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Electrochemical Oxidation of 2-Nitrobenzaldehyde on Boron-Doped Diamond Anodes

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In This work the electrochemical oxidation of aqueous waste polluted with 2-NBA on boron-doped diamond (BDD) has been investigated. The electrochemical oxidation of 2-NBA was performed using a boron doped diamond BDD electrode. The effect of several parameters such as current density, electrolyte type, initial 2-NBA concentration and temperature, was investigated. The 2-NBA degradation demonstrated different behaviors upon operative parameters on this electrode. By the way the results obtained show that the application of electrolysis in 2-NBA allows to reduce the COD for 2% NaCl and 3% NaCl the achieved reduction was 86% and 74% respectively. Beside the influence of initial concentration, current density and supporting electrolyte has shown that mediated oxidation by electro-generated reagents from the anodic oxidation of supporting electrolyte plays an important role in the efficiency of the electrochemical process.

Keywords: 2-nitrobenzaldehyde (2-NBA); Electro-oxidation; Boron doped diamond.

1. INTRODUCTION

The pollutants, especially organic compounds, released from industry to the environment are toxic to humans and other living organisms. Such as manufacturing of 2-NBA compounds with traditional synthetic procedures often leads to serious contamination of the environment by carcinogenic 2-NBA compounds and the release of a large amounts of pollutants to both air and waste water. Traditionally, these wastewaters are treated by chemical methods [1], which are considered inappropriate for removing all the organic matter. Powerful oxidation methods must be developed to destroy these wastewaters to avoid their dangerous accumulation in the aquatic environment. In the recent years, electrochemical oxidation with boron-doped diamond (BDD) electrode appears as one of the most promising technology for the treatment of real and synthetic industrial wastewaters in lab and bench-scale plants due to its high efficiency to combust partially or completely organic pollutants [2-12].The surface of this electrode allows producing large quantity of free hydroxyl radicals from water electrolysis that are well known to be very powerful oxidizing agents [13, 14-23]. Beside this surface does not interact with these radicals (exhibits a non-active behavior) and as a consequence, these radicals can only couple to form oxygen or oxidize the organic matter present in the waste. This anodic material has shown high performance levels for the conversion and/or the combustion of different compounds such as phenol, carboxylic acids, 4-chlorophenol, 3-methylpyridine, benzoic acid, 2-naphtol, polyacrylates, 4-chlorophenoxyacetic acid, amaranth dyestuff, chlorophenols, nitrophenols and polyhydroxybenzenes by electrochemical oxidation [9].

The recent use of a boron-doped diamond thin film anode [8] in anodic oxidation has shown that its O_2 overvoltage is much higher than that of conventional anodes such as PbO_2, doped SnO_2, IrO_2 and Pt, then producing larger amounts of adsorbed $OH^{\cdot}$ by reaction (1) giving a more rapid destruction of pollutants. Anodic oxidation with BDD then seems a suitable procedure to mineralize organics, as found for HClO4 aqueous solutions containing carboxylic acids such as acetic, malic, formic and oxalic [9], 4,chlorophenol [27], phenol [28], and bupirimate [18]. The study of the electrochemical oxidation of 2-NBA has not been presented in the literature.

$$Cl_2 + H_2O \longrightarrow HClO + H^+ + Cl^- \qquad (1)$$

Thus, the current paper presents the study of a prospective electrochemical treatment system for 2-NBA in aqueous solution using a boron-doped diamond electrode (BDD).

In recent studies Salghi and co-workers studied the electrooxidation of various groups pesticides bupirimate [15-16]; methidathion [16, 21], cypermethrin [17], endosulfane [22], difenconazole [19], in brine solution using BDD and SnO_2 anodes. The authors studied the electrooxidation of various organic compound by Iniesta and co-workers, organic substrates [27]; 4-chlorophenol [28]; 1, 2-dichloroethane [29]. 2-NBA (Fig.1) 2-Nitrobenzaldehyde is an organic aromatic compound containing a nitro group ortho to formyl. 2-Nitrobenzaldehyde once was produced as an intermediate in the synthesis of the popular dye Indigo. The reason for it this molecule was chosen as the target molecule for the present study because of seems to be one of the metabolite of cypermethrine [17].

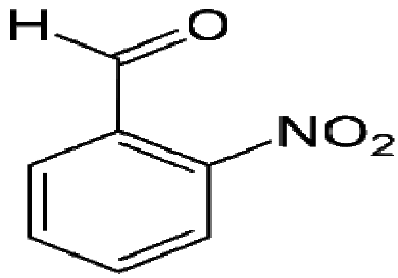

Figure 1. Chemical structure of 2-Nitrobenzaldehyde.

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 0.25 cm. 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 (1440 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 [20]. 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).

3. RESULTS AND DISCUSSION

3.1. Effect of supporting electrolytes

The investigation of the mediator concentration effect has been performed in the range 1- 4% for NaCl. The figure 2 shown effect of chloride ions concentration on the destruction of 2-NBA, carried out at 80mA/cm^2. We observed that the application of electrolysis in this compound have the ability to reduce considerably the COD [21-24]. For example, for 2% mass NaCl and 3% NaCl the achieved reduction was 86% and 47% respectively, while for 1% NaCl was 74%.

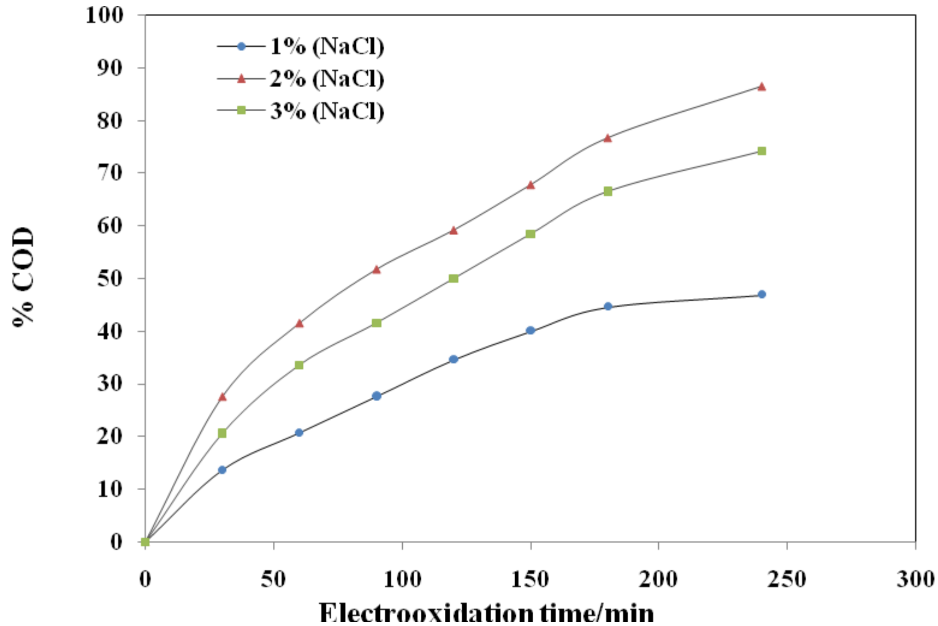

Figure. 2 Direct electrooxidation at BDD anode: effect of NaCl concentration on the % COD (10 mg.L^{-1} 2-NBA solution, 80 mA/cm^2, pH=6,2, and T=25°C).

The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of 2-NBA on the electrode or indirect via some mediators like chlorinated species or other radicals [23-25]. 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):

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

$$Cl^- + Cl^{\cdot}_{ads} \Longrightarrow Cl_2 + e^- \quad (3)$$

$$Cl_2 + H_2O \Longrightarrow HClO + H^+ + Cl^- \quad (4)$$

As cited in reference [22]. That at pH higher than 4.5 the complete dismutation of Cl_2 into HClO and Cl^- is occurred.

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 be explain why until 2% of NaCl concentration the COD removal increases with NaCl concentration. Increasing the chloride concentration more than 3% 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 [23-26]. The balance of all these phenomena results that there is an optimum of NaCl concentration which is 2% mass of NaCl for the degradation of 2-NBA.

Figure 3 illustrates the apparent kinetic constants for oxidation of 2-NBA at different concentration of NaCl as a function of the electrolysis time. The apparent kinetic constants constant of

2-NBA (k) varies from 42×10^{-4} min^{-1} for 1%NaCl, 103×10^{-4} min^{-1} for 2% NaCl and 72×10^{-4} min^{-1} for 3% NaCl.

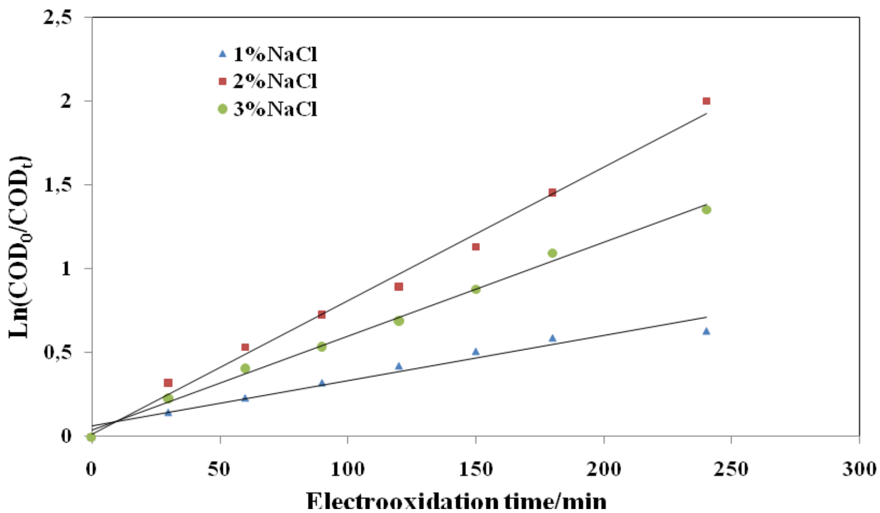

Figure 3. .Pseudo first-order plot oxidation of 2-NBA 25°C, 10 mg/L at 80 mA/cm^2, pH=6,2 for different concentration of NaCl.

3.2. Effect of current density

Applied current is an important factor affecting the electrolysis kinetics and process economics. The effect of applied current on the electrochemical process was demonstrated in several studies [19-25]. In Figure 4 the % COD reduction for 2-NBA is presented under different current inputs (2%NaCl).

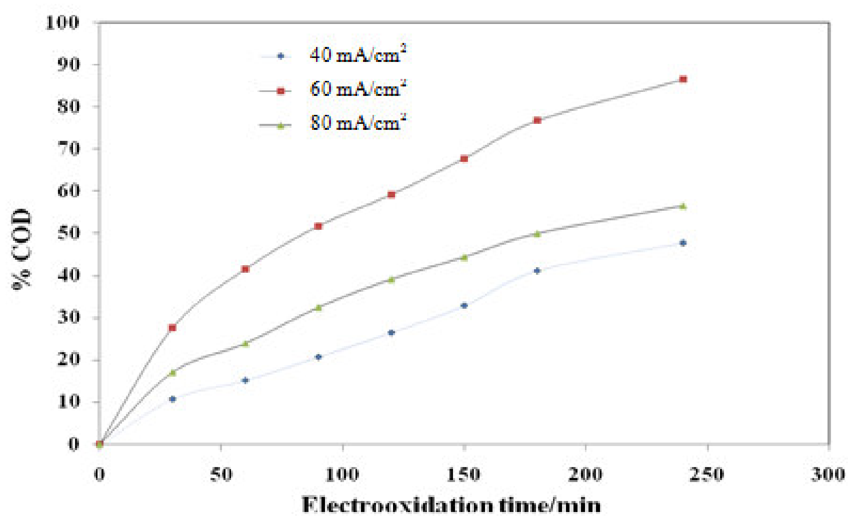

Figure 4. Influence of the applied current density on the trends of % COD electrolysis of 2-NBA (COD_0 = 10 mg/L) using a 1cm^2 BDD anode. 1% (NaCl) and T=25°C.

These studies concluded that applied current increases the rate of electrochemical oxidation process.

The COD of 2-NBA was observed to fall with pseudo first-order kinetics (fig.5), on all the surface studied. This is related to the dependence of the rate of oxidation on the rate of formation of the oxidising species at the electrode surface [15.17-25].

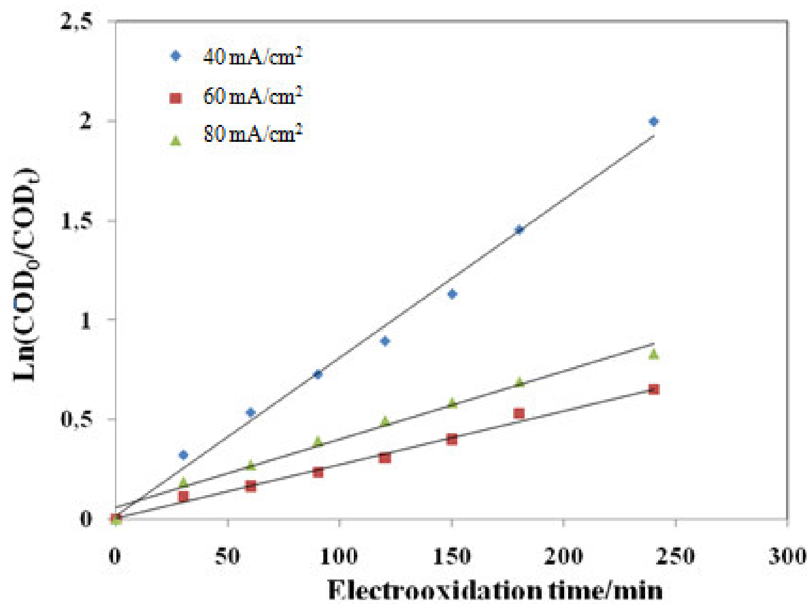

Figure 5. Pseudo first-order plot oxidation of 2-NBA 10 mg/L in 2% NaCl at 25°C under different current inputs.

The pseudo first-order constant of 2-NBA (k) varies from 27×10^{-4} min^{-1} (40 mA) to 83×10^{-4} min^{-1} (80 mA). This is exemplified in Figure 7 where the pseudo first-order plot is presented. From these results it was calculated that the best applied current is 80 mA.

3.3. Effect of initial concentrations of 2-NBA

The initial concentration of a pollutant is always an important parameter in wastewater treatment [15, 17-18]. Figure 6 shows the effect of the initial concentration of 2-NBA on the COD removal during electrolysis at pH = 6,2 ; temperature of 25 °C, supporting electrolyte NaCl (2%NaCl) and using a current density of 80 mA/cm.

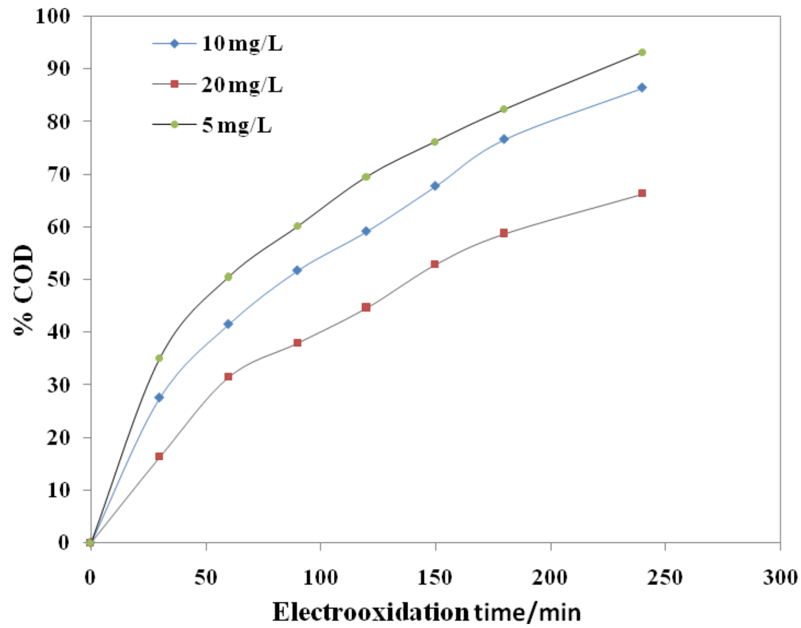

Figure 6. Direct electrooxidation at BDD anode: effect of initial concentration of 2-NBA on the %COD (80 mA/cm^2, pH=6,2, and T=25°C)

Overall 2-NBA 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 45×10^{-4}, $83\times10^{-4}$and 112×10^{-4}min^{-1} for the 2-NBA concentrations of 20 ppm, 10 ppm and 5 ppm, respectively.

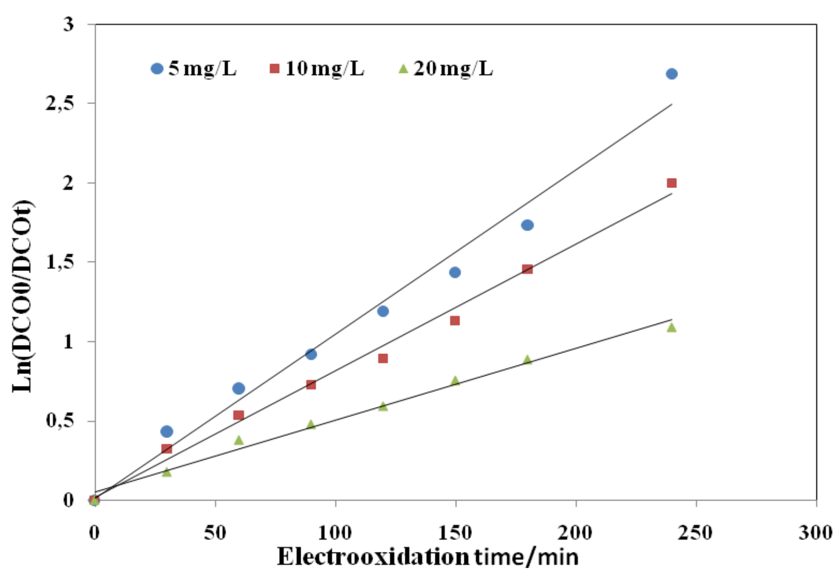

Figure 7. Pseudo first-order plot oxidation of 2-NBA 25°C, 2% NaCl at 80 mA/cm^2, pH=6,2 for different concentration.

3.4 Effect of temperature on the degradation efficiency

In Figure 8 the % COD reduction for 2-NBA at different temperatures under current input 80 mA is presented.

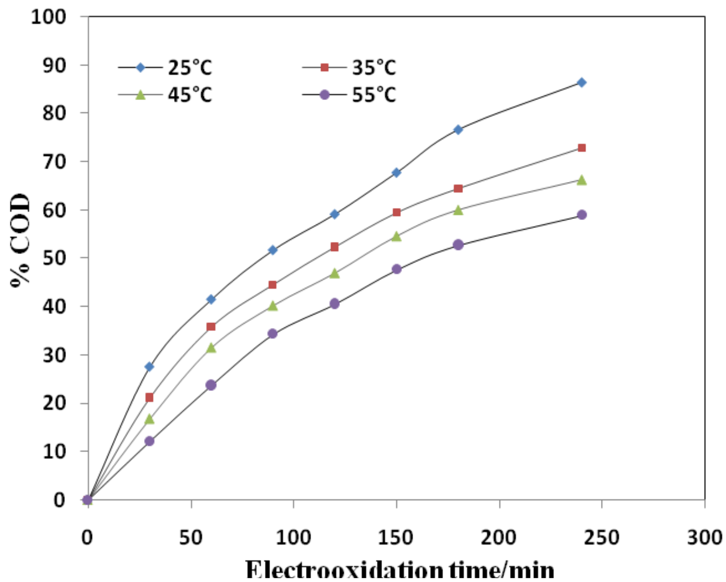

Figure 8. % COD reduction for 2-NBA 10 mg/L in 2% NaCl at 25°C at different temperatures

It is observed that for 25°C and 55°C the achieved reduction was 86% and 59% respectively.

The COD of 2-NBA was observed to fall with pseudo first-order kinetics (fig.9) [20-25]. The pseudo first-order constant of 2-NBA (k) varies from 83×10^{-4}min^{-1} (25 °C) to 37×10^{-4} min^{-1} (55 °C).

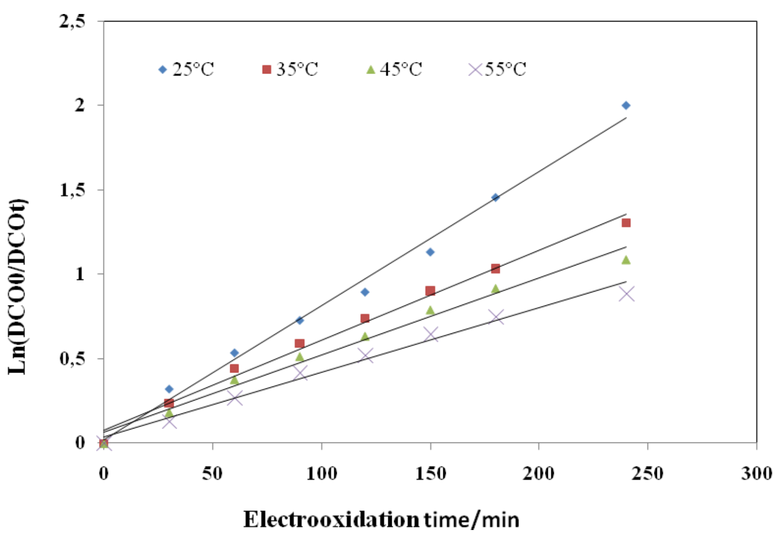

Figure 9. Pseudo first-order plot oxidation of 2-NBA 10 mg/L in 2% NaCl at 80 mA under different temperatures..

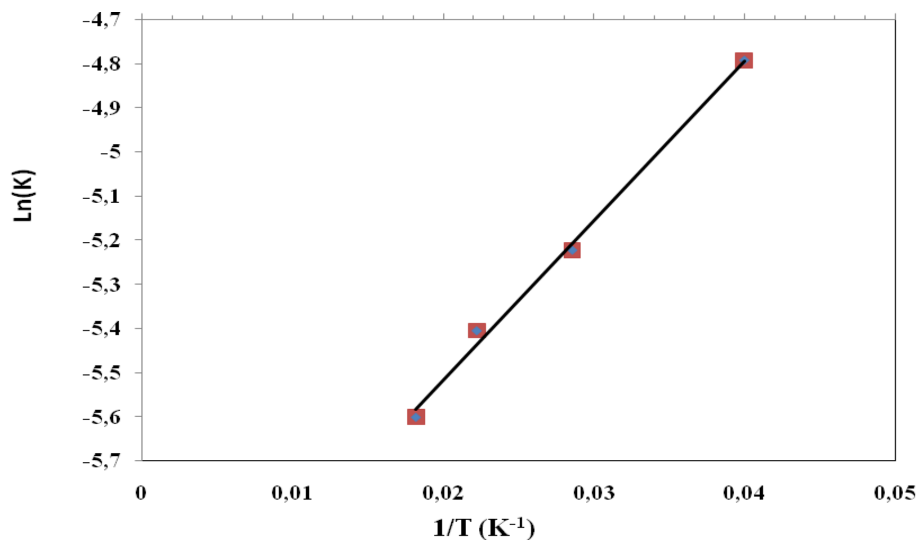

Figure 10. Arrhenius plot of 2-NBA 10 mg/L in 2% NaCl at 80 mA/cm^2 at various temperatures.

The effect of temperature on the rates of constant was modelled using the Arrhenius plots, are shown in (Fig. 10). The apparent activation energies were determined by:

$$K = A. \exp(-Ea/RT) \quad (5)$$

Where K is rate constant, A is constant, Ea is the activation energy, T is the temperature (K) and R is the gas law constant

The obtained activation energy (0,03kj) indicate that the electrochemical degradation is complex.

4. CONCLUSION

The main conclusions of this work can be summarized in the following points:

- BDD-anodic oxidation can be used successfully to remove almost all the COD of synthetic wastewaters polluted with 2-NBA.
- The application of electrolysis in pesticide has the ability reduce the COD. For 2% mass NaCl and 3% mass NaCl the achieved reduction was 86% and 74% respectively. For 4% NaCl was 47%.
- The COD of 2-NBA was observed to fall with pseudo first-order kinetics, on all the surface studied.
- The applied current increases the rate of electrochemical oxidation process.
- The effect of temperature shown that for 25 °C and 55 °C the achieved reduction was 86% and 59% respectively.
- The activation energy indicate that the electrochemical degradation is complex.

This preliminary study suggest that anodic oxidation with BDD electrode constitutes an excellent method for the treatment of effluents contaminated with 2-NBA.

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