Performance of *Terminalia Catappa* Leaves Extract as Bio-Corrosion Inhibitor for Mild Steel in H$_2$SO$_4$ Solution

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Abstract. *Terminalia catappa* leaves extract has a high content of polyphenol compounds. Polyphenol compounds inhibit the corrosion rate for mild steel. This study aimed to assess the ability of *terminalia catappa* leaves extract to inhibit bio-corrosion on the surface of mild steel placed in a corrosive medium of 1M sulphuric acid, and to compare this with that of tannin and sodium phosphate. The method used was the loss of weight at temperatures of 313K, 333K and 353K. It found that the inhibition efficiency was susceptible to increased temperature. The efficiency of bio-corrosion inhibition of sodium phosphate > tannin > *Terminalia catappa* leaves extract; that is, the ability of *Terminalia catappa* leaves extract to inhibit bio-corrosion was relatively lower than that of tannin and sodium phosphate. *Terminalia catappa* leaves extract’s inhibiting corrosion rate of mild steel was very good at 333K and 1250 ppm concentration, with an efficiency inhibition of 64%. The adsorption mechanism is a Langmuir isotherm, and the process is endothermic and spontaneous.

1. Introduction

An inhibitor is defined as a substance that can decrease the rate of corrosion when added to an environment in small concentrations [1]. The addition of inhibitors is common in liquid-containing systems, such as boilers, condensers, heat exchanger, pipelines, and industrial petroleum and other chemical processing industries [2]. The use of chemical inhibitors such as sodium phosphate is considered to have sufficient ability to lower corrosion rates, but its use has an impact on the environment. So, it is necessary to obtain data on inhibitors that would be safe in the environment, and which are abundantly available and renewable. These are known as bio-inhibitors. Bio-inhibitors derived from natural materials ideally would not contain harmful metals, so that they can be used in the food, beverage and pharmaceutical industries. They generally come from natural material extracts that contain several organic compounds, and elements including nitrogen, oxygen, phosphorus and sulphur. These atoms are coordinated, and react with metal ions to form layers on the metal’s surface to prevent corrosion [3].

Several studies on the ability of plant extracts to inhibit corrosion rates have been published, including those on *Sida acuta* [4], *Jasminum nudiflorum* [5] and *Rothmania longiflora* [6]. *Terminalia catappa* a tropical plant, widely found in Indonesia, and belonging to the **Combretaceae** family.

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Terminalia is catappa leaves extract (TLE) contains polyphenol compounds that can inhibit corrosion. Tannin is a widespread polyphenolic compound found in plants, and TLE contains high concentrations of tannins [7], along with saponin, phlobatin, antraquinone, flavonoids, terpene and alkaloids. Tannin is a compound that can form complex compounds with iron ions. Tannins can be used in the environment because the molecules tend to be stable at low pH [8]. The chemical properties of TLE provide it with an excellent potential for development as a corrosion inhibitor, along with its proven ability to survive for 168 days, with an inhibition efficiency of up to 87% at 298K in 1M sulphuric acid solution [9]. Its abilities at higher temperatures have not been tested, however; this is necessary so that its use can be extended.

In this study, a TLE corrosion test was performed at various temperatures (313K, 333K, 353K). As an indicator of TLE capability, corrosion tests were also performed using sodium phosphate, representing a chemical inhibitor, and tannin, representing effective compound in TLE. The results of this study provide information on the thermodynamic and kinetic properties of TLE and, whether its ability can be improved so that it can find wider application.

2. Experimental

2.1. Materials
The mild steel used had a composition (wt%) of 0.54Mn, 0.05Si, 0.01S, 0.01P, 0.16C and the remaining Fe was used. The sample size was 3 x 2 x 0.5 cm. The sample was cleaned using grit 250–1000 abrasion paper, then washed with distilled water and cleaned again with acetone and ethanol.

2.2. Preparation of the Corrosion Inhibitor
The T.catappa leaves used were collected at the Universitas Indonesia Campus. The samples were cleaned, and then dried using sunlight for one week. Following this, a blender was used to reduce the leaves to powder. TLE was obtained through a maceration process for four days, using ethanol as a solvent at a ratio of 1:4 [10]. The TLE solution was then filtered, and separated using a rotary evaporator.

2.3. The Corrosive Medium
The corrosive medium used was 1M sulphuric acid, with the concentration of the inhibitor being 0, 250, 500, 750, 1000 and 1250 ppm. The temperatures used were 313K, 333K and 353K, and the immersion time was 6 h.

2.4. Weight Loss Method and Analysis
Weight loss refers to the difference in mass of a sample before and after being immersed in a corrosive medium. This was measured for various concentrations, temperatures and times. From the data obtained, a corrosion rate was calculated, based on the weight loss, using the formula (ASTM G31):

$$CR (mmpy) = \frac{(87500 \times \Delta W)}{A \rho t}$$

where CR is corrosion rate, \(\Delta W\) is weight loss (g), A is the surface area in cm\(^2\), \(\rho\) is the density of mild steel (g/cm\(^3\)), and t is immersion time (hr).

The efficiency of inhibition was calculated using the formula:

$$I. E \% = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right) \times 100$$

where \(CR_{inh}\) and \(CR_{blank}\) are corrosion rates in the presence and absence of inhibitor, respectively.

Finally, surface coverage was calculated using the equation:

$$\theta = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right)$$
2. Results and Discussion

2.1. Effect of temperature on the corrosion inhibition efficiency of TLE, sodium phosphate and tannin

Table 1 shows the reaction rates derived from the weight loss calculations for the corrosion inhibitors at different concentrations and temperatures. From the data in Table 1, it can be seen that, for all types of inhibitors (sodium phosphate, tannin and TLE), a temperature increase causes an increase in corrosion rate. The higher the temperature, the more reaction occurs. This relates to the theory of collision, whereby, as the temperature rises, the collision between reactants will be faster. Also, in an acidic medium – in this case, sulphuric acid – the corrosion that occurs on the metal (mild steel) will be accompanied by the evolution of hydrogen gas. Higher temperatures cause a faster corrosion reaction, and the solubility of the metal increases as more and more hydrogen gas is produced [13].

Table 1. Corrosion rates for various concentration at different temperature

| T K   | Bio Inhibitor | Concentration ppm |
|-------|---------------|-------------------|
|       | Na_3PO_4      | 575 100 91 77 71 60 |
| 313   | Tannin        | 575 238 227 209 189 175 |
|       | TLE           | 575 245 233 237 238 226 |
| 333   | Na_3PO_4      | 706 228 215 187 184 175 |
|       | Tannin        | 706 338 297 282 275 254 |
|       | TLE           | 706 337 320 315 308 324 |
| 353   | Na_3PO_4      | 813 328 333 317 290 288 |
|       | Tannin        | 813 492 484 459 449 420 |
|       | TLE           | 813 582 560 508 554 456 |

Table 1 shows that the TLE corrosion rate is higher than that of sodium phosphate and tannin (sodium phosphate < tannin < TLE); that is, its ability to inhibit corrosion is less than that of sodium phosphate and tannin. Table 1 also shows the effect of temperature on the corrosion rate of all three inhibitors. At the same temperature, with the highest inhibitor concentration, the rate of corrosion decreases. Table 1 shows that the higher the concentration of the inhibitor, the greater is its ability to inhibit the corrosion rate of mild steel. To obtain the value of the activation energy, Arrhenius’ equation is used[6, 14]:

\[
\log CR = \log A - \left( \frac{E_a}{2.303 RT} \right)
\]

where \( CR \) is the mild steel corrosion rate, \( A \) is the Arrhenius pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the gas constant and \( T \) is the temperature. Table 2 shows the activation energy values for TLE, tannin and sodium phosphate, which are TLE < tannin < sodium phosphate. The activation energy is the minimum energy required for a reaction to proceed. The higher the value, the higher the energy needed to react. When connected to the corrosion rate, the higher the activation energy, the lesser the corrosion rate, and vice versa. Surface coverage is assumed to be an inhibitor molecule that covers a protected steel surface. The Langmuir adsorption kinetics model is used to provide a characteristic description of the adsorption of a metal-ion monolayer on the surface of the adsorbent. The Langmuir isotherm illustrates that, on the surface of the adsorbent, there are a certain number of active sites that are proportional to the surface area, each active site being only one molecule that can be adsorbed.

The efficiency of inhibition indicates the ability of an inhibitor to inhibit the corrosion rate. The higher the efficiency value of inhibition, the better the inhibitory ability. The results on Figure 4 show that the
efficiency of inhibition is ranked sodium phosphate > tannin > TLE. The temperature rise also caused the inhibition efficiency to decrease, since the inhibitory efficiency is related to the corrosion rate. When associated with time, the corrosion rate decreased the longer the mild steel was immersed in the 1M sulphuric acid solution. Although all of the inhibitors saw this decrease, the sodium phosphate inhibitor decrease was lower than that of tannin and TLE.

| Table 2. Activation energy for various concentration | TLE | Tannin | Sodium Phosphate |
|---------------------------------|----------------|----------------|------------------|
| Concentration (ppm) | Ea kJ/mol | Ea kJ/mol | Ea kJ/mol |
| 0 | 7.97 | 7.97 | 7.97 |
| 250 | 21.72 | 20.05 | 27.33 |
| 500 | 21.91 | 19.62 | 29.89 |
| 750 | 22.86 | 24.05 | 32.40 |
| 1000 | 23.37 | 22.67 | 32.46 |
| 1250 | 23.25 | 23.10 | 36.29 |

2.2. Kinetics of Reaction
The natural interaction between a molecular inhibitor and a metal surface is approached through isotherm adsorption. The preferred adsorption method is Langmuir isotherm adsorption. The equivalent isotherm equation is[15]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$ (5)

where $C$ is the concentration of the inhibitor, $\theta$ is the surface coverage and $K_{ads}$ is the adsorption equilibrium constant. Its adsorption properties can explain the mechanism of corrosion protection. Isotherm adsorption is important for explaining the mechanism of the organo-electrochemical reaction. From this, there are known interactions among metal inhibitors, molecular inhibitors and a metal surface. The presence of metal interfaces/solutions is due to the formation of an electrolyte, or covalent bonds between the adsorbate and the atoms on the metal surface [16]. From Table 3, it can be seen that TLE shows that the adsorption of Langmuir isotherm is suitable for use at 313K and 333K.

| Table 3. Langmuir isotherm parameters for the adsorption of Terminalia catappa leaves extract on the surface of mild steel |
|---------------------------------|--------|--------|--------|
| Temperature K | Kads | R² |
| 313 | 15.48 | 0.99 |
| 333 | 74.43 | 0.99 |
| 353 | 0.99 | 0.85 |

In Table 3 the $R^2$ value for 313K and 333K can be seen to be 0.99, while at 353K, $R^2<0.9$. At 313K and 333K, the $K_{ads}$ value increased, while at 333K and 353K, the $K_{ads}$ value decreased. Based on the tendency of the $K_{ads}$ value to rise and fall when associated with temperature, $K_{ads}$ values obtained using Langmuir isotherms, where by the values decreased with increasing temperature, indicated that the adsorption of TLE on mild steel surfaces was excellent when used at low temperatures[17]. Similarly, if the $K_{ads}$ value increases with rising temperature, then high temperatures can be used instead.

2.3. Thermodynamic Activity Parameters $\Delta G$, $\Delta H$ and $\Delta S$
The thermodynamic activity parameters used are $\Delta G$, $\Delta H$ and $\Delta S$, and the equations are as follows[18]:
\[
\Delta G_{ads}^\theta = -2.303 \cdot RT \log(55.5 \cdot K_{ads})
\]  
(6)

\[
K_{ads} = \frac{\theta}{(1-\theta)} [C]
\]  
(7)

\[
\Delta S = \frac{\Delta H_{ads}}{T} \frac{\Delta G_{ads}}{\Delta S}
\]  
(8)

By making a linear graph between \(\log (CR/T)\) and \((1/T)\), then \(\Delta H_{ads}\) is derived from the slope \((-\Delta H_{ads}/2.303 R)\). The thermodynamic parameter shows the ability of the adsorption of the inhibitor on a mild steel surface submerged in a 1M sulphuric acid solution, the data can be seen in Table 4. From the results obtained from the calculations, \(\Delta G\) TLE is negative, which indicates that the adsorption of molecule inhibitors on the surface of mild steel takes place spontaneously; in general, the reaction takes place by physirorption. The value of \(\Delta H_{ads}\) shows the amount of heat adsorbed during the adsorption process. \(\Delta H_{ads}\) on a positive value table show that the process is endothermic. The higher the temperature, the more heat is adsorbed in the inhibition process. The entropy value indicates whether the reaction is reversible or non-reversible, and the stability of the inhibitory layer that formed on the mild steel surface. From Table 4, \(\Delta S\) can be seen to be negative, indicating the instability of the inhibitory layer formed, and that the reaction takes place non-reversibly.

| Table 4. Thermodynamic adsorption parameters at different temperature | Na3PO4 | Tannin | TLE |
|---|---|---|---|
| T K | \(\Delta H_{ads}\) kJ/mol | \(\Delta G\) kJ/mol | \(\Delta S\) kJ/mol.K | \(\Delta H_{ads}\) kJ/mol | \(\Delta G\) kJ/mol | \(\Delta S\) kJ/mol.K | \(\Delta H_{ads}\) kJ/mol | \(\Delta G\) kJ/mol | \(\Delta S\) kJ/mol.K |
| 313  | 6.15 | -14.25 | -0.28 | 8.24 | -15.10 | -0.39 | 8.24 | -17.58 | -0.46 |
| 333  | 6.55 | -12.88 | -0.25 | 8.77 | -15.87 | -0.42 | 8.76 | -23.05 | -0.61 |
| 353  | 6.94 | -11.58 | -0.23 | 9.29 | -14.37 | -0.38 | 9.29 | -11.76 | -0.31 |

3. Conclusions
1. The ability of TLE to inhibit the corrosion rate of mild steel at 333K and at a concentration of 1250 ppm is a 64% inhibition efficiency. At this temperature, the performance of TLE is optimal. The adsorption mechanism is the Langmuir isotherm, the process occurring endothermically, and the inhibition layers tending to be unstable.
2. The inhibition efficiency of TLE is still less than that of sodium phosphate and tannin, so it will be necessary to undertake further research in order to improve this ability in TLE.
3. TLE’s sensitivity to temperature is quite significant, characterised by higher temperatures causing lowered efficiency of corrosion inhibition.

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