Corrosion inhibition effect of Verbena extract (VE) on C38 steel in 1 M HCl medium was investigated for the first time by weight loss, potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) methods. Inhibition efficiency of 85.3% was achieved with 6g/L VE at 298K. The polarization studies showed that VE acts as mixed-type inhibitor. The Nyquist plots showed that on increasing VE concentration, increases charge transfer resistance and decreases double layer capacitance. VE obeys the Langmuir adsorption isotherm.

Keywords: Inhibition, steel, verbena extract, acid medium, polarization curves, EIS, SEM.

1. INTRODUCTION

Steel has found wide application in a broad spectrum of industries and machinery; however its tendency to corrosion. Acid solutions are used in industry to remove mill scale from metallic surfaces [1, 2]. Hydrochloric acid is often used because of the higher soluble ferrous chloride. One way of protecting steel from corrosion is to use corrosion inhibitors. Organic compounds containing heteroatoms are commonly used to reduce the corrosion attack on steel in acidic media [3-12]. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. These advantages have incited us to draw a large part of program of our laboratory to examine natural substances as corrosion inhibitors such as: Fennel oil [13], prickly pear seed oil [14], Argan extract [15-17], Argan oil [18, 19], Rosemary oil [20-22],
Thymus oil [23, 24], Pennyroyal Mint oil [25], Lavender oil [26], Jojoba oil [27] and Artemisia [28-30]. The present work was established to study the corrosion inhibition of C38 steel in 1M HCl solution by verbena extract as corrosion inhibitor using different techniques: weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) methods.

2. MATERIALS AND METHODS

2.1. Solutions preparation

Sample of verbena officinalis was collected in the food supermarket of Agadir, Morocco. Dried and pulping fruits were crushed. Stock solution of the verbena extract was prepared by stirring cold weighed amounts of the chamomile plant for 24 h in 1 M HCl solution (The solution 1M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water). The resulting solution was filtered. This extract was used to study the corrosion inhibition properties and to prepare the required concentrations. The solution tests are freshly prepared before each experiment. Experiments were carried out in triplicate to ensure the reproducibility.

2.2. Weight loss measurements

The gravimetric measurements were carried out at the definite time interval of 6 h at room temperature using an analytical balance (precision ± 0.1 mg). The carbon steel specimens used have a rectangular form (length = 1.6 cm, width = 1.6 cm, thickness = 0.07 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 50 ml of non-de-aerated test solution. After immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighted. Triplicate experiments were performed in each case and the mean value of the weight loss is calculated.

2.3. 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 0.094 cm².

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 tests 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 \( E_{\text{corr}} \) 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.

2.4. Scanning electron microscopy (SEM)

Immersion corrosion analysis of carbon steel samples in the acidic solutions with and without the optimal concentration of the inhibitor was performed using SEM. Immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface morphology. SEM Jeol JSM-5800 was used for the experiments.

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurements

3.1.1. Effect of concentration

The effect of addition of Verbena extract (VE) tested at different concentrations on the corrosion of carbon steel in 1 M HCl solution was studied by weight loss method at 298 K after 6 h of immersion period. The corrosion rate \( C_R \) and inhibition efficiency \( \eta_{\text{WL}}(\%) \) were calculated according to the Eqs. 1 and 2 [31,32], respectively:

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

\[
\eta_{\text{WL}}(\%) = \left(1 - \frac{W_i}{W_0}\right) \times 100
\]

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 carbon steel in uninhibited and inhibited solutions, respectively, \( A \) the total area of the carbon steel specimen (cm\(^2\)) and \( t \) is the exposure time (h).
The obtained values of corrosion rate \( (C_R) \) and inhibition efficiency \( \eta_{WL}(\%) \) are summarized in Table 1. It is obvious from these results that the VE inhibits the corrosion of carbon steel at all concentrations used in this study. The variation of \( C_R \) and \( \eta_{WL}(\%) \) with the VE concentration are shown in Fig. 1. It can be observed from this figure, that the \( C_R \) of carbon steel decreases while the protection efficiency increases as the VE concentration increases in 1 M HCl solutions. This conclusion was also supported by the electrochemical studies reported below. The maximum \( \eta_{WL}(\%) \) of 82.1 % is achieved at 6 g/L and a further increase in concentration did not cause any appreciable change in the performance of the inhibitor. The corrosion inhibition can be attributed to the adsorption of the inhibitor at the steel/hydrochloric acid solution interface [33].

**Table 1.** Corrosion rate of steel in 1M HCl with and without Verbena extract various concentrations, and the corresponding inhibition efficiency.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (g/L)</th>
<th>( C_R ) (mg cm(^{-2}) h(^{-1}))</th>
<th>( \eta_{WL} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>--</td>
<td>1.261</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.597</td>
<td>52.7</td>
</tr>
<tr>
<td>VE</td>
<td>4.0</td>
<td>0.446</td>
<td>64.6</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.325</td>
<td>74.2</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.226</td>
<td>82.1</td>
</tr>
</tbody>
</table>

**Figure 1.** Variation of corrosion rate and inhibition efficiency of carbon steel in 1 M HCl containing various concentrations of VE.

### 3.2. Polarization measurements

The kinetics of the anodic and cathodic reactions occurring on C38 steel electrodes in 1 M HCl solutions with different Verbena extract concentrations was studied through the polarization measurements. The complete potentiodynamic polarization curves are shown in Fig. 2. The
electrochemical parameters, i.e. corrosion current density \( I_{\text{corr}} \), cathodic \( b_c \) and corrosion potential \( E_{\text{corr}} \). Table 2 shows the electrochemical parameters \( (I_{\text{corr}}, E_{\text{corr}} \) and \( b_c \) \) obtained from Tafel plots for the C38 steel electrode in 1M HCl solution without and with different concentrations of MMI. The \( I_{\text{corr}} \) values were used to calculate the inhibition efficiency, \( E_I (\%) \) (listed in Table 2), using the following equation:

\[
E_I (\%) = \left( \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \right) \times 100
\]

(3)

Where \( I_{\text{corr}} \) and \( I'_{\text{corr}} \) are uninhibited and inhibited corrosion current densities, respectively.

Figure 2. Polarisation curves of carbon steel in 1 M HCl for various concentrations of VE.

Table 2. Electrochemical parameters of C38 steel in 1M HCl solution without and with verbena extract at different concentrations at 298K.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (g/L)</th>
<th>Ecorr (mV/SCE)</th>
<th>Icorr (µA/cm²)</th>
<th>-bc (mV/dec)</th>
<th>EI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0</td>
<td>-612</td>
<td>124</td>
<td>149</td>
<td>-</td>
</tr>
<tr>
<td>VE</td>
<td>3.0</td>
<td>-571</td>
<td>61</td>
<td>160</td>
<td>50.8</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>-587</td>
<td>50</td>
<td>171</td>
<td>59.7</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>-593</td>
<td>37</td>
<td>163</td>
<td>70.1</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>-613</td>
<td>24</td>
<td>154</td>
<td>80.6</td>
</tr>
</tbody>
</table>
Regarding the potentiodynamic polarization curves, as previously observed, it can be clearly seen that the $E_{\text{corr}}$ values shifted to more negative potentials with an increase in the verbena extract concentration. This effect may be related to the adsorption of the organic compound at the active sites of the electrode surface, retarding the corrosion reaction. The increase in the verbena extract concentration caused a clear increase in the cathodic current density, but did not change significantly the cathodic Tafel slopes (Table 2), indicating that the hydrogen evolution reaction is diminished exclusively by the surface blocking effect [34] of VE. The parallel cathodic Tafel lines (Fig. 2) suggested that the addition of inhibitor to the 1 M HCl solution do not modify the hydrogen evolution mechanism and the reduction of $H^+$ ions at the C38 steel surface which occurs mainly through a charge transfer mechanism [35]. For the inhibited system, if the displacement in $E_{\text{corr}}$ value is greater than 85 mV relative to uninhibited system than the inhibitor is classified as cathodic or anodic type. In our case, the maximum displacement of $E_{\text{corr}}$ value is 41 mV, hence the VE is classified as a mixed-type inhibitor.

### 3.1.3. Electrochemical impedance spectroscopy measurements

The corrosion behaviour of steel in 1 M HCl solution, in the absence and presence of VE, is also investigated by the EIS at 298 K after 30 min of immersion. The charge-transfer resistance ($R_{\text{ct}}$) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [36]. The double layer capacitance ($C_{\text{dl}}$) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{\text{max}}$) are found as represented in equation:

$$C_{\text{dl}} = \left( \frac{1}{\omega R_t} \right), \quad \text{where} \quad \omega = 2\pi f_{\text{max}}$$

The inhibition efficiency got from the charge transfer resistance is calculated by:

$$\%IE = \left(1 - \frac{R_{\text{ct}}^i}{R_{\text{ct}}^s}\right)$$

where $R_{\text{ct}}^i$ and $R_{\text{ct}}^s$ are the charge transfer resistance in the absence and presence of different concentrations of inhibitor, respectively.

Impedance measurements were studied to evaluate the charge transfer resistance ($R_{\text{ct}}$) and double layer capacitance ($C_{\text{dl}}$) and through these parameters the inhibition efficiency was calculated. Figure 3 shows the Impedance diagrams for C38 steel in 1 M HCl with different concentrations of the verbena extract and the impedance parameters derived from these investigations are given in Table 3.

As noticed from Figure 3, the obtained impedance diagrams are almost in a semi-circular appearance, indicating that the charge - transfer process mainly controls the corrosion of C38 steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode
surface arising from surface roughness or interfacial phenomena. In fact, in the presence of the verbena extract the values of $R_{ct}$ has enhanced and the values of double layer capacitance are also brought down to the maximum extent. The decrease in $C_{dl}$ shows that the adsorption of the inhibitors takes place on the metal surface in acidic solution.

![Nyquist plots of steel in 1 M HCl containing various concentrations of verbena extract at $E_{corr}$ after 30 min of immersion.](image)

**Figure 3.** Nyquist plots of steel in 1 M HCl containing various concentrations of *verbena extract* at $E_{corr}$ after 30 min of immersion.

**Table 3.** Impedance parameters for corrosion of steel in 1M HCl in the absence and presence of different concentrations of verbena extract at 298 K.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc (g/L)</th>
<th>Rct (Ω.cm²)</th>
<th>fmax (Hz)</th>
<th>Cdl (µF/cm²)</th>
<th>ERct (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0</td>
<td>48</td>
<td>50</td>
<td>60.3</td>
<td>-</td>
</tr>
<tr>
<td>VE</td>
<td>3.0</td>
<td>100</td>
<td>60</td>
<td>26.5</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>175</td>
<td>50</td>
<td>18.1</td>
<td>67.7</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>192</td>
<td>45</td>
<td>18.4</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>260</td>
<td>40</td>
<td>15.3</td>
<td>81.1</td>
</tr>
</tbody>
</table>

Inhibition efficiency as a function of concentrations of extract at 298K is plotted in Fig.4. In the three cases, it can be observed, from this figure that the protection efficiency increases with increasing the concentration of extract and inhibits the corrosion of steel in 1 M HCl solution. Maximum of inhibition efficiency was achieved at 6 g/L of the extract. The results of electrochemical studies (impedance and polarization measurements) and weight loss measurements were in good agreement with slight deviations.
### 3.3. The effects of immersion time on the inhibitor performance

To investigate the VE adsorption kinetics and determine the time needed for VE to reach its maximum inhibition efficiency, EIS experiments were carried out in the presence of 6 g/L VE in 1 M HCl at different immersion times at 298K (Fig. 5). A comparison of the results of $R_{ct}$ with 6 g/L VE at different immersion times is presented in Table 4. $R_{ct}$ increased upon increasing the immersion time up to 2 h and then became relatively constant. From the figure, $R_{ct}$ slightly increased upon increasing the inhibitor concentration at a given immersion time. This may indicate that the inhibitor film becomes slightly more effective at higher inhibitor concentrations. Increasing the inhibitor concentration may not yield good performance of the inhibitor film for longer immersion times. The decrease in $C_{dl}$ values was caused by an imperceptible replacement of water molecules due to the adsorption of inhibitor molecules on the steel surface, decreasing the extent of the dissolution reaction [37, 38]. The corresponding corrosion resistance and corrosion inhibition efficiency values were calculated and are presented in Table 4. We can also observe that the carbon steel electrode with longer immersion time has a larger $R_{ct}$ value suggesting the formation of a protective film which grows with increasing exposure time. This observation suggests that an improvement in the quality of the film take place in time.
**Figure 5.** Nyquist plot for steel in 1 M HCl in the presence of different immersion time of 6 g/L verbena extract at 298 K.

**Table 2.** Impedance parameters for corrosion of steel in 1M HCl in the absence and presence of different immersion time of 6 g/L verbena extract at 298 K.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Immersion time (h)</th>
<th>Rct (Ω.cm²)</th>
<th>fmax (Hz)</th>
<th>Cdl (µF/cm²)</th>
<th>ERct (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.5</td>
<td>48</td>
<td>50</td>
<td>66.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>60</td>
<td>63</td>
<td>42.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>80</td>
<td>79</td>
<td>25.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>92</td>
<td>79</td>
<td>21.9</td>
<td>-</td>
</tr>
<tr>
<td>VE</td>
<td>0.5</td>
<td>260</td>
<td>15</td>
<td>40.8</td>
<td>81.1</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>350</td>
<td>25</td>
<td>22.7</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>550</td>
<td>25</td>
<td>13.1</td>
<td>85.4</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>680</td>
<td>25</td>
<td>9.3</td>
<td>86.4</td>
</tr>
</tbody>
</table>

3.4. Adsorption isotherm

The adsorption process of inhibitor is a displacement reaction where the adsorbed water molecule is being removed from the surface of metal [39]:

\[ \text{Org}_{\text{sol}} + n\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{Org}_{\text{ads}} + n\text{H}_2\text{O}_{\text{sol}} \]  

(6)

\[ \text{Org}_{\text{sol}} \] and \[ \text{Org}_{\text{ads}} \] are the organic molecules in the aqueous solution that adsorbed to the metal surface. While \[ \text{H}_2\text{O}_{\text{ads}} \] is the water molecule on the metal surface in which \( n \) is the coefficient that represents water molecules replaced by a unit of VE. To obtain an effective adsorption of an inhibitor on metal surface, the interaction force between metal and inhibitor must be greater than the
interaction force of metal and water molecule [40]. The establishment of isotherms that describe the
desorption behaviour of corrosion inhibitor is important as they provide important clues about the
nature of metal-inhibitor interaction. Values of degree of surface coverage (θ) corresponding to
different VE concentrations were used to determine which isotherm best described the desorption
process. In the present study, values of θ were calculated using the impedance results according to the
following equation [41]:

\[ \theta = \frac{R_{ct} - R_{ct}^\theta}{R_{ct}} \]  
(7)

where \( R_{ct} \) and \( R_{ct}^\theta \) are the charge-transfer resistance values without and with inhibitor,
respectively. The results obtained for VE in 1 M HCl solution fit well Langmuir adsorption isotherm
given by Eq. (8) [42]:

\[ \frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \]  
(8)

where θ is the degree of surface coverage and \( C_{inh} \) is the inhibitor concentration in the
electrolyte. \( K_{ads} \) is the equilibrium constant of the adsorption process.

![Figure 6. Plots of Langmuir adsorption isotherm of verbena extract on the steel surface at 298K.](image)

The plot of \( C_{inh}/\theta \) versus \( C_{inh} \) of VE yields a straight line with correlation coefficient more than
0.99957 showing that the adsorption of this inhibitor can be fitted to Langmuir adsorption (Fig. 6). It is
very important to note that discussion of the adsorption isotherm behaviour using natural product
extracts as inhibitors in terms of thermodynamic parameters (such as the standard free energy of
adsorption value (\( \Delta G_{ads} \))) is not possible because the molecular mass of the extract components is not
known. For example, there are several phenolic compounds in the aqueous extract. Valek and Martinez [43], in their study on acid corrosion with Azadirachta indica leaf extract, noted the same limitation.

3.5. Scanning electron microscopy (SEM)

In order to study the morphology of the carbon steel surfaces in contact with acidic solution, SEM was used. The C38 steel specimens after immersion in 1 M HCl solution for 6 hours at 298K in the absence and presence of optimum concentration of the verbena extract, the specimens were taken out, dried and kept in a dessicator. The SEM images of C38 steel immersed in 1 M HCl in the absence and presence of the optimum concentration of the plant extract are shown in Figures 7 (a, b, c).

![Figure 7. SEM (×2000) of tinplate (a) before immersion (b) after 6 hours of immersion in 1M HCl (C) after 6 hours of immersion in 1M HCl + 6 g/L of VE.](image)

The resulting scanning electron micrographs reveal that, the surface was damaged owing to corrosion in absence of the inhibitor (blank), but in presence of the inhibitor, there is a much less damage on the surface. This is attributed to the formation of a good protective film on the carbon steel surface.

4. CONCLUSION

In this study, the inhibition efficiency of verbena extract on steel in 1 M HCl solution was determined by weight loss and electrochemical techniques such as polarization and impedance measurements. The inhibition efficiency increased upon increasing of the inhibitor concentration. The adsorption of verbena extract on the steel obeyed the Langmuir adsorption isotherm model. A mixed
inhibition mechanism was proposed for the inhibitive effects of verbena extract based on the polarization results. The introduction of verbena extract solution resulted in the formation of a thin inhibitor film on the steel surface, causing a decrease in surface roughness and effectively protecting the steel from corrosion. The inhibition efficiencies were determined by polarization and EIS plots, which were in good agreement with the weight loss measurements. The changes in the impedance parameters confirmed the strong adsorption of the inhibitor on the steel surface, which prevented anodic dissolution of the metal by blocking active metal surface sites. Furthermore, in the presence of the inhibitor, the double layer capacitance decreased, which confirmed adsorption of the inhibitor molecules on the steel surface. The SEM results showed the formation of a protective and dense layer on the steel surface in the presence of the inhibitor.

ACKNOWLEDGEMENTS

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