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Electrochemical Combustion of Insecticides Endosulfan and Deltamethrin in Aqueous Medium Using A Boron-Doped Diamond Anode

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Disposal of agricultral wastewater containing enosulfan and deltamethrin by electrochemical methods has been studied in this paper. The degradation of insecticides enosulfan and deltamethrin in aqueous medium of pHi range 5.8-6.2 has been comparatively studied by anodic oxidation using a boron-doped diamond (BDD) anode. A number of experements were run on a laboratory scale and the resulte are reportude here. GC and chemical oxygen demand measurements were conducted to study the reaction kinetics of two insecticides mineralization. The experimental results showed that the electrochemical process was suitable for almost completely removing COD, due to the production of hydroxyl radicals on the diamond surface. In particular, the COD removal follows a pseudo first-order kinetics and the apparent rate constant increased with applied current, while it is almostun affected by concentrations of pesticides and pH. Under optimal experimental conditions of temperature (T=25 °C), supporting electrolyte NaCl (1 g/L) and current density (i.e. 60 mA cm^{-2}), 81% of COD was removed in 2 h electrolysis for deltamethrin, with 11 kWh($kgCOD^{-1}$), and 7.6 kWh($kgCOD^{-1}$) for endosulfan.

Keywords: Electrooxidation, Pesticide, endosulfan, deltamethrin , Insecticide, agricultral wastewater , BDD.

1. INTRODUCTION

In recent years there has been increasing interest in environmental damage and human injury by agricultre pollution, and the relevant legislation is always being made harsher. The intensive use of pesticides in agriculture and the improper storage or disposal of obsolete pesticides are a source of contamination of soil, ground water, rivers, lakes, rainwater and air. Various innovative technologies have been proposed for the removal of pesticides from water. Among these technologies, the electrochemical processes constitute the emergent methods for the degradation of pesticides.

In this framework electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents. Electrochemical techniques have been receiving greater attention in recent years due to their distinctive advantages such as, environmental compatibility; (the main reactant is the electron which is a clean reagent) and versatility (a plethora of reactors and electrode materials, shapes, and configurations can be utilized). It is noteworthy that the same anode can be used frequently for different electrochemical reactions with only minor changes and also the electrolytic processes can be scaled easily from the laboratory to the plant, allowing treatment volumes ranging from milliliters to millions of liters.

In anodic oxidation, organic pollutants are directly destroyed by reaction with hydroxyl radical ($HO^\bullet$) formed at the anode surface from water oxidation [1, 2]:

$$H_2O \rightarrow HO^\cdot + H^+ + e^- \qquad (1)$$

Hitherto, many electrodes have been examined to improve the effectiveness and efficiency of electrochemical processes, including Pt [3-8], SnO_2 [9-13], PbO_2 [14, 15], and boron-doped diamond (BDD) electrodes [11, 12, 16 - 20] have been used for pesticides removal. The new anode material (BDD) possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous medium [20, 21]. BDD anode has much higher O_2 overvoltage than that of conventional anodes such as PbO_2, doped SnO_2, IrO_2 and Pt, then producing larger amount of $HO^\bullet$ on the anode surface by reaction (1) giving a more rapid destruction of pollutants.

Recently, salghi et al. [11-13, 16, 17] demonstrated that the pesticide methedation and bupirimate can be electrochemically removed from aqueous solutions using SnO_2, and BDD anodes. They found that current density influence is remarkably clear on the BDD electrodes where it was evident that the most efficient current density toward a complete bupirimate mineralization was reached with the application of 60 $mAcm^{-2}$.

The organochlorine insecticide endosulfan is entering the final stages of consideration for listing under the Stockholm Convention on Persistent Organic Pollutants for global elimination. Endosulfan (Table 1) is a Persistent Organic Pollutant (POP) satisfies POPs criteria of persistence, bioaccumulation, long-range transport, and toxicity. In 2009 the POPs Review Committee (POPRC) concluded that “endosulfan is likely, as a result of its longrange environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted”.

The POPRC stated that “Human fatality and chronic poisoning cases, and severe environmental degradation have been reported” and that endosulfan is highly toxic for humans and most animal groups, showing both acute and chronic effects at relatively low exposure levels [22].

Deltamethrin products are among the most popular and widely used insecticides in the area Souss Massa in Morocco and have become very popular with pest control operators and individuals in the United States in the past five years [23]. This material is a member of one of the safest classes of pesticides: synthetic pyrethroids. This pesticide is highly toxic to aquatic life, particularly fish, and therefore must be used with extreme caution around water. It is neurotoxic to humans and has been found in human breast milk [24]. There are many uses for deltamethrin, ranging from agricultural uses to home pest control. Deltamethrin has been instrumental in preventing the spread of diseases carried by tick-infested prairie dogs, rodents and other burrowing animals. It is helpful in eliminating and preventing a wide variety of household pests, especially spiders, fleas, ticks, carpenter ants, carpenter bees, cockroaches and bedbugs. Deltamethrin is also one of the primary ingredients in ant chalk.

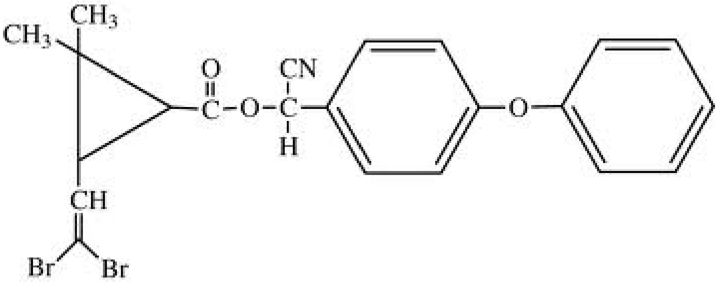
2. MATERIALS AND METHODS

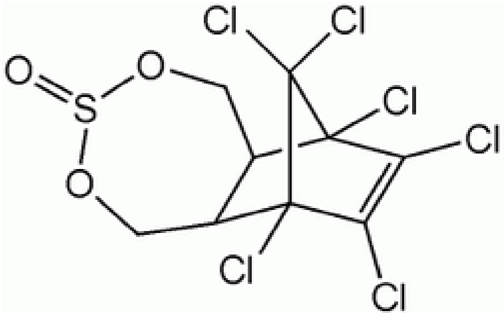
2.1. Chemicals

Deltamethrin is a pyrethroid insecticide. is a local systemic insecticide that is effective for control of Tuta absoluta in the tomato crop in area of Agadir (Morocco). Deltamethrin formulation is commercially available in the Decis expert 25 EC (100 g/L deltarmethrin) (Table 1). It was purchased from Bayer crop science. Endosulfan formulation is commercially available in the Prosulfan (350 g/L Endosulfan) (Table 1). It was purchased from sté Promagri (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).

Table 1. Chemical structure of Deltamethrin and Endosulfan.

Name of pesticide	Structure and Molecular Weight	Chemical structure
Deltamethrin	$C_{22}H_{19}Br_2NO_3$ 505.2 g/mol	

Endosulfan	$C_9H_6Cl_6O_3S$ 406.93 g/mol	

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 BDD 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 30 mg/L de deltamethrin and 6 g/L of endosulfan.

The range of applied current density was 20 to 60 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 [25]. 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 two pesticides was adapted from Charles and Raymond [26]. 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 pesticides 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) (15 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. Effect of the NaCl concentration

Different concentrations of NaCl were applied to study their effect on the removal of endosulfan and deltamethrin elimination as in Fig. 3a and Fig. 3b. The results indicate that an increase of the electrolyte concentration up to 1 g/L lead to increase in the pesticide degradation rate and Concentration removal for both deltamethrin and endosulfan pesticides.

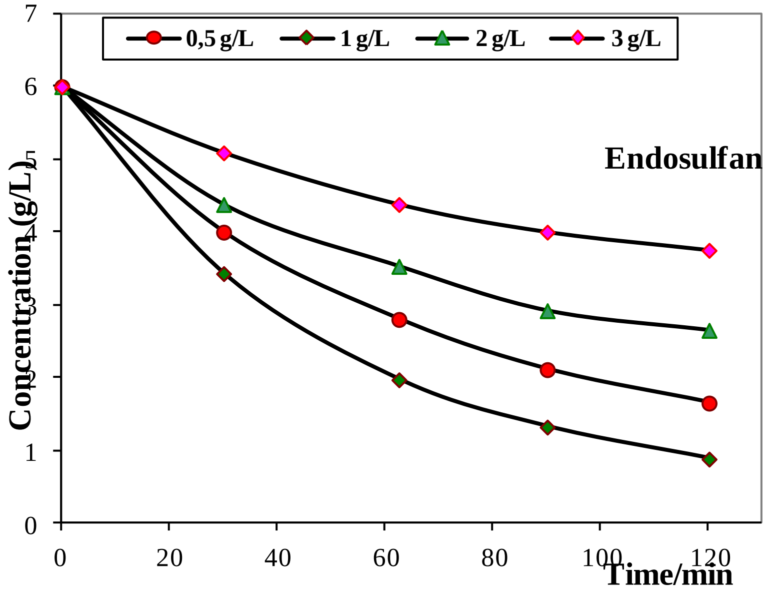


Figure 3. Evolution of concentration endosulfan during the galvanostatic electrolyses of wastes polluted with 6 g.L^{-1} of endosulfan pesticide under effect of NaCl concentration. Operating conditions: T=25°C; pH 5.8; i=60 mA. cm^{-2}.

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 been explain why until 1g/L of NaCl concentration the concentration removal increases with NaCl concentration. Increasing the chloride concentration more than 2g/L 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 1 g/L of NaCl for the degradation of both pesticides.

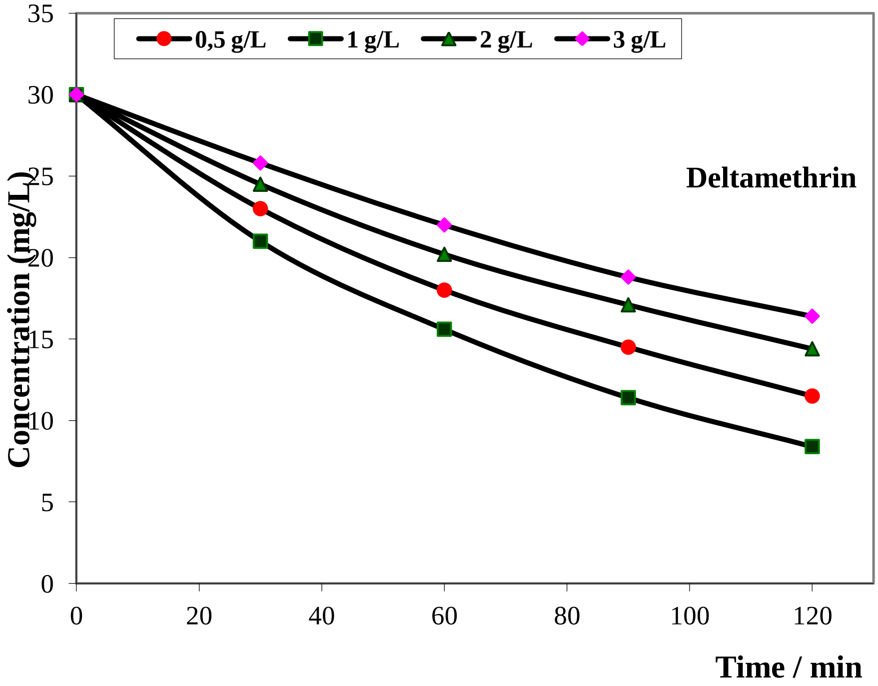


Figure 3. Direct electrooxidation at BDD anode: effect of NaCl concentration (30 mg.L^{-1} deltarmethrin solution, 60 mA.cm^{-2}, pH=6.2, and T=25°C).

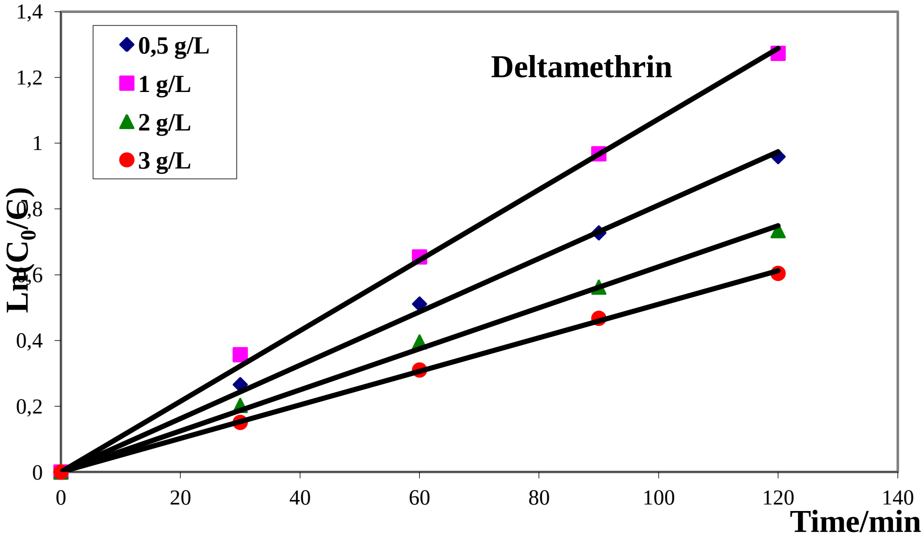


Figure. 4a apparent kinetic constants for oxidation of 30 mg/L deltamethrin at 60 mA cm^{-2}, pH=5.8 and T=25°C.

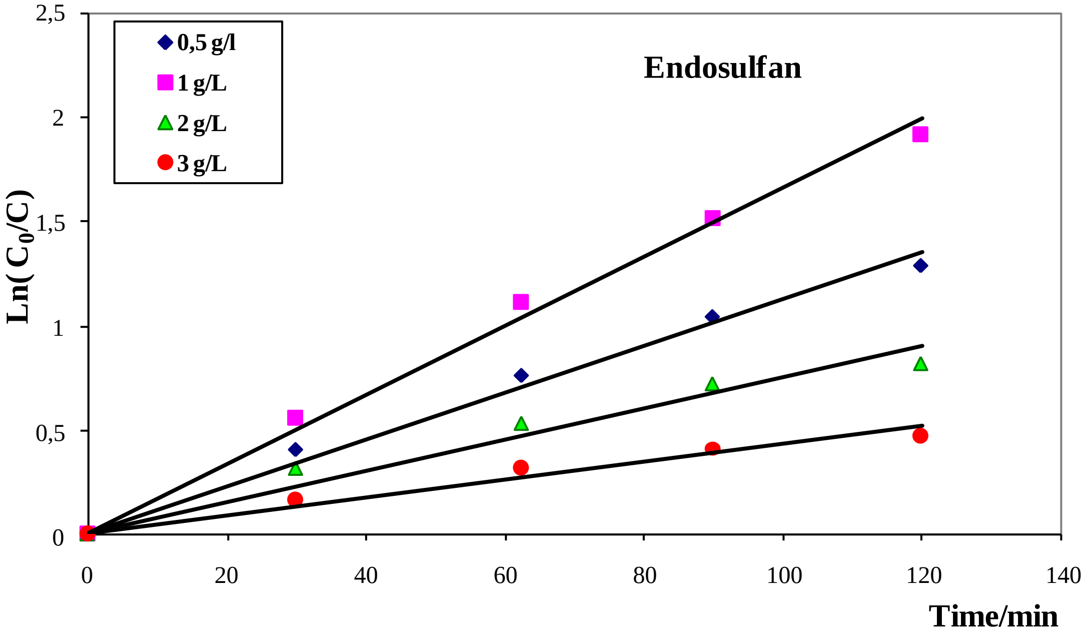


Figure. 4b apparent kinetic constants for oxidation of 6 g/L endosulfan at 60 mA cm^{-2}, pH$_i$=6.2 and T=25°C.

Table 2. Effect of NaCl concentration on the values of the rate constant.

Pesticides	Concentration of NaCl (g/L)	Rate constant, K (min^{-1})
Endosulfan	0.5	113.10^{-4}
	1	166.10^{-4}
	2	75.10^{-4}
	3	53.10^{-4}
Deltamethrin	0.5	81.10^{-4}
	1	107.10^{-4}
	2	62.10^{-4}
	3	51.10^{-4}

Figure 4a and Figure 4b illustrates the apparent kinetic constants for oxidation of deltamethrin and endosulfan at different concentration of NaCl as a function of the electrolysis time. The apparent kinetic constants constant of two pesticides (k). Table 2 indicates the rate of electrochemical degradation of pesticides.

3.2.Effect of pH

Fig. 5a and Fig. 5b illustrate the pH of the brine solution during electrolysis for both pesticides under effect of supporting electrolyte NaCl. In all cases the pH after 30 min of electrolysis was significantly reduced. Finally the pH in all cases became strong basic (pH = 12–13). It is obvious that the continuous addition of high levels of radicals $OH^{\bullet}$ in the electrolytic cell resulted in the increase of pH. This increase of the pH, during pesticides degradation, was also noted from Errami et al. [16] using BDD anode for the decomposition of bupirimate in aqueous solution. It was also reported (Salghi et al., 2011) [12] that while the mineralization goes to completion and the solution pH gets more and more basic, this could affect the speciation of radicals $OH^{\bullet}$, chlorine compounds and their oxidizing power.

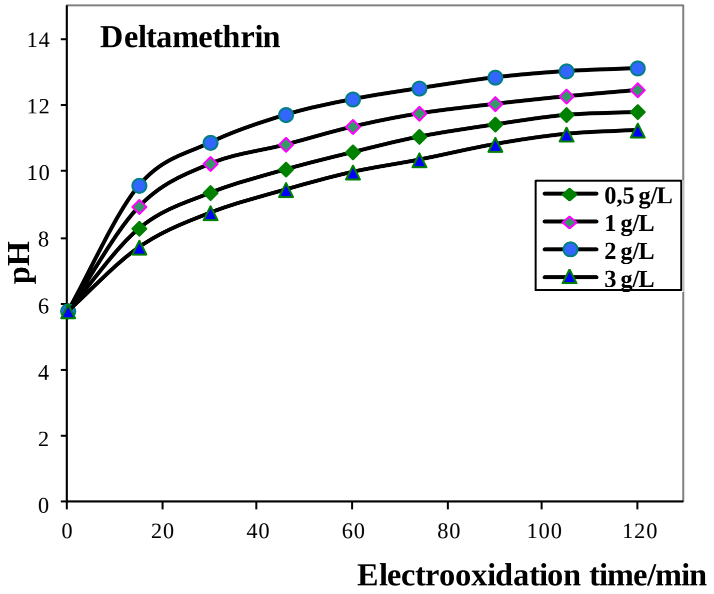


Figure. 5a pH reduction of deltamethrin 30 mg/L for 120 min of electrolysis at 60 mA/cm^2 and 25 °C, volume of treated solution: 75 cm^3

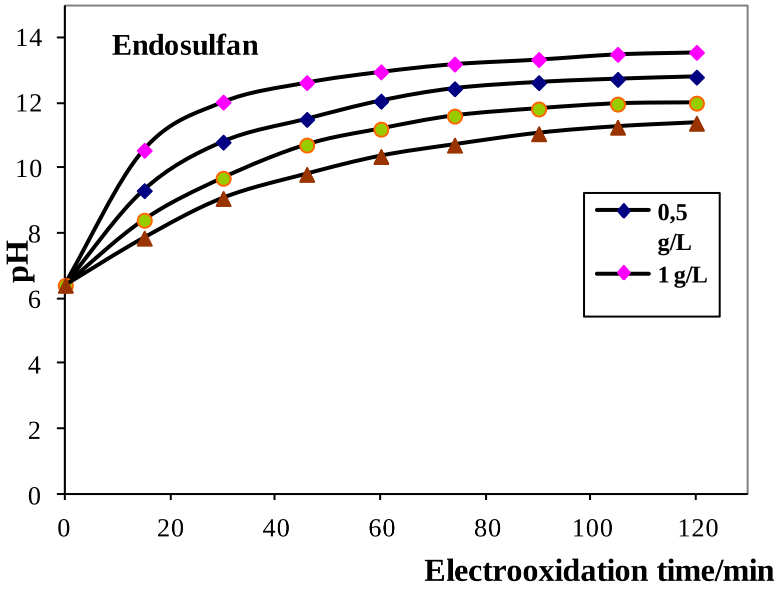


Figure. 5b pH reduction of endosulfan 6 g/L for 120 min of electrolysis at 60 mA/cm^2 and 25 °C, volume of treated solution: 75 cm^3

3.3. Effect of electric current

Different electric currents were applied to investigate the electrochemical degradation of deltamethrin and endosulfane in NaCl solutionsolution (1 g/L) at an 30 mg/L initial concentration of deltamethrin and 6 g/L of endosulfane (Fig. 6). It was found that the COD removal increased with increasing the electric current. The COD removal were about 37%, 48%, 65% and 80% for endosulfane, and 30 %, 40 %, 52 % and 64 % for deltamethrin the electric current of 20, 40, 50 and 60 mA, respectively. The results further indicated that the effect of the apparent electric current on the COD removal was insignificant when the apparent electric current exceeded 60 mA. Since the consumption of electric energy increased with the electric current, the best applied current density in this system was 60 mA when the accepted COD removal and the energy consumption were considered simultaneously.

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:

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

This was confirmed by the fact that the COD (mg/L of O_2) decreased with the current density.

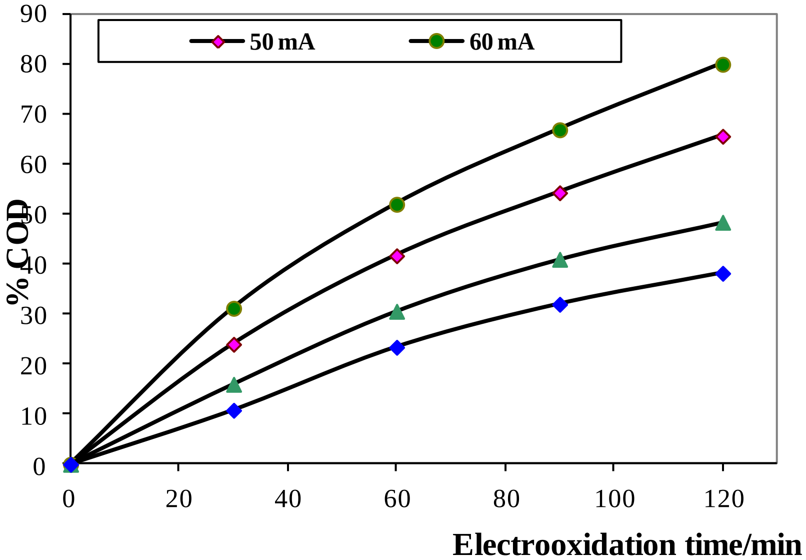


Figure 6. Direct electrooxidation at BDD anode: effect of curent densite on the %COD b(6 g.L^{-1} endosulfan solution, T=25°C, pH$_i$=6.2, and 1 g/L (NaCl)).

The decay of COD concentration exhibits an exponential behavior with all the applied current indicating a first-order reaction kinetics for the oxidation reaction.

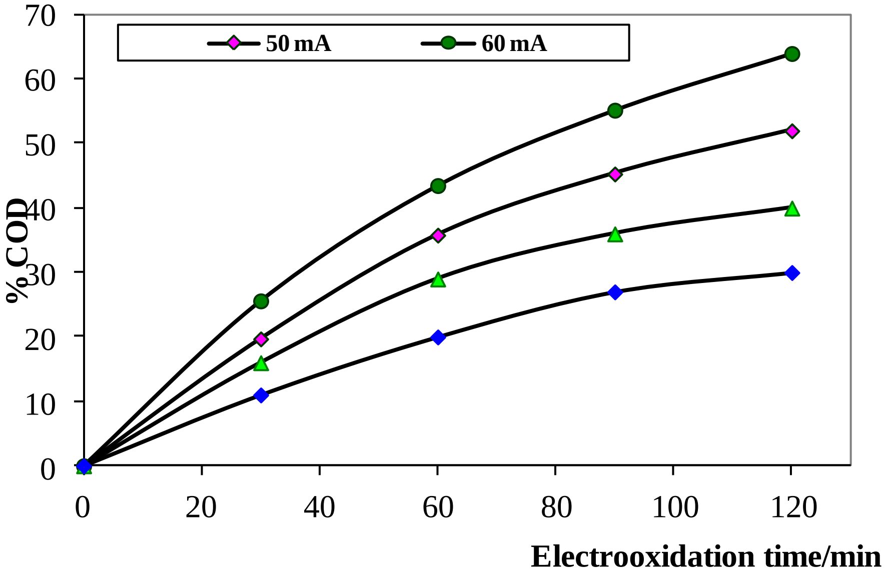


Figure 7. Direct electrooxidation at BDD anode: effect of curent densite on the %COD (30 mg.L^{-1} deltamethrin solution, T=25°C, pH$_i$=5.8, and 1 g/L (NaCl)).

Table 3. Effect of the current intensity on the values of the rate constant for Endosulfan and Deltamethrin.

Pesticides	Current intensity (mA.cm^{-2})	Rate constant, K (min^{-1})
Endosulfan	20	54.10^{-4}
	40	69.10^{-4}
	50	87.10^{-4}
	60	120.10^{-4}
Deltamethrin	20	46.10^{-4}
	40	79.10^{-4}
	50	122.10^{-4}
	60	184.10^{-4}

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:

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

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 3).

3.4. Energy consumption

An important factor in the electrochemical treatment of organic-containing effluents is the energy necessary to achieve the desired results. The efficiency of the electrolysis system depends on the energy consumption for the reduction of 1kg COD of organic matter (in terms of COD), which is one of the most important factors in the economics of electrolysis.

The cost of the electricity depends not only on the electric charge, but also on the potential supplied to the cell; the following figure of merit that may be defined as specific energy consumption (E) defines the amount of energy necessary for abating one gram of COD:

$$E = \frac{VI\Delta t}{(COD_t - COD_{t-\Delta t})v}$$

where V is the average cell potential (V); COD units are mg dm^{-3} and the time interval, Δt, is measured in h, in order to express E in kW h $gCOD^{-1}$ units.

The energy consumption according to this ratio for the four pesticides is depicted in Fig. 8 and Fig. 9. As it is observed from this figure, endosulfan had the lowest energy demand. It must also be noted that in all cases there is a considerable drop in energy consumption after approximately 30min of electrolysis. After that period there is a considerable increase in % COD reduction which probably resulted in lower energy demands.

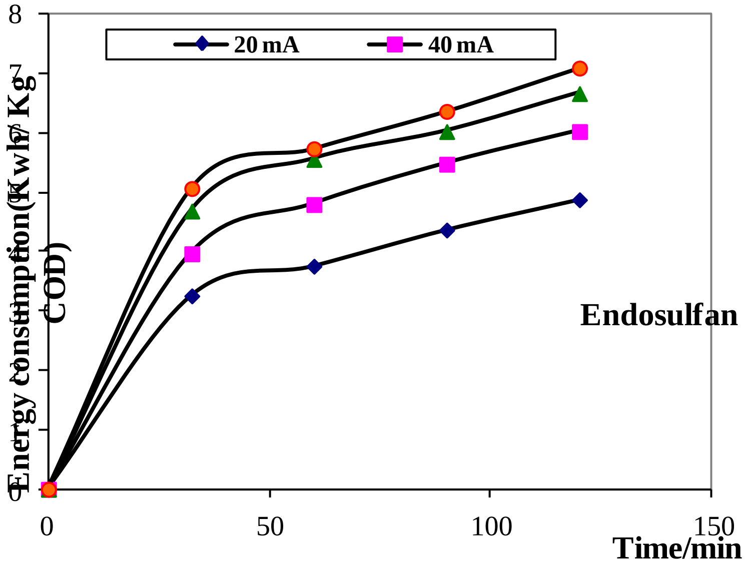


Figure 8. Evolution of Energy consumption ($kWhkgCOD^{-1}$) for ratio kWh/COD reduction during electrolysis of endosulfan.

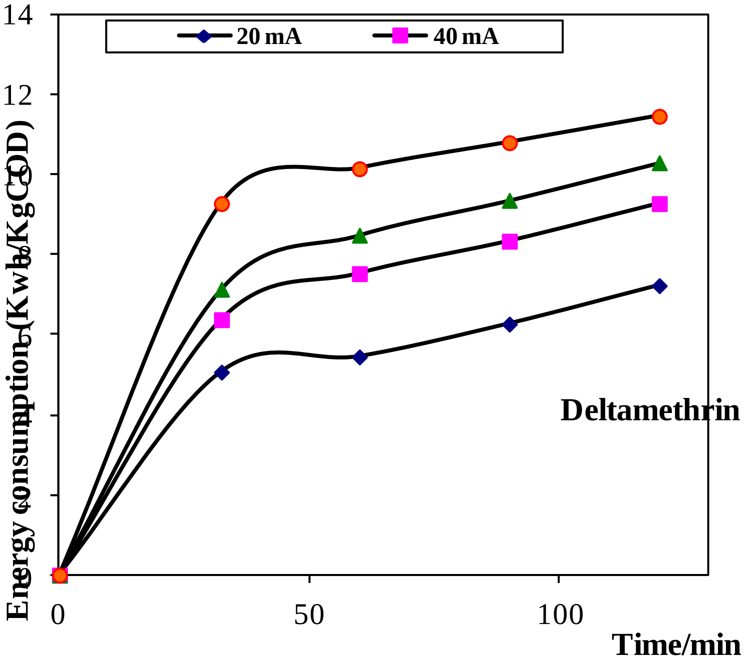


Figure 9. Evolution of Energy consumption (kWhkgCOD^{-1}) for ratio kWh/COD reduction during electrolysis of deltamethrin.

4. CONCLUSION

This work studied the efficiency of an electrochemical oxidation system for the treatment of insecticides. Electrochemical oxidation is a method that has never been applied for the treatment of this type of wastes. This work is a first attempt to investigate the degradation of deltamethrin and endosulfan insecticide in electrochemical treatment with BDD. The electrochemical degradation of deltamethrin (30 mg/L) and endosulfane 6g/L has been investigated using BDD anode under all conditions tested involving, effect of NaCl (0.5 to 3g/L), and applied current density from 20 to 60 mA cm^{-2}. 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, and radicals OH$^{\cdot}$ in the process. The results also indicated that the COD removal eciency was afected by chloride concentration and the optimum one was 1 mg/L (NaCl).
- In all cases, the pH of electrolysis was significantly reduced after 40 min for both pesticides studied.
- 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.
- Applying electrolytic oxidation, the two obsolete insecticides stocks cannot be treated effectively in terms of COD reduction. Nevertheless, the efficiency of the electrolysis system in terms of consumed energy (kWhkgCOD^{-1}) was low in both cases. This ratio is one of the most important

factors in the economics of electrolysis. The low observed kWhkgCOD^{-1} values that were found in the present study indicate that using this method for the treatment of the endosulfane and deltamethrin pesticides obsolete.

- This electrochemical technique can be considered as very clean and very suited for treating agricultural wastewaters containing pesticides.

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