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Electrooxidation of Bupirimate: A Comparative Study of SnO_2 and Boron Doped Diamond Anodes

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The aim of this work was to investigate the approaches to reduce the negative impacts of pesticides on the environment. Specifically, two approaches to electrooxidize bupirimate are compared. The first approach was based on the use of SnO_2 electrode. This electrode is a commercial grid of $1cm^2$ of SnO_2. The second approach was based on the use of Boron Doped Diamond (BDD) electrode. The electrolyses were performed by using a solution composed of an electrolyte support NaCl. The effects of current density, NaCl concentration, pH, and pesticide concentration on the rate of chemical oxygen demand (COD) abatement were investigated. The results showed that the rate of the electrooxidation increases with increasing current density and decreasing NaCl. The overall results indicated that BDD electrode exhibited the best performance.

Keywords: Bupirimate fungicide, Electrooxidation, pesticide, Boron doped diamond, SnO_2

1. INTRODUCTION

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 [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 very low active ingredient content, rather than highly concentrated obsolete pesticide stocks.

In the last few years, interest in direct and indirect electrochemical oxidations of organic pollutants increased significantly. In the direct anodic oxidation, adsorbed $OH^{\bullet}$ radicals are produced from water oxidation at an anode made from Pt, PbO_2, doped SnO_2 [6, 7] or boron-doped diamond (BDD) [8, 9]:

$$H_2O \rightarrow OH\bullet_{ads} + H^+ + e^- \qquad (1)$$

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 $BDD(OH^{\bullet})$ with ability to completely mineralize organics, as reported for several aromatics [10-13] and carboxylic acids [8].

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 [11]. 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 $OH^{\cdot}$ from reaction (2) or (3) and hence, a quicker oxidation of aromatics and pesticides

$$\text{in acidic and neutral media:} \quad BDD(H_2O) \rightarrow BDD(HO^{\bullet}) + H^+ + e^- \qquad (2)$$

$$\text{in basic media (pH} \geq 10\text{):} \quad BDD(OH^-) \rightarrow BDD(HO^{\bullet}) + e^- \qquad (3)$$

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, a systemic fungicide widely 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).

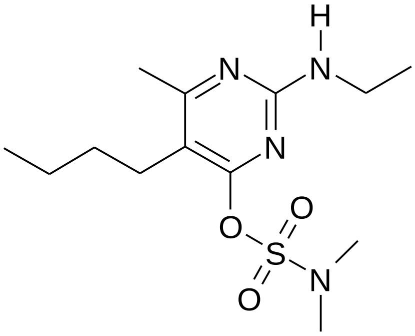


Figure 1. Chemical structure of bupirimate.

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. 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 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 bupirimate 230 mg/L 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 [14]. 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 analyzed 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 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

Figures 2-a and 2-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. 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 [15].

$$d[COD]/dt=-K[COD] \tag{4}$$

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.

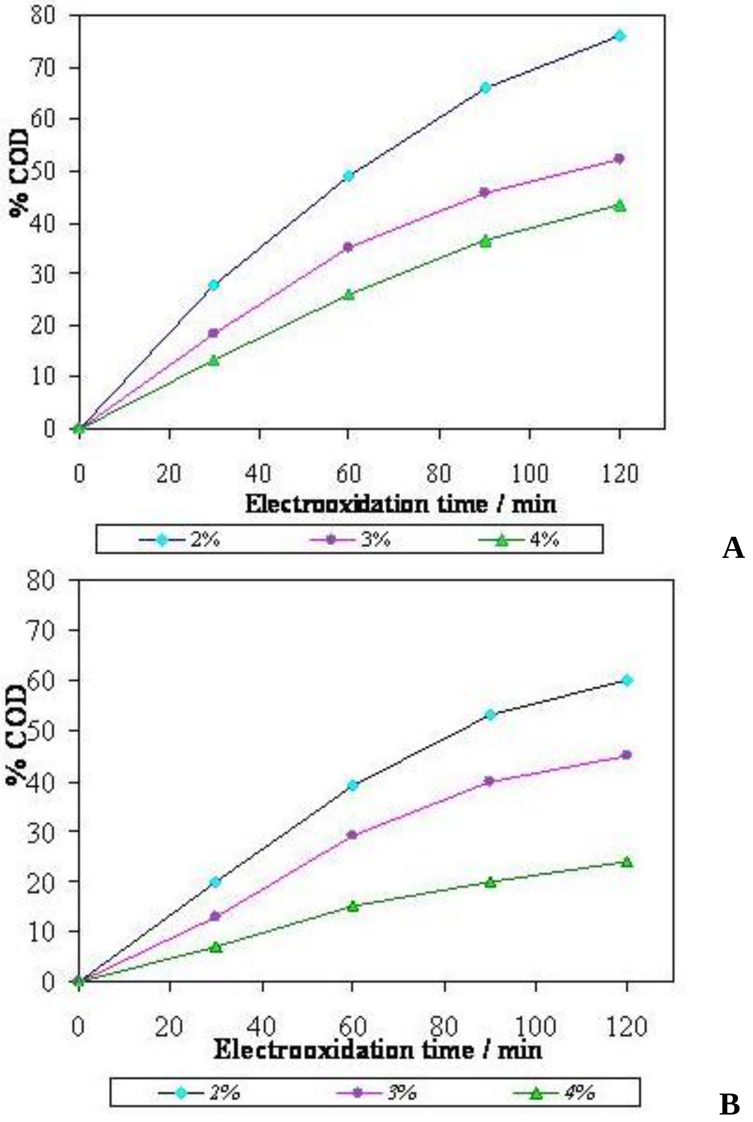


Figure 2 a)Direct electrooxidation at BDD anode: effect of NaCl concentration on the %COD (230 mg.L^{-1} Bupirimate solution, 60mA.cm^{-2}, pH=6.2, and T=25°C) b) Direct electrooxidation at SnO$_2$ anode: effect of NaCl concentration on the %COD (230 mg.L^{-1} Bupirimate solution, 60mA.cm^{-2}, pH = 6.2, and T = 25°C).

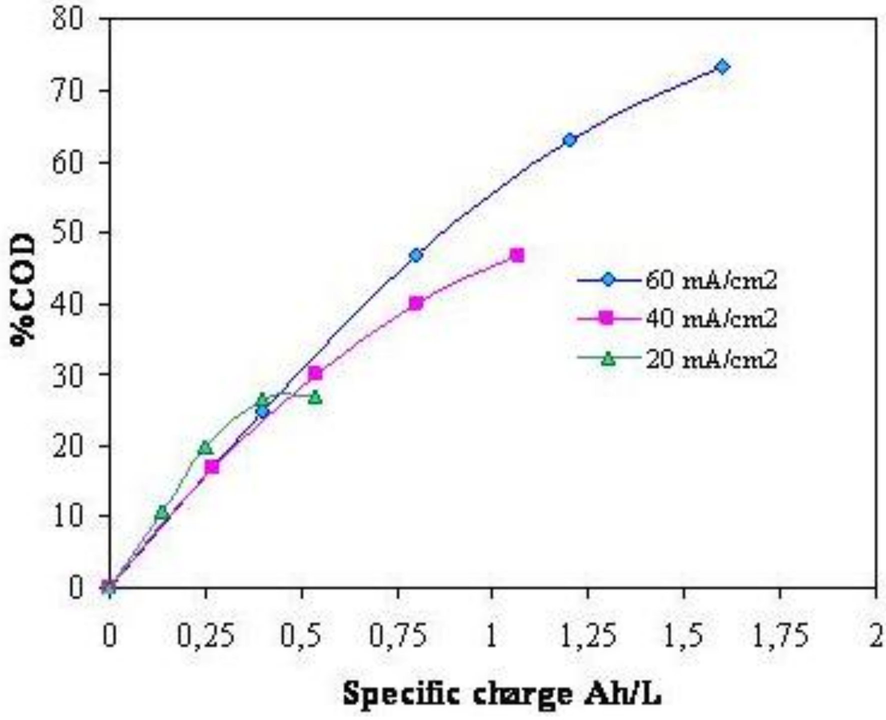
The effect of supporting electrolyte on rate constant increased with decreasing concentration of NaCl and the higher reaction rate constant ($109x10^{-4}$ min^{-1}) was obtained at 2% of NaCl supporting electrolyte. This indicates that the bupirimate molecules were easily attacked by hydroxyl radicals at lower concentration of NaCl. These results are in agreement with previously reported results [9].

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

Electrode	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

3.2. Effect of the applied current density

The effect of applied current density on the electrochemical process was reported in several studies [9, 16]. 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 3-a, 3-b and Table 2).



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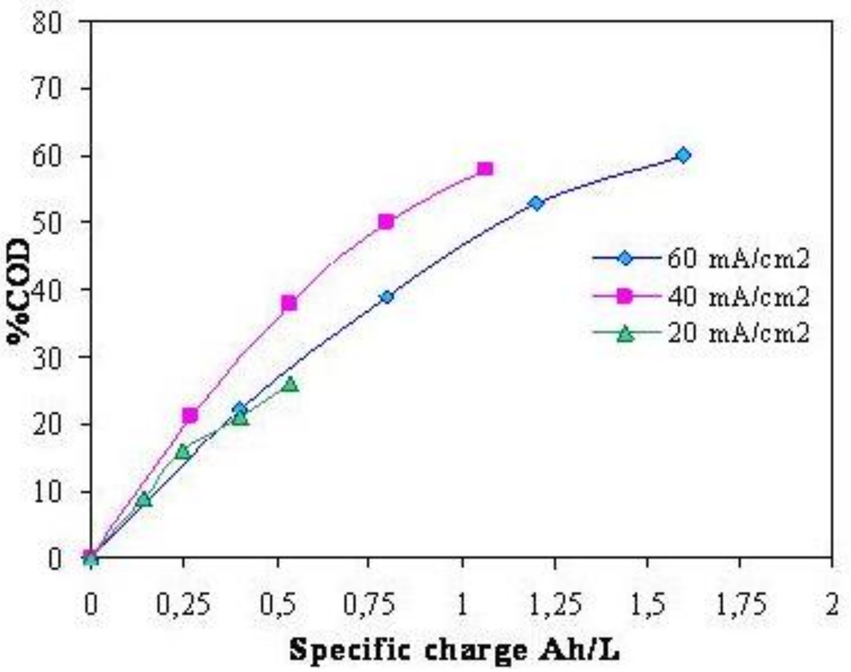

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Figure 3 a)Variation of %COD as a function of the specific charge passed during electrolysis of bupirimate performed with BDD and at several current densities (20, 40 and 60mAcm^{-2}). Initial bupirimate concentration = 230mg/L, pH = 6.2, T = 25°C, electrolyte = 2% NaCl. b) Variation of COD removal as a function of the specific charge passed during electrolysis of bupirimate performed with SnO_2 and at several current densities (Operating conditions: initial bupirimate concentration = 230mg/L, pH = 6.2, T = 25°C, electrolyte = 2% NaCl.

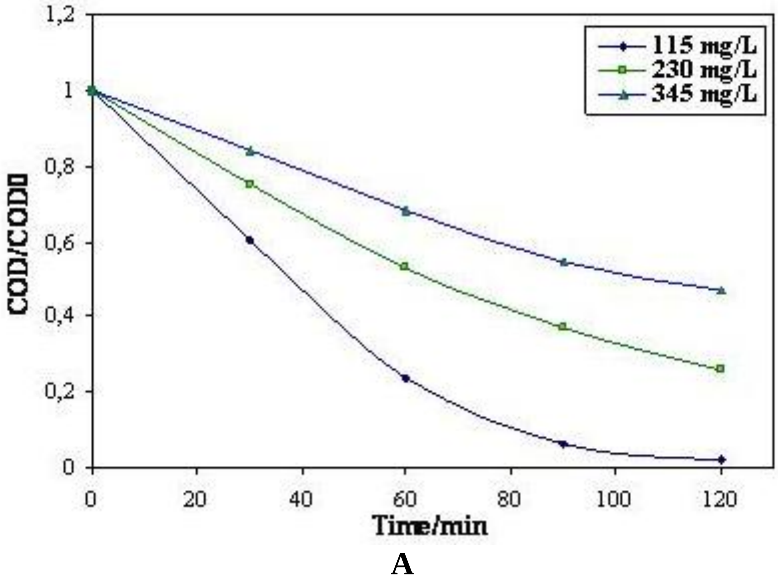
Table 2. Effect of the current intensity on the values of the rate constant and the %COD.

Electrode	Current intensity (mA.cm^{-2})	Rate constant, K (min^{-1})	%COD
BDD	20	109×10^{-4}	74
	40	52×10^{-4}	47
	60	35×10^{-4}	26
SnO_2	20	80×10^{-4}	60
	40	75×10^{-4}	58
	60	28×10^{-4}	24

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.

3.3. 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 4-a and 4-b, complete bupirimate removal can be achieved on 115 mg/L concentration of bupirimate for BDD anode as the electrolysis time was extended.



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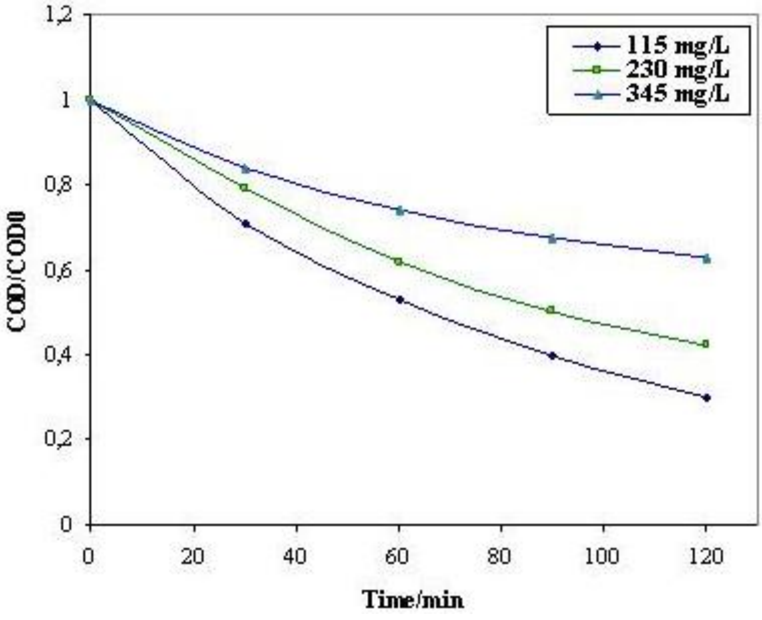

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Figure 4. a)Influence of bupirimate initial concentration on the normalized COD during BDD-anodic oxidation (Operating conditions: electrolyte = 2% NaCl, current density = 60mAcm^{-2}, T = 25°C). b) Influence of bupirimate initial concentration on the normalized COD during SnO_2 anodic oxidation of bupirimate (Operating conditions: electrolyte = 2% NaCl, current density = 60mAcm^{-2}, T=25°C)

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 SnO_2. 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 [17, 18]. 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.

3.4. 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 5).

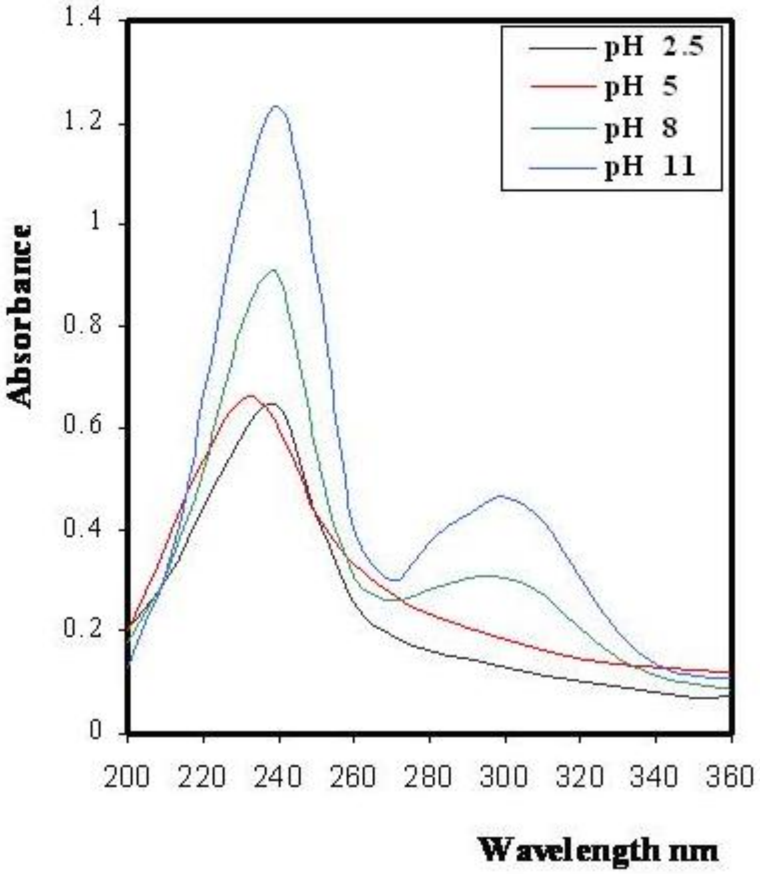

Figure 5. Effect of initial pH on the variations of UV spectra for 2 h of the electrooxidation assays performed at a BDD anode (Operating conditions: Bupirimate initial concentration = 230 mg/L, current density = 60mAcm^{-2}, electrolyte = 2% NaCl).

The decrease of the pH 11 to 2.5 leads to a decrease of the absorbance of the peaks located at 240 nm and 310 nm. At pH=5, the peak located at 310 nm disappeared. This results indicate 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 favors the rate of oxidation [19].

3.5. Comparative study of electrochemical degradation efficiency on BDD and SnO_2 Electrodes

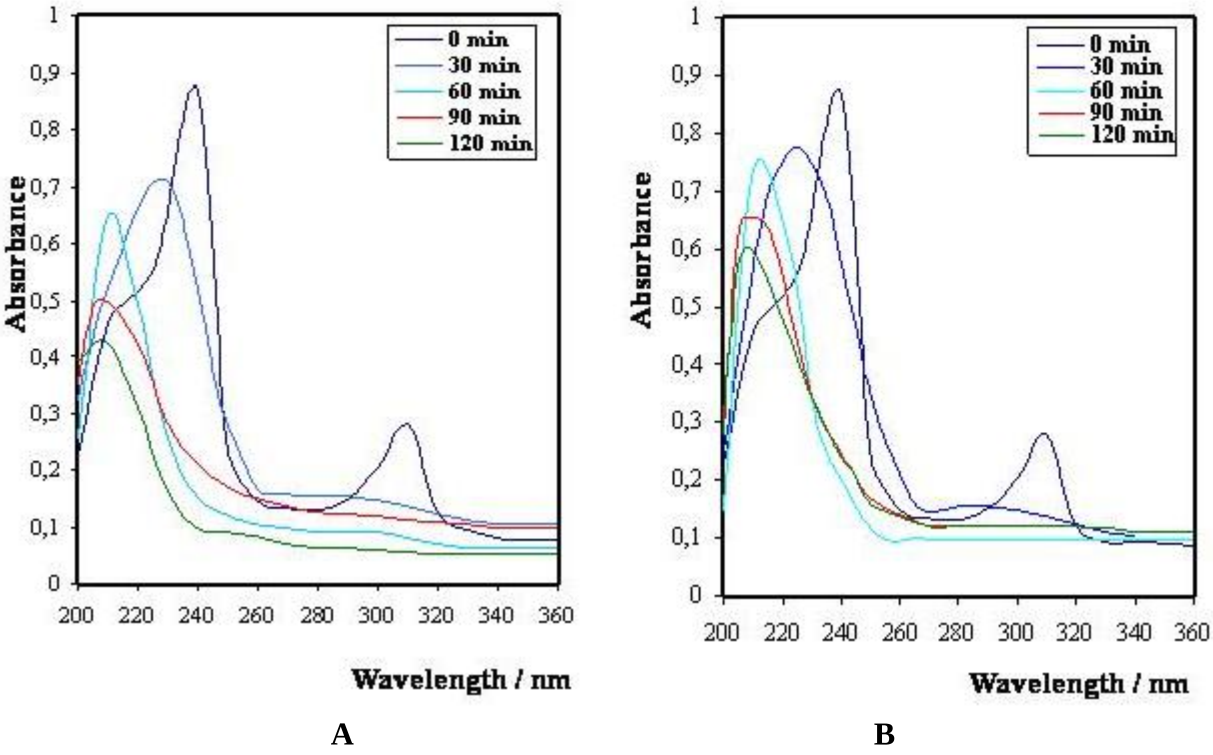

Figure 6. a)UV spectra for the electrooxidation assays performed at the BDD anode (Operating conditions: Bupirimate initial concentration = 230 mg/L, current density = 60mAcm^{-2}, pH = 6.2, electrolyte = 2% NaCl). b) UV spectra for the electrooxidation assays performed at the SnO_2 anode (Operating conditions: Bupirimate initial concentration = 230 mg/L, current density = 60mAcm^{-2}, pH = 6.2, electrolyte = 2% NaCl).

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 6-a and 6-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 6-a). The same observation could be made for SnO_2 electrode but with slower rate.

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 7. 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.

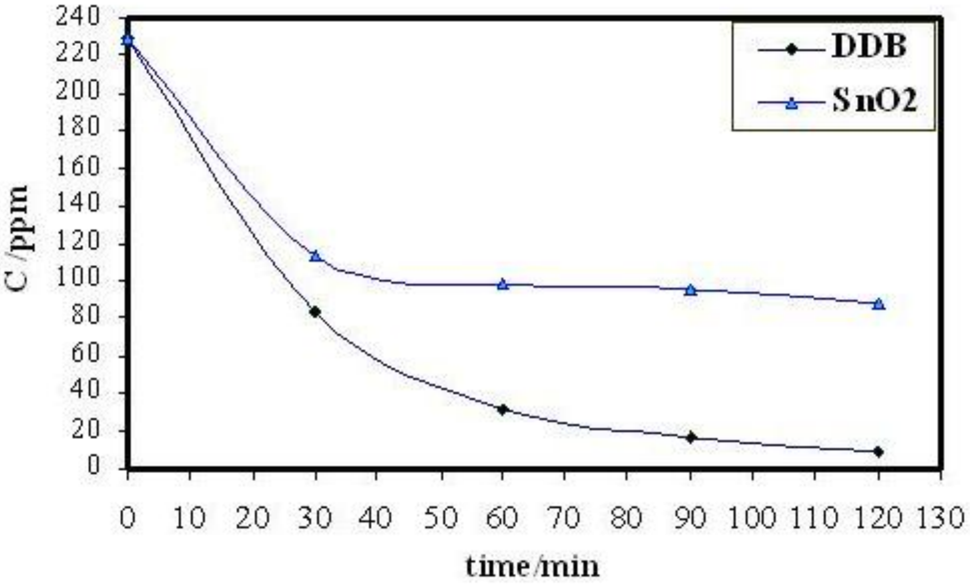

Figure 7. Electrolysis time dependence of bupirimate concentration for two anodes (BDD, SnO_2). Bupirimate initial concentration = 230 mg/L, current density = 60mAcm^{-2}, pH = 6.2, electrolyte = 2% NaCl).

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

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

4. 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.

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