Olive pomace extract (OPE) as corrosion inhibitor for steel in HCl medium

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Objective: To explore the possibility of reuse olive pomace extract as a corrosion inhibition of steel in an acid medium (HCl, 1 mol/L), and to compare the inhibitory effect of olive pomace (OP) samples collected from three extraction process of olive oil: press process, continuous process three–phase and continuous process two–phase and olive pomace continuous process two–phase without stone and stone of olive (both fractions were separated by mill) in the eastern region of Morocco.

Methods: The electrochemical behavior of the C38 steel in HCl medium in the absence and presence olive pomace was studied by gravimetric and electrochemical techniques such as potentiodynamic polarization, linear polarization and impedance spectroscopy. The effect of temperature was also studied. The experimental data with several adsorption isotherms at different temperatures were tested to determine the standard free energy of adsorption process and the adsorption mode of inhibitor on the surface of the steel were studied.

Results: The samples of the olive pomace tested in the corrosion experiment have a very complex and heterogeneous physicochemical composition. They contain a variety of organic and inorganic compounds of very different nature and concentration, allowing the olive pomace play a very important role in anti-corrosion activity. The inhibition efficiency increased with increased olive pomace concentration to attain a maximum value of 92.1% at 1.4×10−5 with small differences among the other samples of olive pomace.

Conclusions: The use of solid waste (pomace) of crushing olives (oil mills) as green inhibitors in the fight of corrosion plays a dual function, firstly, destituting the pollution of the receiving environments (soil, water, etc.) and on the other hand, a recovery of components (bioactive) such as phenolic compounds.

1. Introduction

One major tree crop found naturally in the Mediterranean basin, Asia and Africa is the olive (Olea europaea L. (O. europaea) [1], approximately 900 million olive trees cover over 10 million hectares worldwide, 98% of which located in the Mediterranean basin are cultivated for fruit and oil production especially under Mediterranean climate conditions [2–5]. The olive oil may be produced from olives either by batch or continuous methods [6,7]. In batch (traditional) system using hydraulic presses, oil is extracted by applying pressure [8]. But the continuous system is a modernized method and based on centrifugal separation through the so-called “two and three phase continuous processes”. After the process, three “phases” are produced, i.e. oil, wastewater and olive pomace. In two phase application, no process water is added and only two phases are produced, i.e. oil and olive pomace with moisture [7,9]. The residues generated since the two phases extraction yields a semisolid pomace including both vegetal liquids and solid residues from the olives, contrary to the traditional techniques in which the solid and liquid

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residual fractions are separated and can be more easily managed.

By definition, olive pomace is the solid residue heterogeneous composed of skin, pulp, woody endocarps, seeds, pit and stone fragments of olive fruit[10-16], plus a small amount of vegetation and process water which contains the water soluble compounds of the fruits and a remaining quantity of oil. The quantity of water and soluble compounds depends on the extraction system employed. The olive oil pomace includes olives (6%-8%), water (20%-33%), seeds and pulps (59%-74%)[17], depending on the olive oil extraction processes[11]. The percent of pulp in the system of three phases pomace (traditional and continuous three phases) is 12%-35%; in olive pomace stone percent of three-phase system (traditional and continuous three phases) is 15%-45% and in the two-phase system is 12%-18%[18]. Approximately 35-45 kg of olive solid waste is typically produced from 100 kg of olives[19]. On average, 100 kg of olive produces about 20 kg of oil depending on the case and extraction systems. It also produces the following byproducts: 40 kg of olive pomace (moisture content of 50%) and over 40 kg of olive oil mill wastewaters, if the traditional system is used[20], 55 kg of olive pomace (moisture content of 50%) and over 100 kg olive oil mill wastewaters, if the continuous system is used in three phases[21], 70 kg of olive pomace (moisture content of 60%) and 3.5 kg olive oil mill wastewaters, if the continuous system is used in two phases[22]. This olive solid waste is a solid heterogeneous mixture of olive skin, pulp, woody endocarps and seeds; it composed of 83%-96% water, 3.5%-15% organics and 0.5%-2% mineral salts by weight[23].

The physicochemical characteristics of the olive pomace vary within a broad range according to the type and origin of olives, environmental conditions and storage time[24]; however, they mainly depend on the olive oil extraction process[25]. The olive solid waste is composed of 83%-96% water, 3.5%-15.0% organics and 0.5%-2.0% mineral salts by weight[26]. The characteristics of olive mill pomace in continuous two–phases process are obviously very different than those of three phase pomace (40%-45% water content), with 55%-70% moisture content and higher concentration of sugars due to the presence of vegetable water[24]. Olive pomace leachate are characterized by moderate organic load and they are highly colored[23]. Wet pomace has high chemical and biological oxygen demands (about 100 g/L and 50 g/L, respectively, some 150–200 times higher than urban solid waste[27]). The olive pomace contains approximately 3%-5% of residual oil that can be economically recovered in the pomace oil industry through extraction with n–hexanet[24]. But, the basic first stage in the extraction of the residual oil is the drying of the pomace to reduce its moisture to 8%–10%[28]. The main use of wet pomace is in the extraction of olive pomace oil either through repressing or extraction with solvents[29]. Olive pomace is a potentially harmful by–product for the environment arising from the phytotoxic and antimicrobial properties, mainly due to the phenolic and lipid constituents[23,30]; therefore, the disposal and the removal of the olive pomace make a major social, economic and environmental problem in Mediterranean olive oil producing countries[31].

Due to the recent increasing awareness of green chemistry, the integration of green chemistry principles to corrosion is one of the key issues in green inhibitor research. There is a growing need for environmentally benign inhibitor synthesis processes that do not use toxic chemicals in the synthesis protocols to avoid adverse effects in corrosion applications. The encouraging results of the anticorrosion effect obtained from olive oil mill wastewater[32], encourage us to test olive pomace extract against corrosion. To our knowledge there is no report on the effect of the addition of the olive pomace extract on the corrosion of C38 steel alloy in HCl solution. The byproducts of (O. europaea L.) have attracted growing interests in the scientific community. In the olive–tree cultivation, pruning generates a considerable volume of pomace, offering an abundant, easily available, and low–cost byproducts. Hence, scientific and technical efforts have been made to determine the value of this agricultural waste.

2. Materials and methods

2.1. Samples and materials

The olive pomace was obtained from Taourirt and Oujda Olive mills in eastern Oujda, Morocco during 2013 in olive harvesting season. Five different samples of solid–containing residues were used, three samples from three different oil extraction processes, i.e. press process [olive pomace press process (OPPP)], continuous process three–phase [olive pomace continuous process three–phase (OPCP3P)] and continuous process two–phase [olive pomace continuous process two–phase (OPCP2P)], modern olive crushing units automatically separate solid waste (pomace) into two parts: pomace without stone and stone alone, the latter used to heat water in boiler to separate the olive oil of olive oil mill wastewater, olive pomace continuous process two–phase without stone (OPCP2PWS) and stone of olive (SO). The samples were stored at 20 °C, to avoid auto–oxidation and retard microbial spoilage, until their analysis. Olive pomace was dried at 40 °C for 3 d until constant weight.
Dried olive pomace was milled and sieved (metallic mesh 1 mm) to obtain particles with a diameter of under (1.00±0.01) mm. The extraction of the olive pomace was carried out in sealed containers protected from light and immersed in a thermostatic water bath. The solvent used was water and the ratio between the weight of the olive pomace and the solvent volume was 20 g/30 mL (20 g of olive pomace extracted in 30 mL of bidistilled water). All samples are presented in Figure 1.

2.2. Physicochemical characterization of olive pomace

Dry matter was determined by oven drying at 105 °C overnight [Association of Official Analytical Chemists (AOAC), cod. 930.15, 1995]. The pH and electrical conductivity (EC) were measured using a digital display device (Consort) after homogenization of 5 g of olive pomace for 1 h in 50 mL of distilled water [33]. The pH meter was calibrated by two buffer with pH 4 and pH 7 (analytical standards and sampling of waste NM 00.2.213). For the EC and overall mineralization, a digital calibrated conductivity–meter (Radiometer CDM 230) was used to measure the conductivity of the olive pomace leachate samples. Ash content was determined by combusting for 3 h at 550 °C. The biological oxygen demand (BOD5) was determined by respirometric method (manometric) in a thermostat at 20 °C (AFNOR T 90–103) pregnant, and the chemical oxygen demand (COD) was determined using the standard method (APHA 1992) by oxidation of organic matter in the sample to 150 °C with an excess of potassium dichromate in acid and in the presence of sulfate money. Excess potassium dichromate is determined by colorimetry at 620 nm. Determination of nitrate (NO3−) was done by using sodium salicylate method. Content of orthophosphate was detected by molecular absorption spectrophotometry.

For the extraction of residual oil from the olive cakes, 250 mL of hexane was added to 100 g of the pomace. The mixture was homogenized with a T50 Ultraturrax for 1 min at 44 r/min for 10 min at 20 °C and then filtered with filter paper (Whatman No. 1). The extraction was performed in duplicate. The filtered homogenate was evaporated under vacuum in a nitrogen flow at 35 °C.

The concentrations of total phenols for each olive pomace and experimental diet were determined colorimetrically, according to a previous study [34]. Total phenolic content was determined using Folin–Ciocalteu’s reagent. Briefly, 0.2 mL of sample was mixed with 1.5 mL of Folin–Ciocalteu’s reagent.
reagent (0.2 mol/L). The reaction was kept in the dark for 5 min. Then, 1.5 mL of 7% (w/v) sodium carbonate solution was added to the mixture and the reaction was kept in the dark for 1 h. The absorbance was then read at 725 nm in a double-beam UV/vis spectrophotometer (Helios Alpha Spectrophotometer, Thermo Scientific, Bremen, Germany). Gallic acid was used as phenolic compound standard for calibration curve (20–120 μg/mL; where x and y represent gallic acid concentration (g/mL) and absorbance at 725 nm, respectively)[10].

2.3. Material of the corrosion experiments

The aggressive solution (1 mol/L HCl) was prepared by dilution of 37% HCl of analytical grade with bi-distilled water. Steel sample contained 0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron. Prior to all measurements, the steel samples were polished with different emery paper up to 1200 grade, washed thoroughly with bi-distilled water, degreased and dried with ethanol and acetone.

Weight loss was measured on sheets of pure steel of apparent surface area of 6 cm$^2$. These sheets were abraded successively with fine emery paper. The sheets were then rinsed with distilled water, degreased and dried before being weighed and immersed in the corrosive medium. The immersion time for the weight loss was from 6 h to study the effect of the concentration of the samples and 1 h at different temperatures (40, 50, 55, 65 °C) for the temperature effect.

2.4. Gravimetric and polarization measurements

Gravimetric measurements was carried out in double walled glass cell equipped with a thermostatic cooling condenser. The solution volume was 100 cm$^3$. The steel specimens used had a rectangular form (1.8 cm×1.5 cm×0.2 cm).

Electrochemical trends were carried out in a conventional three electrode cylindrical glass cell. The working electrode, in the form of a disc cut from steel, had a geometric area of 1 cm$^2$. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrode, respectively. The temperature was thermostatically controlled at 308 K. The polarisation curves were recorded with a potentiostat type EG and G 273, at a scan rate of 30 mV/min. The steel electrode was maintained at corrosion potential for 30 min and thereafter pre–polarised at ~800 mV for 10 min. The potential was swept to anodic potentials. The test solution was de–aerated for 30 min in the cell with pure nitrogen which was maintained throughout the experiments.

3. Results

3.1. Olive pomace characterization

All physicochemical analysis was repeated three times, the reported results were averaged. All results of the characterization of olive pomace tested in the present research are presented in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>OPPP</th>
<th>OPCP3P</th>
<th>OPCP2P</th>
<th>OPCP2PWS</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td></td>
<td>5.98</td>
<td>4.99</td>
<td>5.09</td>
<td>4.94</td>
</tr>
<tr>
<td>Electric conductivity</td>
<td>ms/cm</td>
<td>6.16</td>
<td>11.16</td>
<td>8.81</td>
<td>8.64</td>
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<tr>
<td>Mineralization</td>
<td>g/L</td>
<td>5.85</td>
<td>10.59</td>
<td>8.36</td>
<td>8.20</td>
</tr>
<tr>
<td>NaCl</td>
<td>g/L</td>
<td>2.36</td>
<td>4.63</td>
<td>3.58</td>
<td>3.46</td>
</tr>
<tr>
<td>Dry matter</td>
<td>g/L</td>
<td>96.8</td>
<td>94.0</td>
<td>79.6</td>
<td>80.5</td>
</tr>
<tr>
<td>Ash</td>
<td>g/L</td>
<td>3.2</td>
<td>6.0</td>
<td>20.4</td>
<td>19.5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>g/L</td>
<td>13.9</td>
<td>14.8</td>
<td>7.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Carbon content</td>
<td>g/L</td>
<td>41.45</td>
<td>39.60</td>
<td>36.00</td>
<td>37.20</td>
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<tr>
<td>BOD_5</td>
<td>g/L</td>
<td>40</td>
<td>38</td>
<td>41</td>
<td>35</td>
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<tr>
<td>Total COD</td>
<td>g/L</td>
<td>115</td>
<td>110</td>
<td>114</td>
<td>106</td>
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<tr>
<td>Dissolved COD</td>
<td>g/L</td>
<td>102</td>
<td>113</td>
<td>103</td>
<td>98</td>
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<tr>
<td>Biodegradability</td>
<td></td>
<td>0.25</td>
<td>0.35</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>Oxidizable matters</td>
<td></td>
<td>60.7</td>
<td>63.0</td>
<td>61.7</td>
<td>56.0</td>
</tr>
<tr>
<td>fat</td>
<td>g/L</td>
<td>4.60</td>
<td>3.50</td>
<td>10.05</td>
<td>7.52</td>
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<tr>
<td>Total polyphenols</td>
<td>g/L</td>
<td>0.79</td>
<td>1.7</td>
<td>0.82</td>
<td>0.78</td>
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<tr>
<td>Orthophosphate</td>
<td>mg/L</td>
<td>4.13</td>
<td>3.83</td>
<td>4.21</td>
<td>5.75</td>
</tr>
<tr>
<td>Nitrate</td>
<td>g/L</td>
<td>2.31</td>
<td>0.47</td>
<td>0.21</td>
<td>1.37</td>
</tr>
</tbody>
</table>

3.2. Olive pomace corrosion results

3.2.1. Weight loss measurements

Weight loss was measured on sheets of pure steel of apparent surface area of 6 cm$^2$. These sheets were abraded successively with fine emery paper. The sheets were then rinsed with distilled water, degreased and dried before being weighed and immersed in the corrosive medium. The immersion time for the weight loss was from 6 h to study the effect of the concentration of the samples and 1 h at different temperatures (313, 323, 328 and 338 K) for the temperature effect.

The data of Table 2 represent the results obtained from weight loss experiments: the corrosion rate: $W$ (mg/cm$^2$·h) and the inhibition efficiency percentage ($E_{w%}$) of mild steel coupons in 0.1 mol/L HCl solution at 308 K (1 °C=273 Kelvin) after 6 h of immersion period in the presence of different concentrations of olive pomace.

The inhibition efficiencies ($E_{w%}$) was determined by the relation equation (1):

$$E_{w%} = 100\times \left(1- \frac{W_{corr}}{W_{corr}^-}\right)$$  \hspace{1cm} (1)

Where, $W_{corr}$ and $W_{corr}^-$ are the corrosion rates of steel with
3.2.2. Electrochemical polarisation measurements

The cathodic and anodic polarisation curves of C38 steel in 1 mol/L HCl in the absence and presence of different samples of olive pomace at different concentrations at 308 K are presented in Figures 2 and 3.

Table 3 gives the values of corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope ($\beta_c$) of olive pomace samples in 1 mol/L HCl. In the case of polarisation method, the relation (2) determines the inhibition efficiency ($E%$):

$$E\%=100\times \left(1-\frac{I_{\text{corr}}}{I_{\text{corr}}^{\text{blank}}} \right)$$

Where, I_{corr}^{\text{blank}} and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

3.2.3. Electrochemical impedance spectroscopy measurements (EIS)

The corrosion behavior of steel in acidic solution 1 mol/L HCl in the absence and presence of the olive pomace samples was also investigated by EIS method at 308 K after 30 min of immersion (Figures 4 and 5).

The inhibition efficiency can be calculated by the following formula (3):

$$E_{\text{corr}}^\%=100\times \left(1-\frac{R_t}{R_{\text{corr}}} \right)$$

Where, R_t and R_{corr} are the charge transfer resistances in inhibited and uninhibited solutions, respectively.
The Potentiodynamic polarization parameters including corrosion current densities (Icorr), corrosion potential (Ecorr), cathodic Tafel slope (βc), anodic Tafel slope (βa), and inhibition efficiency (%E) are shown in Table 3. The values of the polarization resistance were calculated by subtracting the high frequency intersection from the low frequency intersection, double layer capacitance values were obtained at maximum frequency (fmax), at which the imaginary component of the Nyquist plot is a maximum, and calculated using the following equation (4).

\[
C_d = \frac{1}{2\pi f \sigma L_i} \tag{4}
\]

Where, \(C_d\) represents double layer capacitance (μF cm\(^{-2}\)); \(f\) represents maximum frequency (Hz) and \(R_i\) is charge transfer resistance (Ω cm\(^{-2}\)).

The impedance parameters derived from these investigations are listed in Table 4.

3.2.4. Effect of the temperature

3.2.4.1. Weight loss, corrosion rates and inhibition efficiency

The composition of the medium and its temperature are essential parameters affecting the phenomenon of the corrosion, the effect of the absence and presence of olive pomace tested at concentration 1.4×10\(^{-5}\) mol/L during 1 h of immersion on the corrosion of steel in 1 mol/L HCl solution was studied by using weight–loss at different temperatures from 313 K to 338 K. The inhibition efficiency (Ew%) is calculated a various temperatures as follows equation (5). The corresponding data are shown in Table 5.
Table 5
Effect of temperature on the corrosion rate of steel at various samples of olive pomace in 1h of immersion at the concentration 1.4×10⁻⁵ mL/L.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Temperature (K)</th>
<th>W [g/(cm²·h)]</th>
<th>%E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (HCl)</td>
<td>313</td>
<td>2.070</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>2.519</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>3.067</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>4.019</td>
<td>–</td>
</tr>
<tr>
<td>OPPP</td>
<td>313</td>
<td>0.355</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.607</td>
<td>75.9</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>0.812</td>
<td>73.5</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>1.217</td>
<td>69.7</td>
</tr>
<tr>
<td>OPCP3P</td>
<td>313</td>
<td>0.403</td>
<td>80.5</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.554</td>
<td>78.0</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>0.771</td>
<td>74.9</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>1.370</td>
<td>65.9</td>
</tr>
<tr>
<td>OPCP2P</td>
<td>313</td>
<td>0.327</td>
<td>84.2</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.498</td>
<td>80.2</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>0.684</td>
<td>77.7</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>1.042</td>
<td>74.1</td>
</tr>
<tr>
<td>OPCP2PWS</td>
<td>313</td>
<td>0.210</td>
<td>89.9</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.365</td>
<td>85.5</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>0.668</td>
<td>78.2</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>1.137</td>
<td>71.7</td>
</tr>
<tr>
<td>Stone of olive</td>
<td>313</td>
<td>0.343</td>
<td>83.4</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.585</td>
<td>76.8</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>0.837</td>
<td>72.7</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>1.474</td>
<td>63.3</td>
</tr>
</tbody>
</table>

\[ E\% = 100 \times \left( \frac{W_{corr} - W_{cor}}{W_{cor}} \right) \]  \hspace{1cm} (5)

Where, \( W_{corr} \) and \( W_{cor} \) are the corrosion rates of steel in 1 mol/L HCl in the absence and presence of olive pomace, respectively.

3.2.4.2. Thermodynamic parameters

To calculate activation thermodynamic parameters of the corrosion reaction at various temperatures (313–338 K) in the presence and absence of various temperatures of the olive pomace samples at 1 h of immersion, such as the energy \( E_a \), the entropy \( \Delta S^o_{ads} \) and the enthalpy \( \Delta H^o_{ads} \) of activation, Arrhenius equations 6–8 and its alternative formulation called transition state equations 7–9 were used[36,37].

\[ W = K \exp \left( - \frac{E_a}{RT} \right) \]  \hspace{1cm} (6)

\[ \log (w) = - \frac{E_a}{RT} + K \]  \hspace{1cm} (7)

\[ W = \frac{RT}{Nh} \exp \left( \frac{\Delta S^o_{ads}}{R} \right) \exp \left( \frac{\Delta H^o_{ads}}{RT} \right) \]  \hspace{1cm} (8)

\[ \log(W/T) = \left( \log \left( \frac{R}{Nh} \right) \right) + \left( \frac{\Delta S^o}{R} \right) - \frac{\Delta H^o}{RT} \]  \hspace{1cm} (9)

Where \( T \) is the absolute temperature, \( K \) is a constant, \( E_a \) is the apparent activation corrosion energy, \( R \) is the universal gas constant, \( A \) is the Arrhenius pre-exponential factor, \( h \) is Planck’s constant, \( N \) is Avogadro’s number, \( \Delta S^o_{ads} \) is the entropy of activation and \( \Delta H^o_{ads} \) is the enthalpy of activation.

Figure 5. Nyquist diagrams for steel electrode with and without at OPCP2PWS and stone of olive after 30 min of immersion in 1 mol/L HCl for various concentrations.

Figures 6 and 7 Show the Arrhenius plot for mild steel corrosion in 1 mol/L HCl in the absence and presence at different temperatures of olive pomace samples. The activation energy \( E_a \) is calculated from the slope of the plots of \( \log(W_{corr}) \) vs. \( 1/T \) (Figure 6) for olive pomace samples. Plots of \( \log(W_{corr}/T) \) vs. \( 1/T \) give a straight line with a slope of \( \Delta H^o/\Delta S^o_{ads}/R \) as shown in (Figure 7). The values of \( E_a, \Delta H^o \) and \( \Delta S^o \) are listed in (Table 6).
Figure 7. The relation between log (W/T) vs. 1000/T for steel at different temperature at concentration 1.4×10^−5 mL/L of the different samples of olive pomace.

Table 6
Activation parameters of the dissolution of mild steel in 1 M HCl in the absence and presence of different concentrations of olive pomace at various temperatures 313 to 338 K.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tp  °K</th>
<th>Ea (kJ/mol)</th>
<th>ΔH°ads (kJ/mol)</th>
<th>Ea−ΔH°ads (kJ/mol)</th>
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</thead>
<tbody>
<tr>
<td>Blank</td>
<td>313</td>
<td>23.8</td>
<td>21.1</td>
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<tr>
<td></td>
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<td>338</td>
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<tr>
<td>OPPP</td>
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<td>41.1</td>
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4. Discussion

4.1. Olive pomace characterization

The acidic pH is a fundamental characteristic of olive pomace with values between (4.94 and 5.98) for different processes trituration of olive oil, these results are confirmed with the values obtained by other several researches, pH in continuous two phases process is 4.9 to 6.8[38-40]. The conductivity measurement is a good assessment of the degree of mineralization of olive pomace, where each ion is characterized by its concentration and specific conductivity, the electrical conductivity is strongly related to the concentration of dissolved substances and to their nature; in the case of olive pomace, the conductivity varies from one system of trituration to another, and it can take values ranging between 6 and 11 ms/cm, but it is low for the stone of olive (2 ms/cm). The results obtained in our study are higher to those found in the literature, the electrical conductivity (EC) in continuous two phases process is 1.78−5.24 dS/m[41-43], the highest concentrations of the salt present in these residues due to salting practices for the conservation of olives before crushing in addition to the natural wealth of olive oil mill wastewaters dissolved minerals.

Dry matter in the different samples of olive pomace is changed between 79.6%−96.8%, these results are confirmed with the values obtained by several researches. Dry matter in the solid residue (pressing process and continuous three phases process) is 87.1%−94.4%[44,45].

Ash in the different samples of olive pomace is changed between 3%−20%, Ash percent in the solid residue (pressing process and continuous three phases process) is 1.7%−4.0%, but in continuous two phases process is 1.42%−4.00%[18]. The results obtained in our study are higher to those found in the literature; the ash content is normally low of 3% to 5%. High levels we encounter were due to the lack of washing and presence on the ground picked olives.

The fat in the different samples of olive pomace was changed between 3.5%−4.6% for the OPPP and OPCP3P, but was higher for OPCP2P and OPC2PWS. For the stone olive, the percent of the fats was low. The results obtained in our study are higher to those found in the literature.

The physicochemical characteristics of the olive pomace vary within a broad range according to the type and origin of olives, environmental conditions, storage time and the extraction process; values of the dry matter, mineral matter and fat found by Mennane et al. are: dry matter: 51.8%−74%; mineral matter: 2.1%−13%; fat: 7.6%−11.2%[46]. The dry matter is greater than that of previous studies[47,48], and similar to that of Aloui F et al.[49], then the ash is lower than those of Aloui F et al[49]. For Chaabane K, the dry matter for the raw olive pomace of the press process is dry matter: 70.2%; mineral matter: 3.7%; fat: 8.1%, but for the continuous process (three and two phases) dry matter: 40.6%; mineral matter: 2.4%; fat: 9.1%[50].

Lipids percent in the solid residue (pressing process and continuous three phases process) is 3.5%−8.72%, but in the continuous two phases process is 3.76%−18.0%[18,26,41,43,51,52].

The olive pomace are rich in organic matter expressed in terms of BOD5 (biological oxygen demand) and COD (chemical oxygen demand). From the present results, the values obtained for the process press (OPPP) are about 40 g/L for BOD5 115 g/L for COD, for continuous process three−phases (OPCP3P) we found for (BOD5: 38 g/L) and (COD: 110 g/L) and for continuous process two−phases (OPCP2P) a value of about (BOD5: 41 g/L) and (COD:114 g/L) and for continuous process two−phases with stone (OPCP2PWS)
The nitrates $\text{NO}_3^-$ fertilization, fruit and mature vegetative organs. ponds. However, they have a beneficial effect by playing two-phases, it is 4.21 mg/L, and for the continuous process olive pomace samples are due to the presence of the orthophosphates ($\text{PO}_4^{3-}$) concentrations are varied with process type of trituration of olive, for the press process, it is 4.13 mg/L, the continuous process three-phases process, it is 3.83 mg/L, and for the continuous process two-phases, it is 4.21 mg/L, and for the continuous process two-phases without stone, it is 5.75 mg/L, and for stone of olive, it is 4.76 mg/L. Phosphorus is a biogenic element essential to the growth of algae. High levels of this element in olive pomace can cause eutrophication in storage ponds. However, they have a beneficial effect by playing a regulatory role: they promote all the phenomena of fertilization, fruit and mature vegetative organs.

The nitrates $\text{NO}_3^-$ concentrations are varied with process type of trituration of olive, for the press process, it is 2.31 g/L, the continuous process three-phases, it is 0.47 g/L, and for the continuous process two-phases, it is 0.21 g/L, and for the continuous process two-phases without stone, it is 1.37 g/L and for the stone of olive, it is 0.04 g/L.

4.2. Olive pomace corrosion results

4.2.1. Weight loss measurements

The addition of different samples of the olive pomace reduces the corrosion rate in HCl solution. The inhibitory effect increased with the increase of olive pomace concentration; $E_p$ reaches a maximum of 84.3%, 88.2%, 88.5%, 92.1% and 85.9% at 4.10–5.00 mL/L concentration for (OPPP), (OPCP3P), (OPCP2P), (OPCP2PWS) and stone of olive samples respectively. The effectiveness of the different olive pomace samples are due to the presence of the heteroatom such as N, O and S. The physicochemical composition of olive pomace is rich in organic matter. However, we can classify samples tested according to the efficiency of growth inhibition as follows: OPPP<stone of olive<OPCP3P<OPCP2P<OPCP2PWS. We can conclude that olive pomace samples extracts are good inhibitors of corrosion of steel in 1 mol/L HCl, and the samples tested achieved high efficiencies even at low concentrations.

4.2.2. Electrochemical polarisation measurements

The recording of the anodic and cathodic polarization curves has been conducted to obtain information about the action of inhibitor on the partial corrosion processes; the results showed that the addition of olives pomace samples decreased current density, and the decrease was more pronounced with the increase of the inhibitor concentration. The Tafel plots indicated that the mechanism of hydrogen reduction was activation control, and the presence of olive pomace does not affect the anodic Tafel slope specially for the samples OPPP, OPCP3P, and OPCP2P indicating that the mechanism of H$^+$ oxidation was not modified with the olive pomace concentration. But, the polarization curves of steel in molar HCl with and without the olive pomace samples (OPCP2PWS and stone of olive) showed that the addition of the inhibitor decreased the anodic current densities in the studied domain of potential. It could be concluded that the presence of the olive pomace didn’t affect the anodic dissolution of steel as well but not for the cathodic reduction of hydrogen ions. The mode of action of the inhibitor (different olive pomace samples) was perfectly cathodic.

The inhibition efficiency reached 83.3%, 85.7%, 85.9%, 93.8% and 96.3% at concentration 1.4x10^{-7} mL/L for the different samples of olive pomace, i.e. OPPP, OPCP3P, OPCP2P, OPCP2PWS and stone of olive samples, respectively. This phenomenon was interpreted by the adsorption of the olive pomace on steel surface leading to the increase of the surface coverage $\theta$ defined by $E_p/100$, $E_p$ increases with inhibitor concentration. We may conclude that olive pomace samples are effective inhibitors of steel corrosion in molar HCl acid.

4.2.3. EIS measurements

It is visible from the present study results that the obtained impedance diagrams for different olive pomace samples had a semi-circular appearance, indicating that a charge transfer process mainly controled the corrosion of steel[55]. In fact, the presence of olive pomace samples enhanced the value of the transfer resistance in acidic solution. EIS study showed that the olive pomace samples tested were an efficient inhibitor.

The general shape of the curves was almost similar for all olive pomace samples and the shape was maintained throughout the whole concentration, indicating that almost no change in the corrosion mechanism occurred due to the inhibitor addition[56], the $R_t$ values increased with the increase of the concentration of the olive pomace. The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the EIS. Also, inhibition efficiency values obtained from the gravimetric method agreed with those obtained from the Tafel extrapolation.
4.3. Effect of the temperature

4.3.1. Weight loss, corrosion rates and inhibition efficiency

Results showed that the corrosion rates of steel in 1 mol/L HCl were lower in the presence of olive pomace samples compared to the blank acid solution. The corrosion rate increased with increase in temperature with the highest values obtained at 338 K. Also, the inhibition efficiency decreased with increasing temperature, indicating that at higher temperatures, dissolution of steel predominated on inhibitor adsorption. E% was still significant even at high temperature 69.7%, 65.9%, 74.1%, 71.7% and 63.3% of the different samples of olive pomace (OPP, OPCP3P, OPCP2P, OPCP2PWS and stone of olive samples respectively) at concentration 1.4×10^{-5} mol/L at 338 K, which suggested possible desorption of some of the adsorbed inhibitors from the metal surface at higher temperatures. Such behavior showed that the additive was physically adsorbed on the metal surface[56-58].

4.3.2. Thermodynamic parameters

Inspection of the data showed that the activation energy was higher in the presence of different olive pomace samples than in its absence. The increase in $E_a$ with olive pomace concentration as shown in the present result was typical of physisorption mechanism[59]. The decrease of the olive pomace efficiencies with temperature rise led to a higher value of $E_a$ when compared to that in an uninhibited acid, which was interpreted as an indication for an electrostatic character of the inhibitor’s adsorption[60]. But, $E_a$ variation is not the unique parameter to affirm such mode of adsorption. Others can be free adsorption enthalpy $\Delta G_{ads}$ and enthalpy $\Delta H_{ads}$. The positive values of $\Delta H_{ads}$ in both the absence and presence of additives of olive pomace samples indicated the endothermic nature of the activation process[61]. It can also be seen from the present study that $E_a$ and $\Delta H_{ads}$ varied in the same manner but the values of $\Delta H_{ads}$ were lower than that of $E_a$. This reflects the formation of an ordered stable layer of inhibitor on the steel surface[62]. From previous data, we can conclude that olive pomace is an effective inhibitor. This phenomenon is often interpreted with physical character and formation of an adsorption film of electrostatic character[63].

The samples of the olive pomace collected from the Eastern Morocco have very complex and heterogeneous physicochemical composition. They contain a variety of organic and inorganic compounds of very different nature and concentrations. This variation is mainly due to the following factors: ripening stage of olives, climatic conditions, variety of olive cultivation system, geographic location, and time of storage before crushing olives, techniques and storage space, nature conservation olives and process for extracting olive oil which is the most important element.

Due to the lack of regulations governing the use and disposal of most organic inhibitors, which are, according to the literature, harmful to the environment, it is best to search for inhibitors of corrosion from natural resources such as plant extracts or reuse of effluent from industrial units of mills as in our case study, to reduce the organic load and to enhance the main constituents of these by-products.

From the overall studies, the following conclusions could be deduced that the inhibition efficiency increased with increase of olive pomace concentration to attain a maximum value of 92.1% at 1.4×10^{-5} with small differences between the samples; the inhibition efficiency of olive pomace decreased with the rise of temperature; the inhibition efficiency of olive pomace varied slowly with the temperature; the olive pomace acted as a cathodic inhibitor without modifying the hydrogen reduction mechanism; the presence of olive pomace increases the activation energy of the corrosion process and the inhibitor was physically adsorbed on the steel surface. Therefore, there is a need for guidelines to manage these wastes through technologies that and minimize their environmental impact and lead to a sustainable use of resources. The acidity, the high organic load, and the phototoxic material (high phenol, lipid and organic acid concentrations) of the solid waste present no problems for such application such as the corrosion.

Although the above utilization of olive pomace is technically feasible, it is too early to achieve large-scale application such as in industrial areas.

Conflict of interest statement

We declare that we have no conflict of interest.

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