Green and Black Tea (Camellia sinensis) Extracts as Corrosion Inhibitor for Mild Steel in Acid Medium


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Abstract: The inhibitive behavior of Green (GTE) and Black Tea (BTE) extracts on mild steel in acidic environment was investigated using gravimetric and spectroscopic methods. Results showed that the inhibition efficiency of both extracts increases with increasing the concentration of extract and decreases with increasing the temperature. Maximum inhibition efficiency of 83.1 and 81.7% were obtained for GTE and BTE respectively at 0.25g/L inhibitor concentration. Adsorption behavior of both inhibitors on the mild steel surface obeyed the Langmuir adsorption isotherm and they inhibited the corrosion of mild steel by adsorption mechanism where the adsorption process involved was spontaneous, exothermic and physisorptive. The FTIR spectra also indicated the formation of active compound-Fe complex. GTE and BTE from Camellia sinensis thus represent potential and inexpensive environment friendly corrosion inhibitors for mild steel in acid environment.

Key words: Corrosion • Adsorption • Mild steel • Green tea • Black tea

INTRODUCTION

Corrosion remains a major destructive process that affects the performance of metals in their different areas of applications. Mild steel for example finds wide use as a constructional material in many industries because of its excellent mechanical properties, ductility, weldability and low cost. However, it gets corroded when exposed to the corrosive industrial environment. [1] The adverse consequences of corrosion are considered a serious problem in industry, constructions and civil services such as electricity, water and sewage systems. To abate or reduce internal corrosion in these systems, inhibitors are generally employed, as this remains one of the best options of protecting metals against corrosion [2].

Several techniques used in corrosion control include lubrication, painting, cathodic and anodic protection and electro-painting, material selection, etc.

Corrosion Inhibitors (CI) are either organic or inorganic chemicals, or more commonly, formulations there of that are added in small amounts (parts per million, ppm) to a corrosive environment in order to delay or decrease the corrosion process of the surface to be protected.

A large number of synthetic compounds including heterocyclic compounds are known to be applicable as good corrosion inhibitors (CI) for mild steel [3, 4]. However, most of them are found to be toxic and expensive, hence, their popularity and use as corrosion inhibitors is being diminished as they have adverse effects on living beings and environment [5]. Therefore, there exists a need to develop a new class of corrosion inhibitors with low toxicity, eco-friendly and with good inhibition efficiency.

The use of green inhibitors has generated a lot of attention in recent times. This is due to their biodegradability, ecofriendliness, low cost and easy availability. For example, the extracts of some common plants based chemicals and their by-products have been tried as inhibitors for metals under different environments [6, 7, 8, 9, 10]. Several works have been reported using plants such as Vernonia amydalina (bitter leaf) extracts [11], Nypa fruticans Wurmb leaf extracts [12], Zanthoxylum alatum plant [13] and Telfaria occidentalis extract [14], Emilia sonchifolia [15], Launaea nudicaulis [16] and Sida acuta [17] for the acid corrosion of mild steel.

Studies show that plant products containing tannins, alkaloids, saponins, essential oils, flavonoids, organic and amino acids are known to exhibit corrosion inhibiting action [18, 19, 20, 21, 22]. One of the possible mechanisms employed by the plant molecules is to adhere to the metal
surface thereby retarding the aggressive liquid from coming in contact with the metal surface. Given the growing trend, tea (Camellia sinensis) is one of such plant that has not been fully harnessed in this respect, which this study seeks to address. Tea is an extract of the leaf of the plant Camellia sinensis. The leaf contains several polyphenols, such as epigallocatechin gallate and an enzyme, polyphenol oxidase. Upon harvest, the leaves are heated, these enzymes are deactivated and thus, following drying, the result is green tea. C. sinensis can also be processed to black tea. Processing green and black tea follow almost the same steps of withering, rolling, oxidation and firing, however, in the case of green tea rolling the leaves to break the membranes for oxidation is skipped, hence the oxidation process is also skipped. Tea has both therapeutic and prophylactic benefits to humans. This includes its anti oxidants properties which help to improve body resistant to bacterial infection, reduces the incidence of diabetics, inhibits growth of cancer cells, increases body’s immunity against viral infection. It is a cardio-protective agent; it is an anti-inflammatory and antifibriotic agent [23]. Tea is an important source of caffeine which has mild stimulating effect on the central nervous system. It increases mental alertness and improves heartbeat and breathing rate thus helps to reduce the incidence of hypotension [24]. The health-promoting effects of green tea are mainly attributed to its polyphenol content. Green tea is a rich source of polyphenols, especially flavanols and flavonols, which represent approximately 30% dry weight of the fresh leaf [25]. Catechins (Fig. 1) are the predominant flavanols and are mainly comprised of epigallocatechin gallate (EGCG), epigallocatechin (EGC), epicatechin gallate (ECG) and epicatechin (EC).

In the present study, we reports corrosion inhibitive properties of green tea and black tea extract on mild steel in acidic medium using weight loss method and spectrophotometric analysis.

**MATERIALS AND METHODS**

**Material Preparation:** The mild steel sheets used for this study were sourced locally. The mild steel sheet used was 0.04cm in thickness and mechanically pressed cut into coupons of dimension 1cm x 1cm. For surface treatment, they were degreased using absolute ethanol, dried in acetone and stored in moisture free desiccators until ready for use. The Mild steel specimens were abraded with a series of emery paper (grade 600 and 800), washed with distilled water, degreased with acetone and dried with a cold air stream then used for weight loss measurement.

**Preparation of Plant Extract:** Camellia sinensis was obtained from the Mambilla station of the Cocoa Research Institute of Nigeria. This was processed into Green (GT) and Black tea (BT). Air-dried plant materials of Green and Black tea were first defatted with n-hexane three times at room temperature for 72 h each. The defatted plant materials were then extracted three times with methanol at room temperature for 72 h each. The combined methanol extracts were then concentrated under vacuum at 40 °C until methanol was completely removed. The dried methanolic extract was then used to prepare test solutions of different required concentration in 1.0 M aqueous hydrochloric acid solution.

**Weight Loss Measurements:** Experiments were conducted under total immersion in stagnant aerated condition using 250 mL capacity beakers containing 200 mL test solution at 303, 313 and 323 K maintained in a regulated water bath. The mild steel coupons were weighed and suspended in the beaker with the aid of rod and hook. The coupons were removed at interval, cleaned, dried and reweighed. The weight loss, (in grams), was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions including the blank. The tests were performed in triplicate and the mean value of the weight loss was reported. Inhibition concentrations of 0.05, 0.15, 0.20, 0.25, 0.30 and 0.35g/L were used. From the weight loss values, corrosion rates, degree of surface coverage and inhibition efficiency were calculated accordingly using the following expressions:

\[ IE(\%) = \frac{W_o - W}{W_o} \times 100 \]  
\[ ? = \frac{IE}{100} \]
Where, \( W_0 \) and \( W \) are the weight loss of the mild steel specimens in absence and in presence of inhibitors, respectively while \( \theta \) is the surface coverage.

The corrosion rate (CR) of mild steel was calculated using the equation:

\[
C_R (\text{mm/yr}) = \frac{87.6W}{AtD}
\]

(3)

Where \( W \) is the corrosion weight loss of mild steel (mg), \( A \) the area of the specimen, \( t \) the exposure time (h) and \( D \) is the density of mild steel (g/cm\(^3\)).

**Surface Analysis:** The film formed on the metal surface after 72 h immersion of the steel in a solution containing 0.25 g/L of GT and BT extracts and without inhibitors was carefully removed, mixed thoroughly with potassium bromide (KBr) and made as pellets. The FTIR spectra (KBr pellet) of the film formed on the mild steel samples were recorded with a Perkin–Elmer FTIR spectrophotometer (100 series). FTIR analysis was also performed for the GT and BT extracts.

**RESULTS AND DISCUSSIONS**

**Weight Loss, Corrosion Rate and Inhibition Efficiency:**

The effect of varying concentration of two extracts of *Camellia sinensis*, Green Tea Extract (GTE) and Black Tea Extract (BTE) on mild steel in 1.0 M HCl was examined using the weight loss measurement. The data obtained for the percentage inhibition efficiency, corrosion rate and surface coverage are presented in Table 1, while the effect of inhibition efficiency with different concentrations of the two extracts (GTE and BTE) are shown in Fig. 2.

It is evident that GTE and BTE exhibited effective inhibitory characteristics on mild steel in 1.0 M HCl environment. Inhibition efficiency is directly related to the extracts concentrations as it increases with increasing GTE and BTE concentrations. Also, the corrosion rate of the blank (Table 1) is higher than for the extracts; this confirms the inhibitory characteristics of the extracts.

From Fig. 1, maximum inhibition efficiencies of 83.1 and 81.7% for GTE and BTE were attained at 0.25 g/L and beyond this concentration, no marked increase in inhibition efficiency was noticed. This trend may be attributed to the leaching of GTE and BTE molecules into the inhibitive solution when the concentration of extracts reaches beyond critical, thus resulting to reduced metal – inhibitor interaction [26, 27]. The resultant effect is the observed decreased inhibition efficiency. At 0.25 g/L for both GTE and BTE, minimum corrosion rate of 1.2 and 1.28 mm year\(^{-1}\) respectively were obtained.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>Weight loss (g)</th>
<th>Surface coverage (%)</th>
<th>Corrosion rate mm yr(^{-1})</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (Blank)</td>
<td>1.18</td>
<td>-</td>
<td>2.31</td>
<td>-</td>
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<tr>
<td>0.05</td>
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<td>0.751</td>
<td>1.71</td>
<td>75.1</td>
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<td>0.1</td>
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<td>76.3</td>
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<td>0.777</td>
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<td>77.7</td>
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<td>0.2</td>
<td>0.67</td>
<td>0.813</td>
<td>1.32</td>
<td>81.3</td>
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<td>0.831</td>
<td>1.2</td>
<td>83.1</td>
</tr>
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<td>0.3</td>
<td>0.62</td>
<td>0.827</td>
<td>1.22</td>
<td>82.7</td>
</tr>
<tr>
<td>0.35</td>
<td>0.62</td>
<td>0.827</td>
<td>1.22</td>
<td>82.7</td>
</tr>
<tr>
<td>BTE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>0.674</td>
<td>1.79</td>
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</tr>
<tr>
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<td>0.806</td>
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<tr>
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<td>0.67</td>
<td>0.805</td>
<td>1.32</td>
<td>80.5</td>
</tr>
</tbody>
</table>

**Fig. 2:** Changes in Inhibition efficiency with varying concentration of GTE and BTE.

Corrosion rate increases with temperature as evident in Table 2. Corrosion is an oxidation process and this implies that increase in temperature will increase oxidation rate which in this case is the rate of corrosion.

Coating layer on the surface of material often protect the surface of the steel so as to reduce the corrosion rate. It can be observed that the efficiency of inhibition decreases with increasing temperature. This is due to the increased rate of oxidation of iron in the steel surface with...
increasing temperature, so the adsorbate from the GTE and BTE desorbed easily from the surface of the mild steel [28, 29]. The equilibrium that exists between adsorption and desorption of inhibitor molecules occurring at the metal surface at specific temperature may also be responsible for this trend. With increase in temperature, this equilibrium tend towards desorption until it is reestablished. The implication is that lower inhibition efficiencies were obtained at higher temperatures. Such behavior shows that the additives were physically adsorbed on the metal surface, hence indicating a physisorption nature of inhibition mechanism [16].

Adsorption Isotherm: An inhibitor can be considered as an effective corrosion inhibitor in aqueous solution only when the interaction force between metals and inhibitor is greater than the interaction force of metal and water molecules [30]. There are several types of adsorption isotherms that can be used as a reference point in studying the adsorption mechanism of corrosion inhibitors, including the Langmuir, Frumkin and Temkin adsorption isotherm. To ascertain the nature of adsorption, the surface coverage values for GTE and BTE were theoretically fitted into different adsorption isotherm models and correlation coefficients were used to determine best fit which was obtained with these isotherms for mild steel [31, 32]. Table 3 shows the Thermodynamic parameters for the adsorption of GTE and BTE on the mild steel calculated from Langmuir isotherms using surface coverage calculated from the results of weight loss method.

Free energy value of adsorption provides vital information about the nature of adsorption of inhibitor onto the surface of mild steel and this can be calculated by using the equation below:

\[
\Delta G_{ads} = -RT\ln (K \times 55.5)
\]

K is the adsorption–desorption equilibrium constant, C is the concentration of inhibitor and g is the adsorbate parameter.

Using the degree of surface coverage values (θ) for different concentrations of inhibitors (GTE and BTE) at 298 1 K were used, attempts were made to fit the above named isotherms.

The best fit was obtained with Langmuir isotherm which gave straight line with the slope of the unit, where the regression coefficient r² values for this isotherm were 0.9995 and 0.9997 for GTE and BTE, respectively. The implication of this is that Langmuir isotherm shows the best correlation with the experimental data and also explains the monolayer formation of the inhibitor on the surface of mild steel [31, 32]. Table 3 shows the Thermodynamic parameters for the adsorption of GTE and BTE on the mild steel calculated from Langmuir isotherms using surface coverage calculated from the results of weight loss method.

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\]
It is a generally accepted fact that when the values of $\Delta G_{\text{ads}}$ are around -20 kJ mol$^{-1}$ or lower, it is a physisorption type of adsorption and the inhibition acts through the electrostatic interaction between the charged molecules and the charged metal. When the adsorption value is around -40 kJ mol$^{-1}$ or higher, such interactions are chemisorptions in nature wherein the charge sharing or a charge transfer from the inhibitor molecules to the metal surface occurs to form covalent bond. In Table 3, the negative values for GTE and BTE indicates that both inhibitors spontaneously adsorbed on the mild steel surface. Results from the present study shows that the free energy of adsorption value for GTE and BTE were below -20 kJ mol$^{-1}$ thus showing a physisorption nature of interaction. The implication is that both inhibitors are physically adsorbed on the surface of mild steel.

The other thermodynamic parameters such as enthalpy and entropy of adsorption were also calculated using the equation below:

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}}$$

Where $\Delta H_{\text{ads}}$ and $\Delta S_{\text{ads}}$ are the enthalpy and entropy of adsorption respectively. As shown in Table 3, negative values were obtained for $\Delta H_{\text{ads}}$ for GTE and BTE indicating an exothermic type of reaction and the positive $\Delta S$ shows the spontaneity of the reaction.

**Mechanism of Inhibition:** Green and Black tea were selected as inhibitors because reports have it that they contain high concentrations of polyphenols and are environmentally-friendly as they contain less of damaging contaminating effects of other organic inhibitors. Monomeric flavanols, the major components in green and black tea, are precursors of condensed tannins. These contain mixture of various compounds containing oxygen (O) and nitrogen (N) polar functional groups. These polyphenols are also posse’s high complexion affinity to metals, alkaloids and other biological molecules such as lipids, carbohydrates, proteins and nucleic acids.
The high complexation affinity to metals in particular, in this case inhibitor-Fe$^{3+}$ complex could be responsible for the effective mild steel corrosion inhibition behavior. The inhibition process was a function of the metal, inhibitor concentration and temperature as well as inhibitor adsorption abilities which is a function of the number of adsorption sites.

**CONCLUSIONS**

The corrosion inhibition efficiency of GTE and BTE on mild steel immersed in 1.0 N HCl increases with increasing the concentration until a maximum was attained at 0.25g/L. The FTIR studies on the film showed peak maximums in the regions of hydroxyl and carbonyl functional groups. Formation of the active compound-Fe$^{3+}$ complex was confirmed from the shifts in peaks. GTE and BTE from *Camellia sinensis* can serve as promising eco-friendly corrosion inhibitors.

**REFERENCES**


