CHAPTER 2

EXPERIMENTAL METHODS

2.1 INTRODUCTION

Mild steel finds a wide range of applications in industries such as pulp and paper, power generation, chemical and oil industries, because of its availability, low cost, ease of fabrication and high tensile strength. But mild steel has a high tendency to corrode easily, especially in acid, alkali and other aggressive environment (Vinod Kumar et al 2010). Corrosion is a prevailing destructive phenomenon in science and technology. Corrosion is a major problem that must be confronted for safety, environmental and economic reasons.

The use of inhibitors is one of the most practical methods for protection against corrosion. The role of inhibitor is to form a barrier of one or several molecular layers against acid attack. Protective action is often associated with chemical or physical adsorption involving variation in charge of, adsorbed substance and transfer of charge from one phase to another phase (Anwar Sathiq 2011). Most of the efficient corrosion inhibitors used in industry is organic compounds having multiple bonds and heteroatoms like nitrogen, oxygen, sulphur through which they are adsorbed on the metal surface (Saliyan 2008). They function by interfering with either the anodic or cathodic reactions or both (Nalini 2011).
The present chapter deals with the description of methods used in characterization of the plant material and the corrosion monitoring techniques. The corrosive inhibitive effect of peel, flower and bract extract of *Musa acuminata* in 1N HCl, H$_2$SO$_4$ and H$_3$PO$_4$ on mild steel was carried out using conventional weight loss method, electrochemical potentiodynamic polarization, A.C impedance techniques and surface examination analysis.

2.2 CHARACTERIZATION OF PLANT MATERIAL

2.2.1 Materials and Methods for Phytoanalysis

a) Chemicals and Reagents

All the chemicals and reagents used for screening test, qualitative analysis, quantitative analysis and antioxidant activity were of analytical grade.

b) Collection of plant materials

The study was carried out on the *Musa acuminata* fruit peel, flower and bract. The samples were obtained from cultivated farm in Thirumalayampalayam, Coimbatore, India. The peel was separated from the fruit pulp, the inflorescence was separated into florets and bracts, and then were air dried under shade. The dried samples were ground into powder using an electronic blender, sieved and the fine powder was stored in air tight container.

c) Preparation of the plant extract

Extraction was carried out by maceration using the following solvents with increasing polarity: petroleum ether, chloroform, ethyl acetate, methanol and water. 20 g of each part of *Musa acuminata* peel, floret and bract were separately soaked in 200 ml of the solvents for 48h at room
temperature. The samples were agitated using mechanical shaker to obtain successive extracts and filtered. The filtrates obtained were evaporated to dryness under vacuum using rotary evaporator. These extracts of *Musa acuminata* peel, flower and bract were then analysed for preliminary phytochemical screening.

d) **Phytochemical Screening**

Each extract of the parts of *Musa acuminata* was subjected to preliminary phytochemical screening to identify the chemical constituents of the plant. The methods of analysis were carried out using standard qualitative methods as described by various researchers Kotate (1999) and Harborne (1984). The samples were screened for the presence of bioactive compounds.

2.2.2 **Qualitative Phytochemical Analysis**

(i) **Detection of carbohydrate**

A mixture of 2 ml of Molish’s reagent and 2 ml of concentrated sulphuric acid was added to the extract. Formation of a reddish ring indicated the presence of carbohydrate.

(ii) **Detection of reducing sugar**

2 ml of the extract was added to Fehling’s solution and boiled for 5 min. Formation of a brick red precipitate indicated the presence of reducing sugar.

(iii) **Detection of Alkaloids**

Extracts were treated with Mayer’s reagent and formation of cream coloured precipitate indicated the presence of alkaloids.
(iv) Detection of Saponins

Extracts were diluted with 20 ml of distilled water and shaken in a graduated cylinder for 15 min. Formation of 1 cm layer of foam indicated the presence of saponins.

(v) Detection of Tannins

To 2 ml of the extract, few drops of 1% lead acetate were added and the formation of yellowish precipitate indicated the presence of tannins.

(vi) Detection of Flavonoids

To a small quantity of the extract dilute sulphuric acid was added. The appearance of orange colour indicated the presence of flavonoids.

(vii) Detection of Terpenoids

To 2 ml of extract, 2 ml of acetic acid and sulphuric acid were added. Formation of blue green rings indicated the presence of terpenoids.

(viii) Detection of Phlobotannins

The extract was boiled with 1% hydrochloric acid. Deposition of red precipitate indicated the presence of phlobotannins.

(ix) Detection of Coumarin

2 ml of extract with 10% of 3 ml sodium hydroxide resulted in yellow colour. This indicates the presence of coumarin.

(x) Detection of Cycloglycosides

To 5 ml of extract, 2 ml of acetic acid, 1 drop of 1% ferric chloride and 1 ml of sulphuric acid was added. Formation of brown violet and greenish ring indicated the presence of cycloglycosides.
Detection of Total phenol

Extract with 3% ferric chloride resulted in deep blue colour. This indicated the presence of phenol.

Detection of Quinone

The extract with 5 ml of hydrochloric acid resulted in yellow precipitate, indicating the presence of quinone.

Detection of Anthraquinones

To 2 ml of extract, 2 ml of 10% ammonium hydroxide was added. A bright pink colour indicated the presence of anthraquinones.

Detection of Steroids

2 ml of the extract with 2 ml of chloroform, acetic acid and 1 ml of concentrated sulphuric acid resulted in violet to blue green formation, indicating the presence of steroids.

2.2.3 Quantitative Phytochemical Analysis

Quantitative phytochemical analysis of Musa acuminata flower was done at Herbal Division & Phyto Pharma testing lab, M/s T. Stanes and Company Limited, Coimbatore, India. The various screening methods carried out are:

1. Total amino acid : Ninhydrin method – UV spectroscopy
2. Total terpenoids : Gravimetric method - UV spectroscopy

4. Total flavonoids : Ferric Chloride - UV spectroscopy

5. Antioxidant assay

(a) DPPH radical scavenging activity

(b) Ferric Reducing Power: Ammonium Molybdate method.

(a) Detection of Antioxidant properties

Antioxidant activity basically refers to the action of a molecule that is capable of slowing or preventing the oxidation of other molecules. Antioxidants that scavenge free radicals play an important role in corrosion. The antioxidant activity of *Musa acuminata* flower extract was investigated using DPPH radical scavenging assay because it gives reliable information concerning the antioxidant ability of the tested compounds. DPPH, a commercial oxidizing radical is reduced by antioxidants. The disappearance of the DPPH radical absorption at a characteristic wavelength is monitored by a decrease in optical density. Different concentrations of extract were taken in different test tubes. Methanol solution of DPPH was added to these tubes and shaken vigorously. The tubes were then incubated in dark at room temperature. A control sample was prepared as above without extract, and ethanol was used for the baseline correction. Changes in the absorbance of the samples were measured. Radical scavenging activity is expressed as the inhibition percentage. The percentage of scavenging effect is basically determined by the colour change of DPPH solution from purple to yellow or colourless.
(b) **Ferric Reducing Power**

In this assay, Fe$^{3+}$/ Ferricyanide complex is reduced to the ferrous form by antioxidants. The Fe$^{2+}$ formed is monitored by measuring the formation of Perl’s Prussian blue at 700 nm. Different amounts of sample in 1 ml of distilled water were mixed with phosphate buffer and potassium ferricyanide. The mixture was incubated. A portion of trichloroacetic acid was added to the mixture, which was then centrifuged. The upper layer of the solution and ferric chloride were mixed and the absorbance was measured. Increased absorbance of the reaction mixture indicated increased reducing power (Shyamala 2011).

2.2.4 **Phytochemical Analysis by Spectrophotometer**

Nature always stands as a golden mark to exemplify the outstanding phenomenon of symbiosis. The plants are indispensable to men for his life. Spectroscopic techniques are employed for qualitative and quantitative analysis of plant extract. The spectral studies like UV and FTIR are the preliminary work for the detection of phytochemical contents in the plants.

(i) **Fourier transform infrared spectroscopy**

Fourier transform spectrophotometer is the recent advancement in the field of IR spectroscopy, which has a number of advantages over dispersive instruments. They can scan quickly and therefore used for recording spectra, as compounds are eluted. Instead of recording the intensity of energy absorbed when the frequency of the infra-red light is non constant (monochromator), the infra red light is guided through an interferometer. After passing through the sample under investigation, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal
results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy (Silverstein 2007, Williams and Fleming 2011).

FTIR spectrometers are very cheaper than other conventional spectrometers because building of interferometers is very easier as compared to the fabrication of a monochromator.

The widespread use of FTIR for identification of drugs, polymeric modification, excipients and raw materials used in pharmaceutical manufacturing is due to its sensitivity with which the spectra can be obtained on any type of sample including insoluble solids, polymers, solution and gases. It is very useful tool in the detection of functional groups of biomolecules, thus aiding in their structural elucidation (Kokate et al 2010).

(ii) Ultraviolet-Visible spectroscopy

Ultraviolet (UV) and visible absorption techniques encompass analytical methods based upon measurements of light absorption by substances in the wavelength region from 200 to 800 nm. The region from 200 to 380 nm is known as the UV region and from 380 to 800 nm, the visible region of the spectrum. Absorption in UV-Visible region arises from electronic transitions within the molecule. The colour of the chemicals involved directly affects the absorption in the visible ranges. This technique apposite the fluorescence spectroscopy, in that, fluorescence involved with transitions of molecule from the excited state to the ground state, while in UV-Visible spectroscopy the absorption measures transitions from the ground state to the excited state (Skoog et al 2007, Pavia 2011).

UV-Visible spectroscopy is widely used in the quantitative analysis of transition metal ions and highly conjugated organic compounds. The presence and absence of an analyte gives an indication, which can be
considered to be proportional to the concentration. For perfect results, the instrument's indication about an analyte in the unknown should be compared with the indication of a standard. This is identical to the use of calibration curves. The response or indication (e.g., peak height) for a particular amount of concentration is known as the response factor.

For UV-Vis and FTIR spectrophotometer analysis, the 5% stock solution of extract prepared was used as such. The FTIR spectra of the ethanol, hydrochloric and sulphuric acid were taken on SHIMADZU FTIR - 8400F, at PSG College of Arts and Science College, Coimbatore, India, to detect the characteristic peaks and their functional groups.

To detect the UV-Vis spectrum profile, the extracts of *Musa acuminata*, were scanned in the wavelength ranging from 210–800 nm on SHIMADZU UV-Vis spectrophotometer UV-1700 Pharmuspec model. The characteristic peaks were detected to confirm the different bioactive nutrients present in the sample extracts. The peak values of the FTIR and UV-Vis were recorded.

### 2.3 PREPARATION OF THE INHIBITOR

*Musa acuminata* fruit peel, flower and bract were collected from the farm in Thirumalayampalayam, Coimbatore, Tamilnadu, India, washed and shade dried. Various medium like water, ethanol, HCl, H₂SO₄ and H₃PO₄ were used to prepare the extracts.

When the extract was prepared with distilled water, it was found to be affected by microbes within 12h. The plant material is edible and contains carbohydrates, proteins and amino acids which are easily attacked by the fungus (Figure 2.1). Hence attempt to prepare extract with water was dropped.
Dry powdered samples of *Musa acuminata* were soaked in a solution of ethanol. After 48h, the sample was filtered. The filtrate was subjected to evaporation in order to leave the sample free of ethanol using a vacuum rotary evaporator. It resulted in a dark brownish thick oily resin (Figure 2.2).

**Figure 2.2** Photograph of dark brownish oily resin of ethanol extract of MAN (P)

Its solubility in various solvents including acid was tested. It was either sparingly soluble or insoluble in acids. The results are summarised in the following Table 2.1.
Table 2.1  Solubility test of ethanol extract of MAN (P)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N Hydrochloric acid</td>
<td>- -</td>
<td>Completely insoluble.</td>
</tr>
<tr>
<td>1 N Sulphuric acid</td>
<td>- -</td>
<td>Completely insoluble.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>+ +</td>
<td>Dissolved completely with difficulty. When 1N HCl was added to the solution, it gave a yellow turbid liquid.</td>
</tr>
<tr>
<td>Chloroform</td>
<td>+ +</td>
<td>Dissolved readily. When 1N HCl was added, it separated into two layers, upper light yellow layer and bottom dark brown layer. Oily drops found to float at top.</td>
</tr>
<tr>
<td>1,4 Dioxan</td>
<td>+ +</td>
<td>Dissolved readily. Dark brown solid particles found at the bottom. When 1N HCl was added, it gave a turbid brown liquid. No particles found.</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>+ -</td>
<td>Sparingly soluble. Gave a yellow solution with sticky mass at the bottom. When 1N HCl was added, it gave a yellow liquid evolving heat. Oily drops found to float at the top.</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>+ +</td>
<td>Dissolved completely giving a yellow solution. When 1N HCl was added, it gave a yellow turbid liquid.</td>
</tr>
</tbody>
</table>
Table 2.1 (Continued)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulphoxide</td>
<td>+ -</td>
<td>Light yellow solution, with sticky mass at the bottom. When 1N HCl was added, it gave a yellow liquid. Sticky mass remained undissolved.</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>+ +</td>
<td>Dissolved readily. Dark brown solid particles found at the bottom. When 1N HCl was added, it separated into two layers, upper yellow layer and bottom clear liquid and a scum at the junction of two layers.</td>
</tr>
<tr>
<td>Dichloro methane</td>
<td>+ +</td>
<td>Dissolved readily. Dark brown solid particles found at the bottom. When 1N HCl was added, it separated into two layers, upper clear liquid and bottom dark brown layer. No particles found.</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>+ +</td>
<td>Dissolved readily. Dark brown solid particles found at the bottom. When 1N HCl was added it separated into two layers, upper dark brown layer and bottom clear liquid.</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>+ +</td>
<td>Yellow liquid. Dark particles at the bottom. When 1N HCl was added, it separated into two layers, upper yellow layer and bottom clear liquid.</td>
</tr>
</tbody>
</table>

+++: Completely soluble, + - : Sparingly soluble, - - : Completely insoluble
The results reveal that the extract was soluble in most of the organic solvents but insoluble in acids. Hence ethanol extract was not suitable for the acid medium corrosion study.

The acid extract of the samples when evaporated also resulted in a dark brownish thick oily resin (Figure 2.3) which led to practical difficulties in preparing the inhibitor solution for the study. Because of these constraints the extract of the plant material was prepared in the acid medium and was used as such.

![Figure 2.3](image)

**Figure 2.3  Photograph of dark brownish oily resin of hydrochloric acid extract of MAN (P)**

25 gm of dried powder of peel was boiled in 500 ml of 1N HCl acid with reflux condenser for three hours and was kept overnight to extract its phytonutrients (Figure 2.4). The extract was filtered and the filtrate volume was made up to 500 ml using the respective acids. The extract so prepared was taken as 5% stock solution and from this other concentrations were prepared (Figure 2.5). All other extracts were prepared in the similar manner.
2.4 SELECTION OF MILD STEEL

Mild steel is severely prone to corrosion in acid medium. Acid solutions are often used in industry for acidification of oil wells, cleaning of boilers, descaling and pickling of mild steel. All these processes are normally accompanied by considerable dissolution of the metal. Looking at the
increasing use of the metal, the study of corrosion inhibition is of paramount importance and hence several protective measures are being adopted. Rate of metallic corrosion can be reduced by the addition of inhibitors. Thus, in the present work mild steel is selected for corrosion inhibition studies.

### 2.5 MILD STEEL COMPOSITION

The corrosion tests were performed on coupons cut from sheets of mild steel of 2 mm thickness obtained from Albert Steel House, Coimbatore, India. The chemical composition of the mild steel in terms of element weight percentage as given by the supplier is shown in the Table 2.2.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the Element</th>
<th>Weight percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Carbon</td>
<td>0.123</td>
</tr>
<tr>
<td>2.</td>
<td>Manganese</td>
<td>0.031</td>
</tr>
<tr>
<td>3.</td>
<td>Silicon</td>
<td>0.011</td>
</tr>
<tr>
<td>4.</td>
<td>Phosphorus</td>
<td>0.037</td>
</tr>
<tr>
<td>5.</td>
<td>Sulphur</td>
<td>0.022</td>
</tr>
<tr>
<td>6.</td>
<td>Chromium</td>
<td>0.031</td>
</tr>
<tr>
<td>7.</td>
<td>Molybdenum</td>
<td>0.014</td>
</tr>
<tr>
<td>8.</td>
<td>Nickel</td>
<td>0.012</td>
</tr>
<tr>
<td>9.</td>
<td>Iron</td>
<td>Rest %</td>
</tr>
</tbody>
</table>

Low carbon content of mild steel makes it neither brittle nor ductile. It is hence best used as structural material.
2.6 CHOICE OF ACID MEDIA

The metal gets corroded by exposure to corrosive atmosphere like moist air, salty water, refinery oil, various acids etc. Acids are widely used in industry for derusting and pickling, cleaning of refinery equipment, removal of calcareous deposits from boilers, radiators of vehicles, pipelines carrying water or petroleum products, heat exchangers and so on. Due to its prominent properties, hydrochloric acid, sulphuric acid and phosphoric acid are widely used in industry for acid pickling process. These acids have their own advantages and disadvantages. Hydrochloric acid is cheaper and can be used for pickling at low temperature, but require a large volume for pickling due to its low activity. Sulphuric acid is costly and produces fewer fumes and involves less volume for pickling. Phosphoric acid is non toxic and used in production of fertilizers. It is a medium strong acid and shows strong corrosiveness on ferrous and ferrous alloys. Little work has been done on the inhibition of steel in phosphoric acid solutions.

Present study has been carried out with commercial grade HCl, H$_2$SO$_4$ and H$_3$PO$_4$ acid to simulate industrial conditions.

2.7 CORROSION MONITORING TECHNIQUES

The influence of the inhibitors on the dissolution process of mild steel in acid media was monitored chemically and electrochemically. The scheme of corrosion monitoring study is shown in the following flow chart.
2.7.1 Non Electrochemical Methods

2.7.1.1 Weight loss method

a) Preliminary treatment of mild steel

Rectangular mild steel coupons of size 5 x 1 x 0.2 cm were cut from a large sheet of mild steel, with a small hole of about 1.0 mm diameter near the 1.5 cm side end for suspending (Figure 2.6). The specimens were polished in sequence using silicon carbide emery papers of grade 200, 400, 600 starting with coarse one and proceeding in steps to the finest grade, then washed with distilled water, dried with clean tissue paper, degreased with acetone and dried using hot air drier. The specimens were then kept in desiccator to avoid the adsorption of moisture.

Figure 2.6 Photograph of mild steel coupons
b) **Experimental procedure**

Weight loss studies were conducted at room temperature and elevated temperatures.

Mild steel specimens were weighed accurately in electronic balance (SHIMADZU model AUW 220D). After initial weighing, the specimens were fully immersed using glass hooks in beakers containing 100 ml of 1N HCl/H$_2$SO$_4$/H$_3$PO$_4$ without and with inhibitor of different concentrations (Figure 2.7) at various intervals of time. After the specified period of immersion, the specimens were removed, washed with distilled water, dried and reweighed. The details of inhibitor concentration and time intervals used in the present study are given below,

<table>
<thead>
<tr>
<th>Inhibitor concentrations in % v/v</th>
<th>0.05</th>
<th>0.10</th>
<th>0.50</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time interval in hours</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>12</td>
<td>24</td>
</tr>
</tbody>
</table>

*Figure 2.7 Photograph of specimens fully immersed in acid medium*
c) **Temperature study**

Weight loss determinations were also carried out at the temperature range of 303 K – 353 K.

After initial weighing, the specimens were immersed in 100 ml of acid (1N HCl/H$_2$SO$_4$/H$_3$PO$_4$) without and with various concentrations of the plant extracts and kept in the thermostat (Raaga Lit pump type digital) for 1h duration (Figure 2.8). After the appropriate immersion time, the specimens were removed, washed, dried and reweighed.

The loss in weight was determined. A triplicate was run to ensure the weight loss and the results were averaged.

The parameters considered for temperature study are,

<table>
<thead>
<tr>
<th>Inhibitor concentrations in % v/v</th>
<th>0.05</th>
<th>0.10</th>
<th>0.50</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in Kelvin</td>
<td>303</td>
<td>313</td>
<td>323</td>
<td>333</td>
<td>343</td>
<td>353</td>
</tr>
</tbody>
</table>

*Figure 2.8 Photograph of thermostat (Raaga Lit pump type digital)*
2.7.1.2 Calculation of corrosion parameters

(i) Determination of corrosion rate

The rate of dissolution of metal was calculated in terms of corrosion rate (CR) using the expression,

\[
\text{Corrosion Rate (CR)} = \frac{(87.6 \times W)}{DAT} \text{ (mm/y)}
\]

where, mm/y = millimetre per year

\[ W = \text{loss in weight in milligrams} \]

\[ D = \text{metal density in g/cm}^3 \ (7.86 \text{ g/cm}^3) \]

\[ A = \text{area of the sample in square centimetres} \]

\[ T = \text{time of exposure of the metal surface in hours} \]

87.6 = conversion factor

(ii) Determination of inhibition efficiency

The percentage inhibition efficiency (IE %) of the inhibitor in terms of concentration has been calculated from the expression,

\[
\text{Inhibitor Efficiency (\%)} = \left( \frac{\text{Weight loss without inhibitor}}{\text{Weight loss with inhibitor}} \right) \times 100
\]

(iii) Determination of surface coverage

Surface coverage (\( \theta \)) has been calculated using the expression,
A graph was drawn between \((C/\theta)\) and \(C\) and between \(\theta\) and \(\log C\) to know whether the adsorption of inhibitors follows Langmuir or Temkin adsorption isotherm.

(iv) **Determination of thermodynamic parameters**

Various thermodynamic parameters such as activation energy \((E_a)\), free energy of adsorption \((\Delta G_{\text{ads}})\), enthalpy of adsorption \((\Delta H_{\text{ads}})\) and entropy of adsorption \((\Delta S_{\text{ads}})\) were calculated using the following equations described below obtained from the results of temperature study.

(a) **Determination of activation energy**

The apparent activation energies \(E_a\) for the corrosion in presence and absence of inhibitor were evaluated from Arrhenius equation.

\[
CR = Ae^{\frac{-E_a}{RT}}
\]

where \(CR\) is the corrosion rate, \(E_a\) is the apparent activation energy of the corrosion reaction, \(R\) is the gas constant, \(T\) is the absolute temperature and \(A\) is the Arrhenius pre-exponential factor (Eddy 2008 a).

(b) **Determination of free energy of adsorption**

The free energy of adsorption \((\Delta G_{\text{ads}})\) at different temperature was calculated from the equilibrium constant of adsorption using the expression,

\[
k = \frac{1}{55.5} \exp \left( \frac{\Delta G_{\text{ads}}}{RT} \right)
\]
where,  
\[ k = \frac{\theta}{C(1-\theta)} \] (from Langmuir equation)
\[ \theta = \text{degree of coverage on the metal surface} \]
\[ C = \text{concentration of inhibitor in mM} \]
\[ \Delta G_{\text{ads}} = -RT \ln(55.5k). \]

(c) **Determination of enthalpy and entropy of adsorption**

Enthalpy of adsorption (\(\Delta H_{\text{ads}}\)) and entropy of adsorption (\(\Delta S_{\text{ads}}\)) was calculated from the values of free energy of adsorption (\(\Delta G_{\text{ads}}\)) using Gibbs-Helmholtz relationship,

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

The slope and intercept of the line obtained by plotting \(\Delta G_{\text{ads}}\) against \(T\) furnished \(\Delta S_{\text{ads}}\) and \(\Delta H_{\text{ads}}\) respectively.

(v) **Determination of adsorption isotherms**

Since corrosion inhibition is a surface phenomena involving adsorption of the inhibitor on the surface of the metal, the phenomenon of interaction between the metal surface and inhibitor can be understood with adsorption isotherms. Different adsorption isotherms namely Langmuir and Temkin were tested for their fit into the experimental data.

2.7.2 **Electrochemical Methods**

2.7.2.1 **Potentiodynamic polarization studies**

Potentiodynamic polarization studies were carried out for mild steel of same composition both in absence and presence of inhibitor. A frequency
response analyzer PARSTAT 2273 (Princeton Applied Research, USA) and IBM personal computer which automatically controls linear polarization and Tafel polarization were used for the polarization study (Figure 2.9). The data acquisition was performed using the PowerSuite software and analysed using Zsimpwin software (version 3.21) to evaluate the corrosion kinetics parameters, such as $I_{\text{corr}}$, $E_{\text{corr}}$, Tafel slopes $b_a$ and $b_c$.

![Figure 2.9](image.png)

**Figure 2.9** Photograph of experimental set up of frequency response analyzer, PARASTAT and an IBM personal computer, for polarization measurement

(i) **Electrode surface preparation**

Mild steel rod of 15 cm long and 5 mm diameter mounted in Teflon leaving 0.19625 cm$^2$ of surface area exposed to the solution was used for electrochemical studies. It was then polished using 120, 200, 400, 600, 800, 1000, 1200 grade emery papers and finally degreased using acetone.

(ii) **Polarization cell assembly**

Experiments were carried out in three electrode polarization cell containing platinum foil as auxiliary electrode, saturated calomel as the reference electrode and polished mild steel rod specimen as working electrode.
(Figure 2.10). The electrode potential was allowed to stabilize for 10 min before starting the experiment. All the measurements were carried out in the frequency range of $10^6$–$10^2$ Hz at the open circuit potential by superimposing a sinusoidal A.C signal of small amplitude 10 mV, after immersion for 30 min in the corrosive medium.

The frequency response analyzer measured the linear polarization and Tafel polarization. The data were analyzed using computer software.

The experiments were carried out in 1N HCl, H$_2$SO$_4$ and H$_3$PO$_4$ with various concentrations of the inhibitor. The log of current and the corresponding potentials were fed into the plotter and a potential (E) against log I plot was obtained. The corrosion current $I_{\text{corr}}$ was obtained from the Tafel plot by extrapolation of the linear portion of the curve to $E_{\text{corr}}$ and this slope of the linear region were the Tafel slopes $b_a$ and $b_c$ which were calculated using the software. The inhibitor efficiency by Tafel method was calculated using the expression,

$$\text{Inhibitor Efficiency (\%)} = \frac{I_{\text{corr (blank)}} - I_{\text{corr (inh)}}}{I_{\text{corr (blank)}}} \times 100$$

where,

$I_{\text{corr (blank)}}$ = Corrosion current without inhibitor

$I_{\text{corr (inh)}}$ = Corrosion current with inhibitor.
2.7.2.2 Electrochemical impedance measurements

The electrochemical impedance measurements were carried out for mild steel in acidic media using the same electrochemical measurement unit. The impedance measurements were made at corrosion potentials $1.66 \text{ mVs}^{-1}$. The results are presented in the form of Nyquist plot. The real part ($Z'$) and the imaginary part ($Z''$) were measured at various frequencies and a plot $Z'$ against $Z''$ were made. From the plot, the charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) were calculated using the “Z” view software. Impedance measurements were carried out for mild steel in 1N HCl, H$_2$SO$_4$ and H$_3$PO$_4$ without and with inhibitors for the selected concentration. The inhibitor efficiency by linear polarization method was calculated using the equation,

$$
\text{I.E (\%)} = \frac{R_{ct} \text{ (inh)} - R_{ct} \text{ (blank)}}{R_{ct} \text{ (inh)}} \times 100
$$
where,

\[ R_{ct\ (inh)} = \text{Charge transfer resistance with inhibitor} \]

\[ R_{ct\ (blank)} = \text{Charge transfer resistance without inhibitor} \]

\[ I_{corr} \text{ can be calculated from the Stern Geary equation,} \]

\[ I_{corr} = \frac{b_a \times b_c}{2.303 (b_a + b_c)} \times \frac{1}{R_{ct}} \]

Where,

\[ R_{ct} = \text{Charge transfer resistance} \]

\[ b_a, b_c = \text{Tafel slopes.} \]

2.7.3 Surface Examination Studies

Surface analysis studies of mild steel specimens were done in order to study the changes that occur during the corrosion of mild steel in the presence and absence of the inhibitor in acid medium (Raja and Sethuraman 2009). The nature of the metal surface was analyzed by Scanning Electron Microscope (SEM), Energy Dispersive X-ray spectroscopy (EDX) and Fourier Transform Infrared (FTIR) spectroscopic studies (Sivaraju and Kannan 2010).

(i) Preparation of the specimen for surface analysis

The mild steel specimens (5 x 1 x 0.2 cm) were abraded with emery paper of grade 400 and 600 to a mirror finish, washed with distilled water and then rinsed with acetone and dried by hot air drier (Hegazy et al 2011).
The specimens used for morphological examination were immersed in a beaker having 100 ml of 1N HCl/ H₂SO₄/ H₃PO₄ acid solution containing an optimum concentration of 2% v/v MAN (P)/MAN (F)/MAN (B) extract for 3h at room temperature (Kannan et al 2010). After immersion, the specimens were removed, gently rinsed and dried without disturbing the surface.

(ii) **Surface morphology studies by Scanning Electron Microscope**

SEM photographs of the unprotected and protected samples were taken to examine the morphology of the corrosion product formed on the surface of mild steel specimen using JOEL SEM model JSM 6360 with 1000 x 10 µm magnification (Singh and Quraishi 2011) at Metallurgy Department, PSG College of Technology, Coimbatore, India.

(iii) **Surface morphology studies by Energy Dispersive X-ray study**

EDX analysis was done for mild steel specimens exposed to (i) blank 1N HCl (ii) 1N HCl containing 2% v/v MAN (F) extract and (iii) 1N HCl containing 2% v/v MAN(B) extract at CECRI, Karaikudi, India, using SHIMADZU 720/800 HS Energy Dispersive X-ray fluorescence spectrometer.

(iv) **Surface morphology studies by Fourier Transform Infrared spectroscopy**

The inhibitive action of plant extracts on mild steel corrosion was also investigated by FTIR technique, revealing the formation of protective film. The mild steel specimens were immersed in 1N HCl solution in absence and presence of 2% v/v concentration of MAN(P)/MAN(F)/MAN(B) extract for a period of three hours at room temperature, removed, washed carefully
with distilled water without disturbing the surface and dried. FTIR Spectra of the samples were taken at PSG College of Arts and Science College, Coimbatore, India, with SHIMADZU FTIR -8400F model instrument. The presence of phytochemical constituents such as glycosides, fatty acids, terpenoids etc. in the plant peel, flower and bract extract was investigated using FTIR spectral analysis. Bands associated with stretching vibrations of O-H, N-H, C=C and C-C groups and bending vibrations of C-O and N-H groups have been recorded. FTIR spectra of the *Musa acuminata* peel, flower and bract extracts in ethanol, HCl and H$_2$SO$_4$ were also taken for comparative study.

### 2.8 INDUSTRIAL APPLICATION OF CORROSION INHIBITOR

Major end-use industries for corrosion inhibitors are petroleum refining, oil and gas exploration, chemical production and water treatment industries. The benefit of corrosion inhibitors is that they can be applied in-situ to metals as a corrective action to counter unexpected corrosion.

To find the applicability of the selected plant materials as inhibitor in the industry, the extracts were tested in the local submersible pump manufacturing industry, Mahendra Pumps Pvt Ltd, Puliakulam, Coimbatore, India. The spare parts to be painted were pickled in acid solution for cleaning the surface. The effects produced during this process in the industrial condition were observed with the plain acid as is usually done in the industry, as well as with 2% v/v concentration of plant extract inhibitor.

An attempt has also been made to study the possible use of plant extract on corrosion protection of the spare part components. One set of the components were exposed to the environmental atmosphere, while the other set were coated with the plant extract paste obtained by removing the acid
using vacuum evaporator (Figure 2.11). The extent of corrosion and protection by inhibitor were assessed by visual observation.

Figure 2.11 Photograph showing manual application of plant extract over the metal components using brush