

1. Introduction

The Mediterranean countries are confronted with the problem of the elimination of olives mill wastewaters produced from olive oil extraction. These wastewaters are generally discharged into the natural environment without any prior treatment, thus causing serious problems of environmental pollution. Indeed, these effluents have a high polluting power due to a high load in chemical and biological oxygen demands (COD and BOD5) [1]. In addition, they are saturated by phenolic and aromatic compounds that are very difficult to be biodegraded [2]. Numerous studies have been carried out in order to treat these effluents by proposing economical methods such as biological treatments [3], chemical oxidation [4] and coagulation flocculation [5].

In the case of electrocoagulation (EC), the coagulant is generated by dissolution of a sacrificial anode [6]. EC uses an electrical current to produce several metal ions in solution. In fact, the EC systems can be effective in removing suspended solids, dissolve metals, tannin, dyes and margins. The contaminants present in wastewater are maintained in solution by electrical charges. When metal ions are neutralized with ions of opposite electric charge, provided by an EC system, they become unstable and precipitate in a form that is usually very stable. EC is an electrochemical technique derived from chemical coagulation standard. In the case of the EC, no chemical additions is needed since the metal ions assets come directly from the dissolution of the anodes. This situation allows therefore cost reduction of the use of chemical products and decreases by the fact even the final production of sludge that must be disposed. The characteristics of EC are simple equipment and easy operation, brief reactive retention period, decreased or negligible equipment for adding chemicals and decreased amount of sludge [7]. The electrochemical process is ideal to take advantage of the combined effect due to the production of polyanvalent cations from the oxidation of corroible anodes (such as Fe and Al). The gas bubble carry the pollutant to the top of the solution can be more easily concentrated, collected and removed. The metallic ions can react with the OH-ions produced at the cathode during the evolution of H2 gas, to yield insoluble hydroxides that will remove pollutants out of the solution. It also contributes to coagulation by neutralizing any negatively charged colloidal particles that have been reported to be more compact than sludge obtained by chemical methods [8].

Our work consists in reducing organic matter, color and phenols by EC [9]. The objective of this study is to treat an effluent from the region of Essaouira (Morocco) in order to make it colorless, reduce its chemical oxygen demand (COD) and phenols content, in accordance to world standards [10].

2. Material and methods

2.1. Industrial waste study

The olive mill wastewater was taken from a traditional oil mill in Essaouira, during the 2016-2017...
olive-growing season. No chemical additives were used during the production of olive oil [11]. The Table 1 illustrates the composition and characteristics of olive mill wastewater sample.

**Table 1**
Composition and characteristics of crude olive mill wastewaters [12].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.9</td>
</tr>
<tr>
<td>Polyphenol (g/L)</td>
<td>12</td>
</tr>
<tr>
<td>Dry matter (g/L)</td>
<td>13.0</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>98</td>
</tr>
<tr>
<td>Volatile matter (g/L)</td>
<td>9.5</td>
</tr>
<tr>
<td>Ash (g/L)</td>
<td>3.5</td>
</tr>
<tr>
<td>COD (g O₂/L)</td>
<td>31</td>
</tr>
<tr>
<td>Fatty acid (g/L)</td>
<td>0.9</td>
</tr>
<tr>
<td>Total nitrogen (%)</td>
<td>0.05</td>
</tr>
<tr>
<td>Conductivity (ms/cm)</td>
<td>12.4</td>
</tr>
<tr>
<td>Total sugars (mg/L)</td>
<td>14</td>
</tr>
</tbody>
</table>

### 2.2. Separation of olives mill wastewater

After the storage of the samples, the oily and aqueous phases of OMW can be separated either naturally or by centrifugation. Even if they have the same performance, the slow and the area requirement may limit the first one. The centrifugation allowed us to accelerate the separation of oil and water phase. This separation technique is performed by filling 4 test tubes with 0.250 L of OMW solution, they are then centrifuged at a speed of 4000 rpm during 30 minutes. The oil, having a lower density than water, will be found above the water in the centrifuge. The oil phase was collected using an automatic adjustable pipette. Oil percentage was determined by weight difference.

### 2.3. Electrocoagulation mechanism

Metal hydroxides that are formed during the EC [13] have a very large empowered for the adsorption of pollutants. A current (or potential) imposed between two electrodes (iron or aluminum) immersed in an electrolyte content in a reactor generates ions in situ (Fe²⁺, Fe³⁺, Al³⁺), and likely produces a coagulant. Figure 1 shows the principle of the process with aluminum electrodes. The anodes and cathodes used can have different configurations. They can be in the form of plates, bowls, and spheres to fluidized bed, wire, rod or tube. These electrodes can be made of various metals that are chosen in such a way to optimize the treatment process. The two metals commonly used are the iron and aluminum.

The electrolytic dissolution of the aluminum anodes produces cationic species such as Al³⁺ and Al(OH)³⁺ at relatively low pH level. When the pH increases, these species are transformed into Al(OH)₃, these compounds can be condensed to form dimers such as Al₂[O](OH)₃, and Al₂(OH)₃²⁺ or even form other polymeric compounds more complex.

**Fig.1. Principle of electrocoagulation.**

The chemical reactions encountered during the production of hydroxides are the following:

The aluminum:
- The anode: the main reaction that occurs is:
  \[ \text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- \]  

There may be other secondary reactions during processes of oxidation. The formation of oxygen by electrolysis of water:
- In acid medium: \[ 2 \text{H}_2\text{O} \rightarrow 4 \text{H}^+ + \text{O}_2 + 4 \text{e}^- \]  
- In basic medium: \[ 4 \text{OH}^- + \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \]  

- The cathode: the main reaction led to the reduction of the water:
  - In acid medium:
    \[ 3 \text{H}_2\text{O} + 3 \text{e}^- \rightarrow 3/2 \text{H}_2(\text{g}) + 3 \text{OH}^- \]  
  - In solution:
    \[ \text{Al}^{3+} (\text{aq}) + 3 \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3(\text{s}) + 3 \text{H}^+ (\text{aq}) \]  
  - In basic medium:
    \[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2 \]  

Metal cations form complex with hydroxide ion the majority species depends on pH of the medium. In the case of the aluminum, there are a multitude of complex anionic and cationic. One can distinguish:
- Mono complexes such as Al(OH)³⁺, Al(OH)₂⁺, Al(OH)₄⁺
- Poly complexes such as Al₂OH₅⁺, Al₂OH₇⁺, Al₂OH₉⁺⁺, Al₃OH₁₃⁺⁺, Al₃OH₁₅⁺⁺⁺
- The amorphous species and very little soluble such as Al(OH)₃, Al₂O₃

By the in situ production of ions of aluminum Al³⁺ in an aqueous medium, there is formation of aluminum hydroxides (agents coagulants) which in function of the pH of the solution, may take the following forms (only the aluminum hydroxides mononuclear cells are presented):

\[ \text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}^{2+} + \text{H}^+ \]  
\[ \text{Al(OH)}^{2+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_2^{+} + \text{H}^+ \]
Al(OH)₂⁺ + H₂O → Al(OH)₃ + H⁺  \hspace{1cm} (9)
Al(OH)₃ → Al(OH)₄⁺ + H⁺ \hspace{1cm} (10)

Faraday’s Law:

If we consider that, the only chemical reactions taking place in the reactor EC are:

- At the anode, the oxidation of the metal,
- At the cathode, the reduction of water,

it is possible to determine the mass of dissolved metal and hydrogen formed during a electrolysis time \( t \) at a current \( I \), using Faraday’s law:

\[
m = \frac{I \cdot t \cdot M}{n \cdot F}
\]

where:

- \( m \): mass of dissolved metal or formed gas (g).
- \( I \): intensity of the imposed current (A).
- \( t \): electrolysis time (s).
- \( M \): molecular weight of the element under consideration (g/mol).
- \( F \): Faraday constant (96500 C).
- \( n \): number of electrons involved in the reaction considered.

2.4. Experimental

The electrochemical process relies on the phenomenon of electrolysis which is an electrochemical reaction based on the passage of the current between two electrodes which cause an oxidation of the organic matter present in the effluent and which degrades automatically [14]. This is achieved by a cell comprising anode and cathode immersed in the reaction medium. As soon as the electrodes are switched on, the reaction is activated spontaneously and a foam is formed on the surface of the solution and the inner wall of the reactor. This foam is due to the oxidation of fat and organic.

The assembly consists of a pyrex electrolytic cell with a volume of 400 mL, equipped with two identical aluminum electrodes of dimensions 83 mm × 51 mm × 1 mm. This corresponds to an electrode lateral surface area of \( S = 42.33 \text{ cm}^2 \). The inter-electrode distance is 4 cm is a characteristic value in EC systems [15]. The homogenization of the solution is carried out using a magnetic stirrer (the presence of bubbles permits the homogenization of the effluent, in addition to the forced recirculation of the medium). The advantage of agitation by bubbles has been put forward and their negative influence on the conductivity has been minimized by working in laminar regime inside the electrochemical reactor. This allows rapid evacuation of the micro-bubbles which will be released at the stirred reactor.

The voltage at the terminals of the electrodes is fixed by a DC generator (AL 823 ELC, maximum current 10 A, maximum potential 15 V), a potential between 3 V and 12 V is maintained constant during the experiment at ambient temperature [16]. The electrodes are pretreated with a hydrochloric acid solution for the purpose of cleaning them and avoiding their passivation. The batch experimental apparatus is shown in Figure 2. The cathode and the anode consist of many pieces of cast aluminum spaced 2 cm a part and dipped in the wastewater. EC of-containing aqueous solutions were carried out in 250 mL beakers. The total area of the electrode plates was 0.0106 m². The stirrer was employed in the electrochemical cell to maintain an unchanged composition and avoid the association of flocks in solution [17].

The voltages are directly detected on the display of the stabilized power supply. For each current and sampling time, we have a voltage value that appears directly on the power supply screen. This makes it possible to follow the evolution of the voltage and informs indirectly on the passage of the current between the electrodes.

\[ \text{Fig.2. Experimental setup of the EC system.} \]

2.5. Analytical technique

Continuous measurements of pH were made by a pH meter Consort model C931 equipped with a glass electrode containing a solution of KCl of 4M concentration. The pH meter is calibrated with pH 4, 7, 10 and 12 phosphate standards. The accuracy of the standards given by the supplier is ± 0.02 units at 20 °C. The pH of each sample taken from the agitated reactor was taken immediately. This pH makes it possible to monitor the production of the OH⁻ ions responsible for the rise in pH of the effluent [15].

Conductivity measurements were carried out using a Consort model 832 conductivity meter equipped with a platinum plate-measuring cell. This cell has an automatic compensation of the conductivity value as a function of the temperature of the solution (reference temperature: 25 °C. The measurement range is 0.01 to 200 mS/cm. With KCl solutions of 0.1, 0.01, 0.001 M the conductivity was 12.88, 1.413 and 0.148 mS/cm, respectively.

The absorbance of the different samples was measured on the clear supernatant. Previously, the clear supernatant of the raw untreated crude effluent undergoes several measurements of wavelengths in order to determine the absorption wavelength most suitable for this characterization and also to follow the
reduction of the different colors during the treatment [18]. These measurements were carried out by UV/visible spectrometry after baseline intake with deionized water. Subsequently, each sample was passed with the initial absorbance as that of the crude effluent, and therefore the values read at the predetermined wavelength represent the absorbance of the sample.

The COD can be considered as a measure of the total organic matter contained in the sample [19]. The consumption of oxygen by the sample to be analyzed causes a change in the color whose absorbance is proportional to the amount of potassium dichromate reduced and was measured as oxygen equivalent.

3. Results and discussion

The olive mill wastewater used in this study were taken from a traditional unit in the region of Essaouira. It was undergo the following pretreatment operations: decantation, Filtration and Delipidation by means of a separating funnel.

3.1. Variation in physicochemical parameters during EC

3.1.1. pH variation

From Figure 3, it was observed that the pH increases with the variation of the time until a neutral pH. This increase in pH is due to the formation at the cathode of OH⁻ hydroxide ions. Due to its amphoteric nature, Al(OH)₃ acts as a base in the medium of slightly acid margins and partially dissolves in releasing OH⁻ and Al³⁺. Free OH⁻ ions result in an increase in pH [20].

![Fig.3. Evolution of pH as a function of time.](image3)

3.1.2. Conductivity variation

According to Figure 4, the conductivity decrease as a function of the electrolysis time. This means that the concentration of the dissolved substances has decreased due to the decrease in the H⁺ concentration. As a result of their neutralization, more mobile OH⁻ ions, and the substitution of Cl⁻ ions by heavier AlCl₄ ions [21].

![Fig.4. Evolution of conductivity as a function of time.](image4)

3.1.3. COD variation

The evolution of the residual COD (chemical oxygen demand) concentration as a function of time is useful for determining optimum conditions for the degradation of harmful organic matter (COD and polyphenols) and discoloration of the marginal effluent. The evolution of the residual chemical oxygen demand (COD) over time (Figure 5) shows an abatement of more than 40% after only 60 min of treatment. A quasi stable concentration of 13.9 mg/L obtained after 120 min treatment, knowing that our margins had a COD of the order of 32.7 mg O₂/L. This value is nearby equal to 31 mg O₂/L given in Table 1 [12]. Therefore, the optimum time is 120 min. According to the curve found COD decreases as a function of the electrolysis time, which means that the freshly formed amorphous Al(OH)₃ flocs which are beneficial for rapid adsorption of the soluble organic compounds and trapping of the particles colloid. The elimination of COD is accompanied by the formation of sludge (MES) and foam.

Calculation of effectiveness:

\[
E_f = \frac{COD_0 - COD_f}{COD_0} \times 100
\]

\[
E_f = \frac{(32.7 - 13.9)}{32.7} = 57\%
\]

![Fig.5. Variation of COD as a function of time.](image5)

3.1.4. Treatment effect of discoloration

The absorbance makes possible to estimate the coloration of the effluents indirectly. We have scanned the raw samples to find the most representative wavelength of the absorbance of the effluent [22]. This wavelength corresponding to a fairly flat maximum of
the absorbance is 395 nm. Figure 6 shows the evolution of the absorbance of the effluent during the treatment. We can see a decrease in absorbance during treatment to reach a value of 0.1198 after 2 hours. It can be seen that the UV absorbance at 395 nm has dropped sharply after 120 minutes of electrolysis, the percentages of elimination of the discoloration reaches 78 %. The reduction of the COD is 57 %. Hence, the feasibility of our method of treatment for the elimination of non-biodegradable molecules thus almost complete discoloration of the effluents.

Calculation of the effectiveness of the color reduction:

\[
E_t = \frac{A_{0} - A_{f}}{A_{0}} \times 100
\]

\[
E_t = \frac{0.5546 - 0.1198}{0.5546} = 78 \%
\]

\[Fig.6. \ \text{Sample discoloration as a function of time.}\]

3.2. Effect of current density

The current density is judged as an essential parameter in EC specifically for the kinetics of reduction of COD and that of discoloration. When the current density increases, the processing time decreases due to the high dissolution of the electrodes. This results in more destabilization of the pollutant particles. Moreover, the production rate of the hydrogen bubbles increases and their size decreases when the current density increases. All of these effects are beneficial for efficient removal of the pollutant by flotation [23]. The current density is a critical parameter in EC, since it is the only one that can be controlled directly. The effect of the current density on the removal of the dyes was evaluated by repeating the same test with the same operating conditions but with different intensities. The intensity applied varies between 0.5 and 3 A depending on the capacities of the generator used. The variation of the UV absorbance at max = 395 nm depends strongly on the current imposed during the electrolysis (Figure 7). It is clear that the discoloration of the rejection of margins reached 86 % for electrolysis currents of I ≥ 3 A. This has been confirmed by several authors, when treating an azo dye using iron electrodes [24] these authors explained that high electrical currents would generate a significant level of iron ions which, confirmed that at high current densities, the anodic dissolution of aluminum increases, leading to a higher rate of necessary precipitates For the elimination of pollutants [25]. It should be noted that the size of gas bubbles at the cathode decreases (their number increases) with the increase in the intensity of the applied current. This can be beneficial for a high pollutant removal performance by hydrogen flotation [26].

\[Fig.7. \ \text{Effect of current density.}\]

3.3. Effect of salt concentration

The increase in conductivity by the addition of sodium chloride is known to reduce the voltage U between the electrodes at a constant current density due to the decrease in the resistance of the polluted water [27]. The energy consumption, which is proportional to the applied voltage between electrodes, should therefore decrease and written as follows:

\[
E = \frac{U.I.t}{V}
\]

The choice of sodium chloride results from the fact that chloride ions significantly reduce the undesirable effects of other anions [28]. Thus, the influence of the salt was studied by varying its concentration (g/L) in one liter of solutions. The other parameters were kept constant. A current density of 7038.68 A/m² (3 A) was used. The chloride ion Cl⁻ is considered the most reactive element. It is readily oxidized in aqueous solution. The results obtained (Figure 8) are expressed as percent removal of the coloration and the concentration of NaCl in the case of aluminum electrodes. The effectiveness of the color reduction was 78 % in the case of 5 g/L and 86 % in the case of 2 g/L.

An additional salt intake has a negative effect on the efficiency of the process since a decrease is recorded (78 % for 5 g/L). Overall, the EC treatment gave excellent results with the use of aluminum electrodes with a very low salinity of the order of 0.5-2 g/L (NaCl). Similar effects of improved stain removal and organic matter from margin by increasing conductivity have been reported by various authors who claim that
high conductivity is favorable for high performance of the process EC [30].

![Fig.8. Effect of salt concentration.](image)

### 3.4. Energy consumption

We have carried out a study to estimate the quantity of energy consumed to treat an effluent of vegetable waters of volume 1 L. Table 2 gives the experimental conditions of the experiment carried out during our study. The theoretical load to be circulated is obtained using Faraday’s Law. It can be seen from the results obtained that the quantity of electricity [kWh/L] is of the order of 0.9 kWh/L to obtain a final COD of 13.9 mg O₂/L, knowing that our margins had a COD of the order of 32.7 mg O₂/L, with a rate of COD abatement of the order 57 %. The energy estimate allows us to predict an energy consumption of 1 kWh/L by working at low current densities. Increasing the conductivity of the effluent and reducing the inter-electrode distance could further reduce energy consumption.

**Table 2**
The operating conditions of treatment.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Values</th>
<th>Energy consumed [kwh/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution</td>
<td>10 times</td>
<td>-</td>
</tr>
<tr>
<td>Volume of margines (L)</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Intensity [A]</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Voltage [V]</td>
<td>15</td>
<td>-</td>
</tr>
</tbody>
</table>

### 4. Conclusion

The objective of our study was to reduce the negative impact of vegetation waters on nature without prior treatment by the treatment of margins with EC as pretreatment. During the EC of margins, we determined in a first step the pH of the margins before and after the EC of margins. The acidity of the medium has been neutralized. This result makes it possible to affirm that the technique used constitutes a good choice as pretreatment. The COD of the margins of the order of 13.9 g O₂/L confirms the efficacy of EC as the main process of treatment, knowing that our margins had a COD of the order of 32.7 g O₂/L. We have carried out this treatment by varying the concentration of the margins, the margins diluted 20 times are retained as optimum, experience shows that the best results are obtained for a current density of 416 A/m² under the operating conditions, and for a time (120 min) and a quantity of added salt 2 g/L. Liquid discharges thus obtained can be directly discharged into rivers or mixed with urban wastewater to be treated by sewage treatment plants without risk of disrupting the functioning of the latter.

### References