Cissus quadrangularis as green corrosion inhibitor for mild steel in acid medium

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ABSTRACT
The inhibition effect of Cissus Quadrangularis extract on mild steel in 1N HCl was studied by weight loss measurement. The inhibition effect increases with increase in concentration of green inhibitor and immersion period. Studies on the effect of temperature indicated that the inhibition efficiency increased with temperature. The kinetic and thermodynamic parameters indicated that inhibition was spontaneous chemisorption obeying Langmuir isotherm. Preliminary physiochemical screening of extract supports the presence of active component responsible for adsorption. SEM was used to analyse adsorbed surface film.

Key Words: Green inhibitor, Corrosion inhibitor, mild steel, adsorption, weight loss.

1. INTRODUCTION
Corrosion causes disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety and environmental pollution [1]. Due to these harmful effects corrosion is an undesirable phenomenon that ought to be prevented. There are several ways of preventing corrosion and the use of inhibitors is one of the best methods to reduce and/or prevent corrosion [2]. As organic corrosion inhibitors are toxic in nature, green inhibitors which are biodegradable, without any heavy metals and other toxic compounds, are promoted [3]. Also plant products are inexpensive, renewable, and readily available. Cissus Quadrangularis(CQ) a perennial shrub reaching a height of 1.5 m and has quadrangular-sectioned branches with internodes 8 to 10 cm long and 1.2 to 1.5 cm wide, commonly found in India or Sri Lanka, but is also in Africa, Arabia, and Southeast Asia. It belongs to family Vitaceae (Grape family). Cissus Quadrangularis(CQ) has been used as a medicinal plant. It contains a high percentage of calcium ions (4% by weight) and phosphorous. It has been used to heal broken bones and injured ligaments and tendons. It is also been known as antibacterial, antifungal, antioxidant, anthelmintic, antihemorrhoidal and analgesic agents. However, Cissus Quadrangularis(CQ) has not been exploited as corrosion inhibitor for...
mild steel in HCl medium. In view of its phytochemical investigation, the present paper reporting for the first time the inhibitive performance of Cissus Quadrangularis (CQ) extract as an eco-friendly corrosion inhibitor for mild steel in HCl medium by Weight loss measurements and Scanning Electron Microscope.

2. MATERIALS AND METHODS
Properly double distilled water and Analar grade hydrochloric acid was used throughout the experiment. Analar grade ethanol used as purchased without distillation. Cissus Quadrangularis washed and dried in shade. About 50g of dried leaves were refluxed with 1000ml of 1N HCl for 2 hours. The acid extract was kept overnight and filtered. The extract was made up to 1000ml and taken as 5% stock solution. From this various vol. % ranging from 0.05% to 1% extract have been prepared. Weight loss measurements were performed using specimens with a dimension of 5 × 2 × 0.2cm and 0.2 cm diameter hole near the upper edge of the specimen. The specimens were polished and degreased with ethanol and acetone and dried in a desicator before being immersed in the CQ extract solution. The specimens were immersed in 100ml of 1N HCl without and with inhibitors of different concentration from 0.05%, 0.1%, 0.2%, 0.4%, 0.6%, 0.8% and 1%. Experiments were carried out in 1N HCl at 298K for 0.5, 1, 2, 4, 6, 8, 24, 48 and 72 hrs respectively. The influence of temperature on corrosion of mild steel has been carried out at different temperatures via, 298K, 313K, 323K, 333K and 343K in the absence and presence of inhibitor at 1h immersion period. Each experiment was carried out in triplicate and recorded as an average of three reading taken way to the 4th decimal on an analytical balance. Inhibition efficiency was calculated using the following relation,

IE (%) = (W$_1$ - W$_2$)/W$_1$× 100

Where W$_1$ and W$_2$ are the weight loss in absence and presence of inhibitor respectively.

Corrosion rate $C_R$ (mg cm$^{-2}$ h$^{-1}$), was calculated using the formula,

$C_R = \Delta w/ St$

Where $\Delta w$ is the weight loss (mg), t is the immersion time (h), S is the surface area of the specimen in (cm$^2$). Phytochemical screening was carried out on a freshly prepared extract. The different chemical constituents tested include reducing sugars, saponins, tannins, glycosides, alkaloids and flavonoids [4]. The specimens used for surface morphological examination were immersed in 1N HCl containing 1.0% of Inhibitor and in 1N HCl separately for 1 h. They were removed and washed quickly with rectified spirit and dried. The analysis was performed on HITACHI model S-3000 H scanning electron microscope.

3. RESULTS AND DISCUSSION
WEIGHT LOSS METHOD
Effect of concentration
Weight loss measurements were carried out in 1N HCl in the absence and presence of CQ extract of concentration ranging from 0.05 to 1.0%. Inhibition efficiency increases with respect to increase in the concentration of Inhibitor and showed a maximum value of 97.00% at a concentration of 1.0% for CQ extract. There is a decrease in the corrosion rate with respect to increase in the concentration of Inhibitor. The results indicate that the addition of inhibitor increase the inhibition efficiency of CQ extract on mild steel surface in 1N HCl medium through adsorption and protect against corrosion.

Effect of immersion time
To study the stability of inhibitive behavior of the extract with respect to time, weight loss measurements were performed in the presence and absence of the extract for all concentration ranging from 0.05% to 1.0% at the immersion period of 0.5h to72h in 1N HCl medium. The inhibition efficiency of CQ extract on mild steel as a function of time is presented in Fig. 1. The result shows that inhibition efficiency increases with increase in the immersion period and reaches a maximum value at 24hr and then remains almost constant. The result indicates that effective adsorption of CQ extract on mild steel surface occurs at 24hrs.

Effect of Temperature
It was clear that the corrosion of mild steel was prevented through adsorption process by CQ extract. Hence, the effect of temperature on the inhibition efficiency of green inhibitor on mild steel in 1N HCl medium becomes more important. Weight loss measurements were carried out in the absence and presence of CQ extract of all concentrations on mild surface in 1N HCl at different temperatures from 298K to 343K. The inhibition efficiency and corrosion rate of CQ extract on mild steel at different temperatures with immersion period of 1h are presented in Table 1 & 2.
It is evident from the table that inhibition efficiency increases with increasing temperature. This is due to increased rate of dissolution of mild steel and chemical adsorption of inhibitors on the metal surface with temperature [5]. From the Table 2, it is clear that, the $C_R$ increases with increasing temperature in the absence of the inhibitor. However this increase seems slightly in the presence of CQ extract.

The relationship between the corrosion rate ($C_R$) of mild steel and temperature can be expressed by the Arrhenius equation [6, 7, 8].

$$C_R = K \exp \left( \frac{-E_a}{RT} \right)$$

Where $E_a$ is the activation energy, $K$ is the pre exponential factor, $R$ is the gas constant and $T$ is the absolute temperature. The plots of log $C_R$ vs $1/T$ is presented in Fig 2. The values of $E_a$ and $K$ at various concentrations of extract were computed from slopes and intercepts respectively and tabulated in Table 3. The activation energy decreases with increase in the concentration of the CQ extract. The decrease in the values of activation energy in the presence of CQ extract compared to uninhibited system supports the mechanism of the corrosion process in the presence of adsorbed inhibitor molecule is chemisorptions[9] and it is the indication of the formation of an adsorbed film on metal surface by a chemical process [5].

The values of enthalpy and entropy of activation can be calculated using the following equation.

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

Plots of log ($C_R/T$) vs $1/T$ is presented in Fig.3. $\Delta H^*$ and $\Delta S^*$ calculated from the slope and intercept of the plots of log ($C_R/T$) vs $1/T$ respectively. The activation parameters viz $E_a$, $\Delta H^*$, $\Delta S^*$ are presented in Table 3. The positive values of $\Delta H^*$ both in the absence and presence of inhibitor indicate the endothermic nature of mild steel dissolution process [10].

The negative value of $\Delta S^*$ both in the presence and absence of inhibitor indicate that the activated complex in the rate determining step represents an association rather than dissociation. The decrease in the disorder of the system due to the adsorption of inhibitor molecule on to the metal surface [11]. It reveals the formation of an ordered stable layer of inhibitor on the steel surface [12].

![Figure 1 Inhibition efficiency of Inhibitor vs Time](image-url)
Table 1
Inhibition efficiency of Cissus Quadrangularis extract on mild steel in 1N HCl at 1h immersion period from weight loss method at different temperature.

<table>
<thead>
<tr>
<th>Conc.,(%)</th>
<th>298K</th>
<th>313K</th>
<th>323K</th>
<th>333K</th>
<th>343K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0069</td>
<td>0.0108</td>
<td>0.0689</td>
<td>0.1326</td>
<td>0.1316</td>
</tr>
<tr>
<td>0.05</td>
<td>56.52</td>
<td>46.29</td>
<td>82.43</td>
<td>81.29</td>
<td>76.97</td>
</tr>
<tr>
<td>0.1</td>
<td>62.31</td>
<td>58.33</td>
<td>88.67</td>
<td>85.82</td>
<td>85.94</td>
</tr>
<tr>
<td>0.2</td>
<td>66.66</td>
<td>61.11</td>
<td>91.43</td>
<td>87.07</td>
<td>87.08</td>
</tr>
<tr>
<td>0.4</td>
<td>72.46</td>
<td>66.66</td>
<td>92.74</td>
<td>92.30</td>
<td>88.44</td>
</tr>
<tr>
<td>0.6</td>
<td>75.36</td>
<td>72.22</td>
<td>92.88</td>
<td>92.60</td>
<td>91.41</td>
</tr>
<tr>
<td>0.8</td>
<td>78.26</td>
<td>75.00</td>
<td>95.06</td>
<td>97.73</td>
<td>92.62</td>
</tr>
<tr>
<td>1</td>
<td>79.21</td>
<td>78.70</td>
<td>96.22</td>
<td>98.41</td>
<td>92.85</td>
</tr>
</tbody>
</table>

Table 2
CR of Cissus Quadrangularis extract on mild steel in 1N HCl at 1h immersion period from weight loss method at different temperature.

<table>
<thead>
<tr>
<th>Conc.,(%)</th>
<th>298K</th>
<th>313K</th>
<th>323K</th>
<th>333K</th>
<th>343K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.298246</td>
<td>0.473684</td>
<td>3.02193</td>
<td>5.815789</td>
<td>5.77193</td>
</tr>
<tr>
<td>0.05</td>
<td>0.122807</td>
<td>0.254386</td>
<td>0.530702</td>
<td>1.087719</td>
<td>1.328947</td>
</tr>
<tr>
<td>0.1</td>
<td>0.114035</td>
<td>0.197368</td>
<td>0.342105</td>
<td>0.824561</td>
<td>0.811404</td>
</tr>
<tr>
<td>0.2</td>
<td>0.092105</td>
<td>0.184211</td>
<td>0.258772</td>
<td>0.614035</td>
<td>0.745614</td>
</tr>
<tr>
<td>0.4</td>
<td>0.087719</td>
<td>0.157895</td>
<td>0.219298</td>
<td>0.447368</td>
<td>0.666667</td>
</tr>
<tr>
<td>0.6</td>
<td>0.078947</td>
<td>0.131579</td>
<td>0.214912</td>
<td>0.429825</td>
<td>0.495614</td>
</tr>
<tr>
<td>0.8</td>
<td>0.065789</td>
<td>0.118421</td>
<td>0.149123</td>
<td>0.131579</td>
<td>0.425439</td>
</tr>
<tr>
<td>1</td>
<td>0.057018</td>
<td>0.100877</td>
<td>0.114035</td>
<td>0.092105</td>
<td>0.412281</td>
</tr>
</tbody>
</table>

Figure 2: log CR vs 1/T
Table 3
Activation parameter for mild steel in 1N HCl in the absence and presence of different concentration of Cissus Quadrangularis extract

<table>
<thead>
<tr>
<th>Conc., (%)</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>0</td>
<td>59.97</td>
<td>62.24</td>
<td>0.911</td>
</tr>
<tr>
<td>0.05</td>
<td>44.81</td>
<td>46.99</td>
<td>-57.43</td>
</tr>
<tr>
<td>0.1</td>
<td>38.19</td>
<td>40.88</td>
<td>-80.42</td>
</tr>
<tr>
<td>0.2</td>
<td>38.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>36.24</td>
<td>38.8</td>
<td>-88.2</td>
</tr>
<tr>
<td>0.6</td>
<td>33.91</td>
<td>36.8</td>
<td>-95.52</td>
</tr>
<tr>
<td>0.8</td>
<td>26.53</td>
<td>29.35</td>
<td>-122.06</td>
</tr>
<tr>
<td>1</td>
<td>27.18</td>
<td>28.67</td>
<td>-125.75</td>
</tr>
</tbody>
</table>

Figure 3: $\log C/R$ vs $1/T$

Adsorption isotherm
The interaction between the inhibitors and steel surface is adsorption. The adsorption isotherm is very important to understand the mechanism of adsorption reaction. Weight loss data are quite useful in determining the adsorption characteristics of the inhibitor and are useful in the construction of adsorption isotherms. The surface coverage ($\theta$) values were calculated using the formula

$$\theta = \frac{(W_1 - W_2)}{W_1}$$

Where $W_1$ is the weight loss in the absence of inhibitor. $W_2$ is the weight loss in the presence of inhibitor.
Many attempts have been made to find the best isotherm. Langmuir adsorption isotherm was found to be the best isotherm for the adsorption of CQ extract on mild steel. According to the Langmuir adsorption isotherm, \( \Theta \) is related to the inhibitor concentration via:

\[
\frac{C}{\Theta} = \frac{1}{K_{\text{ads}}} + C
\]

The plot of \( C/\Theta \) vs \( C \) gave a straight line (Fig 4), with a slope equal to unity confirming that the adsorption of CQ extract on mild steel obeys the Langmuir adsorption isotherm. According to this isotherm, there is no interaction between the inhibitor molecules, and the energy of adsorption is independent on the degree of surface coverage(\( \Theta \)). Langmuir isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site occupies one adsorbed species.

The thermodynamic parameters for the adsorption process were calculated, using the following equations.

\[
K_{\text{ads}} = \exp \left( \frac{-\Delta H_{\text{ads}}}{RT} \right)
\]

\[
\log K_{\text{ads}} = \log\left( \frac{-\Delta H_{\text{ads}}}{RT} \right) + \Delta S_{\text{ads}}
\]

The \( \Delta H_{\text{ads}} \) and \( \Delta S_{\text{ads}} \) were calculated from the slope and intercept of plot of \( \log K_{\text{ads}} \) vs \( 1/T \). The plot of \( \log K_{\text{ads}} \) vs \( 1/T \) is presented in Fig 5. The thermodynamic parameters of adsorption process are presented in Table 4. The negative values of \( \Delta G_{\text{ads}} \) indicate the spontaneity of the adsorption process, and the stability of the adsorbed layer on metal surface and strong interaction of the inhibitor molecule on the steel [13]. The \( \Delta G_{\text{ads}} \) value confirmed the chemisorptions process [14].

The process of chemisorption also further confirmed by the negative value of \( \Delta H_{\text{ads}} \) (an exothermic process). An exothermic process with a \( \Delta H_{\text{ads}} \) value closer to 40kJ/mol favours chemisorption. The negative value of \( \Delta S_{\text{ads}} \) implies that activated complex in the rate determining step represents an association rather than dissociation step. The decrease in disordering takes place on going from reactants to the activated complex [15,16,17,18].

**Phytochemical Screening**

From the earlier literature, it was very clear that the presence of phytochemical is responsible for the anticorrosion action. Hence, the presence of various phytochemicals was analysed (Usmanet al.2009). It was presented in the Table 5. CQ extract showed the presence of tannins, saponins and glycosides. The presence of tannin and its derivatives can be used to protect steel from corrosion in saline and strong pickling acids [19].

**Scanning Electron Microscopy**

The protective layer that formed on the metal surface characterised by SEM analysis. Morphologies of mild steel in the absence and presence of 1% of CQ extract at 30°C are shown in Fig.6. It reveals that the mild steel surface after immersion in 1N HCl for 1hr shows an aggressive attack of the HCl on the steel surface. The corrosion products appear very uneven and lepidotreal-like morphology and surface is rather rough. In the presence of 1% of CQ extract, there is an adsorbed film on mild steel surface Fig 6. which conclude that the adsorption film can efficiently inhibit the corrosion of steel.

**4. CONCLUSIONS**

The following conclusions were drawn from the present study.

1. CQ extract act as a good inhibitor for corrosion of mild steel in HCl medium. The inhibition efficiency increase with concentration of the inhibitor.
2. The CQ extract inhibits corrosion upto 97.00% in HCl medium at a concentration of 1% and at a temperature of 343K.
3. Inhibition efficiency of CQ extract with increase of temperature, which is due to chemisorption following Langmuir adsorption isotherm.
   The free energy of adsorption (\( \Delta G_{\text{ads}} \)) values obtained were -13.88 KJ/mol for CQ extract supports the chemisorption mode adsorption.
4. Presence of tannin and saponins are responsible for the formation of adsorption layer on the mild steel.
5. SEM analysis supports the formation of protective layer over the mild steel surface by the CQ extract.
Cissus quadrangular is as green corrosion inhibitor for mild steel in acid medium, Indian Journal of Science, 2015, 13(39), 60-68, http://www.discovery.org.in/ij.htm

Figure 4. C/θ vs C

Figure 5: log K_{ads} vs. 1/T
Table 4
Thermodynamic parameter for adsorption of Cissus Quadrangularis extract on mild steel in 1N HCl from Langmuir adsorption isotherm.

\[
\begin{array}{ccc}
\Delta H_{ads} & \Delta S_{ads} & \Delta G_{ads} \\
kJ mol^{-1} & J mol^{-1} K^{-1} & kJ mol^{-1} \\
-24.59 & -46.68 & -13.88 \\
\end{array}
\]

Table 5
Preliminary phytochemical screening of both Cissus Quadrangularis extract

<table>
<thead>
<tr>
<th>Tests</th>
<th>Cissus Quadrangularis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponins</td>
<td>+</td>
</tr>
<tr>
<td>Tannins</td>
<td>+</td>
</tr>
<tr>
<td>Flavonoids</td>
<td>_</td>
</tr>
<tr>
<td>Alkaloids</td>
<td>_</td>
</tr>
<tr>
<td>Cardiac glycosides</td>
<td>+</td>
</tr>
<tr>
<td>Cyanogenic glycosides</td>
<td>_</td>
</tr>
<tr>
<td>glycosides</td>
<td>+</td>
</tr>
</tbody>
</table>

(a)
Figure 6 SEM image of mild steel (a) in 1N HCl (b) in 1.0% of CQ extract at immersion period of 24h

REFERENCES