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Anodic Destruction of Abamectin Acaricide Solution By BDD-Anodic Oxidation

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This paper presents the study of the electrochemical oxidation of the pesticide Abamectin at a boron-doped diamond (BDD). The effect of using different supporting electrolytes (NaCl, K_2SO_4, Na_2CO_3 and Na_2SO_4) during the galvanostatic electrolysis of Abamectin was investigated.The influence of several operating parameters, such as applied current density, effect of electrolytes (NaCl), was investigated. UV spectroscopy and chemical oxygen demand measurements were conducted to study the reaction kinetics of abamectin 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 flowrate applied current and NaCl concentration.Under optimal experimental conditions of current density (i.e. 80 mA/ cm2), 88% of COD was removed in 2.5 h electrolysis.

Keywords: Abamectin, pesticide; boron-doped diamond (BDD); Oxidation; Degradation, acaricide.

1. INTRODUCTION

Abamectin belongs to the family avermectins which are macrocyclic lactones produced by the actinomycete Strep-tomyces avemitilis. It is a mixture of two homologues containing about 80%

avermectin B1a and about 20% avermectin B1b [1]. Abamectin acts by stimulating the release of c-aminobutyric acid thus causing paralysis [2]. It is used to control motile stages of mites and some other insects on fruits and vegetables and has limited plant systemic activity.

The intensive use of pesticides, particularly Abamectin in agriculture, and their improper storage or disposal of obsolete pesticides are a source of contamination of soil, ground water, rivers, lakes, rainwater, and air. This useful feature of pesticides is naturally a problem in their neutralisation. Various innovative technologies have been proposed for the removal of pesticides from water such as biological treatment [3], photo catalytic oxidation [4, 5], ozonation [6], Fenton's reaction [7], and electrochemical methods [5, 8–17]. Among these technologies, 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 [18, 19]. 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 [5-8]. 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 [9-11]. Oxidative electrochemical processes are among new technologies for the treatment of wastewaters particularly when they are charged with toxic and bioresistant compounds. Direct electrolytic techniques for achieving oxidative degradation of organic compounds can be described as electrochemical incineration (ECI) when the ultimate product of the electrolytic procedure applied to organic compounds is identical to the products anticipated from thermal incineration, i.e. CO_2(g). In ECI, the O-atoms transferred to oxidation products originate from H2O in the electrolysis solution. However, in spite of the surplus of H_2O in these reaction solutions, conventional anode materials, e.g. Au, Pt and glassy carbon, exhibit very slow heterogeneous kinetics for the complete ECI process. Therefore, intensive research continues with the goal of discovering more efficient electrode materials. Examples of electrode materials that appear to function catalytically within ECI processes include synthetic diamond electrodes [18] and various doped metal oxide-film electrodes, e.g. PbO_2 [12-14], SnO_2 [15], and TiO_2 [16].

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].

Abamectin (Fig.1) is a mixture of avermectins containing more than 80% avermectin B1a and less than 20% avermectin B1b. These two components, B1a and B1b have very similar biological and toxicological properties. The avermectins are insecticidal and antihelmintic compounds derived from various laboratory broths fermented by the soil bacterium Streptomyces avermitilis. Abamectin is a natural fermentation product of this bacterium.

In this work the results concerning essays about the oxidation of abamectin mixture of: (10E,14E,16E)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-6′-[(S)-sec-butyl]-21,24-dihydroxy-

5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24]pentacosa-10,14,16,22-tetraene)-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-4-O-(2,6-dideoxy-3-O-methyl-α-L-arabino-hexopyranosyl)-3-O-methyl-α-L-arabino-hexopyranoside and (10E,14E,16E)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-21,22-dihydroxy-6′-isopropyl-5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24]pentacosa-10,14,16,22-tetraene)-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl2,6-dideoxy-4-O-(2,6-dideoxy-3-O-methyl-α-L-arabino-hexopyranosyl)-3-O-methyl-α-L-arabino-hexopyranoside by BDD anode are presented in order to demonstrate the possibilities of this method to remove avermectins compound from waters.

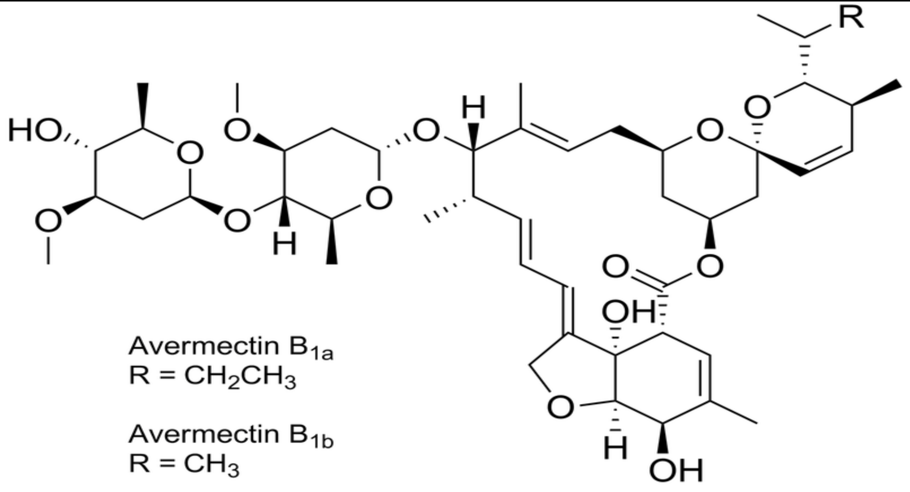	Avermectine B1a : $C_{48}H_{72}O_{14}$ M(C48H72O14) = 873,07 g·mol-1 Avermectine B_{1b} : $C_{47}H_{70}O_{14}$ M($C_{48}H_{70}O_{14}$)=859,05 g·mol^{-1}

Figure 1. Chemical structure of abamaectin acaricide

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) thermo regulated 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 (2340 mg/L). The range of applied current density was 15 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 [20]. The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method.

The UV–Vis spectra of abamactin were recorded in 190–400 nm range using a UV–Vis spectrophotometer (UV-1700 Pharmaspec, Shimadzou) with a spectrometric quartz cell (1 cm path length). All chemicals used in the experiments were of analytical pure grade and used without further purification. The sodium chloride, sodium carbonate, sodium sulphate and potassium sulphate used was of analytical-reagent grade and was obtained from Aldrich (French).

3. RESULTS AND DISCUSSION

3.1. Effect of supporting electrolytes

Electrolytes of 2 g/L of the following salts: NaCl, Na_2CO_3, $K_2SO_4$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 electro-degradation of the investigated abamectin pesticide 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 (2340 mgL^{-1}), and the distance between the two electrodes was 0.5 cm.

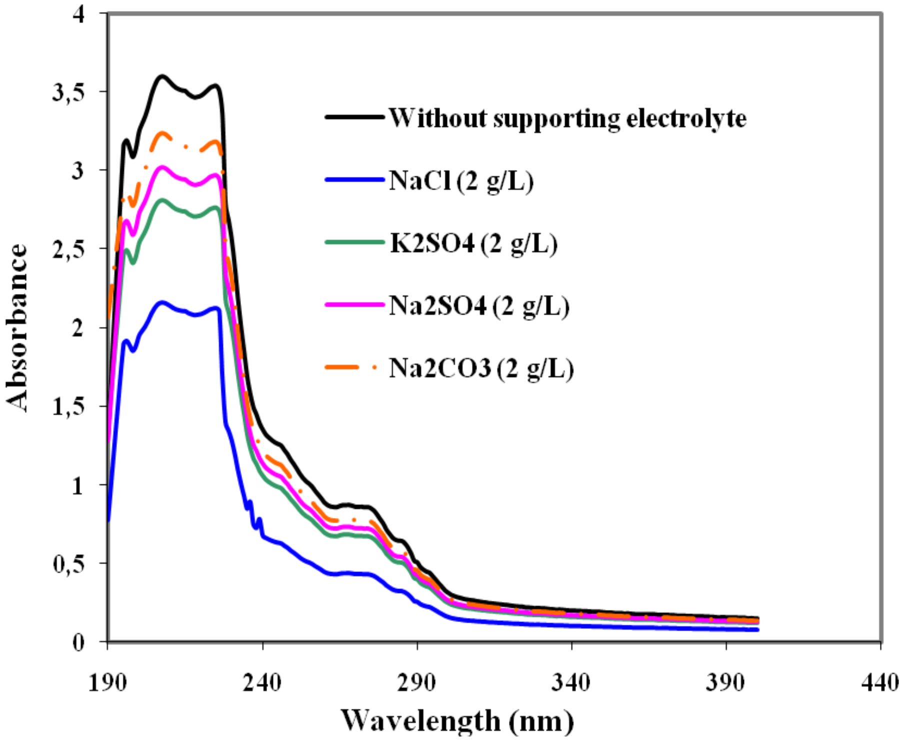

Figure 2. Evolution of the UV spectra with time during galvanostatic electrolysis of Abamectin pesticide under influence of supporting electrolytes. Conditions: Current density 60 A.cm^{-2}; T: 25C.

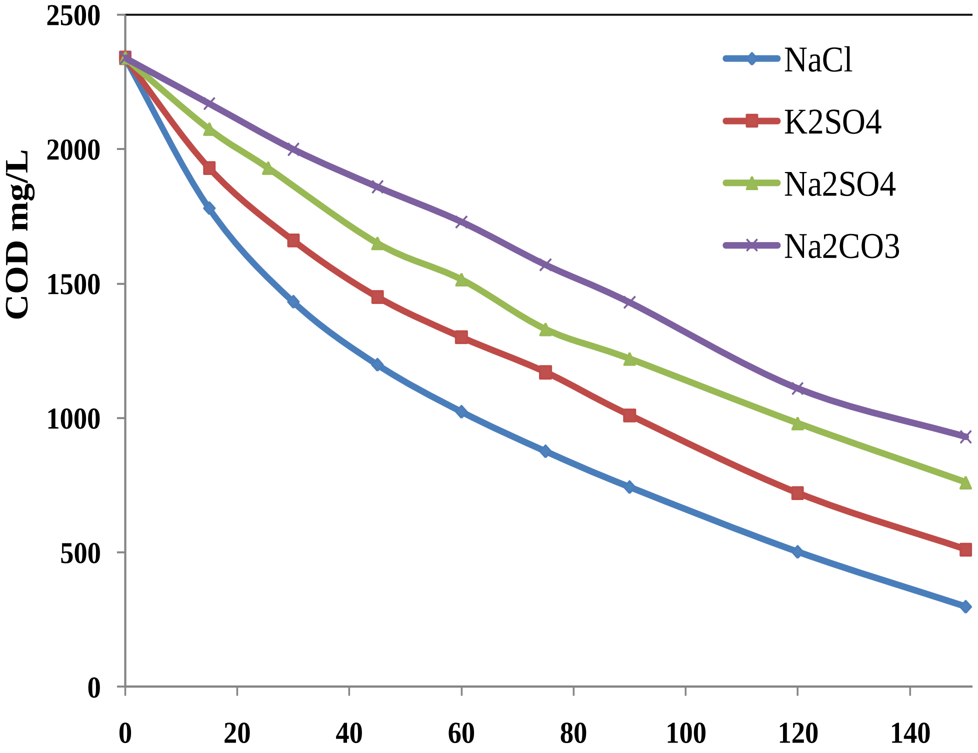

Figure 3. Influence of supporting electrolytes on the decay of COD during electrooxidation of 10 mg. L^{-1} abamactin on BDD anode. Conditions: applied current 60 $mA.cm^{-2}$, pH = 6.7, T = 25 C.

The results of UV-spectra of Abamactin at some supporting electrolytes after treatment are shown in Figure 2. It can be observed that the absorption spectrum of abamactin is characterized by a band in the UV region with its maxima located at 210 nm and by a band in region located at 230 nm.

As can be seen that at the NaCl (2 g/L), the UV-spectrum changed greatly and had a weak absorbance at 230 nm. It is observed that the absorption of the bands ethylene characterized the acaricide increases in the presence of the electrolyte supporting NaCl (2 g/L) and The absorbance decreases rather slowly for authors supporting electrolyte. Figure 3 presents the relative removals of COD. The electrochemical degradation of the acaricide abamactin using the BDD anode. The removal of the pesticide in 2g/L (NaCl) higher than that of K_2SO_4 and much higher than Na_2SO_4. This fact means that, also for this pesticide, the combustion is not complete after 2.5 h assay.

Working in galvanostatic condition, the concentration of $^{\bullet}OH$ can be approximated in a steady state and therefore, the oxidation rate expression can be written as follows [21, 22]:

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

which can be integrated to give the following expression:

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

The $Ln([COD]_t/[COD]_0)$ vs. time plot appears to be linear (Figure 4), which means that the process is kinetic under mass transport control. Thus, we can obtain the mass transport coefficient from the slope of the linear plot. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of pesticide on the electrode or indirect via some mediators like chlorinated species or other radicals [12-14].

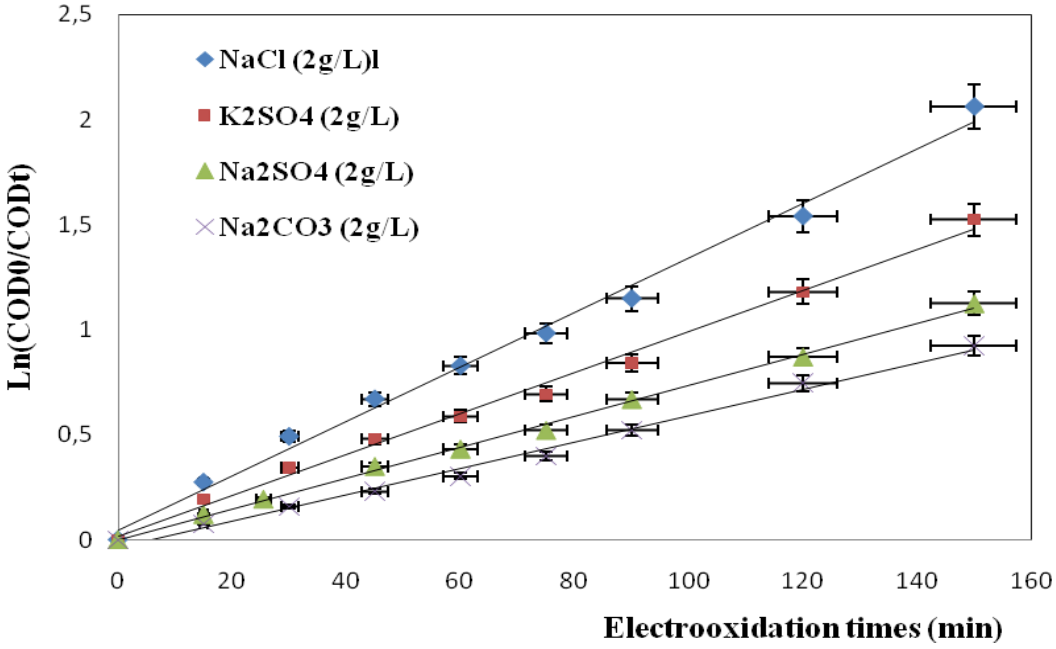

Figure 4. Influence of supporting electrolytes on the decay of COD during electrooxidation of 10 mg. L^{-1} abamactin on BDD anode. Conditions: applied current 60 $mA.cm^{-2}$, pH = 6.7, T = 25 C.

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 (%)
NaCl (2 g/L)	$(1.34 \pm 0.05)\times10^{-2}$	(88 ± 4.5)
K_2SO_4 (2 g/L)	$(0.93 \pm 0.10)\times10^{-2}$	(78± 5.7)
Na_2SO_4 (2 g/L)	$(0.73 \pm 0.08)\times10^{-2}$	(67 ± 6.2)
Na_2CO_3 (2 g/L)	$(0.5 \pm 0.03)\times10^{-2}$	(60 ± 5.4)

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation acaricide abamectin at different supporting electrolytes. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [27]. Figure 4 and table 1 represents the Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation abamectin at of the different supporting electrolyte in a (2 g L^{-1}) NaCl, (2 g L^{-1}) Na_2CO_3, (2g L^{-1}) Na_2SO_4 solution in the presence of 10 mg L^{-1} of abamactin pesticide. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows.

3.2. Effect of the NaCl concentration

The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of abamectin on the electrode or indirect via some mediators like chlorinated species or other radicals [26-27].

Since, some oxidant compounds that are produced during oxidation of water (like O_2, O_3 or hydroxyl radical) or oxidation of chlorine ions following eq (2) to (4):

$$Cl^- \Longrightarrow Cl^{\cdot}_{ads} + e^- \qquad (1)$$

$$Cl^- + Cl^{\cdot}_{ads} \Longrightarrow Cl_2 + e^- \qquad (2)$$

$$Cl_2 + H_2O \Longrightarrow HClO + H^+ + Cl^- \qquad (3)$$

As cited in reference [28]. That 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 [31].

The investigation of the mediator concentration effect has been performed in the range 1-4 g/L for NaCl. The Figure 5 and figure 6 shown effect of chloride ions concentration on the degradation of abamactin solution, carried out at 60 mA.cm^{-2}.

The results indicate that an increase of the electrolyte concentration up to 4g/L (NaCl) lead to decrease in the pesticide acaricide degradation rate and COD removal for electrodegradation by BDD electrode. Further increase of the NaCl concentration reflected negatively on the degradation rate of abamactin and COD removal.

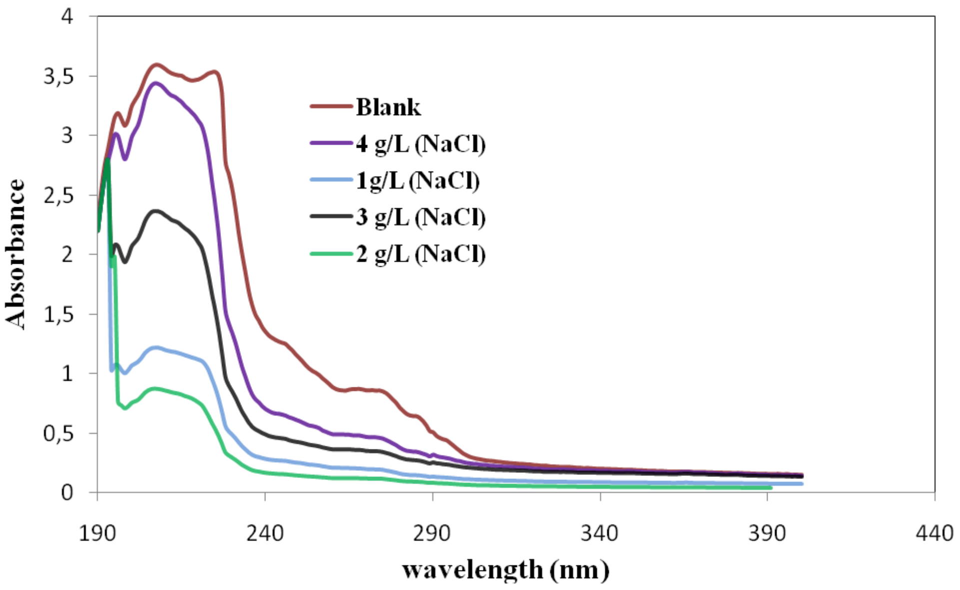

Figure 5. Evolution of the UV spectra with time during galvanostatic electrolysis of Abamectin pesticide under influence of concentration NaCl. Conditions: Current density 60 A.cm^{-2}; T: 25C.

The achieved reduction was 88% and 68% for 2g/L of NaCl and 1g/L of NaCl respectively, while for 4g/L NaCl was 22%. After 2 h of electrodegradtion. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of this abamaetin on the electrode or indirect via some mediators like chlorinated species or other radicals [20-24].

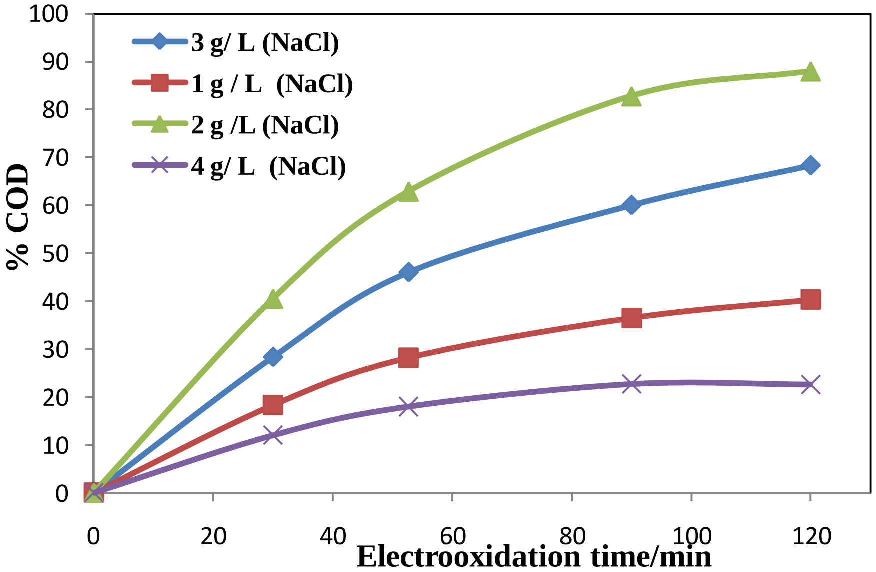

Figure 6. Pseudo first-order plot oxidation of abamectin (COD_0 = 2340 mg/L) in different electrolytes at 60 mA.cm^{-2}.

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation abamectin at different concentration supporting electrolyte NaCl. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [27-29]. The values of rate constant for different supporting electrolyte concentration are summarized in Table 2.

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

Supporting electrolytes (NaCl)	Rate constant, K (min^{-1})	COD removal (%)
1 g/L	$(1.32 \pm 0.12)\times10^{-2}$	(35 ± 5.0)
2 g/L	$(1.34 \pm 0.05)\times10^{-2}$	(88 ± 4.5)
3 g/L	$(0.53 \pm 0.23)\times10^{-2}$	(65 ± 6.2)
4 g/L	$(0.32 \pm 0.13)\times10^{-2}$	(22 ± 5.4)

3.3. Effect of current density

The role of current density has been followed, testing values smaller that the previously considered as the optimum. The influence of current density on abamactin has been investigated in the range 15–80 mA and The results are reported in Fig. 7. Increasing the current density until 80 mA.cm^{-2} resulted in an enhancement of the oxidation rate. After 2.5h time of electrolysis, the COD percent removal increased from (64 ± 3,4) % to (98 ± 4,5) % when the current density increased from 15 to 80 mA.cm^{-2}. This behavior indicates that in these experimental conditions, the oxidation of abamactin is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:

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

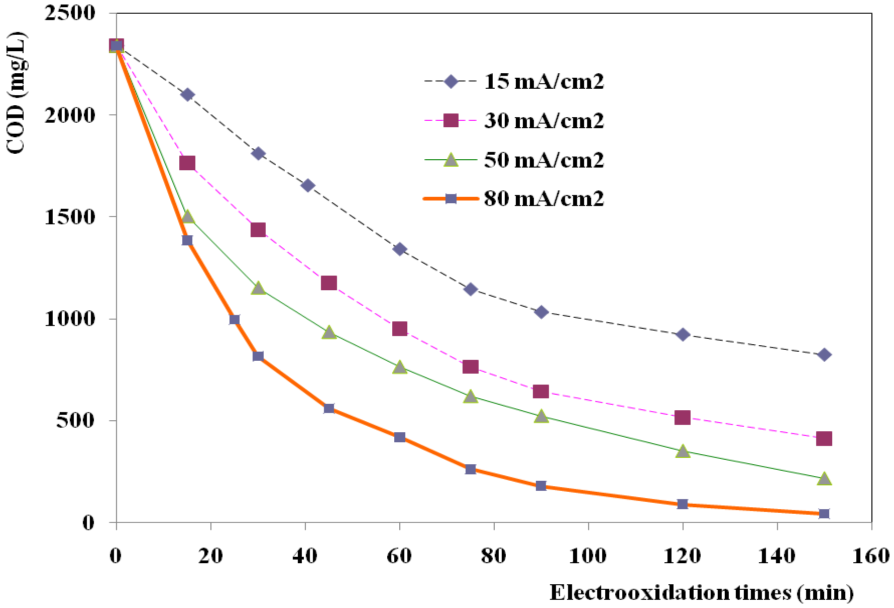

Figure 7. Influence of the applied current density on the trends of % COD electrolysis of abamactine (COD0 = 2340 mg.L−1) using a 1cm2 BDD anode. 1g/l (NaCl) and T=25◦C.

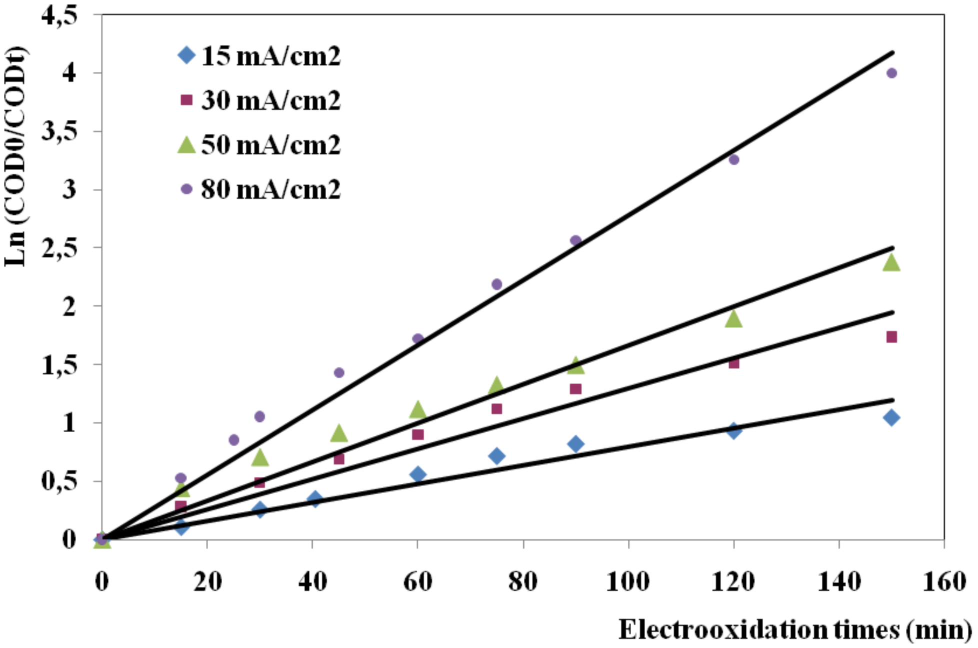

Figure 8. Pseudo first-order plot oxidation of abamectin (COD_0 = 2340 mg/L) in different current density at 2g/l NaCl electrolytes.

The % COD of abamactin was observed to fall with pseudo first-order kinetics on all the surface studied (Figure 8). This is related to the dependence of the rate of oxidation of formation of the oxidizing species at the electrode surface [28-30]. The pseudo first-order constant of abamactin acaricide (k) varies from (7.9 ± 0.15) ×$10^{-3}$$min^{-1}$ (15 $mA.cm^{-2}$) to (2.78 ± 0.12) ×10^{-2} min^{-1} (80 $mA.cm^{-2}$). From these results it was calculated that the best applied current is 80 $mA.cm^{-2}$.

The absorbance spectral changes during galvanostatic electrolysis in aqueous solution are shown in figure 9. It can be observed that the absorption spectrum of abamectin is characterized by a band in the UV region with its maxima located at 215 nm.

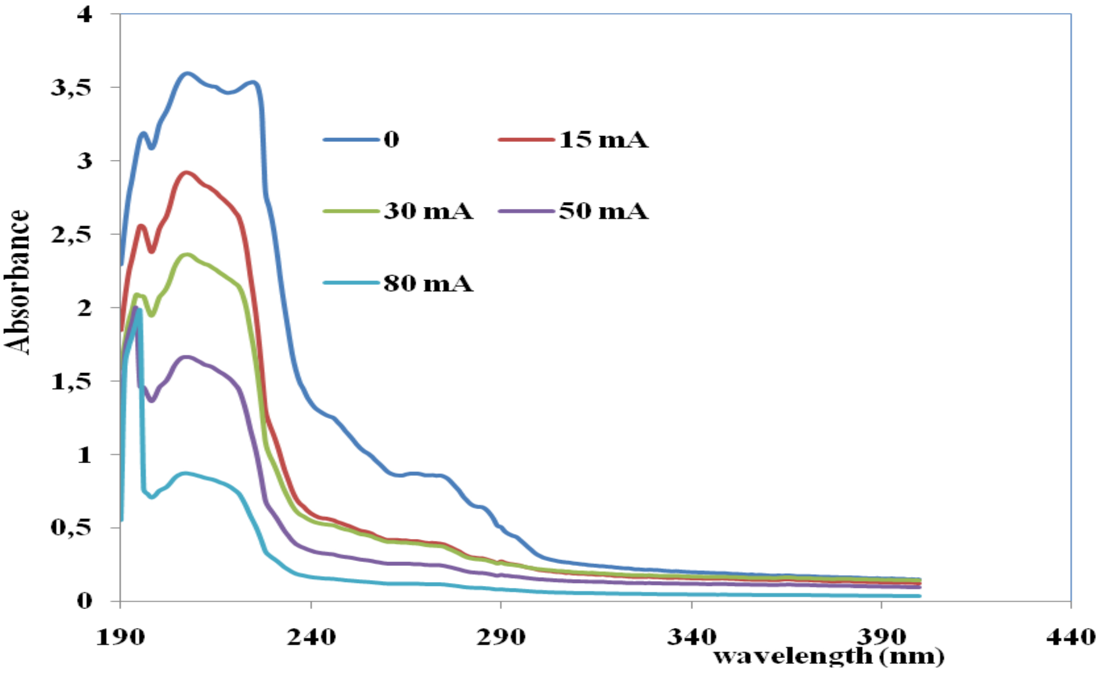

Figure 9. Effect of applied current density on the variations of UV spectra for 2,5 h of the electrooxidation assays performed at a BDD anode (Operating conditions: electrolyte (2g.L^{-1} NaCl), abamectin initial COD concentration =2340 mg/L, T = 25 C).

It is observed that the absorption of the bands decreases with density current. The slower decrease of this absorbance can be related to the formation of intermediates resulting from the electrooxidation of the abamactin.

4. CONCLUSION

A pilot plant study was carried out to investigate the anodic oxidation of abamectin pesticide over BDD anodes at different electrolytes (NaCl, K_2SO_4, Na_2CO_3 and Na_2SO_4) and different concentrations of NaCl. This work is a first attempt to investigate the degradation of this pesticide in electrochemical treatment. The electrochemical degradation of abamectin has been investigated using

BDD anode under applied current density from 15 to 80 mA cm^{-2}. The experimental results allowed us to draw the following conclusions:

The best results were obtained when electrolyses were carried out at high densities, 80 $mAcm^{-2}$, and in the presence of supporting electrolyte 2g/L of NaCl.

Increasing the temperature considerably reduces the time necessary for the complete elimination of abamectin from the solution. After 2,5 h time of electrolysis, the concentration percent removal increased to 98% for 80 mA cm^{-2}.

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