Adsorption Behaviour and Corrosion Inhibition Effect of *N. imperialis* *p. beauv* (Lecythidaceae) Seed Extract on Mild Steel in 1.0 M HCl

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ABSTRACT

The effect of *Napoleona N. imperialis* seed extract on the corrosion of mild steel in 1.0 M solution of HCl was studied using weight loss measurements at 313 and 333 K. The results obtained from the experiment showed that the seed extract of *N. imperialis* functioned as an excellent inhibitor against the corrosion of mild steel in 1.0 M solution of HCl. Inhibition efficiency increased with increase in extract concentration and temperature but decreased with immersion time. $E_a$ values were less than that obtained for the blank, 67.56 kJ/mol and the values of $\Delta G^\circ$were negative and greater than -20 kJ/mol, signifying that the adsorption of *N. imperialis* on the mild steel surface was chemisorptive and spontaneous respectively. Weight loss data gave best fit with the Langmuir adsorption isotherm model. Chemical adsorption mechanism is proposed for the adsorption behaviour of *N. imperialis* seeds extract. The corrosion inhibition aligned with the first order kinetics equations.

Keywords: Adsorption isotherm, Corrosion rate, Inhibition efficiency, Mild steel, *N. imperialis*, Temperature

INTRODUCTION

Corrosion is a natural process, which converts a refined metal/ alloy to a more chemically stable form, such as its oxide, hydroxide, or sulfide thereby leading to the gradual destruction of these metals/ alloys (Roberge, 2000; Ahmad, 2006). Mild steel is most commonly employed because of its desirable structural properties, low cost and availability. However, mild steel is prone to corrosion when it comes in contact with acid solutions during processes such as acid cleaning, pickling, descaling and drilling operations (Jeyinka et al. 2005; Onen, 2010; Dönner et al. 2011).

The corrosion of metallic materials in acidic solution causes undesirable effects in the industries, environment, etc, resulting in waste, pollution and shorter life span of these metallic materials. In order to reduce the corrosion of metals/ alloys, several techniques like cathodic protection and painting of alloy surfaces have been applied. The use of inhibitors is one of the most practical methods for protection against corrosion of metals/ alloys in acidic media because they can serve as additives in the corrosive media (Fouda et al. 2013; Dariva and Galio, 2014; Chakravarthy, 2015; Eddy et al. 2015). Corrosion inhibitors are substances that slow the rate of corrosion of mostly metals/ alloys when added in small amounts to corrosive environments. Most of the effective and efficient corrosion inhibitors are those compounds containing $\pi$ electrons and hetero atoms such as oxygen, nitrogen, sulphur, and phosphorus, which allows for the adsorption of these compounds on the metal/alloy surface (Eddy, 2009; Fouda et al. 2013; Dariva and Galio, 2014; Chakravarthy, 2015; Eddy et al. 2015). The effectiveness of an inhibitor is based on its ability to displace water molecules from the metal surface, interact with the anodic and cathodic reaction sites such as to retard the oxidation and reduction reactions, and to prevent transportation of water and corrosion-active species to the surface of the metal/alloy (Roberge, 2000; Ahmad, 2006; Dariva and Galio, 2014).

Corrosion control by the use of inhibitors have been found to be very effective. However, synthetic chemical inhibitors, commonly chromates, are toxic and pose threat to life and the environment upon their disposal or leaching into the environment (Abiola et al. 2009; Eddy, 2009; Dariva and Galio, 2014; Chakravarthy, 2015). To overcome these challenges, there is need to investigate environmentally friendly, non-toxic and readily available inhibitors as alternatives. Hence, recent focus is on greener approaches to corrosion control using non-toxic and environmentally friendly corrosion inhibotors. The use of plants extract as corrosion inhibitors is one of the green approaches used in controlling the corrosion of metals/ alloys in acidic environments (Abiola and James, 2010; Chahul et al. 2015; Dass et al. 2015; Manimegalai and Manjula, 2015; Chahul et al. 2017; Onen and Buba, 2018).
Plant extracts contain phytochemicals which possess chemical and electronic structures that are similar to those of the synthetic inhibitors hence, their potentials as effective corrosion inhibitors against the corrosion of metals/alloys in acidic environments. Experimental and literature reports on phytochemical screening of n-butanol extract of *Napoleonae imperialis* seeds revealed the presence of saponins, cardiac glycosides, flavonoids, anthraquinones and alkaloids (Ojinnaka and Okpala, 2012; Ndukwe et al. 2016).

This study seeks to investigate and evaluate the inhibitive and adsorptive behaviour of n-butanol extract of *N. imperialis* seeds on the corrosion of mild steel in 1.0 M solution of hydrochloric acid using weight loss measurement.

**MATERIALS AND METHODS**

**Materials**

Steel sheet, obtained from modern market, Makurdi. Analytical balance, dessicator, hand dryer, ethanol, acetone, HCl, SiC paper (#900). All the reagents used for this study were analar grade.

**Preparation of Plant Extract**

*N. imperialis* extract was prepared as reported by Ndukwe et al. (2016).

**Preparation of Mild Steel Coupons**

The mild steel sheets were press cut into pieces of 2 x 3 cm. These coupons were polished with emery cloth (#900), washed with liquid soap under running water, cleaned with ethanol and dried with acetone. The coupons were then placed in a desiccator prior to use.

**Preparation of Inhibitor Solution**

Five different concentrations (0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L, and 1.0 g/L) of the extract were prepared in 250 mL of 1.0 M HCl solution and were used for all the measurements. A blank was also prepared without the plant extract.

**Weight Loss Measurements**

Pre-cleaned and weighed mild steel coupons were suspended in 250 mL of 1.0 M solution of HCl in the absence and presence of different concentrations of the seed extract with the aid of glass hooks and rods at the immersion time of 24, 48, 72, 96, 120, 144 and 168 hours. The coupons in duplicates were removed from test solutions each time, washed in water, cleaned with ethanol, dried with acetone and reweighed. The weight loss was taken to be the difference between the initial and final weights of the mild steel coupons at a given time. Average weight loss of the duplicate coupons was taken in order to obtain reproducible results (Chahul et al. 2015, 2017).

From the weight loss results, weight loss ($\Delta w$) of mild steel, inhibition efficiency (IE) and the degree of surface coverage ($\theta$) of the inhibitor were calculated using equations 1, 2 and 3 respectively (Momoh-Yahaya et al. 2012; Chahul et al. 2015).

$$\Delta w = w_2 - w_1$$

$$IE_{exp} = \left(1 - \frac{W_{inh}}{W_{blank}}\right) \times 100$$

$$\theta = 1 - \frac{W_1}{W_2}$$

where $\Delta w = w_2 - w_1$ is the weight loss of metal after a given time, $w_{inh}$ and $w_{blank}$ are the weight loss (g) of the mild steel in the presence and absence of the inhibitor respectively, and $\theta$ is the degree of surface coverage of the inhibitor.

**RESULTS AND DISCUSSION**

**Effect of Immersion Time on Inhibition Efficiency of *N. imperialis* Extracts**

Fig. 1 shows variation of weight loss with immersion time of mild steel in 1.0 M HCl in the absence and presence of 0.2 g/L-1.0 g/L concentrations of *N. imperialis* extract. From the plot on Fig. 1, it can be deduced that though the corrosion rates of the mild steel coupons increased with time, they were considerably reduced in the presence of the plant extract. This implies that *N. imperialis* seeds extract actually inhibited the corrosion of mild steel in 1.0 M solution of HCl. Fig. 2 indicated this quantitatively.

Fig. 2 depicts the variation of % IE of *N. imperialis* seeds extract as a function of immersion time. From the plots on Fig. 2, it can be observed that the plant extract actually inhibited the corrosion of mild steel in 1.0 M solution of HCl at all the concentrations investigated. However, % IE of *N. imperialis* decreased with immersion time. This phenomenon could be due to the fact that with prolonged immersion time, the adsorbed extract gets desorbed from the surface of the mild steel surface as a result of the aggressive action of the chloride ion in the HCl solution thereby reducing the integrity of the adsorbed *N. imperialis* seeds extract and a decrease in inhibition efficiency (Obot and Obi-Egbedi, 2008, 2010; Oguzie et al. 2010, 2012).
Fig. 1: Effect of Immersion Time (hrs) on Weight Loss (g) of Mild Steel in 1.0 M HCl in the Absence and Presence of *N. imperialis* Seeds Extract.

Fig. 2: Effect of Immersion Time (hrs) on Inhibition Efficiency of *N. imperialis* Seeds Extract for the Corrosion of Mild Steel in 1.0 M HCl.

**Effect of Temperature**

In order to investigate the effect of temperature on the corrosion of mild steel in the absence and presence of the seed extract, weight loss measurements were done after 3 hours of immersion, with the water bath maintained at 303 and 333 K respectively.

Corrosion rates (CR) of mild steel coupons in the test solutions were calculated using equation (4) (Oguzie *et al.* 2010),

\[
CR = \frac{\Delta w}{At} \text{ g} h^{-1} \text{ cm}^{-2}
\]

where \(\Delta w\) is the average weight loss in g, \(A\) is the area of the mild steel coupon in cm\(^2\) and \(t\) is the time of immersion in hours.

The evaluated results are presented in Figs. 3 and 4 respectively. Fig 3 shows the corrosion rate of mild steel in the absence and presence of various concentrations of *N. imperialis* at 313 and 333 K respectively. The results revealed that the corrosion rates of mild steel coupons was higher at 333 K. This was due to increase in the average kinetic energy of the reacting molecules thereby resulting in the increased rate of corrosion of mild steel as reflected in the plots (Obot and Obi-Egbedi, 2008, 2010; Oguzie *et al.* 2010, 2012; Chahul *et al.* 2015). However, the plots showed the corrosion rates of mild steel to be relatively reduced with increased concentrations of *N. imperialis* at both temperatures again revealing the inhibitive action of the plant extract. Also, it can be observed from the plots that the adsorption-desorption equilibrium of the process favoured adsorption of the molecules of the plant extract at a higher temperature thereby resulting in higher % IE values at 333 K compared to 313 K. This behaviour is consistent with the chemisorption of inhibitor molecules on the mild steel surface (Oguzie *et al.* 2012).
Fig. 3: Effect of Concentrations of *N. imperialis* Seeds Extract on the Corrosion Rate of Mild Steel in 1.0M HCl at 313 and 333 K.

Fig. 4: Effect of Concentrations of *N. imperialis* Seeds Extract on Inhibition Efficiency for the Corrosion of Mild Steel in 1.0 M HCl at 313 and 333 K.

Table 1: Values of Inhibition Efficiency and Surface Coverage at 313 and 333 K.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>Average weight loss 313 K</th>
<th>Inhibition efficiency 313 K (%)</th>
<th>Surface coverage 313 K</th>
<th>Average weight loss 333 K</th>
<th>Inhibition efficiency 333 K (%)</th>
<th>Surface coverage 333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0400</td>
<td>-</td>
<td>-</td>
<td>0.1850</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0150</td>
<td>62.50</td>
<td>0.62</td>
<td>0.0550</td>
<td>70.27</td>
<td>0.70</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0140</td>
<td>65.00</td>
<td>0.65</td>
<td>0.0500</td>
<td>72.97</td>
<td>0.73</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0130</td>
<td>67.00</td>
<td>0.67</td>
<td>0.0450</td>
<td>75.67</td>
<td>0.76</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0100</td>
<td>75.00</td>
<td>0.75</td>
<td>0.0400</td>
<td>78.38</td>
<td>0.78</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0065</td>
<td>83.78</td>
<td>0.84</td>
<td>0.0231</td>
<td>87.50</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Kinetics Studies

The relationship between corrosion rate and temperature can be investigated using the Arrhenius equation (Momoh-Yayaha et al. 2013, 2014),

\[
\log\left(\frac{C R_2}{C R_1}\right) = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

where \(C R_1\) and \(C R_2\) are the corrosion rates at temperatures \(T_1\) and \(T_2\) respectively, \(E_a\) is the activation energy and \(R\) is the universal constant. Calculated values of \(E_a\) are presented on Table 2. It can be observed from Table 2 that the values of \(E_a\) in the inhibited solutions were lower than that of the blank which confirms the earlier assertion of a chemisorptive type of adsorption. This implies that the plant extract bonds covalently to the surface of the mild steel.

The kinetics of the corrosion of mild steel in the absence and presence of *N. imperialis* were investigated at 303 K by plotting \(-\log\) (weight loss) versus time as presented in Fig. 6. Linear plots with regression values that were close to unity were obtained indicating that the kinetics of the corrosion process aligned with the first order...
kinetics according to equation (6) (Undiandeye et al. 2014; Ngobiri and Okorosaye-Orubite, 2017),

\[-\log(w) = \frac{k_1 t}{2.303}\]

where \(w\) is the weight loss of mild steel, \(k_1\) is the rate constant for a first order reaction and \(t\) is time in hours.

The half-life \((t_{1/2})\) for the first order reaction is related to the rate constant as follows (Undiandeye et al. 2014; Ngobiri and Okorosaye-Orubite, 2017)

\[t_{1/2} = \frac{0.693}{k_1}\]

Values of \(k_1\) for the corrosion process and \(t_{1/2}\) of mild steel in the absence and presence of the plant extract are presented on Table 2. The rate constant is the tendency of the mild steel to corrode in the various test solutions (Undiandeye et al. 2014). It can be observed from Table 2 that the value of \(k_1\) in the uninhibited test solution was the highest. The value of \(k_1\) in the uninhibited system however, decreased with increasing concentrations of the plant extract showing the inhibitive action of \(N.\) imperialis. This is corroborated by the increasing values of \(t_{1/2}\) of mild steel in the presence of the plant extract. This implies that as the half-life increased, the corrosion rate decreased thereby prolonging the life span of the mild steel in the acid medium.

**Table 2:** Values of Activation Energy and Kinetic Parameters for the Corrosion of Mild Steel in 1.0 M HCl in the Absence and Presence of \(N.\) imperialis Seeds Extract.

<table>
<thead>
<tr>
<th>System</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(k_1) (h s(^{-1})(10(^{-3}))</th>
<th>(t_{1/2}) (h)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>67.56</td>
<td>1.7842</td>
<td>38.84</td>
<td>0.935</td>
</tr>
<tr>
<td>0.2g/L</td>
<td>59.38</td>
<td>0.42679</td>
<td>162.37</td>
<td>0.951</td>
</tr>
<tr>
<td>0.4 g/L</td>
<td>56.50</td>
<td>0.36573</td>
<td>189.48</td>
<td>0.948</td>
</tr>
<tr>
<td>0.6 g/L</td>
<td>55.71</td>
<td>0.25618</td>
<td>270.51</td>
<td>0.965</td>
</tr>
<tr>
<td>0.8 g/L</td>
<td>60.67</td>
<td>0.24335</td>
<td>284.77</td>
<td>0.965</td>
</tr>
<tr>
<td>1.0 g/L</td>
<td>66.51</td>
<td>0.10731</td>
<td>645.79</td>
<td>0.951</td>
</tr>
</tbody>
</table>

### Thermodynamics and Adsorption Studies

The adsorption behaviour of an inhibitor on a metal/alloy surface can be evaluated by the thermodynamic parameter called the heat of adsorption, \(Q_{\text{ads}}\). The relationship between the heats of adsorption \(Q_{\text{ads}}\) and degree of surface coverage at two different temperatures is given by equation (7) (Momoh-Yayaha et al. 2013, 2014):

\[Q_{\text{ads}} = 2.303R \left\{ \log \frac{\theta_1}{1 - \theta_2} - \log \frac{\theta_1}{1 - \theta_1} \right\} \times \frac{T_1 T_2}{T_2 - T_1}\]

where \(\theta_1\) and \(\theta_2\) are values of the degree of surface coverage at temperatures \(T_1\) and \(T_2\), respectively and \(R\) is the gas constant. Calculated values of \(Q_{\text{ads}}\) were all positive as shown on Table 3 signifying that the surface coverage of the plant extract on the mild steel surface increased at 333 K resulting in higher inhibition values at 333 K. This trend has been reported in other works (Momoh-Yayaha et al. 2014; Manimegalai and Manjula, 2015).
Adsorption isotherms provide information about the interaction among adsorbed molecules themselves as well as their interactions with the metal surface (Chahul et al. 2015, 2017). The adsorption characteristics of *N. imperialis* seeds extract were investigated by fitting data obtained for the degree of surface coverage (θ) from weight loss experiments at 313 and 333 K (Table 1) into various adsorption isotherm models. The Langmuir adsorption isotherm best described the adsorption mechanism of the plant constituents on the mild steel surface (equation 8).

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

where C is the concentration of the plant extract, θ is the surface coverage and \( K_{ads} \) is the equilibrium constant of the adsorption process. Fig. 6 presents Langmuir isotherm for the adsorption of *N. imperialis* seeds extract on the mild steel surface.

A plot of \( \frac{C}{\theta} \) against C aligned with the experimental data at both 313 and 333 K. The non-zero intercepts on the y-axis and the divergence of the slope from unity is attributable to interactions between the adsorbed plant molecules on the metal surface as well as changes in the heat of adsorption with increasing surface coverage (Oguzie et al. 2010; Obot et al. 2011; Oguzie et al. 2012). The plots are linear with a correlation coefficient higher than 0.96.

It has been reported that high values of \( K_{ads} \) indicate better adsorption of inhibitor molecules and hence better inhibition efficiency (Momoh-Yahaya et al. 2014). The values of \( K_{ads} \) presented on Table 4 reveals a higher value at 333 K than 313 K revealing that inhibition of the plant extract was more favourable at a higher temperature, a phenomenon that is characteristic of the chemisorptive adsorption mechanism (Obot et al. 2011; Momoh-Yahaya et al. 2014).

Free energy \( (\Delta G_{ads}^*) \) values associated with the adsorption process were also deduced using the relationship between the equilibrium constant for the adsorption process \( (K_{ads}) \) and the standard free energy of adsorption, \( \Delta G_{ads} \) shown in equation (9).

\[
\log K_{ads} = -1.744 \frac{\Delta G_{ads}^*}{2.303RT}
\]

where \( K_{ads} \) is the adsorption equilibrium constant, \( R \) is the gas constant \( (8.314 \text{ J K}^{-1}\text{mol}^{-1}) \), \( T \) is the absolute temperature in Kelvin and the value 55.5 is the concentration of water in solution expressed in \( \text{mol L}^{-1} \) (Obot et al. 2011). Evaluated values of \( \Delta G_{ads}^* \) are presented on Table 4.

Free energy values were negative and above \(-40 \text{ kJ mol}^{-1} \), indicating the spontaneity of the adsorption process and the mechanism of chemisorption (Obot and Obi-Egbedi, 2010, 2011; Chahul et al. 2015).

### Table 3: Values of Heat of Adsorption for the Adsorption of *N. imperialis* on Mild Steel Surface.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>( Q_{ads} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>15.50</td>
</tr>
<tr>
<td>0.4</td>
<td>16.28</td>
</tr>
<tr>
<td>0.6</td>
<td>19.26</td>
</tr>
<tr>
<td>0.8</td>
<td>7.24</td>
</tr>
<tr>
<td>1.0</td>
<td>13.67</td>
</tr>
</tbody>
</table>

Fig. 6: Langmuir Isotherms for the Adsorption *N. imperialis* Seeds Extract on Mild Steel Surface in 1.0 M HCl at 313 and 333 K.
CONCLUSION

From the results of this study, it has been shown that N. imperialis seeds extract inhibited the corrosion of mild steel in 1.0 M HCl. Inhibition efficiency increased with concentration and a rise in temperature but decreased with immersion time. Activation energy values obtained from the study showed the adsorption mechanism of N. imperialis seeds extract on the mild steel surface to be chemisorptive while free energy values revealed the adsorption process to be spontaneous. The adsorption mechanism of the N. imperialis seeds extract on mild steel supports the Langmuir adsorption isotherm model. Weight loss data gave best fit with the Langmuir isotherm while the corrosion process was found to align with a first order kinetics.

REFERENCES


