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Electrochemical oxidation of olive mill waste waters on Tin Oxide Electrode

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- ✓ *Chronopotiometry;*
- ✓ *Decolorization and COD*

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Abstract

Oil mill wastewaters (OMW) are a liquid effluents resulting from the extraction of the olive industry, characterized by their acidic pH (<5), their red-brown color, Chemical Oxygen Demand may exceed 220 g / L, high phosphorus content that accelerates the growth of algae resulting in eutrophication, high salinity and very large quantity of phenolic compounds (>8g/L) which cause the destruction of soil microflora and induce toxic effects on plant crops. In addition, this compounds lead to sterilization of soil and the imbalance of the biological interaction between soil's microflora and plants. To treat these liquid wastes, several techniques have been used, but the results are not satisfactory. For this we have chosen the electrochemical process because it is environmental and economic. In this work the electrochemical degradation of olive oil mill wastewater (OMW) was investigated using a Tin dioxide anode SnO_2 in chloride containing solution by cyclic voltammetry and chronopotentiometry. The electrolytic process was detected by the UV–visible spectrometry and the Chemical Oxygen Demand (COD). The influence of current density, time of electrolysis and the concentration of conductive salt were studied. The results obtained show that after only 4 hours of electrolysis, discolouration was reached at 96% with an abatement of COD 73%. The study of the applied current density shows that the best efficiency of the removal of COD reaches a maximum at 100 mA / cm².

1. Introduction

Morocco is the sixth country after: Spain, Italy, Greece, Turkey and Tunisia, with an annual yield of 120,000 tons of olives. In fact, the world production exceeds 3,269,249 tons, which 98% of the world's production of olives is produced in the Mediterranean region which generates more than 30 million m^3 of oil mill wastewater (OMW) [1-3]. These effluents are characterized by their red-brown color, acidic pH (3-5), Chemical Oxygen Demand may exceed 220 g / L, high salinity and abundance of phenolic compounds which cause the destruction of soil microflora and induce toxic effects on plant crops. In addition, this compounds lead to sterilization of soil and the inbalance of the symbiosis between soil's microflora and plants [4-7]. Trying to treat these effluents, several methods have been employed such as: biological, chemical and physical processes as well as different combinations of them [8]. The biological treatment is considered more economical, but this technique requires a large space and time consuming. On the other hand, the physical adsorption is an expensive technique (the high price of activated carbon) and difficult for the regeneration of the adsorbent. Moreover, the chemical and biological ones produce considerable amounts of sludge, which necessitates other treatments [9].

In the last decades the electrochemical methods has been proven as an efficient, cheaper, no-toxic method (using only the electrons) and it has been applied in several studies for degradation of organic matters by offering encouraging results [10]. According to several authors, the electrochemical degradation of organic pollutants depends on the type and structure of the anode. Therefore, conventional electrodes like graphite and platinum have a low yield, against the Dimensionally Stable Anodes (DSA) such as: PbO_2, RuO_2, SnO_2, and Boron Doped Diamond (BDD)..., which was admitted satisfactory results [11-16]. Belaid *et al* [17] have carried out the electrochemical degradation of OMW diluted 50 times on the electrode of Ti / Pt. The result was obtained 90%

of decolourization and 65% abatement of COD after 4H of electrolysis. Un *et al* [18] reported that the use of Ti / RuO_2 anode allows the reduction of 99.6% of COD under the following conditions of 135mA/cm², 2M NaCl and 40°C. Biological treatment followed by electrochemical treatment, was suggested by Gonçalves et al [19], it was obtained complete removal of COD on RuO_2 without using a supporting electrolyte.

In the present study, SnO_2 was selected as working electrode due to it is widely applied in the electrochemical degradation of organic pollutants and it gives acceptable results than other electrodes. For example, the oxidation of phenol on Ti/SnO_2 leads to total mineralization of organic matters without the production of hydroquinone and benzoquinone [20].

The aim of this work is to study the feasibility of treating wastewater from the olive oil extraction by direct oxidation and decreasing of the risk of environmental pollution from these effluents. The chrono-potentiometry and cyclic voltammetry were applied as electrochemical techniques. The electrocatalytic electrode efficiency based on oxides SnO_2 against the electrodegradation of OMW will be evaluated by physicochemical techniques such as COD measurement and UV spectrophotometry.

2. Materials and methods

2.1. Olive Mill Wastewater (OMW)

The effluent used in this study was taken from a 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 was shown in Table 1. Experiments were carried out with the filtrated OMW which was then diluted with deionised water to achieve the desired initial concentration.

Table 1: Properties of OMW samples used in this study

Property	Before filtration	After filtration
COD (g/L)	320	180
Total polyphenol (g/L)	8	3
pH	5	4.8
Conductivity (ms/cm)	16	18
Chloride (g/L)	6	5

2.2. Electrochemical degradation experiments

The electrochemical measurements and cyclic voltammetry (CV) analysis were carried out using a computer controlled by Potentiostat/Galvanostat model PGP 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 was a SnO_2 grid with a surface area of 1 cm^2, while the counter was a stainless steel with 10 cm² of active surface and a saturated calomel electrode (SCE) were used as the reference electrode. And the distance between the mentioned electrodes was 1 cm. Before each manipulation, the working electrode is generated by the use of a 1N H_2SO_4 solution. The evolution of the OMW color is measured by UV-visible spectrometry at the wavelength 395 nm, [17].

2.3. Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is measured using standard methods for water and wastewater testing [18]. The measured amount of pollutant is diluted in advance and then brought to a commercially available digestion solution containing potassium dichromate, sulfuric acid, mercuric sulphate and the mixture, then the solution is boiled to Reflux for 2 hours at 150 °C. in a COD reactor. The concentration of COD was measured by the colorimetric method using an Aqualytic PCcompact COD vario photometer.

3. Results and Discussion

Electrochemical degradation of organic pollutants is achieved through two mechanisms: direct mechanism by which the organic matter is adsorbed on the surface of the electrode, then oxidized by electron transfer and the other is indirect where the organic pollutants are exchange electrons with the surface of the anode through some oxidants such as chlorine, hypochlorite, hydroxyl...etc. On the point of view hypochlorite is a powerful oxidant and low chlorinating agent, however alkaline media can be used to reduce the formation of halo compounds in such electro-generated chlorine transform to hypochlorite according to equations (1), (2), (3) and (4) [19, 21], that is a reason why the pH value was adjusted at 7 at the beginning of the experience.

$$2Cl^- \longrightarrow Cl_{2\,(g)} \rightleftarrows Cl_{2\,(aq)} + 2e^- \qquad (1)$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (2)$$

$$Cl_{2\,(aq)} + H_2O \longrightarrow HOCl + Cl^- + H^+ \qquad (3)$$

$$HOCl \rightleftarrows H^+ + OCl^- \qquad (4)$$

3.1. Electrochemical techniques

Figure 1 represents the cyclic voltammograms of the four different supporting electrolytes mentioned as 2% NaCl, 2% KNO_3, 2% Na_2SO_4, and 2% Na_2CO_3solution in OMW The interaction of the phenolic compounds with the electrode surface using 2% NaCl was shown the distinct results than the other supporting electrolytes.

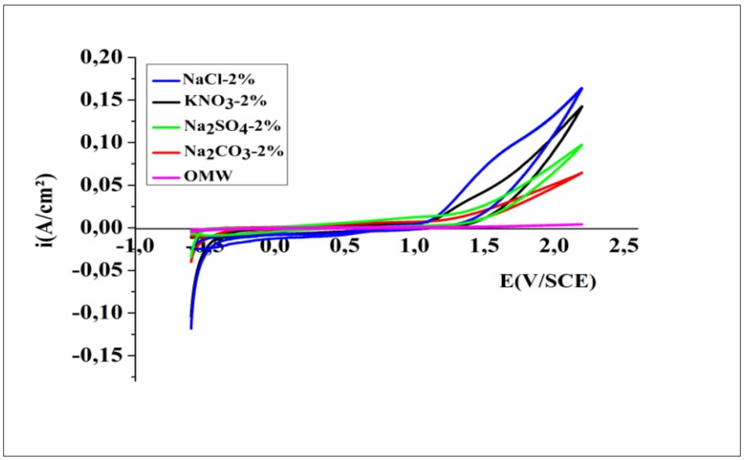

Figure 1: Cyclic voltammograms of OMW on SnO_2: scan rate. 100 mV s^{-1}; concentration of OMW: diluted 50 times.

Figure 2 illustrates effect of chloride ions concentration (range between 1 and 2%) on the degradation of OMW degradation carried out at 100 $mA/cm^{2.}$. In 2% NaCl it can be showed that OMW promotes has an increase in current attached with the oxygen evolution reaction for the SnO_2 electrode. However, the response of the other NaCl concentrations decreased when OMW was added. These results indicate that the interaction of the effluent with the surface of the electrode with 2% NaCl is distinct from that of the other concentrations.

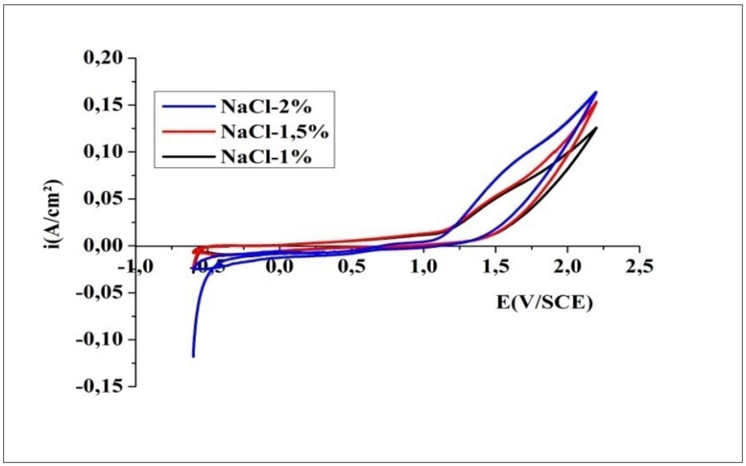

Figure 2: Cyclic voltammograms of omw on SnO_2: scan rate 100 mV s^{-1} at pH=7; concentration of OMW: 50 times diluted

3.1.1. Effect of current density

3.1.1.1 Decolorization studies

Results in Figure 3 show that the removal of colour significantly enhanced with increasing the current density. When the current density was increased from 20 mA/ cm^2 to 100 mA/cm^2, the discoloration changed from 38% to 96.3%.

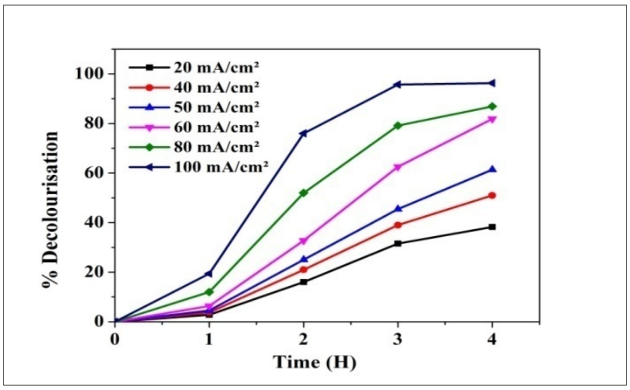

Figure 3: Discoloration of OMW during electrolysis at different current densities.

Figure 4: Discoloration of OMW during electrolysis at 100mA/cm^2

The removal of colour rate increases with increased current density and the highest values obtained at 100 mA/cm^2, which is the optimal current density for the significant electrochemical degradation of OMW. In all tests, the colour intensity decreases during treatment; the colour changes from dark brown to light yellow and it ends with a colourless solution (figure 4). The impact of the current is very important during the first 2 hours of treatment and the dark brown of OMW reflects on its heavy load in phenolic compounds, as reported by Belaid *et al* [22], discoloration was suggested that these toxic compounds are destroyed by electrochemical degradation.

3.1.2 *Effect of pH solution*

3.1.2.1 *Decolourisation studies*

Figure 6 shows the influence of intitial pH to the decolorization, from the same figure it can be seen that the decolorization process has been accelerated with the exposure time. In addition of that, the decolorization keep increasing to reach an important value of 96% at pH=7.

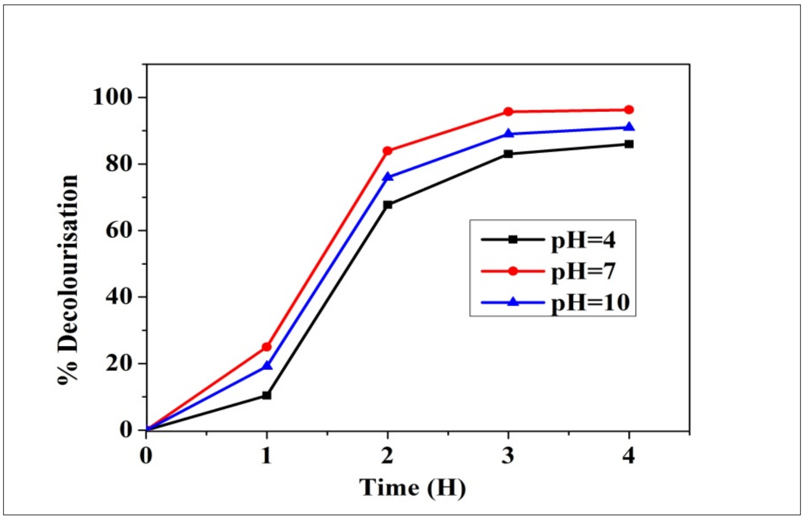

Figure 5: Discoloration of OMW during electrolysis at different at different pH value

3.1.2.2. Variation of pH

The Figure 7 indicates the variation of the pH value of the studied solutions with the exposure time of 240 min. It can be concluded that the pH value of the solution with pHi=10 is decreased until 8. For the electrolyte media with initial pH of 7, the same behavior was observed after a pH rising from 7 to 9. However, the third solution tested (pHi=4), discloses a pH value augmentation from 4 to 8 after the immersion time studied.

By detecting whatever the initial pH of the solution of OMW, the electrolysis at 100 mA/cm² leads to a stabilization of the final pH at about 7 after 3 hours.

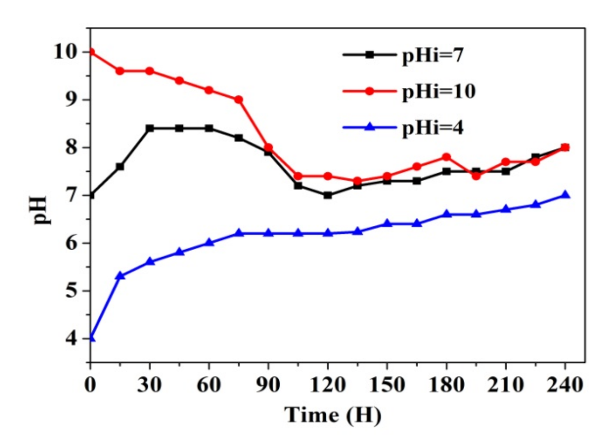

Figure 7: variation of pH as a function of electrolysis time at different values of applied current density i=100mA/cm², T=25°C.

3.2. UV-Visible Spectroscopy

Figure 8 shows that the change in the absorbance as a function of the wavelength of the solution for different electrolysis times at 100 mA/cm².

We find that the control curve (t = 0H) exhibits 2 characteristic peaks, the first peak p_1 is at about 230 nm and the second p_2 at 280 nm. We also find that the velocity of these 2 peaks p_1 and p_2 decreases during the electrolysis time to disappear completely after 3 hours of electrolysis.

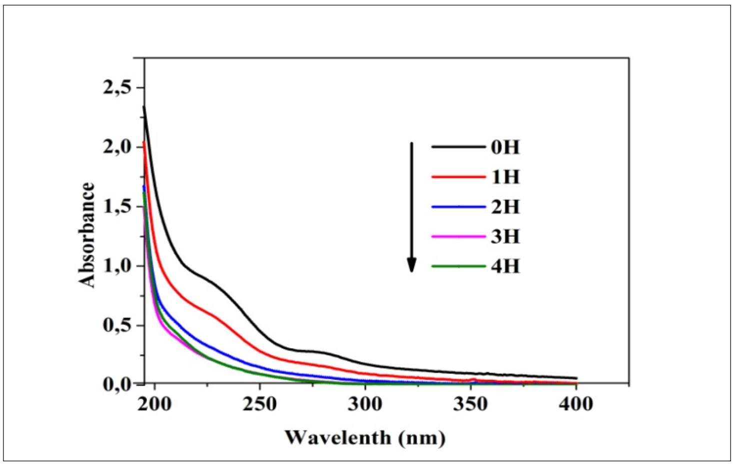

Figure 8: UV–Vis spectrum for Phenolic compounds before and after electrolysis (4 hours) at 100mA/cm²

3.3. Chemical oxygen demand

3.3.1. % abatement of COD

To study the effect of the electrolyte concentration, electrolysis was carried out for 4 hours in a solution containing 1 to 2% NaCl. In figure 9 it was observed that the realization of the electrolysis in this effluent has the ability to significantly decrease the COD. For example, to 2% by weight NaCl and 1.5 % NaCl to the achieved abatement was 73 % and 53% respectively, whereas for 1% of NaCl, it was 43%. This result was in agreement with UV-Visible Spectroscopy.

Figure 10 shown that the mineralization efficiency increased with increased current density, when the current density rises from 60 to 100 mA/cm^2, the % COD reduction increases from 58 to 73 %. This result was agreed with Figure 11,which shown that the degradation of the organic compounds passes through an initial value of 3600 mg /L to 962 mg /L for 2%NaCl obtained the significant yield.

Figure 12 and 13 were shown that the COD evolution with charge during electrolysis at different concentration of NaCl and different current densities, respectively. It was observed that SnO_2 electrode could oxidize OMW.

At charge of 1440 C and after 4 hours of electrolysis, COD was reduced from an initial 3600 mg/L to 972 mg/L. However the variation of the COD with the specific electrical charge passed has a typical exponential form in the range of the concentration studied process [23].

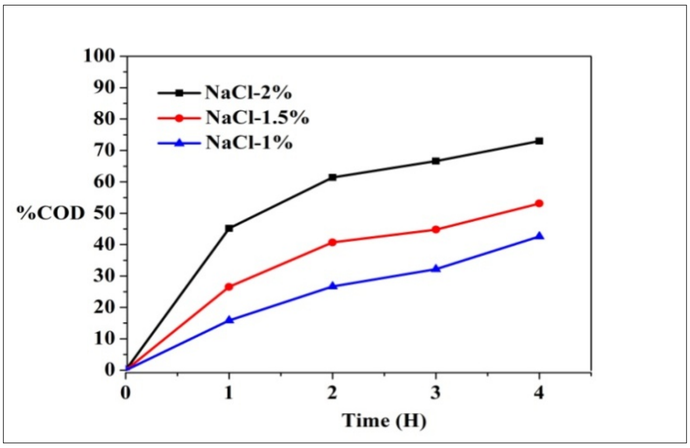

Figure 9: Influence of electrolysis time in the COD removal in the presence of different NaCl concentrations.

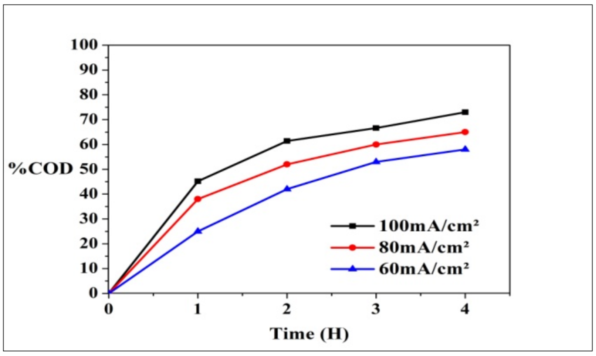

Figure 10: COD reduction during electrochemical treatment of OWM at different current densities

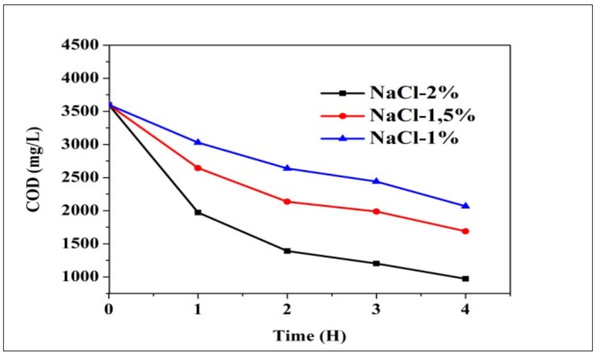

Figure 11: COD reduction during electrochemical treatment of OWM at different concentration of NaCl

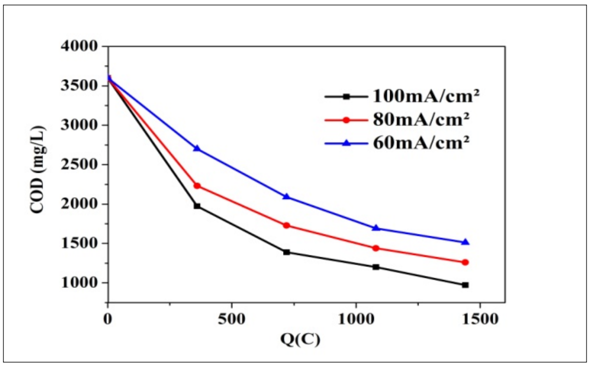

Figure 12: COD reduction during electrochemical treatment of OWM at different concentration of NaCl as a function of charge

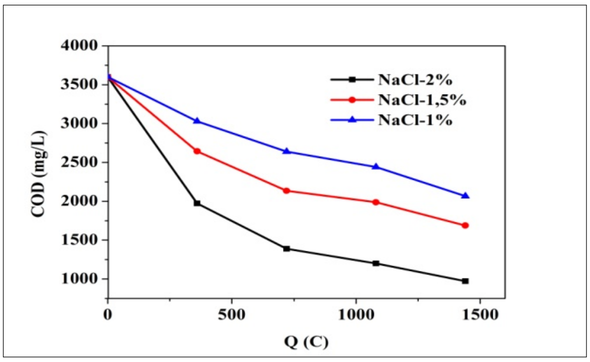

Figure 13: COD reduction during electrochemical treatment of OWM at different current densities as a function of charge

3-4. Energy consumption

To determine the Instantaneous Current Efficiency ICE we used the following formula [24]:

$$\mathrm{ICE} = \frac{((\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}).\,\mathrm{FV}}{8\mathrm{I}\Delta t}$$

F: 96487 C mol^{-1}; V: electrolyte volume (L); I: applied current (A); COD: Chemical oxygen demand (mol O_2/L) and Δt: time interval (s).

Figure 14 shows the instantaneous current efficiency (ICE) as a function of time at 100A/cm². From the figure, it was clearly observed that ICE was fairly right all over the experiment in 2% NaCl and 100mA/cm².

This confirms the results obtained in FIGS. 12 and 13.

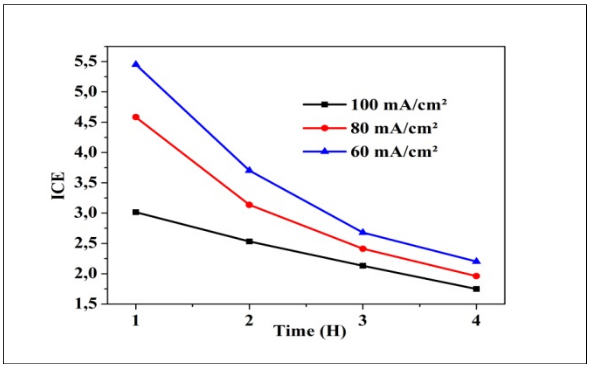

Figure 14: Variation ICE as function as time at different current density.

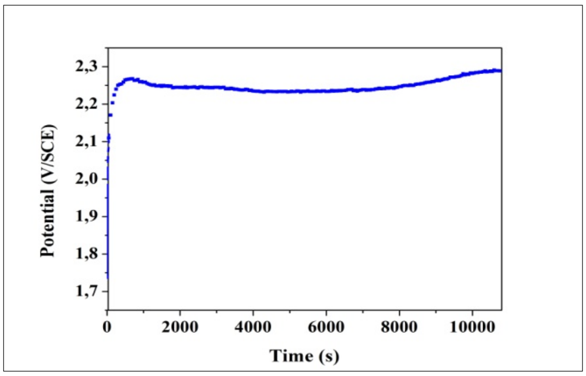

Figure 15: OMW chronopotentiogram at i =100mA/cm², NaCl-2% and pHi=7

Figure 15 shows the evolution of the potential E as a function of time in the galvanostatic mode, according to this figure it can be noted that there is stabilization of the potential after 15 min at 2.3 V.

The quantity of energy necessary during 4 h of electrolysis at 100 mA/cm² for SnO_2 anode was represented in Figure 16; the energy necessary to destroy 73% of the organic compounds was 0.95 kWh/g COD pendant for this electrode.

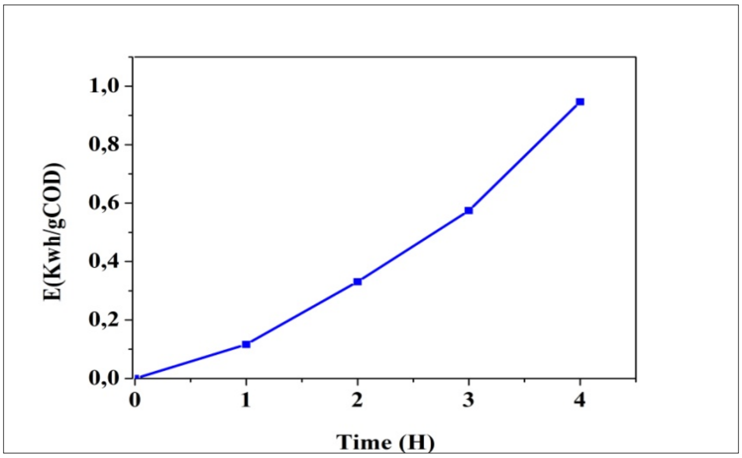

Figure 16: The variation of energy consumption with the electrode SnO2 during 4 hours of treatment at i=100mA/cm², NaCl-2%, and pHi=7.

Conclusion

In this study the electrochemical treatment of Oil Mill Wastewaters containing phenolic compounds was carried in NaCl conductive electrolyte and under several operating conditions using the tin oxide electrode. OMW removal efficiency was depended to NaCl concentration, and applied current density.

Also the results showed that: The best color and COD removal were achieved 96% and 73% respectively at the optimal parameters of 100 mA·cm^{-2} current density, NaCl 2% and 4 hours of electrolysis.

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