Chemical and Electrochemical Investigations of Coffee Husk as Green Corrosion Inhibitor for Aluminum in Hydrochloric Acid Solutions

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ABSTRACT

The inhibition action of coffee husk extract towards the corrosion of aluminum in 0.5 M HCl solution was studied at temperatures 25 and 45°C by weight loss method, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) methods. Surface morphology was tested using energy dispersive X-ray (EDX) and scanning electron microscopy (SEM). The results showed that the inhibition efficiency increased with increasing concentration of extracts. Polarization data showed that this extract acts as mixed type inhibitor. Adsorption of extract on aluminum surface was found to obey Langmuir and Temkin isotherms. The thermodynamic parameters were calculated and discussed. The inhibition efficiencies obtained from all techniques employed are in good agreement with each other.

Keywords: Corrosion inhibition, aluminum, coffee husk extract, HCl, SEM-EDX.

1. INTRODUCTION

Hydrochloric acid solutions are widely used for acid cleaning, pickling, oil well acidizing and acid decaling [1–4]. Aluminum has a remarkable economic, light weight, high thermal and electrical conductivity. The most important feature in aluminum is its corrosion resistance due to the formation of a protective film on its surface upon its exposure to atmosphere or aqueous solutions. Prevention of corrosion of aluminum has been a subject of numerous studies due to their high technological value and wide range of industrial and house hold applications. Using organic compounds as corrosion inhibitors may be the main choice to decrease the corrosion rate of metals and their alloys in acidic media. The presence of hetero atoms in the structure of inhibitor molecules such as O, N, S, P; enhance the adsorption process and inhibition efficiency [5-9]. Despite the broad spectrum of organic compounds, the choice of appropriate inhibitor for a particular application is restricted by several factors. These include increased environmental awareness and the need to promote environmentally friendly process. Many previous studies showed that the naturally occurring substances of plant are successfully used as inhibitors for corrosion [10-12]. The natural products of plant origin are inexpensive, ecofriendly corrosion inhibitors. The extracts from their leave, barks, seeds, and roots compose of a mixture of organic compounds and some have been reported as effective inhibitors for metal corrosion [13-20].

The present work, was aimed to investigate the inhibition of aluminum corrosion in 0.5 M HCl solution in presence of different concentrations of the extract and to study the effect of temperature on the extract efficiency. Also, to study the surface morphology of Al in presence and absence of extract.

2. EXPERIMENTAL

2.1. Materials and solutions

2.1.1 Aluminum electrode

Corrosion tests have been carried out on electrodes cut from sheets of aluminum with composition more than 99.9%.
2.1.2 Hydrochloric acid
The corrosive medium (0.5 M HCl) was prepared from a stock 5 M HCl solution by dilution with bi-distilled water from the concentrated acid solution (37%, Merck). The concentration was checked by standard solution of Na₂CO₃. 0.5 M HCl solution was prepared by dilution from 5 M acid with bi-distilled water. This solution was used as a blank.

2.1.3 Coffee husk solution extract
Coffee husk extract was obtained directly from the powder of dried coffee husk, then soaked in methanol and left standing for 7 days. The solution was filtered and further bi-distilled at 40°C to remove the methanol from the coffee husk solution and then concentrated to dryness.

2.1.4 Chemical composition of coffee husk extract
Coffee husk is rich in organic matter (cellulose, hemicelluloses, pectin and lignin), and chemical nutrients such as nitrogen (N) and potassium (K). Additionally, coffee husk also contains secondary compounds such as caffeine, tannin and polyphenol [21, 22].

Table 1: chemical structure of coffee husk

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td><img src="image" alt="Cellulose structure" /></td>
</tr>
<tr>
<td>Hemicellulose</td>
<td><img src="image" alt="Hemicellulose structure" /></td>
</tr>
<tr>
<td>pectin</td>
<td><img src="image" alt="pectin structure" /></td>
</tr>
</tbody>
</table>
2.2. Weight Loss Measurements

The weight experiments were carried out using specimens of aluminum having dimensions (2x2x0.05cm). The test pieces of aluminum samples were weight up to fourth decimal place using digital electronic balance. The test samples were immersed in 50 mL of 0.5 M HCl in absence and presence of varying concentrations of coffee husk extract taken in beaker at temperatures 25 and 40°C in water thermostat. Initial weight of samples were measured before immersion and after specified period of exposed time, each piece was taken out of the test solution, rinsed with bi-distilled water, dried between two filter papers and weighed again. The difference in weight for an exposed period of 30-180 minutes was taken as the total weight loss. The experiments were carried out at various concentrations (100-500 ppm) of coffee husk extract. Triplicate samples were used to check reproducibility of results. From the average weight loss results (average of three replicate analysis), the corrosion rate, the percentage of inhibition efficiency (% IE) and the degree of surface coverage (θ) were calculated using equations[23]:

\[
\text{Corrosion rate} = \frac{\Delta W}{AT} \text{ mg/cm}^2\text{h}
\]

(1)

Where \(\Delta W\) is the weight loss in mg, \(A\) is the area of the specimen in sq-cm and \(T\) is the exposure time in min.

\[
\text{Inhibition efficiency (%IE)} = (\theta) \times 100 = \left(\frac{W_1 - W_2}{W_1}\right) \times 100
\]

(2)

where \(W_2\) and \(W_1\) are the weight losses (mg) for aluminum sample in the presence and absence of the inhibitor and \(\theta\) is the degree of surface coverage of the inhibitor. The percentage of inhibition efficiency (% IE) and the degree of surface coverage (θ) were tabulated.
2.3. Electrochemical measurements
All electrochemical measurements (potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM)) were carried out using Gamry Potentiostat/Galvanostat/ZRA (model PCI4/300) with a Gamry framework system based on ESA400. Gamry applications include software DC105 for potentiodynamic polarization, EIS300 for EIS measurements and EFM140 for EFM measurements; computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data. All electrochemical measurements carried out using a conventional cell with three electrodes were used. The aluminum sheet (1 cm²) was used as working electrode; the counter electrode was Pt foil and saturated calomel electrode (SCE) as reference electrode. The working electrode was polished and cleaned as mentioned before.

2.3.1 Potentiodynamic polarization measurements
For potentiodynamic polarization measurements, the polarization cell was filled with 100 ml of test solution. The potentiodynamic current – potential curves were recorded by changing the electrode potential automatically from -0.8 to 0.5 V at a scan rate of 1 mVs⁻¹. The degree of surface coverage (θ) and inhibition efficiency (% IE) were calculated using equation (3):

\[
\text{% IE} = \theta \times 100 = \left[1 - \left(\frac{i}{i^\circ}\right)\right] \times 100
\]  

where \(i^\circ\) and \(i\) are the current densities in the absence and presence of the extract, respectively.

2.3.2 Electrochemical impedance spectroscopy (EIS) measurements
Electrochemical impedance spectroscopy (EIS) is a powerful technique for the characterization of electrochemical systems and mechanistic information. For this reason this technique is being applied to an increasing extent to understand corrosion process in solution, to study rate determination, inhibitor performance, coating performance and passive layer characteristics [24-29]. The electrochemical impedance measurements were carried out over a frequency range of \(10^5\) Hz to 0.1 Hz with a signal amplitude perturbation of 5 mV. Experiments were always repeated at least three times. The impedance diagrams were given in Nyquist representations. In the represented electrical equivalent circuit (Figure 1), \(R_s\) is the solution resistance, \(R_{ct}\) is the charge transfer resistance and \(C_{dl}\) is the double layer capacitance.

The inhibition efficiency was calculated from the charge transfer resistance (Rct) values using the following equation (4):

\[
\text{%IE} = \left[\frac{(R_{ct} - R_{ct}^0)}{R_{ct}}\right] \times 100
\]  

Where \(R_{ct}^0\) and \(R_{ct}\) are the charge transfer resistance in the absence and presence of inhibitor, respectively.

Figure (1): Equivalent circuit proposed to fit the EIS experimental data
2.3.3 Electrochemical frequency modulation (EFM) measurements
The electrochemical frequency modulation (EFM) technique is a new tool for monitoring the electrochemical corrosion. The theory of EFM technique is previously reported [30]. The electrochemical frequency modulation has many features [31-35]. EFM is a non-destructive technique, rapid test, gives directly value of the corrosion current without a prior of knowledge of Tafel constants and has a great strength due to casually factors, which serve an internal check on the validity of the EFM measurement.

2.4 Scanning electron microscopy studies
A scanning electron microscope (SEM) model HITACHI S-3000H coupled to an analyzer EDAX –RONTEC, were used to analyze the morphology of the aluminum surface without and with inhibitor added. Images of the samples were recorded after 24h exposure time in 0.5M HCl without and with different concentration of coffee husk extract. These samples underwent the same pre-treatment as those used in the experiments of weight loss and electrochemistry.

3. Results

3.1 weight loss measurements
The weight loss of aluminum both in 0.5 M HCl in the absence and presence of various concentrations (100-500 ppm) of coffee husk extract were determined. In all cases the weight loss decreases with increasing of extract concentration. The experimental data of weight loss (Δw), percentage of inhibition efficiency (%IE), corrosion rate (C.R.) and degree of surface coverage (θ) for aluminum in 0.5 M HCl and in the presence of various concentrations of coffee husk extract at different temperatures are shown in Table.2. The values of corrosion rate were plotted against the concentration of the extract in 0.5 M HCl (Figure 2).

![Figure (2): Corrosion rates of various concentrations of inhibitor on aluminum in 0.5 M HCl at 25 and 45°C](Image)

The characterization of the corrosion of aluminum in the different corrosive solution will carried out by assessment of the inhibition efficiency (%IE) using equation 2. A bar chart of inhibition efficiency to concentration of inhibitor in 0.5 M HCl was plotted as shown in (Figure 3).
Figure (3): The variation of inhibition efficiency with inhibitor concentration of aluminum in 0.5 M HCl solutions

Table 2: data from weight loss of Al in 0.5 M HCl for various concentration of coffee husk after 1.5 h at 25 and 45°C

<table>
<thead>
<tr>
<th>Conc., ppm</th>
<th>298 K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔW mg cm⁻²</td>
<td>θ</td>
</tr>
<tr>
<td>Blank</td>
<td>0.84</td>
<td>0.558</td>
</tr>
<tr>
<td>100</td>
<td>0.43</td>
<td>0.488</td>
</tr>
<tr>
<td>200</td>
<td>0.26</td>
<td>0.690</td>
</tr>
<tr>
<td>300</td>
<td>0.25</td>
<td>0.702</td>
</tr>
<tr>
<td>400</td>
<td>0.17</td>
<td>0.798</td>
</tr>
<tr>
<td>500</td>
<td>0.14</td>
<td>0.833</td>
</tr>
</tbody>
</table>

3.2 Adsorption isotherms
To understand the mechanism of corrosion inhibition, the adsorption behavior of the extract adsorbents on the metal surface must be known. The predominant adsorption mode will be dependent on factors such as the extract composition, chemical changes to the extract and the nature of the surface charge on metal. There are a number of mathematical expressions having thus developed to take into consideration of non-ideal effects. The most used isotherms are, Frumkin, De Boer, Parsons, Temkin, Flory-Huggins and Bockris-Swinkless [36-40]. The values of surface coverage, θ, corresponding to different concentrations of extract at 25 and 45 °C have been used to explain the best isotherm to determine adsorption isotherm process. Figure 4 confirms that the inhibition processes due to adsorption of the coffee husk extract on the Al surface. This is because a straight line is obtained when log (C/θ) is plotted against log C and the linear correlation coefficient of the fitted data is close to 1. This indicates that the adsorption of coffee husk extract molecules obeys the Langmuir adsorption [41] expressed as:

\[
\frac{C}{\theta} = \frac{1}{K} + C
\]

Where C is the inhibitor concentration and K is the equilibrium constant for the adsorption /desorption process of the inhibitor molecules on the metal surface.
The extract also obeys Temkin adsorption isotherm which is present in Figure 5 equation 6. Values of adsorption parameters deduced from the plots are recorded on Table 3

\[ a \theta = \ln K C \]  
\[ (6) \]

'a' is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface.

Plot of log \( \theta/1-\theta \) against log C (Figure 6) at different concentrations of coffee husk extract, straight lines were obtained indicating that adsorption follows kinetic thermodynamic model according Equation (7) [42]:

\[ \log \theta/1-\theta = \log (K') + y \log C \]  
\[ (7) \]

The equilibrium constant of adsorption is \( K_{ads} = K'(1/y) \), where \( 1/y \) is the number of surface active sites occupied by one inhibitor molecule and C is the bulk concentration of the extract. According to the data in this table, it is seen that the values of \( 1/y \) are nearly 1 indicating that each inhibitor molecule occupies one active site.
It is well known that the equilibrium constant of adsorption (K) is related to the standard adsorption free energy ($\Delta G_{ads}^o$) and can be calculated by the following equation [43]:

$$K_{ads} = \frac{1}{55.5 \exp \left[ -\Delta G_{ads}^o / RT \right]}$$

(8)

Values of free energy of adsorption calculated from equation 8 using K values obtained from Langmuir adsorption and Temkin adsorption isotherm are presented in Table 3. The values are negative and less than -40 kJ mol$^{-1}$. This implies that the adsorption of the extract on aluminum surface is spontaneous and confirms the physical adsorption isotherm mechanism [44].

Table 3: Langmuir, Temkin and Kinetic model adsorption parameters for adsorption of coffee husk extract on aluminum in 0.5 M HCl for 90 min immersion period at different temperatures

<table>
<thead>
<tr>
<th>Temp., ºC</th>
<th>Langmuir isotherm</th>
<th>Temkin isotherm</th>
<th>Kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>R$^2$</td>
<td>$-\Delta G_{ads}^o$</td>
</tr>
<tr>
<td>25</td>
<td>9.61</td>
<td>0.99</td>
<td>15.54</td>
</tr>
<tr>
<td>45</td>
<td>7.43</td>
<td>0.98</td>
<td>15.92</td>
</tr>
</tbody>
</table>

The corrosion data fit the first- order reaction rate law according to equation (10) [45]

$$\log[W_i-\Delta W] = -kt / 2.303 + \log W_i$$

(10)

where $W_i$ is the initial weight of aluminum specimen, $\Delta W$ is the weight loss of aluminum specimen at time t, $[W_i-\Delta W]$ is the residual weight of aluminum coupon at time t and k is the first–order rate constant. The linear plots obtained with correlation coefficients close to 1 confirm first –order kinetics for the corrosion of aluminum in 0.5 M HCl solution in the presence and absence of coffee husk extract Figure (7).
Figure (7): Plot of log (Wi-ΔW) versus time for Al in 0.5 M HCl solution without and with coffee husk extract

3.3 Effect of temperature
Temperature is one of the main factors likely to modify the behavior of materials in a corrosive medium. The adsorption of organic compounds on the corroding system by physical and chemical adsorption was described by studying the effect of temperature. Chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The data revealed that the protection efficiency decreases with an increase in temperature whereas the physiosorbed molecules are attached to the metal at the cathode and essentially retard metal dissolution by stifling the cathodic reaction [46]. From our study the protection efficiency decreases with an increase in temperature. This can be due to the decrease in the strength of adsorption process at higher temperature, suggesting that physical adsorption of the inhibitor on the sample surface. The apparent activation energies (E* a) for the corrosion process in absence and presence of inhibitor can be evaluated from Arrhenius equation (11):

\[
\log \frac{(C.R.)_2}{(C.R.)_1} = \frac{E_a}{2.303R} \times \frac{1}{T_1} - \frac{1}{T_2}
\]

Whereas estimates of the heats of adsorption (Q_ads) can be obtained from the trend of surface coverage with temperature as follows [46]:

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

Table 4: Calculated values of apparent activation energy (E* a) and heat of adsorption (Q_ads) of coffee husk extract on aluminum in 0.5 M HCl at different temperatures

<table>
<thead>
<tr>
<th>Concentration, ppm</th>
<th>E* a, kJmol(^{-1})</th>
<th>Q_ads, kJmol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M HCl</td>
<td>7.03</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>9.50</td>
<td>6.09</td>
</tr>
<tr>
<td>200</td>
<td>16.65</td>
<td>15.54</td>
</tr>
<tr>
<td>300</td>
<td>14.62</td>
<td>11.09</td>
</tr>
<tr>
<td>400</td>
<td>14.16</td>
<td>9.20</td>
</tr>
<tr>
<td>500</td>
<td>13.26</td>
<td>8.70</td>
</tr>
</tbody>
</table>

3.4 Potentiodynamic polarization measurements
Polarization curves for aluminium in HCl solutions in the absence and presence of different concentrations of coffee husk extract are shown in Figure 8. These polarization curves demonstrate, as a first sight, that in presence of coffee husk extract the cathodic and anodic branches of the polarization curves are shifted towards lower currents to similar
extent, probably as a consequence of the blocking effect of the adsorbed inhibitor molecules. As it can be seen from Figure 8, the anodic and cathodic reactions are affected by the coffee husk extract. Based on this result, coffee husk extract inhibits corrosion by controlling both anodic and cathodic reactions i.e. mixed-type inhibitor. Meaning that the addition of coffee husk extract reduces the anodic dissolution of aluminium and also retards the cathodic reaction. Electrochemical parameters derived from polarization curves including corrosion potential ($E_{\text{corr}}$), corrosion current ($i_{\text{corr}}$), anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$) have been measured and by Tafel extrapolation and presented in Table 5.

![Graph](image)

**Figure (8):** Anodic and cathodic Tafel polarization curves for aluminum in the absence and presence of various concentrations of coffee husk extract.

**Table (5):** Electrochemical kinetic parameters obtained by Tafel polarization technique for aluminum in absence and presence of various concentration of coffee husk extract.

<table>
<thead>
<tr>
<th>Conc., ppm</th>
<th>$E_{\text{corr}}$, mV vs. SCE</th>
<th>$i_{\text{corr}}$, $\mu$A cm$^{-2}$</th>
<th>$\beta_a$, mV dec$^{-1}$</th>
<th>$\beta_c$, mV dec$^{-1}$</th>
<th>$\theta$</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>729</td>
<td>2600</td>
<td>174.4</td>
<td>358.0</td>
<td>0.712</td>
<td>71.2</td>
</tr>
<tr>
<td>100</td>
<td>744</td>
<td>750</td>
<td>111.7</td>
<td>236.3</td>
<td>0.712</td>
<td>71.2</td>
</tr>
<tr>
<td>200</td>
<td>748</td>
<td>565</td>
<td>112.9</td>
<td>252.6</td>
<td>0.783</td>
<td>78.3</td>
</tr>
<tr>
<td>300</td>
<td>739</td>
<td>533</td>
<td>148.8</td>
<td>312.6</td>
<td>0.795</td>
<td>79.5</td>
</tr>
<tr>
<td>400</td>
<td>748</td>
<td>449</td>
<td>175.6</td>
<td>319.9</td>
<td>0.827</td>
<td>82.7</td>
</tr>
<tr>
<td>500</td>
<td>752</td>
<td>320</td>
<td>200.7</td>
<td>334.9</td>
<td>0.877</td>
<td>87.7</td>
</tr>
</tbody>
</table>

**3.5 Electrochemical impedance spectroscopy (EIS) measurements**

The corrosion behavior of aluminum in 0.5 M HCl solution in the presence of coffee husk extract was investigated by EIS at 25°C. Figure 9 shows the results of EIS experiments in the Nyquist representation. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semi-circles, showing that the corrosion process was mainly charge transfer controlled [47]. The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole concentrations, indicating that almost no change in the corrosion mechanism occurred due to the extract addition (48). The diameter of Nyquist plots ($R_p$) increases on increasing the coffee husk extract concentration. These results suggest the inhibition behavior of coffee husk extract. The Nyquist plots are analyzed in terms of the equivalent circuit composed with classic parallel capacitor and resistor (Figure 1) [49]. The impedance of a CPE is described by the equation 14:
\[ Z_{\text{CPE}} = Y_0^{-1} (j\omega)^n \quad (14) \]

where \( Y_0 \) is the magnitude of the constant phase element (CPE), \( j \) is an imaginary number, \( \omega \) is the angular frequency at which the imaginary component of the impedance reaches its maximum values and \( n \) is the deviation parameter of the CPE: \(-1 \leq n \leq 1\).

The values of the interfacial capacitance \( C_{dl} \) can be calculated from CPE parameter values \( Y_0 \) and \( n \) using equation 15(50):

\[ C_{dl} = (2\pi f_{\text{max}} R_{ct})^{-1} \quad (15) \]

Where \( f_{\text{max}} \) is the frequency value at which the imaginary component (\( Z'' \)) of impedance is maximum. The degree of surface coverage (\( \theta \)) and the inhibition efficiency (\% IE) was calculated from the EIS data using equation 15, listed in Table (6). By increasing the inhibitor concentration, the \( R_{ct} \) values increase and the calculated \( C_{dl} \) values decrease, as it can be seen from Table (6), the \( C_{dl} \) values tend to decrease with the increase of the concentration of coffee husk in 0.5 M HCl. The decrease in the \( C_{dl} \), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that coffee husk extract molecules function by adsorption at the metal/solution interface. Deviations from the ideal semi-circle are generally attributed to the frequency dispersion as well as in homogeneities, roughness of metal surface and mass transport process [51-53]. The resistances between the metal and outer Helmholtz plane (OHP) must be equal to the \( R_{ct} \). The adsorption of inhibitor molecules on the metal surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the metal surface. This modification results in an increase of charge-transfer resistance. The \( R_{ct} \) values increased with inhibitors concentrations may suggest the formation of a protective layer on the aluminum surface. This layer makes a barrier for mass and charge-transfer. The Bode plot, Figure (10) Shows resistive region at high frequencies and capacitive region at intermediate frequencies but do not show a clear resistive region (horizontal line and a phase angle = 0) at low frequencies. These plots show two overlapped phase maxima at intermediate and low frequencies. According to act circuit theory, an impedance plot obtained for a given electrochemical system can be correlated to one or more equivalent circuits.

Table 6: EIS data of aluminum in 0.5 M HCl and in the presence of different concentration of coffee husk extract

<table>
<thead>
<tr>
<th>Conc., ppm</th>
<th>( R_{ct} \ \Omega \text{cm}^{-2} )</th>
<th>( Y^0 \times 10^6 \ \mu\Omega^{-1} \text{s}^n )</th>
<th>( n )</th>
<th>( C_{dl} \ \mu\text{F cm}^{-2} )</th>
<th>( \theta )</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>28.1</td>
<td>53.01</td>
<td>0.970</td>
<td>43.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>67.0</td>
<td>85.67</td>
<td>0.954</td>
<td>66.79</td>
<td>0.58</td>
<td>58.1</td>
</tr>
<tr>
<td>200</td>
<td>106.6</td>
<td>41.17</td>
<td>0.946</td>
<td>30.2</td>
<td>0.74</td>
<td>73.6</td>
</tr>
<tr>
<td>300</td>
<td>135.2</td>
<td>45.95</td>
<td>0.935</td>
<td>32.27</td>
<td>0.79</td>
<td>79.2</td>
</tr>
<tr>
<td>400</td>
<td>153.9</td>
<td>49.53</td>
<td>0.918</td>
<td>32.1</td>
<td>0.82</td>
<td>81.7</td>
</tr>
<tr>
<td>500</td>
<td>197.8</td>
<td>38.8</td>
<td>0.892</td>
<td>21.52</td>
<td>0.86</td>
<td>85.8</td>
</tr>
</tbody>
</table>
Figure (9): Nyquist plots for aluminum in 0.5 M HCl in absence and presence of various concentrations of coffee husk extract.

Figure (10): Bode plots for aluminum in 0.5 M HCl at different concentrations of coffee husk extract.

### 3.6 Electrochemical frequency modulation (EMF) measurements

The electrochemical frequency modulation (EMF) technique is a new tool for monitoring the electrochemical corrosion. The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. The theory of EFM technique is previously reported [54,55]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Figure 11 shows the intermodulation spectra obtained from EFM measurements of aluminum in 0.5 M HCl solution in the absence and presence of different concentrations of the coffee husk extract. The causality factor is calculated from the frequency spectrum of the current response[56-60]. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0, then it can be deduced that the measurements are influenced by noise. If the causality factors
are approximately equal to the predicted values of 2.0 and 3.0, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable [61]. The calculated corrosion kinetic parameters at different concentrations of the coffee husk extract in 0.5 M HCl at 25°C ($i_{corr}$, $\beta_a$, $\beta_c$, CF-2, CF-3 and % IE) is given in Table 7. From this Table, the corrosion current densities decrease and the inhibition efficiencies increase by increasing the concentration of coffee husk extract. Inhibition efficiency (%IE$_{EFM}$) depicted in Table 7 calculated from the following equation:

$$\text{IE\%} = \left[ \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \right] \times 100$$

Where $i_{corr}^0$ and $i_{corr}$ are corrosion current density in the absence and presence of the studied compounds, respectively.

Table 7: Electrochemical kinetic parameters obtained by EFM technique for aluminum in 0.5 M HCl in the absence and presence of different concentrations of coffee husk extract

<table>
<thead>
<tr>
<th>Conc., ppm</th>
<th>$i_{corr}$, $\mu A$ cm$^{-2}$</th>
<th>$\beta_a$, mV dec$^{-1}$</th>
<th>$\beta_c$, mV dec$^{-1}$</th>
<th>CF-2</th>
<th>CF-3</th>
<th>0</th>
<th>% IE</th>
<th>$R_{corr}$ mmy$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>984.8</td>
<td>42.4</td>
<td>75.36</td>
<td>1.58</td>
<td>2.45</td>
<td>593.2</td>
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<tr>
<td>100</td>
<td>291.3</td>
<td>91.49</td>
<td>142.2</td>
<td>1.134</td>
<td>2.054</td>
<td>0.704</td>
<td>70.4</td>
<td>175.4</td>
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<td>200</td>
<td>187.0</td>
<td>105.9</td>
<td>205.8</td>
<td>1.19</td>
<td>1.505</td>
<td>0.810</td>
<td>81.0</td>
<td>112.7</td>
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<td>300</td>
<td>142.3</td>
<td>91.76</td>
<td>142.5</td>
<td>1.279</td>
<td>3.26</td>
<td>0.856</td>
<td>85.6</td>
<td>85.72</td>
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<tr>
<td>400</td>
<td>112.7</td>
<td>105.5</td>
<td>153</td>
<td>1.258</td>
<td>2.14</td>
<td>0.886</td>
<td>88.6</td>
<td>67.89</td>
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<td>500</td>
<td>71.79</td>
<td>108.2</td>
<td>154</td>
<td>1.15</td>
<td>5.75</td>
<td>0.927</td>
<td>92.7</td>
<td>43.24</td>
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3.7 Scanning electron microscopy (SEM) studies

Figure (12) represents the micrograph obtained for aluminum samples in presence and in absence of coffee husk extract after exposure for 24h immersion. It can be seen from Fig. 12(a) that the aluminum samples before immersion seems smooth and appears some abrading scratches on the surface. It is clear that aluminum surfaces suffer from severe corrosion attack in the blank sample as shown in Fig. 12(b). Furthermore, the corrosion products appear very uneven and cube-shaped morphology. It is important to stress out that when the coffee husk extract is present in the solution Fig12(c), the morphology of aluminum surfaces is quite different from the previous one, and the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the aluminum. This may be interpreted as due to the adsorption of the coffee husk extract on the aluminum surface incorporating into the passive film in order to block the active site present on the aluminum surface. Or due to the involvement of inhibitor molecules in the interaction with the reaction sites of aluminum surface, resulting in a decrease in the contact between aluminum and the aggressive medium and sequentially exhibited excellent inhibition effect [62, 63].

Figure (11): Intermodulation spectra recorded for aluminum electrode in 0.5 M HCl solutions in the absence and presence various concentrations of coffee husk extract
Figure (12): Scanning electron microgram of polished aluminum (1500x) (a) alone (b) after exposure to 0.5 M HCl (c) after exposure to 0.5 M HCl containing 500 ppm of extract

The EDX spectra were used to determine the elements present on the surface of aluminum and after 24h of exposure in the uninhibited and inhibited 0.5 M HCl. Figure (13) shows the EDX analysis result on the composition of aluminum only without the acid and inhibitor treatment. Figure 13 shows the EDX spectrum in the absence and presence of inhibitor figure show an additional line characteristic for the existence of O. In addition, the intensities of C signal are enhanced. The appearance of O signal and this enhancement in the C signal is due to the C and O atoms constituting the inhibitor, which indicate that the inhibitor molecules have adsorbed on the metal surface. Data obtained from spectra are presented in Table 8. The spectra show also that Al peaks are considerably suppressed in the presence of inhibitor which is due to the overlying inhibitor film. These results confirm those from electrochemical measurements which suggest that a surface film inhibits the metal dissolution, and hence retard the hydrogen evolution reaction [64,65].

Table 8: Surface composition (weight %) of aluminum before and after immersion in 0.5 M HCl without and with 500 ppm of coffee husk extract at 25 °C

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>C</th>
<th>O</th>
<th>Si</th>
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<td>Pure</td>
<td>73.24</td>
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<td>90.32</td>
<td>9.23</td>
<td>--</td>
<td>0.45</td>
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<tr>
<td>inhibitor</td>
<td>71.54</td>
<td>25.73</td>
<td>2.53</td>
<td>0.19</td>
</tr>
</tbody>
</table>

a) Metal free

b) 0.5 M HCl
c) Presence of coffee husk extract

Figure (13): EDX spectra of aluminum: (a) before of immersion in 0.5 M HCl, (b) after 24 h of immersion in 0.5 M HCl and (c) after 24 h of immersion in 0.5 M HCl + 500 ppm coffee husk extract at 25°C

DISCUSSION

From Table 1 coffee husk contains many O atoms in functional groups (O-H, C=O, C-O, O-heterocyclic ring) as well as conjugated double bonds or aromatic rings which are the major characteristic for typical corrosion inhibitors [66]. As discussed above the thermodynamic and kinetic parameters, the adsorption is mainly electrostatic. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution. In acid solution, the molecules of coffee husk components could be protonated in the acid media due to the interaction between O and H+. Aluminum surface is positively charged due to the accumulation of Al-OH₂⁺ species in the acidic solution [67]. The acid anions (Cl⁻) adsorb electrostatically on the positively charged , giving rise in for a net negative charge on the metal surface ; and the organic cations are physically attracted to the anions layer which is formed on the metal surface , forming electrostatic protective layer on aluminum.

CONCLUSION

1- Coffee husk acts as good inhibitor for aluminum corrosion in 0.5 M HCl solutions.
2- The adsorption of coffee husk on aluminum surface obey Langmuir and Temkin isotherm.
3- The negative values of ΔG°_{ads} shows the spontaneity of the adsorption.
4- Corrosion current densities (i_{corr}) obtained using EFM technique was in good agreement with those obtained from Tafel extrapolation technique. In addition, the Causality factors were good internal check for verifying the validity of data obtained by this technique.
5- EIS measurement reveals that charge transfer resistance increases and the double layer capacitance decreases with increase in concentration of the extract.

REFERENCES

[29]. F. Mansfeld and M. Kendig, Corrosion (1983) 255


