## RESEARCH ARTICLE

# ELECTRODEGRADATION STUDY OF PHENOLIC COMPOUNDS CONTAINING IN OLIVE MILL WASTEWATERS OF THE CHIADMA REGION

[1,*]Rguiti, M. M., [1]Baddouh, A., [1]Amaterz, E., [3]EL Asbahani, A., [2]Bazzi, L,H., [1]Hilali, M. and [1]Bazzi, L.

[1]Applied Chemistry-Physics Team, Faculty of Sciences, IBN ZOHR University, B.P.8106 Cité Dakhla, Agadir. Morocco
[2]Autonomous Control Establishment and Coordination of Agadir Exports, Morocco
[3]Aït Melloul University Campus, Science and Technology Center, IBN ZOHR University, Agadir, Morocco

| ARTICLE INFO | ABSTRACT |
|---|---|
| | The electrochemical oxidation of PP (polyphenols) in Oil Mill Wastewaters (OMW) has been studied on Tin oxide ($SnO_2$) electrode in chloride containing solution. The degradation follows the pseudo-first-order kinetics indicating that the process was controlled by mass transfer. The supporting electrolytes containing nitrate and carbonate exhibited slower kinetics than those obtained using chloride. The PP can be electrochemically degraded effectively in chloride containing solution. The removal efficiency of PP was found to increase with the decrease of temperature and with the increase in both current density and NaCl concentration. The effect of temperature shows that for 25°C and 45°C a removal efficacy of PP was found to be 91% and 79%, respectively. For 1 % NaCl, 1.5 % NaCl and 2% NaCl solutions, the achieved removal of PP was 91%, 86% and 82%, respectively. |

## INTRODUCTION

The olive industry produces two types of waste, solid (olive, leaf and wood) and liquids (OMW). A study carried out for several years by the department of the Environment estimates more than 250,000 m³ as annual production of Morocco in OMW. OMW are considered among the most polluting effluents in the agro-food industry, and when they are evacuated to the environment without any prior treatment, they cause serious environmental damage.

**Their polluting power is mainly due to several causes, among which**

- The presence of phenolic compounds inhibits the development of microorganisms both in the presence and absence of oxygen (Nefzaoui, 1991). These substances have a phytotoxic effect and an antimicrobial activity (Hamdi *et al.*, 1992; Paixao *et al.*, 2002; Benyahia N *et al.*, 2003; Khoufi *et al.*, 2007) and have a—low level of biodegradation.

*Corresponding author:* **Rguiti, M. M.**
Applied Chemistry-Physics Team, Faculty of Sciences, IBN ZOHR University, B.P.8106 Cité Dakhla, Agadir. Morocco.

For these reasons, biological treatments cannot be applied for this type of effluents (Minh *et al.*, 2007).

- Acid pH: this is the first direct cause of the death of fish, when OMW are discharged into the rivers (Lacomelli *et al.*, 2000).
- Organic content that contributes to the consumption of dissolved oxygen and prevents water from self-purifying, and pollution can spread over very long distances (Benyahia *et al.*, 2003).
- The fat content causes the formation of a layer on the surface of the water preventing its proper oxygenation and the passage of light and obstructing the normal development of fauna and flora within rivers. Fatty acids and their derivatives inhibit sporulated soil bacteria (Nefzaoui, 1991).
- The high level of ammonia and other gases gives a bad odor to the places where the OMW are discharged (Mechichi *et al.*, 2005).

Phenolic compounds in OMW are toxic and non-biodegradable, their toxicity is higher than that of domestic water per thousand times (M. Niaounakis, 2006). A single cubic meter (1m³) of OMW is equivalent, depending on its basic composition, to domestic waste from 1000 to 2000 inhabitants (Mbourmad, 2011). Low molecular weight phenolic compounds are distinguished, such as phenolic acids,

phenols, flavonoids, phenolic glucosides and others with high molecular weights such as tannins, anthocyanins and catechins (Belaid *et al*., 2002). In fact, the treatment of OMW remains, until now, a predominant ecological problem for the Mediterranean countries, given the quality and quantity of the chemicals they contain. Indeed, the application of a simple treatment proves insufficient and incomplete {Hamdi, 1992; Benyahia *et al*., 2003; Ranalli, 1991). To reduce their negative effects, several purification processes, in particular physico-chemical, are implemented. Among these processing techniques, the electrochemical process has in recent years received an increased attention due to its unique characteristics, such as versatility, energy efficiency, automation and cost-effectiveness (Morsi *et al*., 2011). Moreover, the electrochemical techniques have several advantages such as the use the electron as the main reagent, it is called "Clean Reagent", and it degrades all the organic materials present in the pollutant without producing any secondary pollutant or by-product / sludge (Morsi *et al*., 2011; Mussa *et al*., 2015). In addition, the electrochemical treatment of organic pollutants requires the choice of a suitable catalytic electrode material as well as suitable electrolysis conditions.

Tin dioxide is characterized by a high oxygen potential, so it is one of the most commonly used anodes for the electrochemical degradation of many pollutants (Hachami *et al*., 2015; Errami *et al*., 2013; Bouya *et al*., 2012; Sarafraz *et al*., 2015; Bouya *et al*., 2013). However, it is important to note that the presence of $Cl^-$ ions in the solution can also increase the activity of the electrodes, as they act as intermediates in the transfer of electrons between the organic molecules and the electrode (Gaber *et al*., 2013; Miwa *et al*., 2006). The present work emphases a method for removal of pp in OMW by the electrochemical oxidation using $SnO_2$ electrode.

## MATERIALS AND METHODS

### Olive Mill Wastewater (OMW)

The effluent used in this study was taken from three locations of Chiadma in Essaouira city (Morocco). The sample was subjected to various filtrations before treatment to eliminate most total suspended solids (TSS) and its main properties before and after filtration are shown in Table 1.

**Table 1. Physicochemical characteristics of olive mill wastewater from Essaouira region**

| Property | Concentration |
|---|---|
| Turbidity (NTU) | 2805 |
| pH | 5,22 |
| conductivity (ms/cm) | 10,52 |
| $BOD_5$ (g/L) | 62 |
| COD (g/L) | 180 |
| K (g/L) | 2,91 |
| Na (g/l) | 2,71 |
| Cl(g/L) | 3,37 |
| Density(g/ml) | 1,03 |

Experiments were carried out with the filtrated OMW which was then diluted with deionised water to achieve the desired initial concentration.

### Analytical methods

### Physicochemical characteristics

The physicochemical characterization of the OMW has been carried out in our laboratory; as it is shown in Table 1,

according to the standard methods of wastewater analysis (AFNOR, 1985), for the quantitative analysis of the total phenols, the Folin method has been used;Folin-Ciocalteau (Singleton *et al*., 1965).

### Fourier Transform Infrared Spectroscopy (FTIR)

The main objective of infrared spectroscopy is to highlight functional groups. The FTIR spectra of the OMW were made using a spectrophotometerIRAffinity-1S in the frequency range between 400 to 4000 cm$^{-1}$. In this study, the absorption band to be detected is that of the phenolic OH groups observable at 3300 cm$^{-1}$. The FTIR spectra (Figure 1) of the effluent sample collected in the Essaouira region.
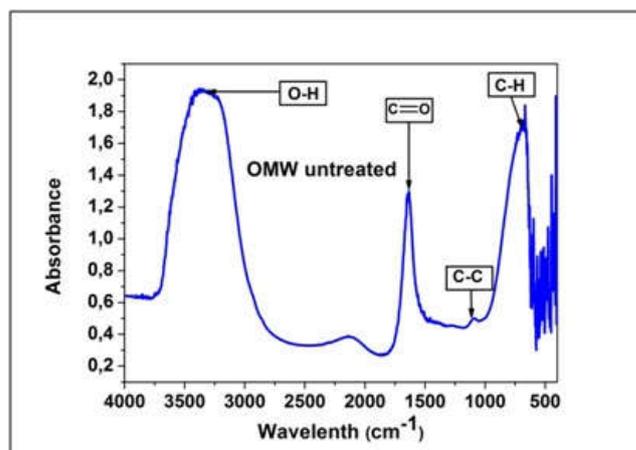


**Figure 1. FTIR spectra of untreated OMW**

### Showed the following characteristics

- A large band was observed at 3000-3600 cm$^{-1}$ which is attributed to OH stretching vibrations (phenolic compounds, organic acids, etc.) (Zghari *et al.*, 2017; Ibarra *et al*., 1996; Apetrei *et al*., 2011).
- The region of 1800-1500 cm$^{-1}$ corresponds to the C=O and CC stretching vibrations (esters, acid, carboxylate, aromatic ring) {Apetrei *et al*., 2011; Aouidi *et al*., 2012).
- A band located between 900-1300 cm-1 which corresponds to C-H elongation vibrations and OH deformation in carboxyl, C-O of ethers on an aromatic ring (El Hajjouji *et al*., 2008).
- The 600-900 cm$^{-1}$ region shows a much higher intensity including the peak at 675 cm$^{-1}$ corresponding to the C-H elongation vibrations (aromatic ethers) (Aouidi *et al*., 2012).
- The detected functions show the presence of the main constituents of vegetable water: organic fatty acids and phenolic compounds (Leouifoudi *et al*., 2014; Dermeche *et al*., 2013).

### Chemicals

In this study, the following reagents were used: NaCl, $Na_2CO_3$, $H_2SO_4$, NaOH, $KNO_3$, $AgNO_3$, Folin-Ciocalteu reagent and Gallic acid. All chemicals listed previously have been provided by: Fluka-kemica, Merck, SD Fine-Chem Limited and Sigma-Aldrich. All these substances were prepared by distilled water.

### Electrochemical degradation experiments

The electrochemical oxidation of PP was carried out using a computer controlled by Potentiostat/Galvanostat model PGZ

301 operated by the "Volta-Master 4" software. A conventional cell thermoregulated glass cell with three electrodes (100 cm $^3$) was used. The working electrode (WE) was a SnO₂ grid with a surface area of 1 cm², while the counter electrode (CE) was a stainless steel with 10 cm² of active surface and a saturated calomel electrode (SCE) was used as the reference electrode. And the distance between the mentioned electrodes was approximately 1 cm². Before each manipulation, the working electrode is generated by the use of a 1N $H_2SO_4$ solution. The pH of the solutions was adjusted using 1.0 mol.L$^{-1}$ $H_2SO_4$ solution and 1.0 mol.L$^{-1}$NaOH.

## RESULTS AND DISCUSSION

### Titration of phenolic compounds

### Calibration curve

The determination of phenolic compounds is carried out using the Folin-Ciocalteu method, it is the most popular method for the estimation of the total phenolic compound, which is based on the transfer of electrons in an alkaline medium from phenolics and other molybdenum reducing species, forming blue complexes that can be detected spectrophotometrically at 750-765 nm (Singleton *et al*., 1965). Gallic acid was used as a standard reference compound to plot a calibration curve. The results were expressed in Gallic acid equivalent (mg/L). It should be emphasized that the blue complexes formed are independent of the structure of the phenolic compounds, thus removing the possibility of coordination of the complexes formed between the metal and the phenolic compounds (Charles, 2012). The determination of the polyphenols was carried out in our laboratory using a Jenway Model 6800 double beam visible spectrophotometer; the maximum absorption was detected at 760 nm. The percentage reduction of polyphenols was calculated using the following equation:

$$\% \text{ Reduction of polyphenols} = \frac{C(0) - C(t)}{C(0)} \times 100 \quad (1)$$

Where C(0): initial concentration; C(t): the final concentration of the polyphenols which are determined by the Folin-Ciocalteu method.

### Effect of electrolytes supports

In this part, NaCl, KNO₃ and Na₂CO₃ were tested as electrolytes to compare their effect on the PP degradation Figure 2.
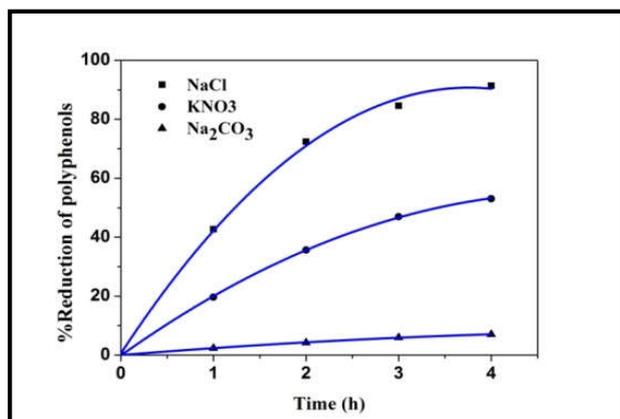


**Figure 2. Effect of supporting electrolyte on PP (60 mg/L) degradation using SnO2 electrode**

shows the influence of the nature of the carrier electrolyte (NaCl, KNO₃, Na₂CO₃) on the percentage reduction of the reduction of pp during electrostatic electrolyses of 60 mg / L of PP using SnO₂ while applying a current density of 80 mA/cm². , pH = 7 and at 25°C. NaCl was observed to give almost a complete mineralization (91.38%) of the PP.On the other hand, KNO₃ (53.1%) and Na₂CO₃(7%) gave only 53.1 and 7%, respectively. As shown in Figure 2, the nature of the supporting electrolyte has an influence on the kinetics during the treatment. As can be seen, the lowering of PP in the presence of NaCl is more efficient than in the presence of KNO₃ and Na₂CO₃. Kinetic studies were performed to determine the reduction efficiency of the electro-oxidation of the pp from different media electrolytes. For this purpose, the elimination rate of pp was assumed to obey first order kinetics (Laviron, 1972) Figure 3. shows the kinetic studies of the different supporting electrolytes in a2% -NaCl, 2% -Na₂CO₃ and 2% -KNO₃, using 60 mg/L of PP. Apparent kinetic constant (k) and electrochemical degradation rate of PP are shown in Table 2.
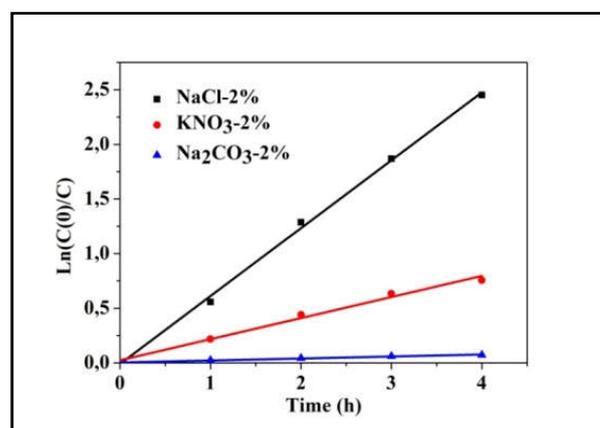


**Figure 3. Pseudo first-order plot oxidation of PP (60 mg/L) in 2% of different electrolyte types at 80mA/cm² and T=25°C.**

**Table 2. Kinetic rate constants of PP removal fitted by a first-order model and %Removal of PP under different electrolytes**

| Supporting Electrolytes | NaCl-2% | KNO₃-2% | Na₂CO₃-2% |
|---|---|---|---|
| K (h$^{-1}$) | 0,621 | 0,193 | 0,018 |
| R² | 0,998 | 0,989 | 0,984 |
| %Removal of PP | 91,38 | 53,08 | 7,03 |

As shown in Figure. 2 and Table 2, the presence of NaCl-2% promoted the best electro-oxidation of PP using SnO₂ electrode.
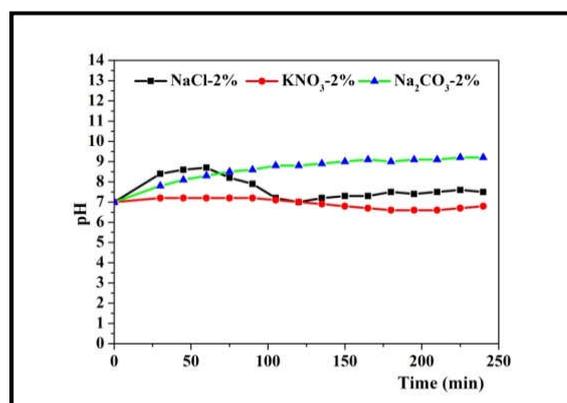


**Figure 4. pH reduction of PP 60 mg/L during 240 min of electrolysis at 80 mA/cm2 and 25 °C**

This result can be explained by the nature of electrogenerated oxidants coming from the oxidation of the support electrolyte during electrolysis on the anode surface. In the case of NaCl, the hypochlorite ion (ClO⁻) is the main electrogenerated oxidant on $SnO_2$ anodes while oxidizing chloride ions, (Dbira *et al.*, 2016; Panizza *et al.*, 2007; Errami *et al.*, 2012) (Equations (2) - (4)):

$$2Cl^- \longleftrightarrow Cl_2 + 2e^- \quad (2)$$

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \quad (3)$$

$$HOCl \longrightarrow H^+ + OCl^- \quad (4)$$

The potential throughout the electrolysis is close to the value 2.3V /SCE> 1.7 V /SCE and at the same time the pH is between 7 and 8 (Figure 4), which allowed us to say that the predominant species is HClO (see Pourbaix diagram Figure 5).
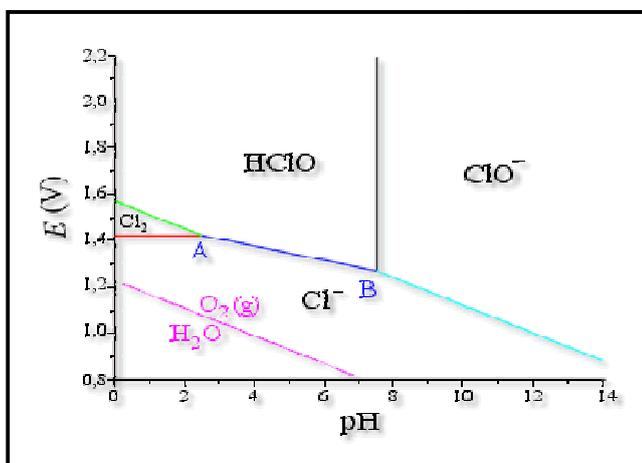


**Figure 5. E-pH diagrams of the system Cl-O-H. T=25°C, P=10⁵ pa**

HClO is the most potent oxidant among active chlorine species for the oxidation of organic compounds (Feng *et al.*, 2016).

**Effect of NaCl concentrations**

In this study, the concentration of NaCl was 1%,1.5% and 2% and the electrocatalytic degradation of the treated PP was carried out under the following operating conditions: current density of 80 mA/cm², pH of 7, temperature of 25°C and a PP initial concentration of 60 mg/L.
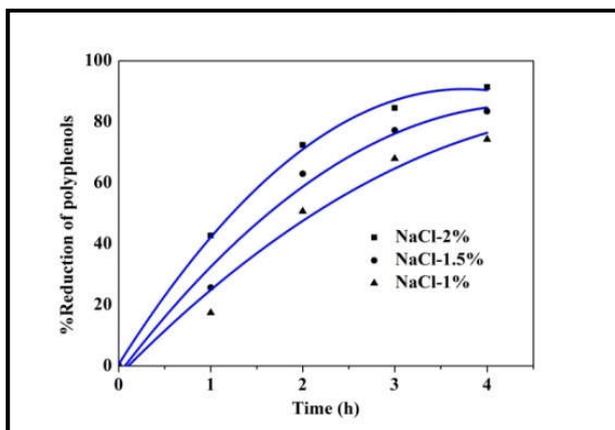


**Figure 6. Effect of NaCl concentration on PP (60mg/L)dgradation using SnO2 electrode**

As can be seen in Figure 5, the variation of the% removal of PP as a function of the electrolysis time at different NaCl concentrations: 1%, 1.5% and 2% for the electrocatalytic degradation of the polyphenols (PP) containing in the OMW studied on the $SnO_2$ electrode under the conditions mentioned above; it is clear from the graphs of the figure 6, that the PP removal percentage increased with the increase of electrolysis time reaching a time limit after 4 hours of electrolysis. On the other hand, the percentage of elimination of the OMW PP has been considerably increased with the increase of the NaCl concentrations; it reached a maximum value of 91.4% using NaCl-2%. For this reason, the NaCl-2% was chosen as the optimum. Kinetic studies were performed to determine the reduction efficiency of the PP on to the tin dioxide electrode at different concentrations of NaCl. For this purpose, the elimination rate of pp was supposed to obey first order kinetics as follows (Hachami *et al.*, 2015).

$$d[COD]/dt = -K[COD] \quad (4)$$

The rate constant values for different concentrations of NaCl are summarized in Table 2. The rate constant K was calculated for all carrier electrolyte masses. At each mass of NaCl, the reduction of PP was estimated at different time intervals and using Eq. (4), the speed constant K was calculated at each time intervals and averaged. Figure 7 illustrates the apparent kinetic constants for the oxidation of PP at different concentrations of NaCl as a function of the electrolysis time.
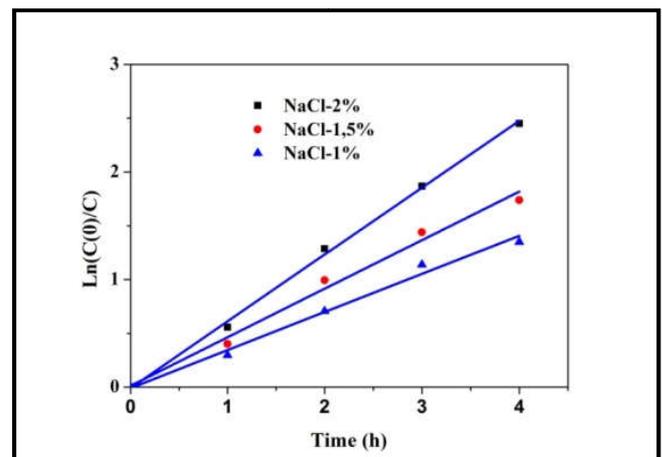


**Figure 7. Pseudo first-order plot oxidation of PP (60 mg/L) at different concentration of NaCl at 80mA/cm², pHi=7and T=25°C**

The apparent kinetic constants of PP (k) vary from 0.354h⁻¹(R²=989)for 1%NaCl, 0.451h⁻¹(R²=0.989) for 1.5% NaCl and 0.621h⁻¹(R²=0.998) for 2% NaCl.

**Effect of initial PP dosage**

The degradation of different concentrations of polyphenols has been studied; the results are shown in Figure 8. It can be seen that the electrochemical degradation efficiency of PP decreased with increasing concentrations. By increasing the concentration from 60mg/L to 300mg/L, the degradation efficiency of PP after 4 hours of treatment decreased from 91.38% to 44.4%, respectively. Indeed, the increase in the concentration of pp caused a decrease in its electrochemical degradation rate. This could be explained by the fact that the concentration of the hydroxyl radical decreases with the increase of the PP initial concentration (Kesselman *et al.*, 1997).
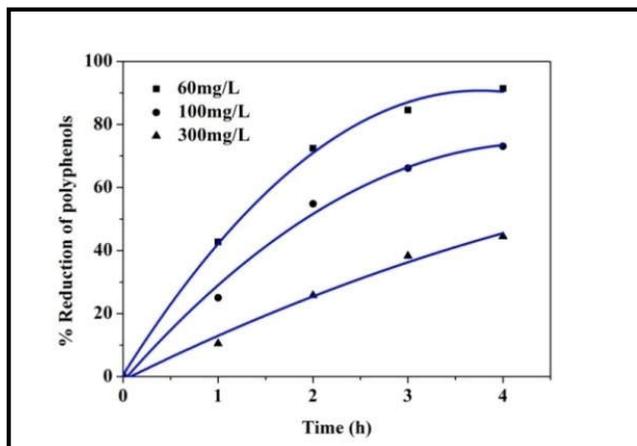
**Figure 8. Effect of initial concentration on phenolic compounds degradation using SnO2 electrode**

### Effect of current density

The effect of current density on the electrochemical process has been examined by several authors (Chiang *et al*., 1995). This is a major factor that affects the kinetics of the oxidation reaction. During electrochemical degradation,

### Two types of reactions can be distinguished

- Direct oxidation reaction that occurs at the anodic surface or the diffusion layer, it is a reaction that is characterized by direct electron transfer to the anode.
- Indirect oxidation reaction that takes place in the electrolyte where the compounds are oxidized by electrogenerated oxidants, like the OH$^\bullet$ radical, which is considered to be the most powerful known oxidant, with a high standard potential ($E_0$ = 2.80 V/SHE), it ensures the total degradation of organic compounds (Chang *et al*., 1990).

To study the electrocatalytic degradation of PP in 2% NaCl solution, we applied different current densities of 40, 60 and 80 mA/cm$^2$ under the following operating conditions: 60 mg/l of PP initial concentration, pH of 7 and temperature of 25 °C Figure 10.
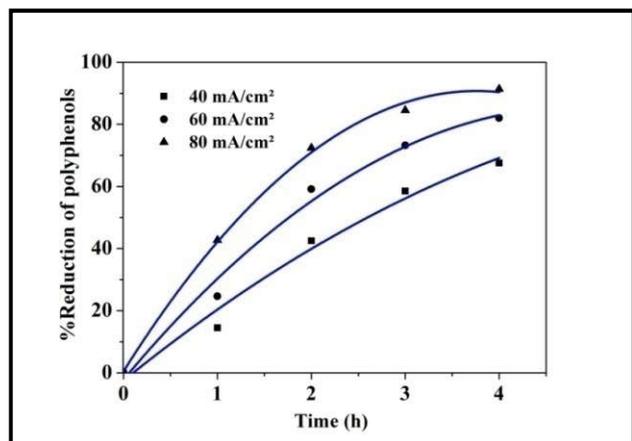


**Figure 9. Effect of current density on the removal of PP (60 mg/L), NaCl-2%, pH 7 and 4 hours time of electrolysis and temperature of 25∘C**

Shows the variation in the percentage of pp removal as a function of electrolysis time at different current densities. In

fact, the graphs analysis of the figure 9 indicates that at given current densities, the percentage of removal of the PP increases with increasing electrolysis time reaching a limit value. In addition, at a given time of electrolysis, the% removal of pp increased from 65.3% to 91.38% with the increase in the applied current density from 40 mA/cm$^2$ to 80 mA/cm$^2$ respectively. This behavior indicates that the oxidation of the PP is total under the control of mass transport and that an increase of the applied current favors only the secondary reaction of the evolution of the oxygen according to the equation (1) (Bouya *et al*., 2012):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- (5)$$
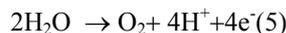
After that, it can be concluded that the current density value of 80 mA/cm$^2$ was considered as the optimal since a PP % removal of 91, 4% was achieved. The pseudo first-order kinetic constant of the elimination of the PP (k) in Figure 10. varies from about 0.621 h$^{-1}$(R²=0.998) for at 80mA/cm², 0.297 × h$^{-1}$ (R²=0.986) for 40mA/cm².
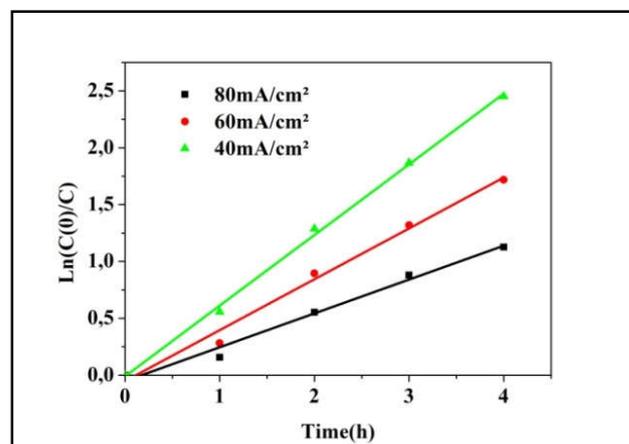


**Figure 10. Pseudo first-order plot oxidation of PP 60 mg/L in 2% NaCl at 25°C under different current inputs**

### Effect of solution pH

Figure 11. shows the variation of the polyphenol removal percentage as a function of electrolysis time at pH values of 4, 7 and 8 for the OMW studied.
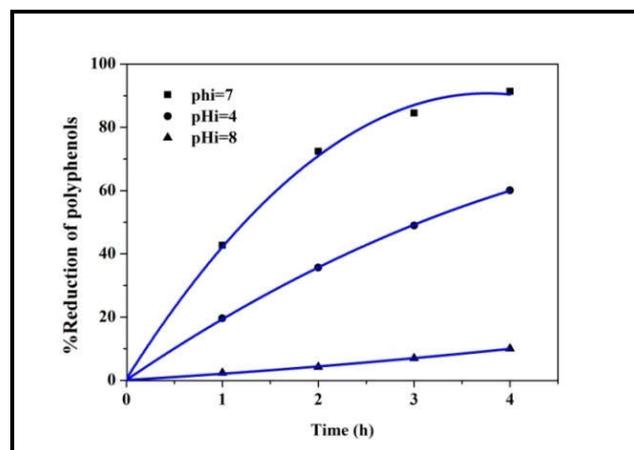


**Figure 11. Effect of initial pH on the removal of PP (60 mg/L), NaCl-2%, 4 hours time of electrolysis and temperature of 25°C**

The electrocatalytic degradation experiments on the SnO$_2$ electrode were carried out in a NaCl-2% solution under the

following operating conditions: current density of 80 mA / cm$^2$, PP initial concentration of 60 mg / l and a temperature of 25 °C. As shown in the graphs of Figure. 12, at given pH values, the% reduction variations of PP increase as a function of the electrolysis time reaching limit values. At a given electrolysis time, the maximum values of the% removal of PP were obtained at the pH values of 4 and 7 and the increase of the pH of the solution considerably decreased the values of the percentage of removal of PP. OMW studied. The reason may be due to the increase of chlorine / hypochlorite in an acidic medium and at a pH less than or equal to 7, the chlorine is present in the solution in the form of hypochlorous acid, which has a higher oxidation potential than that of hypochlorite. For this reason, the pH value of 7 is considered optimal.
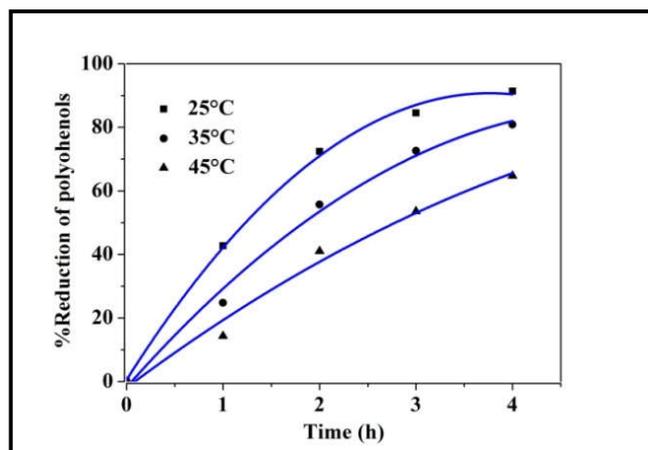


**Figure 12. Effect of temperature on the removal of PP (60 mg/L), NaCl-2%, pH 7 and 4 hours time**

## Effect of Temperature

Figure 12. shows the impact of 3 temperature levels on the efficiency of PP removal (ie 25, 35, 45°C) at a current density of 80 mA/m$^2$, 60 mg/L of initial PP after 4 hours of PP degradation on anode of tin dioxide. The best temperature for PP removal was found to be 25 ° C with a reduction percentage of 91.38%, followed by 35°C with 81.2% and 45°C with 65.3% reduction. The temperature level and the removal efficiency were found to be inversely related. This can be explained as the increasing of the temperature of the solution the chemical reactions accelerate. This reduces the potential of these and decreases the removal of the PP (Pirkarami *et al.*, 2014). The Figure 12 shows that for 25 °C and 45 ° C, the reduction obtained was 91.38% and 59%, respectively. The reduction percentage of PP corresponds to the first order pseudo-kinetics. The first-order pseudo-constant of PP (k) ranges from 0,277h$^{-1}$ (25°C) to 0.115h$^{-1}$ (45°C). The correlation coefficient (R²) of the first order kinetics model is about 0.99 (Figure13). The effect of temperature on the constant rates was modelled using the Arrhenius plots, it is shown in (Figure 14). The apparent activation energies were determined by:

$$K = A exp\left(-\frac{E_a}{RT}\right) \qquad (2)$$

Where Ea is the activation energy, K is rate constant, A is constant, T is the temperature (K) and R is the gas constant. The value of the activation energy is equal to -34.59 kj/mol, which indicates the complexity of the electrochemical degradation (Bouya *et al.*, 2013).

After a number of experiments, it can be concluded that the optimal experimental conditions for achieving a high PP removal efficiency are as follows: initial pH 7, reaction temperature = 25°C, current density =80 mA/cm$^2$, NaCl-2%, 60 mg/L of pp and electrolysis time 240 min.
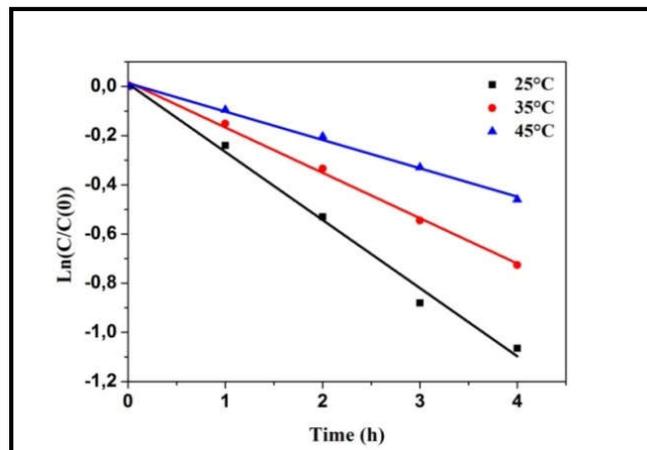


**Figure 13. Pseudo first-order plot for oxidation of 60 mg/L PP at 80mA and 25 °C**
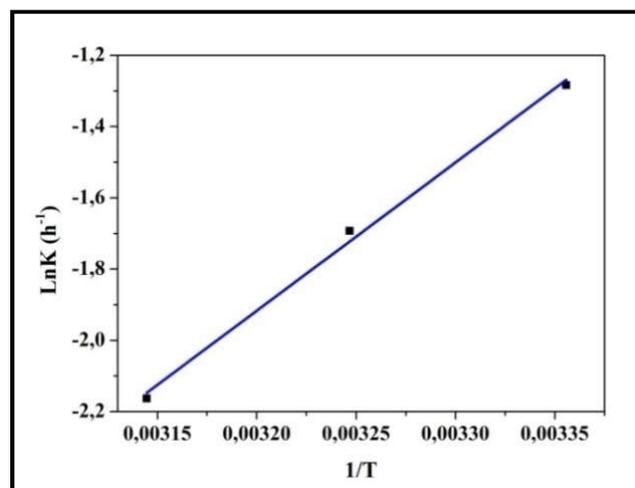


**Figure 14. Arrhenius plot of PP60 mg/L in 2% NaCl at 80 mA/cm2 at various temperatures**

The degradation of PP during the electrocatalytic process under optimal conditions was followed spectrophotometrically Figure 15. illustrates the UV-visible spectra at different stages of degradation of the electrolysis time. Two characteristic absorbance peaks have been observed at 230 nm and 280 nm that can be attributed to phenolic compounds (Zahari *et al.*, 2014; Belaid *et al.*, 2006). These two peaks decrease simultaneously with increasing electrolysis time until their complete disappearance, indicating that the PP was almost completely degraded. This result is confirmed by the figure below which shows the total discoloration of OMW after 240 min of electrolysis, the reddish-brown color reflects the presence of phenolic compounds and vice versa (Khoufi *et al.*, 2007). In order to compare the percentage of COD degradation, PP phenolic compounds of the OMW and the discoloration of the treated solution, we plotted the curves representing the reduction of these 3 parameters as a function of the electrolysis time. The removal efficiencies of COD, PP phenolic compounds and color obtained under these conditions are illustrated in Figure 16.
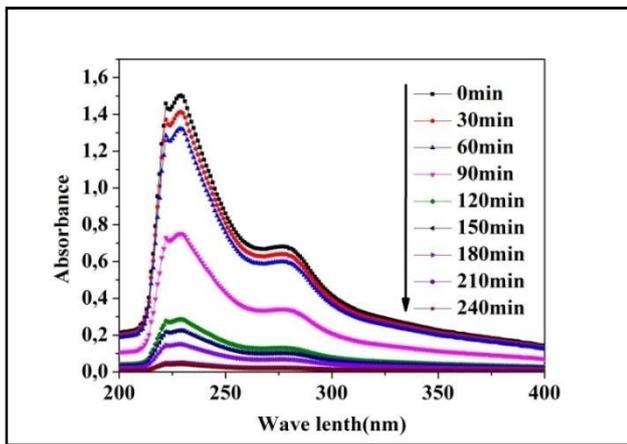
**Figure 15. UV-Vis spectra changes with electrolysis time on electrocatalytic degradation of OMW (conditions: PP concentration 60 mg L-1, initial pH 7, reaction temperature = 25°C, i= 80 mA/cm-2 and electrolysis time=240 min)**
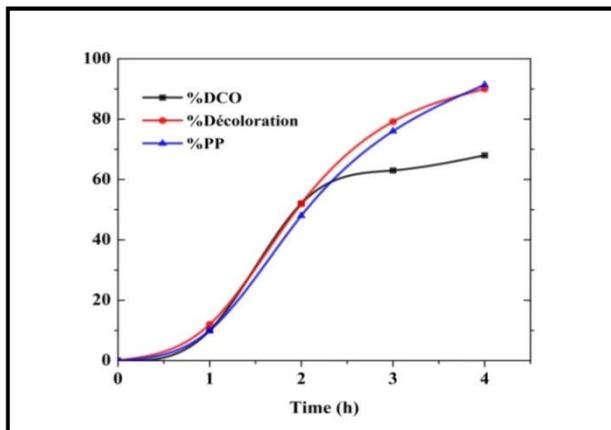


**Figure 16. The removal efficiencies of COD, PP phenolic compounds and color under optimal conditions conditions**

As shown by the results, the highest removal efficiencies were obtained under optimal conditions (Rguiti, 2018) (70 % for COD, 91.38% for PP and 92% for color). It is clear from the results that 80% of the color removal was achieved in the first 3 hours of treatment whereas this value was only 60% for the removal of COD during the same period.

**Conclusion**

This work is considered as a first attempt to study the electrochemical degradation of OMW polyphenols on the $SnO_2$ electrode. Electrochemical oxidation is an efficient method that has been used up to date for the treatment of several types of waste.

**This article provides new results on the electrochemical degradation of phenolic compounds and leads to the following conclusions**

- The application of electrolysis in OMW has the capacity to reduce the phenolic compounds to 2% NaCl mass and 1.5% NaCl mass, the reduction obtained was respectively 91.38% and 83%. For 1% NaCl was 64.76%.
- The applied current densities led to the increase of the rate of the electrochemical oxidation process.

- The effect of temperature showed that for 25 °C and 45 °C, the reduction achieved was respectively 91.38% and 64.76%.

**REFERENCES**

AFNOR, 1985. Recueil des normes françaises des eaux, méthodes d'essais, AFNOR.

Aouidi, F. *et al*., 2012a. Rapid quantitative determination of oleuropein in olive leaves (Olea europaea) using mid-infrared spectroscopy combined with chemometric analyses. *Industrial Crops and Products*, 37(1): 292-297.

Aouidi, F. *et al*., 2012b. Discrimination of five Tunisian cultivars by Mid InfraRed spectroscopy combined with chemometric analyses of olive Olea europaea leaves. *Food chemistry*, 131(1): 360-366.

Apetrei, C. *et al*., 2011. Biomimetic biosensor based on lipidic layers containing tyrosinase and lutetium bisphthalocyanine for the detection of antioxidants. Biosens Bioelectron, 26(5): 2513-9.

Belaid, C. *et al*., 2006. Electrochemical treatment of olive mill wastewaters: Removal of phenolic compounds and decolourization. *Journal of Applied Electrochemistry*, 36(10): 1175-1182.

Belaid, C., Kallel, M. and Elleuch, B., 2002. Identification de nouveaux composés phénoliques présents dans les rejets liquides d'huileries d'olive (margines). Déchets - Revue Francophone D'écologie Industrielle, 27: 30-34.

Benyahia N, K., Z. 2003. Contribution spéciale de Sustainable Business Associates, (Suisse) à SESEC II, pp. 2-7.

Bouya, H. *et al*., 2012. Electrochemical degradation of cypermethrin pesticide on a SnO2 anode. *Int J Electrochem Sci.,* 7(4): 7453.

Bouya, H. *et al*., 2013. Electrochemical Oxidation of 2-Nitrobenzaldehyde on Boron-Doped Diamond Anodes. *International Journal of Electrochemical Science,* 8: 7468.

Bouya, H. *et al*., Electrooxidation of 2-nitrobenzaldehyde: A comparative study of SnO2 and boron doped diamond anodes.

Chang, H. and Johnson, D.C., 1990. Electrocatalysis of Anodic Oxygen-Transfer Reactions Activation of Electrodes in by Addition of Bismuth (III) and Arsenic (III, V). *Journal of The Electrochemical Society,* 137(8): 2452-2457.

Charles, D.J., 2012. Antioxidant properties of spices, herbs and other sources. *Springer Science and Business Media*.

Chiang, L.-C., Chang, J.-E. and Wen, T.-C. 1995. Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. Water Research, 29(2): 671-678.

Dbira, S., Bensalah, N. and Bedoui, A. 2016. Mechanism and kinetics of electrochemical degradation of uric acid using conductive-diamond anodes. *Environmental Technology*, 37(23): 2993-3001.

Dermeche, S., Nadour, M., Larroche, C., Moulti-Mati, F. and Michaud, P. 2013. Olive mill wastes: Biochemical characterizations and valorization strategies. *Process Biochemistry*, 48(10): 1532-1552.

El Hajjouji, H. *et al.*, 2008. Photochemical UV/TiO2 treatment of olive mill wastewater (OMW). *Bioresource Technology,* 99(15): 7264-7269.

Errami, M. *et al.*, 2012. Electrochemical degradation of imazalil and pyrimethanil by anodic oxidation on boron-doped diamond. J Chem Pharm Res, 4(7): 3518.

Errami, M. *et al.*, 2013. Electrochemical degradation of buprofezin insecticide in aqueous solutions by anodic oxidation at boron-doped diamond electrode. *Research on Chemical Intermediates*, 39(2): 505-516.

Feng, Y., Yang, L., Liu, J. and Logan, B.E. 2016. Electrochemical technologies for wastewater treatment and resource reclamation. *Environmental Science: Water Research and Technology,* 2(5): 800-831.

Gaber, M., Abu Ghalwa, N., Khedr, A.M. and Salem, M.F. 2013. Electrochemical Degradation of Reactive Yellow 160 Dye in Real Wastewater Using C/PbO2, Pb; Sn/PbO2;SnO2, and Pb/PbO2 Modified Electrodes. *Journal of Chemistry*, 2013: 9.

Hachami, F. *et al.*, 2015. A comparative study of electrochemical oxidation of methidation organophosphorous pesticide on SnO2 and boron-doped diamond anodes. *Chem Cent J.*, 9: 59.

Hamdi, M. 1992. Toxicity and biodegradability of olive mill wastewaters in batch anaerobic digestion. Applied Biochemistry and Biotechnology, 37(2): 155-163.

Ibarra, J., Muñoz, E. and Moliner, R., 1996. FTIR study of the evolution of coal structure during the coalification process. *Organic Geochemistry*, 24(6): 725-735.

Kesselman, J.M., Weres, O., Lewis, N.S. and Hoffmann, M.R., 1997. Electrochemical production of hydroxyl radical at polycrystalline Nb-doped TiO2 electrodes and estimation of the partitioning between hydroxyl radical and direct hole oxidation pathways. *The Journal of Physical Chemistry B*, 101(14): 2637-2643.

Khoufi, S., Feki, F. and Sayadi, S. 2007. Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes. *J Hazard Mater.*, 142(1-2): 58-67.

Lacomelli A. 2000. In: parties., B.c. (Editor), Work Shop on Agro-industry development in the coastal areas, with special focus on the olive oil industry., Beirut- Lebanon.

Laviron, E. 1972. Influence of the adsorption of the depolarizer or of a product of the electrochemical reaction on polarographic currents: XVII. Theoretical study of a reversible surface reaction followed by a first order chemical reaction in linear potential sweep voltammetry. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 35(1): 333-342.

Leouifoudi, I. *et al.*, 2014. Identification and characterisation of phenolic compounds extracted from Moroccan olive mill wastewater. *Food Science and Technology*, 34: 249-257.

Mbourmad, S. 2011. sciences alimentaires Thesis, ENSA of Elharrach-Alger, 160 pp.

Mechichi, T. and Sayadi, S. 2005. Evaluating process imbalance of anaerobic digestion of olive mill wastewaters. *Process Biochemistry*, 40(1): 139-145.

Minh, D.P., Aubert, G., Gallezot, P. and Besson, M. 2007. Degradation of olive oil mill effluents by catalytic wet air oxidation: 2-Oxidation of p-hydroxyphenylacetic and p-hydroxybenzoic acids over Pt and Ru supported catalysts. Applied Catalysis B: *Environmental,* 73(3): 236-246.

Miwa, D.W., Malpass, G.R.P., Machado, S.A.S. and Motheo, A.J. 2006. Electrochemical degradation of carbaryl on oxide electrodes. *Water Research*, 40(17): 3281-3289.

Morsi, M.S., Al-Sarawy, A.A., El-Dein, W.A.S., 2011. Electrochemical degradation of some organic dyes by electrochemical oxidation on a Pb/PbO2 electrode. *Desalination and Water Treatment*, 26(1-3): 301-308.

Mussa, Z.H., Othman, M.R. and Abdullah, M.P. 2015. Electrochemical Oxidation of Landfill Leachate: Investigation of Operational Parameters and Kinetics Using Graphite-PVC Composite Electrode as Anode. *Journal of the Brazilian Chemical Society*, 26: 939-948.

Nefzaoui, A., 1991. CIHEAM-Mediterranean Options 16: 101-108.

Niaounakis, M. C.P.H. 2006. Waste Management Series. In: Michael, N., Constantinos, P.H. (Eds.), Waste Management Series. Elsevier, pp. v.

Paixao, S.M. and Anselmo, A.M., 2002. Effect of olive mill wastewaters on the oxygen consumption by activated sludge microorganisms: an acute toxicity test method. *J Appl Toxicol,* 22(3): 173-6.

Panizza, M., Barbucci, A., Ricotti, R. and Cerisola, G. 2007. Electrochemical degradation of methylene blue. *Separation and Purification Technology*, 54(3): 382-387.

Pirkarami, A. and Olya, M.E. 2014. Removal of dye from industrial wastewater with an emphasis on improving economic efficiency and degradation mechanism. *Journal of Saudi Chemical Society*,

Ranalli, A. 1991. L'effluent des huileries d'olive proposition en vue de son épuration. Références aux normes italiennes en la matière, première partie olivia, 37: 30-39.

Rguiti, M.M., Baddouh, A., Khadija, E.M., Bazzi, L., Hilali, M., 2018. Electrochemical oxidation of olive mill

Sarafraz, M., Khosravi, M., Bonyadinejad, G., Ebrahimi, A. and Taghavi-Shahri, S.M. 2015. Electrochemical degradation of the acid orange 10 dye on a Ti/SnO2-Sb anode assessed by response surface methodology. *International Journal of Environmental Health Engineering*, 4(1): 31.

Singleton, V.L. and Rossi, J.A. 1965. Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents. *American Journal of Enology and Viticulture*, 16(3): 144-158.

Zahari, A., Tazi, A. and Azzi, M. 2014. Optimization of treatment conditions of Olive Oil Mill Wastewater by superoxidant K3FexMnyO8. *J. Mater. Environ. Sci.*, 5: 2484-489.

Zghari, B., Doumenq, P., Romane, A. and Boukir, A. 2017. GC-MS, FTIR and H, 13 C NMR Structural Analysis and Identification of Phenolic Compounds in Olive Mill Wastewater Extracted from Oued Oussefrou Effluent (Beni Mellal-Morocco).

*******