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# Anodic oxidation of Methidation at boron-doped diamond electrode and degradation mechanism

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## Abstract

This paper presents the study of the electrochemical oxidation of the insecticide Methidathion organophosphorous pesticide, using a boron-doped diamond (BDD) anode. The influence of current density, sodium chloride concentration, temperature and initial Methidathion concentration on the rate of COD abatement has been followed. The electrolyses were performed by using a solution composed of an electrolyte support (2% NaCl) and 1.4mM of Methidathion. Samples were taken during the electrolyses and analysed by UV-vis spectra and chemical oxygen demand (COD). Under laboratory conditions, the electrochemical oxidation removed 85% COD of this pesticide with a specific energy consumption of 0.12 kWhgODC-1. The electrochemical oxidation could be used as a pretreatment methode of the pesticides detoxification. In conclusion the degradation mechanism of Methidathion was carefully studied based on the formation of free radical.

**Keywords:** UV-vis spectra, energy consumption, Methidathion, BDD.

## 1. Introduction

Pesticides are the most abundant environmental pollutants found in soil, water, the atmosphere and agricultural products. Organophosphorous (OP) compounds comprise a diverse group of chemicals that are extensively used as insecticides in modern agriculture. Both their efficiency and acute toxicity stem from their ability to inhibit a group of hydrolytic enzymes called esterases [1]. OP compounds tightly bind to the enzyme acetylcholinesterase (AChE), forming a stable complex that inhibits enzyme phosphorylation and therefore, enzymatic activity. Thus, the detection of organopollutants that threaten living organisms is a crucial civil issue. This study focuses on the degradation electrochemical of industrial wastewaters containing Methidathion organophosphorous pesticide.

Oxidative electrochemical processes are among new technologies for the treatment of wastewaters particularly when they are charged with toxic and bioresistant organics [2-6]. Anodic oxidation is an advanced oxidation process with many advantages compared to other known chemical and photochemical ones. This process aims for the mineralization of organics to $CO_2$ or for its conversion to biocompatible compounds.

Recently, boron-doped diamond (BDD), which are the boundaries of the new electrode materials technology, have been used for oxidation of organics. In fact, the wide potential window and the high anodic stability of the BDD films allow their applications in various fields like electroanalysis, synthesis of powerful oxidants and wastewaters treatment. Diamond anode surfaces allow to produce large quantities of hydroxyl radicals from water electrolysis [7]. The diamond 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. Recent work reported in the literature has shown that several inorganic, organic and bio-molecules can be satisfactorily determined with BDD electrodes [8].

The results of these works show that the electrochemical oxidation with diamond anodes achieves a very high current efficiency [9].

The goal of the work described here was to use the electrochemical oxidation on boron-doped diamond anodes for the treatment of wastewaters containing the Methidathion pesticide (see Fig. 1). The removal of the pesticide from the solution was followed by chemical oxygen demand (COD) analyses and UV-visible spectrophotometry. Finally, the energy mechanism of Méthidathion is also discussed.

## 2. Materials and methods

### *2. 1. Solutions preparation*

Boron-doped diamond films, Diachem®, were synthesized by the hot filament chemical vapor deposition technique (HF CVD) on conducting p-Si substrate (0.1Ωcm, Siltronix).The filament temperature ranged from 2440 to 2560 °C and the substrate one was kept at 830 °C. The reactive gas used was methane in an excess of dihydrogene (1% CH4 in $H_2$). The doping gas was trimethylboron with a concentration of 3 ppm. The gas mixture was supplied to the reaction chamber, providing a 0.24 µm h-1 growth rate for the diamond layer. The diamond films were about 1µm thick. This HF CVD process, produces columnar, randomly textured, polycrystalline films.

Electrochemical measurements using a computer controlled by Potentiostat/Galvanostat model PGP 201 associated to "Volta-Master1" software. A conventional three electrodes cell (100 cm3) was used thermoregulated glass cell (Tacussel Standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode are used as reference and Auxiliary electrodes, respectively. Diamond was used as working electrode (1cm$^2$)

Methidathion [O,O-dimethylS-(5-methoxy-1,3,4-Thiadiazolinyl–3-methyl)dithiophos-phate] (Fig.1) is a widely used organophosphorous insecticide, was chosen as the target molecule for the present study because of chemical toxicity (The acute oral LD50, for rats is approximately 54 mg/kg) [4].

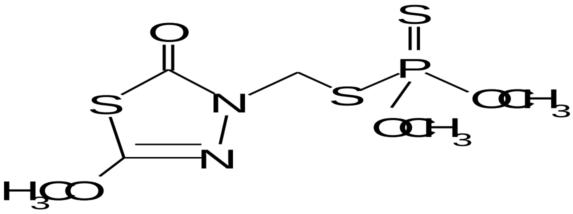

**Figure 1.** Structural formula of methidathion.

Galvanostatic electrolysis ware carried out with a volume of 75 cm$^3$ aqueous solution of Methidathion 1.4mM during 120 minutes. 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.

To characterize the toxicity removal, the global parameter, the chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [10]. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

The commercial formulation Methidaxide (40% methidation) was purchased from Bayer. The chemical sodium chloride used was of analytical-reagent grade and was obtained from Aldrich.

The electrochemical treatment of methidathion pesticide was followed by means of a HP AG/99/00/003 UV-vis spectrophotometer with a 1cm quartz cell recording the spectra over the 190-200 nm range.

## 3. Results and discussion

### *2-1 Influence of the NaCl concentration*

The investigation of the NaCl concentration effect has been performed in the range 1%–2%. As shown in Fig.2, we observed that the application of electrolysis in this pesticide have the ability to reduce considerably the COD. the electrochemical oxidation of the Methidathion solution is higher at 2% and 3% of NaCl concentrations.

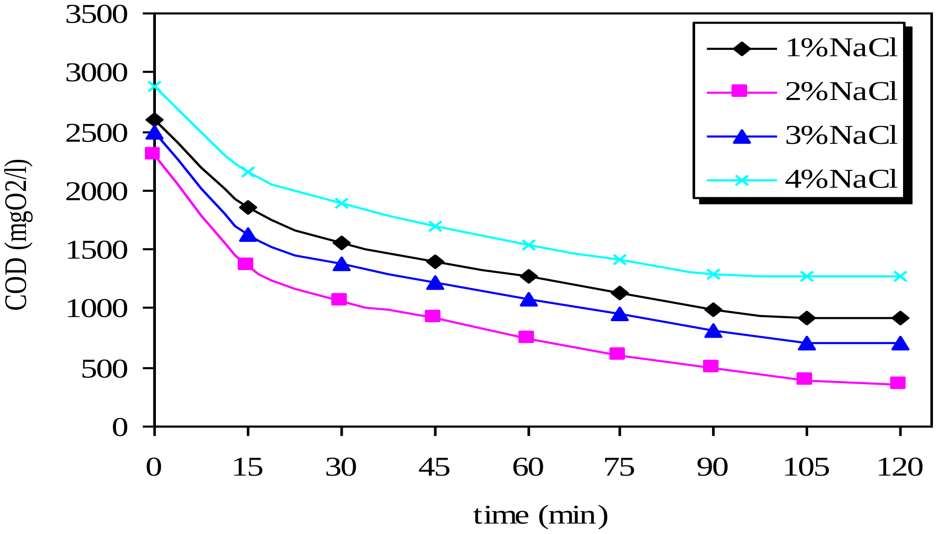

**Figure 2.** COD removal with time for Methidathion 1.4 mM at 60 mA and 25 °C

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 been 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. 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 Methidathion. At this level of the preliminary screening the set of variables allowing the best yield is: 60mA, 2% NaCl, 25°C.

### 2-2 Influence of the current density

The effect of applied current on the electrochemical process was demonstrated in several studies [11, 12]. In Figure 3 the COD removal for the Methidathion pesticide is presented. It is observed that the application of electrolysis for this pesticide has the ability to highly reduce the COD. For 60 mA the achieved reduction was about 85%, while for 40mA and 20 mA it was about 71% and 58% respectively.

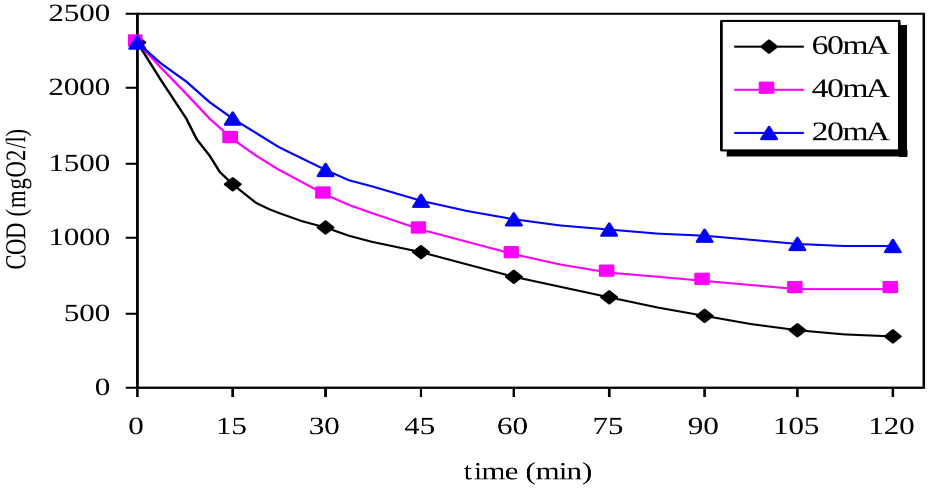

**Figure 3.** COD removal for Methidathion 1.4 mM under different current inputs (chlorides= 2%) and 25°C

These studies concluded that applied current increases the rate of electrochemical oxidation process. Figure 4 illustrates that the pH during the electrolysis is significantly reduced.

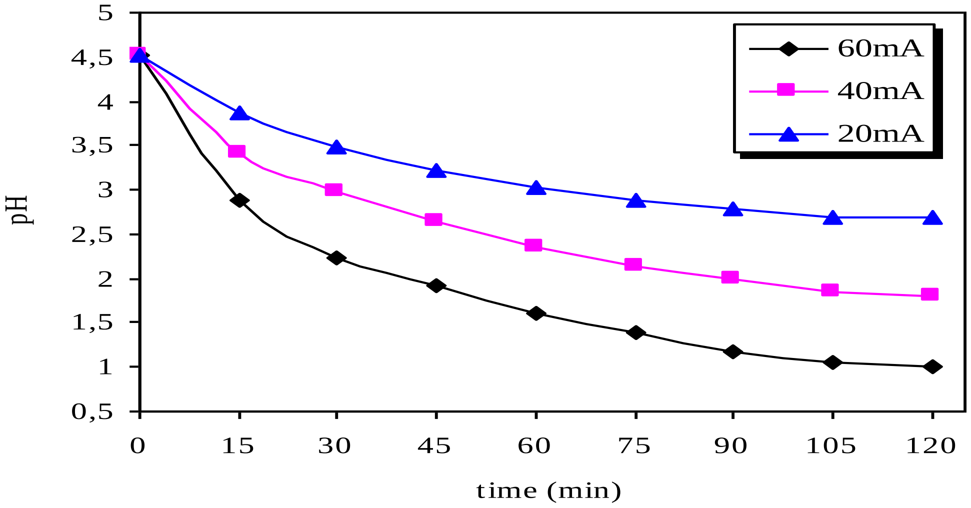

**Figure 4** pH reduction for Methidation 1.4 mM for 120 min of electrolysis at 60 mA and 25 C,

Finally the pH in all cases became strong acidic. The electrolysis was more effective in terms of %COD reduction when the pH was in the acid range. This drop of the pH, during pesticides degradation, was also noted from Kotronarou and al [13]. It was also reported by Bonfatti & al [14] that while the mineralization goes to completion and the solution pH gets more and more acidic.

### 2-3 Influence of temperature

The role of the temperature cannot be easily understood, since the electrochemical process allows more than one reaction, competing one with the other. The results, reported in Fig. 4, show an opposite behavior, compared with those expected on the basis of the Arrhenius law. For 25°C and 65°C the achieved reduction was 85% and 66% respectively. Moreover, considering the mediated mechanism, the temperature has some effects on the chlorine evolution and on the chlorate formation; both reactions lead to a loss in the oxidation mediator [14].

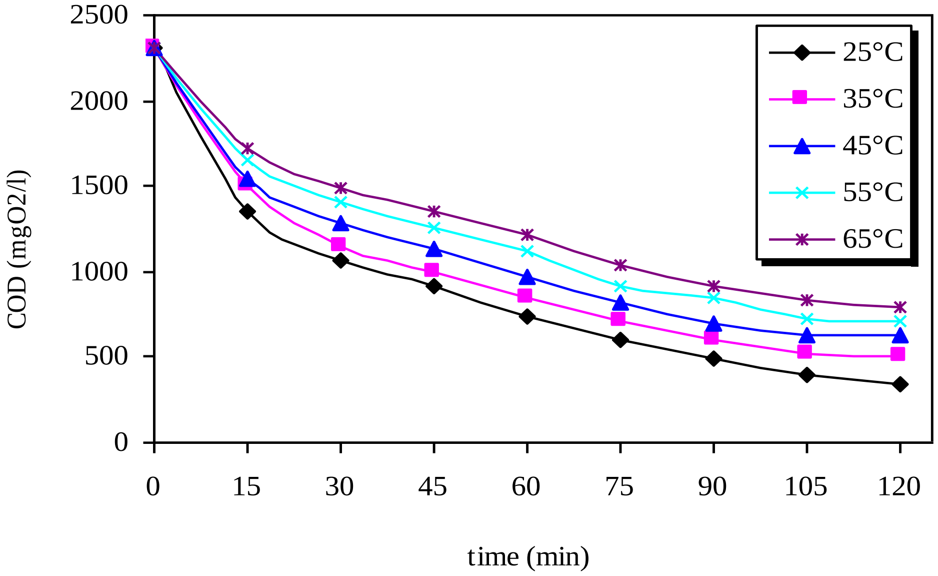

**Figure 5.** COD removal for Methidathion 1.4 mM in 2% NaCl at 25°C

at different temperatures.

Because the temperature was the last parameter under investigation, the ‘best conditions’, considering the one-factor-at-the-time sequential approach, are again the previously reported: 2% NaCl, I=60mA, T=25°C.

The COD of Methidathion was observed to fall with pseudo first-order kinetics (fig.4). The pseudo first-order constant of Methidathion (k) varies from $131.10^{-4}s^{-1}$ (25°C) to $77.10^{-4}$ $s^{-1}$ (65°C).

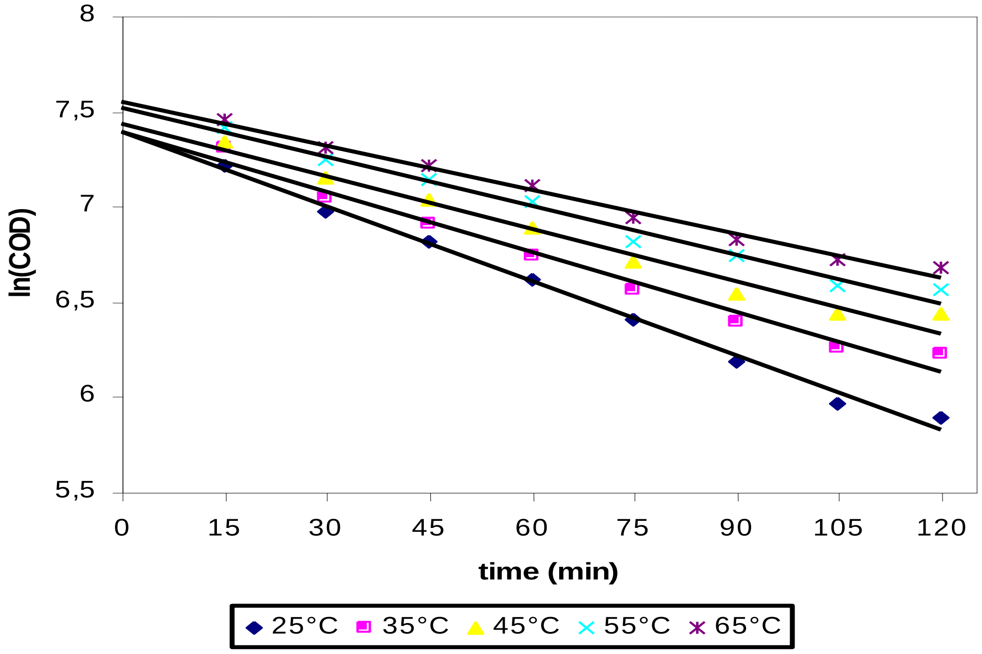

**Figure 6**. Pseudo first-order plot oxidation of Methidation 1.4 mM in 2% NaCl at 60 mA under different temperatures (COD at a given time, t,during electrolysis).

### 2-4 Influence of methidathion concentration

To establish the influence of the initial concentration of Methidathion on the electrodegradation rate, the assay of COD were conducted with initial concentrations of 1.4 and 0.47mM, using 2% NaCl solutions as the support electrolyte. The experiments were conducted at 60mA, for 2h of electrolysis. Removals of COD are presented in Fig. 4. We observe that degradation is more effective when the concentration of Méthidathion is weak

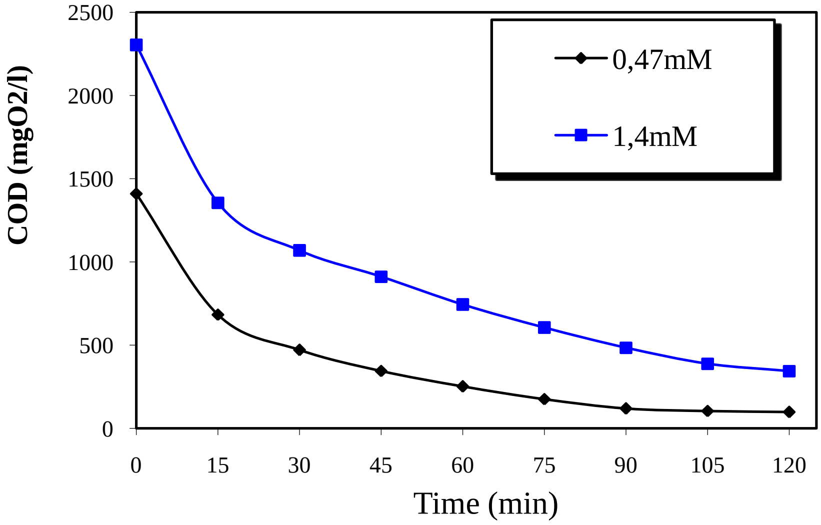

**Figure 7.** COD removal for different concentration of Methidathion in 2% NaCl at 25°C and 60mA.

### 2- 5 Spectrophotometric Measurements

Figure 8 shows the UV spectra of a 1.4mM Methidathion aqueous solution at 60mA, 25°C and 2% of NaCl.

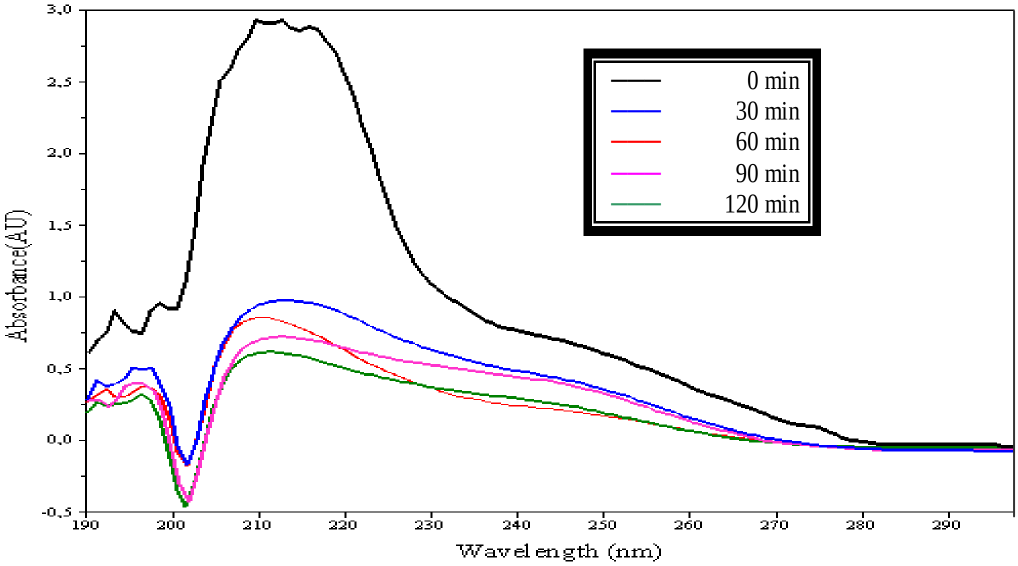

**Figure8.** UV spectum of Methidathion solution from (initial solution concentration: 1,4 mM, courent 60 mA, température 25°C and 2% of NaCl.

In order to have an idea about the nature of the formed species during the electrolyses, UV-vis spectra of the solution samples were taken. Fig. 8 exemplifies the behaviour observed for all the electrolyses performed. The first spectrum at t=0 corresponds to the original solution. For the samples corresponding to the different electrolysis times one band can be observed at 210 nm. The absorbance decreased rapidly reaching low values after 30 min of electrolysis. It is observed that the absorption of the bands decreases with time and almost disappears after about 120 min resulting in the degradation of the solution.

### 2-6 Energetic mechanism the reactions of rupture

After optimization the molecule of Methidathion using `Gaussian 03 program`. The calculations the function of Morse were carried out for the equilibrium distance S-C= 1,84995Å, the fig. 9. represent the Rhythm of the curve of Morse.

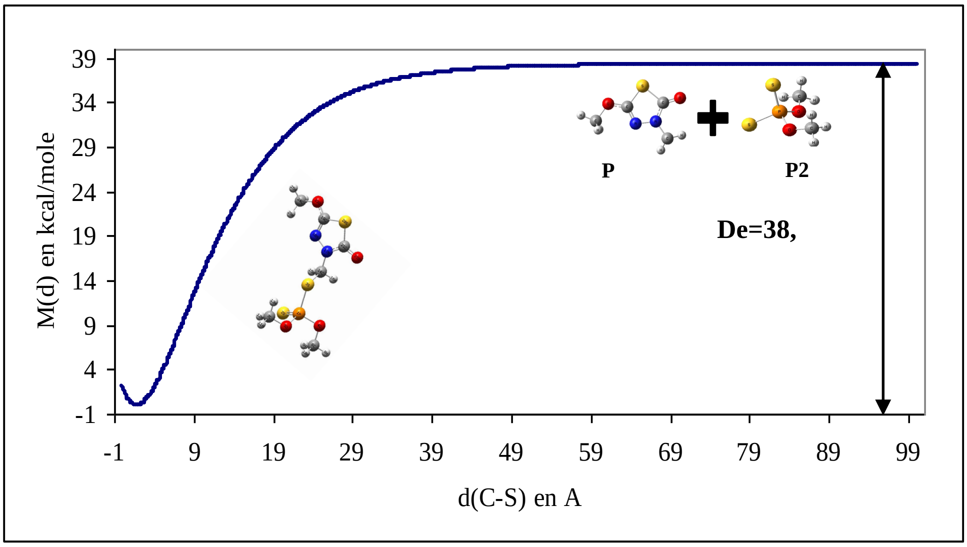

**Figure 9** Energy profiles of the reactions of dissociation Homolytic of the covalent bond $S_3$-$C_{14}$.

We distinguish a field from existence the molecule of Méthidathion it is the field where the curve in parabolic form and a field corresponding to the radicalizing area of dissociation of the molecule in two fragments noted P1 and P2 fig.10.

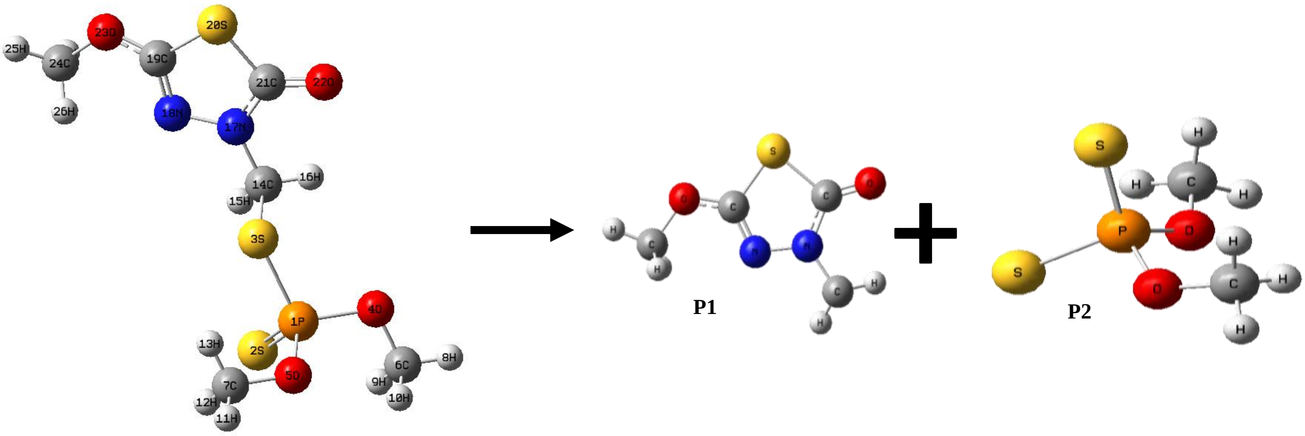

**Figure 10.** Reaction of Homolytic rupture

In the vicinity immediate of the position of equilibrium, the local behavior can be put in a parabolic form (development in Taylor series limited to the second order):

$$E_t = a + bd + cd^2 \qquad (1)$$

Where c is not other than the curve of the potential function of Morse has the following form:

$$M(d) = D_e \{1 - \exp[-\alpha(d - d_{\acute{e}q})]\}^2 \qquad (2)$$

$D_e$ translated the energy gap enters the minimum of potential energy and the asymptote.

The coefficient α of exponential is connected to the curve of the potential function in the vicinity of equilibrium and the radicalizing energy of dissociation according to the following relation:

$$\alpha = \sqrt{\frac{c}{D_e}} \qquad (3)$$

The constant of force K results easily from the relation (1); $k = \frac{\partial^2 E}{\partial d^2})_{d=d\acute{e}q} = 2c$. Thus α takes the following form: $\alpha = \sqrt{\frac{k}{2D_e}}$ (4)

Table1 gather the energy of dissociation (with 0K; 0vib), the distance from balance Déq. is taken as the optimized lengths of the distances S-C and the constant of force which is obtained starting from an adjustment on three energy total: energy corresponding to the structure of equilibrium and two energies corresponding to an elongation and a weak shortening of the central connection compared to the values of equilibrium.

By applying the relations (1), (2), (3) et (4), we deduce the curve from Morse (fig. (2)) the reaction of rupture of the molecule of Méthidathion.

**Table 2.** Energy characteristics of the molecule of Méthidathion

| De | d (Å) | k | E (a.u) | α |
|---|---|---|---|---|
| 38,3214 | $d_{\acute{e}q}$=1,84995506 | 1,038464 | $E_{\acute{e}q}$= -2175,32399 | 0,1164 |
| | $d_1$=1,74995506 | | $E_1$= -2175,31725 | |
| | $d_2$=1,94995506 | | $E_2$= -2175,32035 | |

For the reaction of homolytic rupture of the bond C-S the potential of Morse obtained is:

$$M(d(C\text{-}S)) = 38{,}3214\{ 1 - \exp[ -0{,}1164(d-1{,}84995) ]^2 \} \qquad (5)$$

## Conclusion

This work studied the efficiency of an electrochemical oxidation system for the treatment of organophosphoric pesticides. In this study, a high reduction of COD of the oxidized Methidathion was found. The results demonstrate the feasibility of the electrochemical route for the treatment (total or partial) of waste that contains Methidathion.

The influence of parameters was investigated. The oxidation was successfully achieved within 2 h for most investigated conditions. Highest rates of elimination were achieved at a temperature 25°C, 60mA and 2% of NaCl.

This electrochemical technique can be considered as very clean and very suited for treating industrial wastewaters containing pesticides.

We determined the reaction mechanism of the homolytic rupture of degradation of Méthidathion. The function of Morse established numerically makes it possible to determine the Rhythm of the curve of potential energy of this homolytic rupture.

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