Study of Effects of *Afraegle Paniculata* Extract on Corrosion of Galvanised Steel in H$_2$SO$_4$ Solution

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**Abstract:** The study investigated the corrosion inhibition properties of *Afraegle Paniculata* extract in 1 M H$_2$SO$_4$ solution on galvanised steel with a view to understanding the reaction mechanisms as well as kinetics and thermodynamics of adsorption step in the corrosion reaction. The experimental investigation was conducted using weight-loss and gasometric techniques. The surface morphology of the exposed steel was studied using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). The results of this study revealed that the acidic medium increased the corrosion rate of galvanised steel and the corrosion reaction followed a first order reaction kinetics with a rate constant (k) of 23.7 mm day$^{-1}$ M$^{-1}$. It was deduced that the adsorption of *A. Paniculata* extract on galvanised steel surface obeyed the Langmuir adsorption isotherm with both reaction rate and Standard Change in Gibbs Free Energy of adsorption ($\Delta G_{ads}^\circ$) increasing with increase in temperature. Different values of Standard Change in Gibbs Free Energy of adsorption ($\Delta G_{ads}^\circ$) at different temperatures showed that the reaction was thermodynamically feasible and spontaneous. The Standard Change in Heat of Reaction ($\Delta H_{ads}^\circ$) and Standard Entropy Change ($\Delta S_{ads}^\circ$) were found to be $-10.88$ kJ mol$^{-1}$ and $-0.139$ kJ mol$^{-1}$K$^{-1}$ respectively. The SEM images confirmed that galvanised steel corroded in acidic environment and *A. Paniculata* extract inhibited the rate of corrosion in galvanised steel in 1 M H$_2$SO$_4$ solution. The SEM images revealed that cracks on the metal surface enhanced corrosion, and the corrosion rate were directly proportional to both the number and sizes of cracks. Weight loss, SEM and EDS analyses revealed that galvanised steel can corrode in 1 M H$_2$SO$_4$ and that corrosion rate could be reduced by using *A. Paniculata* extract as an inhibitor.

**Keywords:** *Afraegle Paniculata*, Corrosion, Weight Loss, Gasometric, Inhibition, Adsorption

1. **Introduction**

The transportation of crude petroleum oil and gas in steel pipelines faces several challenges including corrosion due to entrained carbon dioxide and/or hydrogen sulphide (Bai and Bai, 2005). Corrosion causes the degradation of metals due to the transfer of electrons between the solid metal surface and the acidic solution formed as a result of the dissolution of carbon dioxide and/or hydrogen sulphide in water (Ogunrinde and Aribike, 2019; Abdel-Gaber, 2009; Abiola and James, 2009). Corrosion has been identified as one of the major causes of damage and failure in petroleum oil and gas pipelines. The transmission of petroleum crude oil and gas entrained with carbon dioxide, hydrogen sulphide (H$_2$S) and water in steel pipelines can cause severe corrosion problems such as reduction in strength and life-span of steel and transmission pipes, loss of metallic properties, wastage of metal, production losses and open cracks in the pipes. Thus, several experimental studies have been conducted in recent past to investigate prevention of corrosion in steel metals (Ma et al., 2000; Tang, et al., 2010; Karlsdóttir et al., 2017; Wen et al., 2018).

Corrosion inhibitors are being investigated as a means of reducing the propensity of corrosion in metallic pipes. Studies on the inhibition of corrosion of metals using synthetic, natural and organic compounds have been reported in the literature. The synthetic corrosion inhibitors are 3-nitro-5-(2-amino-1,3,4-thiadiazolyl) nitrobenzene (NATN) (Al-Baghdadi et al., 2018), and 2-Amino-5-nitro-4,6-diarylcylohex-1-ene-1,3,3-tricarbonitriles (Chandrabhan et al. (2015). Some organic materials including plant extracts such as Water Hyacinth (Babatunde et al., 2019), *Andrographispaniculata* (Singh et al., 2010), *Spirulinanaplatensis* (Kamal and Sethuraman, 2012), *Ocimum sanctum* (Kumpawat et al., 2010), *Jasminum nudiflorum* Lindl. Leaves (Li et al. 2010), Carica papaya (Okfor et. al. 2007), *Phyllanthus amarus* (okafor et. al. 2008) and *Emblicaofficinalis* (Saratha and Vasudha, 2010), have been reported as anticorrosion substances in various corrosive environments.

Despite the vast research carried out on corrosion inhibitors, little or no work has been carried out on the mechanism, kinetics and the thermodynamics of the process. Some researchers reported that inhibitors minimise corrosion in metals through Langmuir adsorption process with values for Standard Change in Gibbs Free Energy and the equilibrium constant (Abiola et al., 2009; Kamal et al., 2012; Babatunde et al., 2019). However, the corresponding values of Standard Entropy Change and...
Standard Change in Heat of Reaction change were not reported. Thus, the objective of this paper is to investigate experimentally the corrosion inhibitory effect, kinetics and thermodynamics of the adsorption behaviour of *Afraegle Paniculata* extract in acidic medium.

2. Methods and Materials

2.1 Materials

2.1.1 Preparation of Galvanised Steel Metal Specimen

Galvanised steel rod of diameter 0.8 cm and thickness 0.02 cm was obtained from local supplier and cut into 1 cm in length. The specimens were cleaned using absolute ethanol, rinsed with double distilled water, dried with acetone and kept in desiccator until they were ready for use. Analytical grade chemicals were used and appropriate concentrations of acids were prepared using distilled water.

2.1.2 Plant extraction and Solution preparation

*Afraegle Paniculata* leaf was dried, ground to powder form, and soaked with ethyl acetate for 72 hours. The extract was filtered, and the filtered solution was concentrated by distillation and the concentrate air-dried. The dried extract was used for the preparation of inhibitor test solutions with specific concentrations (0.025, 0.05, 0.1, 0.2 and 0.4 g/L) by dissolving extract in 1M H₂SO₄.

2.1.3 Extract Analysis

Chemical composition of the plant extract was analysed using gas chromatography–mass spectrometry (GS-MS). The analysis was carried out using an Agilent Technology Gas Chromatography System 7890, equipped with non-polar fused silica capillary DB-1 column (30m length, 0.32 mm internal diameter, and thickness 0.25 μm). The oven temperature was set at 80°C to 240°C, programmed to increase at the rate of 10°C/min and finally held isothermally for 10 min. The injector and detector temperatures were kept at 200°C and 250°C, respectively. The carrier gas used was helium at a flowrate of 1 mL/min, and the splitting ratio was set at 100:1. The Agilent Technology gas chromatograph was connected to an Agilent Mass Spectrometer 5975. The Mass spectral ionization temperature was set at 230°C. The mass spectrometer was operated using the electron impact ionization mode at a voltage of 70 eV, and the mass spectra were taken over the m/z range of 30-700 amu. The components of the plant extract were identified by WILEY and NIST database matching and by comparison of mass spectra with published data (Adams, 2001).

2.2 Gasometric Method

Gasometric analysis as reported by Onuchukwu (1998), Okafor et al. (2008), and Babatunde et al. (2019) was also used to evaluate the corrosion rate of steel via gas evolution. Clean specimen of galvanised metal pipe was fully submerged into 100 ml of test solutions containing 1M H₂SO₄ with the five different concentrations of *Afraegle Paniculata* extract (0.025, 0.05, 0.1, 0.2 and 0.4 g/L). The test solution was transferred into the reaction vessel, which was connected to a manometer. The initial manometer reading prior to the experiment was taken, after which subsequent manometer readings were taken every 10 seconds for a period of 3 minutes during each experimental run that is after the cleaned metal specimen was dropped into the solution and the reaction vessel was quickly closed. Volume of hydrogen gas evolved was measured and the experiment was carried out at 30, 40, 50, 60 and 70°C. The blank experiment was performed under the same conditions. Each experiment was repeated twice for validation of the results.

2.3 Surface Analysis - Scanning Electron Microscopy

The surface morphologies of the exposed specimens (un-corroded, corroded and corroded with inhibitors metal samples) were carried out using a Tescan VEGA3 scanning electron microscope (SEM) and a Bruker energy dispersive X-ray spectroscopy (EDS) system. Imaging was performed at an accelerating voltage of 15 kV using a secondary electron detector (SEI), and magnifications of 100, 250, 500, 750 and 1000x. For the un-corroded sample, a cleaned steel specimen of 1 cm in length, 0.8 cm in diameter and 0.02 cm in thickness was used for the analysis. For the corroded specimens without inhibitor, a steel specimen of 1 cm in length, 0.8 cm in diameter and 0.02 cm in thickness
was immersed for 72 hrs in 100 mL of 0.5M H₂SO₄ solution; while for the characterisation of the corroded specimens with inhibitor, a steel specimen of similar geometry was immersed for 72 hrs in 100mL of 0.5M H₂SO₄ solution containing *Afraegle Paniculata* extract.

### 3. Results and Discussion

#### 3.1 Characterisation of *Afraegle Paniculata* Extract

The corrosion inhibitive action of phytochemicals has been attributed to the presence of heteroatoms, conjugated or non-conjugated pi bond on the phytochemicals. Lone pair of electrons on heteroatom and delocalized electron on pi bond are regarded as active site of adsorption process by forming coordinate bond with vacant d-orbitals of metal atoms. (De Souza and Spinelli, 2009; Abdel-Gaber et al., 2009).

GC-MS analysis of *A. Paniculata* extract revealed 27 components, which are all oxygenated compounds (see Table 1). All the major components of the extract contained pi electron in addition to heteroatoms on their molecules. Thus, the corrosion inhibitive action of *Afraegle Paniculata* extract observed in this study could be attributed to the adsorption of heteroatom or pi electron containing components onto the metal surface.

#### Table 1. Composition of *Afraegle Paniculata* Extract generated from the Chromatogram

<table>
<thead>
<tr>
<th>S/N</th>
<th>NAME</th>
<th>Molecular Formula</th>
<th>Rt</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Caryophyllene oxide</td>
<td>C_{17}H_{24}O_{2}</td>
<td>11.344</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>Eudesma-4(15),7-dien-1-β-ol</td>
<td>C_{18}H_{26}O</td>
<td>11.777</td>
<td>0.93</td>
</tr>
<tr>
<td>3</td>
<td>10,10-Dimethyl-2,6 dimethylenecyclo[7.2.0]undecan-5β-ol</td>
<td>C_{20}H_{34}O_{2}</td>
<td>11.863</td>
<td>0.66</td>
</tr>
<tr>
<td>4</td>
<td>2-Pentadecanone, 6,10,14-trimethyl</td>
<td>C_{21}H_{36}O_{2}</td>
<td>13.868</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>Dihydrofuran(3,2-F)Coumaranone</td>
<td>C_{10}H_{14}O_{2}</td>
<td>14.345</td>
<td>0.90</td>
</tr>
<tr>
<td>6</td>
<td>n-Hexadecanoic acid</td>
<td>C_{16}H_{34}O_{2}</td>
<td>14.892</td>
<td>3.09</td>
</tr>
<tr>
<td>7</td>
<td>Methoxsalen</td>
<td>C_{10}H_{14}O_{2}</td>
<td>15.063</td>
<td>0.86</td>
</tr>
<tr>
<td>8</td>
<td>7H-Furo[3,2-g][1]benzopyran-7-one, 4methoxy-</td>
<td>C_{17}H_{26}O_{2}</td>
<td>15.330</td>
<td>0.67</td>
</tr>
<tr>
<td>9</td>
<td>Heptadecanoic acid</td>
<td>C_{17}H_{34}O_{2}</td>
<td>15.435</td>
<td>3.21</td>
</tr>
<tr>
<td>10</td>
<td>Phytol</td>
<td>C_{20}H_{42}O_{2}</td>
<td>16.154</td>
<td>0.68</td>
</tr>
<tr>
<td>11</td>
<td>9-Octadecenoic acid</td>
<td>C_{18}H_{36}O_{2}</td>
<td>16.287</td>
<td>0.58</td>
</tr>
<tr>
<td>12</td>
<td>7H-Furo[3,2-g][1]benzopyran-7-one, 4,9-dimethoxy-</td>
<td>C_{19}H_{38}O_{2}</td>
<td>16.711</td>
<td>0.58</td>
</tr>
<tr>
<td>13</td>
<td>Oxirane, 2,2-dimethyl-3-(3,7,12,16,20-pentamethyl-3,7,11,15,19-heneicosapentayl)-,(all-E)-</td>
<td>C_{20}H_{44}O_{2}</td>
<td>17.206</td>
<td>0.43</td>
</tr>
<tr>
<td>14</td>
<td>Sesquiosefuran</td>
<td>C_{17}H_{30}O_{2}</td>
<td>18.044</td>
<td>2.39</td>
</tr>
<tr>
<td>15</td>
<td>alpha.-Amyrin</td>
<td>C_{30}H_{52}O_{2}</td>
<td>18.139</td>
<td>3.47</td>
</tr>
<tr>
<td>16</td>
<td>4,4,6a,6b,8a,11,14b-Octamethyl-2,4a,5,6,7,8,9,10,12a,14a-dodecachydro-1H-picine-3-one</td>
<td>C_{22}H_{46}O_{2}</td>
<td>18.292</td>
<td>26.55</td>
</tr>
<tr>
<td>17</td>
<td>p-(3-Methyl-5-oxo-2-pyrazolin-1-yl)benzoic acid</td>
<td>C_{16}H_{18}N_{2}O_{3}</td>
<td>18.506</td>
<td>3.93</td>
</tr>
<tr>
<td>18</td>
<td>2(1H)Naphthalenone, 3,5,6,7,8a-hexahydro-4,8a-dimethyl-6-(1-methylthiethyl)-</td>
<td>C_{19}H_{26}N_{2}O_{3}</td>
<td>18.611</td>
<td>11.92</td>
</tr>
<tr>
<td>19</td>
<td>7-Isopropenyl-1,4a-dimethyl-4,4a,5,6,7,8-hexahydro-3H-naphthalen-2-one</td>
<td>C_{18}H_{32}O_{2}</td>
<td>18.644</td>
<td>2.29</td>
</tr>
<tr>
<td>20</td>
<td>2(1H)Naphthalenone, 3,5,6,7,8a-hexahydro-4,8a-dimethyl-6-(1-methylthiethyl)-</td>
<td>C_{19}H_{26}O_{2}</td>
<td>18.687</td>
<td>7.91</td>
</tr>
<tr>
<td>21</td>
<td>Lupeol</td>
<td>C_{30}H_{52}O_{2}</td>
<td>18.863</td>
<td>9.15</td>
</tr>
<tr>
<td>22</td>
<td>7,22-Ergostadienol</td>
<td>C_{30}H_{52}O_{2}</td>
<td>18.839</td>
<td>0.94</td>
</tr>
<tr>
<td>23</td>
<td>2H-1-Benzopyran-2-one, 7-[3,7-dimethyl-2,6-octadienyl]oxy]-,(E)-</td>
<td>C_{20}H_{38}O_{2}</td>
<td>19.249</td>
<td>0.37</td>
</tr>
<tr>
<td>24</td>
<td>2,6,9,11-Dodecatetraenal, 2,6,10-trimethyl,-,(E,E,E)-</td>
<td>C_{22}H_{44}O_{2}</td>
<td>19.368</td>
<td>0.47</td>
</tr>
<tr>
<td>25</td>
<td>Urs-20-en-3-ol, (3.beta., 18.alpha, 19,alpha)-</td>
<td>C_{30}H_{52}O_{2}</td>
<td>19.896</td>
<td>11.86</td>
</tr>
<tr>
<td>26</td>
<td>9,19-Cycloergost-24(28)-en-3-ol, 4,14-dimethyl-,-acetate, (3β,4α,5α)-</td>
<td>C_{32}H_{56}O_{4}</td>
<td>19.968</td>
<td>1.55</td>
</tr>
<tr>
<td>27</td>
<td>Curan-17-oic acid, 2,16-didehydro-20-hydroxy-19-oxo-, methyl ester</td>
<td>C_{20}H_{32}N_{2}O_{4}</td>
<td>20.177</td>
<td>1.27</td>
</tr>
<tr>
<td>28</td>
<td>Hop-22(29)-en-3.beta.-ol</td>
<td>C_{18}H_{30}O_{2}</td>
<td>20.635</td>
<td>2.49</td>
</tr>
</tbody>
</table>

#### 3.2 Gravimetric Analysis

**3.2.1 Corrosion Reaction Rate Kinetics.**

The weight loss was calculated in grams as the difference between the initial weight prior to immersion, and weight after removal of the corrosion product.

\[
\Delta W = W_i - W_f
\]  

(1)

**3.2.2 Steel at different concentration of H₂SO₄ after 24 Hours**

As showed in Figure 1, the weight loss of the steel metal increased with an increase in the concentration of the H₂SO₄ and the largest weight loss occurred after the first 24 hours. This can be ascribed to the decrease in the corrosion reaction rate after the first 24 hours (i.e. the initial reaction rate). In Figure 2, it shows that the initial reaction weight loss (first 24 hours) was directly proportional to the concentration. The initial mass loss was used to calculate the time and space average corrosion reaction rate, which was determined using the same methodology as reported by Belarbi et al. (2018):
\[ (-r_{CR}) = \frac{(K \times \Delta W)}{(A \times t \times \rho)} \quad (2) \]

Where \((-r_{CR})\) is the corrosion rate in mm/y, \(K\) is the conversion factor \(8.76 \times 10^4 = 24 \text{ h/d} \times 365 \text{ d/y} \times 10 \text{ mm/cm}\), \(\Delta W\) is the weight loss in g, \(A:\) area in cm\(^2\), \(t\) is the time of exposure in h, \(\rho\) is the density of steel, 7.87 g/cm\(^3\).

3.2.3 Inhibition Efficiency of Afraegle Paniculata

The method reported by Abiola et al. (2009) and Babatunde et al. (2019) was used to determine the percentage inhibition efficiency (% \(I\)) as follows:

\[ I\% = \left( \frac{W_u - W_i}{W_u} \right) \times 100 \quad (4) \]

Where \(I\) is the inhibition efficiency of Water Hyacinth in %, \(W_u\) is the weight loss of uninhibited steel metal in acidic solution, and \(W_i\) is the weight loss of inhibited steel metal in acidic solution with \textit{Afraegle Paniculata} extract.

Figure 5 showed that truly \textit{Afraegle Paniculata} inhibited corrosion of steel by sulphuric acid and the percentage inhibition efficiency increased with increasing extract concentration, but the rate of increase dropped with time after the first 24 hours (i.e. initial reaction).

It was confirmed that the increase in the extract concentration raised the number of inhibitor molecules that were adsorbed onto the steel surface, thus, preventing the adsorption of corrosion species (ions) in the acidic solution. In other words, the adsorption of the inhibitor molecules decreased the number of available active sites, that is, surface area for the corrosion species; thus reducing the rate of corrosion.
Figure 5. Sulphuric Acid Corrosion Inhibition Efficiency of Afraegle Paniculata for a Period of 6 days at different extract Concentrations

The inhibition efficiency at the initial reaction stage (i.e. 24 hours as shown in Figure 6) was used to determine the degree of surface coverage ($\theta$) and the adsorption isotherm. The degree of surface coverage ($\theta$) was deduced as reported by Abiola et. al. (2009), Singh et al. (2011) and Babatunde et al. (2019).

$$\theta = \frac{I\%}{100}$$

(5)

Figure 6. Sulphuric Acid Corrosion Inhibition Efficiency of Afraegle Paniculata after 24 Hours

3.2.4 Adsorption Isotherm

Data of degree of surface coverage were fitted into different isotherms and it was deduced that adsorption relationship follows the Langmuir Adsorption model (see Figure 8), which can be expressed as

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + \frac{C_{inh}}{I}$$

(6)

where $C_{inh}$ is the inhibitor concentration and K the equilibrium constant for the adsorption/desorption process of the inhibitor molecules on the metal surface.

Using the equation that describes Langmuir adsorption isotherm i.e. Equation 6, the equilibrium constant for the adsorption/desorption process (K) was deduced as the inverse of the intercept of Figure 7. The adsorption equilibrium constant was used to deduce the standard change in Gibbs Free Energy of adsorption expression as reported by Abiola et al. (2004), Qiu et al. (2005) and Babatunde et al. (2019) (i.e. Equation 7).

$$K = \frac{1}{5.5} \exp \left( - \frac{\Delta G_{ad}}{RT} \right)$$

(7)

Values of the adsorption equilibrium constant and the standard change in Gibbs Free Energy of adsorption are shown in Table 2. The value of the Standard Change in Gibbs Free Energy estimated in the present was close to those reported in other studies (Abiola et al., 2004; Qiu et al., 2005; Babatunde et al., 2019). Furthermore, the negative value of the Standard Change in Gibbs Free Energy of adsorption ($\Delta G_{ad}$) showed that the adsorption process was spontaneous and exothermic.

Figure 7. Langmuir adsorption model on the steel surface of Afraegle Paniculata extract in 1M H$_2$SO$_4$ solution for 24hrs immersion period at 30°C

<table>
<thead>
<tr>
<th>Table 2. Afraegle Paniculata Adsorption Kinetic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction Kinetics</strong></td>
</tr>
<tr>
<td>Equilibrium Constant ($k_{ads}$)</td>
</tr>
<tr>
<td>Standard Change in Standard Change in Gibbs Free Energy of adsorption ($\Delta G_{ad}$)</td>
</tr>
</tbody>
</table>

3.3 Gasometric Analysis

3.3.1 Corrosion Reaction Mechanism

It was showed in Figures 8 and 9 that the volume of hydrogen gas produced decreases with increasing concentration of inhibitor i.e. Afraegle Paniculata. This was due to the decrease in the corrosion reaction rate due to the decrease in the number of active sites available for the corrosion attack. The same observation was reported in the literature by Abiola et al. (2007), Abiola et al. (2009), and Babatunde et al. (2019).
3.3.2 Inhibition Efficiency of *Afraegle Paniculata*

The volume of hydrogen gas evolved data were used to determine the percentage inhibition efficiency ($\% I'$) using Equation 8.

$$I'\% = \left( \frac{V_a - V_i}{V_a} \right) \times 100$$

Where $I'$ is the inhibition efficiency of *Afraegle Paniculata* in $\%$, $V_a$ and $V_i$ are Volume of H$_2$ gas evolved in the absence and presence of extracts, respectively.

Figure 10 showed that the inhibition efficiency increases with increasing *Afraegle Paniculata* extract concentration. This confirms that an increase in the inhibitor concentration increases the number of its molecules that gets adsorbed onto the steel surface, which in turn reduces the available surface area for the acidic molecule.

3.3.3 Adsorption Isotherm

The inhibition efficiency data were used to determine the degree of surface coverage using the same methodology that was used for the gravimetric analysis. The surface coverage data were further fitted into different isotherms to determine the adsorption isotherm. This was carried out for the various investigated temperatures i.e. 30, 40, 50, 60 and 70°C. It was deduced that the adsorption relationship, irrespective of the temperature of the reaction, follows similar pattern to that of the gravimetric analysis, i.e., the Langmuir Adsorption model, which is described by Equation 6.

3.3.4 Thermodynamic Properties

The thermodynamic properties (Standard Change in Heat of Reaction, Standard Entropy Change and Standard Change in Gibbs Free Energy) were deduced via gasometric analysis whereby each adsorption isotherm was used in calculating the reaction equilibrium constant, which was further used to calculate the Standard Change in Gibbs Free Energy of adsorption ($\Delta G_{ads}$) as previously explained for each temperature considered.

The reaction kinetics parameters shown in Table 3 were used to determine the Standard Change in Heat of Reaction and Standard Entropy Change of the corrosion reaction. The change in Standard Change in Gibbs Free Energy at constant temperature is expressed as Equation 9 below.

$$\Delta G = \Delta H + T\Delta S$$

<table>
<thead>
<tr>
<th>$T$ ($\degree$C)</th>
<th>Intercept</th>
<th>$K$</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.044</td>
<td>22.73</td>
<td>-20.37</td>
</tr>
<tr>
<td>60</td>
<td>0.046</td>
<td>21.74</td>
<td>-19.65</td>
</tr>
<tr>
<td>50</td>
<td>0.068</td>
<td>14.71</td>
<td>-18.01</td>
</tr>
<tr>
<td>40</td>
<td>0.125</td>
<td>8.00</td>
<td>-15.87</td>
</tr>
<tr>
<td>30</td>
<td>0.128</td>
<td>7.81</td>
<td>-15.30</td>
</tr>
</tbody>
</table>
It can be deduced from Figure 11 that the Standard Change in Heat of Reaction was -10.88 kJmol\(^{-1}\) while the Standard Entropy Change was -0.139 kJ mol\(^{-1}\)K\(^{-1}\). The negative Standard Change in Heat of Reaction value showed that the reaction was an exothermic reaction as energy was lost to the surrounding, resulting in the products having a lesser amount of energy. It also confirmed the spontaneity and thermodynamic feasibility of the reaction. Naturally, when heat is added to a system, its molecules would become more active and the randomness of the molecules will increase which would be shown as an increase in the entropy of the system.

However, when heat is removed from a system, the molecules will be less active and will exhibit less chaotic movement, leading to a decrease in the entropy of the molecules, which would be exhibited as a negative entropy change.

The negative value of the entropy change also confirms the exothermic nature of the corrosion process. In addition, the standard entropy change of a system depends on the physical state of the system. For example, the entropy of gases is higher than that of solids because an atom in gas phase has more options for position than the same atom in a solid phase. Hence, the negative value of the Standard Entropy Change confirmed the change of phase of the system as hydrogen sulphide gas molecules dissolved in water, forming the acidic solution which reacts with the iron specie to produce iron sulphate. The phase change exhibited during the process was gas to liquid, and finally solid phase.

3.4 Surface Analysis - Scanning Electron Microscopy
The SEM images of the surface of the un-corroded, corroded and inhibited corroded specimens (i.e., at a magnification of 100\(\times\), 250\(\times\), 500\(\times\), 750\(\times\) and 1000\(\times\)) were in agreement with the conclusions of the gravimetric and gasometric analysis that steel metal corrodes in acidic environment and *Afraegle Paniculata* inhibits the corrosion propensity by acting as an inhibitor. The SEM micrographs of the inhibited corroded steel showed the mechanical polishing on the surface of the inhibited corroded steel and this was an indicator that the corrosion on the inhibited steel was minimal. Comparing that to the surface of the un-inhibited corroded steel suggested that the mechanical polished film formed was due to the adsorption of the *Afraegle Paniculata* molecules.

It was proposed that molecules of the inhibitor and acid adsorbed competitively on the metal surface, and by so doing, affected the morphology and the reaction kinetics of the corrosion products; and the inhibitor molecules adsorption decreases the number of available active sites i.e. surface area for the corrosion species; thus reducing the rate of corrosion attack. Figure 12 confirms the formation of various sizes of pores i.e. cracks due to corrosion, which can lead to the formation of open cracks as the corrosion reaction progresses.

3.4.1 Effect of Cracks
The SEM micrographs in Figure 13 showed that there were larger pores (cracks) sizes on the surface cut-edge section of the inhibited corroded specimen compared to that of the middle section of the same specimen. It can therefore be hypothesized that the presence of cracks on metal surface enhances corrosion, and the corrosion rate is directly proportional to both the number of cracks and the crack sizes. In other words, the higher the number of cracks and the cracks sizes, the higher the rate of corrosion.
3.4.2 Energy Dispersive X-ray Spectroscopy (EDS)
The presence of Sulphur and the absence of Zinc and Aluminium in the EDS analysis of the corroded and inhibited corroded specimens (see Figures 15 and 16), compared to that of the un-corroded specimen (see Figure 14) confirm that galvanised steel corrodes in acidic environment. The weight percentage composition of Iron in the inhibited corroded specimen (see Figure 16) was higher than that of the un-inhibited specimen (see Figure 15); thus, suggesting that *Afraegle Paniculata* acts as an inhibitor in inhibiting sulphuric acid corrosion of steel.
4. Conclusion
The study investigated the corrosion inhibition properties of *Afraegle Paniculata* extract in inhibiting the corrosion propensity of galvanised steel in acidic solution, with a view to understanding the corrosion reaction mechanisms, adsorption behaviour of *A. Paniculata* and the thermodynamics of the reaction. The experimental investigation was conducted using weight-loss (gravimetric analysis) and gasometric analyses. The surface morphologies of the exposed steel were studied using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) system.

Drawn from the study, it could be concluded that:

1. Galvanised steel was corroded in sulphuric acid environment and the corrosion reaction followed a first order reaction kinetics with a corrosion reaction rate kinetic constant (k) of 23.7 mm day⁻¹ M⁻¹. The corrosion reaction was a spontaneous exothermic reaction.

2. *Afraegle Paniculata* extract was a good inhibitor for galvanised steel in sulphuric acid solution and its inhibition efficiency increased with increasing extract concentration.

3. The adsorption of *Afraegle Paniculata* extract on galvanised steel surface obeyed Langmuir adsorption isotherm with Standard Change in Gibb's Free Energy of adsorption (ΔG°_{ads}) and equilibrium constant at different temperatures determined (see Table 4). The Standard Change in Gibb's Free Energy of adsorption (ΔG°_{ads}) at different temperatures confirmed the thermodynamic feasibility of the reaction.

4. The Standard Change in Heat of Reaction (ΔH°_{ads}) was -10.88 kJ mol⁻¹ and the Standard Entropy Change of reaction (ΔS°_{ads}) was -0.139 kJ mol⁻¹K⁻¹. Both values confirmed the exothermic nature of the reaction.

5. The SEM images confirmed the corrosion of galvanised steel metal in acidic environment, and the corrosion inhibitory properties of *Afraegle Paniculata* via forming a mechanical polished film due to the adsorption of the *Afraegle Paniculata* molecules. The SEM images showed the formation of various sizes of cracks which could lead to open cracks on galvanised steel due to corrosion. The SEM images further confirmed that cracks on metal surface enhance corrosion, and the corrosion rate is directly proportional to both the number of crack and the cracks’ sizes.

6. EDS analysis confirmed that galvanised steel corrodes in acidic environment and the corrosion propensity can be reduced using *Afraegle Paniculata*, which acted as an inhibitor to corrosion attacks of sulphuric acid.

**Table 4. Adsorption equilibrium constant and Standard Change in Gibb's Free Energy of corrosion inhibition via *Afraegle Paniculata***

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>K</th>
<th>ΔG°_{ads} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>22.73</td>
<td>-20.37</td>
</tr>
<tr>
<td>60</td>
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<td>-19.65</td>
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<td>50</td>
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<td>-15.87</td>
</tr>
<tr>
<td>30</td>
<td>7.81</td>
<td>-15.30</td>
</tr>
</tbody>
</table>

**References:**


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