Prickly Pear Seed Oil Extract: A Novel Green Inhibitor for Mild Steel Corrosion in 1 M HCl Solution

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Prickly pear seed oil extract (PPSO1) was tested as corrosion inhibitor for mild steel in 1M HCl. Weight loss measurements, potentiodynamic polarizations and electrochemical impedance spectroscopy (EIS) methods are used. The inhibiting action increases with the concentration of the tested inhibitor. The highest efficiency 90% is obtained at 5 g/L of PPSO. We note good agreement between gravimetric and electrochemical methods (potentiodynamic polarization and EIS). Effect of temperature is also studied between 298 K and 328 K; PPSO presents best inhibition efficiency even at elevated temperature. Polarization measurements show also that PPSO1 act as good mixed inhibitor. PPSO1 is adsorbed on the steel surface according to a Langmuir isotherm adsorption model. The thermodynamic data of activation are determined. In this study fatty acid composition contents of prickly pear seeds were determined. Palmitic acid contents of seed oils ranged between 7.3% (PPSO15) and 12.6% (PPSO3). While oleic acid contents varied between 15.0% (PPSO12) and 20.8% (PPSO5), linoleic acid contents ranged from 61.8% (PPSO16) to 68% (PPSO15).

Keywords: Corrosion; Steel; Inhibition; Prickly pear seed oil extract; Acid medium, Fatty Acids, GC.

1. INTRODUCTION

Steel is widely used in most industries because of its low cost and availability for the manufacture of reaction vessels such as cooling tower reservoirs, pipelines, etc…[1]. Acid solutions
are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulfuric acids are widely used in the pickling processes of metals [2]. Organic compounds containing heteroatoms are commonly used to reduce the corrosion attack on steel in acidic media.

These compounds adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion process [3-8]. The toxic nature of these organic inhibitors has required research activities in recent times toward finding alternative environmentally friendly acid corrosion inhibitors.

These advantages have incited us to draw a large part of program of our laboratory to examine natural substances as corrosion inhibitors such as: Menthol [9], Rosemary oil [10-12], Thymus oil [13-14], Artemisia [15-17], Black Pepper Extract [18], Eugenol and Acetyleneugenol [19], Ginger [20], Lavender oil [21], Limonene [22], Pulegone and Pulegone oxide [23], Jojoba oil [24] and Bifurcara bifurcata extract [25].

Salvia aucheri mesatlantica [26], Pennyroyal Mint oil [27], Argan oil [28], Argania plant extract [29] and Argania spinosa Kernels Extract and Cosmetic Oil [30].

The encouraging results obtained by naturally oils as corrosion inhibitor of steel in acid solutions permit to test more substance oils. There is no report to our knowledge on the effect of the addition of prickly pear seed oil (PPSO) extract on the corrosion of C38 steel alloy in hydrochloride solution.

Prickly pear (Opuntia ficus-indica L.), belong to Cactaceae family, is a tropical or subtropical plant originally grown in South America and cultivated in dry regions as an important nutrient and food source [31].

Recently, the demand for nutraceuticals, natural ingredients and health-promoting foods increased constantly [32-35]. The main studies on the Opuntia fruits were the chemical analysis of pulp, skin and seeds [36], analysis of volatile constituents of pulp [37-38], use of pulp in juice production [39], production of alcoholic beverage [40], jam production [41] and the production of cocoa butter equivalents from prickly pear juice fermentation by an unsaturated fatty acid auxotroph [42].

The Opuntia ficus-indica (OFI) fruit, commonly known as prickly pear, is an important and abundant potential raw material for the Moroccan industry. Within the last decade, prickly pear fruits have become an important crop in the semi-arid lands of Morocco, where they play a strategic role in subsistence agriculture.

Efforts are currently made to develop the fruit production and to find new applications in the food industries. With an average production of about 800 000 tons per annum from which 50% is exported mainly to European markets [43].

The aim of this study was to determine the Fatty acid methyl esters composition of prickly pear seed oil extract (PPSO1) in Morocco, and (ii) to study the inhibitive action of (PPSO1) as a cheap, eco friendly and naturally occurring substance on corrosion behaviour of C38 steel in 1M HCl by gravimetric method and electrochemical techniques such as potentiodynamic polarisation, linear polarisation and electrochemical impedance spectroscopy (EIS).
2. MATERIALS AND METHODS

2.1. Prickly pear seed oil extract solution

The samples of prickly pear seed oil extract were collected in different locations and provinces of Morocco (Table 1).

Table 1. Prickly pear seed oil extract samples collected different locations.

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Locations</th>
<th>Sample codes</th>
<th>Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPSO1</td>
<td>Imimkourne (Ait Baha)</td>
<td>PPSO9</td>
<td>Ait-Baamrane (Sidi Ifni)</td>
</tr>
<tr>
<td>PPSO2</td>
<td>Hilala (Ait Baha)</td>
<td>PPSO10</td>
<td>Belfaâ (Tiznit)</td>
</tr>
<tr>
<td>PPSO3</td>
<td>Asdim (Ait Baha)</td>
<td>PPSO11</td>
<td>Mesti (Tiznit)</td>
</tr>
<tr>
<td>PPSO4</td>
<td>Tizi ntarga ntouchka (Ait Baha)</td>
<td>PPSO12</td>
<td>Taksbit (Tiznit)</td>
</tr>
<tr>
<td>PPSO5</td>
<td>Idawgnidif (Ait Baha)</td>
<td>PPSO13</td>
<td>Biougra (Ait Baha)</td>
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<tr>
<td>PPSO6</td>
<td>Ltnine (Ait Baha)</td>
<td>PPSO14</td>
<td>Tamri (Agadir)</td>
</tr>
<tr>
<td>PPSO7</td>
<td>Sbouya (Tiznit)</td>
<td>PPSO15</td>
<td>Ouâroune (Guelmim)</td>
</tr>
<tr>
<td>PPSO8</td>
<td>Khmis (Ait Baha)</td>
<td>PPSO16</td>
<td>Kleaa (Ait Melloul)</td>
</tr>
</tbody>
</table>

2.2. Fatty acid composition

The fatty acid composition was determined following the ISO standard ISO 5509:2000 (ISO 2000) [44]. In brief, one drop of the oil was dissolved in 1 mL of n-heptane, 50 µg of sodium methyleate was added, and the closed tube was agitated vigorously for 1 min at room temperature. After addition of 100 µL of water, the tube was centrifuged at 4500 × g for 10 min and the lower aqueous phase was removed. Then 50 µL of HCl (1 mol with methyl orange) was added, the solution was shortly mixed, and the lower aqueous phase was rejected. About 20 mg of sodium hydrogen sulphate (monohydrate, extra pure; Merck, Darmstadt, Germany) was added, and after centrifugation at 4500 × g for 10 min, the top n-heptane phase was transferred to a vial and injected in a Agilent Technologies 6890N gas chromatograph equipped with a capillary column (30 m x 0.32 mm; Supelco, Bellefonte, PA, USA) and flame ionization detection. The column was programmed to increase from 135 to 160°C at 2°C/min and from 160 to 205°C at 1.5°C/min; the detection temperature was maintained at 220°C, injector temperature 220 °C. The vector gas was helium at a pressure of 5520 Pa. Peaks were identified by comparing retention times with those of standard fatty acid methyl esters.

2.3. Weight loss measurements

Coupons were cut into $2 \times 2 \times 0.08$ cm$^3$ dimensions having composition (0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance) are used for weight loss measurements. Prior to
all measurements, the exposed area was mechanically abraded with 180, 320, 800 grades of emery papers. The specimens are washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 80 cm$^3$. The immersion time for the weight loss is 8 h at 298 K.

2.4. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte is 0.056 cm$^2$.

Potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from $-800$ mV to $-400$ mV at 298 K. The solution test is there after de-aerated by bubbling nitrogen.

Gas bubbling is maintained prior and through the experiments. In order to investigate the effects of temperature and immersion time on the inhibitor performance, some test were carried out in a temperature range 298–328 K.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at $E_{corr}$ after immersion in solution without bubbling.

After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

2.5. Solutions preparation

The solution 1M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water. The solution tests are freshly prepared before each experiment by adding the oil directly to the corrosive solution. The test solutions were freshly prepared before each experiment by adding the oil directly to the corrosive solution. The test solution is there after de-aerated by bubbling nitrogen. Gas pebbling is maintained prior and through the experiments. Experiments were carried out in tripllicate to ensure the reproducibility.
3. RESULTS AND DISCUSSION

3.1. Fatty acid composition

The fatty acid composition of the seed oils from the Opuntia ficus-indica is given in Table 2.

**Table 2.** Fatty acid compositions of prickly pear seed oil (%).

<table>
<thead>
<tr>
<th></th>
<th>C14:0</th>
<th>C15:0</th>
<th>C16:0</th>
<th>C16:1</th>
<th>C17:0</th>
<th>C17:1</th>
<th>C18:0</th>
<th>C18:1</th>
<th>C18:2</th>
<th>C18:3</th>
<th>C20:0</th>
<th>C20:1</th>
</tr>
</thead>
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<td>0.1</td>
<td>&lt; 0.1</td>
<td>12.5</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3.3</td>
<td>17.3</td>
<td>65.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
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<td>&lt; 0.1</td>
<td>12.5</td>
<td>0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3.2</td>
<td>18.9</td>
<td>63.7</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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<td>0.6</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>3.5</td>
<td>19.7</td>
<td>62.6</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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<td>12.2</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>_</td>
<td>3.3</td>
<td>17.2</td>
<td>65.8</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
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<td>0.7</td>
<td>0.1</td>
<td>_</td>
<td>3.5</td>
<td>20.8</td>
<td>61.9</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
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<td>12.3</td>
<td>0.6</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>3.4</td>
<td>18.3</td>
<td>63.8</td>
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<td>0.5</td>
<td>0.2</td>
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<td>0.6</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>3.2</td>
<td>18.0</td>
<td>64.7</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
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<td>&lt; 0.1</td>
<td>12.3</td>
<td>0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3.2</td>
<td>18.7</td>
<td>63.7</td>
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<td>0.2</td>
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<tr>
<td>PPSO9</td>
<td>0.1</td>
<td>_</td>
<td>11.0</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>_</td>
<td>3.2</td>
<td>17.6</td>
<td>66.3</td>
<td>0.2</td>
<td>0.2</td>
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</tr>
<tr>
<td>PPSO10</td>
<td>0.1</td>
<td>_</td>
<td>11.8</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>3.2</td>
<td>18.1</td>
<td>64.4</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>PPSO11</td>
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<td>&lt; 0.1</td>
<td>12.0</td>
<td>0.7</td>
<td>0.1</td>
<td>_</td>
<td>3.1</td>
<td>17.4</td>
<td>64.9</td>
<td>0.3</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>PPSO12</td>
<td>0.1</td>
<td>&lt; 0.1</td>
<td>12.4</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3.1</td>
<td>15.0</td>
<td>66.9</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>PPSO13</td>
<td>0.1</td>
<td>_</td>
<td>11.9</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>3.3</td>
<td>16.5</td>
<td>66.0</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
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<td>PPSO14</td>
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<td>_</td>
<td>12.3</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>3.2</td>
<td>17.2</td>
<td>64.7</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>PPSO15</td>
<td>0.1</td>
<td>_</td>
<td>7.3</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>3.2</td>
<td>20.0</td>
<td>68.0</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>PPSO16</td>
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<td>_</td>
<td>12.1</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>_</td>
<td>3.5</td>
<td>20.0</td>
<td>61.8</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Myristic acid (C14:0), Pentadecanoic acid (C15:0), Palmitic acid (C16:0), Palmitoleic acid (C16:1), Heptadecanoic acid (C17:0), Heptadecenoic acid (C17:1), Stearic acid (C18:0), Oleic acid (C18:1), Linoleic acid (C18:2), Linolenic acid (C18:3), Arachidic acid (C20:0), Gadoleic acid (C20:1).

As usual for the fatty acid composition in prickly pear seeds, there is a wide variation in fatty acid composition (Table 2). The major fatty acids found in cactus seed oils had palmitic, oleic, and linoleic acids. Palmitic acid contents of seed oils ranged between 7.3% (PPSO15) and 12.6% (PPSO3).

While oleic acid contents varied between 15.0% (PPSO12) and 20.8% (PPSO5), linoleic acid contents ranged from 61.8% (PPSO16) to 68% (PPSO15). These results are in good agreement with those reported by Ramadan and Morsel [45] and Coskuner and Tekin [46]. The observed differences in the concentrations of oleic, palmitic and linoleic acid could be due to maturity of the fruit.

According to the literature, saturated fatty acid content of Opuntia fruit increases with maturation [46]. The data indicate that cactus grown at the different locations are significantly differ from each other in individual fatty acid contents. It is well known that the fatty acid composition of cactus seeds is very much influenced by the climatic factors, soil type and genetic factors under which they are grown [45].
3.2. Effect of concentration

3.2.1. Polarization curves

Potentiodynamic polarisation curves of C38 steel in 1M HCl in the absence and presence of prickly pear seed oil extract (PPSO1) at different concentrations at 298 K are presented in Fig. 1. The corrosion parameters including corrosion current densities ($I_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), cathodic Tafel slope ($\beta_c$), anodic Tafel slope ($\beta_a$) and inhibition efficiency ($E_I$ %) are listed in Table 3. In this case, the inhibition efficiency is defined as follows:

$$E_I\% = (1 - \frac{I'_{\text{corr}}}{I_{\text{corr}}})\times100$$

(1)

Where $I_{\text{corr}}$ and $I'_{\text{corr}}$ are current density in absence and presence of prickly pear seed oil extract respectively. We noted that $I_{\text{corr}}$ and $I'_{\text{corr}}$ was calculated from the intersection of cathodic and anodic Tafel lines.

![Figure 1](image.png)

**Figure 1.** Potentiodynamic polarisation curves of C38 steel in 1M HCl in the presence of different concentrations of prickly pear seed oil extract.

The examination of Fig. 1 and Table 3 reveals that the corrosion current hence, it can be said to be a mixed-type inhibitor in 1 M HCl. We also remark that the cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the PPSO1 does not modify the mechanism of this process (Fig.1) [47]. The inhibition efficiency reaches 90% at 5g/L. Consequently, PPSO1 is a good inhibitor.
Table 3. Electrochemical parameters of C38 steel at various concentrations of prickly pear seed oil extract in 1M HCl and corresponding inhibition efficiency.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Concentrations (g/l)</th>
<th>(E_{\text{corr}}) (mV/SCE)</th>
<th>(I_{\text{corr}}) (µA/cm(^2))</th>
<th>(b_c) (mV/dec)</th>
<th>(b_a) (mV/dec)</th>
<th>(E_i) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>0.0</td>
<td>-567</td>
<td>94</td>
<td>99</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td>PPSO1</td>
<td>0.5</td>
<td>-627</td>
<td>51</td>
<td>99</td>
<td>51</td>
<td>45</td>
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<tr>
<td></td>
<td>2.0</td>
<td>-698</td>
<td>42</td>
<td>90</td>
<td>46</td>
<td>55</td>
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<tr>
<td></td>
<td>3.0</td>
<td>-668</td>
<td>28</td>
<td>93</td>
<td>43</td>
<td>70</td>
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<tr>
<td></td>
<td>4.0</td>
<td>-637</td>
<td>13</td>
<td>95</td>
<td>36</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>-674</td>
<td>9</td>
<td>91</td>
<td>34</td>
<td>90</td>
</tr>
</tbody>
</table>

3.2.2. Electrochemical impedance spectroscopy measurements

In order to get more information about the corrosion behavior of steel, in acidic solution with and without PPSO, electrochemical impedance spectroscopy (EIS) measurements have been carried out at 298 K (Fig. 2). The electrochemical impedance parameters derived from these investigations are mentioned in Table 4.

Figure 2. Nyquist diagrams for C38 steel electrode with and without at \(E_{\text{corr}}\) after 30 min of immersion.

The inhibition efficiency can be calculated by the following formula:

\[ E_{R_t}\% = \left(\frac{R_t - R_t^0}{R_t}\right) \times 100 \]  

(2)

Were \(R_t\) and \(R_t^0\) are the charge transfer resistances in inhibited and uninhibited solutions respectively.
The values of the polarization resistance were calculated by subtracting the high frequency intersection from the low frequency intersection [48]. Double layer capacitance values were obtained at maximum frequency \( f_{\text{max}} \), at which the imaginary component of the Nyquist plot is maximum, and calculated using the following equation:

\[
C_{\text{dl}} = \frac{1}{2\pi f_m R_t}
\]

with \( C_{\text{dl}} \): Double layer capacitance (\( \mu \text{F.cm}^{-2} \)); \( f_{\text{max}} \): maximum frequency (Hz) and \( R_t \): Charge transfer resistance (\( \Omega \cdot \text{cm}^2 \)).

The electrochemical impedance parameters deduced from Fig. 2 are summarized in Table 4.

Table 4. Electrochemical Impedance parameters for corrosion of steel in acid medium at various contents of prickly pear seed oil extract.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C (g/L)</th>
<th>( R_t )(k( \Omega )·cm(^2))</th>
<th>( f_{\text{max}} )(Hz)</th>
<th>( C_{\text{dl}} )(( \mu \text{F/cm}^2 ))</th>
<th>( E_{\text{RT}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>0.0</td>
<td>23</td>
<td>50</td>
<td>138</td>
<td>-</td>
</tr>
<tr>
<td>PPSO</td>
<td>0.5</td>
<td>40</td>
<td>44</td>
<td>90</td>
<td>46</td>
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<tr>
<td></td>
<td>2.0</td>
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</tbody>
</table>

The Nyquist plots in Fig. 2, at high frequencies are not perfect semicircles. Deviations of this kind are often referred to as the frequency dispersion of interfacial impedance [49]. This anomalous phenomenon can be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [50]. The shape is maintained throughout the whole concentrations, indicating that almost no change in the corrosion mechanism occurred due to the inhibitor addition [51].

From the impedance data, we notice an increase of the polarization resistance and decrease of the double layer capacity with increasing inhibitor concentration indicate that PPSO inhibits the corrosion rate of mild steel by an adsorption mechanism [52]. The efficiency reaches 81% at 5g/L. Values of double layer capacitance are also brought down to the maximum extent in the presence of the inhibitor, the decrease being more effective with rise of concentration, and the decrease in the values of \( C_{\text{dl}} \) follow the order similar to that obtained for the \( I_{\text{corr}} \) studies. The decrease in \( C_{\text{dl}} \) is due to the adsorption of this compound on the metal surface leading to the formation of a surface film in the acidic solution [53].

The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) with a small variation.
3.2.3. Weight loss, corrosion rates and inhibition efficiency

The effect of the addition of PPSO1 tested at different concentrations on the corrosion of steel in 1M HCl solution was studied by using weight-loss at 298 K. Inhibition efficiency $E_w (%)$ is calculated as follows:

$$E_w(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100$$  \hspace{1cm} (6)

Where $W_{corr}$ and $W'_{corr}$ are the corrosion rate of C38 steel in 1M HCl in absence and presence of inhibitor, respectively.

Table 5 regroups the results of weight loss of steel in 1M HCl with and without the addition of various concentrations of the PPSO1.

**Table 5. Effect of PPSO1 concentration on corrosion data of steel in 1M HCl**

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>concentrations (g/l)</th>
<th>$W_{corr}$ (mg. cm$^{-2}$)</th>
<th>$E_w$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>0.0</td>
<td>1.8614</td>
<td>-</td>
</tr>
<tr>
<td>Prickly pear seed oil extract</td>
<td>0.5</td>
<td>1.0094</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.7371</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.4226</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.3242</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.2976</td>
<td>84</td>
</tr>
</tbody>
</table>

From Table 5, it can be seen that corrosion rate values in 1.0 M HCl solution containing PPSO1, decreased as the concentration of inhibitor increased. This result is due to fact that the adsorption amount and coverage of inhibitor on mild steel surface increases with inhibitor concentration. The highest inhibition efficiency of 84% was obtained at 5g/L concentration of PPSO1. This result suggests that increase in PPSO1 concentration increases the number of inhibitor molecules adsorbed onto mild steel surface and reduces the surface area that is available for the direct acid attack on the metal surface. The results obtained from weight loss are in good agreement with electrochemical studies.

3.3. Effect of temperature

3.3.1. Polarization curves

The effect of temperature on the corrosion rate of steel in free acid and added with 5g/L of PPSO1 is made from 298 to 328 K as shown in fig 3. and 4 and Table 6.
Figure 3. Potentiodynamic polarisation curves of C38 steel in 1M HCl at different temperatures.

Figure 4. Potentiodynamic polarisation curves of C38 steel in 1M HCl in the presence of 5g/L of PPSO1 at different temperatures.

From these results, we can deduce that the corrosion rate increases in the blank with the rise of temperature, but in the presence of PPSO1, the dissolution of pure steel is widely retarded. The inhibitive efficiency of the inhibitor roughly changes with the rise of temperature. From this result, we can conclude that PPSO1 is an excellent inhibitor in high temperatures.
Table 6. Effect of temperature on the steel in free acid and at 5g/L of PPSO1.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Temperature (K)</th>
<th>$E_{\text{corr}}$ (mV/SCE)</th>
<th>$I_{\text{corr}}$ (µA/cm²)</th>
<th>$-b_c$ (mV/dec)</th>
<th>$b_a$ (mV/dec)</th>
<th>$E$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>298</td>
<td>-567</td>
<td>94</td>
<td>99</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-544</td>
<td>157</td>
<td>126</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-545</td>
<td>305</td>
<td>129</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-537</td>
<td>399</td>
<td>136</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>PPSO1</td>
<td>298</td>
<td>-675</td>
<td>9</td>
<td>91</td>
<td>34</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-672</td>
<td>16</td>
<td>89</td>
<td>30</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-678</td>
<td>43</td>
<td>111</td>
<td>45</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-675</td>
<td>76</td>
<td>83</td>
<td>51</td>
<td>80</td>
</tr>
</tbody>
</table>

3.3.2 Kinetic parameters

In acidic solution, the corrosion rate is related to temperature by Arrhenius equation:

$$I_{\text{corr}} = k \exp \left( -\frac{E_a}{RT} \right)$$

and

$$I'_{\text{corr}} = k' \exp \left( -\frac{E'_a}{RT} \right)$$

Where, $I_{\text{corr}}$ and $I'_{\text{corr}}$ are the corrosion rates of steel with and without inhibitor, respectively. $E_a'$ and $E_a$ are the apparent activation energies in the presence and absence of inhibitor, respectively. $k$ and $k'$ are the constants.

The apparent activation energy was determined from the slopes of $\ln I_{\text{corr}}$ vs $1/T$ graph depicted in Fig.5.

![Figure 5. Arrhenius plots of steel in 1 M HCl with and without 5 g/L PPSO1.](image-url)
$E_a = 60.01 \text{ kJ/mol}$ and $E_a = 40.74 \text{ kJ/mol}$ are the apparent activation energies with and without PPSO1 respectively.

We remark that the activation energy change slightly in the presence of inhibitor. Furthermore, the increase of $E\%$ is explained by Ammar and El Khorafi [54] as chemisorption of inhibitor molecules on the steel surface. The lower value of $E_a$ of the corrosion process in an inhibitor’s presence when compared to that in its absence is attributed to its chemisorption [55].

Kinetic parameters, such as enthalpy and entropy of corrosion process, may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation is (6) [56]:

$$I = \frac{RT}{Nh} \cdot \exp\left(\frac{\Delta S^*}{R}\right) \cdot \exp\left(-\frac{\Delta H^*}{RT}\right)$$

(8)

Where $N$ is the Avogadro’s number, $h$ the Plank’s constant, $R$ is the perfect gas constant, $\Delta S^*$ and $\Delta H^*$ the entropy and enthalpy of activation, respectively.

Fig. 6 shows a plot of $\ln(I_{corr}/T)$ against $1/T$ of PPSO. Straight lines are obtained with a slope of $(-\Delta H^*/R)$ and an intercept of $(\ln R/Nh + \Delta S^*/R)$ from which the values of $\Delta H^*$ and $\Delta S^*$ are calculated respectively (Table 7).

![Figure 6. Relation between $\ln(I_{corr}/T)$ and 1000/T at different temperatures.](image)

From the following results, it can be concluded that:

- The positive values of $\Delta H^*$ show that the corrosion process is an endothermic phenomenon.
- The negative values of $\Delta S^*$ show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [57].
Table 5. The values of activation parameters $\Delta H^*$, $\Delta S^*$ and $\Delta G^*$ for mild steel in 1M HCl in the absence and the presence of 5 g/L of PPSO1.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$E_a$ (kJ/mole)</th>
<th>$\Delta H^*$ (kJ/mole)</th>
<th>$\Delta S^*$ (J/mole)</th>
<th>$E_a - \Delta H^*$ = RT (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>40.74</td>
<td>38.16</td>
<td>-79.0</td>
<td>2.58</td>
</tr>
<tr>
<td>PPSO1</td>
<td>60.03</td>
<td>57.59</td>
<td>-35.0</td>
<td>2.44</td>
</tr>
</tbody>
</table>

-We remark that $E_a$ and $\Delta H^*$ values vary in the same way with the inhibitor concentration. This result permit to verify the known thermodynamic relation [58] between $E_a$ and $\Delta H^*$:

$$E_a - \Delta H^* = RT$$  \hspace{1cm} (9)

The calculated values are very close to RT which is equal 2.48 kJ mol$^{-1}$ at 298 K.

3.4. Adsorption isotherm

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor, which obeys to [59]:

$$\frac{C}{\theta} = \frac{1}{K} + \frac{C}{K}$$  \hspace{1cm} (10)

Where C is the PPSO1 concentration, $\theta$ the fraction of the surface covered determined by E/100, K the equilibrium constant. Fig. 7 shows the dependence of the ratio C/ $\theta$ as function of C.

**Figure 7.** Plots of Langmuir adsorption isotherm of PPSO1 on the steel surface at 298K.
The data fit straight line, with slope nearly equal unity (1.03), indicating that these compounds adsorb according to Langmuir adsorption isotherm. $\Delta G_{\text{ads}}$ is not accessible because of the unknown molecule responsible on the inhibition process. In such case, the inhibitory is explained as a synergistic intermolecular effect of the various components of the natural oil [18].

6. CONCLUSION

From the above results and discussion, the following conclusions are drawn:
- Palmitic acid contents of seed oils ranged between 7.3% (PPSO15) and 12.6% (PPSO3). While oleic acid contents varied between 15.0% (PPSO12) and 20.8% (PPSO5), linoleic acid contents ranged from 61.8% (PPSO16) to 68% (PPSO15).
- Prickly pear seed oil extract (PPSO) acts as an excellent inhibitor without modifying the hydrogen reduction mechanism.
- The inhibition efficiency increases with increased PPSO1 concentration to attain a maximum value of 90% at 5 g/L.
- The data obtained from the three different methods: potentiodynamic polarisation, EIS and weight loss, are in good agreements.
- The inhibition efficiency of PPSO1 increases slightly with the rise of temperature.
- PPSO1 studied was adsorbed chemically on the steel surface according to the Langmuir isotherm model.

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References

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