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## DEGRADATION OF CHLOROTHIAZIDE IN ACIDIC AQUEOUS SOLUTION BY ELECTRO-FENTON PROCESS

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### Abstract

The aim of this study is the treatment of Chlorothiazide in an aqueous medium by Electro-Fenton process using a Platinum anode. This pharmaceutical product is used to treat hypertension. Removal rates and mineralization efficiency have been analyzed under different operational conditions. Degradation kinetics well fitted to a pseudo-first-order reaction. Apparent rate constant of the oxidation of Chlorothiazide by electrochemically generated hydroxyl radicals was determined to be  $9.49 \times 10^{-2} \text{ min}^{-1}$  at a temperature of 25°C. Chlorothiazide mineralization in an aqueous solution was followed by the analysis of chemical oxygen demand (COD), the degree of mineralization of 93% was achieved after 7 hours of electrolysis.

*Key words:* Activation energy, Chlorothiazide degradation, Electro-Fenton process

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### 1. Introduction

The aquatic pollution caused by chemicals and pharmaceuticals contained in wastewater is mainly due to a lack or failure of treatment systems. These pollutants tend to accumulate in the aquatic environment and thus contribute to the deterioration of the water ecosystems quality even at low concentrations (Baronti et al., 2000; Gomez et al., 2007; Yu and Chu, 2009). Chlorothiazide (Fig. 1) is a diuretic used within the hospital setting or for personal use to manage excess fluid associated with congestive heart failure. It is commonly used to treat hypertension (Al-Odaini et al., 2010).

After consuming, the substance is metabolized in the liver and its shape is excreted non-metabolized in urine or stool, and eventually discharged into the conventional urban wastewater treatment. The rising concerns about pharmaceuticals in recent years are

due to the fact that these substances are continuously introduced into the environment which can consequently arouse resistance against these products (Najat et al., 2013; Patrick, 2006). In fact, many diseases would be more difficult to treat and would have implications in terms of morbidity and economic cost. Therefore, it is urgent to develop low cost treatment systems for their removal.

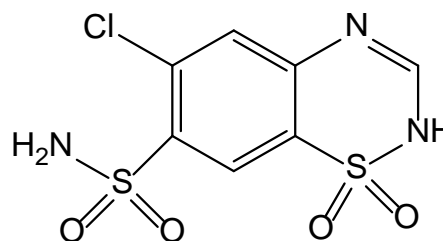
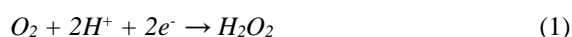


Fig. 1. Structure of Chlorothiazide

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Lodha and Chaudhari (2007) developed biological treatment processes which were considered cheaper, but these systems are insufficient for the degradation of products with complex pharmaceutical structures. Recently, new oxidation processes appeared such as the advanced oxidation processes (AOP) (Eslami et al., 2016; Mansour et al., 2012; Oturan et al., 2001; Trabelsi et al., 2009). These technologies are based on the production of hydroxyl radicals; highly reactive species have proved the effectiveness of the treatment of toxic organic pollutants, which promote the degradation of persistent organic pollutants. Among these advanced oxidation processes: photo-Fenton (Abdesslem et al., 2010), H<sub>2</sub>O<sub>2</sub>/ozonation UV (Karkare and Murthy, 2016; Shu and Chang, 2005) and the high voltage electrical discharge (corona plasma) (El-Aragi, 2008; Trifi et al., 2012). In the electro-Fenton process, hydroxyl radicals, known as the oxidizing species, are obtained from the combination of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> named "Fenton's reagent" according to the reactions (1-3). The process is based on the electrogeneration of hydrogen peroxide in aqueous solution by two-electron reduction of dissolved oxygen (Eq. 1):



The generated H<sub>2</sub>O<sub>2</sub> reacts with the externally added Fe<sup>2+</sup> ions to produce hydroxyl radicals ( $\cdot OH$ ) and Fe<sup>3+</sup> ions according to the classical Fenton's reaction (Eq. 2):



Ferrous ions consumed by Fenton's (Eq. 2) are generated electrochemically at the cathode (Eq. 3):



This system allows continuous regeneration of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> at the cathode according to the reactions (1) and (3), thus allowing control of the formation of hydroxyl radicals according to reaction (2). Hydroxyl radicals formed are effective for a wide variety of organic substances such as dyes, pesticides, polycyclic aromatic pharmaceuticals. They have many advantages in the treatment of organic compounds. They react very quickly with organic compounds, leading to the mineralization, where the final products are H<sub>2</sub>O, CO<sub>2</sub>, inorganic ions. In addition they are easy to handle and environmentally safe.

Thus, the objective of this study is to investigate the degradation and mineralization of Chlorothiazide by electro-Fenton process in aqueous solutions at different temperatures (25°C, 35°C, 40°C and 50°C) and to determine their corresponding activation energies. The present work reports the total mineralization of the title compound using Pt as the anode. The effectiveness of electro-Fenton process to degrade Chlorothiazide with this type of anode was assessed by the analysis of chemical oxygen demand (COD) during electrolysis. The ions formed at the end

of the electrolysis were identified and their evolution was followed by ion chromatography.

## 2. Materials and methods

### 2.1. Chemicals

Chlorothiazide (6-chloro-2H-benzo [1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide) (Fig. 1) was provided by Sigma-Aldrich. FeSO<sub>4</sub>·7H<sub>2</sub>O (purity 97%) and Na<sub>2</sub>SO<sub>4</sub> (99% purity) were obtained from Prolabo. MgSO<sub>4</sub>·7H<sub>2</sub>O and CuSO<sub>4</sub> (purity 97%) were supplied by Across. HPLC analysis were carried out in a C18 column using a mobile phase of 95/5% v/v phosphate buffer (0.05 M) – methanol. The flow rate was fixed to 1 mL/min and the detection wavelength was fixed at 254 nm (European Pharmacopoeia 7.0).

### 2.2. Electrochemical apparatus and procedure

All solutions were prepared with distilled water. The electrolysis were performed at room temperature in a 250mL undivided cylindrical glass cell of diameter intern of 6 cm equipped with two electrodes. The carbon felt piece of 80cm<sup>2</sup> (Carbone Lorraine RVG 4000 Mersen, Paris La Défense, France) was used as a cathode. It was placed on the inner wall of the cell covering the totality of the internal perimeter. The counter electrode was a 0.5 cm<sup>2</sup> sheet of Pt placed on the centre of the cell.

The initial pH of the solutions, measured with a Mettler Toledo EL20 pH-meter (USA), was adjusted to 3 by Sulphuric Acid. Prior to the electrolysis, a moderate compressed air is bubbled for 10 min through the cell to saturate the solution, which was agitated continuously by a magnetic stirrer. FeSO<sub>4</sub>·7H<sub>2</sub>O, CuSO<sub>4</sub> and MgSO<sub>4</sub>·7H<sub>2</sub>O were introduced to the cell just before the beginning of the electrolysis. Electrolysis were carried out under current controlled conditions. The current was kept at the desired level with an Amel 2053 (Italy) potentiostat-galvanostat and samples were withdrawn at regular electrolysis times. The ionic strength was maintained constant by additions of 50 mM Na<sub>2</sub>SO<sub>4</sub>. The thermostatic bath we used in this work is RM20 LAUDA (USA).

### 2.3. Analytical methods

The evolution of Chlorothiazide concentration was detected using Thermo Separation Products (TSP) High Performance Liquid Chromatography (HPLC) (USA) using Spectra system (P1000), equipped with an isocratic pump and UV/Visible detector model Spectra series UV100, fitted with reversed phase C-18 analytical column (Agilent, 5 μm; 4.6 mm × 250 mm).

The ion chromatography instrument we used in this work is 761 Compact IC (Switzerland) (a Metrosep Anion Dual 2 (6.1005.300), a Metrosep Cation column (6.1010.000)). The device is equipped with a conductivity detector.

The mineralization degree of initial and electrolyzed samples was monitored by the abatement of their COD content. COD measurements were taken at every 1h of electrolysis, by sampling 2 cm<sup>3</sup> of the electrolyzed solution. Then, aliquots of an acidic solution (1 cm<sup>3</sup>) containing K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and HgSO<sub>4</sub> were added to the electrolyzed samples followed by the addition (3 cm<sup>3</sup>) of concentrated H<sub>2</sub>SO<sub>4</sub> containing AgSO<sub>4</sub>. These solutions were heated at 150 °C for 2h in a COD block reactor to completely oxidize the remaining organic matter. Finally, the COD value was monitored using HANNA photometer COD (Italy).

### 3. Results and discussion

#### 3.1. Effect of current variation on Chlorothiazide degradation

Among a different operating parameter affecting the efficiency of the electro-fenton process the most important is the applied current intensity. The study of the kinetics of degradation was performed at room temperature in dilute acid solutions at pH = 3. Several experiments were performed on aqueous solutions of Chlorothiazide (0.5 mM) at different current values, in range of 100 to 300 mA in the presence of 0.2 mM of Fe<sup>2+</sup> as a catalyst and 50 mM Na<sub>2</sub>SO<sub>4</sub> as an inert support electrolyte. The results of the Chlorothiazide degradation obtained are illustrated in Fig 2. The kinetic curves were characterized by a decrease from a steady decline and relatively rapid exponential concentration with time of electrolysis. It was found that the degradation rate increased significantly with the increasing current.

The observed results can be explained by the increasing of the production rate of H<sub>2</sub>O<sub>2</sub> and the regeneration of Fe<sup>3+</sup> which lead to accelerating the formation of hydroxyl radicals on the anode surface and thus increasing the rate of Chlorothiazide degradation.

#### 3.2. Effect of activator variation on Chlorothiazide degradation

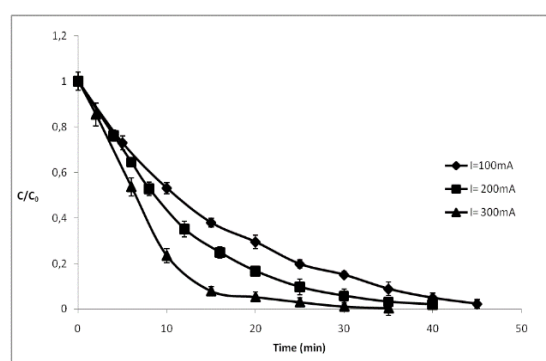
The influence of various catalysis (Fe<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>) on the kinetics of Chlorothiazide degradation during the electro-Fenton process was investigated. Experiments were performed at room temperature in a dilute acid medium (pH = 3) in which we have introduced the active ingredient (concentration = 0.5mM) and 50 mM Na<sub>2</sub>SO<sub>4</sub> for a current = 200 mA. The decay of the initial concentration of Chlorothiazide was followed by HPLC.

As shown in Fig 3, the curves of the degradation obtained with an electro-Fenton with a Pt anode using Fe<sup>2+</sup>, Cu<sup>2+</sup> and Mg<sup>2+</sup> catalysis (concentrations = 0.2mM) were characterized by a steady decline and relatively rapid decrease of Chlorothiazide concentration with Fe<sup>2+</sup> more than Cu<sup>2+</sup> that Mg<sup>2+</sup>. This can be explained by the higher oxidative potential of Fe<sup>3+</sup>/Fe<sup>2+</sup> (E<sub>0</sub> = 0.77 V /SHE) compared to Cu<sup>2+</sup>/Cu<sup>+</sup> (E<sub>0</sub> = 0.16 V/SHE) and consequently, low production of hydroxyl radicals

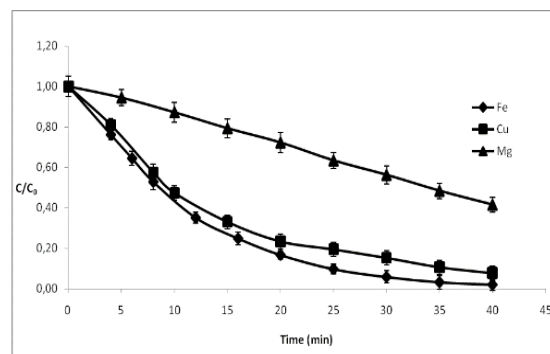
from Fenton reaction between the generated Cu<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>.

#### 3.3. Kinetics of Chlorothiazide degradation by hydroxyl radicals

The Electro-Fenton degradation process with hydroxyl radicals generated with the conditions described above (current intensity of 200 mA, concentration of Chlorothiazide 0.5 mM, concentration of Fe<sup>3+</sup> 0.2 mM and a concentration of 0.05 M Na<sub>2</sub>SO<sub>4</sub> at pH = 3), shows the complete disappearance of Chlorothiazide after 40 minutes. Fig 2 shows also that the decay of Chlorothiazide concentration in function of the electrolysis time is exponential indicating that the oxidation reaction obeys with pseudo-first-order kinetics.



**Fig. 2.** Effect of the current intensity on the degradation kinetics of Chlorothiazide by the electro-Fenton process. Experimental conditions: [Chlorothiazide] = 0.5mM, [Fe<sup>2+</sup>]=0.2 mM, pH=3.0, T= 25°C, [Na<sub>2</sub>SO<sub>4</sub>]=50 mM, V=250 mL



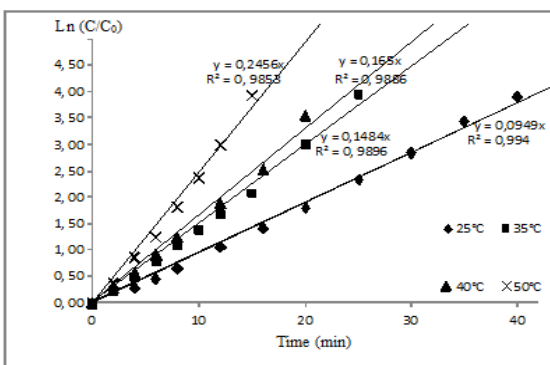
**Fig. 3.** Effect of the catalysts on the degradation kinetics of Chlorothiazide by the electro-Fenton process. Experimental conditions: [Chlorothiazide] = 0.5mM, I= 200 mA, [Fe<sup>2+</sup>] =0.2 mM; [Cu<sup>2+</sup>] = 0.2mM; [Mg<sup>2+</sup>] = 0.2mM, pH =3.0, [Na<sub>2</sub>SO<sub>4</sub>]=50 mM, T=25°C, V=250 mL

In fact, the reaction of Chlorothiazide with hydroxyl radicals can be described by pseudo-first-order kinetics. Moreover, in the electro-Fenton process, the •OH formation rate is controlled by electrical current applied to the cathode during electrolysis and the O<sub>2</sub> concentration in the solution. The current and O<sub>2</sub> concentration being kept constant during electro-Fenton process, the •OH production rate is also kept constant (Eq. 4).

$$V = -\frac{d[\text{Chlorothiazide}]}{dt} = k_{\text{abs}(\text{Chlorothiazide})} [\text{OH}^-] [\text{Chlorothiazide}] = k_{\text{app}} [\text{Chlorothiazide}] \tag{4}$$

where:  $k_{\text{app}} = k [\text{OH}^-]$ ;  $k$  is the absolute rate constant ( $\text{L mol}^{-1}\text{s}^{-1}$ ).

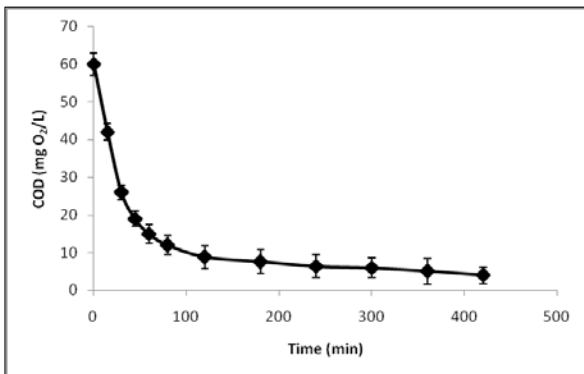
Assuming a first-order kinetics for the Chlorothiazide degradation, the apparent rate constant were determined analytically from the plot slope of concentration versus time in accordance with the  $\text{Ln}(C/C_0) = k_{\text{app}}t$ . The degradation rate constant  $k_{\text{app}}$  was calculated from the linear regression model of pseudo-first-order kinetics (Fig. 4) with coefficients higher than 0.98 and the apparent constant is  $9.49 \times 10^{-2} \text{ min}^{-1}$  at  $25^\circ\text{C}$ .



**Fig. 4.** Plots of  $\text{Ln}(C/C_0)$  versus time at different temperatures. Experimental conditions:  $[\text{Chlorothiazide}] = 0.5\text{mM}$ ,  $I = 200 \text{ mA}$ ,  $[\text{Fe}^{2+}] = 0.2 \text{ mM}$ ,  $\text{pH} = 3.0$ ,  $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$ ,  $V = 250 \text{ mL}$

### 3.4. Chemical analyses by Chemical Oxygen Demand

Chemical analyses were performed by the chemical oxygen demand during electrolysis of Chlorothiazide to show the effectiveness of the mineralization by using electro-Fenton process. Fig 5 shows the reduction in COD with time spent during the electro-Fenton process for Chlorothiazide under the conditions described in the experimental section.



**Fig. 5.** Chemical oxygen demand (COD) evolution of Chlorothiazide solution ( $[\text{Chlorothiazide}] = 0.5\text{mM}$ ) during the electro-Fenton process. Experimental conditions:  $I =$

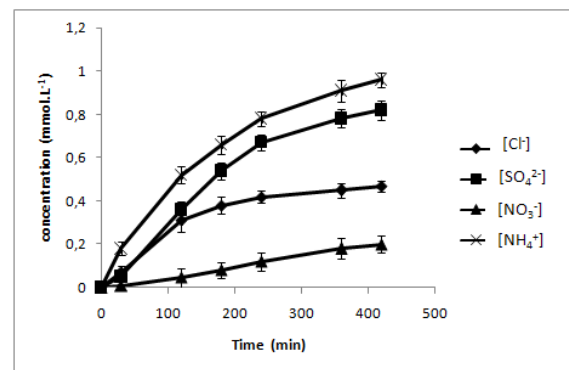
$200 \text{ mA}$ ,  $[\text{Fe}^{2+}] = 0.2 \text{ mM}$ ,  $\text{pH} = 3.0$ ,  $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$ ,  $V = 250 \text{ mL}$ ,  $T = 25^\circ\text{C}$

The COD of the solution decreased regularly slightly faster at the beginning of electrolysis. For Chlorothiazide, the yield of mineralization is 93% after 7 hours of electrolysis at  $25^\circ\text{C}$ .

Fig 5 shows the decrease of COD represented by the weakening of the slope which can be explained by the transformation of aromatic groups in aliphatic hydrocarbons by ring-opening reactions. This hypothesis has also been reported by Oturan et al. (2000). Due to the inactivation of electrophilic attack centers, aliphatic molecules have a lower reactivity towards hydroxyl radicals as aromatic structures (Oturan et al., 2008).

### 3.5. Identification and monitoring of inorganic ions

Previous studies (Stylidi et al., 2003; Stylidi et al., 2004; Tanaka et al., 2000) showed that the mineralization of organic molecules, contains nitrogen and sulfur leads to their conversion to carbon dioxide, water and  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Thus, the release of inorganic ions such as nitrate, ammonium, chloride and sulfate was followed by ion chromatography. The evolution of these ions during the mineralization of Chlorothiazide solution in the optimal conditions was shown in Fig 6. Four ions started to be formed at the beginning of electrolysis.



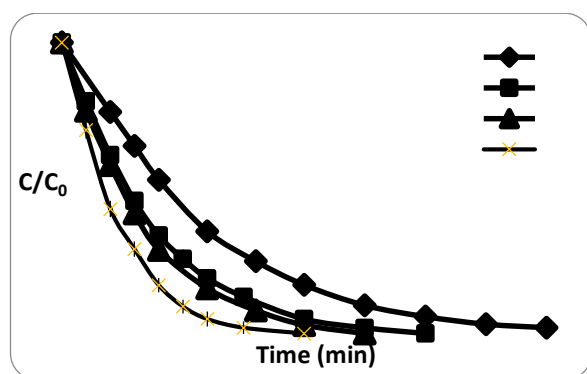
**Fig. 6.** Evolution of inorganic ion concentration formed during the treatment on the degradation kinetics of Chlorothiazide by the electro-Fenton process. Experimental conditions:  $[\text{Chlorothiazide}] = 0.5\text{mM}$ ,  $I = 200 \text{ mA}$ ,  $[\text{Fe}^{2+}] = 0.2 \text{ mM}$ ,  $\text{pH} = 3.0$ ,  $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$ ,  $V = 250 \text{ mL}$ ,  $T = 25^\circ\text{C}$

As it can be seen, the release of  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  was relatively slower than that of  $\text{NH}_4^+$  ions. This phenomenon was observed in many previous works (Chun et al., 2001; Flox et al., 2006; Vautier et al., 2001). The Total balance of nitrogen

mineralization at the end is 94% of the theoretical total nitrogen value, which is in agreement well with the rate of mineralization obtained (93% of the COD). This can be attributed to the mass conservation and the loss of nitrogen by formation of volatile compounds such as  $N_2$  or  $NO_2$  that were detected in other studies (Stylidi et al., 2004). Moreover, Fig 6 shows the importance of sulfate ions release at the beginning of electrolysis. This leads to the suggestion that the rapid attack of sulphonated molecules done by hydroxyl radicals. This result is proved in other works dealing with the deterioration by hydroxyl radicals of various organic molecules (Diagne et al., 2007; Hammami et al., 2007). At the end of the treatment period a percentage of 81.5% was obtained with regards to the theoretical  $SO_4^{2-}$  concentration of sulfur in the initial solution.

### 3.6. Effect of temperature on the Chlorothiazide degradation: the apparent activation energy

The reaction rate depends on a number of factors such as temperature. For this reason we investigated in this work the effect of temperature on the Chlorothiazide degradation at 25°C, 35°C, 40°C and 50°C (Fig. 7).



**Fig. 7.** Effect of the temperature on the degradation of Chlorothiazide by the electro-Fenton process. Experimental conditions: [Chlorothiazide] = 0.5mM, I= 200 mA.  $[Fe^{2+}] = 0.2$  mM, pH =3.0,  $[Na_2SO_4] = 50$  mM, V=250 mL

Indeed, the degradation efficiency of Chlorothiazide increases with temperature. The apparent kinetic constants ( $K_{app}$ ), degradation of Chlorothiazide, obtained at 25°C, 35°C, 40°C and 50°C (Fig.7), were gathered in Table 1.

**Table 1.** Values of  $k_{app}$  of chlorothiazide degradation at different temperatures in the following electrolysis conditions:  $[Chlorothiazide]_0 = 0.5$  mM,  $[Fe^{2+}] = 0.1$  mM,  $[Na_2SO_4] = 50$  mM, I= 200 mA, pH=3, V=250mL

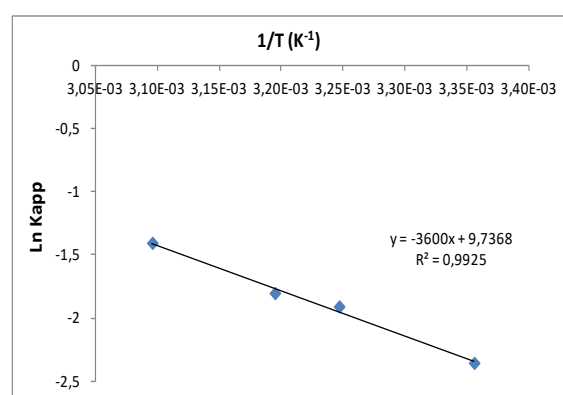
T (K)	$K_{app}$ ( $min^{-1}$ )	$R^2$
298	0.0949	0.994
308	0.1485	0.989
313	0.1650	0.988
323	0.2456	0.985

According to the apparent kinetic constants at different temperatures, the apparent activation energy for the Chlorothiazide degradation by electro-Fenton process was calculated with the Arrhenius law according to (Eq. 5):

$$k_{app} = A e^{\frac{-E_a}{RT}} \quad (5)$$

where: A is the frequency factor (constant);  $E_a$  is the activation energy ( $J \cdot mole^{-1}$ ); R is the ideal gas constant ( $8.314 J \cdot mol^{-1} K^{-1}$ ); T is the reaction temperature (K).

The curve shows that the variation of  $\ln k_{app}$  vs  $1/T$  was linear ( $R^2 > 0.99$ ) (Fig. 8) with an activation energy of 29.916 kJ.  $mol^{-1}$ . This result shows that the degradation of Chlorothiazide in an acidic aqueous medium (pH 3) by Electro-Fenton process requires low activation energy and hence can be easily achieved (Mansour et al., 2012).



**Fig. 8.** The Arrhenius plot of  $\ln k_{app}$  f(1/T) for the degradation of Chlorothiazide by electro-Fenton process. Experimental conditions: [Chlorothiazide] = 0.5 mM,  $[Fe^{2+}] = 0.1$  mM,  $[Na_2SO_4] = 50$  mM, I= 200 mA, pH=3, V=250mL

## 4. Conclusions

The obtained results show that the electrochemical advanced oxidation process (electro-Fenton) is effectively able to degrade Chlorothiazide, which is a pharmaceutical product used by patients with hypertension. The yield of mineralization is 93% after 7 hours of electrolysis. Indeed, the degradation of Chlorothiazide by electro-Fenton process using a carbon felt cathode and a platinum anode was studied with different experimental conditions, including current intensity, nature of activator and temperature.

The results of the mineralization study of Chlorothiazide showed that the COD decreases exponentially during treatment, and it is much faster at the beginning of treatment than at the end. The efficiency of degradation of the active target was enhanced by increasing the temperature of the reaction or by increasing the duration.

Chlorothiazide degradation follows pseudo first-order kinetics and its apparent rate constant of the degradation kinetics at 50 °C is better than at 25 °C.

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