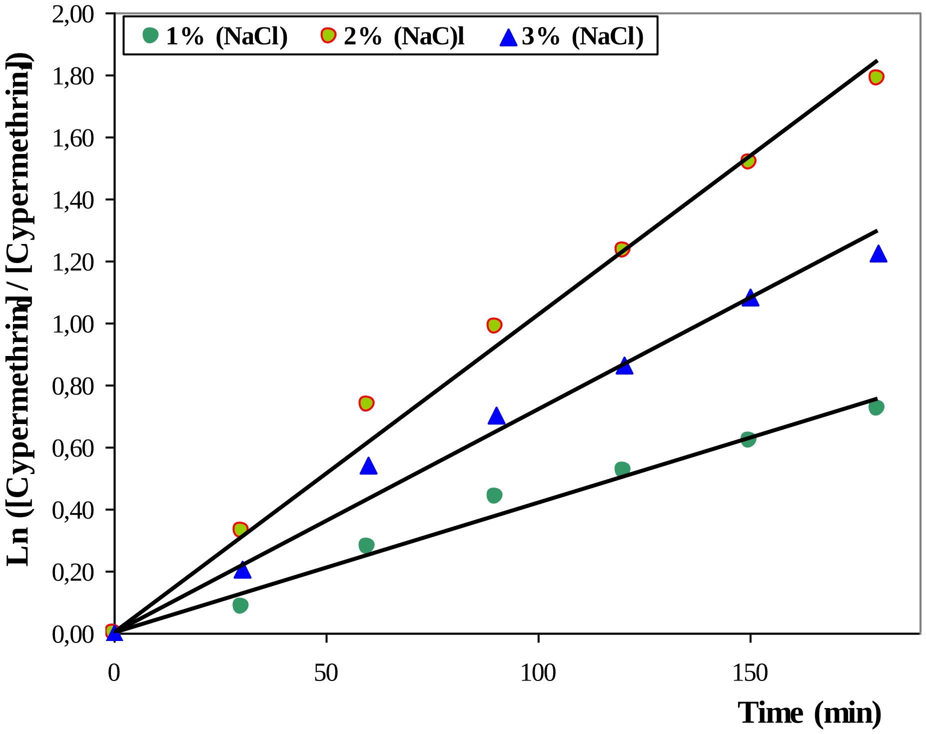

Figure. 5 apparent kinetic constants for oxidation of 50 mg/L Cypermethrin at 80 mA. cm^{-2}, pH=5.4 and T=25°C.

3.3. Effect of current density

The influence of the current density on the COD removal during the electrochemical oxidation of cypermethrin at the anode is shown in Fig. 6. Increasing the current density until 80 mA.cm^{-2} resulted in an enhancement of the oxidation rate [11-13]. After 3h time of electrolysis, the COD percent removal increased from 44% to 76% when the current density increased from 40 to 80 mA.cm^{-2}. This behavior indicates that in these experimental conditions, the oxidation of cypermethrin is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

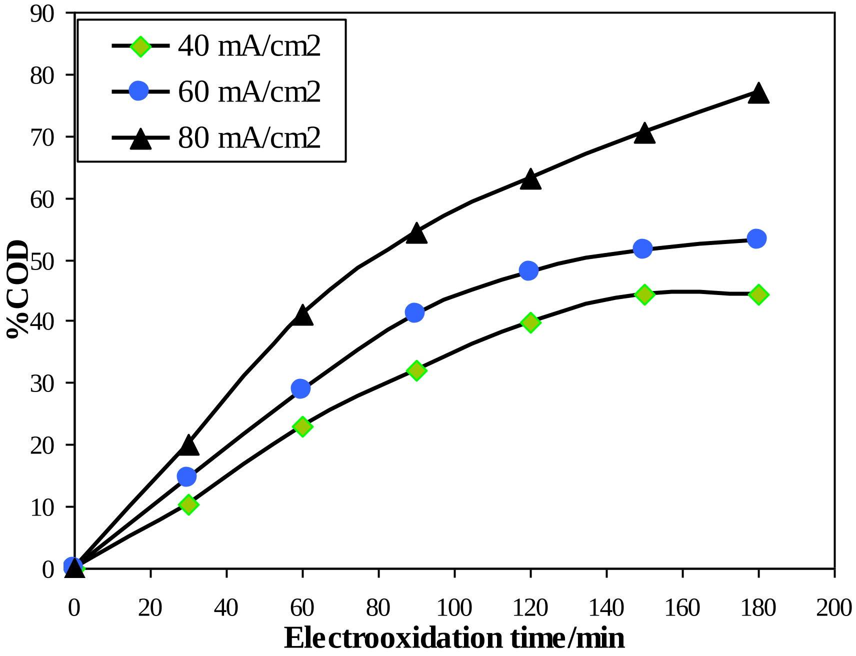

Figure. 6 Influence of the applied current density on the trends of % COD electrolysis of cypermethrin (C_0 = 50 mg.L^{-1}) using a 1cm^2 SnO_2 anode. pH=5.4 and T=25°C.

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 a first-order reaction kinetics for the oxidation reaction. Working in galvanostatic condition, the concentration of $^{\bullet}$OH or Cl$^{\cdot}$ can be approximated in a steady state and therefore, the oxidation rate expression can be written as follows:

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

which can be integrated to give the following expression:

$$Ln\left(\frac{COD_0}{COD_t}\right) = K_{app}t$$

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 observed pseudo first-order rate constant. Apparent rate constants determined by plotting the ln (COD_0/COD_t) against time at different applied current (Table 2).

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

Current intensity (mA.cm^{-2})	Rate constant, K (min^{-1})	COD removal (%)
40	37.10^{-4}	44
60	56.10^{-4}	53
80	103.10^{-4}	76

3.4. Effect of initial concentrations of pesticide

The initial concentration of pollutants is always an important parameter in wastewater treatment. Figure 7 shows the effect of the initial concentration of cypermethrin (25, 50 and 75mgL^{-1}) on the Concentration removal during electrolysis at pH 5.4, temperature of 25°C and using a current density of 80 mAcm^{-2}. 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].

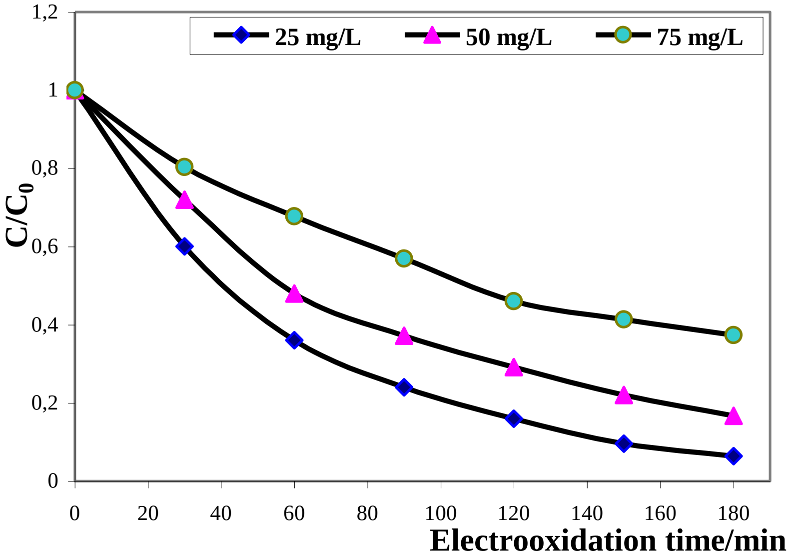

Figure 7. Influence of pesticide initial concentration on the normalized concentration cypermethrin during SnO_2-anodic oxidation (Operating conditions: electrolyte = 2% NaCl, current density = 80 mAcm^{-2}, T = 25°C, and pH=5.4).

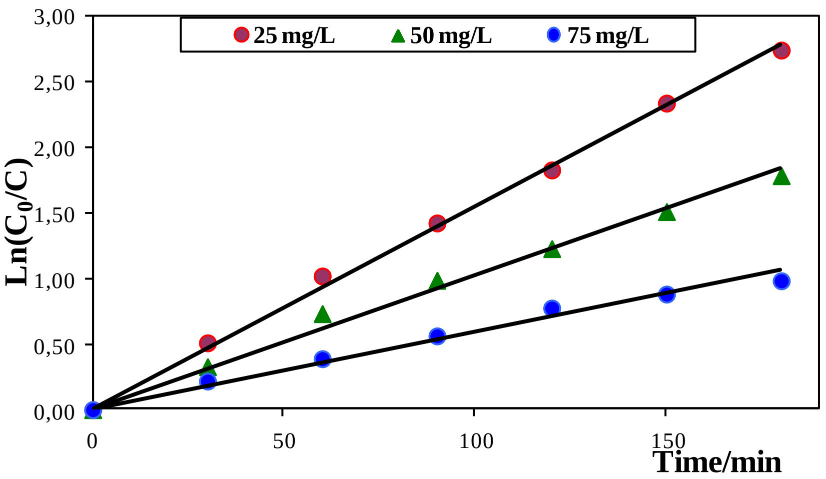

Figure 8. Linear regression for concentration removal with time during the electrochemical oxidation of cypermethrin on the SnO_2 anode for different concentrations. iapp =80mAcm^{-2}; pH=4.5 andv T=25°C.

For all the concentrations the pesticide removal follows pseudo first-order kinetics and the apparent rate constants were 155.10^{-4}, 103.10^{-4} and 59.10^{-4} min^{-1} for the cypermethrin concentrations of 25, 50 and 75 mg/L, respectively. These study was similar of the results obtained by several papers [12,14].

3.5. Effect of temperature on the degradation efficiency

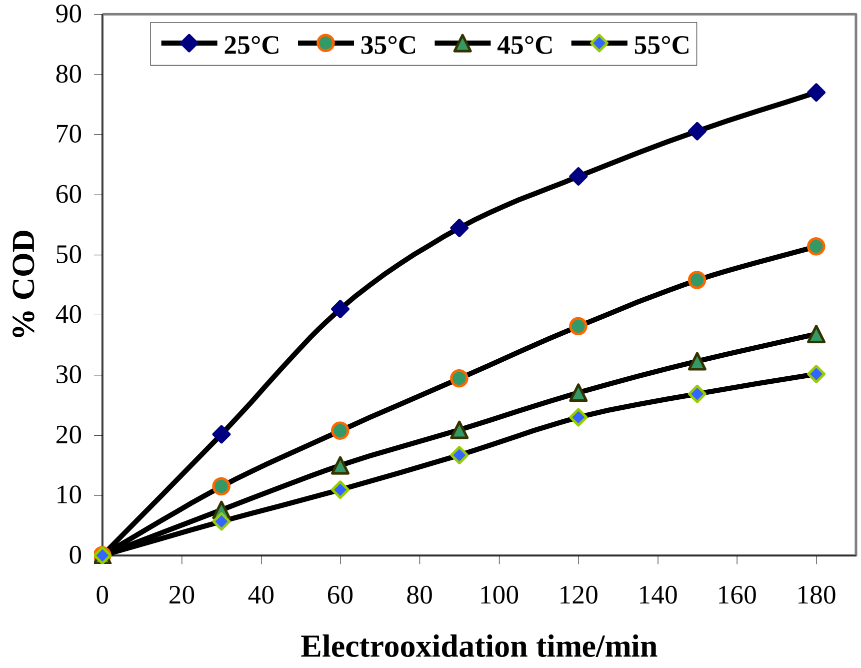

Figure 9. Influence of temperature on the decay of %COD during electro-oxidation of 50 mg/L cypermethrin on SnO_2 anode. Conditions: current density 80mA cm^{-2}; pH=5.4; 2% (NaCl).

Figure 9 shows the effect of temperature on the variation of %COD during the electrolysis of 50 mg/L cypermethrin at 80 mAcm^{-2}. The higher was the temperature, the faster was the %COD removal [10]. In fact, when the temperature increased from 55 to 25 °C the time for the mineralization of the cypermethrin decreased from 180 to 60 min.

In fact, as shown in Figure 10, the COD removal follows a pseudo first-order kinetics and the apparent rate constant decreased with temperature, Apparent rate constants determined by plotting the Ln (COD_0/COD_t) against time at different temperature (Table 3).

Table 3. Apparent rate constants of cypermethrin removal fitted by a first order model and %COD for SnO_2 anodes under different temperature.

Temperature (°C)	Rate constant, K (min^{-1})	COD removal (%)
25	103.10^{-4}	76
35	40.10^{-4}	52
45	26.10^{-4}	37
55	21.10^{-4}	30

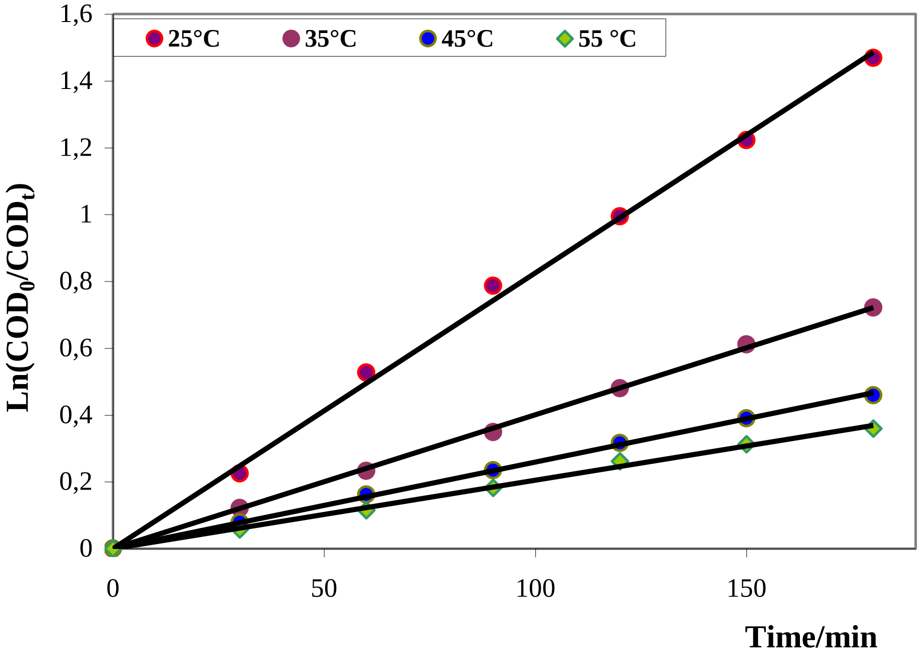

Figure 10. Pseudo first-order plot oxidation of cypermethrin 50 mg/L in 2% NaCl at 80 mA under different temperatures (COD at a given time, t during electrolysis).

4. CONCLUSION

This work is a first attempt to investigate the degradation of cypermethrin insecticide in electrochemical treatment with SnO_2. The electrochemical degradation of cypermethrin (50 mg/L) has been investigated using SnO_2 anode under all conditions tested involving, effect of different supporting electrolyte, effect of NaCl (1% to 3%), applied current density from 40 to 80 mA cm^{-2}, temperature varying from 25 to 55 °C and for different concentration of pesticide. The experimental results allowed us to draw the following conclusions:

- The addition of sodium chloride to the solution resulted in an increase in the organic oxidation rate due to the participation of electrogenerated hypochlorite ions in the process. The results also indicated that the COD removal was affected by chloride concentration and the optimum one was 2% (NaCl).
- In our experimental conditions, the oxidation was under mass transport control and the COD removal was well described by a pseudo-first-order kinetic. The applied current increases the rate of electrochemical oxidation process.
- The effect of temperature shown that for 25 ºC and 55 ºC the achieved reduction was 76% and 30 % respectively.
- The best obtained conditions for COD removal on the SnO_2 anode to degrade cypermethrin solutions (concentration = 50mgL^{-1}) include operating at 80 mAcm^{-2}, 2% NaCl and 25 $^{\circ}$C.

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