Corrosion inhibition of mild steel by Camellia Sinensis extract as green inhibitor
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Abstract
Corrosion inhibition of mild steel used in water station in 35 ppm aluminum sulfate and 10 ppm chloride solution by Camellia Sinensis leaves extract was studied using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques at 30 °C. Results show that the inhibition efficiency increases with increasing temperature and concentration of the extract. Inhibitive effect was afforded by adsorption of the extract’s components which was found to accord with Langmuir adsorption isotherm. Inhibition mechanism is deduced from the temperature dependence of the inhibition efficiency and was further corroborated by the values of activation parameters obtained from the experimental data.

Keywords:
Corrosion inhibition, Mild steel, Aluminum sulfate, Chloride solution, Camellia Sinensis extract

1. Introduction
Industrial processes such as acid pickling, acid cleaning and etching often involve contact between mild steel and acidic media (in our case NaCl and Al₂(SO₄)₃), which implied that the use of inhibitors is necessary[1-3]. Most corrosion inhibitors are either synthesized from cheap raw materials or are chosen from organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds. The presence of aromatic rings and hetero atoms are the major adsorption centers for these inhibitors [4-6]. Despite the broad spectrum of organic compounds available as corrosion inhibitors, the successful utilization of most corrosion inhibitors has been hindered by their toxic nature [7]. Green corrosion inhibitors have the advantage of, biodegradable, inexpensive, non-toxic and eco-friendly. These advantages have provoked numerous and intensive searches on the use of naturally occurring substances or their extracts for the inhibition of the corrosion of metals [8-37].

It has been published that the inhibitory actions of plant extracts are due to the presence of some organic compounds such as saponins, tannin, alkaloid, steroids, glycosides and amino acids [37]. Most of these compounds have centers for π-electrons and functional groups (such as -C=C-, -OR, -OH, -COOH, -NR₂, -NH₂ and -SR), which provide electrons that facilitate the adsorption of the inhibitor on the metal surface. Also, the presence of hetero atoms such as P, O and S enhances the adsorption of the inhibitor on the metal surface. Amino acids in the plant extracts play an important role in the inhibition mechanism [38-47]. Tea leaves contain many compounds, such as polysaccharides, volatile oils, vitamins, minerals, purines, alkaloids (e.g. caffeine) and polyphenols (catechins and flavonoids).

This work reports the results obtained in the evaluation of the corrosion inhibitive effectiveness of the tea extract on the corrosion of mild steel immersed in 35 ppm aluminum sulfate and 10 ppm NaCl solution at ambient temperature.

2. Experimental procedure
2.1 Materials and Solutions
Materials used for the study were mild steel sheet (Talkha water plant) of composition (wt %) 0.13% C, 0.029% Si, 0.018% S, 0.0067% P, 0.397% Mn, 0.025% Ni, 0.0076% Cr, 0.0020% Mo, 0.0010% V, 0.036% Cu, 0.0010% Sn, 0.0057% Co, 0.126% Al, 0.023% Zn, 0.0020% Mg, 0.0046% Nb, and 0.0025% Bi, the rest Fe. They were then ground with silicon carbide abrasive papers, polished, cleaned thoroughly, rinsed in ultrasonic cleaner, dried and kept in desiccator for further weight-loss tests. The weight loss was determined at room by weighing the cleaned samples before and after hanging the sample in to 100 ml of corrosive solution in the absence and presence of various concentrations of the extract. After the time elapsed the coupons were washed with distilled water and ethanol.

For the electrochemical tests, mild steel with dimension of 1 x 1 cm, welded with Cu-wire for electrical connection and was

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mounted in epoxy resin, to expose geometrical surface areas of 1 cm². Prior to these measurements, the exposed surface was pretreated in the same manner as for weight loss experiments. All reagents (NaCl, Al₂(SO₄)₃) used for the study were Analar grade and double distilled water was used for their preparation.

2.2 Extract of Camellia Sinensis

The Camellia Sinensis extract was obtained directly from the tea bags of Lipton green tea. Stock solutions of the inhibitor extract were prepared by boiling 1.5 grams of dried tea bags in 250 ml of double distilled water for 30 min. The extract was left all night, then filtered and completed to 1000 ml with double distilled water. Both the freshly prepared extract and that aged in a refrigerator for one month gave almost the same results.

2.3 The corrosive media

Stock solutions of 100 ppm NaCl were prepared by dissolving 0.12 gram of NaCl in 1000 ml of double distilled. Stock solutions of 1000 ppm aluminum sulfate were prepared by dissolving 1 gm of aluminum sulfate in 1000 ml bidistilled water. The required concentrations were obtained by dilution.

2.4 Electrochemical measurements

The electrochemical measurements were conducted using a conventional three electrode cell, using counter electrode (Pt) and a saturated calomel electrode (SCE) as reference electrode and mild steel as working electrode. A Potentiostat/Galvanostat / ZRA (Gamry PCI 300/4) was used in all electrochemical measurements. All potential values referred to SCE. The experiments were performed in 100 ml volume cell. The potentials were scanned at a scan rate 1 mV sec⁻¹ from the corrosion potential value (Ecorr) in the negative sense and subsequently in the positive sense. Impedance measurements were carried out using AC signals of amplitude 10 mV peak to peak at the open circuit potential in the frequency range 100 kHz to 10 mHz. After immersion of specimen, prior to the test measurements, a stabilization period of 30 min was observed, which proved sufficient for open circuit potential value (Eocp) to attain a stable value.

3. Results and discussion

3.1 Weight-loss method

From the experimental data of the weight loss measurements, the protection efficiency %P, was calculated from the following equation:

\[ P\% = 100 \left[ 1 - \frac{W_2}{W_1} \right] \]  

where W₁ and W₂ are, respectively the corrosion rates in the absence and presence of the predetermined concentration of the inhibitor. All the experiments were performed at 30-50°C. Values of %P of Camellia Sinensis extract are summarized in Table (1). The %P increases with increasing inhibitor concentration. This behavior can be attributed to the increase of the surface coverage and due to the adsorption of natural compounds on the surface of the metal. The optimum concentration required to achieve an efficiency of 90 % is found to be 700 ppm. The results confirmed the very good effect of the Camellia Sinensis extract on the corrosion inhibition of mild steel in aluminum sulfate and sodium chloride solution as corrosive media. Figure (1) shows the weight loss-time curves for the corrosion of mild steel in 35 ppm aluminum sulfate and 10 ppm chloride solution in the absence and presence of Camellia Sinensis at 30°C.

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. loss mg/cm²</td>
<td>%P</td>
<td>Wt. loss mg/cm²</td>
</tr>
<tr>
<td>Blank</td>
<td>0.87</td>
<td>-----</td>
<td>1.05</td>
</tr>
<tr>
<td>100</td>
<td>0.36</td>
<td>58.6</td>
<td>0.83</td>
</tr>
<tr>
<td>200</td>
<td>0.30</td>
<td>65.5</td>
<td>0.61</td>
</tr>
<tr>
<td>300</td>
<td>0.19</td>
<td>78.2</td>
<td>0.60</td>
</tr>
<tr>
<td>400</td>
<td>0.12</td>
<td>86.2</td>
<td>0.45</td>
</tr>
<tr>
<td>600</td>
<td>0.10</td>
<td>88.4</td>
<td>0.37</td>
</tr>
<tr>
<td>700</td>
<td>0.09</td>
<td>89.7</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 1: Effect of Camellia Sinensis extract concentrations on weight loss(mg/cm²) and inhibition efficiency (%P) for mild steel in 35 ppm aluminum sulfate and 10 ppm chloride solution at different temperatures

![Figure 1](image1.png)

**Figure 1** Weight loss-time curves for the corrosion of mild steel in 35 ppm aluminum sulfate and 10 ppm chloride solution in the absence and presence of Camellia Sinensis at 30°C

3.2 Influence of temperature

In 35 ppm aluminum sulfate and 10 ppm chloride solution in the absence and presence of Camellia Sinensis at 30°C

![Figure 2](image2.png)

**Figure 2** the effect of inhibitor dose and temperature on the inhibition efficiency of Camellia Sinensis
3.2 Effect of temperature

The effect of temperature on the corrosion parameters of mild steel with the addition of *Camellia Sinensis* extract was studied using weight loss technique. A major advantage of this method is its relative simplicity and availability. The data of corrosion behavior of mild steel in 10 ppm sodium chloride and 35 ppm aluminum sulfate solution containing different concentrations of *Camellia Sinensis* extract for 21 hours in temperature range 30-50°C were presented in Table 1. Inspection of this Table reveals that the corrosion rate of steel increases with increased temperature. On the other hand, the inhibition efficiency of *Camellia Sinensis* extract decreased with increasing temperature (Fig. 2). This suggests possible desorption of some of the adsorbed inhibitor molecules from the metal surface at higher temperatures. Such behavior shows that the additives were physically adsorbed on the metal surface.

**Table 2:** Kinetic parameters for the corrosion of mild steel in steel in 35 ppm aluminum sulfate and 10 ppm chloride solution at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>K_{adv} M^{-1}</th>
<th>-ΔG_{ads}^{0} kJ mol^{-1}</th>
<th>ΔH_{ads}^{0} kJ mol^{-1}</th>
<th>ΔS_{ads}^{0} J mol^{-1} K^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.166</td>
<td>13.3</td>
<td>86.5</td>
<td>66.0</td>
</tr>
<tr>
<td>40</td>
<td>0.060</td>
<td>20.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.018</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Arrhenius-type dependence is observed between corrosion rate and temperature often expressed as:

\[
CR (k) = A \cdot e^{\left(\frac{-E_a}{RT}\right)}
\]  

where CR is the corrosion rate, \( E_a \) is the apparent activation energy, R is the universal gas constant, T is the absolute temperature, and A is the frequency factor. Fig.3 depicts Arrhenius plot (log CR (k) against the reciprocal of temperature (1/T)) for mild steel in 10 ppm sodium chloride and 35 ppm aluminum sulfate solution in the absence and presence of different extract concentrations. Straight lines of high correlation coefficients were obtained.

The values of activation energy, \( E_a \), were 16.4, 62.9 kJ mol\(^{-1}\) for the blank and in the presence of *Camellia Sinensis* extract, respectively. The increase in the activation energy is proportional to the extract concentration, indicating that the energy barrier for corrosion process is also increased [48]. An alternative formulation of Arrhenius equation is [49]:

\[
CR (k) = \frac{RT}{Nh \exp(\Delta S_{\text{ads}}/R) \exp(-\Delta H_{\text{ads}}^{0}/RT)}
\]

where h is the plank's constant, N is the Avogadro's number, T is the absolute temperature, R is the universal gas constant, Fig. 4 shows a plot of log CR/T as a function of 1/T for mild steel. Straight lines were obtained with a slope of \( -\Delta H_{\text{ads}}^{0}/R \) and an intercept of \( \ln R/Nh + \Delta S_{\text{ads}}^{0}/R \) from which the values of \( \Delta H^{0} \) and \( \Delta S^{0} \) were calculated for the blank and *Camellia Sinensis* extract.

The values of the activation enthalpy, \( \Delta H^{0} \) were 5.9 and 26.1 kJ mol\(^{-1}\) and the values of the activation entropy, \( \Delta S^{0} \) were -2, -259 J mol\(^{-1}\)K\(^{-1}\) for the blank and extract, respectively. It known that values of \( \Delta H^{0} \) lower than 41.9 kJ mol\(^{-1}\) indicative of physical adsorption [50]. Since, the absolute values of \( \Delta H^{0} \) obtained in this study was lower than 41.9 kJ mol\(^{-1}\), this indicative of physisorption.

The increase in the activation enthalpy (\( \Delta H^{0} \)) in presence of the inhibitors means that the addition of the *Camellia Sinensis* extract to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present extract. The adsorption of extract molecules on the metal surface leads to a lower number of hydrogen atoms adsorbed on it; this will cause a decrease in hydrogen evolution rate rather than the rate of metal dissolution, because of the blocking of the surface of the metal by the extract molecules.
Figure 5: Temkin adsorption isotherms for *Camellia Sinensis* extract at different temperatures for mild steel immersed in 35 ppm aluminum sulfate and 10 ppm chloride solution.

**3.3 Adsorption Isotherm**

The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface, which consists of the replacement of water molecules at the corroding interface. If it is assumed that the metals are corroding uniformly, then the corrosion rate in the absence of inhibitor is representative of the total number of corroding sites. To ascertain the nature of adsorption, the surface coverage values for *Camellia Sinensis* extract at 30-50°C were theoretically fitted into different adsorption isotherm models and correlation coefficients were used to determine the best fit which was obtained with Temkin’s and EL Awady isotherm for mild steel.

Temkin’s isotherm:

\[ a \theta = \ln K_{ads} C \]  

where \( a \) is the heterogeneity factor, \( C \) is the concentration of the extract, \( \theta \) is the degree of surface coverage, and \( K_{ads} \) is the adsorption equilibrium constant, which is related to the standard free energy of adsorption \( (\Delta G^{\circ}_{ads}) \) by the equation:

\[ K_{ads} = \frac{1}{55.5} \exp \left( \frac{\Delta G^{\circ}_{ads}}{RT} \right) \]  

where 55.5 is the concentration of water in mol/l at metal/solution interface. The plot of surface coverage \( \theta \) as a function of logarithm of *Camellia Sinensis* extract concentration is shown in Fig.5. From the plot, straight lines were obtained for *Camellia Sinensis* extract indicating that the experimental data fit well into Temkin adsorption isotherm. The Temkin isotherm characterizes the chemisorptions of uncharged molecules on a heterogeneous surface [50]. Though the calculated values of molecular interaction parameter ‘a’ and adsorption equilibrium constant obtained from Temkin’s plot indicate that all values of ‘a’ are positive in all cases (showing that there is an attraction force between the adsorbed molecules [50].

Values of \( K_{ads} \) decrease (Table 2) with increasing temperature, suggesting that the inhibitor is physically adsorbed on the mild steel surface. Generally, \( K_{ads} \) denotes the strength between adsorbate and adsorbent. The \( \Delta G^{\circ}_{ads} \) values were calculated (Table 2) from this plot were negative this means spontaneous adsorption of the extract molecules on the surface of the mild steel. The surface coverage values obtained from the weight loss measurements were also fitted into the adsorption isotherm of the thermodynamic-kinetic model of El-Awady et al. [50] which is given by:

\[ \log K + \frac{1}{y} \log C = \log \left[ \frac{\theta}{(1-\theta)} \right] \]  

where \( C \) is the concentration of the exudates, \( \theta \) is the degree of surface coverage, \( K_{ads} \) is the equilibrium constant of adsorption process, \( 1/y \) is the number of inhibitor molecules occupying one active site or the number of water molecules replaced by one molecule of *Camellia Sinensis* extract. Curve fitting of the data to the thermodynamic-kinetic model is shown in Fig.6. The calculated value of \( y = 0.9-0.52-0.64 \), respectively for 30-40-50°C; the number of active site, \( y \), is less than one. This means that, on adsorption, the inhibitor molecule displaced more than one water molecule. The heat of adsorption \( (\Delta H^{\circ}_{ads}) \) can be calculated according to the Vant Hoff’s equation:

\[ \log K_{ads} = \frac{(-\Delta H^{\circ}_{ads})}{2.303 RT} + \text{constant} \]
In order to calculate heat of adsorption ($\Delta H^º_{ads}$), Log $K_{ads}$ was plotted against $1000/T$ (Fig. 7). A straight line was obtained, its slope is equal to $\Delta H^º_{ads}/2.303R$. Since, the absolute values of $\Delta H^º_{ads}$ obtained in this study was lower than 100 kJ mol$^{-1}$, this indicative of physisorption, and this support the above mechanism of adsorption. The negative value of $\Delta H^º_{ads}$ (-86.5 kJ mol$^{-1}$) in the presence of the extract reflects the exothermic nature of mild steel dissolution process. It is clear that the activation enthalpies vary in the same manner as the activation energies, supporting the proposed inhibition mechanism. According to the basic equation:

$$\Delta G^º_{ads} = \Delta H^º_{ads} - T\Delta S^º_{ads}$$  \hspace{1cm} (7)

The entropy of adsorption, $\Delta S^º_{ads}$ was calculated (Table 2). Large and negative values of entropies imply that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactant to the activated complex. Similar observations have been reported in the literature [49].

### 3.4 Tafel polarization

The Tafel plots for mild steel in 10 ppm sodium chloride and 35 ppm aluminum sulfate solution with and without *Camellia Sinensis* extract are presented in Fig. 8. Corrosion current densities were obtained from polarization curves by linear extrapolation of anodic and cathodic branches of Tafel slopes at point 50 mV more positive and more negative than the corrosion potential values ($E_{corr}$). The protection efficiency ($%P$) was calculated from the following equation:

$$% P = 100 \left[ 1 - \frac{I_{corr}(inh)}{I_{corr}} \right]$$  \hspace{1cm} (8)

where the $I_{corr}$ is the corrosion current density in the absence of inhibitor and the $I_{corr}(inh)$ is the corrosion current density in the presence of inhibitor.

The electrochemical parameters such as: corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), anodic Tafel constant ($b_a$) and cathodic Tafel constant ($b_c$) are given in Table 3. From the Figure 8 and Table 3 we see, when the concentration of *Camellia Sinensis* extract was increased, the corrosion current density gradually decreased and the protection efficiency increased. The nearly steady values of ($E_{corr}$) indicate that *Camellia Sinensis* extract might have predominantly acted as mixed inhibitor to retard both the rates of hydrogen ion reduction and anodic dissolution of mild steel. Addition of *Camellia Sinensis* extract enhances both cathodic and anodic polarization and decreases the corresponding partial anodic and cathodic current density. These data show that *Camellia Sinensis* extract act as mixed type inhibitor. Addition of *Camellia Sinensis* extract has no significant effect on the values of anodic and cathodic Tafel slopes ($b_a$, $b_c$). Therefore, the addition of this inhibitor is simple site blocking of the electrode surface and decreasing the surface area available for corrosion reaction. Therefore the presence of various concentration of *Camellia Sinensis* extract does not alter the corrosion mechanism.

The experimental findings of Tafel curves were in good agreement with the corrosion weight loss data.

### 3.5 Mechanism of inhibition

The inhibition performance of *Camellia Sinensis* extract may be due to the presence of mixture of various compounds containing oxygen (O) and nitrogen (N) polar functions (such as tannins, Monomeric flavonols, polyphenols, etc) which all can be adsorbed on the corroded metal. The adsorption of components of *Camellia Sinensis* extract onto the surface of mild steel may take place through all these functional groups. As the corrosion resistance concentration increases, the area of metal also increases, leading to an increase in the inhibition efficiency. The inhibition process is a function of the metal, inhibitor concentration, and temperature as well as inhibitor adsorption abilities which is so much dependent on the number of adsorption sites. The mode of adsorption (physisorption and chemisorption).
observed could be attributed to the fact that Changing Sinensis extract contain many different chemical compounds which some can adsorbed chemically and others adsorbed physically. One of the main criticisms of the use of plant extracts as corrosion inhibitors is the inability to pinpoint the major active component that is responsible for the corrosion inhibition effect owing to complex chemical composition of the crude extract.

**Table 3** Corrosion parameters in the presence and absence of Changing Sinensis extract obtained from polarization measurements

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>$E_{corr}$ mV vs SCE</th>
<th>$I_{corr}$ µA cm$^{-2}$</th>
<th>$\beta_0$ V dec$^{-1}$</th>
<th>$\beta_1$ V dec$^{-1}$</th>
<th>C.R. mm$^{-1}$</th>
<th>Rp x 10$^3$ Ω cm$^2$</th>
<th>% P</th>
</tr>
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<tr>
<td>Blank</td>
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<td>6.20</td>
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<td>442</td>
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<td>1.12</td>
<td>0.33</td>
<td>8.45</td>
<td>76.5</td>
</tr>
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4. Conclusions

From the present study, it is found that Changing Sinensis extract can be used as inhibitor for mild steel in aluminum sulfate and sodium chloride solution. While the green inhibitor molecules most supposedly act by being adsorbed on mild steel surface, the overall inhibition is provided by a synergistic effect. It has been found that the inhibitive action of Changing Sinensis extract is basically controlled by temperature and the concentration of the inhibitor. A probable sequel to the present study would be to perform in-depth chemical and analytical investigations using techniques like NMR or IR spectroscopy together with electrochemical studies so as to depict which are the active components of the Changing Sinensis extract involved in the corrosion inhibition reaction, and also elucidate the corrosion inhibition mechanism.

References