Adsorptive, Kinetic, Thermodynamic and Inhibitive Properties of Cissus Populnea Stem Extract on the Corrosion of Aluminum in Acid Medium.

1*Chahul, H. F., 2Ayuba, A. M. and 3Nyior, S.

1, 3Department of Chemistry, University of Agriculture Makurdi, P.M.B. 2373, Benue State, Nigeria.
2Department of Pure and Industrial Chemistry, Bayero University, P.M.B. 3011, Kano State, Nigeria.
Email: momohbat2007@gmail.com

ABSTRACT

The adsorption of Cissus populnea stem extract and its subsequent corrosion inhibition properties on aluminum in 0.5 M HCl solutions have been investigated using weight loss measurements. Inhibition efficiency of the plant extract increased with concentration but decreased with rise in temperature. The adsorption of the inhibitor on the aluminum surface was spontaneous and found to align with Langmuir, Freundlich, Temkin and Flory-Huggins adsorption isotherms. From the values of E_0 and ΔG° obtained, the mechanism of physical adsorption has been proposed. Some thermodynamic and activation parameters were also calculated.

Keywords: Adsorption isotherm, Cissus populnea, corrosion, physiosorption, thermodynamics

INTRODUCTION

Corrosion of aluminum and its alloys have been a subject of numerous studies due to their high technological value and wide range of industrial applications especially in aerospace and household industries. There is therefore need to protect it in aggressive acid and alkaline media.

Usually the corrosion of metals and alloys in acid solution is very severe and this kind of attack can be inhibited by a large number of organic substances. In general, nitrogen, oxygen and sulphur containing compounds with a hydrocarbon part attached to the polar group are used as inhibitors (Oguzie, 2005; Asshasi-Sorkhabi et al., 2006; El Ashry et al., 2006; Shukla and Quraish, 2009; Ebenso et al., 2010).

Plant materials are the richest source of heterocyclic compounds and adsorption of these compounds play a key role in corrosion inhibition of metals. Recent development in the area of corrosion control has been on the screening of various plant extracts for anticorrosive properties (Zucchi and Omar, 1985; Khamis et al., 2005; Umoren et al., 2006; Abiola et al., 2007; Oguzie, 2005; 2008; Oguzie et al., 2010; 2012).

The exploration of natural products of plant origin as inexpensive and ecofriendly corrosion inhibitors is an essential field of study. In addition, plant products are of low cost, readily available and renewable source of materials. In view of this, the present work attempts to investigate the use of Cissus populnea stem extract as an inhibitor for the corrosion of aluminum in 0.5 M HCl. Alkanoids have been identified as the major chemical constituent of the stem extract of Cissus populnea. Other chemical compounds are flavonoids, saponins, tannins, cyanogenic and cardiac glycosides, anthraquinones and terpenoids (Soladoye and Chukwuma, 2012; Akomolafe et al., 2013).

MATERIALS AND METHODS

Material Preparation

The aluminum sheets used for this study (99.8% purity) was obtained commercially from Oshodi in Lagos State, Nigeria. The sheet was 0.15 cm thick. They were mechanically press cut into 3.0 x 2.0 cm coupons and were used without further polishing. These coupons were however degreased in ethanol, dried in acetone and warm air, and stored in moisture free desiccators prior to use.

Preparation of Cissus populnea Stem Extract

Fresh stems of the Cissus populnea plant were cut at Tse-Negeh Mbayion in Gboko Local Government Area of Benue State, Nigeria. The stem of the plant was first of all scrapped with the aid of a knife to remove the whitish substance covering it, the stem was later shredded using a knife. The shredded plant stem was soaked in hot water for about 15 minutes to allow for easy extraction and then squeezed with hands to remove the extract which was then filtered using a sieve to obtain a chaff free extract.

The air dried extract was blended with an electric blender into fine powder and kept dry in an air-tight container prior to use. Appropriate quantities of the extract powder were dissolved in 250 cm³ 0.5 M HCl to obtain inhibitor test solutions of 0.2 g/L - 1.0 g/L concentrations while 0. 05 M KI was added for synergistic studies.
Weight Loss Measurements

Preweighed aluminum coupons were immersed in triplicate in 250 cm$^3$ 0.5 M HCl solution in the absence and presence of 0.2 g/L – 1.0 g/L of the stem extract with the aid of glass hooks at 303 K for 24 hours. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight. In order to determine the character of the inhibiting action of the stem extract at short exposure times as well as to assess the effect of temperature change (303−333 K) on corrosion and corrosion inhibition processes, weight loss measurements were also undertaken after 3 hrs of immersion. Average values for each experiment were used in subsequent calculations (Momoh-Yahaya et al., 2012).

From the initial and final weights of aluminum coupons, the weight loss (g h$^{-1}$), corrosion rate (gh$^{-1}$cm$^{-2}$), inhibition efficiency (%IE) and the degree of surface coverage ($\theta$) were calculated using equations 1 to 3 respectively (Eddy et al., 2010; Momoh-Yahaya et al., 2012; 2013; 2014).

\[
CR(gh^{-1}cm^{-2}) = \frac{\Delta W}{At}
\]

\[
IE_{exp} = \left(1 - \frac{W_1}{W_2}\right) \times 100
\]

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

where $W_1$ and $W_2$ are the weight losses (g) for aluminum coupons in the presence and absence of the *Cissus populnea* stem extract respectively, $\theta$ is the degree of surface coverage of the inhibitor, $A$ is the area of the metal coupon (in cm$^2$), $t$ is the period of immersion (in hrs) and $\Delta W = W_2 - W_1$ is the weight loss of aluminum coupon after time, $t$.

RESULTS AND DISCUSSION

Effect of Inhibitor Concentration

The effect of *Cissus populnea* stem extract concentration on corrosion rate and inhibition efficiency at 303 K for the corrosion of aluminum in 0.5 M HCl in the absence and presence of various concentrations of the plant stem extract are shown on Figures 1 and 2 respectively.

From the plots (Fig. 1) it is evident that the corrosion rate of aluminum coupons in 0.5 M HCl decreased with increase in the concentration of the plant extract. This suggests that as the concentration of the plant extract increased, there was an increase in surface coverage of the adsorbed extract on the aluminum coupons which provided a barrier and prevented further corrosion. This result is in agreement with findings of Abiola and James, (2010); Olasehinde et al. (2013). Furthermore, the inhibition efficiency (Fig. 2) of the extract was observed to increase with increasing plant concentrations. This may be due to increase in the fraction of the aluminum surface covered by the adsorbed constituents of the extract.

 Corresponding values of corrosion rates of aluminum coupons and inhibition efficiencies, %IE, of various concentrations of *Cissus populnea* stem extract in 0.5 M HCl obtained from the plots, were as presented in Table 1.

![Graph 1: Variation of Corrosion Rate (g cm$^{-2}$ h$^{-1}$) of Aluminum against Various Concentrations of *Cissus populnea* Stem Extract in 0.5 M HCl at 303 K.](image)
Fig 2: Variation of Inhibition Efficiency (%IE) against Various Concentrations of Cissus populnea Stem Extract for Aluminum Corrosion in 0.5 M at 303 K.

Table 1: Corrosion Rates of Aluminum and Inhibition Efficiencies of Cissus populnea Stem Extract in 0.5 M HCl at 303 K and 24 hrs Immersion.

<table>
<thead>
<tr>
<th>Conc.g/L</th>
<th>Corrosion rate g/cm²/hr</th>
<th>Inhibition efficiency (% IE)</th>
<th>Surface coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0035</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0022</td>
<td>39.72</td>
<td>0.40</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0021</td>
<td>42.40</td>
<td>0.42</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0017</td>
<td>54.20</td>
<td>0.54</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0015</td>
<td>60.25</td>
<td>0.60</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0010</td>
<td>72.44</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Effect of Immersion Time

Fig. 3 shows the effect of immersion time on the weight loss of aluminum in 0.5 M HCl at 303 K in the absence and presence of 0.1, 0.6 and 1.0 g/L concentrations of the extract. From the figure, it can be deduced that although the weight loss of aluminum increased over time, the corrosion rates of aluminum coupons in the presence of the extract decreased with increasing inhibitor concentrations.

Fig. 4 illustrates the effect of immersion time on inhibition efficiency for different concentrations of Cissus populnea stem extract in 0.5 M HCl from which it can be observed that the extract actually inhibited the corrosion of aluminum in 0.5 M HCl with %IE > 60% with 1 g/L inhibitor concentration for up 120 hrs but remained above 50% for up to 168 hrs. This phenomenon could be due to the fact that after 120 hrs, the aggressive action of the chloride ion in the acid medium reduced the integrity of the adsorbed stem extract resulting in reduced inhibition efficiency with longer immersion time (Oguzie et al., 2012).
Fig 3: Effect of Immersion Time (hrs) on Corrosion Rate of Aluminum in 0.5 M HCl in the Absence and Presence of *Cissus populnea* Stem Extract at 303 K.

**Figure 4:** Effect of Immersion Time (hrs) on Inhibition Efficiency (%IE) of *Cissus populnea* Stem Extract on the Dissolution of Aluminum in 0.5 M HCl at 303 K.

**Effect of Temperature**

From the plots on Fig. 5, it is evident that the corrosion rate of aluminum with or without extract increased with increase in temperature. This is because as the temperature increased from 303 to 333 K, the rate of corrosion of the aluminum coupons also increased due to increasing average kinetic energy of the reacting molecules (Obot and Obi-Egbedi, 2010). The corrosion rate is however retarded in the presence of the plant extract.

Fig. 6 presents the variation of inhibition efficiency with temperature for a 3 hrs immersion period and show that corrosion rates in both uninhibited and inhibited process increased with rise in temperature. While on the other hand, the inhibition efficiency of plant extract decreased with increasing temperature. This may be as a result of increasing solubility of the adsorbed protective inhibitor films on the aluminum coupons, thereby increasing the susceptibility of these coupons to dissolution in the acid media (Olasehinde *et al.*, 2013).

Table 2 presents the values of inhibition efficiencies (%IE) and corrosion rates for corrosion of aluminum in the absence and presence of various concentrations of the extract in 0.5 M HCl at 303 - 333 K.
Fig 5: Variation of Corrosion Rate of Aluminum Against Temperature (303 – 333 K) in the Absence and Presence Different Concentrations of *Cissus populnea* Stem Extract in 0.5 M HCl.

![Corrosion Rate Graph]

Fig 6: Variation of Inhibition Temperature (%IE) Against Temperature for the Corrosion of Aluminum in 0.5 M HCl in the presence and absence of *Cissus populnea* stem extract.

![Inhibition Efficiency Graph]

Table 2: Inhibition Efficiencies (%IE) and Corrosion Rates for Corrosion of Aluminum in the Absence and Presence of Various Concentrations of the Extract in 0.5 M HCl at 303 - 333 K.

<table>
<thead>
<tr>
<th>System</th>
<th>Corrosion rate (g/cm²/hr)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
<td>313K</td>
</tr>
<tr>
<td>Blank</td>
<td>0.018</td>
<td>0.015</td>
</tr>
<tr>
<td>0.2g/L</td>
<td>0.012</td>
<td>0.010</td>
</tr>
<tr>
<td>0.6 g/L</td>
<td>0.006</td>
<td>0.007</td>
</tr>
<tr>
<td>1.0 g/L</td>
<td>0.005</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Effect of Iodide Ions (I\textsuperscript{-}).

Fig. 7 shows the combined effect of the addition of 0.05 M potassium iodide (KI) on the corrosion of aluminum in 0.5 M HCl in the absence and presence of 0.2 g/L, 0.6 g/L and 1.0 g/L Cissus populnea stem extract at 303K and 24 hrs immersion period. From the plot, it is evident that the weight loss and corrosion rate of aluminum coupons decreased on addition of KI resulting in remarkable increase in inhibition efficiencies of 78.95%, 90.59% and 93.52% for 0.2 g/L, 0.6 g/L and 1.0 g/L concentrations of the extract respectively.

It is generally accepted that the presence of halide ions in acidic media synergistically increases the inhibition efficiency of some organic compounds. It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions (Oguzie et al., 2007).

Adsorption Characteristics.

Adsorption isotherms provide information about the interaction among adsorbed molecules themselves as well as their interactions with the metal surface. The adsorption characteristics of Cissus populnea stem extract were investigated by fitting data obtained for the degree of surface coverage from weight loss experiment at 303 - 333K into various adsorption isotherms and were found to best fit the Langmuir, Freundlich, Temkin and Flory-Huggins models. The functional and linear forms of these isotherm models are given in Table 3 (Oguzie et al., 2012).

Table 3: Functional and linear forms of adsorption isotherm models tested.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Functional form</th>
<th>Linear form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( k_{ads}C = \frac{\theta}{1 - \theta} )</td>
<td>( \frac{C}{\theta} = C + \frac{1}{k_{ads}} )</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( k_{ads}C^n = 0 ) with ( 0 &lt; n &lt; 1 )</td>
<td>( \log \theta = \log k_{ads} - n \log C )</td>
</tr>
<tr>
<td>Temkin</td>
<td>( k_{ads}C = \exp(f \theta) ) with ( f = -2 \alpha )</td>
<td>( -2 \alpha \theta = 2.303(\log k_{ads} + \log C) )</td>
</tr>
<tr>
<td>Flory-Huggins</td>
<td>( k_{ads}C = \frac{\theta}{x(1 - \theta)} )</td>
<td>( \log \left( \frac{\theta}{C} \right) = \log k_{ads} + x \log (1 - \theta) )</td>
</tr>
</tbody>
</table>
Where \( \theta \) is the degree of surface coverage of the inhibitor, \( C \) is the concentration of the inhibitor, \( \alpha \) is the molecular interaction parameter and \( K_{ads} \) is the equilibrium constant of the adsorption. The data from the study gave best fit with adsorption models presented on Table 3 taking into cognizance that the plots gave linear slopes with regression coefficients, \( R^2 \), values greater than 0.9 (Saratha et al., 2009). Table 4 shows the parameters of linearization for each adsorption model.

### Table 4: Parameters of Various Adsorption Isotherms for the Adsorption of Cissus populnea Stem Extract on Aluminum Surface at 303- 333 K.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Intercept</th>
<th>Slope</th>
<th>( k_{ads} )</th>
<th>( R^2 )</th>
<th>( \Delta G_{ads} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303 K</td>
<td>0.445</td>
<td>0.904</td>
<td>2.247</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td>313 K</td>
<td>0.403</td>
<td>1.188</td>
<td>2.481</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>323 K</td>
<td>0.400</td>
<td>1.579</td>
<td>2.500</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>333 K</td>
<td>0.814</td>
<td>1.408</td>
<td>1.229</td>
<td>0.975</td>
</tr>
<tr>
<td>Freundlich</td>
<td>303 K</td>
<td>0.110</td>
<td>0.558</td>
<td>1.116</td>
<td>0.966</td>
</tr>
<tr>
<td></td>
<td>313 K</td>
<td>0.185</td>
<td>0.461</td>
<td>1.203</td>
<td>0.971</td>
</tr>
<tr>
<td></td>
<td>323 K</td>
<td>0.286</td>
<td>0.371</td>
<td>1.331</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>333 K</td>
<td>0.326</td>
<td>0.598</td>
<td>1.385</td>
<td>0.966</td>
</tr>
<tr>
<td>Temkin</td>
<td>303 K</td>
<td>0.747</td>
<td>0.617</td>
<td>1.211</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>313 K</td>
<td>0.636</td>
<td>0.466</td>
<td>1.365</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>323 K</td>
<td>0.508</td>
<td>0.323</td>
<td>1.573</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>333 K</td>
<td>0.452</td>
<td>0.389</td>
<td>1.162</td>
<td>0.985</td>
</tr>
<tr>
<td>Flory- Huggins</td>
<td>303 K</td>
<td>0.317</td>
<td>0.751</td>
<td>1.373</td>
<td>0.931</td>
</tr>
<tr>
<td></td>
<td>313 K</td>
<td>0.411</td>
<td>1.398</td>
<td>1.508</td>
<td>0.966</td>
</tr>
<tr>
<td></td>
<td>323 K</td>
<td>0.540</td>
<td>2.707</td>
<td>1.716</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>333 K</td>
<td>0.086</td>
<td>1.586</td>
<td>1.090</td>
<td>0.879</td>
</tr>
</tbody>
</table>

Values of \( k_{ads} \) show the strength between adsorbate and adsorbent. Large values of \( k_{ads} \) signify greater adsorption and hence better inhibition efficiency and vice versa (Obot and Obi-Egbedi, 2008). From Table 4, it is clear that values of \( k_{ads} \) are low indicating weak interactions between the extract and the aluminum surface. It therefore suggests that electrostatic interaction (physisorption) exists between the extract molecules and the aluminum surface (Obot and Obi-Egbedi, 2008; Momoh-Yahaya et al., 2014).

It is also significant to state that the value of the equilibrium constant of adsorption (\( k_{ads} \)) obtained from the intercept of the adsorption isotherm is related to the free energy of adsorption as follows.

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

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

Generally, negative \( \Delta G_{ads} \) values indicate spontaneity of the adsorption process (Ebenso et al., 2008; Eddy and Ebenso, 2010; Quraish and singh, 2010) and \( \Delta G_{ads} \) values with magnitude < -40 kJ mol\(^{-1}\) have typically been correlated with electrostatic interactions between inhibitor molecules and charged metal surface (physisorption), whilst those of magnitude in the order of 40 kJ mol\(^{-1}\) and above are associated with charge sharing or transfer from the inhibitor molecules to the metal surface (chemisorption) (Ebenso et al., 2008; Eddy and Ebenso, 2010; Eddy et al., 2010). From Table 4, it can be observed that evaluated values of \( \Delta G_{ads} \) were negative and < -20 kJ mol\(^{-1}\) indicating that the adsorption of the extract is spontaneous and that the mechanism of adsorption is physisorption.
Fig 8: Langmuir Isotherm for the Adsorption of *Cissus populnea* Stem Extract on Aluminum Surface in 0.5 M HCl at 303 – 333 K.

Fig 9: Temkin Isotherm for the Adsorption of *Cissus populnea* Stem Extract on Aluminum Surface in 0.5 M HCl at 303 – 333 K.

**THERMODYNAMICS**

The dependence of corrosion rate on temperature can be represented by a modified form of Arrhenius equation (equation 7). The logarithmic form of which is as given in equation 8. While if the corrosion rates of the metal at two temperatures, \(T_1\) (303 K) and \(T_2\) (333 K) are known, (i.e \(CR_1\) and \(CR_2\) respectively), then equation 8 can be transformed to equation 9.

\[
CR = A \exp^{-E_a/RT} 
\]

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

\[
\log(CR_2/CR_1) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) 
\]
Where $CR$ is the corrosion rate of the metal, $A$ is the Arrhenius constant $E_a$ is the activation energy, $R$ is the universal gas constant and $T$ is the absolute temperature of the system in Kelvin (K).

$$\text{Ea} = -\frac{\Delta H}{2.303R}$$

An estimate of the heats of adsorption ($Q_{ads}$) was also obtained from the trend of surface coverage with temperature as follows (Momoh-Yahaya et al., 2012):

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

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.

The calculated values of $E_a$ and $Q_{ads}$ are presented on Table 5 from which the values for the apparent activation energy for the corrosion process in the presence of the extract are higher than those in the absence of the extract (blank). The increase in activation energy in the presence of the extract symbolizes physical adsorption with the formation of an adsorptive film of an electrostatic character. This signifies that the adsorbed plant extract provided a physical barrier to the change and mass transfer leading to the decrease in corrosion rate. This conforms to the findings of Oguzie et al. 2006; Adeyemi and Olubomehin, 2010; Olasehinde et al., 2013. Studies have also shown that values of $E_a > 80$ kJ mol$^{-1}$ implies chemisorptions whereas $E_a < 80$ kJ mol$^{-1}$ shows physisorption (Ebenso et al., 2008; Eddy and Ebenso, 2010; Olasehinde et al., 2013). From Table 5, it can be observed that values of $E_a$ where less than 80 kJ mol$^{-1}$ confirming a physical or columbic type of adsorption which is characterized by decrease in inhibition efficiency with a rise in temperature.

Negative values of $Q_{ads}$ presented on Table 5 infers that the adsorption of the extract on the metal surface is an exothermic process (Eddy and Odiongenyi, (2010); Ismail et al., (2011); Momoh-Yahaya et al., (2014)).

The values of enthalpy of activation, $\Delta H$ and entropy of activation $\Delta S$ were obtained from the transition state equation (Obot and Obi-Egbedi; 2008; Quraish and Singh, 2010):

$$\Delta H = \Delta H_{2303R}$$

where $h$ is the Planck’s constant, $N$ is the Avogadro’s number, $T$ is the absolute temperature and $R$ is the universal gas constant.

A plot of $\log(CR/T)$ as a function of $1/T$ is a straight line graph (Fig. 11) with a slope $(-\Delta H/2.303R)$ and an intercept $[\log(R/Nh) + \Delta S/2.303R]$ from which the values of $\Delta H$ and $\Delta S$ were computed and presented in Table 5. It can be observed from the Table that the values of $\Delta H$ in the presence of Cissus populnea stem extract increased over that of the uninhibited solution. This implies that energy barrier of the corrosion reaction in the presence of the stem extract increased. The positive values of $\Delta H$ reflects the endothermic nature of aluminum dissolution process. Also, values of $\Delta S$ were positive and increased in the presence of the inhibitor compared to the uninhibited solution, this could be related to the phenomenon of ordering and disordering of inhibitor molecules on the aluminum surface meaning that disorderness is increased on going from reactant to activated complex and that the reaction was spontaneous and feasible (Obot and obi-Egbedi, 2008; Quraish and Singh, 2010).
**CONCLUSION**

From the study, it was observed that *Cissus populnea* stem extract inhibited the corrosion of aluminum in 0.5 M HCl. The values of activation energies (E_a) and standard free energies of adsorption (ΔG_ads) obtained showed that *Cissus populnea* extract adsorbed on the aluminum surface through physical interactions, and that the adsorption process was spontaneous. The negative values of heats of adsorption (Q_ads) obtained from the study signified that the adsorption of *Cissus populnea* stem extract on the metal surface is exothermic while adsorption characteristics of the plant extract gave best fit with Langmuir, Freundlich, Temkin and Florry-Huggins isotherms.

**REFERENCES**


<table>
<thead>
<tr>
<th>System</th>
<th>E_a (kJ mol\textsuperscript{-1})</th>
<th>Q_ads (kJ mol\textsuperscript{-1})</th>
<th>Enthalpy (J mol\textsuperscript{-1})</th>
<th>Entropy (kJ mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>11.33</td>
<td>12.31</td>
<td></td>
<td>1.06</td>
</tr>
<tr>
<td>0.2g/L</td>
<td>16.16</td>
<td>-20.66</td>
<td>16.89</td>
<td>1.09</td>
</tr>
<tr>
<td>0.6g/L</td>
<td>26.47</td>
<td>-29.44</td>
<td>27.80</td>
<td>1.12</td>
</tr>
<tr>
<td>1.0g/L</td>
<td>26.27</td>
<td>-34.00</td>
<td>27.99</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table 5: Heat of Adsorption and Thermodynamic Activation Parameters for the Dissolution of Aluminum in 0.5 M HCl in Absence and Presence of *Cissus populnea* Stem Extract at 303- 333 K


