

*METHODS AND
MATERIALS*



3. METHODS AND MATERIALS

In a research work the materials used and the methods adopted are the aspects which decide and determine qualitatively and quantitatively the outcome of the research. In this chapter, the selection of material, preparation of the material, preparation of the extract, test medium and techniques adopted for the evaluation of the inhibitors are described.

3.1. Mild steel coupons

The sheets of cold rolled mild steel, which is commercially available in the market, were machined into coupons of area $5 \times 1 \text{ cm}^2$. Holes were drilled on the center of one end of all the coupons for suspension. These coupons were degreased, cleaned with emery paper and washed with double distilled water. The coupons were stored in desiccators in the absence of moisture before their use for the investigation.

The composition of mild steel has been analyzed using ARL 3460 metal analyzer (Optical emission spectrometer). It was found to have the following elemental composition. Carbon-0.100%, Silicon-0.013%, Manganese-0.27%, Phosphorus-0.026%, Sulphur-0.011%, Chromium-0.059%, Molybdenum-0.016%, Nickel-0.012% and Iron-99.493%.

3.2. Selection of the medium

Acid solutions are widely used in various industries for pickling of ferrous alloys and steels. They are also used in oil and gas production to stimulate and increase oil and gas flow and to descale encrustations in production wells. Hence the study of corrosion and inhibition on commercial mild steel in acid medium is of much interest and it has gained great importance in the field of engineering and industries involving electrochemical process. 1M HCl and 0.5M H₂SO₄ is chosen for the present study. All the solutions used for the experiment were prepared with commercial grade reagents in distilled water.

3.2.1. Hydrochloric acid

Among various acids, hydrochloric acid is widely used for pickling. The use of HCl has technological advantages over other acids because the scale removing process

is quicker and surface is cleaner. This is due to the many fold aggressive nature of Cl^- ions, which attack oxide layer either to dissolve it or to loosen it from the surface of the steel.

3.2.2. Sulphuric acid

Sulphuric acid is used directly or indirectly in nearly all industries and is a vital commodity in our national economy. The principal uses of H_2SO_4 are for production of chemicals and their derivatives, pickling of steel and other metals, manufacture of fertilizers, dyes, drugs, pigments, explosives, synthetic detergents, rayon and other textiles refining process and production of rubbers. The widespread use of this acid in nearly all industries, places it in an important position with regard to costs and destruction of corrosion. In some cases corrosion increases with concentration of the acid and in others it decreases. For these reasons it is important to have a good picture of corrosion by sulphuric acid. Therefore the present experiment was carried out by using 0.5M H_2SO_4 of commercial grade.

3.3. Selection of inhibitor

Plant materials which are readily available and ecofriendly are selected to act as inhibitor. The selected plant materials are

- ❖ *Cassia fistula* Leaves (Sarakondrai)
- ❖ *Bougainvillea spectabilis* Leaves (Kakithapu)
- ❖ *Mirabilis jalapa* Flowers(Anthimalli or 4'O' Clock)

3.4. Sample Collection

The leaves of *Cassia fistula*, *Bougainvillea spectabilis* and the flowers of *Mirabilis jalapa* were collected in the north Coimbatore area in Tamilnadu state, India. The leaves and flowers were shade dried and powdered.

3.5. Preparation of the Inhibitor

3.5.1. Refluxing method

The extract was prepared by refluxing 50 grams of the powdered leaves/ flowers in 1000 ml of 1M HCl for 3 hours and kept overnight and was filtered and made upto 1000 ml with the same acid. From this stock solution, different concentrations of the inhibitor were prepared.

The same procedure was followed for the preparation of the extract in 0.5 M H₂SO₄.

3.5.2. Extract prepared by soaking the leaves/flowers in acid for 12 hours

5 g of the powdered leaves/flowers were soaked for 12 hours in 100 ml of the 1M HCl and 0.5 M H₂SO₄, stirred well, filtered and made up to the same volume with the respective acid.

3.5.3. Extract prepared after washing the leaves/flowers with Petroleum Ether

5 g of the powdered leaves were soaked overnight in 100 ml of petroleum ether, stirred well and filtered and dried. Then the dried leaves were used for acid extraction by refluxing method.

3.6. Equipments used

- Denver balance
- Thermostat
- Solartran Electrochemical measurement unit (1280 B)
- FTIR Spectrophotometer (NICOLET 15 10)

Corrosion monitoring

Corrosion is the leading cause of production and process equipment, storage and piping failure worldwide, where industries of many types struggle with corrosion prevention, detection, maintenance and control on a daily basis. It is often responsible for major breakdowns and costly downtime.

Various corrosion monitoring techniques are

- ❖ Weight loss method
- ❖ Electrical Resistance
- ❖ Linear polarization
- ❖ Hydrogen penetration
- ❖ Galvanic current

Corrosion rate of the mild steel and the inhibition efficiency are evaluated in this study using the following measurement techniques.

Weight loss method

- At various concentrations of the extract
- At different time intervals
- At elevated temperatures

Electrochemical method

- Tafel polarization method
- Linear polarization method
- AC Impedance techniques

Surface Analysis

FTIR spectroscopy

3.7. Laboratory methods of Testing

3.7.1. Weight Loss Method

Mild steel coupon accurately weighed using Denver balance were fully immersed in triplicate in 100 ml of 1 M HCl and 0.5M H₂SO₄ in the absence and presence of various concentrations of the extract. At the end of the test, the coupons were soaked in sodium bicarbonate, washed with distilled water, dried, desiccated for half an hour and then reweighed. The loss in weight was calculated from the difference between the before and end of the experiment weights. The average of the triplicate values were used for CR calculation.

The weight loss method was adopted for various concentrations of the extract, different time intervals of immersion and at elevated temperatures.

i) Various Concentrations

Different concentrations of the extracts were prepared using the stock solution and the test media. (1M HCl and 0.5 M H₂SO₄). Various concentrations of the inhibitor used in the study are – 0.05, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 (%v/v).

ii) Different time intervals of immersion

Various concentrations of the extract were used at different time intervals as 1 h, 3 h, 5 h, 7 h, 12 h, 24 h and 48 h and tested for the efficiency.

iii) Different temperatures

Temperature has a great effect on the rate of metal electrochemical corrosion. Temperature dependence of the inhibitor efficiency and the comparison of the values of effective activation energy of the corrosion process both in the absence and in the presence of inhibitors help to identify the mechanism of the inhibiting action. Since temperature is one of the significant parameters in corrosion studies, the effect of temperature on the inhibitive property was studied gravimetrically.

The effect of temperature was determined at various concentrations at the temperatures (303, 313, 323, 333 and 343) \pm 2 K for a fixed immersion time of 1 h.

Determination of corrosion rate

Many expressions are available to express the corrosion rate. The widely used one is miles per year. The corrosion rate in mpy was calculated using the formula,

$$CR \text{ (mpy)} = \frac{534W}{DAT}$$

Where W is the weight loss in mg

D is the density of the specimen in gm/cm²

A is the area of the specimen in cm²

T is the exposure time in hours.

Determination of percentage of inhibition efficiency

The inhibition efficiency was obtained from the following formula

$$I.E = \frac{CR - CR_0}{CR_0} \times 100$$

I.E = Inhibition efficiency in %

CR₀ = Corrosion rate in the absence of the inhibitor

CR = Corrosion rate in presence of the inhibitor

3.8. Determination of thermodynamic parameters

Thermodynamic parameters are very essential to explain the various adsorption isotherm and mechanism of the corrosion reaction. Activation energy (E_a) and thermodynamic parameters such as change in free energy of adsorption (ΔG_{ads}), enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) are calculated by the following equations.

a) Determination of activation energy

The corrosion reaction can be regarded as an Arrhenius type process the rate of which is given by

$$R_{\text{corr}} = Ke^{-E_a/RT}$$

R_{corr} = Corrosion rate

E_a = Apparent activation corrosion energy
= - (slope of log CR vs $1/T$) x 2.303 x R

T = Absolute temperature

K = Arrhenius pre exponential constant

R = Universal gas constant

b) Determination of free energy of adsorption

The free energy of adsorption at different temperatures were calculated using the equation given below

$$G = 2.303 RT (1.74 + \log (\theta/1-\theta) - \log C)$$

Where G = Free energy of adsorption

R = Gas constant

T = Temperature in Kelvin

θ = Degree of coverage on the metal surface

C = Concentration of inhibitor in %v/v

c) Determination of free energy of enthalpy (ΔH) and free energy of entropy (ΔS)

The free energy of enthalpy (ΔH) and free energy of entropy (ΔS) are calculated from the slope and intercept of the Eyring equation

$$\log CR/T = \{\log R/N_A h + \Delta S/2.303 * R\} - \Delta H/2.303RT$$

where h - Plank's constant

N_A - Avogadro number

R - Universal gas constant

Slope = $\Delta H/2.303 R$

Intercept = $\log RT/ N_A h + (-\Delta S/2.303 * R)$

3.9. Adsorption isotherms

The degrees of surface coverage (θ) corresponding to different concentrations of the extract (C) and at different temperatures have been extracted to deduce the best isotherm. The following isotherms were tested for their fit into the experimental data.

Langmuir isotherm $\log (\theta/1-\theta)$ vs $\log C$

Freundlich isotherm $\log \theta$ vs $\log C$

Temkin isotherm θ vs C

From the Temkin equation,

$$e^{a\theta} = KC$$

The standard free energy of adsorption can be calculated using the equation

$$\Delta G^{\circ}_{\text{ads}} = RT \ln (55.5 K_{\text{ads}})$$

where K is the equilibrium constant of the adsorption process and

55.5 is the concentration of water in the solution in moles.

3.10. Electrochemical Studies

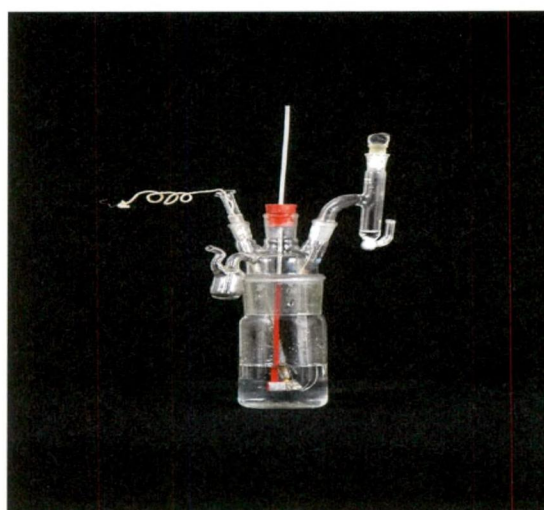
Electrochemical experiments were carried out in a glass cell with a capacity of 100ml. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The working electrode (WE) was mild steel coupon used for weight loss method but lacquered as to expose an area of 1 cm^2 .

3.10. i) Potentiodynamic polarization method

Potentiodynamic polarization was conducted using a Solartran Electrochemical measurement unit (1280 B) with a software package of Corrware, Corrview, Z-plot and Z-view (Fig 3.1). The a.c impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 KHz to 20 MHz, with a signal amplitude perturbation of 10mv. Nyquist plots were obtained from the results of these experiments.

Figure 3.1

Electrochemical measurement unit and Three electrode cell



Corrosion potentials and corrosion current densities were determined by extrapolating the cathodic and anodic Tafel regions from the potentiodynamic polarization curves. The intersect gives the corrosion current and corrosion potential.

Inhibition efficiencies I.E % were calculated as follows

a) Tafel method

$$I.E \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100$$

Where,

I_{corr} is the corrosion current density in the absence of inhibitor

I'_{corr} is the corrosion current density in presence of the inhibitor.

b) Linear polarization method

$$I.E \% = \frac{R_{p(inh)} - R_{p(blank)}}{R_{p(inh)}} \times 100$$

where,

$R_{p(inh)}$ is the polarization resistance in the presence of inhibitor

$R_{p(blank)}$ is the polarization resistance in the absence of inhibitor

3.10. ii) Impedance Studies

Values of the charge transfer resistance R_{ct} were obtained from the plots by determining the difference in the values of impedance at low and high frequencies. Values of the double-layer capacitance C_{dl} were calculated from the frequency at which the impedance imaginary component Z'' was maximum using the equation

$$f(Z_{i_{max}}) = 1 / 2\pi C_{dl} R_{ct}$$

The inhibition efficiency is calculated from the charge transfer resistance using the formula,

$$I.E \% = \frac{R_{ct/inh} - R_{ct}}{R_{ct/inh}} \times 100$$

Where R_{ct} and $R_{ct/inh}$ are the charge transfer resistance values in absence and in presence of the inhibitor, respectively.

3.11. FT –IR Analysis

The mild steel specimen was immersed in 100ml of 1M HCl and 0.5 H₂SO₄ in the presence of the inhibitors for 24 hours. The samples were taken out and dried. The film formed on the surface of the specimen was scratched and the powder was analyzed by using Nicolet iS 10 FT-IR spectrometer using KBr pellet method.

3.12. Bio accumulation studies

The standardization of environmental testing of inhibitors for bioaccumulation by finding out partition co-efficient gives a measure of the distribution of inhibitor between an Octanol- Water mixture, expressed as log of Octanol/Water partition co-efficient (log P_o/W). Bioaccumulation means an increase in the concentration of a chemical in a biological organism compared to the chemicals concentration in the environment. A PC based Double beam UV-Visible spectrophotometer (Systronics 2202) was used for this purpose.

3.13. Phytochemical analysis

Phytochemical analysis of the acid extracts of *Cassia fistula*, *Bougainvillea spectabilis* and *Mirabilis jalapa* was carried out using spot test for alkaloids, flavanoids, terpenoids, saponins, steroids and carbohydrates. The presence of these constituents in the plant extract was confirmed by positive result of the test.