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Physicochemical characterization and inhibitive performance evaluation of *Commiphora kestingii* gum exudate in acidic medium

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Gas chromatographic-mass spectrometry (GCMS), fourier transformed infra-red spectroscopy (FTIR) and physicochemical analysis of *Commiphora kestingii* gum have been carried out. The corrosion inhibition characteristics of *C. kestingii* (CK) gum on aluminium in sulphuric acid media were also investigated at 303 and 333K using gravimetric and scanning electron microscopic studies (SEM) method. The study revealed that the gum contains significant amount of Sucrose, Octadecanoic acid, Alpha camphorenal, Nerolidol isobutyrate, Diisopropenyl-1-methyl-1-vinyl cyclohexane, Abetic acid, Oleic acid, Verbenol, 2,6-dimethylhepta-1,5-diene, Naphthalene, Limonene, 7-hexadecenal and 10-methyl-8-tetradecen-1-ol acetate. Corrosion inhibition tests suggest that GS gum is a good inhibitor for the corrosion of Al in solution of H₂SO₄. The inhibition efficiency of this inhibitor increased with increasing temperature suggesting chemisorption mechanism. Also, the inhibition efficiency of these extract was found to increase in the presence of CK. Inhibition of Aluminium by *C. kestingii* gum occurred through synergistic adsorption of the various components of the gums hence the formation of multiple adsorption layer is proposed.

**Key words:** *Commiphora kestingii* gum, corrosion inhibitors, adsorption, aluminium.

INTRODUCTION

Aluminium has wider application ranging from all sorts packaging, vital in powerlines, the building and construction industry and common household objects (Hatch, 1984). The key features that lend aluminium to these uses are low density, ductility, electrical conductivity and strength in alloys. Aluminium has a natural corrosion protection from its oxide layer. However, the following factors may affect the stability of the aluminium oxide and thereby cause corrosion:

i. The oxide is not stable in acidic (pH < 4) or alkaline (pH > 9) environments (Shimizu et al., 1991).

ii. Aggressive ions (chlorides, fluorides) may attack the oxide locally.

iii. Certain elements (Ga, Ti, In, Sn, Pb) may become incorporated in the oxide and destabilize it (Nisancioglu, 1992).

Several methods have been employed to improve and enhance the metal’s life span, with the use of corrosion inhibitor being the most practical (Migahed and Nassar, 2008; Fouda and Ellithy, 2009). Corrosion inhibitors are
Compounds or chemicals that react with metal surface and corrosion medium to protect the metal against corrosion. Most inhibitors are organic compounds synthesized from cheap raw materials. These non-toxic, benign, inexpensive, renewable and readily available alternative corrosion inhibitors have been found in different parts of plant extracts (Okafor et al., 2010; Ameh et al., 2012a, b; Eddy et al., 2012a, b).

Commiphora kestingii commonly called, Fula-fufulde (fulani), Mbiji (igbo), Nupe (Esha), Yoruba (Origbo) and Hausa (árár(r)ábií) belongs to the Burseraceas family. The tree usually approaches height of 2 to 5 m and is found mostly in rocks within the low altitudes dry woodland and bush of the savanna from Togo to Nigeria, and on to Ubangi-Shari. Notably, in most developing nations, the washed bark mixed with salt is applied to snakebites, and the fruit provides remedy for stomach ailments (Meer, 1980). The tree exudes a pale yellow liquid, which soon hardens to form yellowish red or reddish brown tears or masses that are then collected when the bark is incised (Meer, 1980).

The present study is aimed at elucidating the chemical structure of C. kestingii gum and investigating the corrosion inhibition and adsorption potentials of C. kestingii gum for the corrosion of Al in 0.1 M H₂SO₄ using gravimetric, SEM and fourier transformed infra-red spectroscopy (FTIR) techniques.

Collection of sample

Crude gum of C. kestingii (CK) was obtained as dried exudates from the parent trees grown at Samaru, Zaria in Sabon Gari LGA of Kaduna State. The outer bark of the tree was broken using a small axe. The cut was extended upward and downward to a significant depth and the gum formed was collected. The rate of formation of gum was found to depend on weather conditions. Gum formation was favoured by dry and retarded by cold or wet weather. The first set of gum was collected six weeks after tapping, while other samples were collected at an interval of two to three weeks. Gum droplets collected, were 2.0 to 7.5 cm in diameter. They dried and hardened on exposure to atmosphere.

Purification of gum

The crude sample of the gum consisted of a mixture of large and small modules and other impurities. These were hand sorted to remove fragments of bark and other visible impurities and then were spread out in the sun to dry for one to two weeks. The gum was then dissolved in cold distilled water and the solution strained through muslin, and centrifuged to obtain a small quantity of dense gel. The straw coloured supernatant liquor obtained was separated and acidified to a pH of 2 with dilute hydrochloric acid. Ethyl alcohol was added until it was 80%. The gum precipitated out was removed by centrifugation at a rate of 2000 revolution per minute, washed with alcohol, ether and then dried in a desiccator.

Determination of physiochemical properties

Preliminary tests were performed to confirm the nature of the gum obtained. The test that were conducted are pH and solubility test.

Determination of pH

The pH of 2% w/v of the gum mucilage was determined using a Jenway pH meter (Model; 3505). The pH meter electrode was dipped into a buffer at a room temperature of 28°C after which it was removed, shaken a little to remove droplets of the buffer before immersion into the gum mucilage. The reading on the meter was recorded in triplicate measurements were made.

Determination of solubility in various solvents

The solubility of the gum was determined in cold and hot distilled water, acetone and chloroform. 10 mg sample of the studied gum exudate was added to 10 ml each of the solvents and left overnight. 5 ml of the clear supernatant was taken in small pre-weighed evaporating dishes and heated to dryness over a digital thermostatic water bath (Model. HHS, McDonald Scientific International). The weight of the dried residue with reference to the volume of the solutions was determined using a digital analytical balance (Model. XP-300, Denver instrument, USA) and expressed as the percentage solubility of the gum in the solvents (Carter, 2005).

MATERIALS AND METHODS

Corrosion studies

Aluminum alloy sheet of composition (wt. %, as determined by quantiometric method) Mn (1.28), Pb (0.064), Zn (0.006), Ti (0.029), Cu (0.81) and Si (0.381), Fe (0.57), and Al (96.65%) was used. The sheets were mechanically pressed cut into different coupons, each of dimension, 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation.

Gravimetric studies

The clean and dried previously weighed aluminum alloy coupon was completely immersed in 250 ml of the test solution in an open beaker. After every 24 h the corrosion product was withdrawn from the electrolyte, kept for 3 to 4 min in 70% nitric acid, washed thoroughly with distilled water and then dried and weighed. The
Table 1. Physiochemical properties of Commiphora kestingii gum.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
<tr>
<td>Taste</td>
<td>Bland</td>
</tr>
<tr>
<td>pH (28°C)</td>
<td>5.2</td>
</tr>
<tr>
<td>Percentage yield (%w/w)</td>
<td>63.5</td>
</tr>
<tr>
<td>Solubility (%w/v)</td>
<td></td>
</tr>
<tr>
<td>Cold water</td>
<td>14.00</td>
</tr>
<tr>
<td>Hot water</td>
<td>11.00</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.00</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.00</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.00</td>
</tr>
</tbody>
</table>

experiment was repeated at 333 K. In each case, the difference in weight for a period of 168 h was taken as the total weight loss. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of aluminum (CR) were calculated using 3.1 to 3.3, respectively (Ameh et al., 2012a).

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

\[
\theta = \left(1 - \frac{W_1}{W_2}\right)
\]

\[
CR = \frac{\Delta W}{A \times t}
\]

where \(W_1\) and \(W_2\) are the weight losses (g) for aluminum in the presence and absence of the inhibitor, \(\theta\) is the degree of surface coverage of the inhibitor, \(\Delta W = W_2 - W_1\), \(A\) is the area of the aluminum coupon (in cm\(^2\)), \(t\) is the period of immersion (in hours) and \(\Delta W\) is the weight loss of aluminum after time, \(t\).

Gas chromatography–mass spectrometry (GC-MS) analysis

GC-MS analysis was carried out on a GC Clarus 500 Perkin Elmer system. Interpretation on mass spectrum GC-MS was conducted using the database of National Institute Standard and Technology (NIST) Abuja, having more than 62,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library. The name, molecular weight and structure of the components of the test materials were ascertained. Concentrations of the identified compounds were determined through area and height normalization.

RESULTS AND DISCUSSION

Physiochemical parameters of CK gum

Table 1 presents physical (pH, colour, taste and percentage yield) and chemical properties (solubility in ethanol, acetone, chloroform, cold and hot water) of CK gum. The gum is odourless, pale yellow in colour (Figure 1) and has a characteristic bland taste. The gum has a pH of 5.2 indicating that it is mild acidic. It is soluble in both cold and hot water. However, its solubility tends to decrease with increase in temperature indicating that the gum is ionic. It has been found that the solubility of some ionic solutes tends to decrease due to the change of properties and structure of liquid water; the lower dielectric constant results in a less polar solvent. Also, an increase in temperature will increase the motion of dissolved particles by weakening the forces acting between the solute and solvent. This allows the dissolved gum to re-coagulate without dissolution hence the decrease in solubility (Ebbing and Gammon, 2005). CK gum is also found to be slightly soluble in ethanol and acetone. The solubility of the gum in ethanol may be due to the presence of polar and non-polar ends in ethanol,
which makes it to dissolve some polar and non-polar compounds. On the other hand, aprotic solvents such as acetone tend to have large dipole moment (separation of partial positive and partial negative charges within the same molecule) and solvate positively charged species via their negative dipole. This probably explains why CK gum is soluble in acetone to some extent.

**GC-MS study on CK gum**

Figure 2 shows the GC-MS spectrum of CK gum. In Table 2, IUPAC names as well as concentrations of compounds identified from various lines in the spectrum are presented while their chemical structures are presented in Figure 3. The gas chromatographic-mass spectrometry (GCMS) spectrum of CK displayed 14 significant peaks. Since area under the chromatogram is proportional to concentration, area normalization was carried out and percentage concentrations of the respective chemical constituents were evaluated. The results obtained shows that the most abundant component of CK gum is sucrose (37.11%), followed by Octadecanoic acid (20.44%). The least abundant constituent was found to be 0.82% alpha camphorenal. Others constituents of the gum included nerolidolisobutyrate (1.72%), diisopropenyl-1-methyl-1-vinyl cyclohexane (13.10%), abetic acid (4.10%), oleic acid (2.14%), verbenol (1%), 2,6-dimethylhepta-1,5-diene (6.11%), Naphthalene (1.40%), Limonene (2.34%), 7-hexadecenal (1.71%) and 10-methyl-8-tetradecen-1-ol acetate (6.20%). The molar mass and chemical formulas of these compounds are also presented in Table 2. Resolutions of each line in the spectrum of CK gum also revealed the occurrence of several fragmentation peaks for each fraction.

**FTIR**

Figure 4 presents the FTIR spectrum of CK gum. The spectrum displayed peaks due to C-H bend in phenyl ring (722.37 cm\(^{-1}\)), C-H stretch due to alkene at 981.8 cm\(^{-1}\), C-O stretch vibrations due to carboxylic acid, alcohol, ether or esters at 1164.08 and 1239.31 cm\(^{-1}\), C-H scissoring and bending vibrations at 1378.18 and 1465.95 cm\(^{-1}\), C=O stretch due to aldehyde, ketone, carboxylic acid or esters at 1745.64 cm\(^{-1}\), OH stretch due to carboxylic acid at 2853.78 and 2927.08 cm\(^{-1}\) and OH stretch due to alcohol or phenol at 3474.88 cm\(^{-1}\).

**Corrosion study**

**Effect of CK gum on the corrosion of Al in 0.1 M H\(_2\)SO\(_4\)**

Figures 5 and 6 show the variation of weight loss with time for the corrosion of Al in 0.1 M H\(_2\)SO\(_4\) containing
various concentrations of CK gum at 303 and 333K. The figures revealed that the rate of corrosion of Al in solutions of H$_2$SO$_4$ increases with the period of contact but decreases with increase in the concentration of CK gum, indicating that CK gum is an adsorption inhibitor for the corrosion of aluminium. It has been found that for an adsorption inhibitor, the corrosion rate decreases with increase in the concentration of the inhibitor (Emregul and Hayvali, 2006).

Calculated values of corrosion rate of Al, inhibition efficiency of CK gum and degree of surface coverage calculated from Equations 1 to 3 are presented in Table 4. The results confirmed that the corrosion rate decreases with increase in temperature, while the inhibition efficiency increases with increase in temperature indicating chemical adsorption. For chemical adsorption mechanism, inhibition efficiency increases with temperature while for physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature (Ebenso et al., 2008). The inhibition efficiency of CK gum was found to range from 65.40 to 83.20% and from 74.90 to 83.22%, indicating that CK gum is a good inhibitor compare to values obtained for other inhibitors (Ameh et al., 2012b).

Kinetic study

Most corrosion reactions have been found to be first order and are consistent with the following equation (Ameh et al., 2012a)

\[ -\log \text{(weight loss)} = k_1 t/2.303 \]

(4)

where $k_1$ is the first order rate constant which is related to the half-life ($t_{1/2}$) through Equation 5:

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

(5)

Figures 7 and 8 depict plots for the variation of $-\log$ (weight loss) versus time for the corrosion of Al in solutions of H$_2$SO$_4$ containing various concentrations of CK gum at 303 and 333K, respectively. Kinetic parameters deduced from Equations 4 and 5 are presented in Table 5. The results obtained indicated that the corrosion of Al in solutions of H$_2$SO$_4$ obeys Equations 4 and 5. The half-lives in the presence of the CK gum are higher than those for the blanks at all temperature and concentrations of CK gum indicating that CK gum has the
<table>
<thead>
<tr>
<th>Line no</th>
<th>C (%)</th>
<th>Compound</th>
<th>MF</th>
<th>MW</th>
<th>RT</th>
<th>Fragmentation peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.20</td>
<td>10-methyl-8-tetradecen-1-ol acetate</td>
<td>C_{10}H_{20}O_{2}</td>
<td>240</td>
<td>8.2</td>
<td>27(15%), 41(15%), 43(15%), 65(10%), 77(50%), 93(100%), 105(2%), 121(2%), 136(10%)</td>
</tr>
<tr>
<td>2</td>
<td>1.81</td>
<td>n-Hexadecanoic acid</td>
<td>C_{16}H_{32}O_{2}</td>
<td>256</td>
<td>10.1</td>
<td>27(15%), 41(20%), 53(10%), 67(100%), 77(35%), 93(100%), 105(10%), 121(20%), 136(10%)</td>
</tr>
<tr>
<td>3</td>
<td>1.71</td>
<td>7-hexadecenal</td>
<td>C_{16}H_{30}O</td>
<td>238</td>
<td>35.2</td>
<td>41(80%), 55(90%), 71(78%), 85(50%), 98(40%), 121(40%), 135(20%), 141(10%)</td>
</tr>
<tr>
<td>4</td>
<td>2.34</td>
<td>Limonene</td>
<td>C_{10}H_{16}O</td>
<td>136</td>
<td>9.8</td>
<td>27(40%), 39(60%), 53(45%), 68(100%), 79(40%), 93(65%), 107(20%), 121(20%), 136(25%)</td>
</tr>
<tr>
<td>5</td>
<td>1.40</td>
<td>Naphthalene</td>
<td>C_{20}H_{16}</td>
<td>272</td>
<td>10.1</td>
<td>27(10%), 41(20%), 67(10%), 81(30%), 9(35%), 105(40%), 121(20%), 136(50%), 143(20%), 157(20%), 171(10%), 185(20%), 213(30%), 241(40%), 259(50%)</td>
</tr>
<tr>
<td>6</td>
<td>6.11</td>
<td>2,6-dimethylhepta-1,5-diene</td>
<td>C_{10}H_{16}</td>
<td>136</td>
<td>10.5</td>
<td>27(20%), 41(100%), 53(20%), 69(80%), 77(25%), 93(100%), 107(8%), 121(10%), 136(5%)</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>Verbenol</td>
<td>C_{10}H_{18}O</td>
<td>152</td>
<td>11.6</td>
<td>27(35%), 41(65%), 43(40%), 59(55%), 79(60%), 94(100%), 109(90%), 119(30%), 137(20%)</td>
</tr>
<tr>
<td>8</td>
<td>0.82</td>
<td>alpha-campholenal</td>
<td>C_{10}H_{18}O</td>
<td>152</td>
<td>12.0</td>
<td>27(15%), 39(20%), 55(20%), 67(25%), 81(20%), 93(55%), 108(100%), 119(5%), 137(2%), 152(2%)</td>
</tr>
<tr>
<td>9</td>
<td>2.14</td>
<td>Oleic acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>282</td>
<td>12.8</td>
<td>25(35%), 39(60%), 43(40%), 55(50%), 78(60%), 94(100%), 108(100%), 119(30%), 135(20%)</td>
</tr>
<tr>
<td>10</td>
<td>37.11</td>
<td>Sucrose</td>
<td>C_{12}H_{22}O_{11}</td>
<td>152</td>
<td>14.3</td>
<td>25(20%), 39(40%), 43(20%), 67(20%), 78(100%), 94(50%), 108(40%), 119(30%), 134(20 %), 151(10%)</td>
</tr>
<tr>
<td>11</td>
<td>4.10</td>
<td>Abetic acid</td>
<td>C_{20}H_{30}O_{2}</td>
<td>302</td>
<td>14.8</td>
<td>25(10%), 39(32%), 55(35%), 69(20%), 81(30%), 83(55%), 108(100%), 119(20%), 134(10 %), 152(10%)</td>
</tr>
<tr>
<td>12</td>
<td>13.10</td>
<td>diisopropenyl-1-methyl-1-vinylcyclohexane</td>
<td>C_{18}H_{24}</td>
<td>204</td>
<td>31.8</td>
<td>27(32%), 41(100%), 53(60%), 68(100%), 81(100%), 93(80%), 107(40%), 121(35%), 133(15 %), 147(20%), 161(15%), 189(15%)</td>
</tr>
<tr>
<td>13</td>
<td>20.44</td>
<td>Octadecanoic acid</td>
<td>C_{18}H_{36}O_{2}</td>
<td>284</td>
<td>33.2</td>
<td>27(12%), 39(18%), 43(38%), 59(100%), 81(50%), 93(70%), 107(40%), 121(30%), 135(22 %), 147(10%), 161(40%), 189(20%), 204(10%)</td>
</tr>
<tr>
<td>14</td>
<td>1.72</td>
<td>nerolidolisobutyrate</td>
<td>C_{10}H_{18}O_{2}</td>
<td>292</td>
<td>35.3</td>
<td>41(42%), 43 (100%), 69(25%), 71(50%), 93(30%), 107(10 %), 121(40%), 127(5 %), 143(2%), 161(2%)</td>
</tr>
</tbody>
</table>
tendency of extending the half-life of Al in solution of $H_2SO_4$, hence it is a good inhibitor.

The effect of temperature on the rate of corrosion of Al in solutions of $H_2SO_4$ containing various concentrations of CK gum was investigated using the Arrhenius equation, which can be written as follows (Ebenso, 2003a, b):

$$CR = A \exp(-E_a/RT)$$

(6)

where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the gas constant and $T$ is the temperature. By taking logarithm of Equations 6 and 7 was obtained:

$$\log(CR) = \log A - \frac{E_a}{R}$$

(7)

Between the temperature range of 303 ($T_1$) and 333 K ($T_2$) and the corresponding corrosion rates of $CR_1$ and $CR_2$, Equation 7 can be simplified to Equation 8 as follows:

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

(8)

In Table 6, calculated values of activation energy are recorded. The activation energies are relatively low when compared to the threshold value (80 kJ/mol) required for the mechanism of chemical adsorption. According to Oguzie (2006), lowered value of $E_a$ in inhibited system compared to the blank as observed in the study (Table 6) is indicative of chemisorption possibly because some of the energy is used up in the chemical reaction. $E_a$ tends to decrease in the presence of an inhibitor by decreasing the available reaction area.
Figure 4. FTIR spectrum of *Commiphora kestingii* gum.

**Figure 5.** Variation of weight loss with time for the corrosion of Al in HCl containing various concentrations of *CK* gum at 303K.

It is also significant to note that $E_a$ values tend to increase with increase in the concentration of *CK* gum indicating better adsorption strength with increasing concentration.

**Thermodynamic/adsorption study**

The heat accompanying the adsorption of *CK* gum on
Figure 6. Variation of weight loss with time for the corrosion of Al in HCl containing various concentrations of CK gum at 333 K.

Table 3. Peaks and intensity of adsorption of FTIR by CK gum.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Intensity</th>
<th>Area</th>
<th>Assignments/functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>469.68</td>
<td>0.619</td>
<td>10.211</td>
<td>C-H bend due to phenyl ring substitution</td>
</tr>
<tr>
<td>722.37</td>
<td>30.649</td>
<td>39.968</td>
<td></td>
</tr>
<tr>
<td>981.8</td>
<td>44.661</td>
<td>16.031</td>
<td>C-H stretch due to alkene</td>
</tr>
<tr>
<td>1164.08</td>
<td>5.805</td>
<td>84.851</td>
<td>C-O stretch due to carboxylic acid, alcohol, ether, and esters</td>
</tr>
<tr>
<td>1239.31</td>
<td>5.805</td>
<td>16.031</td>
<td>C-O stretch due to carboxylic acid, alcohol, ether, and esters</td>
</tr>
<tr>
<td>1378.18</td>
<td>26.289</td>
<td>18.176</td>
<td>C-H scissoring and bending due to alkane</td>
</tr>
<tr>
<td>1465.95</td>
<td>13.963</td>
<td>15.642</td>
<td>C-H scissoring and bending due to alkane</td>
</tr>
<tr>
<td>1745.64</td>
<td>0.593</td>
<td>42.869</td>
<td>C=O stretch due to aldehyde, ketones, carboxylic acid and esters</td>
</tr>
<tr>
<td>2853.78</td>
<td>0.957</td>
<td>86.542</td>
<td>OH stretch due to carboxylic acid</td>
</tr>
<tr>
<td>2927.08</td>
<td>0.321</td>
<td>47.798</td>
<td>OH stretch due to carboxylic acid</td>
</tr>
<tr>
<td>3474.88</td>
<td>65.27</td>
<td>5.111</td>
<td>OH stretch due to alcohol or phenol</td>
</tr>
</tbody>
</table>

Table 4. Corrosion rates for Al, inhibition efficiency and degree of surface coverage of CK gum in 0.1M H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>C (g/L)</th>
<th>CR (g/cm$^2$/h) at 303K</th>
<th>%I (303K)</th>
<th>$\theta$ (303K)</th>
<th>CR (g/cm$^2$/h) at 333K</th>
<th>%I (333K)</th>
<th>$\theta$ (333K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>$1.09 \times 10^{-4}$</td>
<td>-</td>
<td>-</td>
<td>$1.63 \times 10^{-5}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>$3.77 \times 10^{-5}$</td>
<td>65.40</td>
<td>0.654</td>
<td>$4.10 \times 10^{-5}$</td>
<td>74.90</td>
<td>0.749</td>
</tr>
<tr>
<td>0.2</td>
<td>$303 \times 10^{-5}$</td>
<td>72.30</td>
<td>0.723</td>
<td>$3.80 \times 10^{-5}$</td>
<td>76.70</td>
<td>0.767</td>
</tr>
<tr>
<td>0.3</td>
<td>$2.61 \times 10^{-5}$</td>
<td>76.10</td>
<td>0.761</td>
<td>$3.24 \times 10^{-5}$</td>
<td>80.20</td>
<td>0.802</td>
</tr>
<tr>
<td>0.4</td>
<td>$2.08 \times 10^{-5}$</td>
<td>81.00</td>
<td>0.810</td>
<td>$3.09 \times 10^{-5}$</td>
<td>81.10</td>
<td>0.811</td>
</tr>
<tr>
<td>0.5</td>
<td>$1.84 \times 10^{-5}$</td>
<td>83.20</td>
<td>0.832</td>
<td>$2.76 \times 10^{-5}$</td>
<td>83.22</td>
<td>0.831</td>
</tr>
</tbody>
</table>
Figure 7. Variation of $-\log$(weight loss) with time for the corrosion of Al in 0.1 M HCl containing various concentrations of CK gum at 303K.

Figure 8. Variation of $-\log$(weight loss) with time for the corrosion of Al in 0.1 M HCl containing various concentrations of CK gum at 333K.

Aluminum surface was calculated using the following equation (Eddy et al., 2012b):

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

(9)

Where $Q_{ads}$ is the heat of adsorption, $R$ is the universal gas constant, $\theta_2$ and $\theta_1$ are the degree of surface coverage at the temperatures $T_1$ (303K) and $T_2$ (333K), respectively. Calculated values of $Q_{ads}$ are also recorded in Table 6. The results obtained reflect an endothermic process. Adsorption characteristics of a corrosion inhibitor can be simplified, using adsorption isotherms. In order to achieve this, the degrees of surface coverage at
Table 5. Kinetic parameters for the corrosion of Al in 0.1 M H_2SO_4 containing various concentrations of CK gum.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>C (g/L)</th>
<th>Slope</th>
<th>Intercept</th>
<th>k_1</th>
<th>R^2</th>
<th>t_{1/2} (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 K</td>
<td>Blank</td>
<td>-0.0036</td>
<td>0.986</td>
<td>0.008291</td>
<td>0.9634</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.0031</td>
<td>1.4282</td>
<td>0.007139</td>
<td>0.9764</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.0035</td>
<td>1.5612</td>
<td>0.008061</td>
<td>0.9883</td>
<td>2</td>
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<tr>
<td></td>
<td>0.3</td>
<td>-0.0037</td>
<td>1.6571</td>
<td>0.008521</td>
<td>0.996</td>
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<tr>
<td></td>
<td>0.4</td>
<td>-0.0032</td>
<td>1.6797</td>
<td>0.00737</td>
<td>0.9658</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-0.0038</td>
<td>1.8088</td>
<td>0.008751</td>
<td>0.9353</td>
<td>2</td>
</tr>
<tr>
<td>333 K</td>
<td>Blank</td>
<td>0.0028</td>
<td>0.6843</td>
<td>0.006448</td>
<td>0.9377</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.0032</td>
<td>1.3563</td>
<td>0.00737</td>
<td>0.9583</td>
<td>2</td>
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<tr>
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<td>0.2</td>
<td>0.0034</td>
<td>1.4186</td>
<td>0.00783</td>
<td>0.9455</td>
<td>2</td>
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<tr>
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<td>0.3</td>
<td>0.0032</td>
<td>1.4147</td>
<td>0.00737</td>
<td>0.8920</td>
<td>2</td>
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<tr>
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<td>0.4</td>
<td>0.0029</td>
<td>1.4427</td>
<td>0.006679</td>
<td>0.9270</td>
<td>2</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.0029</td>
<td>1.5094</td>
<td>0.006679</td>
<td>0.9700</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6. Activation energy and heat of adsorption of various concentrations of CK gum on Al surface.

<table>
<thead>
<tr>
<th>C (g/L)</th>
<th>E_a (kJ/mol)</th>
<th>Q_{ads} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>11.27</td>
<td>52.83</td>
</tr>
<tr>
<td>0.1</td>
<td>2.35</td>
<td>32.93</td>
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<td>0.2</td>
<td>6.34</td>
<td>41.85</td>
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<tr>
<td>0.3</td>
<td>6.35</td>
<td>1.34</td>
</tr>
<tr>
<td>0.4</td>
<td>11.08</td>
<td>3.46</td>
</tr>
<tr>
<td>0.5</td>
<td>11.15</td>
<td></td>
</tr>
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</table>

Various concentrations of the inhibitor were used to test for the fitness of Langmuir, Freundlich, Flory-Huggins, Elawardy et al., Temkin and Frumkin adsorption isotherms. The tests indicated that Freundlich, Temkin and Flory-Huggins adsorption isotherms are applicable to the adsorption of CK gum on aluminum surface. Expression of Flory-Huggins isotherm is given by Equation 10:

\[ \log \left( \frac{\theta}{1 - \theta} \right) = \log b + x \log (1 - \theta) \]  (10)

where x is the number of inhibitor molecules occupying one site (or the number of water molecules replaced by one molecule of the inhibitor). Other parameters are as defined earlier. From Equation 10, a plot of \( \log(\theta/C) \) versus \( \log(1-\theta) \) should produce a straight line if the adsorption of the inhibitor follows Flory-Huggins isotherm. Flory-Huggins isotherm for the adsorption of CK gum is presented in Figure 9. Adsorption parameters deduced from the plots are presented in Table 7. From the results, it can be seen that R^2 values are very close to unity confirming the application of the Flory-Huggins adsorption parameters.

Temkin adsorption isotherm operates on the assumptions that relate the concentration of the inhibitor to the degree of surface coverage according to Equation 11:

\[ \exp(-2a\theta) = bC \]  (11)

where a is molecular interaction parameter; \( \theta \) is degree of surface coverage, C is inhibitor concentration and b is equilibrium constant of the adsorption process. From the logarithm of both sides of Equation 11 and 12 is obtained

\[ \theta = -\frac{\ln K}{2a} - \frac{\ln C}{2a} \]  (12)

From Equation 12, a plot of \( \theta \) versus \( \log(C) \) should give a straight line with slope equal to 2.303 x a/2 and intercept equal to 2.303 a logK/2 provided assumptions of Temkin isotherm are valid (Emregul et al., 2003, Emregul and Hayvali, 2006). Figure 10 presents Temkin isotherm for the adsorption of CK gum on aluminum surface while Temkin adsorption parameters are recorded in Table 7. The results indicated that the interaction parameters, ‘a’ are positive indicating the attractive behaviour of the inhibitor. The parameter tend to increase with increasing...
Figure 9. Flory-Huggins isotherm for the adsorption of CK gum on aluminum surface at 303 and 333 K.

Table 7. Adsorption parameters for Flory-Huggins, Temkin and Freundlich adsorption isotherms.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>T (K)</th>
<th>Slope</th>
<th>Intercept</th>
<th>a or x</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flory-Huggins</td>
<td>303</td>
<td>0.2563</td>
<td>0.9057</td>
<td>0.26</td>
<td>-30.62</td>
<td>0.9901</td>
</tr>
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<td></td>
<td>333</td>
<td>0.1208</td>
<td>0.8631</td>
<td>0.12</td>
<td>-51.57</td>
<td>0.9459</td>
</tr>
<tr>
<td>Temkin</td>
<td>303</td>
<td>1.8266</td>
<td>1.6068</td>
<td>4.49</td>
<td>-19.44</td>
<td>0.9584</td>
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<tr>
<td></td>
<td>333</td>
<td>3.4301</td>
<td>2.8426</td>
<td>9.53</td>
<td>-26.61</td>
<td>0.9169</td>
</tr>
<tr>
<td>Freundlich</td>
<td>303</td>
<td>0.1508</td>
<td>1.965</td>
<td>6.63</td>
<td>-21.52</td>
<td>0.9946</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.065</td>
<td>1.9365</td>
<td>15.38</td>
<td>-21.35</td>
<td>0.9552</td>
</tr>
</tbody>
</table>

Figure 10. Temkin isotherm for the adsorption of CK gum on aluminum surface at 303 and 333 K.
temperature, which also indicate that the strength of adsorption increases with temperature and points toward chemisorption, which is expected to have chemical bond between the inhibitor and the metal surface.

Freundlich adsorption isotherm is an established isotherm for adsorption through physisorption. The assumptions establishing the isotherm given in Equation 13 which simplifies to 14:

\[
\frac{x}{m} = kC^{\frac{1}{n}}
\]

\[
\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C
\]

The fraction \( \frac{x}{m} \) in Equation 14 is approximately the inhibition efficiency of a given inhibitor. Therefore from Equation 14, a plot of \( \log(\text{inhibition efficiency}) \) versus \( \log C \) should give a straight line if Freundlich isotherm is obeyed. Figure 11 shows Freundlich plots for the adsorption of CK gum on Al surface. Adsorption parameters deduced from the plots are also presented in Table 7.

Adsorption of organic adsorbate on the aluminum electrode surface is regarded as substitutional adsorption process between the organic molecule in the aqueous phase (\( \text{Org}_{\text{ads}} \)) and the water molecules adsorbed on the Al surface (\( \text{H}_2\text{O}_{\text{ads}} \)):

\[
x\text{H}_2\text{O}_{\text{ads}} + \text{Org}_{\text{sol}} \xrightleftharpoons{} x\text{Org}_{\text{ads}} + \text{H}_2\text{O}_{\text{sol}}
\]

where \( x \) is the size ratio, that is, the number of water molecules replaced by one organic molecule.

From the Flory-Huggins adsorption isotherm, the value of \( x \) was computed to be 0.26 and 0.12 at 303 and 333K and the corresponding number of available adsorption site (n) computed from Freundlich adsorption isotherms were 6.63 and 15.38, respectively. These results show that the fraction of CK molecule adsorbed is temperature dependent, which point towards chemisorption, a mechanism whose extent of adsorption is expected to increase with increasing temperature.

**Scanning electron microscopy (SEM) study**

The scanning electron micrograph of the polished aluminium, uninhibited and inhibited aluminium in the presence of acid are shown in Figure 12a to c, respectively. It can be observed that there are distinct differences between the three SEM microphotographs. The SEM micrograph of aluminium surface (control) shows the smoothness of the metal surface implying the absence of any corrosion product formed on the metal surface.

The micrograph of the bared aluminum (Figure 12b) compared to the inhibited one (Figure 12c) shows that the former had suffered more severe corrosion than inhibitor protected one. The surface of the aluminum in the absence of the inhibitor was completely damaged after the exposure time while the CK–modified aluminium sheet was not so severely damaged. This means the
presence of CK gum can partially protect aluminum from corrosion.

Conclusion

This study shows that CK gum contains significant amount of Sucrose, Octadecanoic acid, Alpha camphorenal, Nerolidolisobutyrate, Diisopropenyl-1-methyl-1-vinyl cyclohexane, Abetic acid, Oleic acid, Verbenol, 2,6-dimethylhepta-1,5-diene, Naphthalene, Limonene, 7-hexadecenal and 10-methyl-8-tetradecen-1-ol acetate. Corrosion inhibition tests suggest that CK gum is a good inhibitor for the corrosion of Al in solution of H2SO4. The inhibition efficiency of this inhibitor increased with increasing temperature suggesting chemisorption mechanism. Also, the inhibition efficiency of these extract was found to increase in the presence of CK. Inhibition of aluminium by C. kestingii gum occurred through synergistic adsorption of the various components of the gums hence the formation of multiple adsorption layer is proposed.

Conflict of Interests

The author(s) have not declared any conflict of interests.

REFERENCES


Ameh PO, Eddy NO, Gimba CE (2012b). Physiochemical and rheological studies on some natural polymers and their potentials as corrosion inhibitors. Published by Lambert Academic Publishing, UK.


