Corrosion behaviour of mild steel in acidic solution using the aqueous seed extract of *Phoenix dactylifera L (Date seeds)*


*King Abdulaziz University, Girls College, Chemistry Department, Jeddah KSA*

**ARTICLE INFO**

**ABSTRACT**

The effect of some factors such as: acid concentration, immersion time, temperature and the presence of *Phoenix dactylifera L* (date seeds) on the corrosion behaviour of mild steel has been investigated using mass loss (ML) and hydrogen evolution (HE) measurements. The results obtained show that the corrosion rate for mild steel was found to increase with increasing acid concentration and temperature but it decrease with increasing immersion time and inhibitor concentration. The inhibition efficiency of the corrosion of mild steel by aqueous seed extract of *Phoenix dactylifera L* (date seeds) was found to vary with concentration, immersion time and temperature. The adsorption of date seeds extract was found to obey Langmuir adsorption isotherm. Scanning electron microscopy (SEM) of mild steel sample was performed on mild steel surface to account for adsorption of inhibitor molecules on metal surface. Various thermodynamic parameters were also calculated to investigate the mechanism of corrosion inhibition.

© 2013 Journal of Chemica Acta

**Keywords:**

Mild steel  
Phoenix dactylifera seeds  
Date seeds  
Corrosion inhibition

**1. Introduction**

Corrosion in general is the destructive results of chemical reaction between the metal and its environment. Furthermore, the definition of corrosion can be classified as corrosion science and corrosion engineering. Corrosion science is the study of the chemical and metallurgical processes that occur during corrosion. Corrosion engineering is the design and application of methods to prevent corrosion [1].

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Sulphuric acid is widely used in the pickling of metals, industrial acid cleaning, acid descaling and oil well acidizing, etc [2, 3].

The use of mild steel as construction material in industrial sectors has become a great challenge for corrosion engineers or scientists nowadays. In practice, most of the acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes use mild steel as their material. Corrosion of mild steel is the most common form of corrosion, especially in acid solution. It has practical importance, for example, in the acid pickling of iron and mild steel, chemical cleaning of scales in metallurgy, in the oil recovery and petrochemical industry [1, 4]. Therefore, there is a need to protect these metals against corrosion. The use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion [5].

Concentration, time of immersion, temperature, pH and the presence of inhibitor are the major factors which affected the corrosion behaviour of materials in the submerged zone. Use of some inhibitors, such as chromates, has been banned because of toxicity and the environmental hazards they create. Hence there is a strive to make use of environmental friendly, non toxic/less toxic, extracts of naturally occurring plant materials as corrosion inhibitors [6-13]. It is interesting to observe the remarkable inhibitive effect of different parts of plant extracts reported as corrosion inhibitors for inhibitors for mild steel [14-16].

Seed extract of various plant materials were proved to be promising inhibitor for mild steel acid corrosion [19-21]. An overview of Emerging Scenario in the frontiers of eco friendly corrosion for mild steel lists the numerous plant extracts that has been reported as corrosion inhibitor for MS in acidic media [22].
Extracts of plant materials contain a wide variety of organic compounds. Most of them contain hetero-atoms such as P, N, S, O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented [14,15].

Figure 1 Date and Date seeds.

In this research the effect of some factors such as concentrations of sulphuric acid, temperature, immersion time and aqueous extract of date seeds as inhibitor on the corrosion behaviour of mild steel has been studied. Also, the influence of exposure time and temperature on the inhibition efficiency of date seeds is evaluated.

Inhibitor used in the study is date seeds of date palm tree (Phoenix dactylifera L.) which were collected from Jeddah region; Saudi Arabia , Fig. 1. The fruit is composed of a fleshy pericarp and seed which constitutes between 10% and 15% of date fruit weight [16]. Several Phoenix seeds species are cultivated as powdered cores are roasted and used as a beverage similar to coffee, Used in the treatment of diseases, used oil from powder cores for the treatment of scabies and vitiligo.

Table 1 Approximate composition of date seeds.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>5-10%</td>
</tr>
<tr>
<td>Protein (N x 6.25)</td>
<td>5-13%</td>
</tr>
<tr>
<td>Oil</td>
<td>7-10%</td>
</tr>
<tr>
<td>Crude fibre</td>
<td>10-20%</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>81-83%</td>
</tr>
<tr>
<td>Ash</td>
<td>41-47%</td>
</tr>
<tr>
<td>Fat</td>
<td>5-13%</td>
</tr>
<tr>
<td>Noleic acid</td>
<td>41-47%</td>
</tr>
<tr>
<td>Dietary fiber</td>
<td>22.5-80.2%</td>
</tr>
</tbody>
</table>

Adapted from a number of literature references (17-21) an indicative picture of the chemical composition of the date seed has been collated in the following table: Also, date seeds contain high levels of phenolics (3102-4430mg gallic acid equivalents/ 100 g), antioxidants (580-929 ml trolox equivalents/g) and dietary fiber (78-80 g/100 g) [22,23].

2. Experimetal
2.1. Materials
The mild steel used in the study had the following composition (wt %), C (0.19), Si (0.26), Mn (0.64), S (0.05), P (0.06), Ni (0.09), Cr (0.08), Mo (0.02), Cu (0.27), and the remainder iron (Fe) and was obtained from Ejison Resources (Nig.) Ltd. The mild steel coupons were prepared, degreased and cleaned as previously reported [24-26]. The corrosive medium was H_2SO_4 prepared from 98% analytical grade supplied by BDH Chemical Supplies Laboratory, England. Deionized water was used for the preparation of all reagents.

Figure 2 Variation of hydrogen/ time curves for mild steel corrosion in different concentrations of H_2SO_4 at 30° C.

2.2. Preparation of Date seeds extract
Phoenix dactylifera L (date seeds) were dried and ground to powder using a blender. 100 gram of the dry powdered was extracted using 200ml deionised water for 24 h. The aqueous extract was separated by filtration and then kept the filtrate solution in a flask at low temperatures in a refrigerator. From the stock solution of aqueous extract of date seeds, the inhibitor test solutions were prepared in a concentration range (1.0%v/v–60%v/v) for mass loss (ML) and hydrogen evolution (HE) measurements.

2.3. Methods
The apparatus and procedure followed for weight loss and hydrogen evolution methods were similar to that earlier reported [27-30]. In both techniques, the experiments were conducted in the temperature range 30 to 60°C maintained in a thermostat bath.

From the mass loss values, corrosion rates were computed using the expression:

\[
CR = \frac{m_1 - m_2}{At}
\]

(1)

Where \(m_1\) and \(m_2\) are mass loss (mg) of mild steel before and after immersion, respectively, in test solutions, \(A\) is the area of specimen (cm\(^2\)) and \(t\) is the exposure time (h).

\[
IE\% = \frac{CR\text{blank) - CR(inh)}}{CR\text{blank)}} \times 100
\]

(2)

Where \(CR\text{blank) and CR(inh)\) are the corrosion rates in the absence and presence of the inhibitor, respectively in 2.0 M H_2SO_4 at same temperature.
Hydrogen evolution rate \( (RV_H) \) that can be correlated to the mild steel corrosion rate was computed based on the volume of \( H_2 \) evolved using the expression:

\[
RV_H = \frac{V_T - V_i}{T_T - T_i} \times 100
\]

where \( V_T \) and \( V_i \) are volumes of hydrogen evolved at times \( T_T \) and \( T_i \), respectively.

The inhibition efficiency (IE) was computed using the equation:

\[
IE\% = \frac{RV_H(\text{blank}) - RV_H(\text{inh})}{RV_H(\text{blank})} \times 100
\]

where \( RV_H(\text{blank}) \) and \( RV_H(\text{inh}) \) are the rates of hydrogen evolution in the absence and presence of extract, respectively.

Scanning electron microscope (SEM) model, Digi scope II V2, was used to study the morphology of corroded surface in presence and absence of inhibitor.

### Table 2

<table>
<thead>
<tr>
<th>CH(_2)SO(_4) (M)</th>
<th>0.25</th>
<th>0.50</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR(_{HE}) ( \times 10^2 ) (ml. cm(^{-2}). min(^{-1}))</td>
<td>1.99</td>
<td>2.22</td>
<td>2.47</td>
<td>3.03</td>
<td>3.65</td>
<td>4.49</td>
</tr>
<tr>
<td>CR(_{ML}) ( \times 10^5 ) (g. cm(^{-2}). min(^{-1}))</td>
<td>4.99</td>
<td>5.14</td>
<td>5.52</td>
<td>6.84</td>
<td>8.39</td>
<td>9.94</td>
</tr>
</tbody>
</table>

As observed from Table 2, both CR\(_{HE}\) and CR\(_{ML}\) increases with increasing acid concentration, this indicates acceleration behaviour for the metal dissolution and mild steel corrosion in \( H_2\)SO\(_4\) is concentration dependent. This is due to increase in acidity and \( SO_4^{2-} \) ion concentration with increase in acid concentration. The corrosion is attributed to the presence of water, air and \( H^+ \) which accelerate the corrosion process [31]. This observation agrees with the fact that the rate of a chemical reaction increases with increasing concentration.

### Table 3

<table>
<thead>
<tr>
<th>Immersion time (hour)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>4.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR(_{ML}) ( \times 10^6 ) (g. cm(^{-2}). min(^{-1}))</td>
<td>7.7702</td>
<td>7.9501</td>
<td>7.8289</td>
<td>7.6438</td>
<td>7.3147</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion:

#### 3.1 Effect of acid concentration on the corrosion of the mild steel electrode

Figure 2 shows the plot of hydrogen gas evolved against time for mild steel corrosion in different concentrations (0.25-2.5) M of \( H_2\)SO\(_4\). Slopes of such lines are estimated and taken as the rates of corrosion reaction. The good linearity in the relations indicates the absence of insoluble film on the metal surface during corrosion.

The calculated corrosion rates (CR\(_{HE}\) and CR\(_{ML}\)) obtained from HE and ML measurements, respectively, are tabulated in Table 2.

#### 3.2 Effect of immersion time on the corrosion of the mild steel electrode

Corrosion rate of the metal obtained by mass loss method at various periods of immersion in 2.0 M \( H_2\)SO\(_4\) are depicted in Table 3. It is found that as the immersion period increases the corrosion rate decrease. This behavior may be attributed to the increase of the surface area covered by the adsorbed molecules of acid ions. But it found that at 0.5h of immersion the corrosion rate of mild steel was less than that at 1.0h, this can be attributed to the short time of exposure of the metal specimens in the corrosive medium.

#### 3.3 Effect of temperature on the corrosion of the mild steel electrode

Temperature has a great influence on the rate of metal corrosion in acidic medium. Temperature studies were carried out at 303 K, 313 K, 323 K, 333 K and 343 K. The results are presented in Fig. 3. The results obtained indicated that the corrosion rate of mild steel increase with rising temperature, i.e., the slope of the straight lines increases, this is due to decrease in hydrogen evolution. In general, the increase in dissolution rates at
higher temperatures are related to the case of destruction the protective film and the healing process is slowed down.

Figure 4 Hydrogen gas vs. time for the corrosion of mild steel in 2.0 M H₂SO₄ in the presence of different concentrations of aqueous extract of date seeds at 30º C.

Table 4 corrosion rates and inhibition efficiencies for mild steel in 2.0 M H₂SO₄ in presence of different concentrations of aqueous extract of date seeds at 30º C.

<table>
<thead>
<tr>
<th>C_inh (v/v)</th>
<th>CRML × 10⁵ (g/cm²·min⁻¹)</th>
<th>IEML%</th>
<th>CRHE × 10⁵ (ml/cm²·min⁻¹)</th>
<th>HE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.3976</td>
<td>0.0%</td>
<td>3.652</td>
<td>0.0%</td>
</tr>
<tr>
<td>1.0</td>
<td>6.4141</td>
<td>23.61</td>
<td>2.773</td>
<td>24.06</td>
</tr>
<tr>
<td>3.0</td>
<td>3.7436</td>
<td>55.42</td>
<td>1.684</td>
<td>53.88</td>
</tr>
<tr>
<td>10.0</td>
<td>3.7320</td>
<td>55.55</td>
<td>1.617</td>
<td>55.72</td>
</tr>
<tr>
<td>15.0</td>
<td>3.7320</td>
<td>55.55</td>
<td>1.617</td>
<td>55.72</td>
</tr>
<tr>
<td>30.0</td>
<td>3.5334</td>
<td>57.92</td>
<td>1.489</td>
<td>59.22</td>
</tr>
<tr>
<td>40.0</td>
<td>2.5655</td>
<td>69.44</td>
<td>1.096</td>
<td>69.98</td>
</tr>
<tr>
<td>50.0</td>
<td>1.5523</td>
<td>81.51</td>
<td>0.7257</td>
<td>80.12</td>
</tr>
<tr>
<td>60.0</td>
<td>0.3213</td>
<td>96.17</td>
<td>0.08549</td>
<td>97.65</td>
</tr>
</tbody>
</table>

3.4. Effect of inhibitor on the corrosion of the mild steel electrode

The effect of addition aqueous extract of date seeds on mild steel corrosion in 2.0 M H₂SO₄ solution was studied in the concentration range (1.0%v/v – 60%v/v) of inhibitor and the following factors were studied to obtain their effectiveness on the corrosion of mild steel sample.

3.4.1. Effect of inhibitor concentration

The corrosion rates of mild steel in the presence of aqueous extract of date seeds were assessed by monitoring the volume of hydrogen gas evolved at fixed time intervals. Fig. 4 shows representative plots of the volume of hydrogen gas evolved as a function of reaction time at 30ºC for mild steel in 2.0 M H₂SO₄ without and with different concentrations of aqueous extract. It is observed from the figure that the volume of hydrogen gas evolved varies linearly with time and was less in the presence of aqueous extract of date seeds compared to the blank solution (2.0 M H₂SO₄).

Figure 5 The variation of inhibition efficiency (IE%) against C_inh for mild steel corrosion in 2.0 M H₂SO₄ in the presence of date seeds at 30º C.

Table 4 represents the computed values of the mass loss rate (CRML), hydrogen evolution rate (CRHE) and the inhibition efficiency (IE%) of the various additives. Results presented in the table reveal that the rates of hydrogen evolution were reduced on the introduction of the date seeds extract to the uninhibited solution. The increase of the rate of hydrogen evolution in the uninhibited solution can be rationalized on the basis that sulphuric acid reacts with iron and forms metal complexes that are soluble in aqueous media [32]. There are two reactions occurring, namely the anodic reaction and cathodic reaction. The following equations represent iron reaction in acidic solutions [32]:

Anodic reaction (oxidation reaction):

\[ Fe \rightarrow Fe^{2+} + 2e^- \] (5)

Cathodic (reduction reaction or hydrogen evolution reaction):

\[ 2H_+ + 2e^- \rightarrow H_2 \] (6)

The values of inhibition efficiency percentage (IE%) and corrosion rates (CR) obtained from mass loss at different concentration of date seeds aqueous extract at 30ºC are summarized in Table 3. It has been found that the aqueous extract of date seeds inhibit the corrosion of mild steel in 2.0 M H₂SO₄ solution at all concentrations used (1%v/v – 60%v/v). The maximum inhibition efficiency is found equal to 96.17% from ML method and 97.56% from HE method, respectively at 60%v/v of date seeds extract. The inhibitive behavior could be attributed due to the adsorption of
phytochemical constituents present in date seeds extract on the mild steel surface.

**Figure 6** the relation between C/Θ against C_{inh.} of aqueous extract of date seeds for steel corrosion in 2.0 M H_{2}SO_{4} at 30º C (Langmuir isotherm).

Figure 5 illustrates the relationship between IE % deduced from the two chemical methods and the concentration of the studied inhibitors.

In Fig. 5, the inhibition efficiency IE % of the extract is described. An increase in inhibition efficiency with increasing the extract concentration, the inhibition efficiency increase is proposed to form an insoluble complex adsorbed on mild steel surface, leading to more inhibition efficiency, this complex may leads to blocking most of the active centers on mild steel surface, thereby increasing the surface coverage in which a steady inhibition is found.

### 3.5 Adsorption isotherm

Adsorption isotherm values are important to explain the mechanism of corrosion inhibition.

Basic information on the interaction between the inhibitor and mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either by physical (electrostatic) adsorption or chemisorptions with the metal. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage (Θ) values for different concentrations of the inhibitor in H_{2}SO_{4} medium have been evaluated from the weight loss data [33] using the formula,

\[ Θ = \frac{W_o - W_i}{W_o} \]  

(7)

where, \( W_o \) and \( W_i \) are the values of weight loss of uninhibited and inhibited specimens, respectively.

\[ K_c = \frac{Θ}{1 - Θ} \]  

(8)

where, \( c \) is the concentration of the inhibitor, \( Θ \) is the fractional surface coverage.

The Langmuir isotherm, Eq. (8), which is based on the assumption that all adsorption sites are equivalent and that molecular binding occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant \( K \) is related to the free energy of adsorption \( ΔG_{ads} \) as,

\[ K = \frac{1}{C_{solution}} \exp(-\frac{ΔG_{ads}(T)}{R T}) \]  

(9)

where, \( C_{solution} \) represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm\(^{-3}\), \( R \) is the gas constant and \( T \) is the thermodynamic temperature in K. The Langmuir isotherm, Eq. (8), can be rearranged to obtain the following expression,

\[ \frac{C}{Θ} = \frac{1}{K_c} + C \]  

(10)

so that a linear relationship can be obtained on plotting \( C/Θ \) as a function of \( C \), with a slope of unity. The thermodynamic parameters \( K \) and \( ΔG_{ads} \) for the adsorption of the studied inhibitors on mild steel is obtained by Langmuir’s adsorption isotherm are plotted in Figure 6.

**Figure 7** Volume of hydrogen / time curves for mild steel corrosion in 2.0 M H_{2}SO_{4} at different temperatures.

**Figure 8** Volume of hydrogen / time curves for mild steel corrosion in 2.0 M H_{2}SO_{4} in the absence and presence of 1% of aqueous extract of date seeds at different temperatures.
It was found that the linear correlation coefficients clearly prove that the adsorption of the date seeds from 2.0 M H₂SO₄ acid solutions on the mild steel corrosion obeys the Langmuir adsorption isotherm. The negative value of ΔG⁰_ads for the addition of inhibitors indicates that the process of adsorption of studied inhibitors is spontaneous in nature [34]. The free energy of adsorption of (ΔG_ads), in 2.0M H₂SO₄ was found to be -4.827 kJmol⁻¹. It is well known that the values of ΔG_ads in the order of -20 kJ mol⁻¹ or lower indicate a physisorption while those about -40 kJ mol⁻¹ or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [35].

### Table 5

<table>
<thead>
<tr>
<th>Immersion time (hour)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>4.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRₘₐₓ × 10⁻⁷ (g. cm⁻². min.⁻¹)</td>
<td>2.4427</td>
<td>3.1721</td>
<td>3.2420</td>
<td>3.3446</td>
<td>3.1509</td>
</tr>
<tr>
<td>IE%</td>
<td>68.56</td>
<td>60.09</td>
<td>58.58</td>
<td>56.24</td>
<td>56.92</td>
</tr>
</tbody>
</table>

3.6. Effect of immersion time

The effect of period of immersion at 10% v/v concentration of the inhibitor on mild steel in 2.0 M H₂SO₄ are listed in Table 5. It is observed that for 10% v/v concentration of date seed extract with increase in time of immersion, IE decreases from 68.54% (1/2h) to 56.92% (6h). This behaviour can be discussed on the following basis: prolonged immersion of steel in acidic solutions, allows the cathodic or hydrogen evolution kinetics to increase presumably as more cathodic or carbon containing sites are exposed by the corrosion process and increase the concentration of ferrous ion which is known for its stimulation of corrosion attack of the acid on the base metal. It is obvious from the table that date seed extract is promising inhibitor for 2.0 M H₂SO₄ at various time of immersion [19, 36].

![Figure 9](image1.png)  
**Figure 9** Volume of hydrogen / time curves for mild steel corrosion in 2.0 M H₂SO₄ in the absence and presence of 3% of aqueous extract of *date seeds* at different temperatures.

![Figure 10](image2.png)  
**Figure 10** Volume of hydrogen / time curves for mild steel corrosion in 2.0 M H₂SO₄ in the absence and presence of 10% of aqueous extract of *date seeds* at different temperatures.

![Figure 11](image3.png)  
**Figure 11** Arrhenius plots for the dissolution of mild steel in 2.0 M H₂SO₄ in the absence and presence of 10% v/v of aqueous extract of *date seeds*. 

The calculated adsorption values for the studied inhibitor shows that the adsorption is physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the adsorption of date seeds at 1 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

**Table 5** Leverage of immersion time with presence of aqueous extract of date seeds as an inhibitor at 30°C.
3.7. Effect of temperature

The effect of temperature on the inhibited acid-metal reaction is highly complex, because many changes occur on the metal surface such as rapid etching and desorption of inhibitor and the inhibitor itself may undergo decomposition and/or rearrangement.

The change of the corrosion process rate with the temperature increase was studied in 2.0 M H₂SO₄, in the presence of aqueous extract of date seeds. We were interested in exploring the activation energy of the corrosion process and the thermodynamic functions of adsorption of date seeds.

Table 6 Corrosion rates for mild steel in 2.0 M H₂SO₄ with different concentration of aqueous extract of date seeds at different temperature.

<table>
<thead>
<tr>
<th>C inh</th>
<th>30ºC</th>
<th>40ºC</th>
<th>50ºC</th>
<th>60ºC</th>
<th>70ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inh.HE%</td>
<td>Inh ML%</td>
<td>Inh.HE%</td>
<td>Inh ML%</td>
<td>Inh.HE%</td>
</tr>
<tr>
<td>1.0</td>
<td>24.06</td>
<td>32.53</td>
<td>20.88</td>
<td>29.06</td>
<td>22.24</td>
</tr>
<tr>
<td>3.0</td>
<td>44.66</td>
<td>45.45</td>
<td>38.04</td>
<td>44.00</td>
<td>36.38</td>
</tr>
<tr>
<td>10.0</td>
<td>53.88</td>
<td>62.09</td>
<td>57.33</td>
<td>61.86</td>
<td>55.40</td>
</tr>
</tbody>
</table>

It can be seen from Figs. 7-10 and the Table 6 that the corrosion rate has increased with rising temperature for a given concentration of the inhibitor, there is no regular trend in the change of inhibition efficiency this may be explained on the basis of the time lag between the process of adsorption and desorption. The decreasing trend with increasing experimental temperatures for all concentrations of the inhibitor suggests possible desorption of some molecules of inhibitor from the metal surface at higher temperatures. Such behavior shows that the components of the date seeds extract were physically adsorbed on the mild steel surface [37].

According to Dehri and Ozcan [38], the relationship between the temperature dependence of percent inhibition efficiency (IE%) of an inhibitor and the activation energy found in its presence was given as follows: (a) Inhibitors whose IE% decrease with temperature increase, the value of activation energy (E_a) found is greater than that in the uninhibited solution; (b) Inhibitors whose IE% does not change with temperature variation, the activation energy (E_a) does not change with the presence or absence of inhibitor; (c) Inhibitors whose IE% increases with temperature increase, the value of activation energy (E_a) found is less than that in the inhibited solution.

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

$$\log R = \frac{-E_a}{2.303R'T} + \log A \tag{11}$$

where CR is the corrosion rate, E_a is the apparent activation energy, R' is the molar gas constant, T is the absolute temperature and A is the frequency factor.

The parameter E_a can be computed from the slope of the straight lines and are listed in Table 7. Enthalpy and entropy of activation ΔH* and ΔS* were obtained by applying the transition state equation:

$$\log (R/T) = \log \left( \frac{R'}{Nh} \right) + \frac{\Delta S^*}{2.303R'} - \frac{\Delta H^*}{2.303R'} \tag{12}$$

where, h is blank's constant, N is Avogadro's number, ΔS* is the entropy of activation and ΔH* is the enthalpy of activation. Straight lines were obtained (Fig. 12) with a slope of (-ΔH*/2.303R') and an intercept of (log(R'/Nh)+ΔS*/2.303R'), from which the values of ΔH*, ΔS* were calculated from ML and HE and listed in Table 7.

Figure 12 The relation between log(R/T) vs. 1/T for the corrosion of mild steel in 2.0 M H₂SO₄ in the absence and presence of 10 % v/v of aqueous extract of date seeds.
The values of $\Delta H^*$ and $E_a$ are nearly the same in the presence of the inhibitor. This indicates that the energy barrier of the corrosion reaction increased in the presence of inhibitor without changing the mechanism of dissolution. In the present investigation $\Delta H^*$ is positive and $\Delta S^*$ is positive using ML method & negative in HE method. The large negative value of $\Delta S^*$ in 2.0 M H$_2$SO$_4$ implies that the activated complex is the rate-determining step, rather than the dissociation step. In the presence of the inhibitor, the value of increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes. The positive values of reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of the inhibitor onto the steel surface [39].

3.8. Scanning Electron Microscopy Analysis (SEM)

Scanning Electron Microscope (SEM) morphologies of mild steel after immersing in 2.0 M H$_2$SO$_4$ in the absence and presence of date seeds extract were shown in Figure 13 (a-d) respectively. Figure 13a shows the clean surface of mild steel sample before immersing in acid solution. This figure reveals the homogeneity of the surface. Figure 13b shows the general appearance of mild steel in 2.0 M H$_2$SO$_4$ without inhibitor. It can be seen from the figure that the surface of mild steel was damaged extremely in the absence of the inhibitor. Figure 13c & 13d reflect the SEM morphology of the mild steel specimen at low concentration (1%v/v) and at higher concentration (6%v/v) of the date seeds extract under investigation at 30 $^\circ$C. From the figures it is imperative that at low concentration (1%v/v) of the extract only a few constituents cover the surface which are not enough to afford a protective layer and hence dissolution of mild steel is observed to some extent where as at higher concentration (6%v/v) the constituents present are large enough to form a protective layer retarding the dissolution of mild steel.

<table>
<thead>
<tr>
<th>Method</th>
<th>$C_{inh.}$ (%v/v)</th>
<th>$E_a$ (kJ.mol.$^{-1}$)</th>
<th>$\Delta H^*$ (kJ.mol.$^{-1}$)</th>
<th>$\Delta S^*$ (J.mol.$^{-1}$K.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML</td>
<td>0.0</td>
<td>49.18</td>
<td>30.90</td>
<td>$1.94 \times 10^{10}$</td>
</tr>
<tr>
<td></td>
<td>10%v/v</td>
<td>49.18</td>
<td>30.90</td>
<td>$1.94 \times 10^{10}$</td>
</tr>
<tr>
<td>HE</td>
<td>0.0</td>
<td>49.70</td>
<td>31.41</td>
<td>- $1.94 \times 10^{10}$</td>
</tr>
<tr>
<td></td>
<td>10%v/v</td>
<td>49.70</td>
<td>31.41</td>
<td>- $1.94 \times 10^{10}$</td>
</tr>
</tbody>
</table>

3.9. Suggested mechanism of inhibition

From the chemical measurements, it was clear that the extract in acid medium behaves as a mixed inhibitor by reducing H$_2$ evolution and metal dissolution process. The approximate composition present in the extract is enlisted in Table 1. Literature survey related to the Phytochemical aspects of date seeds revealed the presence of the major unsaturated fatty acid –oleic acid (41.3-47.7%) and the main saturated fatty acid-lauric acid (17.8%), palmitic acid, capric acid, myristic, myristoleic, palmitoleic, stearic, linoleic and linolenic acid.

Figure 13 SEM images for mild steel surface immersed for 1h in 2.0 M H$_2$SO$_4$ in the absence and presence of low and high concentrations of aqueous extract of date seeds at 30 $^\circ$C. [a] polished sample before immersion, [b] in 2.0 MH$_2$SO$_4$, [c] in the presence 1%v/v of inhibitor and [d] in the presence of 60%v/v of inhibitor.
This makes them more ready to form strong links with metal surface. In addition they may form complexes with metal cations, which are sparingly soluble in aqueous environment. The complexes have been suggested [40] to cause blocking of micro anodes and/or micro cathodes that are generated on the metal surface when in contact with electrolytes, and so can retard the subsequent dissolution of the metal.

4. Conclusion
Phoenix dactylifera L seeds aqueous extract has been evaluated as an eco friendly inhibitor for mild steel in sulphuric acid medium. Effect of various factors namely acid concentration, immersion time, temperature, inhibitor concentration on the corrosion of mild steel investigated using ML and HE measurements. The results reflect the increase of inhibition efficiency with increasing inhibitor concentration and increasing immersion time but were found to decrease with increasing acid concentration and temperature. The adsorption of the phyto constituents on to the surface of mild steel was approximate by Langmuir adsorption isotherm. The values obtained by mass loss measurements and hydrogen evolution measurements were comparable to reasonable extent. The effectiveness of the inhibitor was further confirmed by SEM studies.

References: