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Electrochemical degradation of thiabendazole by BDD anode

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ABSTRACT

This paper explores the degradation of a model pollutant, 2-(4-thiazolyl) benzimidazole by electrochemical process. The degradation of the real Agricola effluent is followed by COD abatement and UV spectroscopy. The electrochemical oxidation of fungicide thiabendazole has been studied on boron doped diamond (BDD) electrodes on acid medium by bulk electrolysis. The influence of several operating parameters, such as applied current density, effect of electrolytes (NaCl), effect of concentration and effect of temperature was investigated. UV spectroscopy and chemical oxygen demand measurements were conducted to study the reaction kinetics of thiabendazole mineralization. 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: Electrochemical oxidation, boron-doped diamond, Triazole pesticide, fungicides, Reaction kinetics

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INTRODUCTION

In recent years there has been increasing interest in environmental damage and human injury by pollution resulted by the use of pesticide in agriculture, and the relevant legislation is always being made harsher [1]. 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 [1,2]. Various innovative technologies have been proposed for the removal of pesticides from water. For the disposal and degradation of pesticide waste have recently been well reviewed by several auteurs [3-7]. Various methods for pesticide treatment methods are available, according to the World Health Organisation, including high temperature incineration, chemical treatment or removal to specially engineered landfill sites [8]. Amongst the possible methods of treatment of pesticides, ozonation [9], oxidation with Fenton's reagent [10], photodegradation [11] and photocatalysis with TiO_2 have been investigated for a wide variety of pesticides [12]. Since the 1990s, electrochemical methods have been widely studied for the removal of organic substances and a number of reviews are available in the literature [13-15]. Recently, electro oxidation has received great attention due to the use of boron-doped diamond (BDD) thin film electrodes, which possess so high O2-overvoltage that favors the production of great quantity of reactive BDD ($OH^{\cdot}$) with ability to completely mineralize organics, as shown for several aromatics [16-18]. In recent studies Salghi and co-workers studied the electrooxidation of various groups pesticides sach as bupirimate [3,5-6]; methidathion [23] and cypermethrine [7] in brine solution using BDD and SnO_2 anodes. The authors studied the electrooxidation of various organic compound by Outuran et al (2015) [24, 29], Tissot et al (2012) [25]. Benito et al (2017) [26], Chaplin et al (2014) [27], and Panizza et al (2014) [28]. Thiabendazole is used to control a variety of fruit and vegetable diseases such as mold, blight, rot and stains caused by various fungi. Thiabendazole is formulated as a ready-to-use, dusts, flowable concentrates, emulsifiable concentrates, wettable powders, granules, and water dispensable granules (Fig. 1) [29].

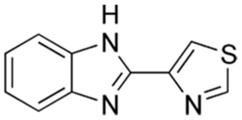

Fig. 1: Structural formula of thiabendazole

MATERIALS AND METHODS

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 0,5 cm. A saturated calomel electrode (SCE) was used as a reference electrode. Galvanostatic electrolysis was carried out with a volume of 75 cm^3 aqueous solution of initial COD_0 (1680 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 [3]. 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. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

RESULTS AND DISCUSSION

Effect of supporting electrolytes

The investigation of the mediator concentration effect has been performed in the range 2% - 4% for NaCl. As shown in Fig. 2, the electrochemical degradation of the pesticide is achieved at reasonable rates only in the presence of the mediator and is higher at higher NaCl concentrations, up to values around 2% of NaCl. Further increase, above this limit, causes and inversion of the trend. The operating conditions of the treatment process were: current density of 60 mA cm^{-2}, temperature of (25 ± 3)°C, initial concentration COD (1680 mgL^{-1}), and the distance between the two electrodes was 0.5 cm. The addition of NaCl to the pesticide solutions during electrolysis, the degradation efficiency increased for thiabendazole. From this observation it was concluded that the introduction of NaCl as electrolyte can enhance the degradation efficiency and shortens electrolysis time, which may be attributed to the reaction between the electrogenerated chlorine/hypochlorite and the TBZ molecule. The possible mechanism of electrochemical degradation in the presence of NaCl is as given below:

Anode reaction:

Anode reaction	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Cathodereaction	$2H_2O + 2e- \longrightarrow H_2 + 2OH^-$
Bulksolutionreaction	$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$
Bulksolutionreaction	$HOCl \longrightarrow H^+ + OCl^-$

The above mechanism was classified as indirect electrooxidation of pollutant. Moreover, the increased concentration of NaCl results in a decrease in the operating voltage at the given current density.

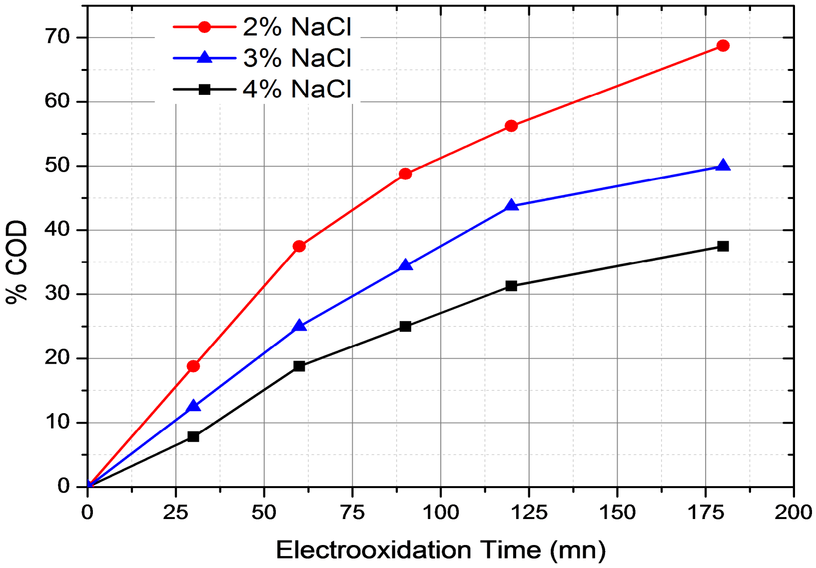

Fig. 2. Influence of supporting electrolytes on the decay of COD during electro-oxidation of 1680 mg/L thiabendazole on BDD anode. Conditions: Current density 60 A.cm^{-2}; T: 25°C

The electrochemical degradation of the fungicide TBZ using the BDD anode. The removal of the pesticide in 2% (NaCl) higher than that of 3% (NaCl) and much higher than 4% (NaCl). Working in galvanostatic condition, the concentration of •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 (Fig. 3), 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 [3-6]. Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation fungicide Thiabendazole at different concentration of supporting electrolyte NaCl. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [6].

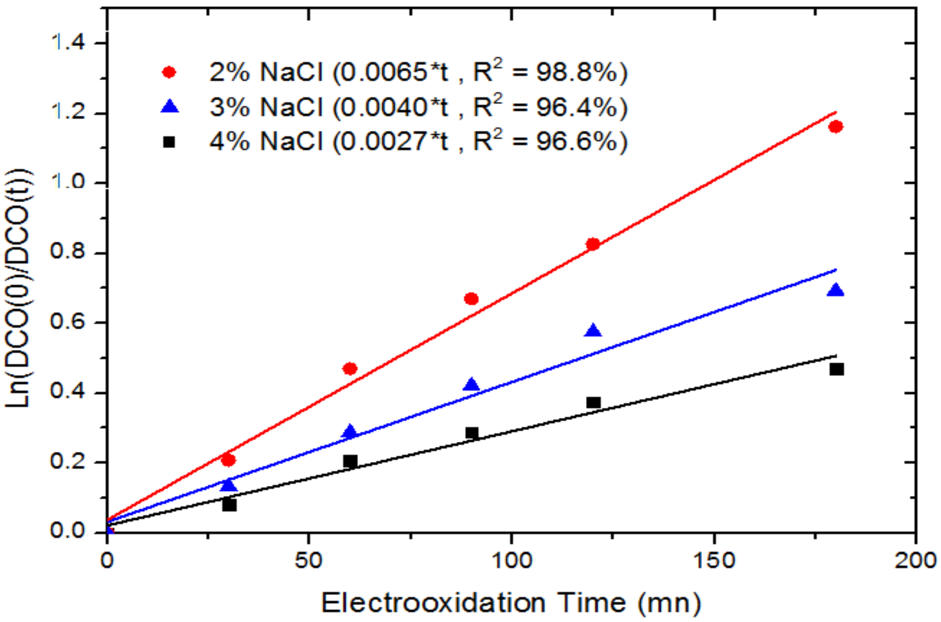

Fig. 3. Pseudo first-order plot oxidation of 2g/L thiabendazole (COD_0 = 1680 mg/L) in different concentration of electrolyte at 60 mA.cm^{-2}

Fig. 3 and Table 1 represents the Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation thiabendazole at of the different concentration of NaCl supporting electrolyte solution in the presence of COD_0 = 1680 mg/L of thiabendazole. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows.

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 %)	$(6.50 \pm 0.05)\times10^{-3}$	(70 ± 2.25)
NaCl (3 %)	$(4.00 \pm 0.10)\times10^{-3}$	(50 ± 3.7)
NaCl (4 %)	$(2.70 \pm 0.08)\times10^{-3}$	(39 ± 2.2)

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 [3-6, 12, 19, 25, 26]. In Fig. 4 the % COD reduction for thibandazole is presented under different current inputs (2%NaCl). These studies concluded that applied current increases the rate of electrochemical oxidation process. As shown in Figs (4-5) thiabendazole COD removal increase with increasing the applied current density up to80 mAcm^{-2} by using DDB electrode. Further increase of the current density was followed by gradual decrease in COD removal due to increase in temperature [14-19]. In other words, the rate of degradation of pesticide increases with increase in current density by maintains a moderate temperature. The COD of thiabendazole 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 oxidizing species at the electrode surface, the pseudo first-order constant of thiabendazole (k) varies from, 2, 5×10^{-3} min $^{-1}$ (40 mA) to $8,1\times10^{-3}$ min $^{-1}$ (80 mA). From these results it was calculated that the best applied current is 80 mA.

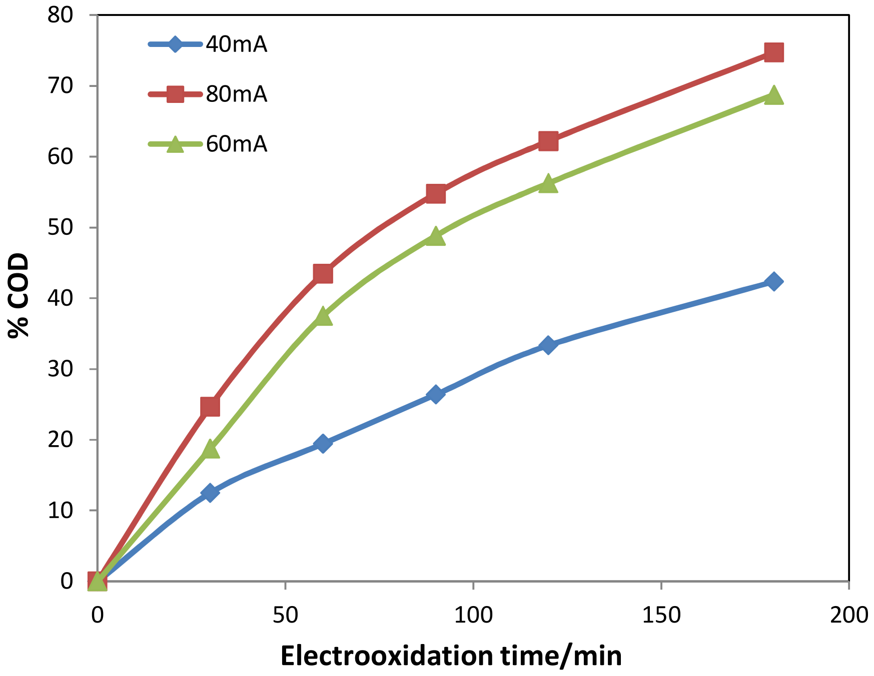

Fig. 4. Influence of the applied current density on the trends of % COD electrolysis of Thiabendazole (COD_0 = 1680 $mg.L^{-1}$) using a $1cm^2$ BDD anode

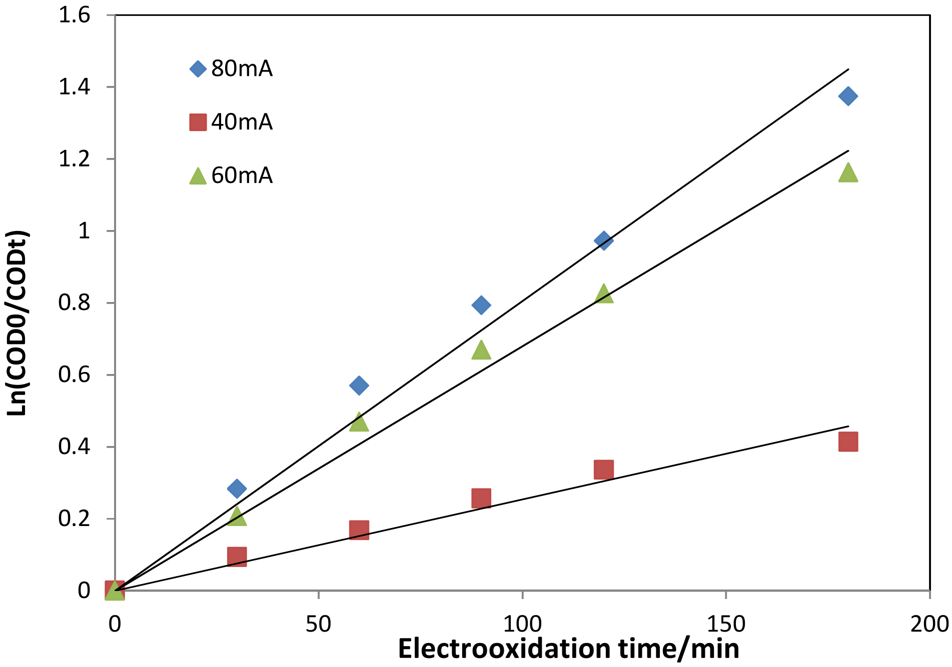

Fig. 5. Influence of applied current density on the decay of %COD during electro-oxidation of thiabendazole 2g/l on BDD anode. Conditions: current density 80 mA cm^{-2}, 2% NaCl

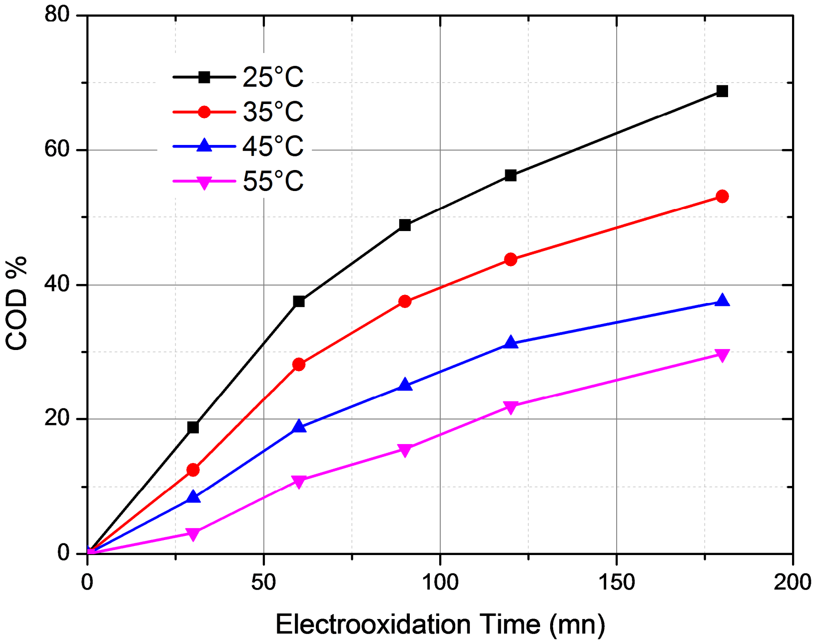

Fig. 6. % COD reduction for thiabendazole in 2% NaCl at 25°C and volume of treated solution: 75 cm^{3}at different temperatures, 80 mA

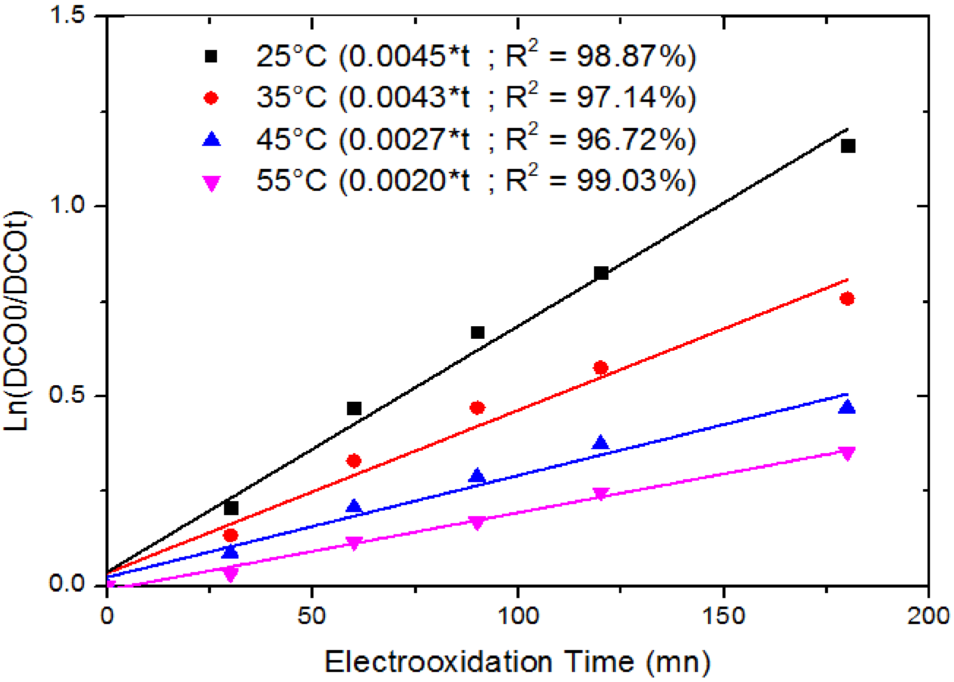

Fig. 7. Pseudo first-order plot oxidation of thiabendazole in 2% NaCl at 80 mA and volume of treated solution: 75 cm^3 under different temperatures (COD at a given time, t, during electrolysis)

Effect of temperature

To determine the effect of temperature on the % COD reduction for the thiabendazole, experiments were carried under current input 80 mA for which degradation of the thiabendazole is more important. Fig. 6 shows the % COD reduction for thibendazole at different temperatures. It was observed that, the % COD reduction decrease with temperature, for 25°C and 55°C the achieved reduction was 70% and 30% respectively. Fig. 7 illustrates the the pseudo first-order of thiabendazole at different temperature under 80 mA current inputs. The pseudo first-order constant of thiabendazole (k) varies from 0.0045min^{-1} at 25 °C to 0.002 min^{-1} at 55 °C.

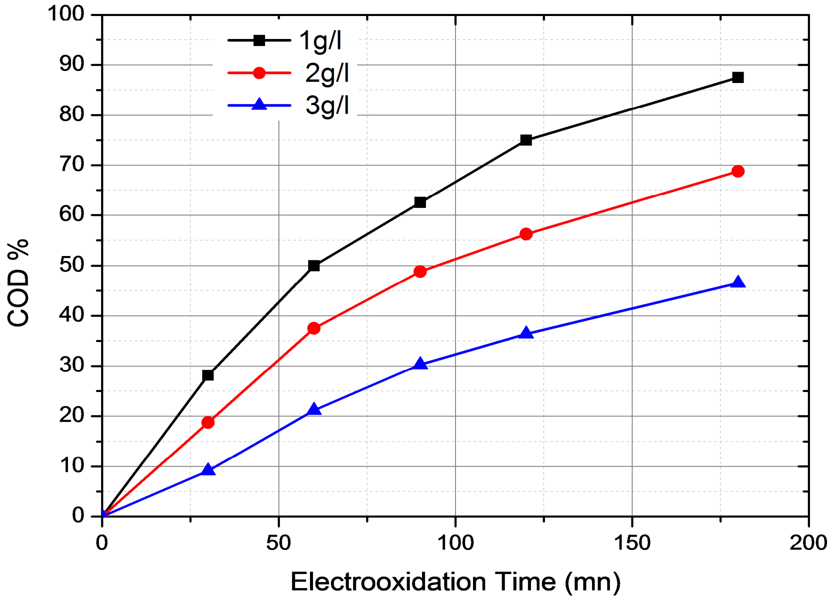

Fig. 8. Direct electrooxidation at BDD anode: effect of initial concentration of thiabendazole on the %COD (80 mA.cm^{-2}, and T=25°C)

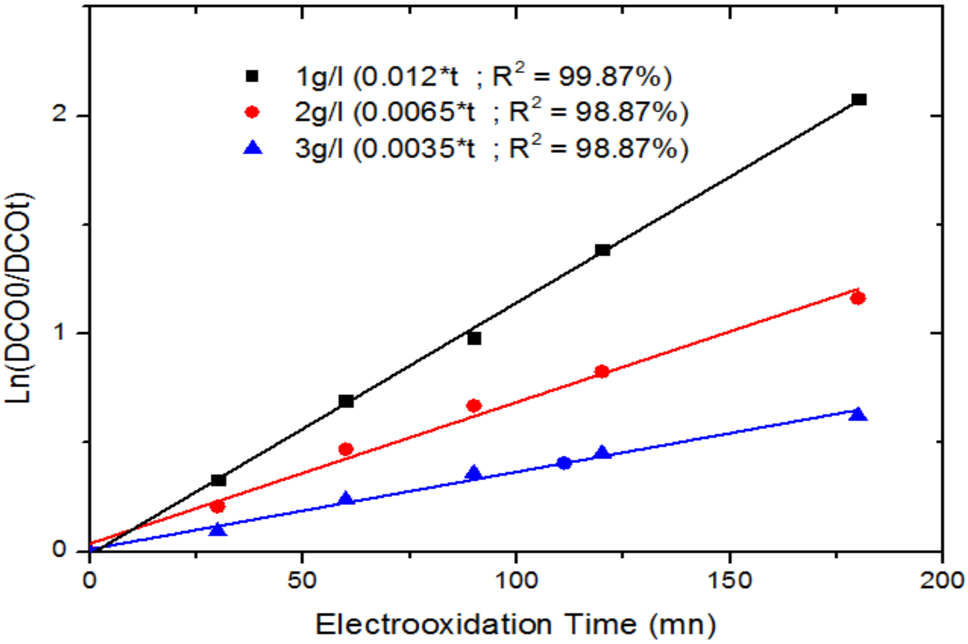

Fig. 9. Pseudo first-order plot oxidation of thiabendazole:T= 25°C, 2% NaCl at 80 mA.cm^{-2}, for different concentration

Effect of concentrations of pesticide

The initial concentration of pesticide is always an important parameter in wastewater treatment. The % COD reduction was studied at three different concentration of thiabendazole pesticide 1 g/L, 2 g/L and 3 g/L) under the previous optimum conditions. Fig. 8 shows the effect of different initial Thiabendazole concentrations on the rate of fungicide degradation and corresponding Concentration removal during electrolysis at temperature of 25 °C, NaCl (2%) and using a current density 80 $mAcm^{-2}$. The increased rate of pesticide degradation is due to the diminution of thiabendazole concentration and formation of chlorine gas at anode and hypochlorite after reaction with OH at the cathode. The degradation of different concentration of pesticide was observed with pseudo first-order kinetics (Fig. 9). The pseudo first-order kinetics constant of thiabendazole removal (k) varies from approximately 12×10^{-3} min^{-1} for 1g/L to 35×10^{-4} min^{-1} for 3 g/L.

CONCLUSION

This work studied the efficiency of an electrochemical oxidation system for the treatment of fungicides thiabendazole. Electrochemical degradation is a method that has never been applied this type of wastes. The electrochemical degradation of thibendazole has been investigated using BDD anode under all conditions tested involving, applied current density from 40 to 80 mA, type of electrolyte, effect of temperature 25°C to 55°C , effect supporting electrolyte NaCl and initial concentration of pesticide 1g/L to 3g/L. The experimental results allowed us to draw the following conclusions:

- The best results were obtained when electrolyses were carried out at high densities, 80 mA, and in the presence of supporting electrolyte NaCl (2%) .
- The COD of pesticide thaibendazole 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 different experimental conditions tested using the BDD anode allow us to conclude that the increases of the initiale concentration of pesticide in the solutions, from 1g /L to 3g /L, slightly decreases the rate of electrooxidation of pesticides.
- BDD-anodic oxidation can be used successfully to remove almost all the COD of synthetic wastewaters polluted with thiabendazole fungicide.

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