An investigation of carbon steel corrosion inhibition in 1 M HCl by Lepidium sativum oil as green inhibitor

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Abstract

The extracted lipid of Lepidium sativum L was examined for fatty acid composition. Oleic (22.03 g/100 g) and Linolenic (29.22 g/100 g) acids were the predominant unsaturated fatty acids, while palmitic acid (8.03 g/100 g) was found as the major saturated acid. The inhibition of the corrosion of carbon steel in hydrochloric acid medium by Lepidium sativum L oil has been studied using weight loss, electrochemical impedance spectroscopy (EIS) and Tafel polarisation methods. Inhibition was found to increase with increasing concentration of the oil but decreases with temperature. Polarization curves showed that Lepidium sativum L oil behaves as a mixed-type inhibitor. The adsorption of the oil on the carbon steel surface obeyed the Langmuir adsorption isotherm. The thermodynamic parameters for activation processes were calculated and discussed. Values of inhibition efficiency calculated from weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy are in good agreement.

1. Introduction

Cress L.S, otherwise known as garden cress, garden cress pepper weed or garden pepperwort, in Morocco is called hab-rachad. Is a fast growing annual herb belonging to the Brassicaceae family that is native to Egypt and West Asia but is widely cultivated in temperate climates throughout the world for various culinary and medicinal uses [1].

Seeds contain 27% of protein, 14-26% of lipids, 35-54% of carbohydrates and 8% of crude fiber [2]. that contains 20-25% of oil and the main fatty acid is linolenic acid (32-35%) it also contains natural antioxidants (tocopherols and carotenoids) which protect the oil from rancidity. Imidazole alkaloids, lepidine, monomeric alkaloids, sinapic acid and sinapin were reported in seeds of L. sativum [3]. α-tocopherol and β-sitosterol were reported in the unsaponifiable matter of the Cress seeds [4]. It has been reported that phytochemicals which are considered as secondary metabolites components are directly responsible for activity such as antioxidant, antimicrobial, antifungal, anticancer, anti-inflammatory among others [5].

A molecule of an organic compound must have the ability to act as a corrosion inhibitor.Which are generally used to reduce corrosion of metallic material in different media. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. Actually, researchers seem to retain many attempts and are focused on the use of natural products extracted from aromatic herbs, spices and medicinal plants. Their use as corrosion inhibitors has been preferred because of both economic and environmental objectives which can encourage us to replace toxic chemicals used.
Several researchers used natural products as corrosion inhibitors [6-8]. And some of them have used vegetable oil as corrosion inhibitors such as: Castor oil [9], Jojoba oil [10], Argan oil [11], Prickly pear seed oil [12], Neem oil [13], Olive oil [14] and Sesame oil [15].

Inhibitors are generally used to reduce corrosion of metallic material in different media. The use of plant extracts as corrosion inhibitors are preferred because of both economic and environmental objectives which can encourage us to replace toxic chemicals habitually used. Therefore, the aim of this work is to study the inhibition action of Lepidium sativum oil (LSO), on the corrosion of carbon steel in hydrochloric acid. The inhibition performance is evaluated by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The thermodynamic parameters for activation processes were calculated and discussed.

2. Experimental details

2.1. Plant seeds collections
Cultivated *Lepidium sativum* seeds were collected from Tafraout city, in the Souss Massa region (South west of Morocco) (29°44'16.4"N 8°58'16.9"W), Seeds were harvested in June 2014. After harvest, the seeds were sun dried and stored at 4 °C until processed.

2.2. Cress oil extraction
Cress seeds were ground in a coffee grinder, 30.0 g triplicates of ground seeds were extracted for 8 h with a Soxhlet apparatus, and after hexane was removed under reduced pressure the weights of the residual oils were calculated [16].

2.3. Fatty acid composition
Fatty acid composition was determined following regulation EEC/2568/91 (EEC/2568, 2003). Before analysis, fatty acids (FAs) were converted to fatty acid methyl esters (FAMEs) by shaking for 25 min. a solution of 60 mg oil and 3 mL of hexane with 0.3 mL of 2 N methanolic potassium hydroxide. FAMEs were analyzed by gas chromatography using a Varian CP-3800 (Varian Inc.) chromatograph equipped with a FID. A split injector was used and the injected volume was 1 µl. The column used was a CP-Wax 52CB column (30 m × 0.25 mm i.d.; Varian Inc., Middelburg, The Netherlands). The carrier gas was helium and the total gas flow rate was 1 mL/min. The initial and final column temperature was 170 and 503K, respectively, and the temperature was increased by steps of 277 K/min. The injector and detector temperature was 503 K. Data were processed using a Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA, USA). Results were expressed as the relative percentage of each individual FA [17].

2.4. Materials
The steel used in this study is a carbon steel (CS) (Euro norm: C35 E carbon steel and US specification: SAE 1035) with a chemical composition (in weight%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 600, 800, 1500 and 2000 grades of emery papers. The specimens were washed thoroughly with bi-distilled water, degreased and dried with ethanol.

2.5. Solutions preparation
The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37 % HCl with distilled water. Inhibitor were dissolved in acid solution at the required concentrations (in g/L), and the solution in the absence of inhibitor was taken as blank for comparison purposes. The test solutions were freshly prepared before each experiment by adding *Lepidium sativum* oil directly to the corrosive solution. Concentrations of *Lepidium sativum* oil are 0.25, 0.50, 1.00, 1.50 and 2.00 g/L.

2.6. Corrosion tests
2.6.1. Weight Loss Measures
Testing the inhibitory action in the absence and presence of *Lepidium sativum* oil (LSO) at various concentrations on the corrosion of the carbon steel in 1 M hydrochloric acid is carried out at room temperature by gravimetry for an immersion time of 6 h. In effect, the weight loss method allowed a more practical in application [18]. After weighing accurately, the specimens [0.3cm x 0.9cm x 3.5cm] were immersed in a 100 mL beaker containing 250 mL of 1.0 M HCl solution with and without addition of different concentrations inhibitor. All the aggressive acid solutions were
open to air. After 6 h of acid immersion, the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility, all measurements were performed few times and average values were reported to obtain good reproducibility. The corrosion rate and the inhibition efficiency \( \eta_{WL}(\%) \) are given by the following equation:

\[
C_R = \frac{W_b - W_a}{At}
\]

(1)

\[
\eta_{WL}(\%) = \left(1 - \frac{W_i}{w_0}\right) \times 100
\]

(2)

where \( W_b \) and \( W_a \) are the specimen weight before and after immersion in the tested solution, \( w_0 \) and \( w_i \) are the values of corrosion weight losses of mild steel in uninhibited and inhibited solutions, respectively, \( A \) the total area of the mild steel specimen (cm\(^2\)) and \( t \) is the exposure time (h).

2.6.2. Electrochemical measurements

2.6.2.1. Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. The working electrode was carbon steel of surface area of 0.27 cm\(^2\). All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solutions for 30 minutes to establish steady state open circuit potential \( E_{ocp} \). After measuring the \( E_{ocp} \), the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 303 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 10 mHz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation \[19\]:

\[
E\% = \frac{R_{ct}^\circ - R_{ct}^i}{R_{ct}^\circ} \times 100
\]

(3)

Where, \( R_{ct}^\circ \) and \( R_{ct}^i \) are the charge transfer resistance in absence and in presence of inhibitor, respectively.

2.6.2.2. Potentiodynamic polarization

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 to 0 mV versus corrosion potential at a scan rate of 2 mV.s\(^{-1}\). The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities \( I_{corr} \). The inhibition efficiency was evaluated from the measured \( I_{corr} \) values using the relationship:

\[
E_i(\%) = \frac{I_{corr}^\circ - I_{corr}^i}{I_{corr}^\circ} \times 100
\]

(4)

Where \( I_{corr}^\circ \) and \( I_{corr}^i \) are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

3. Results and Discussion


The fatty acid composition of the Lepidium sativum L oil is given in Table 1. Fatty acid composition is an important characteristic of oil. The physical, chemical, and nutritional characteristics of oils are influenced by the kinds and proportions of the fatty acid components and their position on the glycerol radical.

Linolenic (29.22\%) and oleic (22.03\%) were the major acids present in the oil followed by Gadoleic acid (13.15\%) and Linoleic acid (11.5\%), which together represent 75.9\% of the total fatty acids. Thus, this oil can be regarded as Linolenic-Oleic oil. Myristic, Palmitic, Pamlitoleic, Arachidic, Stearic, lignoceric and behenic acids constituted about 19\%. 
3.2. Weight loss corrosion rate and effectiveness of inhibition

The data obtained for the corrosion behavior of carbon steel in 1.0 M HCl solution with and without addition of different concentrations (LSO) after 6 h of immersion period at 303 K are presented in table 2.

Table 1: Fatty acid composition of Lepidium sativum oil.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid C 14:0</td>
<td>0.09</td>
</tr>
<tr>
<td>Palmitic acid C 16:0</td>
<td>8.03</td>
</tr>
<tr>
<td>Palmitoleic acid C 16:1</td>
<td>0.22</td>
</tr>
<tr>
<td>Stearic acid C 18:0</td>
<td>2.90</td>
</tr>
<tr>
<td>Oleic acid C 18:1</td>
<td>22.03</td>
</tr>
<tr>
<td>Linoleic acid C 18:2</td>
<td>11.50</td>
</tr>
<tr>
<td>Linolenic acid C 18:3</td>
<td>29.22</td>
</tr>
<tr>
<td>Arachidic acid C 20:0</td>
<td>3.70</td>
</tr>
<tr>
<td>Gadoleic acid C 20:1</td>
<td>13.15</td>
</tr>
<tr>
<td>Behenic acid C 22:0</td>
<td>0.90</td>
</tr>
<tr>
<td>Lignoceric acid C 24:0</td>
<td>4.50</td>
</tr>
</tbody>
</table>

Table 2: Gravimetric results of carbon steel corrosion in 1.0 M HCl without and with various concentrations of (LSO) at 303 K.

<table>
<thead>
<tr>
<th>(LSO) g/L</th>
<th>Wcorr/(g.cm².h⁻¹)</th>
<th>Ecorr/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.1173</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>0.0432</td>
<td>63</td>
</tr>
<tr>
<td>0.50</td>
<td>0.0308</td>
<td>73</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0185</td>
<td>84</td>
</tr>
<tr>
<td>1.50</td>
<td>0.0129</td>
<td>89</td>
</tr>
<tr>
<td>2.00</td>
<td>0.0086</td>
<td>93</td>
</tr>
</tbody>
</table>

It is obvious from these results that the (LSO) inhibits the corrosion of carbon steel at all concentrations used in this study. It can be observed from this table, that the corrosion rate of carbon steel decreases while the protection efficiency increases as the (LSO) concentration increases in 1.0 M HCl solutions. The maximum \( \eta_{wL} \) of 93 % is achieved at 2 g/L and a further increase in concentration did not cause any appreciable change in the performance of the inhibitor. This behavior can be attributed to the increase in the area covered due to the adsorption of natural compounds on the surface of the carbon steel [20]. The concentration of the inhibitor increases. We can conclude that (LSO) is a good corrosion inhibitor for steel in 1.0 M HCl solution.

3.3. Polarization curves
3.3.1. Effect of concentration

The cathodic and anodic polarization curves of carbon steel in 1.0 M HCl in the absence and presence of (LSO) OF different concentrations at 303 K are presented in Figure 1. Values of the associated electrochemical parameters are given in Table 3.

Inspection of the Figure 1 reveal that the addition of (LSO) to 1.0 M HCl solution reduces the anodic dissolution of steel and also retards the cathodic hydrogen evolution reaction. These results indicated that this organic inhibitor exhibit cathodic and anodic inhibition effects. Therefore, (LSO) can be classified as an inhibitor of relatively mixed effect (anodic/cathodic inhibition) in 1.0 M HCl.

From the results in Table 3, it can be noticed that the values of corrosion current densities (Icorr) of carbon steel in the inhibitor containing solutions were lesser than those for the blank solution. At all inhibitor concentrations, the Icorr values are reduced. Corrosion potential (Ecorr) of carbon steel is -447.6 mV in the blank medium, this value is -466.5 mV for LSO at 0.25 g/L concentration. But these values do not vary regularly with changing of inhibitor concentration. Furthermore, if the change in Ecorr value was more than 85 mV, a compound could be identified as an anodic or a cathodic type inhibitor. In our case, the Ecorr value is 20.2 mV, the smallest change indicates that the tested Lepidium sativum oil (LSO) is performed as mixed-type inhibitor [21-24]. The values of ba and bc are slightly changed indicating that the inhibition mechanism occurred by simple blocking of the available cathodic and anodic sites of the mild steel surface [25].
The displayed data show that increasing (LSO) concentration decreases the I\text{corr}, reaching 86% at 2 g/L, but slightly affect the values of E\text{corr} signifying that it could act as pickling inhibitor \[26\]. The higher inhibition efficiency obtained at these concentrations suggests that, the oil could serve as effective corrosion inhibitor. The values of ba and bc are slightly changed indicating that the inhibition mechanism occurred by simple blocking of the available cathodic and anodic sites of the metal surface \[27\].

3.3.2. Effect of temperature

Temperature is a factor that can modify both the behavior of the inhibitors and the substrates in a given aggressive medium \[28\]. The organic compounds can dissolve more easily as the temperature rises. Increasing the temperature can thus cause a reduction in the corrosion resistance of steel \[29-32\].

In order to examine the influence of this parameter on the inhibitory efficiency of the inhibitors, we carried out the stationary electrochemical measurements in potentiodynamic mode in a temperature range between 303 K and 333 K. We then plotted the polarization curves of carbon steel in 1.0 M HCl without and with the inhibitor at 2 g/L (figures 2,3). The table 4 summarizes the values associated with the electrochemical parameters of carbon steel in 1.0 M HCl as a function of temperature in the presence of (LSO) at a concentration of 2 g/L.

It is obvious that the values of I\text{corr} increases by increasing the temperature in both solutions and the efficiency value decreases. Inhibitory efficiency decreases with increasing temperature of 303-333 K in the presence and absence of (LSO), this behavior leads to the rise of the current density, this increase in temperature affects the bonds linking between inhibitor and the carbon steel surface.

To investigate the mechanism of inhibition and to calculate the activation energies of the corrosion process, polarization measurements are taken at various temperatures in the absence and the presence of 2 g/L concentration of this inhibitor.
Figure 2: Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl at different temperatures.

Figure 3: Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl in the presence of 2 g/L of (LSO) at different temperatures.

Table 4. Polarization parameters for carbon steel in 1 M HCl with and without (LSO) at different temperatures.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T (K)</th>
<th>-E_corr (mV/SCE)</th>
<th>I_corr (µA/cm²)</th>
<th>-b_c (mV/dec)</th>
<th>b_a (mV/dec)</th>
<th>E_I (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>303</td>
<td>447</td>
<td>778</td>
<td>93.3</td>
<td>85.0</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>444</td>
<td>1100</td>
<td>125.5</td>
<td>115.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>451</td>
<td>1500</td>
<td>111.1</td>
<td>111.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>443</td>
<td>2118</td>
<td>170.3</td>
<td>161.8</td>
<td></td>
</tr>
<tr>
<td>(LSO) 2 g/L</td>
<td>303</td>
<td>450</td>
<td>107</td>
<td>137.8</td>
<td>87.8</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>472</td>
<td>215</td>
<td>160.0</td>
<td>99.4</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>484</td>
<td>320</td>
<td>104.4</td>
<td>91.6</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>508</td>
<td>600</td>
<td>170.4</td>
<td>119.5</td>
<td>71</td>
</tr>
</tbody>
</table>

Corresponding data are given in Table 5. The activation parameters for the corrosion process are calculated from Arrhenius type plot according to the following equation:

\[ I_{corr} = A \exp \left( \frac{-E_{ai}}{RT} \right) \]  

\[ (5) \]
and from transition state plot according to the following equation:

\[
I_{corr} = \frac{RT}{Nh} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( \frac{-\Delta H_a}{RT} \right)
\]

(6)

where, \(E_a\) is the activation energy, \(R\) is gas constant, \(h\) is Planck’s constant, \(T\) is absolute temperature, \(A\) is Arrhenius pre-exponential factor, \(\Delta H_a\) is enthalpy of activation, \(N\) is Avogadro’s number and \(\Delta S_a\) is entropy of activation.

The apparent activation energy of the inhibitors has been calculated by linear regression between Ln \(I_{corr}\) and 1/T (Fig. 4); the results are presented in Table 5. Inspection of Table 5 shows that apparent activation energy increases on addition of inhibitors in comparison to the blank solution. The increase in \(E_a\) can be interpreted as the physical adsorption. Thus, the studied molecules create a barrier to charge and mass transfer. The higher values of \(E_a\) in inhibited solution may also be correlated with the increased thickness of double layer, which enhances the \(E_a\) values of the corrosion reaction [33].

![Figure 4](image_url)

**Figure 4**: Arrhenius plots for carbon steel in 1.0 M HCl and 1.0 M HCl + 2 g/L \(LSO\).

The relationship between Ln \(I_{corr}/T\) and 1/T are shown in Fig. 5. Straight lines are obtained with a slope \((-\Delta H_a/R)\) and an intercept of \([\text{Ln}(R/Nh) + (\Delta S_a/R)]\), from which the value of \(\Delta H_a\) and \(\Delta S_a\) are calculated and presented in Table 5.

![Figure 5](image_url)

**Figure 5**: Transition state plots for carbon steel in 1.0 M HCl and 1.0 M HCl + 2 g/L \(LSO\).
Table 5. Activation parameters for carbon steel in 1.0 M HCl medium without and with the addition of the inhibitor at optimum concentration.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$R^2$</th>
<th>$E_a$ (KJ mol$^{-1}$)</th>
<th>$\Delta H_a$ (KJ mol$^{-1}$)</th>
<th>$-\Delta S_a$ (J mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.99941</td>
<td>27.79</td>
<td>25.15</td>
<td>106.74</td>
</tr>
<tr>
<td>LSO</td>
<td>0.99555</td>
<td>46.74</td>
<td>44.10</td>
<td>60.44</td>
</tr>
</tbody>
</table>

The positive sign of enthalpy reflects the endothermic nature of steel dissolution process meaning that dissolution of steel is difficult. On comparing the values of entropy of activation ($\Delta S_a$) listed in Table 5, it is clear that entropy of activation increases in presence of the studied inhibitors compared to free acid solution. Such variation is associated with the phenomenon of ordering and disordering of inhibitor molecules on the mild steel surface. The increased entropy of activation in the presence of inhibitor indicates that disorderness is increased on going from reactant to activated complex. The increase in values of entropy by the adsorption of inhibitor molecules on metal surface from the acid solution can be regarded as quasi-substitution between the inhibitor molecules in the aqueous phase and H$_2$O molecules on electrode surface. In such condition, the adsorption of inhibitor molecules is followed by desorption of H$_2$O molecules from the electrode surface. Thus increase in entropy of activation is attributed to solvent (H$_2$O) entropy.

3.4. Electrochemical impedance spectroscopy measurements

EIS is a rapid and convenient method for investigation of protective properties of inhibitors on metals. More reliable results can be obtained by this method, since it does not disturb the double layer at the metal/solution interface [34]. The impedance plots a of carbon steel in 1.0 M HCl in absence and presence of studied inhibitor at 303 K are presented in Fig. 6.

**Figure 6**: Nyquist diagrams for the steel electrode with and without (LSO) after 30 min of immersion at 303 K.

All the impedance spectra displayed in Fig. 6 reveal a single depressed capacitive semicircle across the studied frequency range, which denotes that the dissolution process is related to the charge transfer process [33]. Noticeably, these impedance loops are not perfect semicircles, which can be termed as frequency dispersion effect as a result of the roughness and inhomogeneity of the metal electrode surface [36,37]. Furthermore, the diameters of the capacitive loops increase sharply with the increasing concentration of (LSO) and the shape of the loops doesn't modify.

The impedance parameters derived from these plots are given in Table 6. Double layer capacitance values ($C_{dl}$) and charge-transfer resistance values ($R_{ct}$) were obtained from impedance measurements.

The double layer capacitance ($C_{dl}$) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation 7:

$$C_{dl} = \frac{1}{\omega R_{ct}} \quad \text{Where} \quad \omega = 2\pi f_{max}$$  \hspace{1cm} (7)
Table 6: Impedance parameters for the corrosion of carbon steel in acid at various concentrations of (LSO).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Conc (g/L)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$f_{max}$ (Hz)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
<th>$E_{Ret}$ (%)</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>—</td>
<td>20.26</td>
<td>70.20</td>
<td>111.90</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(LSO)</td>
<td>2.00</td>
<td>445.40</td>
<td>6.12</td>
<td>58.40</td>
<td>95</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>138.50</td>
<td>15.82</td>
<td>72.67</td>
<td>85</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>111.30</td>
<td>17.00</td>
<td>84.15</td>
<td>82</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>110.00</td>
<td>15.82</td>
<td>85.15</td>
<td>81</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>80.77</td>
<td>20.00</td>
<td>98.57</td>
<td>75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The data shown in Table 6 reveal that the value of $R_{ct}$ increases with addition of (LSO) as compared to the blank solution, the increase in $R_{ct}$ value is attributed to the formation of a protective film at the metal/solution interface. The $C_{dl}$ value decreases on increasing the concentration of both the inhibitors, indicating the decrease in local dielectric constant and/or to an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface [38].

3.5. Adsorption isotherm

The values of surface coverage to different concentrations of inhibitors, obtained from EIS measurements at 303 K, have been used to explain the best isotherm to determine the adsorption process. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions [39]. The most frequently used isotherms are Langmuir, Temkin, Frumkin, Parsons, Hill de Boer, Flory-Huggins and Dahar-Flory-Huggins and Bockris-Swinkel. However, the best fit is obtained from Langmuir isotherm (Figure 7). All these isotherms are of the general form:

$$\int (\theta, x) \exp(2a\theta) = KC_{inh}$$  \(8\)

where $\int (\theta, x)$ is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. “$\theta$” is the surface coverage degree, “$C$” is the inhibitor concentration in the bulk of solution “$a$” is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface. “$K$” is the adsorption-desorption equilibrium constant. The surface coverage $\theta$ for different concentrations of (LSO) in 1.0 M HCl at 303 K has been evaluated from EIS. The data were tested graphically, see Fig. 9, by fitting to Langmuir isotherm which given by equation 9.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$  \(9\)

where $C_{inh}$ is the equilibrium inhibitor concentration, $K_{ads}$ adsorptive equilibrium constant, $\theta$ representing the degree of adsorption ($E_{Ret}/100$).

Figure 7: Langmuir plots of ($C_{inh}/ \theta$) versus $C_{inh}$ for LSO.
From the intercepts of the straight lines C/θ - axis, the K value was calculated; K = 8.43 L/g. K is related to the standard Gibbs free energy of adsorption, $\Delta G_{\text{ads}}^*$, according to:

$$K = \frac{1}{C_{\text{H,O}}} \exp \left( \frac{-\Delta G_{\text{ads}}^*}{RT} \right)$$  \hspace{1cm} (10)

Where R is the universal gas constant, T the thermodynamic temperature and the concentration of water in the solution is 1000 g/L. Generally, for values of $\Delta G_{\text{ads}}^*$ around -20 kJ mol$^{-1}$ or less negative, the type of adsorption is regarded as physisorption; those around -40 kJ mol$^{-1}$ or more negative are associated with chemisorption [40,41]. However, it is difficult to distinguish between chemisorption and physisorption only based on these criteria, especially when charged species are adsorbed. The possibility of Coulomb interactions between adsorbed cations and specifically adsorbed anions can increase the Gibbs energy even if no chemical bond appears [42]. However, the calculation of the $\Delta G_{\text{ads}}^*$ value of (LSO) is not possible because the molecular mass of the oil components is not known. This limitation is noted by some authors in the case of the plant extracts used as corrosion inhibitors for steel in acidic media [43,44].

Conclusions

The main finding of present work can be summarized as follows:

- The analyses of the of Lepidium sativum oil (LSO) plant reveal 11 components which accounted for fatty acid methyl esters (96.243%).
- The inhibition efficiency of (LSO) increases with increase in inhibitor concentration but decreases with increasing temperature.
- The potentodynamic polarization studies showed that the studied inhibitor is mixed type inhibitor.
- EIS measurements showed that charge transfer resistance (R$_{ct}$) increases and double layer capacitance (C$_{dl}$) decreases in presence of inhibitors, suggested the adsorption of the inhibitor molecules on the surface of carbon steel.
- The adsorption of the inhibitor tested follows the adsorption of Langmuir isotherm.

References

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