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# Optimization and characterization of a green corrosion inhibitor using *Costus speciosus* extract for the corrosion of mild steel in 1 M HCl

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## Abstract

*Corrosion inhibition by natural compounds has gained attention over traditional methods due to the adverse effects associated with traditional synthetic inhibitors which are harmful for humans as well as the environment. In this study, Costus speciosus, a native plant found widespread in Sri Lanka, known commonly as Thebu, was investigated as a potential corrosion inhibitor. A 10% extract of Thebu leaves in 1 M HCl was shown to have maximum inhibition efficiency when tested for corrosion of mild steel. This was verified by weight loss and electrochemical measurements. As shown by adsorption isotherm studies the mechanism of adsorption of inhibitor molecules to metal surface was identified as chemisorption by forming a monolayer.*

**Keywords:** Corrosion, inhibitor, natural, Thebu, mild steel, HCl

## Introduction

Corrosion inhibitors are chemical substances which slow down the rate of corrosion of metals and metal alloys, when added in small amounts. These inhibitors act by adsorbing themselves to the metal surface by forming a thin film, and thereby protecting the metal from corrosion. Most of the conventional corrosion inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms and are toxic. Therefore, recently the focus has been changed to develop natural corrosion inhibitors which are biodegradable and environmentally friendly. Natural corrosion inhibitors are extracted from herbs, medicinal plants, fruits and vegetable peels and spices. Many studies can be found in literature where different plant extracts were tested as potential natural corrosion inhibitors[1–13]. Sri Lanka, being a tropical country, has a rich ecosystem with a wide variety of plants which are naturally abundant. Therefore, being a resourceful nation it should be easy to find inexpensive and eco-friendly alternatives for the existing synthetic corrosion inhibitors.

The definition of corrosion is "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties"[14]. Different types of corrosion are, uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, microbial corrosion, erosion or abrasion corrosion etc. Corosion can be categorized as atmospheric corrosion, corrosion in water and corrosion in soil, which is based on the medium that it takes place. Corrosion in water is for example very important in cooling water systems, in steel pipelines used in oil and petroleum industries and in mine water. Regardless of the type of corrosion, its inhibition is based on two main principles; either change the material or change the environment. Corrosion inhibitors act by changing the environment by lowering the molecular oxygen activity at the surface of the metal. For example, in acidic medium, the additive adsorbs on the metal-solution interface and inhibits the anodic and/or cathodic reaction.

The natural products in *Occimum viridis*, *Telferia occidentalis*, *Azadiracta indica*, *Hibiscus subdarifa*, *Garcinia kola*, *Murraya koenigii*, *Uncaria gambir* and *Prunus cerasus* have been identified as potential corrosion inhibitors[10]. Some other examples include the study of potato (*Solanum tuberosum*) peel extract (PPE) on mild steel in 2 M HCl solution[9] and a study of *Allium Cepa* (Onion) in industrial chill wastewater systems[12]. Moreover, methanol extracts of matured tea leaves have shown inhibition of corrosion of copper in aerated HCl solutions[10].

In the current study, extracts from the leaf of Thebu plant was investigated as a potential corrosion inhibitor. Corrosion rates and percentage inhibition efficiencies of the Thebu leaf extract were tested against the corrosion of mild steel in acidic media. Thebu is listed as a native plant of Sri Lanka belonging to the family Costaceae and the plant was identified as *Costus speciosus* by the National Herbarium of Sri Lanka, at Peradeniya. An analysis has revealed that the leaves of *Costus speciosus* contain alkaloids, flavonoids, saponins, tannin, terpenes, steroids, polyphenolic compounds and carbohydrates[15]. While decreasing the rate of metal dissolution, corrosion inhibitors form a protective layer by adsorbing onto the metal surfaces. Most of the compounds listed above which have been identified in Thebu leaf extract are organic compounds containing heteroatoms such as oxygen, nitrogen and sulphur. At the same time, they have electronegative

functional groups and conjugated bonds which help in inhibition activity. The presence of heteroatoms also facilitates the adsorption of inhibitor molecules onto the metal surface[16].

## Materials and methods

**Preparation of 1 M HCl solution:** A solution of 1 M HCl was prepared by diluting concentrated (analytical reagent) hydrochloric acid with distilled water.

**Preparation of metal plates:** Metal plates (2 cm × 2 cm × 0.7 mm) were sanded with two grades of sand paper (grade 600 followed by 1000) to obtain a smooth surface free of visible grooves. This was followed by washing first with distilled water, then with ethanol and finally with acetone. Metal plates were air dried before weighing.

**Preparation of inhibition medium:** A mass of 1 g of dry leaves of *Costus speciosus* was placed in 50 ml of double distilled methanol and stirred for four hours. It was then filtered followed by centrifugation at 4500 rpm for 20 minutes. The volume was topped up to 50 ml. Plant extract was mixed with 1 M hydrochloric acid solution to make a 10% inhibition medium.

**Weight loss measurements:** Inhibition efficiency for corrosion of mild steel in 1 M HCl by Thebu leaves (10%) were studied by weight loss experiments. Pre-weighed metal plates were immersed in inhibition medium and final weights were measured every 24 hours up to a total of five days. Metal plates were washed with distilled water and air dried prior to the final weight measurement.

**Electrochemical measurements: Preparation of electrodes:** A three-electrode system was used. Working electrode was a mild steel plate (2 cm × 2 cm × 0.7 mm). They were sanded with sand paper followed by washing with distilled water, then with ethanol and finally with acetone. A Ag/AgCl electrode was used as the reference electrode with a carbon counter electrode.

**Open circuit potential (OCP) measurement:** A two electrode system was prepared (mild steel working electrode and Ag/AgCl reference electrode) and immersed in 1 M hydrochloric acid medium with and without inhibitor. Corrosion potential of mild steel was measured as a function of time for a duration of one hour.

**Linear sweep voltammetry:** Before each experiment, metal plates (working electrode) were dipped in acid solution to reach their corrosion potential. Linear sweep voltammetry was then performed at a sweep rate of 1 mV/s within a range of ± 400 mV from corrosion potential.

**Impedance spectroscopy:** Inhibition efficiency of *Costus speciosus* plant extract was determined by using electrochemical impedance spectroscopy technique from 1 kHz to 1 mHz at 2 mV scan rate. Nyquist plots for corrosion of mild steel in 1 M HCl were recorded at different inhibitor concentrations.

**Adsorption isotherms:** To determine the mechanism of adsorption between the metal and inhibitor, several adsorption isotherms were tested such as Langmuir, Frumkin and Temkin. Langmuir, isotherm describes monolayer formation on the surface assuming the availability of only one binding site per molecule and no interaction between adjacent molecules. Temkin isotherm describes the linear decrease of adsorption heat with increasing surface coverage. Frumkin isotherm is used to describe lateral interactions of molecules. Mass loss experiments were carried out for a duration of six hours with inhibitor concentrations of 2%, 4%, 6%, 8%, and 10%. By plotting the data and fitting into the following equations, a possible mechanism for adsorption was suggested.

$$\frac{C}{\theta} = \frac{1}{k} + C \qquad \text{Langmuir isotherm}$$

$$\exp(-2a\theta) = kC \qquad \text{Temkin isotherm}$$

$$\frac{\theta}{(1-\theta)}\exp(-2a\theta) = kC \qquad \text{Frumkin isotherm}$$

Where: C is inhibitor concentration, k is binding constant and α describes lateral interaction of molecules. θ is the surface coverage.

## Results and discussion

**Weight loss measurements:** Corrosion of mild steel in 1 M HCl was studied by weight loss measurements. In a separate experiment, the maximum inhibition efficiency was found to be shown in the presence of an inhibitor concentration of 10% in 1 M HCl, for the extract of leaves of *Costus speciosus.* Therefore, this concentration has been used throughout the weight loss measurement experiments. From weight loss experiments, corrosion rate and corrosion inhibition efficiency were calculated daily, for a total duration of five days. According to the results in Table-1 and Figure-1, corrosion rate has decreased after 48 hours and it remains a constant thereafter. Accordingly, percentage inhibition efficiency (Figure-2 and Table-1) has increased from 86% to 91% after 48 hours and remains fairly constant after that, except for the decrease observed after 72 hours.

**Table-1:** Corrosion rate and percentage inhibition efficiency within the duration of experiment.

| | Day 1 | Day 2 | Day 3 | Day 4 | Day 5 |
|---|---|---|---|---|---|
| Corrosion rate mg $cm^{-2}$ $h^{-1}$ | 0.06 | 0.04 | 0.04 | 0.04 | 0.04 |
| Inhibition efficiency % | 86 | 91 | 87 | 92 | 91 |

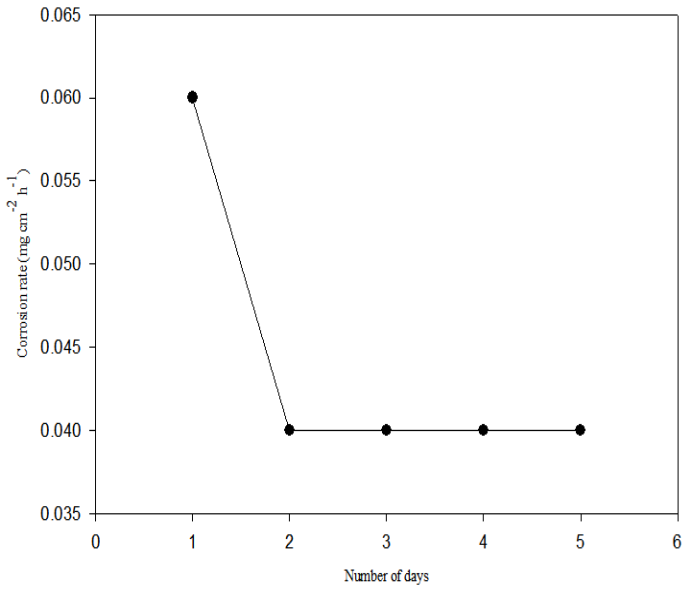


**Figure-1:** Rate of corrosion measured daily for the duration of experiment.

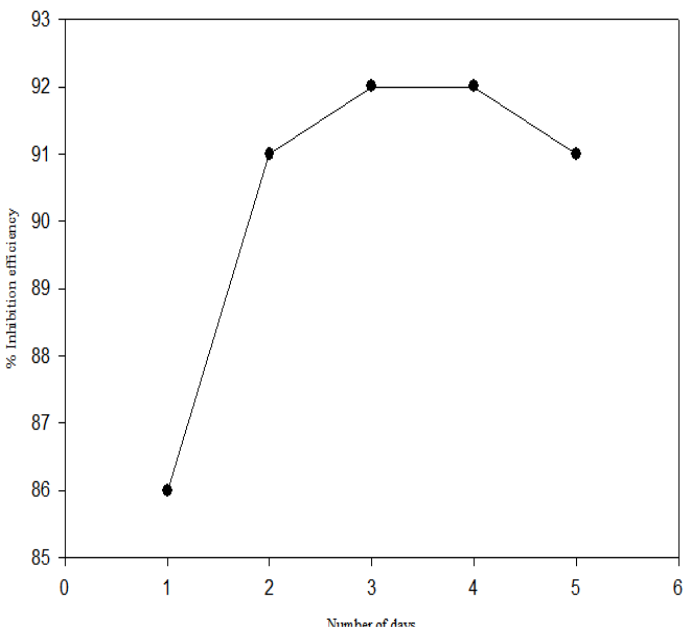


**Figure-2:** Percentage inhibition efficiency for the duration of experiment.

**Potentiodynamic scans:** Corrosion potential of mild steel in 1 M HCl was measured by recording the open circuit potential which was around -0.5 V. Linear sweep voltammetry was performed at a sweep rate of 1 mV/s within a range of ± 400 mV from corrosion potential. Figure-3 shows the cyclic sweeps of mild steel in 1 M HCl solution without the inhibitor as well as with the inhibitor at concentrations of 2%, 4%, 6%, 8% and 10%. Data derived from Figure-3 are shown in Table-2. Electrochemical analysis using Tafel plots showed the maximum corrosion inhibition efficiency for an inhibitor concentration of 10%.

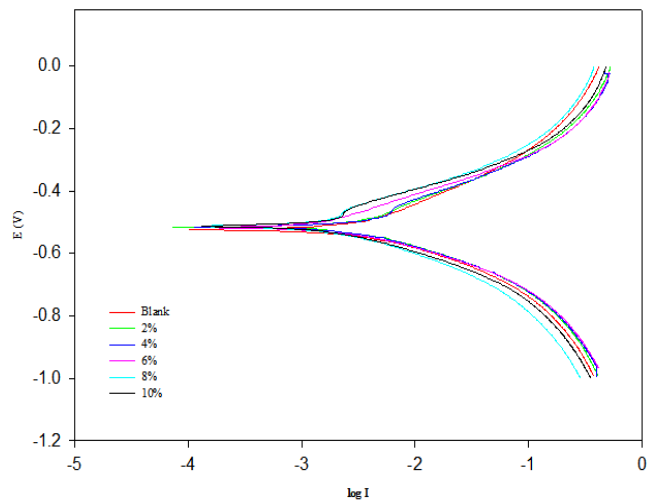


**Figure-3:** Tafel plots of mild steel in 2 M HCl with and without Thebu (*Costus speciosus*) leaves extract.

**Table-2:** Tafel plot parameters and inhibition efficiency for the corrosion of mild steel in 1 M HCl containing different concentrations of Thebu (*Costus speciosus*) leaves extract.

| | Blank | 2% | 4% | 6% | 8% | 10% |
|---|---|---|---|---|---|---|
| $E_{corr}$ (mV) | -517 | -509 | -506 | -505 | -502 | -500 |
| $I_{corr}$ (μA/cm$^2$) | 4881 | 4360 | 4014 | 1893 | 1326 | 1184 |
| $b_a$ (mV/div) | 184 | 162 | 153 | 127 | 120 | 111 |
| $b_c$ (mV/div) | 157 | 152 | 150 | 124 | 114 | 104 |
| %IE | - | 11 | 18 | 61 | 73 | 76 |

The value of corrosion potential ($E_{corr}$) has changed from -517 mV for the blank to -500 mV for the medium with 10% inhibitor. The value of $I_{corr}$ has decreased from 4881 μA cm$^{-2}$ for the blank to 1184 μA cm$^{-2}$ for the medium with 10% inhibitor. Both anodic ($b_a$) and cathodic ($b_c$) constant values decreased with increasing inhibitor concentration but decrease of anodic Tafel slopes with different inhibitor concentrations was higher than the change in cathodic Tafel slope. This indicates the decrease of the oxidation rate of the metal in the presence of higher concentrations of inhibitor. However, due to the reduction of both cathodic and anodic slopes and anodic shift of open circuit potential in the presence of higher concentrations of inhibitor, it can be inferred that these inhibitors behave as mixed type inhibitors with predominant anodic effect. The reduction in current densities results in overall reduction in the corrosion rate. The inhibition efficiency increases with increasing concentration of inhibitor. This indicates that the inhibitor does not change the mechanism of metal dissolution and hydrogen evolution reactions of steel but decreases the rates of both reactions by adsorption on steel surface.

**Electrochemical impedance spectroscopy:** Electrochemical impedance spectroscopy (EIS) was performed on mild steel in the absence and presence of the inhibitor and the results are summarized in Figure-4 and Table-3. According to the results in Figure-4, the semicircular shape of impedance spectra suggests the occurrence of a single charge transfer process during corrosion of the metal. According to the data in Table-3, the numerical value of charge transfer resistance ($R_{ct}$) increases from 36 Ω for the blank to 166 Ω for a medium with 10% inhibitor. This increase is due to the formation of a protective, insulating film at the metal-solution interface.

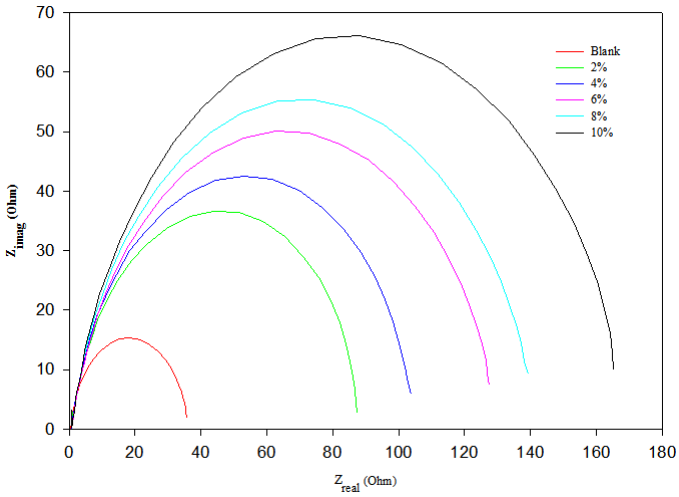


**Figure-4:** Nyquist plots of mild steel in 1 M HCl with and without Thebu (*Costus speciosus*) leaves extract.

**Table-3:** Corrosion parameters derived from impedance spectroscopy for the corrosion of mild steel in 1 M HCl containing different concentrations of Thebu (*Costus speciosus*) leaves extract.

| Inhibitor concentration | $R_{ct}$ (Ohm) |
|---|---|
| Blank | 36 |
| 2% | 88 |
| 4% | 104 |
| 6% | 128 |
| 8% | 140 |
| 10% | 166 |

**Adsorption isotherms:** Results from mass loss experiments were analyzed by fitting into Langmuir, Frumkin and Temkin isothers. Only Langmuir isotherm exhibited a good fit according to the higher linear regression value greater than 0.99. Also, the slope close to unity (1.08) supported a good fit to Langmuir isotherm. This suggests monolayer adsorption of inhibitor molecules on the metal surface.

## Conclusion

The inhibition efficiency for corrosion of mild steel in 1 M HCl was investigated using the leaf extracts of *Costus speciosus* (commonly known in Sri Lanka as Thebu). A methanol extract of Thebu leaves showed maximum inhibition efficiency at a concentration of 10% in HCl media, as evidenced by the results from weight loss measurements as well as electrochemical measurements (both Tafel plot analysis and impedance spectroscopy). Adsorption mechanism of inhibitor molecules onto mild steel surfaces was determined to be monolayer chemisorption by fitting data to different adsorption isotherms. Considering all of these results, Thebu leaves extract can be proposed as an efficient corrosion inhibitor for mild steel in acidic media.

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