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Electrochemical Treatment of Aqueous Wastes Agricole Containing Oxamyl By BDD-Anodic Oxidation

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Laboratory experiments were carried out on the kinetic of the electrochemical degradation of aqueous solutions containing Oxamyl Nematicide of carbamate pesticide. This pesticide is a broad-spectrum insecticide/ nematicide for the control of key pests in field, fruit and vegetable crops. The electrochemical oxidation of oxamyl (Methyl N'N'-dimethyl-N-[(methylcarbamoyl) oxy]-1-thiooxamimidate)), was studied by galvanostatic electrolysis using boron-doped diamond (BDD) as anode. The influence of several operating parameters, such as applied current density, initial oxamyl concentration, temperature, and initial pH value, was investigated. The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the instantaneous current efficiency. 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 temperature, and by applied current while it is almost unaffected by pH.

Keywords: Oxamyl, Pesticide; Boron-Doped Diamond (BDD); Oxidation; Degradation.

1. INTRODUCTION

Removing pesticides from agricole wastewaters is a difficult and expensive process [1]. Oxamyl pesticide belongs to the group of most durable nematicide, so they are often used in products that must satisfy strict requirements concerning resistance to solar radiation and ambient conditions [2]. This useful feature of pesticides is naturally a problem in their neutralisation. The classical processes of physico-chemical and biological oxidation used in their degradation are not always sufficient, and so it becomes necessary to introduce new, more efficient oxidants [3-6]. The most advantageous method of agricole wastewaters degradation seems to be chemical and/or photochemical oxidation, and then (if necessary) elimination of decomposition products by biological methods. Chemical treatment processes often yield insufficient results if the water contains high amounts of non-biodegradable (refractory) organic substances [7-9]. Oxidative electrochemical processes are among new technologies for the treatment of wastewaters particularly when they are charged with toxic and bioresistant compounds. In this framework electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents. In recent years, electrochemical methods are drawing attention and starting to substitute traditional processes due to the advantages such as high efficiency, ease of operation and environmental compatibility [10-12]. 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 [13]. 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 [14-17].

In recent studies Salghi and co-workers studied the electrooxidation of various groups pesticides bupirimate [1-20, 21]; methidathion [18,19], cypermethrin[22], endosulfane[23], difenconazole [24], in brine solution using BDD and SnO_2 anodes. The authors studied the electrooxidation of various organic compound by Bonfatti and co-workers, organic substrates [25]; 4-chlorophenol [26]; 1, 2-dichloroethane [27]. Oxamyl (Fig.1) is a broad-spectrum insecticide/ nematicide for the control of key pests in field, fruit and vegetable crops. This pesticide is active on many pest species of beetles, aphids, thrips, leafperforators, fleahoppers, leafhoppers, leafminers, lygus bugs, mites and multiple species of economically important nematodes. The mode of action for Oxamyl is the inhibition of acetylcholinesterase, an enzyme that functions in nerve impulse transmissions. oxamyl is active via direct contact or by ingestion[28]. Treated insects will exhibit symptoms that include hyperactivity, incoordination, convulsions, paralysis and death. Nematode symptoms include inhibition of hatching, movement, and feeding [28]. Oxamyl can cause cholinesterase inhibition in humans; that is, it can overstimulate the nervous system causing nausea, dizziness, confusion, and at very high exposures (e.g., accidents or major spills), respiratory paralysis and death [28]. In this work the results concerning essays about the oxidation of oxamyl [Methyl

N’N’-dimethyl-N-[(methylcarbamoyl) oxy]-1-thiooxamimidate] by BDD anode are presented in order to demonstrate the possibilities of this method to remove carbamate compound from waters.

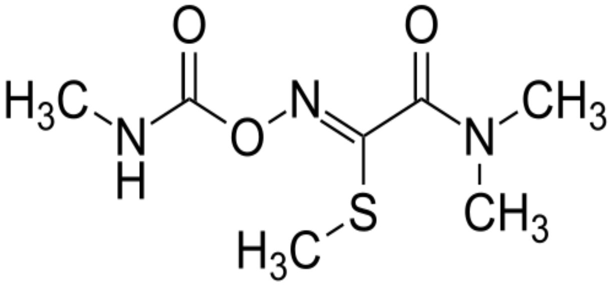

Figure 1. Chemical structure of oxamyl nematicide.

2. MATERIALS AND METHODS

2.1. 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 initial COD_0 (1344 mg/L). 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 [20]. The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method. The UV–Vis spectra of 4MP 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. 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 Analytical procedures

The method used for the extraction of oxamyl was adapted from Charles and Raymond [**25**]. 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 acetonitrile. 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 High performance liquid chromatography (HPLC).

2.3. High performance liquid chromatography (HPLC) analysis

The HPLC system was standardized on the same day as the samples were analyzed by injecting 20 ml of freshly prepared oxamyl in acetonitrile with concentrations ranging from 0.0 to 10 ppm. Areas under the peak versus concentrations were plotted and fit by simple linear regression to obtain an equation for the standard curve. The amount of oxamyl in each sample was thus calculated based on the slope of the standard curve. Extracts were chromatographed with a Perkin Elmer HPLC system model 200 equipped with a degasser, quaternary LC pump model 2000Q/410, 20 ml loop, Spheri-10 RP-18 column (25 cm _4.6 mm i.d., 10 mm, Perkin Elmer), oven column, a LC200 UV detector. The Turbochrom Workstation Software package was used for instrument control, data acquisition, and data analysis. The column temperaturewas kept at 25 °C. Oxamyl was eluted using an isocratic gradient of acetonitrile:H2O in a ratio of 80:20 (v/v) and detected at l of 220 nm with flow rate of 1 ml min^{-1}. The retention time for oxamyl under these conditions was 3.60 min. The limits of detection (LOD) and quantification (LOQ) were calculated according to Keith et al. (1983) [26].

3. RESULTS AND DISCUSSION

3.1. Effect of supporting electrolytes

Electrolytes of 1 % of the following salts: NaCl, Na_2CO_3, and Na_2SO_4 were studied by boron doped diamond electrode. As appears in Fig. 2, the NaCl were the most effective conductive electrolytes for the electrocatalytic degradation of the investigated oxamyl carbamate and COD removal while Na_2SO_4 and Na_2CO_3 electrolytes show poor results. The operating conditions of the treatment process were: current density of 60 mA cm^{-2}, temperature of (25 ± 3) °C, initial concentration COD (1344 mgL^{-1}), and the distance between the two electrodes was 0.5 cm. The UV spectrum studies were carried out to determine the absorbance of oxamyl at λ=220 nm. The absorbance reduction efficiency for electrooxidation oxamyl at different supporting electrolytes was decrease with time of electrooxidation. Fig. 3 represents the Effect of supporting electrolytes on the decay of absorbance at 220 nm for carbamate pesticide. In 1% NaCl it can be observed that oxamyl promotes has a significant increase in absorbance at 220 nm. However, the auther supporting electrolyte response presents a considerable decrease in absorbance when oxamyl is added. These results would indicate that the interaction of the pesticide molecule with the anode surface using 1% NaCl is distinct to that of the other supporting electrolyte.

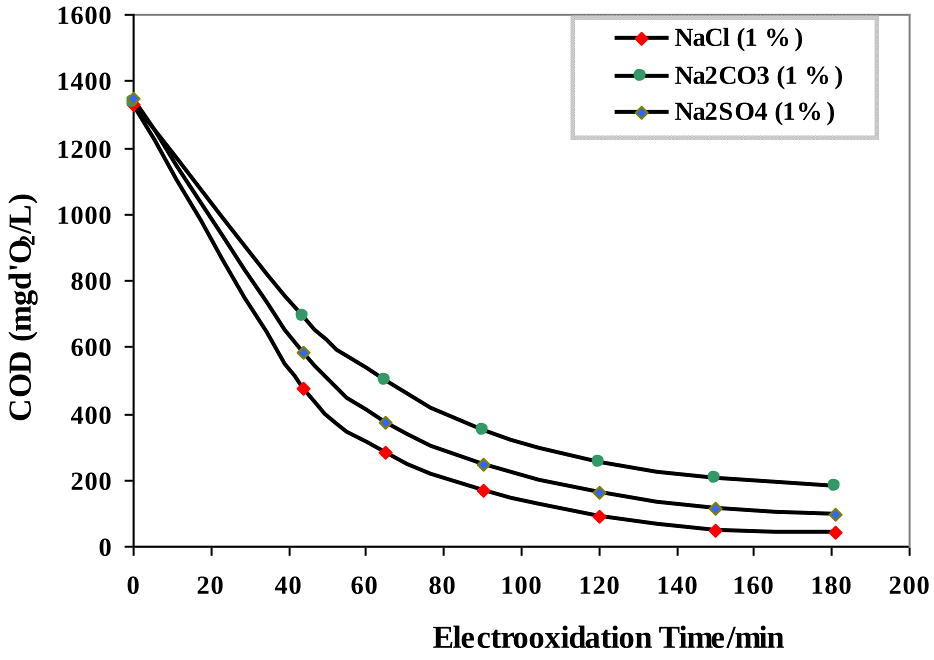

Figure. 2 Influence of supporting electrolytes on the decay of COD during electro-oxidation of 1344 mg/L oxamyl pesticide on BDD anode. Conditions: Current density 60 A.cm^{-2}; T: 25°C.

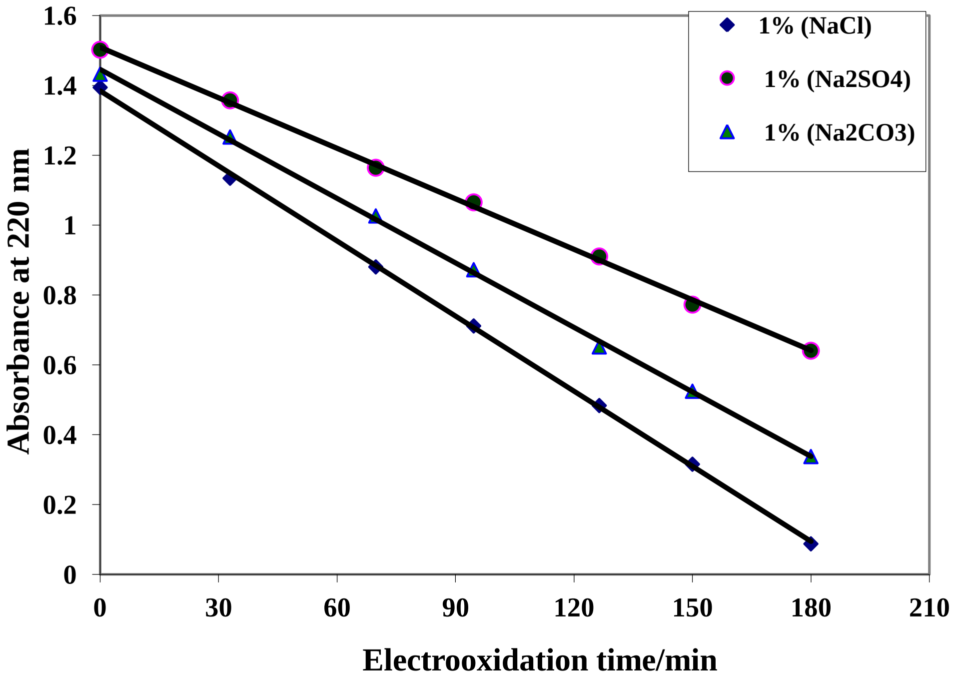

Figure 3. Effect of supporting electrolytes on the decay of absorbance at 220 nm (on the variations of UV spectra) during electro-oxidation of 1344 mg/L oxamyl pesticide on BDD anode. Conditions: Current density 60 A.cm^{-2}; T: 25°C.

3.2. Effect of the NaCl concentration

The investigation of the mediator concentration effect has been performed in the range 1- 4% for NaCl. The Fig. 4 shown effect of chloride ions concentration on the degradation of oxamyl solution, carried out at 60 mA.cm^{-2}. The results indicate that an increase of the electrolyte concentration up to 4% (NaCl) lead to decrease in the pesticide carbamate degradation rate and COD removal for electrodegradation by BDD electrode. Further increase of the NaCl concentration reflected negatively on the degradation rate of oxamyl and COD removal. The achieved reduction was 88% and 68% for 1% NaCl and 2% NaCl respectively, while for 4% NaCl was 22% after 2h of electrooxidation. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of this pesticide on the electrode or indirect via some mediators like chlorinated species or other radicals [20-24].

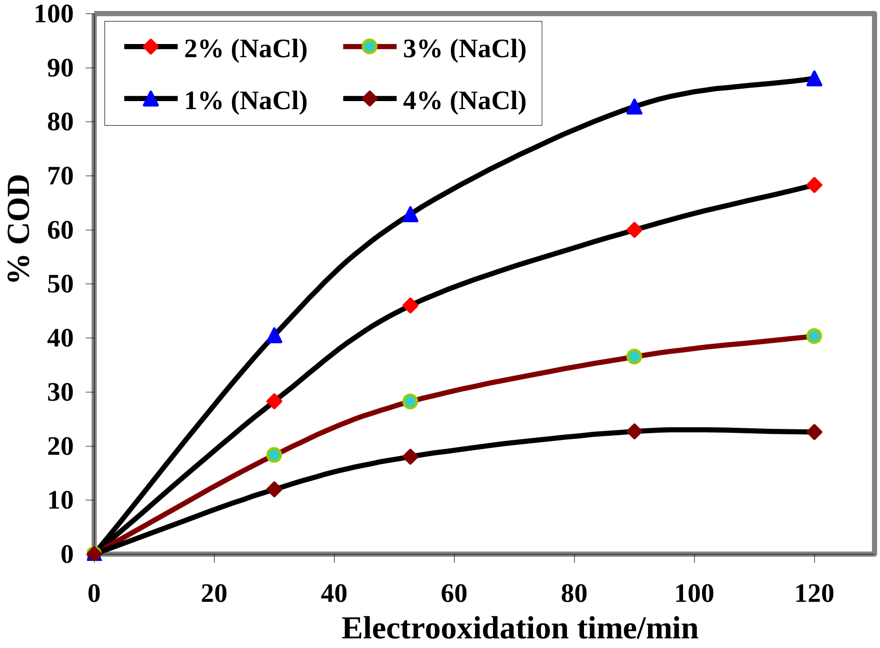

Figure 4. Influence of supporting electrolytes on the decay of COD during electro-oxidation of 1344mg/L oxamyl on BDD anode. Conditions: Current density 60 mA.cm^{-2}; T: 25°C.

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation oxamyl at different concentration supporting electrolyte NaCl. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [1,18,19]. Figure 5 represents the kinetic studies of the different concentration of supporting electrolyte in the presence of COD_0=1344 mg. L^{-1} of oxamyl nematicide. The values of rate constant for different supporting electrolyte concentration are summarized in Table 1.

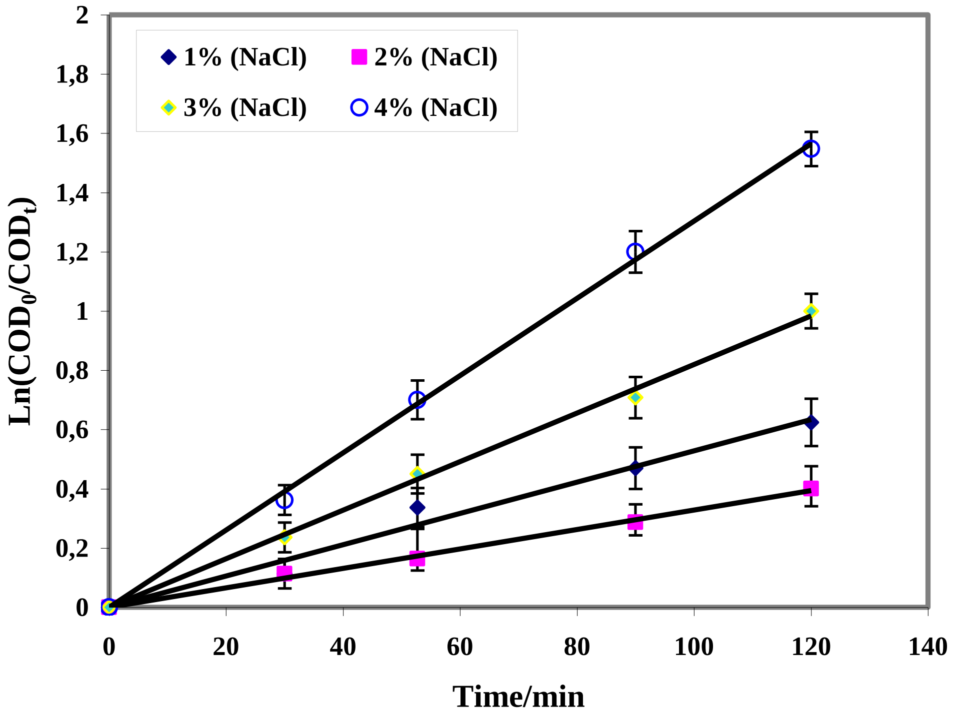

Figure 5. Pseudo first-order plot oxidation of oxamyl (COD_0 = 1344 mg/L) in different electrolytes at 60 mA.cm^{-2}.

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

Supporting electrolytes	Rate constant, K (min^{-1})	COD removal (%)
1% (NaCl)	$(1.32 \pm 0.12)\times10^{-2}$	(88 ± 5)
2% (NaCl)	$(0.82 \pm 0.15)\times10^{-2}$	(68 ± 5.7)
3% (NaCl)	$(0.53 \pm 0.23)\times10^{-2}$	(41 ± 6.2)
4% (NaCl)	$(0.32 \pm 0.13)\times10^{-2}$	(22 ± 5.4)

3.3. Effect of current density

The influence of the current density on the COD removal during the electrochemical oxidation of oxamyl at the anode is shown in Fig. 6. Increasing the current density until 60 mA.cm^{-2} resulted in an enhancement of the oxidation rate. After 2h time of electrolysis, the COD percent removal increased from (63.3 ± 5.4) % to (88 ± 5) % when the current density increased from 20 to 60 mA.cm^{-2}. This behavior indicates that in these experimental conditions, the oxidation of oxamyl is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:

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

The % COD of oxamyl was observed to fall with pseudo first-order kinetics on all the surface studied (Fig. 6). This is related to the dependence of the rate of oxidation of formation of the oxidizing species at the electrode surface. The pseudo first-order constant of nematicide (k) varies from (0.82 ± 0.15) $\times10^{-2}$ min^{-1} (20 mA.cm^{-2}) to (1.32 ± 0.12) $\times10^{-2}$ min^{-1} (60 mA.cm^{-2}). From these results it was calculated that the best applied current is 60 mA.cm^{-2}.

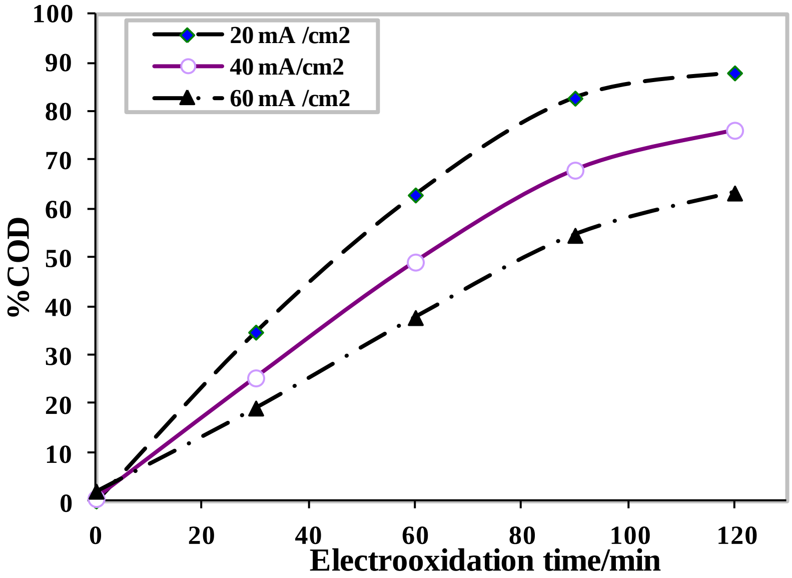

Figure 6. Influence of the applied current density on the trends of % COD electrolysis of oxamyl (COD$_0$ = 1344 mg.L^{-1}) using a 1cm^2 BDD anode. 1% (NaCl) and T=25°C.

3.4. Effect of initial concentrations of oxamyl

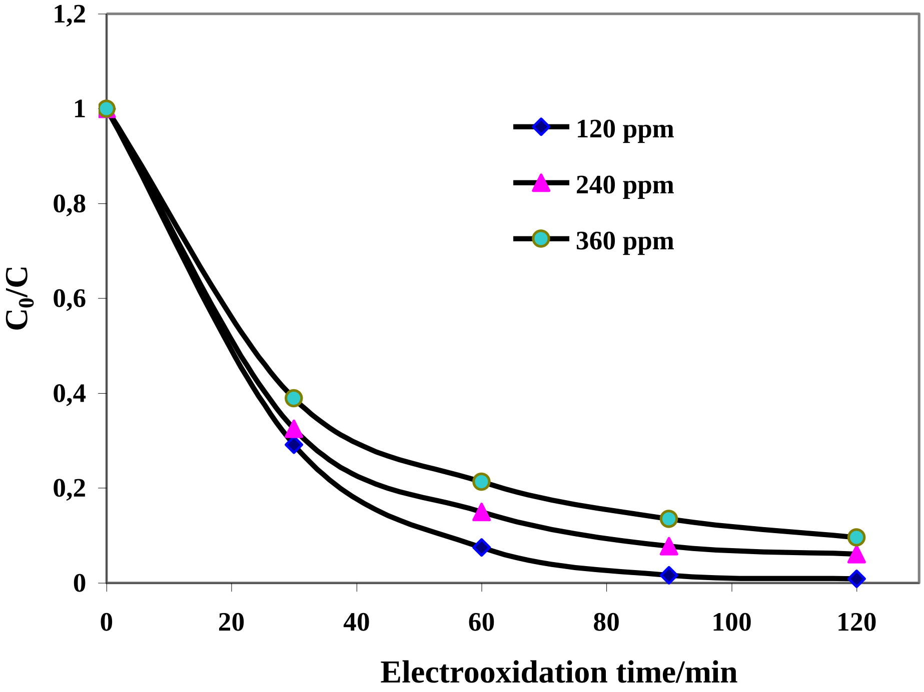

Figure 7. Influence of pesticide initial concentration on the normalized concentration oxamyl during BDD-anodic oxidation (Operating conditions: electrolyte = 1% NaCl, current density = 60 mAcm^{-2}, and T = 25°C).

The initial concentration of pesticide is always an important parameter in wastewater treatment. Fig. 7 shows the effect of different initial nematicide pesticide concentrations on the rate of oxamyl degradation and corresponding concentration removal during electrolysis at temperature of 25°C and using a current density of 60 $mAcm^{-2}$ and concentration NaCl (1%). Overall oxamyl oxidation was achieved in all cases but the time for the complete removal increased with initial pesticide concentration due to the presence of a greater amount of organics in the medium.. For all the concentrations removal follows pseudo first-order kinetics and the apparent rate constants were 98×10^{-4}, $88\times10^{-4}$and $74\times10^{-4}min^{-1}$ for the oxamyl concentrations of 120 ppm, 240 ppm and 360 ppm, respectively.

3.5 Effect of temperature on the degradation efficiency

Table 2. Apparent rate constants of oxamyl removal fitted by a second order model for BDD anodes under different temperature.

Temperature (°C)	Rate constant, K (min^{-1})	R^2
25	88.10^{-4}	0.9979
35	109.10^{-4}	0.9985
45	148.10^{-4}	0.9928

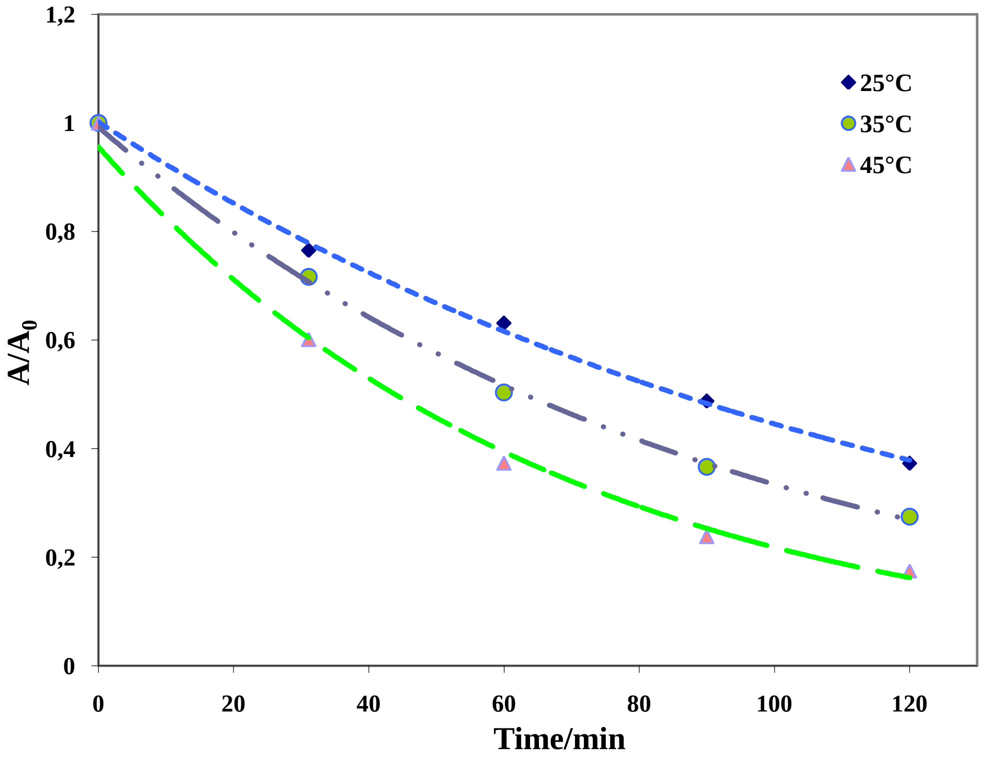

Figure 8. The variation of A/A_0 ratio as a function of time at specified oxamyl concentrations at different temperatures.

Electrolyses of oxamyl pesticide solutions (COD_0 = 1344 mgL^{-1} and 1% NaCl) on BDD at an applied anodic current density of 60 $mAcm^{-2}$ were carried out at different temperatures in the range 25–45 °C. Increasing the temperature considerably reduces the time necessary for the complete elimination of pesticide from the solution (Fig. 8). After 2 h time of electrolysis, the concentration percent removal increased from 88 to approximately 98% when the temperature increased from 25 to 45 °C. This result is probably due to the increase in the indirect oxidation reaction of organics with ClO^-. This powerful oxidizing agent can oxidize organic matter by chemical reaction whose rate increases with temperature leading to an increase in concentration removal rate. These results are in agreement with those obtained by other authors [1, 20, 21]. In fact, as shown in Fig. 8, the apparent rate constant decreased with temperature, Apparent rate constants determined were shown in Table 2.

4. CONCLUSION

Electrooxidation using a BDD anode has been successfully applied to treat aqueous solutions containing oxamyl. This work is a first attempt to investigate the degradation of this pesticide in electrochemical treatment. The electrochemical degradation of oxamyl has been investigated using BDD anode under all conditions tested involving, effect of different supporting electrolyte, applied current density from 20 to 60 mA cm^{-2}, and temperature varying from 25 to 45 °C . The experimental results allowed us to draw the following conclusions:

- The best results were obtained when electrolyses were carried out at high densities, 60 $mAcm^{-2}$, and in the presence of supporting electrolyte NaCl (%).
- The removal rate of COD increases with applied current density until 60 $mAcm^{-2}$ due to the increase of the mass transport caused by oxygen evolution reaction, but decreases for higher values due to the improvement of this reaction.
- Increasing the temperature considerably reduces the time necessary for the complete elimination of oxamyl from the solution. After 2 h time of electrolysis, the concentration percent removal increased from 88 to approximately 98% when the temperature increased from 25 to 45 °C.

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