

Corrosion Inhibition of Mild Steel by Phytochemicals in Acidic Media

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Abstract

Corrosion inhibition of mild steel using extract of leaves, roots and stem bark of coffee plum (*Flacourtia jangomas*) plant extract in 1M HCl and 0.5 H₂SO₄ solutions was investigated by weight loss method at 30°C. Corrosion rate decreased significantly in presence of extract and inhibition efficiency increased with increasing concentration of extract. Inhibition efficiency performance followed the trend Leaf extract > Root extract > Stem Bark extract at 5% inhibitor concentration. No considerable changes in inhibition efficiency were observed above 5% in all the cases. The decreased corrosion rate and adsorption behavior have been explained by Langmuir, Temkin and Freundlich adsorption isotherm. The constituents responsible for inhibition were identified by Phytochemical analysis and Fourier Transform Infrared Spectroscopy FTIR spectroscopy.

Key Words: Coffe plum (*Flacourtia jangomas*), corrosion inhibitor, mild steel, adsorption, weight loss, Langmuir, Temkin isotherm, FTIR.

Introduction

Metallic corrosion is a natural phenomenon which possess very serious problem in industries. Mineral acids are corrosive towards metal and alloys especially iron base alloys and it is extensively used in various industrial operations like metal finishing, de-scaling of rust, pickling etc., where a notable amount of metal loss has been observed as metal dissolution. Inhibitors are used for protection of metal against corrosion in acidic solution to prevent undesired metal dissolution. Organic inhibitors have been used for corrosion inhibition of mild steel [1, 2]. Organic compounds containing Nitrogen, Sulfur or Oxygen atoms act as corrosion inhibitor by adsorption on metal surface though co-ordinate bonding [3-10]. Such inhibitors are generally toxic to the environment and human being as well. Plant extracts have been found more useful, naturally occurring low cost and environment friendly corrosion inhibitors instead of using organic compound [11-16]. A large number of works are reported on biodegradable natural products as corrosion inhibitors [17-19].

The present work deals with the corrosion inhibition and adsorption behavior of constituents of coffee plum extract as an environmentally begin inhibitor on mild steel corrosion in dilute hydrochloric acid and sulfuric acid solution. Its local name is Paniala. The plant is well known for its good medicinal values. It is useful in toothache, bleeding gums etc. [20-21].

Experimental

Materials and Methods

Alloy Used

Commercially available mild steel (C 0.15% by weight) was used for all experiments. The mild steel sheet was mechanically press-cut into 2.5×2.5×0.1 cm coupons. The steel coupons were immersed in 5% HCl to remove rust and sequentially polished using SiC emery

papers of grade 220, 400, 600 and 1000, washed thoroughly with distilled water and degreased with acetone.

Chemicals Used

1M HCl and 0.5M H₂SO₄ solutions were prepared using analytical grade concentrated 37% HCl and 95% H₂SO₄ (Merck products) respectively and double distilled water.

Preparation of Plant Extract

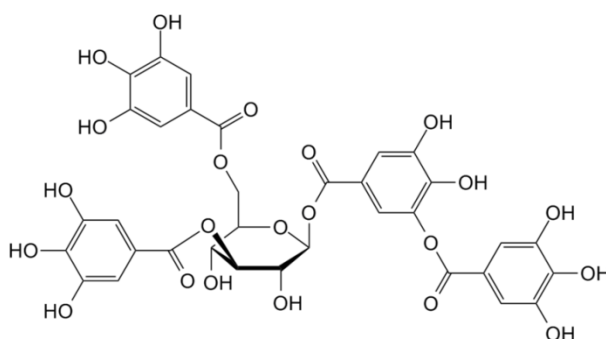
Fresh leaves stem bark and roots of Coffee plum (Paniala) were collected from Gorakhpur city of U.P., India. The parts of the plant were air-dried and kept in an oven maintained at 50°C for constant weight to remove the moisture content. Dried leaves, stem bark and roots were crushed and ground to make powder. Extract was prepared separately in 1M HCl and 0.5M H₂SO₄ for investigation in both the media. 10 g of dried powder of leaves were digested in 200 mL 1M HCl and kept overnight. Next day it was filtered and the filtrate volume was made up to 200 mL using 1M HCl. Similarly another extract was prepared in 0.5M H₂SO₄ solution. The extracts so prepared were taken as stock solutions from which 0.1, 0.5, 1 and 5 % test solutions were prepared. Similarly extracts of stem bark and root were also prepared.

Phytochemical Screening

Test for Tannin

1 g of powdered sample was boiled with 20 ml distilled water for five minutes in a water bath and is filtered while hot.

1 ml of cool filtrate is diluted to 5 ml with distilled water and a few drops of 10 % ferric chloride are added and observed, A bluish-black or brownish-green precipitate indicated the presence of tannins.



Tannin

Test for Saponins

1 g of powdered dried sample is boiled with 10ml of distilled water for 10 minutes. The mixture was filtered while hot and allowed to cool. The following tests are then carried out.

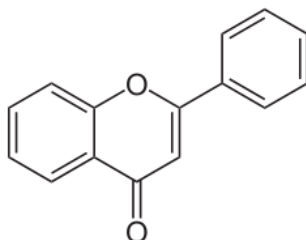
Frothing: 2.5 ml of filtrate is diluted to 10ml with distilled water and shaken vigorously for 2 minutes (frothing indicates the presence of Saponins in the filtrate).

Emulsifying properties: 2 drops of olive oil was added to the solution obtained from diluting 2.5 ml filtrate to 10 ml with distilled water (above), shaken vigorously for a few minutes (formation of a fairly stable emulsion indicates the presence of saponins).

Test for flavonoids

1 g of the powdered dried leaves of sample is boiled with 10 ml of distilled water for 5 minutes and filtered while hot. Few drops of 20 % sodium hydroxide solution is added to 1 ml of the

cooled filtrate. A change to yellow colour which on addition of acid changed to colourless solution indicates the presence of flavonoids.

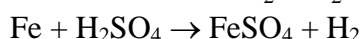
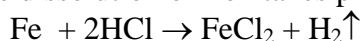


Structure of Flavone (2-Phenyl-1-benzopyran-4-one)

Weight Loss Studies

The weight loss studies were carried out at 30°C by immersing steel coupons of known weight and surface area in 100 ml each of blank 1M HCl and test solutions containing various concentrations of extracts for 48 hours.

The dissolution of iron takes place and reaction can be written as



After 48 hours of reaction, the specimens were taken out, washed with water, dried and weighed. Similarly reactions were performed in 0.5M H₂SO₄ in absence and presence of different concentrations of extracts. Corrosion rates (in terms of g.cm⁻²h⁻¹) were calculated using following expression.

$$\text{Corrosion rate (CR)} = \frac{W_i - W_f}{\text{Surface area (cm}^2\text{)} \times \text{Time (h)}}$$

Where, W_i = initial weight of coupon,

W_f = weight of coupons after treatment

W_i - W_f = weight loss (g)

The surface coverage (θ) as a result of adsorption of inhibitor and inhibition efficiency (η%) were calculated from corrosion rates using the following expression:

$$\theta = \frac{\text{CR}_{\text{blank}} - \text{CR}_{\text{inhibitor}}}{\text{CR}_{\text{blank}}}$$

$$\eta \% = \frac{\text{CR}_{\text{blank}} - \text{CR}_{\text{inhibitor}}}{\text{CR}_{\text{blank}}} \times 100$$

Where,

CR_{blank} = corrosion rate in absence of inhibitor

CR_{inhibitor} = corrosion rate in presence of the inhibitor

Fourier Transform Infrared Spectroscopy (FTIR)

The identification of the corrosion inhibitor components in the extract was carried out by FTIR spectroscopy. FTIR spectra were recorded for aqueous extract of the leaves of coffee plum (Paniala).

Results and Discussion

Analysis in 1M HCl

Table1 shows the variation of corrosion rate, surface coverage (θ) and percent inhibition efficiency (η %) in 1M HCl. The values revealed that corrosion rates were significantly lowered down in presence of inhibitor. The corrosion rate decreased with increasing extract concentration. The maximum lowering in corrosion rate was calculated in presence of 5% leaf extract of Paniala. 5% of extract concentration was also evaluated as the optimum concentration as on increasing the extract concentration above 5% no significant change in corrosion rate lowering was observed. In case of leaf extract maximum inhibition efficiency (98.1%) was noticed and no considerable change in inhibition efficiency was observed after this. With roots it was found 97.3 % and with stem bark 96.4% as maximum inhibition efficiency at the same concentration of inhibitor.

Analysis in 0.5M H₂SO₄

Table-2 shows the change in corrosion rate, surface coverage (θ) and percent inhibition efficiency (η %) in 0.5M H₂SO₄. Similar behavior was observed regarding lowering in corrosion rate and increase in inhibition efficiency in presence of inhibitor. Maximum (95.8%) was found in presence of 5% leaf extract followed by (91.2%) with roots and 68.8% with stem bark extract. The performance of inhibition followed the trend;

Leaf extract > Root extract > Stem Bark extract

The decreasing corrosion rate and increasing inhibition efficiency was attributed to the fact that the adsorption of inhibitor on the metal surface. Adsorption of Paniala extract depends on its chemical composition which showed the presence of various secondary metabolites such as flavonoids, steroids, tannins and phenolic compounds etc. which have oxygen atoms with lone pair of electrons for coordinate bonding with metal substrate.

| Corrosion Rate (g cm ⁻² h ⁻¹) | | | | Surface Coverage (θ) | | | % Inhibition efficiency (% η) | | |
|--|-----------------------|-----------------------|-----------------------|-------------------------------|-------|-----------|-------------------------------------|-------|-----------|
| Extract conc.% | leaves | Roots | Stem bark | Leaves | roots | Stem bark | Leaves | roots | Stem bark |
| Blank | 1.16×10^{-3} | — | — | — | — | — | — | — | — |
| 0.1 | 8.85×10^{-5} | 1.02×10^{-4} | 1.95×10^{-4} | 0.924 | 0.912 | 0.833 | 92.4 | 91.2 | 83.3 |
| 0.5 | 3.09×10^{-5} | 8.82×10^{-5} | 9.95×10^{-4} | 0.973 | 0.924 | 0.913 | 97.3 | 92.4 | 91.3 |
| 1.0 | 2.95×10^{-5} | 6.84×10^{-5} | 5.94×10^{-5} | 0.975 | 0.941 | 0.948 | 97.5 | 94.1 | 94.8 |
| 5.0 | 2.24×10^{-5} | 3.13×10^{-5} | 4.12×10^{-5} | 0.981 | 0.973 | 0.964 | 98.1 | 97.3 | 96.4 |

Table1: Variation of corrosion rate, surface coverage and inhibition efficiency in 1M HCL

| Corrosion Rate ($\text{g cm}^{-2}\text{h}^{-1}$) | | | | Surface Coverage (θ) | | | % Inhibition efficiency ($\% \eta$) | | |
|--|-----------------------|-----------------------|-----------------------|-------------------------------|-------|-----------|---------------------------------------|-------|-----------|
| Extract conc. % | leaves | Roots | Stem bark | Leaves | roots | Stem bark | Leaves | roots | Stem bark |
| Blank | 3.75×10^{-3} | — | — | — | — | — | — | — | — |
| 0.1 | 1.96×10^{-3} | 2.11×10^{-3} | 3.04×10^{-3} | 0.477 | 0.437 | 0.189 | 47.7 | 43.7 | 18.9 |
| 0.5 | 1.02×10^{-3} | 1.48×10^{-3} | 2.23×10^{-3} | 0.728 | 0.605 | 0.405 | 72.8 | 60.5 | 40.5 |
| 1.0 | 5.62×10^{-4} | 1.02×10^{-3} | 2.06×10^{-3} | 0.850 | 0.728 | 0.451 | 85.0 | 72.8 | 45.1 |
| 5.0 | 1.57×10^{-4} | 3.0×10^{-4} | 1.17×10^{-3} | 0.958 | 0.912 | 0.688 | 95.8 | 91.2 | 68.8 |

Table 2: Variation of corrosion rate, surface coverage and inhibition efficiency in 0.5M H_2SO_4

FTIR Analysis of Leaf Extract

FTIR data for aqueous extract of leaves and prominent peaks are given in table-3. The data furnished relevant information that reflects the corrosion inhibition was due to adsorption of such groups present in the extract.

| Frequency (cm^{-1}) | Band Assignment |
|--------------------------------|-------------------------------|
| 3421 | —OH (Hydroxyl group) |
| 2923 | Aromatic (Ar—H) stretching |
| 2854 | Alkane C—H stretching |
| 1621 | Alkene C=C and C=O stretching |
| 1519 | Aromatic rings |
| 1256 | Amines C—N stretching |
| 1075 | Oligosaccharide linkage O—C—O |

Table-3: Prominent FTIR peaks for Paniala extract

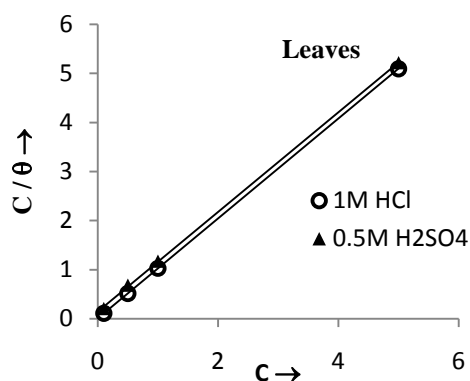


Figure 1 – Langmuir Adsorption isotherm -for Paniala leaves

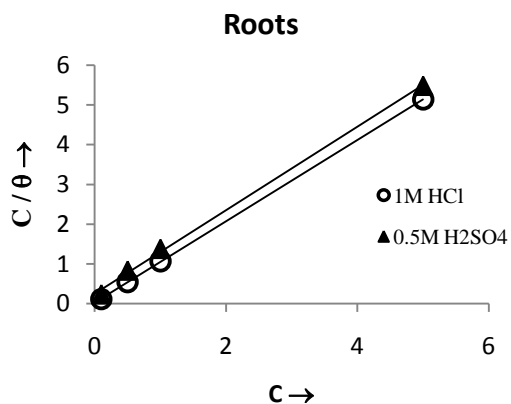


Figure 2 - Langmuir Adsorption isotherm for Paniala roots

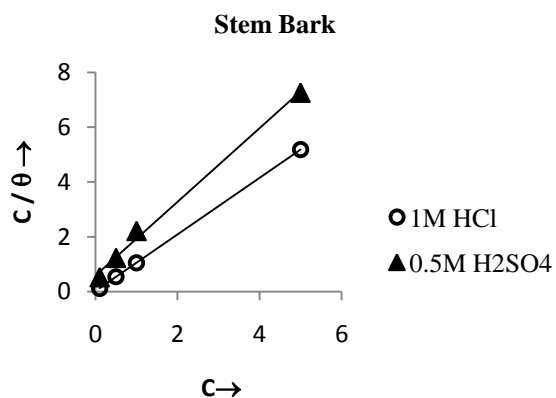


Figure 3 - Langmuir Adsorption isotherm for Paniala stem bark

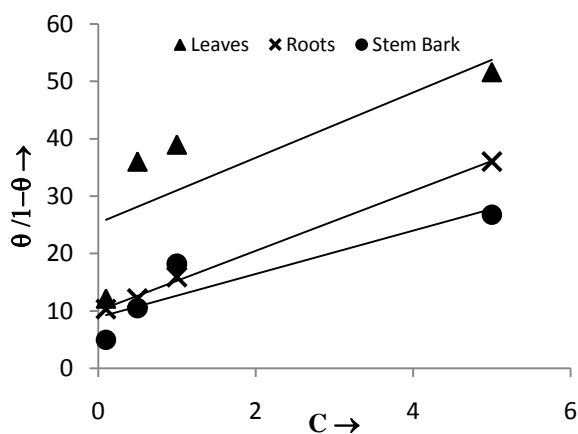


Figure 4 - Freundlich Adsorption isotherm in 1M HCl for paniala leaves, roots and stem bark

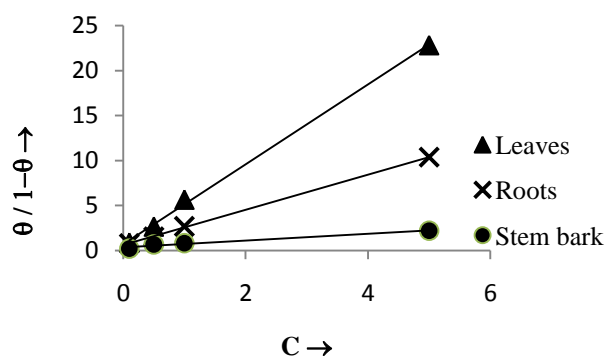


Figure 5 - Freundlich adsorption isotherm in 0.5M H₂SO₄ for paniala leaves, roots and stem bark

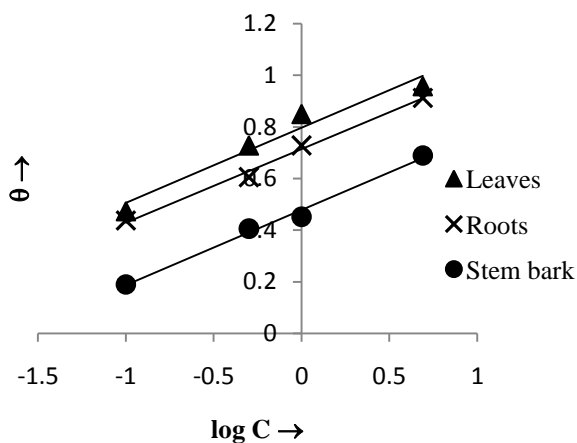


Figure 6 – Temkin adsorption isotherm in 0.5M H₂SO₄

Adsorption Behavior

The plant extracts are rich source of naturally synthesized chemical compounds which can form organo-metallic intermediates [22-24]. The formation of insoluble intermediates on the surface of metal substrate, are responsible for inhibitive action [25]. Secondary metabolites present in extract have complicated molecular structure and number of O, S and N atoms. The adsorption of such compounds creates a barrier for metal dissolution [26]. The experimental findings were applied to various adsorption isotherms and suitable isotherms were found.

As a general consideration of FTIR spectra, the groups such as hydroxyl –OH, phenolic, ketone and amine are responsible for inhibition by adsorption of organic Phytochemicals through O and N atoms. The adsorption of Phytochemicals is also attributed to the presence of π -electrons and aromatic rings [27].

Langmuir Adsorption Isotherm

A plot of C/θ against C (Figures 1-3) showed a straight line indicating that adsorption follows the Langmuir adsorption isotherm.

Freundlich Adsorption Isotherm

A plot between $\theta/1-\theta$ & C showed a straight line indicating that the adsorption obeys a Freundlich adsorption isotherm (Figures 4-5).

Temkin Adsorption Isotherm

A plot between θ and $\log C$ showed straight line indicating Temkin adsorption isotherm for 0.5M H_2SO_4 (Figure 6).

Conclusions

Corrosion inhibition of mild steel using leaves, roots and stem bark of Paniala (*Flacourtia jangomas*) plant extract in 1M HCl and 0.5 H_2SO_4 solutions was investigated by weight loss method at room temperature. The result showed that corrosion rate was significantly decreased in presence of the extract and percent inhibition efficiency increased with increasing the concentration of extract. 98.1% inhibition efficiency was found in 1M HCl and 95.8% in 0.5M H_2SO_4 at 5% inhibitor concentration of leaf extract. No considerable changes in inhibition efficiency were observed above extract concentration 5% in all the cases. The performance of inhibition as over all results followed the trend

Leaf extract > Root extract > Stem Bark extract

The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of Langmuir, Freundlich and Temkin adsorption isotherm.

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