CHAPTER 2

CORROSION INHIBITION POTENTIAL OF PLANT EXTRACTS

BY WEIGHT LOSS METHOD

It is a well known fact that corrosion control can be achieved by the effective use of organic inhibitors which are mostly N, S and 0 containing heterocyclic compounds. Most of these organic inhibitors, though effective, suffer from such drawbacks like toxicity, non-biodegradability, high cost etc. Hence there is a growing trend for the development of green inhibitors which do not have the drawbacks usually encountered with organic inhibitors. The present study involves the screening of the extracts of the following plants for their corrosion inhibition effect on mild steel in acid media.

a) *Datura metel*
b) *Datura stramonium*
c) *Solanum nigrum*
d) *Solanum tuberosum*
e) *Piper nigrum*
f) *Rauvolfia serpentina*
g) *Strychnos nux-vomica*

2.1. Inhibitor sample preparation

Usually the test samples are dissolved in water / any other appropriate solvent and the solutions of definite concentrations are prepared. Alternatively, the test samples are dissolved in the corrosive environment itself and solutions of various concentrations are prepared. Perusal of the literature shows that extracts prepared
with distilled water were used for sample preparation [1]. There are also reports available wherein the plant extracts were prepared by directly refluxing a known quantity of powdered plant material with acid solutions [2].

In the case of *Datura metel*, the preparation of inhibitor samples was done by taking the acid extracts directly as detailed below. 5 g of the leaves were macerated and extracted with acids under reflux condition. The resultant acid solutions were filtered and made upto known volume. The made up solutions were diluted suitably to get various concentrations of the inhibitor.

However, the above method was refined subsequently as given under. The refining was necessitated so as to make the extract alkaloid rich.

### 2.2. Preparation of alkaloid enriched extract

The plant parts which are rich in alkaloids were powdered well and 500 g of the material was refluxed with 10% HCl for 6 hours, with a view to extract the basic components present in the plant parts to the acid layer. After this extraction, the resultant acid solutions contained the salts of basic component. Then the extracts were filtered off and neutralized with 10% NaOH up to pH 8 in order to liberate the base from the salt. The neutralized solutions were then extracted with chloroform. The organic (chloroform) layers consisting of basic organic compounds were evaporated and the resultant gummy materials obtained were dried and powdered. Various concentrations of the plant extracts were made by dissolving the known quantity of the resultant powder in the acid medium. Schematically this process can be explained as follows (Fig. 2.1).
Fig. 2.1. Schematic diagram of alkaloid enriched inhibitor preparation

The different concentrations of corrosive media were prepared using AR grade reagents and bidistilled water. The resultant powder tested positively for alkaloids and examination by thin layer chromatography (TLC) revealed the presence of alkaloids as the major constituent present in the plant extract [3]. Thus the plant extracts prepared mostly contained only alkaloidal constituents.

2. 3. Specimen preparation

Mild steel (MS) is a material of choice in various industries due to its cheaper cost and easy availability. MS is used extensively in boiler and other industries as a
construction material. Since MS undergoes rapid corrosion in the acid medium it was proposed to test the various test samples for their corrosion inhibiting effect on MS in acid medium. MS specimens containing C = 0.15 %, Mn = 1.02 %, P = 0.025 % and Fe = remaining were used for the study. The surface preparation of the mechanically polished specimens were carried out using different grades of emery paper (hard, medium and soft then 1/0, 2/0, 3/0 and 4/0) and then degreased with acetone.

2. 4. Weight loss determination

Weight loss method is the simplest and the most accurate method for estimating inhibition efficiency and corrosion rate [4-7]. The technique requires no complex equipment or procedures, merely an appropriately shaped coupon, a carrier for the coupon (coupon holder, if any) and a reliable means of removing corrosion products without disruption of the metal substrate. The weight loss measurement is still the most widely used means of determination. It has a number of attractive features that account for its sustained popularity. Some of the reasons being:

• Simple - no sophisticated instrumentation is required to obtain a result.

• Direct - a direct measurement is obtained, with no theoretical assumptions or approximations

• Versatile - it is applicable to all corrosive environments, and gives information on all the forms of corrosion

The method is commonly used as a calibration standard for other means of corrosion monitoring techniques, such as linear polarization and electrical resistance measurements. In instances where metal wastage is slow and averaged data are acceptable, weight loss monitoring is the preferred technique. The choice of
technique for initial preparation of the coupon surface, and for cleaning the coupon after use, is critical in obtaining useful data.

Large numbers of reports are available on the investigation of corrosion inhibitory effect by weight loss studies. By using weight loss measurements Tariq Saeed [8] studied the inhibitory properties of bicyclic isoxazolidines during corrosion of mild steel in sulphuric acid medium using weight loss studies. Abdallah [9] investigated Guar gum as corrosion inhibitor for corrosion for carbon steel in sulphuric acid solution. Quarishi et al, [10] have extensively studied the inhibition of mild steel in acid solution using 4-amino-5-mercapto-3-n-propyl-1-2-4-triazole as inhibitor and calculated various kinetic parameters from weight loss results.

2. 4.1. Experimental

In the present study, weight loss determination was carried out in the following manner. Mild steel specimens of size 3 x 1 x 0.21 cm were employed for the determination of the corrosion rate by weight loss method. A small hole near the upper edge of the specimen was made. They were abraded into uniform surfaces with the help of grinding machine and by using different grades of emery papers. These were finally polished by various polishing papers to a mirror like surface. The specimens were thoroughly washed with running water and finally degreasing was done with acetone.

These specimens were hung into the experimental solution with the help of the glass hooks. The volume of the solution used was 100 ml. The initial weight of the specimens was noted and the specimens were completely immersed in the corrosive environment for two hours. After two hours, the specimens were taken out then
washed thoroughly with distilled water, dried completely and their weights were noted using Mettler balance. From the initial and final weights, the loss in weights were calculated. The experimental solutions used were 1M HCl and 1M H₂SO₄. Weight loss measurements with and without the presence of the inhibitors for both the media were performed. The study was carried out in three different temperatures viz., 303, 313 and 323 K (± 3K) by using a thermostat. Triplicate measurements were carried out and the mean value of the weight loss is recorded.

Inhibition efficiency was calculated from the weight loss values by using the following formula.

$$\text{Inhibition efficiency} = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \times 100$$  \hspace{1cm} (2.1)

Corrosion rate was calculated using the following formula in mpy (miles per year) unit.

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Loss of weight (mg)}}{\text{Density} \times \text{area (sq. inch)} \times \text{time (hr)}}$$  \hspace{1cm} (2.2)

2. 4. 2. Results and Discussion

From the weight loss measurements in HCl and H₂SO₄ media at different temperatures, the percentage of inhibition efficiency was calculated for various test samples and the values are depicted in Tables 2.1-2.7.
### Table 2.1. Effect of *D. metel* extract on MS corrosion in acid media  
(weight loss studies)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of Inhibitor (V/V)</th>
<th>% of IE (in HCl)</th>
<th>% of IE (in H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>303 K 313 K 323 K</td>
<td>303 K 313 K 323 K</td>
</tr>
<tr>
<td>1</td>
<td>10%</td>
<td>43.11 72.39 81.25</td>
<td>59.62 62.82 63.88</td>
</tr>
<tr>
<td>2</td>
<td>20%</td>
<td>57.35 77.91 84.55</td>
<td>72.34 74.34 75.40</td>
</tr>
<tr>
<td>3</td>
<td>30%</td>
<td>77.04 79.14 87.86</td>
<td>82.60 83.70 84.40</td>
</tr>
</tbody>
</table>

### Table 2.2. Effect of *D. stramonium* extract on MS corrosion in acid media  
(weight loss studies)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of Inhibitor (ppm)</th>
<th>% of IE (in HCl)</th>
<th>% of IE (in H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>303 K 303 K 303 K</td>
<td>303 K 313 K 323 K</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>32.74 58.18 62.55</td>
<td>52.38 54.83 77.25</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>39.82 65.40 71.75</td>
<td>56.49 65.13 81.99</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>52.21 72.01 78.66</td>
<td>59.15 71.45 86.49</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>63.71 76.41 82.01</td>
<td>63.12 77.32 89.57</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>69.91 78.30 88.07</td>
<td>71.22 79.94 91.46</td>
</tr>
</tbody>
</table>
Table 2.3. Effect of *S. nigrum* extract on MS corrosion in acid media (weight loss studies)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of Inhibitor (ppm)</th>
<th>% of IE (in HCl)</th>
<th>% of IE (in H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>303 K</td>
<td>313 K</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>41.18</td>
<td>63.69</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>52.94</td>
<td>68.56</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
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<td>66.70</td>
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<tr>
<td>4</td>
<td>40</td>
<td>63.64</td>
<td>82.86</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>70.66</td>
<td>89.35</td>
</tr>
</tbody>
</table>

Table 2.4. Effect of *S. tuberosum* extract on MS corrosion in acid media (weight loss studies)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of Inhibitor (ppm)</th>
<th>% of IE (in HCl)</th>
<th>% of IE (in H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>303 K</td>
<td>313 K</td>
</tr>
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<td>1</td>
<td>4</td>
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</tr>
<tr>
<td>2</td>
<td>8</td>
<td>64.71</td>
<td>76.82</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>68.47</td>
<td>80.64</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>74.59</td>
<td>85.82</td>
</tr>
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<td>5</td>
<td>20</td>
<td>78.35</td>
<td>87.05</td>
</tr>
</tbody>
</table>
Table 2. 5. Effect of *P. nigrum* extract on MS corrosion in acid media (weight loss studies)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of Inhibitor (ppm)</th>
<th>% of IE (in HCl)</th>
<th>% of IE (in H$_2$SO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>303 K 313 K 323 K</td>
<td>303 K 313 K 323 K</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>68.24 70.35 73.54</td>
<td>77.23 85.62 89.24</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>72.17 73.68 77.63</td>
<td>80.14 88.63 91.46</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>75.46 75.87 81.15</td>
<td>84.22 90.71 93.37</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>79.35 80.44 85.08</td>
<td>88.31 92.83 94.68</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>81.62 83.84 88.35</td>
<td>90.86 94.32 95.53</td>
</tr>
</tbody>
</table>

Table 2. 6. Effect of *R. serpentina* extract on MS corrosion in acid media (weight loss studies)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of Inhibitor (ppm)</th>
<th>% of IE (in HCl)</th>
<th>% of IE (in H$_2$SO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>303 K 313 K 323 K</td>
<td>303 K 313 K 323 K</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>59.92 88.25 92.14</td>
<td>81.37 88.54 89.33</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>70.53 89.00 93.05</td>
<td>84.67 88.80 90.04</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>75.89 89.22 94.24</td>
<td>88.22 92.33 92.95</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>80.35 91.16 94.86</td>
<td>91.61 94.84 94.96</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>84.82 94.68 95.68</td>
<td>93.38 95.44 95.97</td>
</tr>
<tr>
<td>S. No.</td>
<td>Concentration of Inhibitor (ppm)</td>
<td>% of IE (in HCl)</td>
<td>% of IE (in H\textsubscript{2}SO\textsubscript{4})</td>
</tr>
<tr>
<td>-------</td>
<td>---------------------------------</td>
<td>------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>51.41</td>
<td>52.61</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>58.58</td>
<td>60.56</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>65.93</td>
<td>68.31</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>70.06</td>
<td>75.98</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>75.61</td>
<td>78.78</td>
</tr>
</tbody>
</table>

Careful examination of Table 2.1 reveals that *D. metel* shows a dose dependent inhibition in both the acid media. The efficacy of this inhibitor is more in H\textsubscript{2}SO\textsubscript{4} than in HCl medium at room temperature. At higher temperatures, efficiency is high in HCl medium compared to H\textsubscript{2}SO\textsubscript{4} medium. At a concentration of 30%, this plant extract shows a maximum of 87.86% inhibition in HCl medium at 323 K. Similar observations with regard to the variation of IE in various acids have been reported by earlier researchers. Mehta *et al* [11] have reported the corrosion inhibition efficiency of several plant extracts by following the method of extraction directly with dilute acids. Hence, this method was followed in the present study also and the corrosion inhibition potential of the plant extract was evaluated. It is likely that the corrosion inhibition potential is not only due to the alkaloidal constituents as no attempt has been made to extract the alkaloidal constituents alone. This shortcoming
has been rectified in the subsequent studies wherein the extract preparation included methods that enriched the alkloidal content. Alkaloids with the heterocyclic atoms can very well donate the lone pair of electrons and can bring about inhibition.

In the evaluation of corrosion inhibition potential of *D. stramonium*, the crude alkaloidal fraction of the plant extract was taken up and as could be seen in Table 2.2 at a concentration of 20 ppm, the maximum inhibition efficiency was attained. Like *D. metel* this plant also showed increase in the inhibition efficiency with rise of temperature. Thus at 323 K *D. stramonium* at a concentration of 20 ppm shows an IE of 91.46% in H$_2$SO$_4$ medium. Beyond this concentration, the plant does not show much variation in IE.

Careful perusal of the literature shows that *Datura* plants contain atropine and scopolamine as the major alkaloidal constituents. The corrosion inhibition potential of these plants can very well be correlated to the presence of these phytoconstituents. Both these compounds have heterocyclic ring structure which aids the process of adsorption through the participation of the lone pair of electrons present over nitrogen, oxygen and the $\pi$–electron clouds. The likely synergistic influence of other phytoconstituents cannot be ruled out at this stage.

*S. nigrum* belonging to the Solanaceae family is very much useful in the preparation of food stuffs. This plant also has medicinal properties. The extract of leaves of this plant has also been found to possess corrosion inhibiting nature. In sulphuric acid medium, the inhibition percentage is 92.07% at room temperature at a concentration 50 ppm. In sulphuric acid medium the IE is higher compared to the HCl medium. This plant extract also shows dose dependent inhibition with IE increasing
with rise of temperature. It is to be noted that solasodine a glyco alkaloid is present to the extent of 3000 ppm in this plant.

*S. tuberosum* commercially known as potato plant is one of the most widely used vegetables in India. Potato known for its rich starch content has paved way for the development of boiler compounds. Extract of this plant at a very low concentration of 4 ppm shows 60% of IE in HCl medium and nearly 69% in H2SO4 medium. At a concentration of 20 ppm the IE reached a maximum of 80.11% in H2SO4 medium. From the Table 2.4 it could be seen that with rise of temperature, *S. tuberosum* shows a steady increase in the IE. This plant too belongs to Solanaceae family and contains solanesol, a glyco alkaloid. It is worth recalling that the plants of this family are the house of tropane alkaloids which are also known as solanaceous alkaloids. It is likely that these alkaloids play a vital role in the corrosion inhibition activities.

Piperaceae is a family famous for pepper and other spices. Black pepper botanically known as *Piper nigrum* is often called as black gold. The fruits of the black pepper are evaluated for its corrosion inhibition potential. Srivatsava *et al* [12] has studied the anticorrosion efficiency of leaves of this plant. In an effort to pinpoint the active ingredient responsible for the anticorrosion effect, study has been carried out first with extract of black pepper. At a concentration of 50 ppm, *P. nigrum* shows a maximum IE of 81.62% and 90.86% in HCl and H2SO4 medium respectively. Careful examination of the test coupons after the weight loss study revealed the formation of an adherent coating over the coupons. Further there was no visible evolution of hydrogen gas either at room temperature or at higher temperatures.
*P. nigrum* in addition to terpenoidal constituents like citral also contains piperine as the major alkaloidal ingredient. The concentration of this alkaloid is as high as 90,000 ppm. This certainly tells that the role of piperine in anticorrosion effect of *P. nigrum* cannot be ruled out.

*Rauvolfia serpentina* is a medicinally important plant found in tropical regions in India [13]. It is cultivated commercially for its export value. Reserpine the major alkaloid present in this plant has been proved to be a very effective antihypertensive drug [14]. The plant belongs to the family of Apocyanaceae. The leaves of this plant are now investigated for the corrosion inhibition potential. This plant shows almost the same inhibition efficiency in both HCl and H₂SO₄ media at higher temperatures. Examination of Table 2.6 reveals that at 50 ppm concentration the increase in the IE with rise of temperature is not appreciable.

Generally it can be inferred that the protective action of plant extracts can be attributed to the adsorption of the phytoconstituents over the surface of the metal. This protective layer formed, shields the metal from further corrosion [15]. The increase of temperature decreases the hydrogen evolution overvoltage that leads to the spurt in the cathodic reaction. On the other hand, increase of temperature accelerates the chemisorption of the inhibitor on the metal surface [16]. When the latter effect is predominant, the final result is an increase of inhibiting effect, which was observed in our studies.

In the case of *R. serpentina*, it is likely that all active sites are blocked by the adsorbed layer of phytoconstituents and any further rise in temperature does not
increase the number of active sites as the protective action seems to be near complete even at 323 K.

The corrosion inhibition effect of *Strychnos nux – vomica* resembles that of *S. tuberosum*. One inexplicable observation is that (Table 2.7) the increase of temperature does not alter the IE appreciably in H₂SO₄ medium while in HCl medium there is a significant rise of IE with rise of temperature. *S. nux – vomica* the poisonous plant of Loganaiceae is medicinally useful as a stimulant in small doses and is also rich in alkaloids such as brucine and strychnine.

2. 5. **Mechanism of corrosion inhibition**

The adsorption isotherms are very important to understand the mechanism of organo-electrochemical reactions [17]. The adsorbed layer combats the action of corrosive media (HCl and H₂SO₄) and enhances the protection of metal surface. Weight loss data are quite useful in determining the inhibitor’s adsorption characteristics and are useful in the construction of adsorption isotherms. Adsorption mechanism could be assigned from these plotted adsorption isotherms. The surface coverage (θ) values were evaluated using weight loss values.

\[
\text{Surface coverage (}\theta\text{)} = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \quad (2.3)
\]

The θ values for different concentrations of inhibitors were tested graphically by fitting into several isotherms viz., Temkin, Langmuir, Frumkin, and Freundlich adsorption isotherms. The equations (2.5) and (2.6) represent the mathematical form of Temkin and Langmuir adsorption isotherms.

\[
K_{\text{ads}} C = e^{\theta} \quad (2.4)
\]

\[
\theta (1 - \theta) = K_{\text{ads}} C \quad (2.5)
\]
Where, $K_{ads}$ is the equilibrium constant of the adsorption process.

A plot of surface coverage $Vs \ln C$ is usually called Temkins plot while Langmuir adsorption isotherm involves a plot of $\ln (\theta/1-\theta)$ vs $\ln C$. From the figures 2.2-2.29, it can be observed that all the seven plant extracts follow Temkin and Langmuir adsorption isotherms. The regression coefficient (closer to unity) supports the linearity in the plot. Thus it is evident that adsorption plays a very vital role in the control of corrosion by these plant extracts.
Fig. 2. 2. Temkin plot of *D. metel* extract on MS corrosion in 1M HCl medium

Fig. 2. 3. Temkin plot of *D. metel* extract on MS corrosion in 1M H₂SO₄ medium

Fig. 2. 4. Temkin plot of *D. stramonium* extract on MS corrosion in 1M HCl medium
Fig. 2.5. Temkin plot of *D. stramonium* extract on MS corrosion in 1M H$_2$SO$_4$ medium

Fig. 2.6. Temkin plot of *S. nigrum* extract on MS corrosion in 1M HCl medium

Fig. 2.7. Temkin plot of *S. nigrum* extract on MS corrosion in 1M H$_2$SO$_4$ medium
Fig. 2.8. Temkin plot of \textit{S. tuberosum} extract on MS corrosion in 1M HCl medium

Fig. 2.9. Temkin plot of \textit{S. tuberosum} extract on MS corrosion in 1M H\textsubscript{2}SO\textsubscript{4} medium

Fig. 2.10. Temkin plot of \textit{P. nigrum} extract on MS corrosion in 1M HCl medium
Fig. 2.11. Temkin plot of *P. nigrum* extract on MS corrosion in 1M H₂SO₄ medium

Fig. 2.12. Temkin plot of *R. serpentina* extract on MS corrosion in 1M HCl medium

Fig. 2.13. Temkin plot of *R. serpentina* extract on MS corrosion in 1M H₂SO₄ medium
Fig. 2.14. Temkin plot of *S. nux-vomica* extract on MS corrosion in 1M HCl medium

Fig. 2.15. Temkin plot of *S. nux-vomica* extract on MS corrosion in 1M H₂SO₄ medium
Fig. 2.16. Langmuir plot of *D. metel* extract on MS corrosion in 1M HCl medium

Fig. 2.17. Langmuir plot of *D. metel* extract on MS corrosion in 1M H₂SO₄ medium

Fig. 2.18. Langmuir plot of *D. stramonium* extract on MS corrosion in 1M HCl medium
Fig. 2.19. Langmuir plot of *D. stramonium* extract on MS corrosion in 1M \( \text{H}_2\text{SO}_4 \) medium

Fig. 2.20. Langmuir plot of *S. nigrum* extract on MS corrosion in 1M \( \text{HCl} \) medium

Fig. 2.21. Langmuir plot of *S. nigrum* extract on MS corrosion in 1M \( \text{H}_2\text{SO}_4 \) medium
Fig. 2.22. Langmuir plot of *S. tuberosum* extract on MS corrosion in 1M HCl medium

Fig. 2.23. Langmuir plot of *S. tuberosum* extract on MS corrosion in 1M H₂SO₄ medium

Fig. 2.24. Langmuir plot of *P. nigrum* extract on MS corrosion in 1M HCl medium
Fig. 2.25. Langmuir plot of *P. nigrum* extract on MS corrosion in 1M H₂SO₄ medium

Fig. 2.26. Langmuir plot of *R. serpentina* extract on MS corrosion in 1M HCl medium

Fig. 2.27. Langmuir plot of *R. serpentina* extract on MS corrosion in 1M H₂SO₄ medium
Fig. 2. 28. Langmuir plot of *S. nux-vomica* extract on MS corrosion in 1M HCl medium

Fig. 2. 29. Langmuir plot of *S. nux-vomica* extract on MS corrosion in 1M H2SO4 medium
From the equation of Temkin adsorption isotherm, free energy of adsorption \((\Delta G)\) was calculated using following derivation.

\[
e^{\theta} = K_{ads} C \quad (2.6)
\]

\[
f \theta = \ln K_{ads} C \quad (2.7)
\]

\[
\theta = 1/f \ln K_{ads} + 1/f \ln C \quad (2.8)
\]

plotting \(\theta\) Vs \(\ln C\) (Tempkin plot)

slope = \(1/f\)

Intercept = \(1/f \ln K_{ads}\)

Therefore, Intercept = slope x ln \(K_{ads}\)

\[
\ln K_{ads} = \text{Intercept} / \text{slope} \quad (2.9)
\]

\[
K_{ads} = \text{Anti ln (intercept / slope)} \quad (2.10)
\]

The adsorption of inhibitor molecules from an aqueous solution can be regarded as a quasi-substitution process between the inhibitor molecules in the aqueous phase and water molecules at the surface. The equilibrium constant of the adsorption process \(K_{ads}\) is related to the free energy of adsorption \(\Delta G^0_{ads}\) by,

\[
K_{ads} = (1/55.5) e^{(-\Delta G^0_{ads}/RT)} \quad (2.11)
\]

\[
\Delta G^0_{ads} = -RT \ln (55.5 \text{ K}) \quad (2.12)
\]

where, 55.5 is the molar concentration of water in solution, \(R\) is the gas constant \((8.314 \text{ JK}^{-1}\text{mol}^{-1})\) and \(\Delta G^0_{ads}\) is the adsorption energy. The values of activation energy \((Ea)\) were calculated using the Arrhenius equation \((2.13)\) \([2]\).

\[
\ln \left( \frac{r_2}{r_1} \right) = -\frac{Ea \Delta T}{RT_1 T_2} \quad (2.13)
\]
where, $T_1$ and $T_2$ are Temperatures 1 and 2, $r_1$ and $r_2$ are corrosion rates 1 and 2. Table 2.8 represents the average values of free energy of adsorption ($\Delta G^o_{ads}$) and activation energy ($Ea$).

**Table 2.8. Free energy of adsorption ($\Delta G^o_{ads}$) and activation energy ($Ea$) for mild steel in 1M HCl and 1M H$_2$SO$_4$ solution in the presence and absence of inhibitor**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the plant</th>
<th>$\Delta G^o_{ads}$ $\text{kJmol}^{-1}$</th>
<th>$Ea$ $\text{kJmol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HCl</td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>1.</td>
<td>Blank</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td><em>D. metel</em></td>
<td>12.83</td>
<td>29.43</td>
</tr>
<tr>
<td>3.</td>
<td><em>D. stramonium</em></td>
<td>15.60</td>
<td>21.50</td>
</tr>
<tr>
<td>4.</td>
<td><em>S. nigrum</em></td>
<td>16.57</td>
<td>78.01</td>
</tr>
<tr>
<td>5.</td>
<td><em>S. tuberosum</em></td>
<td>31.27</td>
<td>32.50</td>
</tr>
<tr>
<td>6.</td>
<td><em>P. nigrum</em></td>
<td>25.86</td>
<td>35.09</td>
</tr>
<tr>
<td>7.</td>
<td><em>R. serpentina</em></td>
<td>47.42</td>
<td>68.07</td>
</tr>
<tr>
<td>8.</td>
<td><em>S. nuix-vomica</em></td>
<td>14.33</td>
<td>72.21</td>
</tr>
</tbody>
</table>

The negative values of $\Delta G^o_{ads}$ ensure the spontaneity of the adsorption process, stability of the adsorbed layer on metal surface and strong interaction of the inhibitor molecules on the mild steel surface [18, 19]. Donahue et al [20] and Kamis et al [21] reported that chemisorption plays a main role when the values of $\Delta G^o_{ads}$ exceeds more than -40 kJmol$^{-1}$. Physisorption plays a main role if it is lower than -40kJmol$^{-1}$. Tariq Saeed [22] reported that when $\Delta G^o_{ads}$ values are more negative than
-30 kJmol⁻¹ the inhibitor system involves both electrostatic adsorption and chemisorption. On the basis of the values of ΔG°_ads, it can be inferred that D. metel and D. stramonium follow physisorption in both acid media while R. serpentina follows chemisorption in both acid media. S. nigrum, P. nigrum, S. nux-vomica follow physisorption in HCl media, S. nigrum and S. nux-vomica follow chemisorption in H₂SO₄ medium, S. tuberosum follows both electrostatic adsorption and chemisorption in both acid media and P. nigrum follows chemisorption in H₂SO₄ medium. The above observations however are not supported by the variation of IE with increase of temperature.

The values of energy of activation energy (Ea) give an insight into the mode of adsorption. The Ea values when being smaller than that in free acid media is generally interpreted by a specific type of adsorption of the inhibitors [23, 24]. Machu et al [25] also stated that corrosion process taking place in the presence of powerful inhibitors is characterized by smaller activation energy than in uninhibited solution. These explanations agree with our results and this decrease of activation energy may be attributed to the process of chemisorption of phytoconstituents on the MS surface [26, 27].

As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitor at the metal – solution interface is the first step in the mechanism of action of inhibitors in aggressive media. Four types of adsorption may take place involving organic molecules at the metal – solution interface.
i. electrostatic interaction between charged molecules and the charged metal

ii. interaction of unshared electron pairs in the molecule with the metal

iii. interaction of π – electrons with the metal and

iv. a combination of the above [28].

The data obtained from the temperature dependence of the inhibition process suggest a chemical adsorption. To further elucidate the mechanism of inhibitor adsorption, it is necessary to establish the adsorption modes of the inhibiting species. The predominant adsorption mode depends upon factors such as the extract composition, type of acid anion as well as chemical changes to the extract. Since, the isolated inhibitor from chloroform layer is basic in nature; protonation occurs easily in HCl and H₂SO₄ media. The protonated species can get adsorbed on cathodic sites of the MS surface and reduce H₂ gas evolution.

Plant extracts inhibit the dissolution reaction by adsorption at the metal surface in two different ways [29]. First, the inhibitor may compete with Cl⁻ or SO₄²⁻ ions for sites at the water covered anodic surface. In doing so, the protonated inhibitor loses its associated protons in entering the double layer and chemisorbs by donating electrons to the metal. In addition, the protonated inhibitor electrostatically adsorbs onto the anion covered surface, through its cationic form. Both the modes are depicted in Figure. 2.30. But, since chemisorption plays a main role, competitive adsorption of the green inhibitor which involves the donation of electron pair to the metal surface appears predominant.
Fig. 2. 30. a) competitive and b) cooperative adsorption of green inhibitor in acid solutions.

Moreover, all the green inhibitors show good inhibition efficiency in H₂SO₄ medium than in HCl medium. This may be due to the well known fact that chloride ions are strongly adsorbed on the metal surface leaving less space for organic molecules to get adsorbed. But, sulphate ions adsorb considerably to a lesser extent than chloride ions on the metal surface leaving more space on the metal surface for organic molecules to get adsorbed [30]. Thus the availability of more sites on the metal surface in H₂SO₄ leads to the greater inhibition of mild steel in H₂SO₄ medium.

From the weight loss studies it is found that all these extracts inhibit corrosion in both the acid media in a dose dependent manner. Temperature studies and calculated thermodynamic parameters revelaed that the inhibitor preferably followed the chemisorption mode. All the green inhibitors showed better inhibition efficiency in H₂SO₄ medium rather than in HCl medium.
References:


