Introduction
The use of mild steel in chemical industries cannot be overemphasized owing to its mechanical properties and usefulness as structural material for vessels reactor, pipelines, tank, construction works and other industrial equipment which are known to corrode invariably in contact with various solvents (Junae et al., 2012). Acid solutions especially sulfuric acid used for industrial processes such as acid pickling, industrial cleaning, acid descaling, etching of metal and acid operations may cause damage to metal surface (Akalezi et al., 2012; Okorokwo et al., 2015; Peter et al., 2016; Akalezi and Oguzie, 2015). Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases thereby affecting the tensile strength and utility efficiency of the material (Samuel et al., 2015). In view of the nation’s economy and financial implications of corrosion menace, researchers are compelled to do copious scientific studies in an attempt to improve the resistance of metals.

Corrosion inhibitors have proven to be the most convenient means of protecting metals due to their unique properties which enhance their capability to resist the corrosion process as compared to other methods (i.e. electroplating, coatings, alloying elements, and plastic deformation) (León-Silva et al., 2010; Gutiérrez et al., 2016; EL-Basiony et al., 2019). A corrosion inhibitor is a chemical compound which when added to liquid or gas decreases corrosion rate of a material, typically metal or alloys (Yiguang et al., 2006). The effectiveness of a corrosion inhibitor depends on the fluid composition, quantity of water and flow regime (Umoren et al., 2008; Ulakeo et al., 2012). Corrosion inhibitors could be additives to the fluids that surround the metal (Schmit, 2000).

In recent time, great achievement has been made in developing the efficiency of organic compounds containing hetero-atoms as corrosion inhibitors for mild steel in acid media (Banu et al., 2016; EL-Basiony et al., 2019). The interaction between the mild steel and hetero-atoms such as O, N, P, S and double/triple bonds or aromatic rings in the form of a wall, shows a vital role in corrosion prevention processes caused by the free electron pairs (Shubham et al., 2018). However, due to the known hazardous effects of most synthetic corrosion inhibitors coupled with increasing ecological awareness and strict environmental regulations, as well as the inevitable drive toward sustainable and environmentally friendly processes, attention has now focused toward the development of nontoxic alternatives. The exploration of natural products of plant origin as inexpensive eco-friendly corrosion inhibitors are becoming more important. In addition to being environmentally friendly and ecologically acceptable, plant products are low-cost, readily available, biodegradable, non toxic and renewable sources of materials, and they are widely used as corrosion inhibitors for the protection of metals in acid and alkaline environment (Akalezi and Oguzie, 2015; Okorokwo et al., 2015).

The use of plant extracts as corrosion inhibitors is not a new phenomenon and the following plants have been investigated and found to possess inhibitory efficacy. Gliricidia sepium (Okorokwo et al., 2015), Azadirachta indica (Peter et al., 2017), Pterocarpus soyauxii Taul (Onukwude et al., 2016), Momordica charantia (Kavitha et al., 2017), Boscia senegalensis (Awe et al., 2015) and lots more. Brachystegia eurycoma (achi as its popularly called in eastern part of Nigeria) is an economically valuable tree crop mostly grown in the tropical rain forest of West Africa. In Eastern Nigeria, the edible seed is used in soup making as a thickener and is common among the rural dwellers. It helps in maintaining heat within the body when consumed in other words; it is a good source of nutrient and helps to control body temperature (Ndukwu et al., 2009; Uzoma et al., 2011). Due to their absorption capacity, they are useful as functional agents in fabricated foods such as bakery products and meat formulations (Ndukwu et al., 2009; Uzoma et al., 2011). In Nigeria, the seed is used for its anti-Inflammation, anti-malaria, anti-diabetics and anti-corrosion properties (Michael et al., 2000; Okafor et al., 2008). Brachystegia eurycoma seed has been reported to contain 10.47% protein, and 71.94% total carbohydrate content, the timber products are used as building material in carpentry and related applications (Nwosu et al., 2012).
Materials and Methods

Collection of plant material and preparation of seed extracts

The study was carried out on Brachystegia eurycoma seeds (BE). The Brachystegia eurycoma seeds were purchase from Eke-Okigwe market in Okigwe local government area of Imo state, Nigeria. The sample was dried and grounded into powder. Four hundred and fifty gram (450 g) of the dehydrated and grounded seeds were soaked in a 500ml solution of ethanol for 48hrs. Sequentially, sufficient grams of the ground seeds were measured into the ethanol and were extracted until the 450 g of the ground seeds were exhausted. After 48hrs, the samples were filtered using Whatman filter paper No. 1 (QUALIGEN- Germany). The filtrates were further subjected to evaporation by rotatory evaporator at 358K in order to leave the sample free of the ethanol. The stock solutions of the extract obtained were used in preparing different concentrations of the extract by dissolving 1.0, 2.0, 3.0, 4.0 and 5.0 g of the extract in 1 L of 1M HCl acid, respectively.

Phytochemical screening on BE

Screening of phytochemicals is significant for identification of bioactive principles present in plants. Phytochemical screening was carried out on BE extracts by standard procedures (Khadom et al., 2017). Plant extracts were screened for reducing sugar, alkaloids, protein, phenols, flavonoids, amino acids, tannin, steroids, glycosides and carbohydrates. These compounds are potential corrosion inhibitors for many metals in an acidic medium (Verma and Mehta, 1997).

Preparation of specimen

The specimens were cut using a saw into the required dimension of 4 x 3 x 0.017 cm then descaled by brushing with a emery paper. They were cleaned and dried with acetone, then stored properly in desiccators for further use. The elemental composition of mild steel specimen analyzed and used for this study with iron (Fe) having the highest elemental composition of 93.65%.

Gravimetric techniques

One hundred millilitres (100 ml) each of the 1.0M H2SO4 solution was measured into six different beakers with one as the blank (uninhibited solution) and the remaining five labeled A to E containing different concentrations of the inhibitors BE, respectively (Okorokwo et al., 2017). The solution was measured into six different beakers with one as the blank (uninhibited solution) and the remaining five labeled A to E containing different concentrations of the inhibitors BE, respectively (Okorokwo et al., 2017). The coupon in each beaker was noted to avoid mix ups during the practical work. The immersion period was 24 h interval, after 24 h the coupons were retrieved from the acids, washed with tap water, degreased with ethanol and dried with acetone before the corresponding weights after immersion were recorded. The corresponding weights after immersion were recorded as well after each day. The differences in weight of the coupons were again taken as the weight loss (Kavitha et al., 2017). The rate of corrosion (CR), inhibition efficiency (IE), and degree of corrosion inhibition process takes place through the adsorption of the phytochemical constituents on the mild steel surface. The spectra of BE seed extract were recorded in a Perkin-Elmer 1600 spectrophotometer using KBr pellet.

Scanning electron microscopy (SEM) analysis

The surface morphology of the mild steel before and after immersion were examined with scanning electron microscopy to analyze the elements on the surface, using a phenom pro X Scanning Electron Microscope (SEM). The elements interact with atoms in the sample, producing various signals that can be detected and that contain information about the samples surface topography and composition (Okoronkwo et al., 2012).

Table 1: Phytochemical constituents of BE seed extract

<table>
<thead>
<tr>
<th>Phytochemical constituents</th>
<th>Tannins</th>
<th>Flavonol</th>
<th>Amino acids</th>
<th>Alkaloid</th>
<th>Carb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanolic extract of AAS</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Carb.</td>
<td>Carbohydrates; + = Sparingly Present; ++ = Moderately Present; +++ = Highly Present</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Kinetics and Thermodynamic Studies of Brachystegia eurycoma seed extracts as Corrosion Inhibitor

Table 2: Deduced data for inhibition efficiency, corrosion rate, rate constant and half life obtained from gravimetric method for mild steel in 1M H$_2$SO$_4$ after 24 h

<table>
<thead>
<tr>
<th>Concentration of inhibitor (g/l)</th>
<th>$\Delta W$ (g)</th>
<th>Corrosion Rate (g/cm$^2$-h)$^{-1} \times 10^{4}$</th>
<th>% IE</th>
<th>Rate Constant (day$^{-1}$) $10^{3}$</th>
<th>Half Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.336</td>
<td>57.76</td>
<td>-----</td>
<td>1.90</td>
<td>3.65</td>
</tr>
<tr>
<td>1</td>
<td>0.144</td>
<td>24.75</td>
<td>57.15</td>
<td>0.79</td>
<td>8.77</td>
</tr>
<tr>
<td>2</td>
<td>0.096</td>
<td>16.50</td>
<td>71.43</td>
<td>0.52</td>
<td>13.33</td>
</tr>
<tr>
<td>3</td>
<td>0.047</td>
<td>8.08</td>
<td>86.01</td>
<td>0.25</td>
<td>27.72</td>
</tr>
<tr>
<td>4</td>
<td>0.027</td>
<td>4.64</td>
<td>92.00</td>
<td>0.15</td>
<td>46.20</td>
</tr>
<tr>
<td>5</td>
<td>0.015</td>
<td>2.58</td>
<td>95.53</td>
<td>0.08</td>
<td>86.63</td>
</tr>
</tbody>
</table>

Weight loss measurements

The weight loss of mild steel coupons due to their immersion in solutions of 1M H$_2$SO$_4$ containing different concentrations of BE seed extract was measured as shown in Table 2. The results clearly shows a general reduction in the original weight of the metal coupons in the presence of the inhibitor compared to the uninhibited solution (blank), indicating that ethanol extract of BE seed inhibited the corrosion of mild steel in 1M H$_2$SO$_4$ at the end of the corrosion monitoring process. This is further supported by the decrease in Corrosion rate and Rate constant as the concentration of the extract increases, this also is in tandem with what was observed in the inhibitory action of Monordica charantia seed extracts on the corrosion of mild steel (Kavitha et al., 2017). This may be attributed to the adsorption of inhibitor on the mild steel surface, producing a barrier, which isolates the metal with acid (Lahodny-Sarc and Kapor, 2002).

The corrosion rate for the mild steel and the inhibition efficiency of the plant extract in 1M H$_2$SO$_4$ containing different concentrations of the plant extracts as a function of time (in days) are also presented in Figs. 1 – 2.

The inhibition efficiency increased with increase in concentration of inhibitor from 1.0 to 5.0g/l at room temperature (Fig. 2). Maximum inhibition efficiency was 95.53% in case of BE/1MH$_2$SO$_4$ for immersion period of 24 h at a concentration of 5.0 g/l (Fig. 2). These results suggest that adsorption model arrangement and orientation of constituents present in Brachystegia eurycoma seed extract on the surface of mild steel may change with time (Rekha et al., 2010). Decrease in inhibition efficiency thereafter with increasing time may be due to shift in adsorption and desorption equilibria which takes place simultaneously on prolonged exposure to corrosive media (Kavitha et al., 2016). Adsorbed organic molecules prevent further interaction of metal with acid (Lahodny-Sarc and Kapor, 2002).

Figure 3 shows the plot of log W against Time (hrs), for BE seed extracts indicating a linear variation at all concentrations. The linearity of the plots confirmed a first order reaction kinetics with respect to the corrosion of mild steel in the acidic medium (1M H$_2$SO$_4$). This implies that the rate of the reaction was directly proportional to the concentration of the extracts (Rozenfeld, 1981). From Table 2, the values of rate constant of the reaction decreases as the concentration of BE seed extracts increased and were in agreement with the assertion that the rate of the reaction was directly proportional to the concentration of the of BE seed extracts (James and Akaranta, 2009). Since the rate of the reaction was first order, the half-life of the reaction which were determined using the expression for the half-life for a first order reaction, showed the time required for the concentration of BE seed extracts to be reduced to half its initial value. Table 2, also shows that the half-life of the reaction increased as the concentration increased. The increase in half-life as the concentration of the extracts increased indicated a decrease in the dissolution rate of the mild steel and hence more protection of the metals by the BE seed extracts (Akalezi and Oguzie, 2015; James and Akaranta, 2009).

![Fig. 1: Variation of corrosion rate of mild steel corrosion in 1M H$_2$SO$_4$ with different concentration of BE seed extract showing the effect of time](image1)

![Fig. 2: Variation of inhibition efficiency of BE seed with concentration and time](image2)

![Fig. 3: Variation of log Wt with time for mild steel of in 1M H$_2$SO$_4$ solutions containing BE seed extract](image3)

![Fig. 4: Effect of Temperature on inhibition efficiency for mild steel corrosion in 1M H$_2$SO$_4$ at different concentration of Brachystegia eurycoma seed extract for immersion period of 2 h](image4)
The weight loss experiment was also carried out at different temperature range of 313 – 333K in 1M H₂SO₄ to investigate the influence of temperature on the rate of corrosion and inhibition efficiency for immersion time of 2 h. The variation of inhibition efficiency with temperatures at different concentration of BE seed extract is shown in Fig. 4. From the plot, the inhibition efficiency increases with an increase in BE seed extract concentration but decreases with an increase in temperature.

According to Alinor and Ejimeke (2012), at higher temperatures, the average kinetic energy of components of extracts increases, thus making adsorption between components of extracts and a metal surface insufficient to retain the species at the binding site and this could lead to desorption or cause the species to bounce off the surface of the metal instead of colliding and combining with it. Moreover, the solubility of the protective films on the metal surface would have occurred at a higher temperature, hereby exposing the metal surface to the aggressive medium, leading to more dissolution at this temperature.

The values of the corrosion rate at different temperatures are summarised in Table 3. It is clear from the table that the corrosion rate increases with a rise in temperature. This happened to be the case because, as the temperature increases, the average kinetic energy of the reactant molecules increases, thereby increasing the rate of the reaction. A decrease in inhibition efficiency with a rise in temperature and a corresponding increase in activation energy (Eₐ) in the presence of an inhibitor is termed physical adsorption mechanism (Ebenso et al., 2008).

Table 3: Temperature effect on corrosion rate (CR), activation energy (Eₐ), standard free energy (ΔG°,ads) and heart of adsorption for mild steel in 1M H₂SO₄ in absence and presence of BE seed extract for an immersion time of 2 h

<table>
<thead>
<tr>
<th>Concentration of inhibitor (g/l)</th>
<th>Temperature</th>
<th>CR (g/cm²·hrs⁻¹·10⁻⁶)</th>
<th>IE %</th>
<th>CR (g/cm²·hrs⁻¹·10⁻⁶)</th>
<th>IE %</th>
<th>CR (g/cm²·hrs⁻¹·10⁻⁶)</th>
<th>IE %</th>
<th>Eₐ KJmol⁻¹</th>
<th>Kₐbs</th>
<th>ΔG°,ads KJmol⁻¹</th>
<th>Q°,ads KJmol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313K</td>
<td>1.0</td>
<td>57.76</td>
<td>86.63</td>
<td>44.74</td>
<td>132.01</td>
<td>40.74</td>
<td>35.81</td>
<td>1.00</td>
<td>-10.45</td>
<td>-16.32</td>
</tr>
<tr>
<td>Blank</td>
<td>323K</td>
<td>2.0</td>
<td>57.10</td>
<td>73.88</td>
<td>50.00</td>
<td>123.76</td>
<td>44.44</td>
<td>39.70</td>
<td>0.67</td>
<td>-9.41</td>
<td>-17.19</td>
</tr>
<tr>
<td></td>
<td>333K</td>
<td>3.0</td>
<td>67.86</td>
<td>66.01</td>
<td>58.90</td>
<td>107.26</td>
<td>51.85</td>
<td>46.00</td>
<td>0.71</td>
<td>-9.56</td>
<td>-12.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>24.75</td>
<td>58.75</td>
<td>49.51</td>
<td>92.82</td>
<td>58.33</td>
<td>57.26</td>
<td>2.88</td>
<td>-13.21</td>
<td>-41.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>14.44</td>
<td>37.13</td>
<td>76.32</td>
<td>76.32</td>
<td>65.74</td>
<td>72.12</td>
<td>4.24</td>
<td>-14.21</td>
<td>-56.19</td>
</tr>
</tbody>
</table>

The values of activation energy (Eₐ) for the corrosion process were calculated using Arrhenius equation represented by Equation 7:

\[ \log(\frac{C_1}{C_2}) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

Where: C₁ is the corrosion rate at temperature, T₁. C₂ is the corrosion rate at temperature, T₂. Eₐ is the Activation Energy, R is the universal gas constant. Protective films formed on the surface of the mild steel increases the activation energy of the metal dissolution. In a chemical reaction, when the activation energy increases, the rate of the reaction decreases (Okoronkwo et al., 2015). This is also seen in the results shown in Table 3; the addition of the inhibitor increases Eₐ, thereby reducing the rate of the metal dissolution into the electrolyte.

Thermodynamics and adsorption mechanism

The heat of adsorption (Q°ads) of BE seed extract on the surface of mild steel has been calculated using equation 2.5 (Ebenso, 2003a,b, 2004; Umoren et al., 2006a, 2006b, 2007).

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

Values of Q°ads calculated through equation 8 are recorded in Table 3. These values are negative and ranged from -16.32 to -56.19 KJ/mol indicating that the adsorption of the extract is exothermic (Ebenso, 2003a,b, 2004; Bhajiwala and Vashi, 2001). Values of free energy of adsorption of BE seed extract were calculated using equation 9,

\[ ΔG°_{ads} = -RT\ln(55.5K_{ads}) \]

Where: K_{ads} = \frac{θ}{C(θ-1)} is the adsorption equilibrium constant, C is the concentration of the inhibitor, R is the universal gas constant. The calculated values of ΔG°_{ads} for the plant extract are also recorded in Table 3. From the result obtained, The values are found to be negatively less than the threshold value of ~40 KJ mol⁻¹ required for the mechanism of chemical adsorption to take place. This indicates that the adsorption of the studied plant extract on the mild steel surface is spontaneous and is consistent with the mechanism physical adsorption (Ebenso, 2003a, b, 2004; Bhajiwala and Vashi, 2001; Loto, 2011).
Kinetics and Thermodynamic Studies of Brachystegia eurycoma seed extracts as Corrosion Inhibitor

Fig. 5: Langmuir adsorption isotherm plot for the adsorption of BES on the surface of mild in 1M H$_2$SO$_4$ acid solution

Fig. 6: (a) SEM of the mild steel immersed in 1M H$_2$SO$_4$ solution without inhibitor for 5 hrs at 50 magnification and (b) SEM of the mild steel alone and in the presence of BE seed extract

Surface studies by scanning electron microscopy
Morphological analysis using SEM shows differences in the morphologies of the samples in the uninhibited and inhibited medium. Fig. 6 showed the SEM image of the mild steel surface immersed in the uninhibited medium for 5 h, big pits and cracks observed in the image are due to the effect of corrosion on the specimen infused by the acid. Similar image of mild steel immersed in the inhibited medium are also shown in Fig. 6. Smoother surfaces with little cracks observed are due to the formation of a thin film layer infused by the complexation between the mild steel and the phyto-chemical constituents in the extract. This implies corrosion rate was lowered by the extract which is in agreement with the results obtained from the weight loss analysis.

Infra red spectroscopy analysis
FTIR analysis is used to ascertain the fact that the corrosion inhibition process takes place through the adsorption of the phytochemical constituents on the mild steel surface. The spectra of the extract are presented in Fig. 7. From the result obtained, the strong and broad peak of O–H stretching that obscured the appearance of other peaks basically N–H peak occurs at 3419 cm$^{-1}$ with C–H stretching vibration occurring at 2927 cm$^{-1}$. The strong band at 1630 cm$^{-1}$ is assigned to C=C and C=O stretching vibration. Owing to the conjugation effect of flavonoids of BE seed extract, the C=O peak shifts from about 1700 cm$^{-1}$ to lower wave number (approximately 1630 cm$^{-1}$), C=C and C=O stretching vibration bands are superposition (Deng et al., 2007). The C–H bending bands in –CH$_2$ and –CH$_3$ are found to be at 1409 cm$^{-1}$. The absorption bands at 1272 cm$^{-1}$ could be assigned to the framework vibration of aromatic ring.

Fig. 7: FTIR spectra of Brachystegia eurycoma seed extract (BESE)

The IR spectra of the extracts showed peaks attributed to the characteristics of the functional groups. The presence of these functional groups indicates the effectiveness of the extract constituents to interact with the mild steel surface and that adsorption between the extract and the mild steel occurs through the identified functional groups (Okoronkwo et al., 2015). Hence, protection of metallic surface is done via the functional groups presented in the flavonoids, tannin, carbohydrates, alkaloid and amino acids as the main constituents of Brachystegia eurycoma seed extracts.

Conclusion
From the above results and discussions, the following conclusion was drawn:
All the studied phytochemical constituent of the seed extracts acts as an effective corrosion inhibitor of mild steel in 1M...
Kinetics and Thermodynamic Studies of Brachystegia eurycoma seed extracts as Corrosion Inhibitor

H₂SO₄ acid solution and their inhibition efficiency increases with increase in the concentration of the seed extracts with maximum efficiency obtained at an optimum concentration of 5.0g/l within the first 24 hours. The adsorption data was best fitted into Langmuir adsorption models. The results of SEM and Fourier transform infrared spectroscopy (FTIR) all indicate that the corrosion reaction was inhibited by the adsorption of the extract’s organic matter onto the corroding mild steel surface.

The trends of inhibition efficiency with temperature as well as values of kinetic and activation parameters for corrosion and corrosion inhibition processes point toward significant physisorption of the extract constituents on the mild steel surface.

Acknowledgement
The authors express their profound gratitude to Dr. Kufre for his technical advice and help in the analysis of the extract. Also they sincerely thank the other staffs of the department of chemistry Akwa Ibom State University for their support in providing the enabling environment for the lab work.

Conflict of Interest
Authors have declared that there is no conflict of interest reported in this work.

References


