The inhibition of mild steel corrosion in 0.5 M sulphuric acid solution by ethanol extracts of *Parinari polyandra* as an eco-friendly inhibitor was studied at different temperatures by weight loss technique and linear polarization. The test plant extracts has a promising inhibitory action against corrosion of mild steel in the sulphuric acid media. The inhibition efficiencies increase with a corresponding increase in the concentration of the inhibitor. The adsorption of the inhibitor on mild steel surface is exothermic, spontaneous and is best described by Freundlich and Temkim adsorption models. Calculated values of activation energy, enthalpy of activation, entropy of activation, free energy of adsorption and the trend in the variation of inhibition efficiency with temperature, the mechanism of the process is by physical adsorption. Ethanol extract of *Parinari polyandra* is a good adsorption inhibitor for the corrosion of mild steel in sulphuric acid. Tafel polarization analyses indicate that the studied plant extract is a mixed type inhibitor.

**Key words:** Isotherm, polarization, adsorption, inhibitor, *Parinari polyandra*.

**INTRODUCTION**

Corrosion is the deterioration of materials by chemical interaction with their environment. The consequences of corrosion are many and its effects on the safe, reliable and efficient operation of equipment or structures are severe. Most corrosion inhibitors are synthetic chemicals that are expensive and hazardous to the environment (Okoro, 2007). Basically, attention is however shifting away from the use of synthetic organic compounds as metal corrosion inhibitors. This is because many of them have been found to be toxic to humans and the environment. In recent years, a lot of research efforts have gone into the search for non-toxic naturally occurring substances for use as metal corrosion inhibitors. In this regard, a number of amino acids (Fu et al., 2011; Eddy et al., 2010) as well as extracts from leaves, roots and stem barks of plant (biomass) and even fruits or fruit peels have been reported as effective inhibitors of metal corrosion (Oguzie, 2008; Rosliza and
Wan Nik, 2010; Kumar et al., 2011; Oguzie, 2005; Ostovari et al., 2009; Satapathy et al., 2009; Ekanem et al., 2010; Oguzie et al., 2006; Umoren et al., 2009; Oguzie and Ebenso, 2005; Oguzie, 2007; Okafor et al., 2008; Ameh et al., 2012). The crucial property of the plant extracts is because they contain phytochemical compounds such as alkaloids, tannins, flavonoids, saponins, amino acids, ascorbic acid, phenolic acids, pigments, resins, triterpenoids, phlobatans, anthraquinone, cardiac glycosides, with molecular electronic structures close to conventional corrosion inhibitors. Such plant extracts could thus serve as sources of non-toxic and inexpensive corrosion inhibiting additives. In spite of the large numbers of green corrosion investigated and tested, literature is scantly on the inhibitive properties of ethanol extract of *Parinari polyandra* for the corrosion of mild steel in sulphuric acid media. Therefore the objective of the study is to investigate the inhibitive properties of ethanol extract of *P. polyandra* leaves for the corrosion of mild steel in sulphuric acid.

**MATERIALS AND METHODS**

**Materials and sample preparation**

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.6), P (0.36), C (0.15), and Si (0.03) and Fe (balance). The sheet was mechanically pressed cut into different coupons, each of dimension, 3 cm x 2 cm x 0.12 mm of thickness 0.12 mm². Each coupon was polished with different size of emery paper grids (600 – 1200), and was later degreased by washing with ethanol, rinsed with acetone and air dried before they were preserved in a desiccator. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

**Plants extraction**

Samples of *P. polyandra* leaves were obtained from Zango – Shaniu, Sabon Gari Local Government, Kaduna State Nigeria. The samples were later taken to Herbarium in Department of Biological Sciences, Ahmadu Bello University Zaria Nigeria for identification and was assigned a batch number. The leaves were dried, ground, and soaked in a solution of ethanol for 48 h. After 48 h, the samples were filtered. The filtrates were further subjected to evaporation at 352 K in order to make it free of ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5 g of the extract in 1L of 2.5 M H₂SO₄, respectively. For gravimetric analysis as well as linear polarization analysis, the concentration of H₂SO₄ used for the preparation of the inhibitor-acid solutions was 0.5 M (Eddy and Odoemelam, 2009).

**Chemical analysis**

Phytochemical analysis of the ethanol and aqueous extract of the sample was carried out according to the method reported elsewhere (Odiongenyi et al., 2009). Frothing and Na₂CO₃ tests were used for the identification of saponin, bromine water, ferric chloride tests were used for the identification of tannin while Leberman’s and Salkowski’s tests were used for the identification of cardiac glycosides while Dragendorf, Hagger, and Meyer reagent tests were used for the identification of alkaloid.

**Scanning electron microscopy (SEM)**

Morphological studies of the mild steel electrode surfaces exposed to uninhibited and inhibited 0.5 M H₂SO₄ solutions for seven days at 303 K were taken by using a Jeol JSM – 7500 F scanning electron microscope (Eddy and Ita, 2010)

**Gravimetric analysis**

A previously weighed metal (mild steel) coupon was completely immersed in 250 ml of the test (in a close beaker). The beaker was inserted into a water bath maintained at a temperature of 303 K. After every 24 h, each sample was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100 g/L of zinc dust. The washed steel coupon was rinsed in acetone and air dried before re-weighting. The difference in weight for a period of 168 h was taken as the total weight-loss. The effect of temperature on mild steel corrosion and corrosion inhibition was investigated by performing experiments in 0.5 M H₂SO₄ at 303, 313, 323 and 333 K for 3 h immersion period. All tests were run in triplicates and the data showed good reproducibility. From the weight loss results, the inhibition efficiency (%) of the inhibitor, the degree of surface coverage (θ), and the corrosion rate of mild steel (CR) were calculated using the Equations (1), (2) and (3) respectively (Sethuran and Raja, 2005).

\[
\% I = \frac{(W_1 - W_2)}{W_1} \times 100
\]

\[
\theta = 1 - \frac{W_1}{W_2}
\]

\[
CR (\text{gm}^{-2} \text{cm}^{-2}) = \frac{\Delta W}{At}
\]

Where \( W_1 \) and \( W_2 \) are the weight losses (gm/L) of mild steel in the presence and absence of inhibitor (0.5 M H₂SO₄) solution, respectively, \( \theta \) is the degree of surface coverage, \( A \) = area of specimen (cm²), and \( t \) = period of immersion (hours), \( \Delta W = W_2 - W_1 \) is the weight loss of mild steel after time, \( t \).

**Electrochemical measurements**

Metal samples for electrochemical experiments were of dimensions 1.0 cm x 1.0 cm of thickness 0.12 mm. These were subsequently sealed with epoxy resin in such a way that only one square surface of area 1.0 cm² was left uncovered. The exposed surface was degreased in acetone, rinsed with distilled water and dried in warm air. Linear polarization studies were carried out in the potential -1000 to 2000 mV at a scan rate of 0.333 mV s⁻¹ at room temperature of 303 K. Each test was run in triplicate to verify the reproducibility of the systems (Oguzie et al., 2010).

**RESULTS AND DISCUSSION**

**Phytochemical constituent**

Table 1 shows the phytochemical composition of ethanol extract of *P. polyandra*. The results obtained, indicate that saponnin, tannin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid are present in ethanol extract of *P. polyandra* hence the inhibition efficiency of ethanol extract of *P. polyandra* may be attributed to the
Table 1. Phytochemical composition of the ethanol extract of P. polyandra.

<table>
<thead>
<tr>
<th>Phytochemicals</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponins</td>
<td>+</td>
</tr>
<tr>
<td>Tanins</td>
<td>+</td>
</tr>
<tr>
<td>Phlobatanins</td>
<td>---</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>+ + +</td>
</tr>
<tr>
<td>Cardiac glycoside</td>
<td>+ +</td>
</tr>
<tr>
<td>Flavanoid</td>
<td>+ +</td>
</tr>
<tr>
<td>Terpene</td>
<td>+ + +</td>
</tr>
<tr>
<td>Alkaloid</td>
<td>+ + +</td>
</tr>
</tbody>
</table>

+ present; ++ moderately present; +++ present in large amount; - absence or presence in negligible quantity.

**Effect of ethanol extract of P. polyandra (PB)**

Figure 1 shows the variation of weight loss with time for the corrosion of mild steel in various concentrations of H₂SO₄. The figure indicates that the rate of corrosion of mild steel in sulphuric acid increases with increase in concentration. It is evident from the plot that weight losses of mild steel increases with increase in the concentration of H₂SO₄ and contact time. It is also important to note that weight loss of mild steel decreases with increasing concentration of ethanol extract of P. polyandra which indicates that ethanol extract of P. polyandra is an adsorption inhibitor for the corrosion of mild steel. It is also noted that as the temperature increases, the weight-loss were found to be more higher than at room temperature and was also found to decrease with increase in concentration of inhibitors similar to those obtained at 303 K. However, the inhibition efficiency of ethanol extract of P. polyandra decreases with increasing temperature. This also suggests that the adsorption of ethanol extract of P. polyandra on mild steel surface is consistent with the mechanism of physical adsorption. In order to sustain further, the inhibition efficiencies and corrosion rate was determined, the inhibition efficiencies of ethanol extract of P. polyandra and the corrosion rates of mild steel in H₂SO₄ in the absence and presence of ethanol extract of P. polyandra as an inhibitor. From the results obtained, it is evident that the corrosion rate of mild steel decreases with increasing concentrations of the extract while the inhibition efficiency increases with increasing...
Table 2. Corrosion rates (CR) of mild steel of ethanol extract of *P. polyandra*.

<table>
<thead>
<tr>
<th>Conc.(g/L)</th>
<th>333K</th>
<th>303K</th>
<th>313K</th>
<th>323K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>37.79</td>
<td>13.84</td>
<td>8.71</td>
<td>6.68</td>
</tr>
<tr>
<td>0.1</td>
<td>34.31</td>
<td>10.99</td>
<td>6.86</td>
<td>5.58</td>
</tr>
<tr>
<td>0.2</td>
<td>33.83</td>
<td>10.49</td>
<td>6.86</td>
<td>5.58</td>
</tr>
<tr>
<td>0.3</td>
<td>32.14</td>
<td>10.99</td>
<td>6.86</td>
<td>5.58</td>
</tr>
<tr>
<td>0.4</td>
<td>31.22</td>
<td>10.99</td>
<td>6.86</td>
<td>5.58</td>
</tr>
<tr>
<td>0.5</td>
<td>29.57</td>
<td>10.99</td>
<td>6.86</td>
<td>5.58</td>
</tr>
</tbody>
</table>

Table 3. Inhibition efficiencies (% I) of ethanol extract of *P. polyandra*.

<table>
<thead>
<tr>
<th>333K</th>
<th>323K</th>
<th>313K</th>
<th>303K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>09.88</td>
<td>31.77</td>
<td>37.09</td>
</tr>
<tr>
<td>1.59</td>
<td>22.28</td>
<td>45.01</td>
<td>50.46</td>
</tr>
<tr>
<td>4.78</td>
<td>30.70</td>
<td>50.26</td>
<td>55.92</td>
</tr>
<tr>
<td>5.39</td>
<td>38.83</td>
<td>56.43</td>
<td>59.65</td>
</tr>
<tr>
<td>8.61</td>
<td>41.08</td>
<td>60.18</td>
<td>65.47</td>
</tr>
</tbody>
</table>

concentration of the extract. This implies that ethanol extract of the inhibitor retarded the rate of corrosion of mild steel in H$_2$SO$_4$. From the calculated values of corrosion rate of mild steel and of the inhibition efficiency of the plant extracts (Tables 2 and 3), it can be seen that the inhibition efficiency of *P. polyandra* for mild steel in solutions of sulphuric acid increases with increase in the concentration of the inhibitor, but decreases with increasing temperature, indicating that *P. polyandra* is an adsorption inhibitor for the corrosion of mild steel in solutions of H$_2$SO$_4$ and that the adsorption of *P. polyandra* favours the mechanism of physical adsorption (Chetounani et al., 2004).

**Effect of temperature**

The effect of temperature on the corrosion of mild steel in the absence and presence of various concentration of *P. polyandra* was investigated using the Arrhenius state equation shown in Equations (4) and (5) (Lebrini et al., 2010).

\[
\log CR = \log A - \frac{E_a}{2.303RT} \tag{4}
\]

\[
\log \left( \frac{CR}{T} \right) = \left\{ \log \left( \frac{R}{N_A h} \right) + \frac{\Delta S_a}{2.303R} \right\} - \frac{\Delta H_a}{2.303RT} \tag{5}
\]

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, $E_a$ is the activation energy (that is, the minimum energy needed before the corrosion reaction of the metal can proceed), $R$ is the universal gas constant and $T$ is the temperature of the system, $N_A$ is the Avogadro’s constant, $\Delta S_a$ is the entropy of activation and $\Delta H_a$ is the enthalpy of activation.

From Equation (4), plot of log CR versus reciprocal of absolute temperature, 1/T, as shown in Figure 2 gives a straight line with slope equal to $-E_a/2.303R$, from which the activation energy for the corrosion process can be calculated. From Equation (5), plot of log CR/T versus reciprocal of absolute temperature, 1/T, as shown in Figure 3 gives a straight line with slope equal to $-\Delta H_a/2.303R$ and intercept of $\log R/N_A h + \Delta S_a/2.303R$, from which the enthalpy and entropy of activation for the corrosion process can be calculated. Values of $E_a$, $\Delta S_a$, and $\Delta H_a$ are presented in Table 4. Figure 2 and 3 also show a linear relationship between the corrosion rate and the temperature of the environment.

Values of the extrapolated activation energy $E_a$ were found to be greater where corrosion rates were inhibited than those obtained where there were no inhibition indicating that the ethanol extract of *P. polyandra* retarded the corrosion of mild steel in H$_2$SO$_4$. It is also found that the activation energy was lowered than the value of 80 kJmol$^{-1}$ required for chemical adsorption to take place, confirming that the adsorption of the ethanol extract of *P. polyandra* occur through the mechanism of physical adsorption (Sethuran and Raja, 2005). Table 3 shows the enthalpies of activation of the corrosion.
Figure 2. Variation of logCR of mild steel with inverse temperature for the corrosion of mild.

Figure 3. Variation of logCR/T of mild steel with inverse temperature for the corrosion of mild steel in 0.5 M H$_2$SO$_4$ containing various concentration of inhibitor.

Table 4. Activation energy parameters for the dissolution of mild steel in H$_2$SO$_4$ in the absence and presence of different concentration of *P. polyandra*.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H_a$ (kJ/mol)</th>
<th>$\Delta S_a$ (kJ/molK)</th>
<th>$(E_a-\Delta H_a)$ (kJ/mol)</th>
<th>$Q_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>28.80</td>
<td>26.15</td>
<td>-0.194</td>
<td>2.65</td>
<td>-229.48</td>
</tr>
<tr>
<td>0.1</td>
<td>40.52</td>
<td>37.87</td>
<td>-0.160</td>
<td>2.65</td>
<td>-115.81</td>
</tr>
<tr>
<td>0.2</td>
<td>46.64</td>
<td>44.00</td>
<td>-0.142</td>
<td>2.64</td>
<td>-90.30</td>
</tr>
<tr>
<td>0.3</td>
<td>48.60</td>
<td>45.95</td>
<td>-0.136</td>
<td>2.65</td>
<td>-91.04</td>
</tr>
<tr>
<td>0.4</td>
<td>50.64</td>
<td>48.00</td>
<td>-0.130</td>
<td>2.64</td>
<td>-83.94</td>
</tr>
<tr>
<td>0.5</td>
<td>54.17</td>
<td>51.52</td>
<td>-0.120</td>
<td>2.65</td>
<td></td>
</tr>
</tbody>
</table>
process to be positive which reflect endothermic nature of dissolution process. Moreover, the average difference value of \( (E_a - \Delta H_a) \) is 2.6467 kJ/mol which is approximately equal to the average value of RT is 2.6438 kJ/mol. Therefore, the corrosion process is a unimolecular reaction as it is characterized by the equation given below:

\[
E_a - \Delta H_a = RT
\]

The entropy of activation in the presence and absence of the inhibitor also has negative values which indicates that the activated complex in the rate determining step represents an association rather than dissociation, implying that a decrease in disordering took place on going from the reactant to the activated complex (Lebrini et al., 2011).

**Adsorption thermodynamic considerations**

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm, gives an insight into the adsorption process. Several adsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir, Freundlich, Temkin, Flory-Huggins. The surface coverage (\( \theta \)) values for different concentrations of the inhibitor in 0.5 M \( \text{H}_2\text{SO}_4 \) have been evaluated from the weight-loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of \( \log(C/ \theta) \) against \( \log C \) (Figure 4) gave a straight line indicating that adsorption follows the Langmuir adsorption isotherm and a straight line was also obtained in the plot between \( \log \theta \) versus \( \log C \), this shows that the adsorption also obeys Freundlich adsorption isotherm (Figure 5). The weight-loss data obtained were also tested in other adsorption isotherm, among the entire adsorption isotherm tested, Freundlich was found to be the best fit. The heat of adsorption of ethanol extract of PB on mild steel was also calculated using the Equation (7) (Eddy et al., 2009a),

\[
Q_{ads} = 2.303R[\log(\frac{\theta_2}{1-\theta_2}) - \log\left(\frac{\theta_1}{1-\theta_1}\right)](\frac{T_{ads}}{T_1-T_2}) \text{kJ/mol} - 1
\]

Where \( \theta_1 \) and \( \theta_2 \) are the degrees of surface coverage of the inhibitor at the temperature, \( T_1 \) (303 K) and \( T_2 \) (333 K) respectively and \( R \) is the molar gas constant. Calculated values of \( Q_{ads} \) are presented Table 4. The values are negative and ranged from indicating that the adsorption of the ethanol extract of the inhibitor on mild steel surface is exergonic. The free energies for the adsorption of ethanol extract of \( P. \text{polyandra} \) were calculated using the Equation (8) (Eddy et al., 2008b),

\[
\Delta G_{ads}^o = -2.303RT\log(55.5K_{ads})
\]

Where \( R \) is the molar gas constant, \( T \) is the temperature in Kelvin, 55.5 is the molar concentration of water and \( K_{ads} = \theta/(1-\theta)[C] \).

Calculated values of \( \Delta G_{ads}^o \) are also presented in Table 5, the values ranged from -9.67 to 13.58 kJmol\(^{-1}\) and tend to be more negative as concentration of the inhibitor increases. These indicate that the adsorption of ethanol extract of \( P. \text{polyandra} \) on mild steel surface is spontaneous and that the strength of the adsorption
increases with increase in concentration of the inhibitor. It is also significant to note that values of $\Delta G^\circ_{\text{ads}}$ greater than $\ll-40$ kJ mol$^{-1}$ are consistent with the transfer of electron from the inhibitor to the metal surface which represent a chemical adsorption whereas, values of $\Delta G^\circ_{\text{ads}}$ less than $\ll-40$ kJ mol$^{-1}$ signifies that the adsorption is a physical process. Therefore the adsorption of ethanol extract of $P. polyandra$ on mild steel surface supports the mechanism of physical adsorption from the values of $\Delta G^\circ_{\text{ads}}$ obtained from this study.

**SEM surface analysis**

Surface morphology of the mild steel specimens in uninhibited and inhibited acid solutions was carried out by SEM after immersion in the test solutions after 7 days at 303 K. Figure 6 (a) and (b) shows the SEM images of the mild steel in the absence of inhibitor and presence of the inhibitor. A severely corroded surface morphology was observed after the immersion in the uninhibited system, due to the corrosive attack of the acid solution. Corrosion was relatively general with no evidence of localized attack. The corrosion product layer on the metal surface in uninhibited is clearly very loose and porous and would thus offer insignificant corrosion protection. With addition of $P. polyandra$, the corrosion damage is visibly reduced, there is slight evidence of the adsorbate presence on the metal surface.

**Linear polarization resistance**

Linear polarization experiment was taken to understand the effect of $P. polyandra$ on both the cathodic and anodic dissolution of the mild steel. A typical polarization
curves for mild steel in 0.5 M H₂SO₄ in the absence and presence of *P. polyandra* is shown in Figure 7, and also parameters derived from the curves were also presented in Table 6. It can be observed that both cathodic and anodic reactions were suppressed with the addition of various concentration of *P. polyandra* which indicate that the inhibitor affected the cathodic as well as the anodic partial reactions, shifting the corrosion potential slightly towards more positive values, thus reducing the anodic and cathodic current densities and the corresponding corrosion current density. This indicates that the extracts functioned as a mixed-type inhibitor in the acid solution. From the value of the corrosion current densities in both the absence and presence of the inhibitor, the inhibition efficiencies were calculated using the equation given below:

\[ \text{Inhibition Efficiency} = \frac{I_{corr, \text{blank}} - I_{corr, \text{inhibitor}}}{I_{corr, \text{blank}}} \times 100 \]
From the study, we found that ethanol extract of P. polyandra is an adsorption inhibitor for the corrosion of mild steel in sulphuric acid. The adsorption characteristics of the inhibitor favours the mechanism of charge transfer from the charged inhibitor’s molecule to the charged metal surface (Physical adsorption) and supported Freundlich adsorption model. Linear polarization results, indicate that the inhibitor is a mixed type inhibitor on the surface of mild steel.

### Conflict of Interest

The authors have not declared any conflict of interest.

### ACKNOWLEDGEMENTS

The authors are grateful to Dr. I. A. Bello and Mr. C. O. Ochigbo, both of Chemistry Department, Ahmadu Bello University, Zaria Nigeria, for their assistance in the procurement of the plant.

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**Table 6. Polarization parameters for mild steel in 0.5 M H2SO4 in the presence and absence of P. polyandra.**

<table>
<thead>
<tr>
<th>System</th>
<th>Ecorr (mV vs SCE)</th>
<th>icorr(μA/cm²)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-1004.4</td>
<td>1642.0</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>-926.15</td>
<td>1069.8</td>
<td>34.85</td>
</tr>
<tr>
<td>0.2</td>
<td>-956.73</td>
<td>861.27</td>
<td>47.55</td>
</tr>
<tr>
<td>0.3</td>
<td>-1003.4</td>
<td>722.32</td>
<td>56.01</td>
</tr>
<tr>
<td>0.4</td>
<td>-932.84</td>
<td>480.84</td>
<td>70.71</td>
</tr>
<tr>
<td>0.5</td>
<td>-935.00</td>
<td>372.01</td>
<td>77.34</td>
</tr>
</tbody>
</table>

\[ IE\text{,}% = \left(1 - \frac{i_{\text{inh}}}{i_{\text{corr}}}\right) \times 100 \] (9)


