Abstract:
The main purpose of this study was to investigate the removal of the chemical oxygen demand (COD) from olive mill wastewater (OMW) by electrocoagulation process. Olive mill wastewater (OMW) (COD about 1.1 g dm\(^{-3}\)) was treated by electrochemical reactor equipped with bipolar iron cylindrical electrodes. The effect of the experimental parameters such as voltage, pH, and NaCl concentration on COD removal was assessed. The results showed that the optimum COD removal rate was obtained at a voltage of 2V, pH ranging from 3 to 6.8 and salt concentration of 0.5g dm\(^{-3}\). At the optimum operational parameters for the experiments, electrocoagulation process could reduce COD from 1.1 g dm\(^{-3}\) to 78 mg dm\(^{-3}\), allowing direct discharge of the treated OMW as that meets the Algerian wastewater discharge standards (< 125 mg dm\(^{-3}\)).

Key words: olive mill wastewater- electrocoagulation-bipolar electrodes.

1. Introduction:
The industry of olive oil counts among the generative industries of contrary pollution and often even but that no preliminary treatment is preceded to it. This constitutes a major problem especially in the countries of the Mediterranean Basin. Olive mill wastewater is produced in large quantities (0.5-0.8 m\(^3\) treated / ton of olives) (Tsioulpas and al. 2002). In the Mediterranean countries, the production of olive mill wastewater is superior to 30 million m\(^3\) / year (Casa and al., 2003). These discharges are characterized by a very strong load of organic compounds, toxic products and high chemical oxygen demand values (COD between 50 g O\(_2\) / l and 250g O\(_2\) / l) (Benyahia and al. 2003, Andreozzi and al. 1998). Olive mill wastewaters are composed on average by 80 % of water, 18 % of organic matter and 2 % of mineral matter. The composition of the organic part is rather complex; Fats, proteins, organic acids, polyalcohol’s, pectin’s, tannins, glycosides’ and polyphenols. The mineral part consists
essentially of carbonates, phosphates, sodium and potassium (Fiestas and al., 1990). Olive mill wastewater causes severe problems in plants and phenols inhibit the growth of certain microorganisms particularly bacteria (Iconomou and al. 1998).

The ultrafiltration is a process adapted to olive mill wastewater (Borsani and al., 1996, Mameri and al., 2000 and Drouiche and al., 2004). The electrocoagulation was successfully used in the treatment of olive mill wastewater (Adhoum and al. 2004, Khoufi and al., 2007, Hanafi and al., 2010).

The electrocoagulation is an electrochemical process which allows generating during the treatment the metallic cations of iron or aluminum necessary for the formation of hydroxides in which the organic pollutants are included. The passage of the electric current in the water allows the dissolution of anodes. These bubbles of H₂ and O₂ attract the flocculated particles and float the pollutants to the surface. In the case of iron electrodes, the following mechanisms are proposed.

At the anode:

\[
\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\, \text{e}^- \quad (1)
\]

\[
2\text{H}_2\text{O}(l) \rightarrow 4\text{H}^+(\text{aq}) + \text{O}_2(g) + 4\text{e}^- \quad (2)
\]

At the cathode:

\[
\text{Fe}^{2+}(\text{aq}) + 2\, \text{e}^- \rightarrow \text{Fe(s)} \quad (3)
\]

\[
2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \quad (4)
\]

The present work investigates the efficiency of the electrocoagulation process to remove COD from OMW. The effect of electric potential, pH and NaCl concentration (NaCl used as supporting electrolyte) has been performed.

2. Materials and Methods:

Olive mill solid wastewater was obtained from an olive oil processing plant located in Tadmait (east of Algiers) and transported to the laboratory at low temperature, T= 4°C. The main physicochemical characteristics of OMW are given in the Table 1.

Table 1: The main physicochemical characteristics of OMW
<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS (g/dm$^3$)</td>
<td>49.5</td>
</tr>
<tr>
<td>pH</td>
<td>4.8</td>
</tr>
<tr>
<td>Electrical conductivity (mS/cm)</td>
<td>32</td>
</tr>
<tr>
<td>Total polyphenols(as C$_6$H$_5$OH in g/ dm$^3$)</td>
<td>2.9</td>
</tr>
<tr>
<td>COD (g/ dm$^3$)</td>
<td>28</td>
</tr>
<tr>
<td>BOD$_5$ (g/ dm$^3$)</td>
<td>17.6</td>
</tr>
</tbody>
</table>

2.1. Electrochemical reactor:

The electrochemical reactor (Figure 1) was equipped with cylindrical coaxial

![Figure1: Schematic representation of electrochemical reactor. (1) potentiostat, (2) two views of the electrochemical cell and (3) pump. Note in the electrochemical reactor shown on the left hand side a) is the outlet, b) the bipolar electrodes, c) the iron anode electrode, d) the steel cathode electrode, and e) the inlet.]
The internal electrodes were iron metal and the external electrode used as the cathode was stainless steel. The cathode had a diameter of 85 mm and length of 300 mm. The smallest iron electrode diameter was used as the anode. Two sacrificial cylindrical electrodes were placed between the two parallel electrodes without any electrical connection when an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared with the parallel side beside it. The sacrificial electrodes are known as bipolar electrodes. This electrode is commonly called the bipolar electrode. Three intern electrodes have diameters of about 55, 65, and 75 mm and height of about 275 mm.

2.2. Analysis techniques

The influence of the different experimental parameters was studied by following the change of COD during the experiments. The kinetic curves describing the abatement of the COD of the water were drawn by following the evolution of the COD of the treated water at short and regular intervals. COD values were determined by the spectrophotometer SHIMADZU, 1240CE at wave length of $\lambda=600$ nm as recommended by Standard Methods, 2005.

All experimental results presented below were triplicate and average values are presented with standard error less than ±8%.

3. Results and Discussion:

3.2. The effects of parameters on electrochemical treatment

To determine the optimum experimental conditions of the electrocoagulation process, the influence of different parameters such as electrical potential, initial pH and concentration of supportive electrolyte (NaCl) were studied. We studied the influence of the electric potential on the abatement of the DCO and the discoloration of OMW. For that purpose, we kept the initial value of the pH of OMW equal to pH=6.8 and we fixed the concentration of the salt at 0.5g / l. The figure 3 shows that the curves of the variation of the residual COD with the electrocoagulation time present the same profile, also we obtain a landing of mean value from 75 to 111 mg d'O$_2$/l after 60 minutes of manipulation.
Besides, the obtained curves by operating in 2V, 2.5V and 3V are practically confused, the electric potential of 2V was considered thus optimal with the aim of minimizing the energy consumed during the treatment.

By making vary the initial pH of OMW by simple addition of H$_2$SO$_4$ or KOH we obtain the curves of the variation of the residual DCO according to the time of electrocoagulation (figure 4). The curves of pH=3 and 6.8 present a faster decrease of the COD. Rates of 89 % and 91 % are obtained 60 min from treatment respectively. The value of pH of 6.8 is thus the optimal.

This result may be explained using the concept of a Pourbaix diagram; at positive potentials and at pH value ranging near 6, the formation of Fe(OH)$_2$ and Fe(OH)$_3$ is encountered.
We made vary the concentration of NaCl going from 0.5 to 4 g/l. For other parameters we kept the values already optimized to know pH=6.8 and U=2V.

The evolution of the residual COD in time for the various values of the salinity is represented in figure 5. The obtained curves are confused, a salinity of 0.5g / l is considered sufficient to insure the conduction in OMW to treat.

**Figure 3: Influence of pH on COD abatement. U=2V and S=0.5g/l**

**Figure 4: Influence of NaCl concentration on COD abatement. U=2V and pH=6.8.**
The conditions operating optimized for the cylindrical reactor are the following ones:

- Potential applied of 2V
- pH OMW of 6.8
- NaCl concentration of 0.5g/l

Thus, the optimum experimental conditions of the electrochemical reactor were as follows:

Table 2: Experimental results during OMW treatment and standards

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before Treatment</th>
<th>After Ultrafiltration</th>
<th>After ultrafiltration and electrocoagulation</th>
<th>standards *</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD mg dm$^{-3}$</td>
<td>28 000</td>
<td>1100</td>
<td>78</td>
<td>&lt; 125</td>
</tr>
<tr>
<td>Abatement ratio</td>
<td></td>
<td>96</td>
<td>99.8</td>
<td></td>
</tr>
</tbody>
</table>


4. Conclusion:

COD removal from olive mill wastewater by means of ultrafiltration membranes was satisfactory as the process reduces COD from 28 g dm$^{-3}$ to 1.1 g dm$^{-3}$, a COD abatement ration of about 96 %. The obtained values are still higher than the wastewater discharge standards (<125 mg dm$^{-3}$). The proposed combination of the use of ultrafiltration process as pre-treatment and an electrochemical reactor equipped with iron bipolar electrodes as second treatment was very satisfactory as the COD was further reduced to 78 mg dm$^{-3}$. This process is very efficient and may be considered ecologically friendly wastewater treatment technology. Further work needs to be carried out at pilot scale to assess the technical and economic feasibility of the process.
5. References:


