Corrosion Inhibition Performance of Ethanol Extract Leaves of *Cucurbita pepo* (Pumpkin) on Mild Steel in Acidic Media

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**ABSTRACT**

The use of inorganic and synthetic organic compounds as corrosion inhibitors is becoming unpopular due to environmental concerns. The focus of most corrosion mitigation research is now on the use of environmentally friendly substances. This paper reports on the use of the ethanol extract of the leaves of *Cucurbita pepo* against the corrosion of mild steel in 1.0 M solution of hydrochloric acid using weight loss and linear polarization measurements at 303-333 K. The plant extract was found to retard the corrosion of steel coupons in the acid media at 95% inhibition efficiency thereby functioning as a good corrosion inhibitor against the dissolution of steel in 1.0 M solution of hydrochloric acid. Apparent activation energy values in the inhibited systems (16.42 kJ/mol, 16.52 kJ/mol/17.26 kJ/mol, 19.34 kJ/mol) were found to be greater than that of the free acid solution (10.48 kJ/mol) showing the adsorption of the plant extract on the steel surface to be by physical mechanism. In the study, values of enthalpy, $\Delta H^*$ were all negative showing the exothermic nature of the corrosion and inhibition processes while free energy values for the inhibition processes at 303 K and 333 K were -16.48 kJ/mol and -15.59 kJ/mol respectively revealing the inhibition of mild steel in the acid media by the plant extracts to be spontaneous.

**Keywords:** Acid, Adsorption, Corrosion, Mild steel, Temperature, Weight loss

**INTRODUCTION**

Industries depend heavily on the use of metals and alloys for operation. One of the most challenging and difficult tasks for industries is the protection of these metals and alloys from corroding due to their contacts with electrolytes like acids. Steel is an important type of alloy due to its wide range of industrial applications (Ahmad, 2006). It has the advantage of being one of the cheapest alloys because of its low cost of production. Corrosion of steel structures results in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. This has been a source of concern to many corrosion scientists and engineers resulting in many investigations and researches on ways to checkmate this problem.

The use of corrosion inhibitors is an economical and practical way of checkmating the corrosion of steel parts in an acidic environment (Oguzie et al. 2014; Eddy et al. 2015). Corrosion inhibitors are chemicals either synthetic or natural which, when added in small amounts to an environment decrease the rate of attack by the environment on the metals/alloys. A large number of synthetic compounds are known to be good corrosion inhibitors of steel (Eddy et al. 2015; Ramya et al. 2015; Tourabi et al. 2017). Nevertheless, the reputation and use of these synthetic compounds as corrosion inhibitors is diminishing due to strict environmental regulations and health concerns over their toxic effects on man and animals.

The use of extracts from plants parts as corrosion inhibitors perhaps is the answer to all the environmental concerns and fears surrounding the use of synthetic corrosion inhibitors. Plant extracts are environmentally friendly phytochemicals with structures that are similar to those of the synthetic corrosion inhibitors. They possess hetero atoms like oxygen, sulphur, phosphorus, nitrogen and/or conjugated carbon chains that may have aromatic rings (Umoren et al. 2008; Oguzie et al. 2014; Chahul et al. 2018).

In a work by Akpuaka et al (2011) on the phytochemical screening of *Cucurbita pepo*, the leaves of the plant were found to contain phytochemical components which are rich in heteroatoms including alkaloids, tannins, saponins, flavonoids, phenols, steroids, coumarins, reducing sugars and anthocyanins. Perusal of literatures reveals that the leaves of this plant have not been studied for their corrosion inhibitory properties. This paper reports our findings on the use of ethanol extract of the leaves of *Cucurbita pepo* (CP) (pumpkin) against the corrosion of mild steel in 1.0 M HCl using weight loss and linear polarization measurements.
MATERIALS AND METHODS

Materials
Steel sheet were purchased from building materials market, Jos. Analytical balance, dessicator, hand dryer, ethanol, acetone, HCl, SiC paper (#600 and #1200). Analar grade reagents.

Materials Preparation
Mild steel coupons of composition (w %) Fe: 99.14, C: 0.15, Mn: 0.60, P: 0.04, and Si: 0.03; Dimensions: 3.0cm x 2.0cm x 0.6 cm were used for the experiments. They were abraded with emery papers of variable grades, starting with a coarse one (#600) and proceeding to the finer grade (#1200). The coupons were degreased in ethanol, dried in acetone and warm air, and stored in moisture free desiccators prior to use.

Preparation of the Leaf Extracts of Cucurbita pepo
The leafy parts of Cucurbita pepo were collected from Pankshin Local Government Area of Plateau state and identified at the Department of botany, University of Jos. A voucher specimen of the plant was dried by air at 40 °C until all the solvents were completely removed. The dried plant alcoholic extract was used for the corrosion inhibition experiments by preparing inhibitor test solutions in the concentrations 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L. This was achieved by transferring 0.05 g, 0.10 g, 0.15 g, 0.20 g and 0.25 g of the extract into 250 mL of 1.0 M HCl solution in glass jars (Chahul et al. 2017; 2019).

Gravimetric Measurements
Gravimetric experiments were conducted using methods reported in previous studies (Chahul et al. 2017; 2019). Already cleaned and weighed coupons were suspended in the test solutions in glass jars. Weight loss was calculated as the difference between the initial and final weights of the coupons at a fixed time intervals. The effect of immersion time on the corrosion rate of the mild steel with and without CP extract was studied by conducting the experiment for 24 hours, 48 hours, 72 hours, 96 hours, 120 hours, 144 hours and 168 hours.

Inhibition efficiency (% IE) and surface coverage (θ) of CP extract were quantified using equations 1 and 2 (Olasheinde et al. 2013; Chahul et al. 2015).

\[
\text{IE}_{\text{exp}} = \left(1 - \frac{w_1}{w_2}\right) \times 100
\]

\[
\theta = 1 - \frac{w_1}{w_2}
\]

where \(w_1\) and \(w_2\) are the weight losses (g) for mild steel in the presence and absence of CP and \(\theta\) is the degree of surface coverage of CP.

Linear Polarization
Linear polarization measurements were carried as reported elsewhere (Ijau et al., 2016). A three-electrode flask having a saturated calomel electrode (SCE) as reference electrode, platinum (Pt) as an auxiliary electrode and mild steel working electrode, was employed for the experiments.

In quantifying the corrosion current densities \(I_{\text{corr}}\), the linear tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential. Inhibition efficiency was calculated using equation 1 (Ijau et al. 2016; Alhaffar et al. 2018):

\[
\% IE = \frac{I_{\text{corr(bink)}} - I_{\text{corr(ih)}}}{I_{\text{corr(bink)}}} \times 100
\]

where %IE is the inhibition efficiency of the extract of \(CE\), \(I_{\text{corr(ih)}}\) is the corrosion current density of mild steel with CE and \(I_{\text{corr(bink)}}\) is the corrosion current density of mild steel without CE.

RESULTS AND DISCUSSION

Gravimetric Measurements
Fig. 1 is the plot of the effect of time on the weight loss of the mild steel in 1.0 M HCl solution in the absence and presence of various concentrations of CP. The plots reveal that the loss in weights of the steel coupons in the uninhibited and free acid medium generally increased slowly with exposure time up to 96 hours. A significant increase in weight loss of the steel coupons and hence, the corrosion rates of the coupons was noticed just after 96 hours. This phenomenon can be attributable to the anodic dissolution of iron to produce hydrogen gas along with the high solubility of the metal oxides formed as corrosion products (Oguzie et al. 2012). Corrosion rate was however observed to be relatively higher for the mild steel coupon in the free acid solution compared to the test solutions containing CP extracts. This signifies a decrease in the rate of the anodic dissolution of iron in the presence of CP as reflected in Fig. 1.

Fig. 2 is the plot of % IE as a function of time for 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L concentrations of CP extract. Inhibition efficiency increased as follows: 93.12 %, 95.01 %, 96.22 %, 97.64 % and 98.01 % at 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L concentrations respectively, up to 96 hours, before gradually decreasing to 69.71 %, 76.54 %, 80.45 %, 84.39 %
and 89.26% respectively, at 168 hours. This gradual decrease maybe due to desorption of the plant extract from the steel surface on prolonged exposure to the aggressive acid species in the solution (Chahul et al. 2017). Fig. 2 also revealed that CP extract inhibited the corrosion of mild steel within the concentration range studied with higher concentrations of CP extract giving higher values of inhibition efficiency. This observation is attributable to greater surface coverage of the steel coupons by the extract species when they adsorbed on the steel surface thereby preventing more dissolution of iron atoms from the steel surface (Umoren et al. 2008, 2016).

**Linear Polarization Measurement**

Fig. 3 is the linear polarization plot for the corrosion of mild steel in 1.0 M HCl with and without different concentrations of CP. The plot was obtained by measuring the change in corrosion currents by varying applied potentials. The plot revealed that the introduction of CP to the blank solution influenced both the anodic and cathodic half reactions at the surface of the steel coupons by inhibiting both the anodic dissolution of mild steel and cathodic reduction of hydrogen ions. Values of $E_{corr}$ were however more negative at higher CP concentrations. This signifies a mixed-type inhibition mechanism of CP at lower concentrations with predominant cathodic effects at higher concentrations (Nnana et al. 2011; Chidiebere et al. 2012; Oguzie et al. 2012).
Fig. 3: Linear Polarisation Plot for Mild Steel in 1.0 M HCl with and without Different Concentrations of CP.

Table 1: Linear Polarisation Parameters for the Corrosion of Mild Steel in 1.0 M HCl with and without Different Concentrations of CP.

<table>
<thead>
<tr>
<th>Conc (g/L)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>$b_a$(V/dec)</th>
<th>$b_c$(V/dec)</th>
<th>CR(mm/yr)</th>
<th>% I E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-1396.90</td>
<td>262.50</td>
<td>237.13</td>
<td>201.10</td>
<td>3047.30</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>-1728.50</td>
<td>24.73</td>
<td>54.69</td>
<td>63.40</td>
<td>287.37</td>
<td>90.48</td>
</tr>
<tr>
<td>0.4</td>
<td>-1056.60</td>
<td>10.70</td>
<td>56.92</td>
<td>64.62</td>
<td>124.30</td>
<td>95.92</td>
</tr>
<tr>
<td>0.6</td>
<td>-1254.40</td>
<td>5.32</td>
<td>33.22</td>
<td>61.86</td>
<td>18.06</td>
<td>97.88</td>
</tr>
<tr>
<td>0.8</td>
<td>-984.19</td>
<td>0.15</td>
<td>12.04</td>
<td>12.11</td>
<td>99.41</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>-792.14</td>
<td>0.23</td>
<td>6.24</td>
<td>25.04</td>
<td>99.82</td>
<td></td>
</tr>
</tbody>
</table>

Effect of Temperature on the Corrosion of Mild Steel in 1.0 M HCl in the Absence and Presence of CP

The effect of temperature on the corrosion of the steel coupons in inhibited and free acid solutions was investigated with the water bath maintained at 303 K, 313 K, 323 K, and 333 K respectively, for 3 hours. Table 2 presents the values of corrosion rates of steel and inhibition efficiencies of various concentrations of CP at the understudied temperatures. Table 2 also depicts the influence of temperature on the inhibition efficiency of CP extracts.

Table 2: Effect of temperature on the inhibition efficiency (%) and corrosion rate (gh⁻¹cm⁻²) of mild steel in 1.0 M HCl in the absence and presence of Cucurbita pepo (CP).

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>Inhibition efficiency (%)</th>
<th>Corrosion Rate (gh⁻¹cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303 K</td>
<td>313 K</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>68.59</td>
<td>66.97</td>
</tr>
<tr>
<td>0.4</td>
<td>84.29</td>
<td>81.82</td>
</tr>
<tr>
<td>0.6</td>
<td>86.91</td>
<td>85.76</td>
</tr>
<tr>
<td>0.8</td>
<td>89.53</td>
<td>87.88</td>
</tr>
<tr>
<td>1.0</td>
<td>91.10</td>
<td>88.18</td>
</tr>
</tbody>
</table>

The values of inhibition efficiency of CP extract on Table 2 were observed to decrease with temperature at all the concentrations studied. This behaviour has been reported by other researchers to be due to the agitation of the adsorbed inhibitor and its consequent desorption from the surface of the mild steel at higher temperatures, signifying physisorption (Umoren et al. 2008; Oguzie et al. 2012; Chahul et al. 2017).

The Arrhenius equation (equation 4) explains the influence of temperature on the corrosion rates of mild steel in the presence of CP extract (Shukla and Ebenso, 2011; Refat and Ishaq, 2013).
\[ \log CR = \log A - \frac{E_a}{2.303RT} \]

where \( CR \) is the rate of corrosion of the mild steel, \( A \) is the Arrhenius constant, \( E_a \) is the apparent activation energy, \( R \) is the universal gas constant and \( T \) is the absolute temperature of the system in Kelvin (K).

Fig. 4a is the Arrhenius plot of mild steel in 1.0 M HCl with CP at different temperatures. The plot is linear. Values of the apparent activation energy \( (E_a) \) evaluated from the plots are presented on Table 3.

The transition state equation is given as equation 5 (Shukla and Ebenso, 2011; Refat and Ishaq, 2013).

\[
\log \frac{CR}{RT} = \left[ \log \left( \frac{R}{nh} \right) + \frac{\Delta S^*}{2.303R} \right] - \frac{\Delta H^*}{2.303RT} 
\]

where \( CR \) is the corrosion rate at temperature \( T \), \( h \) is the Planck’s constant \( (6.6261 \times 10^{-34} \text{J} \cdot \text{s}) \), \( n \) is Avogadro’s constant \( 6.0225 \times 10^{23} \) and \( R \) is the molar gas constant.

Fig. 4b shows the transition state plot for the corrosion of mild steel in 1.0 M HCl with CP at different temperatures. The plot is also linear with values of \( \Delta H^* \) and \( \Delta S^* \) obtained from the plot presented on Table 3.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>( E_a ) (kJ/mol)</th>
<th>( \Delta H^* ) (kJ/mol)</th>
<th>( \Delta S^* ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>10.48</td>
<td>-44.54</td>
<td>-183.32</td>
</tr>
<tr>
<td>0.2</td>
<td>16.42</td>
<td>-40.94</td>
<td>-158.20</td>
</tr>
<tr>
<td>0.4</td>
<td>16.52</td>
<td>-39.75</td>
<td>-149.03</td>
</tr>
<tr>
<td>0.6</td>
<td>17.26</td>
<td>-38.05</td>
<td>-148.06</td>
</tr>
<tr>
<td>0.8</td>
<td>17.78</td>
<td>-37.82</td>
<td>-147.00</td>
</tr>
<tr>
<td>1.0</td>
<td>19.34</td>
<td>-24.13</td>
<td>-131.83</td>
</tr>
</tbody>
</table>
Investigation of the temperature dependence of corrosion rates, % IE as well as comparison of corrosion apparent activation energies in the inhibited and free acid solutions gives some insight into the likely mechanism of the adsorption of the inhibitor. A decrease in the % IE with a rise in temperature (Table 2) with a corresponding increase in the corrosion activation energy in the presence of an inhibitor compared to its absence (Table 3) is frequently interpreted as being suggestive of formation of an adsorbed film of physical-electrostatic-nature. The opposite outcome, analogous to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of an inhibitor, suggest a chemisorption mechanism (Ashassi-Sorkhabi et al., 2006; Umoren et al. 2008; Mejeha et al., 2010). In this study, % IE decreased at all the concentrations of the plant extract with increase in temperature (Table 2) signifying physisorption. Also, the Ea value obtained for the corrosion of mild steel in the free acid (10.48 kJ/mol) was lower than those obtained for the inhibited acid solutions (Table 3). This confirms the physisorptive nature of the adsorption of CP on the steel surface. Table 3 also shows that values of enthalpies of activation are all negative for all the test solutions which reflect the exothermic nature of the mild steel dissolution process. Also, values of entropies of activation energy are negative and increased in the presence of the plant extract compared to the free acid solution. This implies an increase in disordering on going from reactant to activated complex signifying that the activation complex represents dissociation steps. These results are in excellent agreement with the reports of previous work by (Shukla and Ebenso, 2011; Refat and Ishaq, 2013).

Adsorption Considerations

The establishment of isotherm models that explain the adsorption mechanism of a corrosion inhibitor is very imperative as these isotherms provide significant knowledge about the nature of metal-inhibitor interaction. It has been reported that the adsorption of the inhibitor molecules on a metal substrate depends on a variety of factors such as the presence of functional groups (either electron donating or withdrawing), steric factors, charge distribution at the donor atom, the π orbital character of donating electrons, the nature of substrate metal and the type of interaction between the organic molecules and the metal surface (Niu et al. 2005; Morad, 2008).

In trying to understand the adsorption mechanism of CP extract on the steel surface, surface coverage values obtained from weight loss measurement were fitted into various adsorption models. The adsorption studies indicated that the Langmuir isotherm described the adsorption of CP molecules on the steel surface. This signifies a monolayer adsorption of CP molecules on the steel surface and that there was the formation of a layer of insoluble complex of the iron on the steel surface which acted as a barrier between the metal surface and the corrosive ions in HCl. Equation 6 is the linearized form of Langmuir isotherm (Chahul et al. 2017, 2019):

$$\frac{C}{\Theta} = \frac{1}{K_{ads}} + C$$

where C is the concentration of CP, $K_{ads}$ is the adsorption equilibrium constant, $\Theta$ is the degree of surface coverage of CP. The plot of $\frac{C}{\Theta}$ vs C with slope as $\frac{1}{K_{ads}}$ was linear with a regression coefficient value, $R^2 \geq 0.99$ (Chahul et al. 2017, 2019).

Equations 7 and 8 show the relationship between $K_{ads}$ and free energy of adsorption (Shukla and Ebenso, 2011; Refat and Shukla, 2013),

$$\log K_{ads} = -1.744 - \frac{\Delta G_{ads}}{2.303 RT}$$

$$\Delta G_{ads} = -2.303 \times RT \log (55.5 K_{ads})$$

Fig. 5: Graph of the Langmuir Isotherm for the Adsorption of CP onto Mild Steel Surface in 1.0 M HCl at 303K and 333K respectively.
Table 4: Langmuir Isotherm Adsorption Parameters for the Corrosion of Mild Steel in 1.0 M HCl with CP Extract.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Intercept</th>
<th>Slope</th>
<th>$K_{ads}$ (M⁻¹)</th>
<th>$R^2$</th>
<th>$\Delta G^0$ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.080</td>
<td>1.015</td>
<td>12.50</td>
<td>0.999</td>
<td>-16.484</td>
</tr>
<tr>
<td>333</td>
<td>0.199</td>
<td>1.006</td>
<td>5.03</td>
<td>0.997</td>
<td>-15.592</td>
</tr>
</tbody>
</table>

Table 4 presents the adsorption parameters evaluated from the plots. Generally, the value of $\Delta G_{ads}^0 \leq -20$ kJ mol⁻¹ signifies physisorption and values more negative than $-40$ kJ mol⁻¹ signifies chemisorption (Saratha et al. 2011; Shukla and Ebenso, 2011; Oguzie et al. 2012; Refat and Ishaq, 2013; Umoren et al., 2016). The values of $\Delta G_{ads}$ presented on Table 4 are negative at both temperatures and $\geq -40$ kJ mol⁻¹. This implies that the adsorption of the inhibitor on metal surface is spontaneous and confirms physisorption adsorption mechanism.

CONCLUSION

The findings from this study revealed that ethanolic extract of Cucurbita pepo leaves acted as an excellent inhibitor against the corrosion of mild steel in 1.0 M HCl solution. Inhibition efficiency of the plant extract increased with increase in the concentration of the inhibitor. Linear polarisation results indicate that Cucurbita pepo leaves extracts behaved as a mixed inhibitor at lower concentrations and cathodic at higher concentrations. The values of activation energy, enthalpy of activation and free energy obtained in this work suggest a physisorptive, exothermic and spontaneous adsorption mechanism respectively, of CP molecules on the steel surface while Langmuir isotherm described this adsorption behaviour. Values of entropy of activation reveal the activation complex represents dissociation steps.

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REFERENCES


