

Anodic Destruction of 4-methyl Pyrimidine Solution Using a Boron-Doped Diamond Anode

M. Errami¹, R. Salghi^{1,*}, A. Zarrouk², S. S. Al-Deyab³, H. Zarrok⁴, B. Hammouti²

¹ Equipe Génie de l'Environnement et de Biotechnologie, Ecole Nationale des Sciences Appliquées, Université Ibn zohr, B.P 1136, 80000 Agadir, Morocco.

² LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, B.P. 4808, 60046 Oujda, Morocco

³ Department of Chemistry, College of Science, King Saud University, B.O. 2455, Riyadh 11451, Saudi Arabia.

⁴ Laboratoire des procédés de séparation, Faculté des Sciences, Université Ibn Tofail BP 242, 14000 Kénitra, Morocco.

*E-mail: r_salghi@yahoo.fr

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Degradation of 4-methyl pyrimidine (4MP), a refractory toxic chemical emitted to the environment from the industrial production of pyrimidine pesticide was studied in aqueous solution. This paper presents the study of the electrochemical oxidation of 4MP in alkaline media in the presence of sodium chloride, has been investigated. The process has been followed through the dependence of Chemical Oxygen Demand (COD) and by UV spectrophotometer. The influence of current density, supporting electrolytes (NaCl, NaOH, and Na₂SO₄) and temperature on the rate of COD abatement has been followed. The rate of the degradation was found to increase with increasing the current density and temperature. The best obtained conditions for COD removal on the boron-doped diamond anode (BDD) to degrade 4MP solutions (initial COD₀ = 900 mg.L⁻¹) include operating at 30 mAcm⁻² and 25 °C. The high efficiency of this technology can be explained in terms of the direct electro-oxidation at the BDD surface and the oxidation carried out by hydroxyl radicals (OH[·]) and other electro-generated oxidants (Cl[·], ClO[·]).

Keywords: Electrochemical treatment, Pesticide, Electrooxidation, 4-methyl pyrimidine.

1. INTRODUCTION

The increase in animal and vegetable production obtained by using new technologies and methods has undoubtedly raised the productivity. However, it is not possible to provide an

everlasting increase of product through the new methods and techniques implemented [1]. Even though a quantitative product increase is provided by this way, some environmental problems also appear. Chemical products implemented in soil and plants with developed agricultural applications, various wastes pollute air, soil and water resources and make them uninhabitable for a live things living on them. Pesticides come first among the inputs used to increase product amount to be obtained from unit of area. Pesticides are chemical compounds used with the aim of removing micro and macro pests in the agriculture. Use of pesticides in agricultural struggle applications appears the easiest and the cheapest method. This situation increases use of these compounds for long years [1]. The intensive use of organic compound 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.

Various innovative technologies have been proposed for the removal of pesticides from water. There are many treatment processes that have been used or investigated extensively to treat agriculture wastewaters such as biological treatment [2], photo catalytic oxidation [3], ozonation [4], Fenton's reaction [5] and electrochemical methods [6-14].

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 [15-17].

Electrochemical techniques have been proposed for the treatment of wastewater containing bio refractory and toxic organic pollutants. According to this process electro-conversion and electro-combustion reactions transform the non-biodegradable organic species, dissolved in aqueous solutions, respectively, to biodegradable organic compounds or final inorganic ones, like CO_2 and H_2O [6-7]. The advantages of electrochemical treatment are various and well documented: the catalyst/electrode is immobilized (thus reducing the need to separate the catalyst from the reaction mixture), the variables (i.e. current and potential) are easily controlled and facilitate automation of a process and the cost of the equipment is generally not that high [8].

In recent studies Salghi and co-workers studied the electrooxidation of various groups pesticides bupirimate [10,12-14]; methidathion [11,12] in brine solution using BDD and SnO_2 anodes. The authors studied the electrooxidation of various organic compound by Bonfatti and co-workers, organic substrates [21]; 4-chlorophenol [22]; 1, 2-dichloroethane [23].

The nitrogenous heterocyclic compounds, such as 4-methyl pyrimidine (4MP) (fig.1) are frequently found in surface and groundwater sources in the Europe and other parts of the world. 4MP presence in the environment is due to their widespread use as solvents and pesticide, paint stripping, in the dry cleaning industry and in various household products.

In this work the results concerning essays about the oxidation of 4MP by BDD anode are presented in order to demonstrate the possibilities of this method to remove pyrimidine compound from waters.

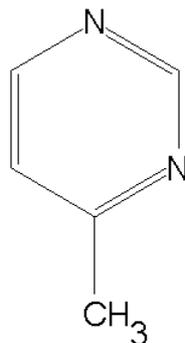


Figure 1. Chemical structure of 4-methyl pyrimidine. (4MP)

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 cm³) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of BDD electrode with effective surface area of 1 cm², 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 cm³ aqueous solution of initial COD₀ (900 mg/L). The range of applied current density was 10 to 30 mA/cm² c 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 [12]. The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method.

The UV–Vis spectra of 4MP were recorded in 200–400 nm range using a UV–Vis spectrophotometer (UV-1700 Pharmaspec, Shimadzu) with a spectrometric quartz cell (1 cm path length). 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).

All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

3. RESULTS AND DISCUSSION

3.1. Effect of supporting electrolytes

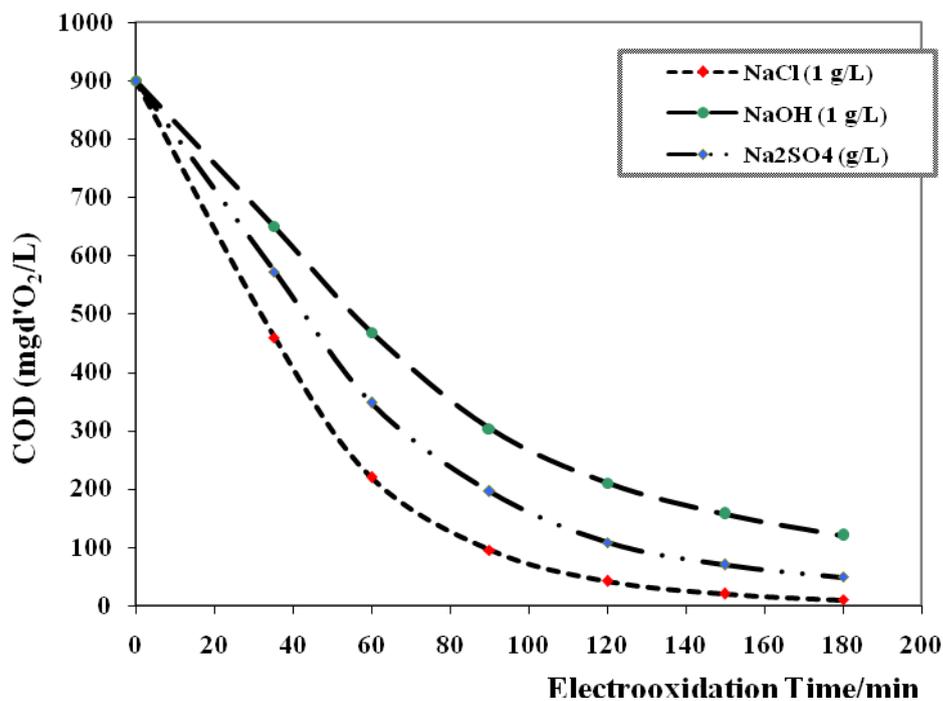


Figure 2. Influence of supporting electrolytes on the decay of COD during electro-oxidation of 900mg/L 4-methyl pyrimidine on BDD anode. Conditions: Current density 30 A.cm⁻²; T: 25°C.

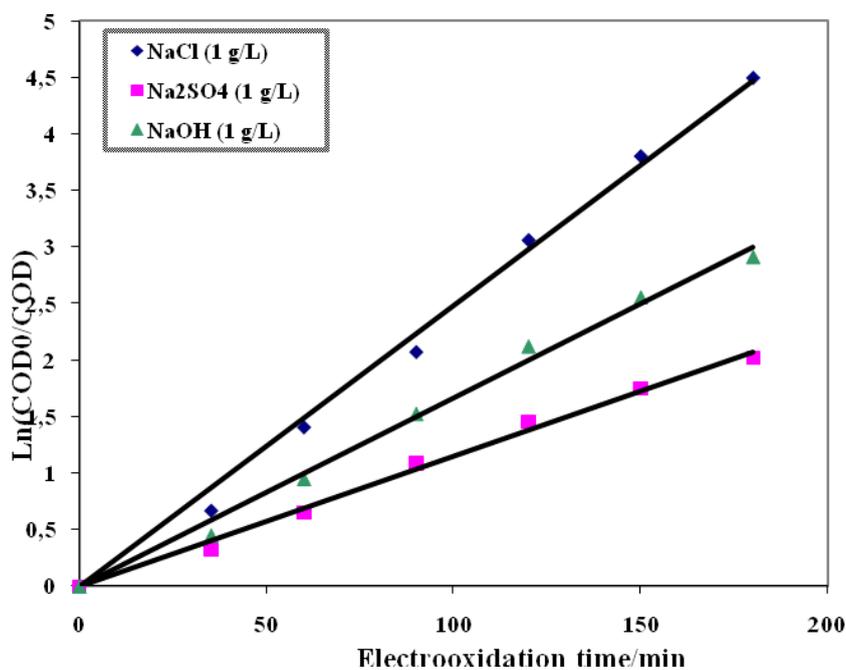


Figure 3. Pseudo first-order plot oxidation of 4MP (COD₀ = 900 mg/L) in different electrolytes at 30 mA.cm⁻².

Electrolytes of 1 g.L^{-1} of the following salts: NaCl, NaOH, 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 electrocatalytic degradation of the investigated 4MP and COD removal while Na_2SO_4 and NaOH electrolytes show poor results. The operating conditions of the treatment process were: current density of 30 mA cm^{-2} , pH (8.4), temperature of $(25 \pm 3) \text{ }^\circ\text{C}$, initial concentration COD (900 mg.L^{-1}), and the distance between the two electrodes was 0.5 cm.

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation 4MP at different supporting electrolytes. For this purpose, the removal rate of COD was assumed to obey a first order kinetic as follows [24]. Fig. 3 represents the Kinetic studies of the different supporting electrolyte in a 1 g.L^{-1} NaCl, (1 g.L^{-1}) NaOH, (1 g.L^{-1}) Na_2SO_4 solution in the presence of 900 mg.L^{-1} of 4-methyle pyrimidine. The values of rate constant for different supporting electrolyte concentration are summarized in table 1.

It was disclosed above that in the Na_2SO_4 medium BDD was more suitable for electrochemical incineration of 4MP than NaOH. In The presence of a less concentration of chloride ions (1 g/L of NaCl) allows inhibiting the water discharge into oxygen, and promotes hydroxyl, chloride, and oxychloride radical's formation [22].

Therefore, in the present work, the degradation of 4MP was investigated in three systems of mixture supporting electrolyte: (1 g.L^{-1} NaOH + 1 g.L^{-1} NaCl), (1 g.L^{-1} NaOH + 1 g.L^{-1} Na_2SO_4) and (1 g.L^{-1} Na_2SO_4 + 1 g.L^{-1} NaCl).

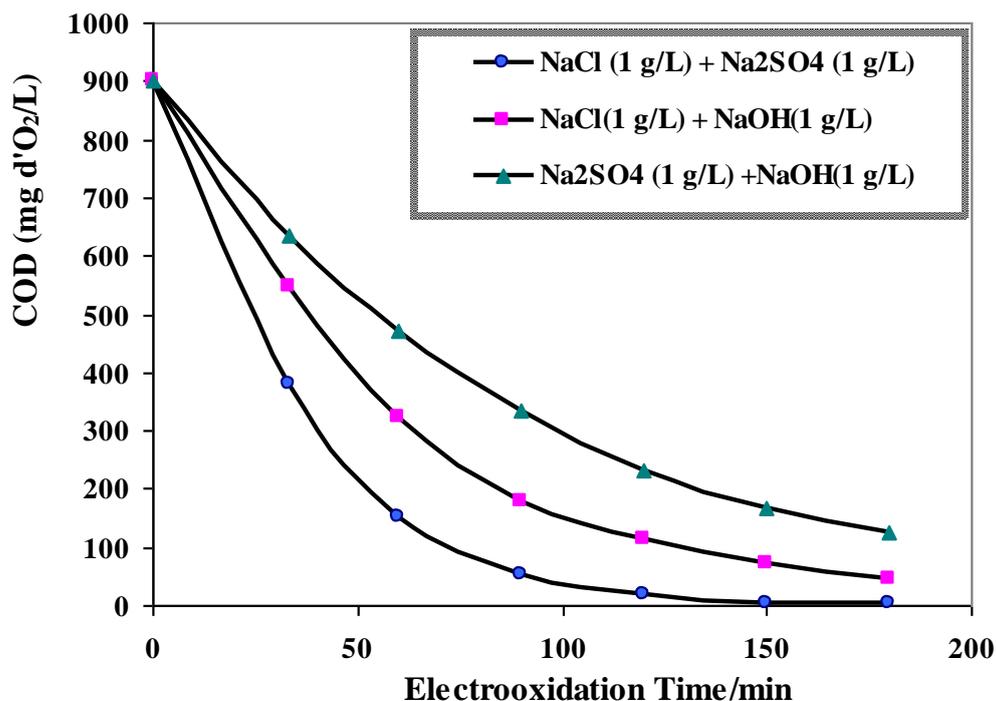


Figure 4. Influence of supporting electrolytes on the decay of COD during electro-oxidation of ($\text{COD}_0 = 900 \text{ mg/L}$) 4MP on BDD anode. Conditions: Current density 30 mA.cm^{-2} ; T: 25°C .

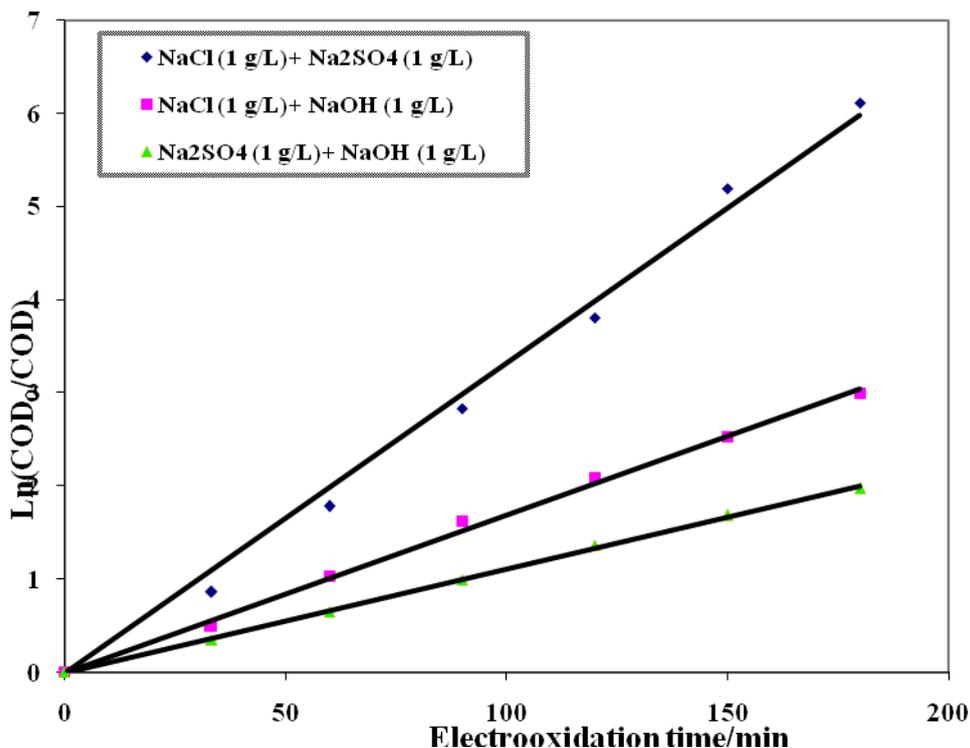


Figure 5. Pseudo first-order plot oxidation of 4MP ($COD_0 = 900 \text{ mg/L}$) in different electrolytes at $30 \text{ mA}\cdot\text{cm}^{-2}$.

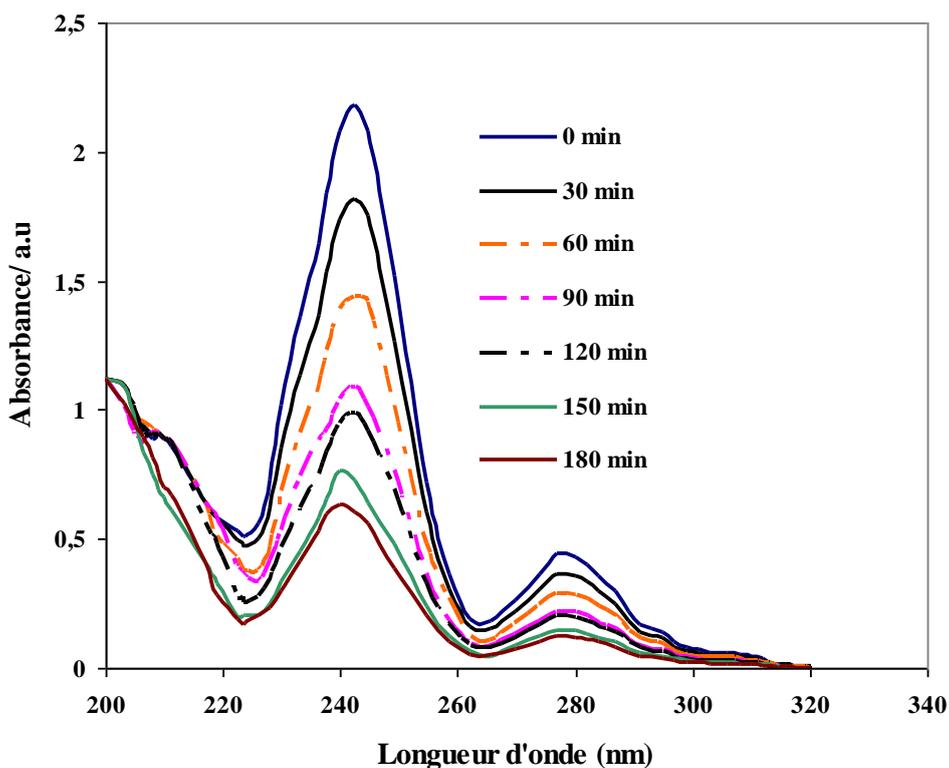


Figure 6. Effect of initial temperature on the variations of UV spectra for 3 h of the electrooxidation assays performed at a BDD anode (Operating conditions: electrolyte ($1 \text{ g}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4 + 1 \text{ g}\cdot\text{L}^{-1} \text{ NaCl}$), 4MP initial COD concentration = 900 mg/L , current density = $30 \text{ mA}\cdot\text{cm}^{-2}$).

The absorbance spectral changes during galvanostatic electrolysis in aqueous solution are shown in figures 6. It can be observed that the absorption spectrum of 4MP is characterized by a band in the UV region with its maxima located at 245 nm and by a band in region located at 290 nm.

The absorption spectral changes during galvanostatic electrolysis (30 mA cm^{-2}) in aqueous ($1 \text{ g.L}^{-1} \text{ Na}_2\text{SO}_4 + 1 \text{ g.L}^{-1} \text{ NaCl}$) solution are shown in figures 6. It can be observed that the absorption spectrum of 4MP is characterized by a band in the UV region with its maxima located at 245 nm and by a band in the visible region located at 290 nm. It is observed that the absorption of the bands decreases with time and almost disappears after about 200 min resulting in the complete degradation of the solution. The absorbance at 290 nm decreases rather slowly. The slower decrease of this absorbance can be related to the formation of intermediates resulting from the electrooxidation of the 4MP.

Table 1 Kinetic rate constants of 4MP removal fitted by a first order model and %COD for BDD anode under different electrolytes.

Supporting electrolytes	Rate constant, K (min^{-1})	% COD
NaCl (1 g/L)	$(24.8 \pm 4.0) \times 10^{-3}$	92%
Na_2SO_4 (1 g/L)	$(16.7 \pm 5.0) \times 10^{-3}$	86%
NaOH (1 g/L)	$(11.5 \pm 3.2) \times 10^{-3}$	77%
NaOH (1 g/L) + NaCl (1 g/L)	$(11.8 \pm 4.2) \times 10^{-3}$	74%
NaOH (1 g/L) + Na_2SO_4 (1 g/L)	$(16.9 \pm 2.0) \times 10^{-3}$	84%
NaCl (1 g/L) + Na_2SO_4 (1 g/L)	$(33.2 \pm 1.4) \times 10^{-3}$	99%

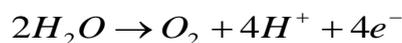
3.2. Effect of current density

The role of current density has been followed, testing values smaller than the previously considered as the optimum [12, 28]. The influence of the current density on the COD removal during the electrochemical oxidation of 4-methyl pyrimidine at the anode is shown in Fig. 7.

As expected, the COD abatement is faster as the current density is greater, but the results are a logical

consequence of the major quantity of charge passing in solution. On the other hand, the application of the highest current density can be suggested in order to obtain the complete abatement of the organic content in the smallest time; obviously, the efficiency of the oxygen evolution reaction is larger at higher current densities.

After 3h time of electrolysis, the COD percent removal increased from 80% to 96% when the current density increased from 10 to 30 mA.cm^{-2} . This behavior indicates that in these experimental conditions, the oxidation of 4MP is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution [30]:



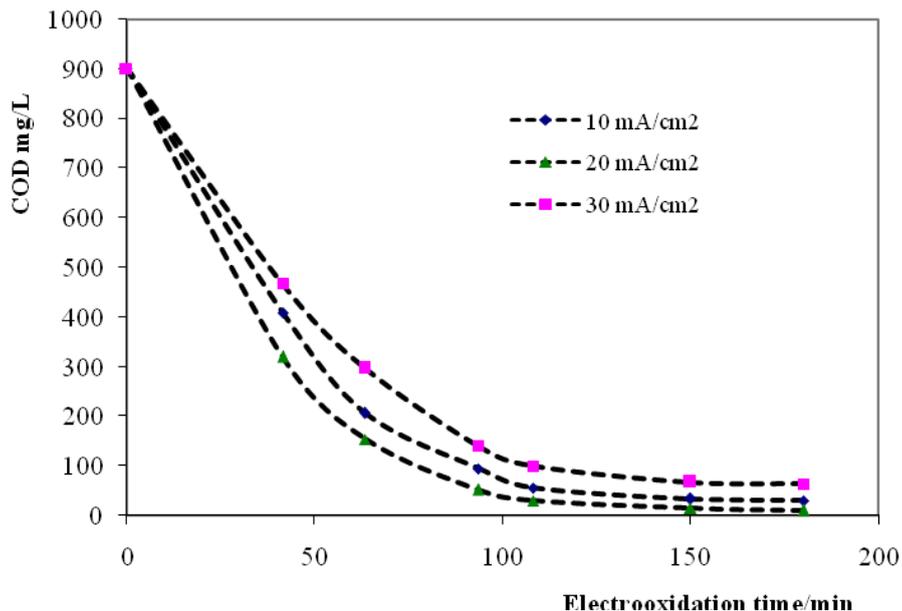


Figure 7. Influence of the applied current density on the trends of % COD electrolysis of 4MP (COD₀ = 900 mgL⁻¹) using a 1cm² BDD anode. pH=8.4 and T=25°C.

This was confirmed by the fact that the COD (mg/L of O₂) decreased with the current density. The decay of COD concentration exhibits an exponential behavior with all the applied current indicating a first-order reaction kinetics for the oxidation reaction. 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 [12, 26, 29]:

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

which can be integrated to give the following expression:

$$\ln\left(\frac{COD_0}{COD_t}\right) = K_{app}t$$

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

Current intensity (mA)	Constant, K (min ⁻¹)	COD removal (%)
10	(11.2 ± 1.8) × 10 ⁻³	77%
20	(2.42 ± 2) × 10 ⁻³	86%
30	(33.2 ± 1.4) × 10 ⁻³	99%

where COD_0 and COD_t are the COD of the solution at the beginning and at time t respectively, and k_{app} is the apparent observed pseudo first-order rate constant. Apparent rate constants determined by plotting the $\ln(COD_0/COD_t)$ against time at different applied current (Table 2).

3.3. Effect of temperature on the degradation efficiency

Like other electrochemical reactions, temperature could have a significant effect on the rate of COD removal. Therefore, experiments were conducted at different temperatures of 25, 35, 45 and 55 °C. Figure 8 shows the effect of temperature on the variation of % COD during the electrolysis of $COD_0 = 900$ mg/L 4MP at 30 mA cm^{-2} and 1g/L NaCl.

The results of UV-spectra of 4MP at different temperature after 180 min of electrooxidation time are shown in Fig. 10. As can be seen that at the temperature 55°C after 180 min of treatment, the UV-spectrum changed greatly and had a weak absorbance at 290 nm. The absorbances at 245 nm also decreased much. This results confirmed that obtained with COD removal for 4MP under different temperature.

The increase of the COD removal with increasing reaction temperature suggests a strong temperature dependence on the electrochemical reaction[12]. The influence of temperature on the rates of COD removal was modeled using the Arrhenius equation (Fig. 11) [22]. From the data shown in Fig. 11, the activation energy for the degradation reaction is 7.31 J mol^{-1} .

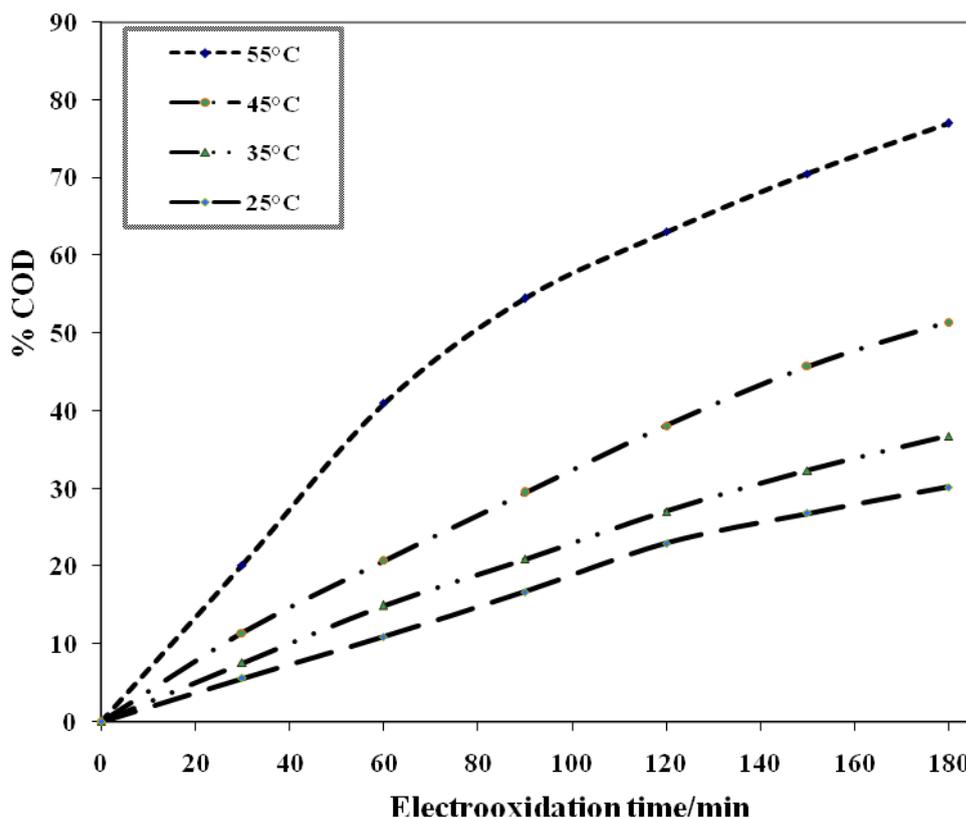


Figure 9. Influence of temperature on the decay of %COD during electro-oxidation of 4MP on BDD anode. Conditions: current density 30 mA cm^{-2} ; pH=8.4, 1g/L NaCl

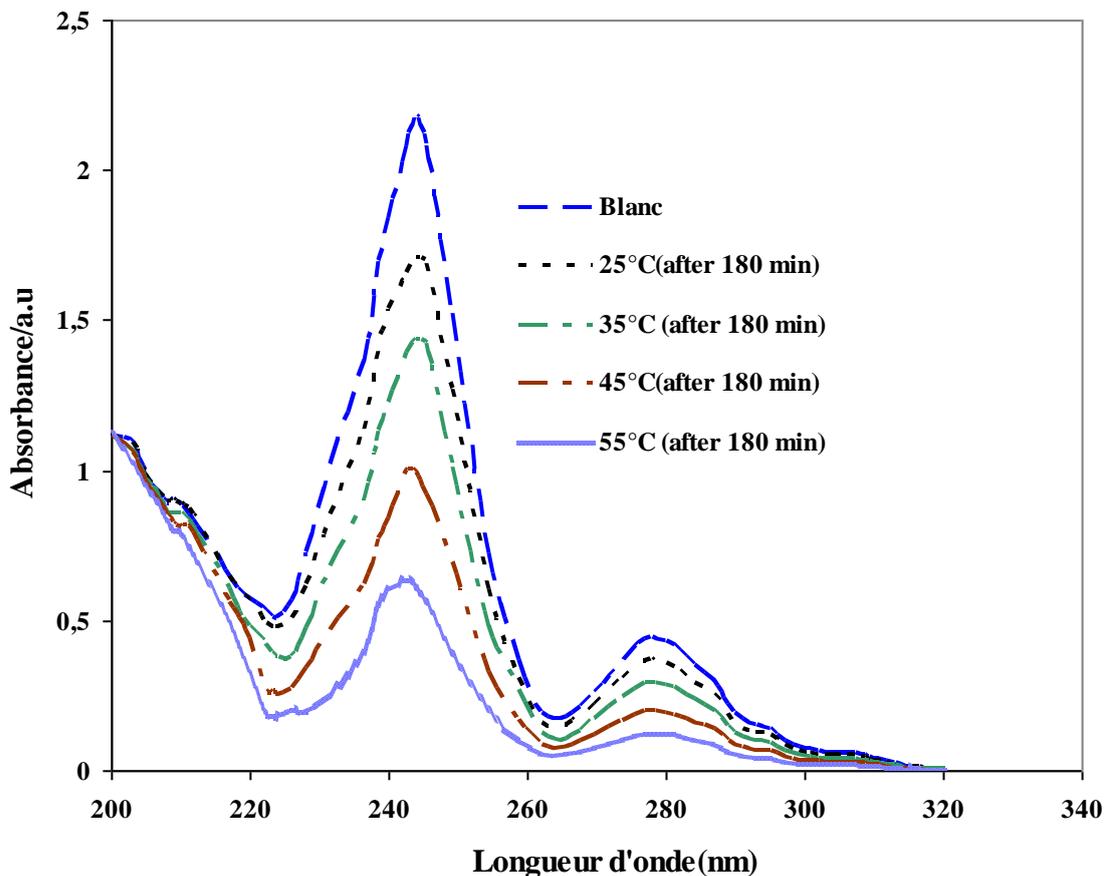


Figure 10. UV visible spectral changes of 4MP in aqueous with time during the galvanostatic electrolysis (30 mA cm^{-2}), 1 g/L NaCl under effect of temperature.

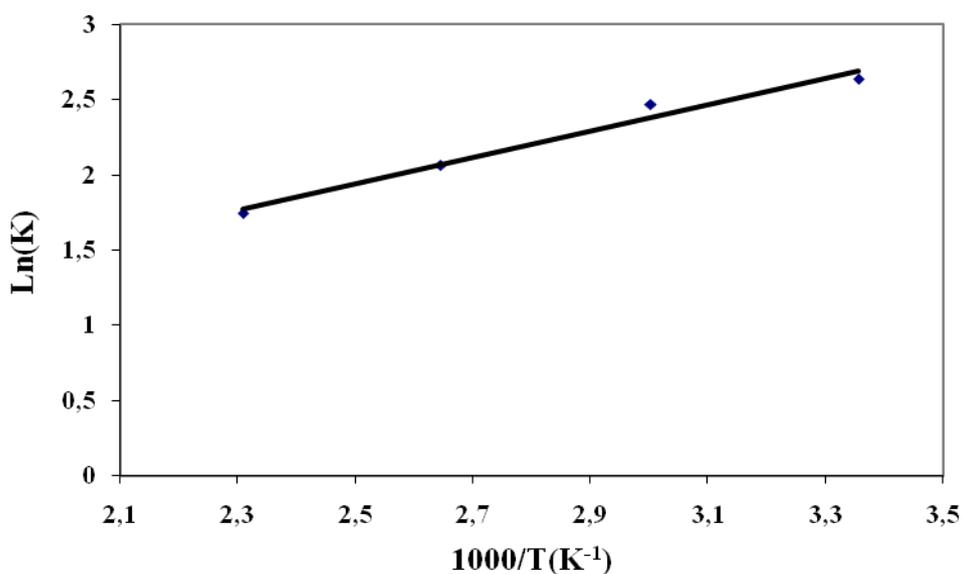


Figure. 11. Arrhenius plots for the COD removal process during electrolysis of 4MP at different reaction temperatures.

4. CONCLUSION

This work is a first attempt to investigate the degradation of 4-methyl pyrimidine in electrochemical treatment. The electrochemical degradation of 4-methyl pyrimidine has been investigated using BDD anode under all conditions tested involving, effect of different supporting electrolyte, applied current density from 10 to 30 mA cm⁻², and temperature varying from 25 to 55 °C. The experimental results allowed us to draw the following conclusions:

- The best results were obtained when electrolyses were carried out at high densities, 30 mAcm⁻², and in the presence of mixture supporting electrolyte NaCl (1g/L) with Na₂SO₄ (1g/L).
- The removal rate of COD increases with applied current density until 30 mAcm⁻² due to the increase of the mass transport caused by oxygen evolution reaction, but decreases for higher values due to the improvement of this reaction.
- The reaction temperature affected the COD removal rates, which was modeled using the Arrhenius equation. The activation energy for the degradation reaction was determined to be 7.3 J mol⁻¹.

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