Inhibition of C-steel Corrosion by Green Tea Extract in Hydrochloric Solution

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Inhibition ability of green tea extract (GTE) on the C38 steel (CS) in 1.0 M HCl was evaluated using different methods such as: weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) methods at various temperatures. Polarisation curves show that GTE acts essentially as mixed-type inhibitor controlling cathodic and anodic reactions with slight predominant in cathodic branches. EIS results indicate the increase of resistance transfer (Rt) while double layer capacitance (Cdl) decrease in the rise of green tea extract (GTE) concentrations. Obtained results also showed that the inhibition efficiency decreased with a rise in the temperature. Activation energy (Ea), enthalpy (ΔH⁺a) and entropy and (ΔS⁺a) of corrosion process were estimated using experimental measurements.

Keywords: Inhibition, Corrosion, Green Tea Extract, Steel
1. INTRODUCTION

Steel and different steel based alloys have many applications in industries and the study of their corrosion problems in aggressive mediums is an important class of research. Acid solution used extensively in industrial processes which is cause dissolution and damage of the industrial equipment [1-4]. Among the steel corrosion protection methods, the organic compounds is widely used for protecting steel and ferrous alloys against deterioration due to corrosion phenomenon [5-19]. However, the major problems related with most of these inhibitors are their expensive cost and their toxicity.

Recently, extracts and oils of natural plats have attracted some attention as green and nontoxic corrosion inhibitor [20-23] and these compounds can be obtained by using simple procedures with low cost. The use of this type of compounds can be one of the most practical method in view of the various constituents in these compounds which can rise their interactions with metal surface and consequently protect metals against deterioration. An overview of the literature shows that many natural resources such as Juniper oxycedrus extract [24], Fennel oil [25], Argan oil [26] and Artemisia [27] tested as corrosion inhibitors. The inhibitors extracted from these natural products showed important effectiveness for CS in hydrochloric acid environments. For example, Euphorbia falcata extract [28] gives inhibition efficiency higher than 93% in 1 M HCl solution and Anemone coronaria extract tested in the same solution gives up to 90.07% of inhibition at 2 g/L [29].

The positive results obtained for natural compounds have motivated our team to test the inhibitive properties of Green Tea Extract (GTE) on the behavior of CS corrosion in molar hydrochloric solution by gravimetric method and electrochemical techniques.

2. EXPERIMENTAL METHODS

2.1. Materials preparation and inhibitor

The aggressive medium (1M HCl) were prepared by diluting a reagent of analytical grade HCl 37% (from Sigma-Aldrich) with double-distilled water. The compositions of the CS used in this study are 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and balance Fe. The green tea extract GTE used as corrosion inhibitor was prepared by stirring cold weighed amounts of the Green Tea for 24 h in 1 M HCl solution and their concentration employed was 0.25 to 2.00 g/L in 1 M HCl.

2.2. Weight loss tests and electrochemical measurements

The effect of the green tea extract GTE on the C38 steel corrosion were carried out using electrochemical techniques (EIS and weight loss (WL) at 298 K), while the PDP experiments performed at 298 to 328 K. More details of experiments and used materials can be obtained in our previous works such as [30–32].

In this study, the PDP measurements were obtained in the interval of −800 mV to −200 mV/SCE with a scan rate 1 mV/s. The IE (%) for PDP measurements were calculated with the help of
the corrosion current densities in blank solution ($I_{\text{corr}}$) and with green tea extract GTE concentrations as follows:

$$EI_{\text{corr}} = \frac{I_{\text{corr}}^{\text{w}} - I_{\text{corr}}^{\text{g}}}{I_{\text{corr}}^{\text{w}}} \times 100$$  \hspace{1cm} (1)

where $I_{\text{corr}}^{\text{w}}$ and $I_{\text{corr}}^{\text{g}}$ are the without and with green tea extract GTE concentrations.

*EIS* study were performed with a small alternating voltage perturbation (10 mV) at frequencies between 100 kHz and 10 mHz at open circuit potential at 298 K. The inhibition efficiencies (%) in the case of the *EIS* measurements were calculated using charge transfer resistance values in blank solution ($R_{t}^{\text{w}}$) and with green tea extract GTE concentrations ($R_{t}^{\text{g}}$) as follows:

$$EI_{R_t} = \frac{R_{t}^{\text{w}} - R_{t}^{\text{g}}}{R_{t}^{\text{w}}} \times 100$$  \hspace{1cm} (2)

3. RESULTS AND DISCUSSION

3.1. Weight loss tests

Table 1 exhibits the parameters derived from gravimetric method such as the $IE\%$ and the corrosion rate ($\nu$), before and after immersion period (6h) using different green tea extract concentrations in 1 M HCl solution at 298 K. The Eq. 4 was used to calculate the $IE\%$ after the evaluation of the corrosion rate (Eq. 3) in blank medium ($\nu_{o}$) and with presence of green tea extract ($\nu$) during $t = 6h$ of immersion of mentioned $S$ surface of metal:

$$\nu = \frac{w}{St}$$  \hspace{1cm} (3)

$$EI_{wt} = \frac{\nu_{o} \cdot \nu}{\nu_{o}} \times 100$$  \hspace{1cm} (4)

The results obtained by weight loss measurements (Table 1), indicate that 2 g/L of GTE is the concentration which exhibit higher $IE\%$ of the corrosion of the CS. The increase of the GTE concentration beyond 2 g/L decreasing the value of the $IE\%$. The good value of the inhibition efficiency of GTE is mainly attributed to the rise of surface coverage as result of great interactions of the constituents of tested green tea extract on CS surface. The $IE\%$ become very important with the rise of the concentration of our inhibitor. This behavior indicates that more molecules of green tea extract constituents are adsorbed on electrode surface resulting stable inhibitor film [33]. In this case, Its very reported that the inhibitive action, *i.e.* the adsorption of the chemical compounds used as corrosion inhibitors is mainly due to the presence of the reactive sites such as heteroatoms, $\pi$-bonds and aromatic rings which let us concluded that these characteristics are very probably presented in our eco-friendly compound which result a protective film on the surface of the CS and consequently retards the corrosion rate from 1.26 to 0.1237 mg. cm$^{-2}$·h$^{-1}$ leading high protection of the metal.
Table 1. C38 steel weight loss data and inhibition efficiency of Green Tea Extract at 298 K.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>$\eta$ (mg. cm$^{-2}$·h$^{-1}$)</th>
<th>$EI_{wt}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.26</td>
<td>56.08</td>
</tr>
<tr>
<td>0.25</td>
<td>0.5533</td>
<td>75.23</td>
</tr>
<tr>
<td>0.50</td>
<td>0.3121</td>
<td>80.36</td>
</tr>
<tr>
<td>1.00</td>
<td>0.2474</td>
<td>90.18</td>
</tr>
<tr>
<td>2.00</td>
<td>0.1237</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Tafel polarization curves

The PDP curves obtained for CS in HCl medium containing various concentrations of green tea extract are shown in Fig. 1. From these results, it is very observed that the green tea extract decrease the reaction of anodic and cathodic process; these observation indicate that green tea extract retards metallic deterioration and also reduce the hydrogen evolution reaction [34-35].

Figure 1. The PDP curves of CS in 1M HCl containing different concentrations of GTE at 298K

The electrochemical parameters derived from PDP experiments such as corrosion potential ($E_{corr}$), cathodic Tafel slopes ($\beta_c$) and corrosion current density ($I_{corr}$) as well as calculated $IE\%$ are collected in the Table 1. It is noted that if the displacement of $E_{corr}$ is $> 85$ mV, an inhibitor can be classified as cathodic or anodic. From Table 2, mixed type inhibitor can be attributed to GTE [36-37] with predominant anodic effectiveness. As is illustrated in the same Table, we can see also that green tea extract decreases the values of the $I_{corr}$. This decrease is very observed in the maximum concentration of green tea extract. On the other hand, insignificant change observed in $\beta_c$ after the
addition of green tea extract which explain that the hydrogen evolution mechanism is unaffected. Recently, Anupama et al., [38] investigated the corrosion inhibition of the MS using Phyllanthus amarus leaf extract, noted PAE, the authors reported that the presence of this extract in 1M HCl solutions decrease steadily the $I_{\text{cor}}$ from 1.052 to 0.031 mA cm$^{-2}$ at 4 (V/V%) of PAE. The authors also verified that Phyllanthus amarus leaf extract exhibit as cathodic and anodic inhibitor supporting the mixed type behavior in tested medium. Similar results are presented in our previous study [39] using natural compound namely Chenopodium Ambrosioides, noted CAE for MS corrosion inhibition in H$_2$SO$_4$ medium.

Table 2. The $PDP$ parameters and inhibition efficiency of CS at different contents of GTE in 1M HCl.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>$I_{\text{cor}}$ (µA/cm$^2$)</th>
<th>$E_{\text{cor}}$ (mV/SCE)</th>
<th>$-\beta_c$ (mV/dec)</th>
<th>$E_{\text{Icor}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>594</td>
<td>-450</td>
<td>186</td>
<td>----</td>
</tr>
<tr>
<td>0.25</td>
<td>286</td>
<td>-510</td>
<td>135</td>
<td>51.85</td>
</tr>
<tr>
<td>0.50</td>
<td>120</td>
<td>-516</td>
<td>133</td>
<td>79.79</td>
</tr>
<tr>
<td>1.00</td>
<td>97</td>
<td>-520</td>
<td>147</td>
<td>83.67</td>
</tr>
<tr>
<td>2.00</td>
<td>64</td>
<td>-516</td>
<td>136</td>
<td>89.22</td>
</tr>
</tbody>
</table>

3.3. Electrochemical impedance spectroscopy measurements

Graphical presentations of the Nyquist plots performed in 1 M HCl and in the presence of green tea extract at 298K are presented in Fig. 2.

Figure 2. The EIS diagrams for CS with and without GTE concentrations at 298K.
If the Nyquist plot is given under a semicircle form, it can be electrically modeled using an equivalent circuit containing double layer capacitance in parallel with charge transfer resistance in addition to electrolyte resistance ($R_s$) in series.

In the Fig.2, one single capacitive loop in high frequency range observed in all diagrams, this is attributed to the charge transfer process. From the same figure, we can see that capacitive loops in this medium are not perfect semicircles. This phenomenon can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [40-41]. For this reason, it must be introduce the CPE (constant phase element) to an equivalent circuit for obtained pure double layer capacitor. For this purpose, a simple Randel’s circuit can give a more accurate fit [42]. The Nyquist representations of EIS obtained experimentally were simulated to the appropriate equivalent circuit model (Fig. 3). The EIS parameters are given in Table 3.

Table 3. The EIS parameters related to corrosion of CS in studied medium with different contents of GTE.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>$R_t$ (Ω.cm²)</th>
<th>$C_{dl}$ (µF.cm²)</th>
<th>$E_{Rt}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>18</td>
<td>92.91</td>
<td>----</td>
</tr>
<tr>
<td>0.25</td>
<td>54</td>
<td>49.00</td>
<td>66.67</td>
</tr>
<tr>
<td>0.5</td>
<td>93.41</td>
<td>19.55</td>
<td>81.00</td>
</tr>
<tr>
<td>1.0</td>
<td>118</td>
<td>5.62</td>
<td>84.74</td>
</tr>
<tr>
<td>2.0</td>
<td>147</td>
<td>3.76</td>
<td>87.75</td>
</tr>
</tbody>
</table>

The value of double layer capacitance ($C_{dl}$) are evaluated using the following relation [43, 44]:

$$C_{dl} = (Q.R_t^{-n})^{1/n}$$  \hspace{1cm} (5)

where $Q$ are the constant phase element (CPE) and $n$ are a coefficient can be used as a measure of surface inhomogeneity [45].

With the addition of green tea extract, the value of the $C_{dl}$ decrease, which is often attributed to the decrease in the local dielectric constant and/or an increase in the thickness of the double layer resulted from adsorption of the constituents of the green tea extract GTE [46, 47].

Figure 3. Equivalent electrical circuit used to fit the experimental data.

These results can be compared in view of the published findings, in this case, Jokar et al., [48] studied the inhibition mechanism of the MS corrosion in hydrochloric acid (1M), the results presented in the electrochemical impedance section showed that the addition of the morus alba pendula leaves extract, noted MAPLE, increase the charge transfer resistance from 95.6 to 832 Ω cm² at 0.4 g/L and
decreases the $C_{dl}$. The authors associated these results to the increase of extract molecules adsorption with a rise of the concentration of morus alba pendula leaves which can lead a high protection of the steel against deterioration in hydrochloric solution. Others authors [49] applied the electrochemical techniques for investing the inhibition of CS corrosion in 1M of HCl using orange peel extract, similar conclusions are reported, *i.e.*, the extract reduce the corrosion effect of the aggressive medium leading an important protection of the metal. These works further support the use of natural compounds to protect metals against dissolution.

3.4. Effect of temperature

Basic information on the adsorption process of CS can be achieved by the calculation of the activation energies from the effect of the temperature conducted at 298 to 328 K using *PDP* measurements at 2 g/L of GTE (Figs. 4. and 5.). Derived parameters of C38 steel are given in the Table 4. The results collected in the Table 4, showed that when the temperature increases, a great increase of the current density observed in uninhibited solution. While a little decrease observed with the addition of the GTE. The inhibitory action of GTE decreased when the temperature increases. This results are mainly associated to the desorption process of the GTE molecules which caused an increase in the contact of the CS with the aggressive environment.

![Figure 4. The PDP plots of CS in 1M HCl at different temperatures](image-url)
Figure 5. The PDP plots of the CS in 1M HCl with 2 g/L of GTE at different temperatures.

With the help of the Arrhenius and transition-state plots (Eq. 6-7), the activation parameters for the corrosion process were calculated [50, 51]

\[ I_{\text{cor}} = A \exp \left( -\frac{E_a}{RT} \right) \]  

(6)

where \( I_{\text{cor}} \), \( A \), \( E_a \) and \( R \), are the the corrosion current density, the Arrhenius constant, the apparent activation energy and the universal gas constant, respectively.

\[ I_{\text{cor}} = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right) \]  

(7)

where \( N \), \( h \), \( \Delta S^* \), and \( \Delta H^* \) are the Avogadro’s constant, the Planck’s constant, the change of the entropy of activation and the change of enthalpy of activation, respectively.

Table 4. The results of the temperature effect of CS steel corrosion performed in 1M HCl and with 2 g/L of GTE.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>T (K)</th>
<th>( E_{\text{cor}} ) (mV/SCE)</th>
<th>( I_{\text{cor}} ) (( \mu )A/cm(^2))</th>
<th>(-\beta_c) (mV/dec)</th>
<th>( EI_{\text{cor}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>298</td>
<td>-450</td>
<td>594</td>
<td>186</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-467</td>
<td>896</td>
<td>165</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-470</td>
<td>3428</td>
<td>137</td>
<td>---</td>
</tr>
</tbody>
</table>
The plots of $ln(I_{cor})$ vs. $10^3/T$ and $ln(I_{cor}/T)$ vs. $10^3/T$ are graphically presented in the Figs. 6 and 7 respectively.

**Figure 6.** Arrhenius plots of steel in 1M HCl with and without 2 g/L of GTE

**Figure 7.** Relation between $ln(I_{cor}/T)$ and $1000/T$ at different temperatures.

The values of the activation parameters including, $E_a$, $\Delta H_a^*$ and $\Delta S_a^*$ are calculated and collected in the Table 5. The results showed that the values of $\Delta H_a^*$ and $E_a$ are higher for the solutions
containing the inhibitor than that obtained for the aggressive solutions. The higher values of $E_a$ suggested that more energy barrier have been achieved in presence of green tea extract [52]. The positive signs of $\Delta H_a$ reflected the endothermic nature of the CS dissolution process. The increase of $\Delta S_a$ suggests that, an increase in disordering takes place on going from reactants to the activated complex due to adsorption of green tea extract on the surface of CS [53]. Comparing to others results such as published work of Belkhouda et al., [54] it can be seen that the inhibition efficiencies values of extracted compound can be increased with the rise of the temperature resulting high protection at higher temperature. The Juniper Oxycedrus Extract investigate by Belkhouda increase the $IE\%$ from 90.9 to 92.2 % at 298 to 328 K. While the effect of the temperature on the corrosion inhibition of steel performed by Bammou et al, [39] using the Chenopodium Ambrosioides (CAE) extract indicate that the $IE\%$ slightly decreased with the rise of the temperature.

**Table 5.** The activation parameters related to the corrosion inhibition of CS in 1M HCl with 2 g/L of GTE.

<table>
<thead>
<tr>
<th></th>
<th>$E_a$ (kJ.mol$^{-1}$)</th>
<th>$\Delta H_a^*$ (kJ.mol$^{-1}$)</th>
<th>$\Delta S_a^*$ (J.mol$^{-1}$K$^{-1}$)</th>
<th>$E_a-\Delta H_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>69.82</td>
<td>67.23</td>
<td>-24.91</td>
<td>2.59</td>
</tr>
<tr>
<td>2g/L</td>
<td>83.79</td>
<td>81.19</td>
<td>4.43</td>
<td>2.60</td>
</tr>
</tbody>
</table>

3.6. Adsorption isotherm

The results obtained in this investigation demonstrated the better efficiency of tested green tea extract against dissolution of CS in HCl medium. This efficiency is very probably attributed to good adsorption of green tea extract on the surface of CS. It’s reported that the most compounds used as corrosion inhibitors contain various reactive centers such as aromatic ranges and heteroatoms especially the nitrogen, oxygen and sulfur atoms. In addition, the natural resources are containing many aromatic and/or pharmaceutics compounds which further rise the adsorption of these inhibitors on studied surface. In this case, basic information about the interactions between CS and green tea extract can be obtained by performing the isotherm models. The $EIS$ measurements were used to calculate the $\theta$ values (degree of surface coverage) of green tea extract in 1M HCl. The results presented in the Fig. 8 shows the best fit which found that Langmuir adsorption isotherm (Eq. 8) is the best descriptor of the GTE-CS interactions:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$  \hspace{2cm} (8)

where $C_{inh}$ is the Concentration of GTE and $K_{ads}$ is the adsorption equilibrium constant of the adsorption process.
4. CONCLUSION

Green tea extract (GTE) can act as an eco-friendly and biodegradable for the inhibition of the CS steel corrosion in 1 M of hydrochloric environments. The PDP results indicate the mixed type nature of GTE, while the EIS data show that the Cdl decreased when the concentration of green tea extract increases. Same trend of the values of IE% of GTE are obtained by all used methods. The inhibitory action of GTE decreased when the temperature increases. The adsorption of the green tea extract on the steel surface follow the isotherm of Langmuir.

References


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