# 3 MATERIALS AND METHODS

In the present investigation entitled **"Inhibitive performance of selected biomass - *Passiflora vitifolia, pyrostegia venusta* and marine algae- *Sargassum polycystum and Padina boergesenii* on acid and alkali corrosion of Mild steel and Aluminium alloy – Experimental and Theoretical approach"** is phased out in the following manners.

- ❖ Selection of Material, inhibitor, corrosive media solution and characterization of inhibitor using analytical techniques
- ❖ Ascertaining corrosion inhibitive nature using electrochemical measurements and mass loss techniques
- ❖ Surface analytical techniques
- ❖ Quantum chemical studies

## 3.1 SELECTION OF METAL, MEDIA, INHIBITORS AND CHARACTERIZATION OF INHIBITORS

### 3.1.1 Selection of Sample

Due to the low price and physicochemical properties of MS and AA materials are commonly utilized in industries, but it is inevitable that various degrees of corrosion occur in different environments. Industrial, army equipment, petroleum manufacturing and fertilizers industries widely use MS. After iron aluminium is the second most used metal, it is used in a large number of industrial applications by itself and is used in a wide range of alloys. Aluminium works as an anode material for power sources with high energy densities due to negative values of standard potential. To improve the quality of the aluminium and to reduce the dissolution of aluminium in aluminium/ air battery corrosion inhibition studies in NaOH medium are performed using natural inhibitors.

MS and Aluminium samples were locally obtained in Coimbatore. Metal samples were abraded with emery sheets of 600 to 1200 grades washed with double distilled water, degreased and dried for doing experiments as per standard **ASTM G1-03.** The chemical composition of MS/AA are given below (Figure 3.1)

**Mild Steel**

C 0.019%, Mn 0.352%, Si 0.049%, P 0.019%, S 0.013%, Cr 0.010%, Mo 0.008%, Ni 0.010%, C 0.026% and Fe 99.33%

**Aluminium**

Si 0.056%, Fe 0.184%, C 0.010%, Mn 0.013%, Mg 0.015%, Cr 0.010%, Ni 0.053%, Zn 0.040%, Sn 0.026%, Ti 0.013%, Pb 0.029%, Bi 0.021%, Cd 0.013%, Ga 0.024% and Al 99.49%.

**Figure 3.1 Chemical composition of metal specimens**

### 3.1.2 Corrosive Media

HCl and NaOH are extensively used in industries for various activities. Corrosion of metal in aggressive solution is a vital problem in industrial cleaning and pre-treatment processes such as acid pickling, industrial acid cleaning, acid rescaling and oil well acidizing.

### 3.1.3 Selection of the studied Inhibitor

In the current study, the plants/ marine algae - seaweeds are used as green inhibitors. Considering the following reasons

- Inexpensive nature
- High recoverability and it possess the gold mine of novel chemical compounds.
- Environmentally benign
- Easily available and renewable resource

### 3.1.4 Preparation of inhibitor solutions

The leaves extract of *Passiflora vitifolia* (PAVL), *Pyrostegia venusta* (PVL), were collected from Maruthamalai area, Coimbatore district, and *Sargassum polycystum* (SP), *and Padina boergesenii* (PB) seaweeds/marine algae were collected from Mandapam. The studied leaves/seaweeds were cut into small pieces and shade dried. The investigated plants/seaweeds were authenticated by Botanical Survey of India (BIS), Coimbatore, Tamilnadu.(Figure 3.2)

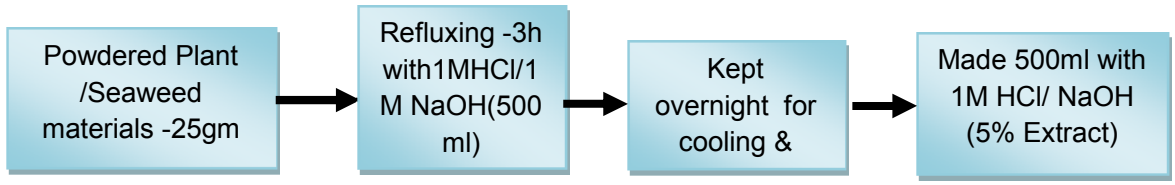


**Figure 3.2 Preparation method for the inhibitor solution**

### 3.1.5 CHARACTERIZATION OF INHIBITORS

Characterization of PAVL/PVL/SP/PB extracts were carried out using the following analytical techniques such as UV-Vis, FTIR, HPTLC and GC-MS.

#### 3.1.5.1 Phytochemical screening Test

Phytochemicals present in the investigated inhibitors PAVL, PVL, SP and PBextracts were found out using the standard procedure given in **Harborne, 1973.** (Appendix-I)

#### 3.1.5. 2 GC- MS Analysis

10µ ethanolic extract of PAVL / PVL / SP / PB was subjected to GC-MS analysis using GC and MS JEOL GC Mate equipped with secondary electron multiplier and HP5 fused silica column (50m, 0.25mm. i.d). Analysis conditions were -20min at 100$^{o}$C, 3min at 235$^{o}$C column temperature and 240$^{o}$ injector temperature, carrier gas was Helium, split ratio 5:4. Run time was 22 minutes.

#### .3.1.5.3 HPTLC analysis

HPTLC analysis of plants/seaweed extracts was carried on silica gel 60 $f_{254}$, 20X10 cm HPTLC plates (Merck, Germany-5642). Ethyl acetate, methanol, formic acid and water [20:2.5:0.5:2 (v/v)] were utilized for the mobile phase. The sample was applied with CAMAG-Linomat IV automated spray on band applicator equipped with a 100µL syringe with standard solutions (5.0µL of each concentration 1mg/mL) are applied to the plates as 10mm bands. The application rate was 10sec/µL, the distance between 4mm, distance from the plate side edge1.5cm and distance from the bottom of the plate 2cm and band length 10mm are the setting for the instrument operation. The scan was performed at 500nm to arrive at peak table, peak display and peak densitogram.

### 3.2 INSTRUMENTATION TECHNIQUES ADOPTED

Electrochemical techniques and Mass loss measurements were chosen for the present investigation

#### 3.2.1 Electrochemical Methods

Potentiodynamic polarisation method (PDP)

Linear Polarisation Resistance Method (LPR)

Electrochemical Impedance Spectroscopy (EIS) Techniques were employed.

| Details of Methods Adopted | Instrument Employed | Surface Area | Frequency Range | IE (%) |
|---|---|---|---|---|
| Electrochemical Impedance and Linear Polarisation method | Frequency Response Analyser (Biologic model v1023 EC Lab software version 10.4) (Reference – calomel, counter – Pt, Working – MS electrode) | $1cm^2$ | Linear Polarization Resistance: 0.02V Vs OCP.The scan rate of 0.125 mV $s^{-1}$ | $\frac{R_{p(inh)}-R_{p(blank)}}{R_{p(inh)}}$ x 100 (3.1) |
| | | | PDP: -0.1 to -1 V at 2 mV/sec | $\frac{I_{corr(blank)}-I_{corr(inh)}}{1_{corr(blank)}}$ x 100 (3.2) |
| | | | Impedance Spectroscopy AC signal 5-10mV and frequency 20 kHz to 0.1Hz at open circuit potential | $\frac{R_{ct(inh)}-R_{ct(blank)}}{R_{ct(inh)}}$ x 100 (3.3)<br>$C_{dl} = \frac{1}{2\pi \times f_{max}} \times R_{ct}$ (3.4)<br>Surface Covarage ($\theta$) = $\frac{C_{dl(blank)}-C_{dl(inh)}}{C_{dl(blank)}}$ x 100 (3.5) |

### 3.2.2 Mass Loss Methods

Mass loss measurements were performed as per **ASTM G1-2** standard procedure. After a particular immersion period, the samples were removed from the experimental setup, dried and reweighed. The experiments were carried out by different concentration, at various time of immersion at room temperature and higher temperature.

| Details of Methods Adopted | Instrument Employed | Surface Area | Inference |
|---|---|---|---|
| Gravimetric Method | Electronic balance with 0. 00001g accuracy | 5X1cm$^2$ | Mass losses are directly converted into the corresponding corrosion rates and inhibition efficiencies |

| Parameter | Equation |
|---|---|
| Corrosion Rate (mpy) | $\frac{K \times W}{DAT}$ (3.6) |
| Inhibitor Efficiency (%) | $\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100$ (3.7) |

### 3.2.3 Adsorption Isotherm

The adsorption behaviour of the inhibitor molecule on the metal surface reflects the mechanism of corrosion inhibition. Adsorption isotherms provide the relation between the coverage of an interface with the adsorbed species. The dependence of surface coverage on concentration is studied through the following adsorption isotherm.

| | |
|---|---|
| Langmuir | **Langmuir, 1917** |
| Temkin | **Temkin,1940** |
| Freundlich | **Freundlich, 1907** |
| Frumkin | **Frumkin, 1964** |
| Flory – Huggins | **Flory-Huggins,1941** |
| Bockris-Swinkel's | **Bockris, 1964** |
| El-Awady | **El-Awady, 1985** |

Various adsorption isotherms are tested graphically to fit a suitable adsorption model for the inhibitor. A statistical estimation of correlation for the adsorption isotherms data was carried out using a statistical package.

### 3.2.4 Kinetic Parameters

**Energy of Activation ($E_a$) and Activation parameters**

Arrhenius equation was applied for calculating $E_a$ and activation parameters **(Radovici, 1965).**

| Parameter | Equation | Parameters obtained |
|---|---|---|
| Corrosion Rate | $A \exp(-E_a/RT)$ (3.8) | $E_a$ |
| log CR | $\log A - E_a/2.303RT$ (3.9) | $E_a$ |
| CR/T | $R/Nh \times \exp(\Delta S_a/R) \times \exp(\Delta H_a/RT)$ (3.10) | $\Delta S_a, \Delta H_a$ |
| log (CR/T) | $\log R/Nh + \Delta S_a/2.303R - \Delta H_a/2.303RT$ (3.11) | $\Delta S_a, \Delta H_a$ |

### 3.2.5 Thermodynamic Parameters

**Free Energy of Adsorption ($\Delta G°_{ads}$)**

The change in free energy of adsorption at high temperature at various concentrations has been calculated using the formula furnished by **Abd-El-Rehim *et al*, 1999.**

| Parameter | Equation |
|---|---|
| log C | $[\log(\theta/1-\theta)] - \log B$ (3.12) |
| $-\Delta G^{o}_{ads}$ | $2.303\,RT\,(1.744 + \log(\theta/1-\theta) - \log C)$ (3.13) |
| $\Delta G^{\circ}_{ads}$ | $\Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads}$ (3.14) |

## 3.3 SURFACE ANALYTICAL TECHNIQUES

| Name of the Technique | Instrument Make | Specimen format | Immersion time | Range | Influence to be ascertained |
|---|---|---|---|---|---|
| UV-Visible spectroscopy (UV) | AU-2701 UV-Vis Double beam spectrophotometer | 1. Crude plant/seaweed extract<br>2. MS/AA in HCl<br>3. AA/1M NaOH | 3h | 200-800nm | Formation of a metal- inhibitor complex |
| FT-IR Spectra photometer | Shimadzu IR Affinity-1S Fourier Transform Infrared Spectrometer | | 3h | 4000-400cm$^{-1}$ | Interaction between the metal and the studied inhibitors |
| SEM , EDX | JEOL MODEL JSM 6390 | 1. Plain<br>2. Blank<br>1. All Inhibitors/MS/AA in HCl<br>3. All Inhibitors/AA/1M NaOH | 3h | - | Surface morphology(SEM), Elemental composition(EDX) |
| X-Ray Diffraction Analysis (XRD) | XPERT-PRO X-ray diffractometer | | 3h | - | Film formed on the metal surface |
| Laser Profilometer | Zeta-20 3D Optical Profiler | | 3h | 100x magnified surface | Surface profiles and pores |

## 3.4 QUANTUM CHEMICAL STUDIES USING MOPAC SOFTWARE

The quantum-chemical study is one of the important methods to interpret the mechanism of reaction that occurs in the molecule and on its electronic structure levels by means of theoretical calculations **(Eddy *et al*, 2018)**. Mopac software was used for the quantum chemical investigation. Several electronic structures parameters were calculated for selected phytochemical constituents of the investigated inhibitors applying the equations given below.

| Structural parameters | Equations | Approximation Methods | Ref |
|---|---|---|---|
| Ionisation potential (IP) | $-E_{HOMO}$ (3.15) | Finite | **Martinez, 2002; Chattaraj *et al*, 2007** |
| Electron Affinity (EA) | $-E_{LUMO}$ (3.16) | | |
| Energy gap ($\Delta E$) | $E_{HOMO} - E_{LUMO}$ (3.17) | | |
| Global Hardness ($\eta$) | $\frac{E_{HOMO} - E_{LUMO}}{2}$ (3.18) | | |
| Global Softness ($\sigma$) | $\frac{1}{2\eta}$ (3.19) | | |
| Electronegativity ($\chi$) | $\frac{IP + EA}{2}$ (3.20) | | |
| Electrophilic Index ($\omega$) | $\frac{\mu^2}{2\eta}$ (3.21) | | |

where, $E_{HOMO}$ = Highest occupied molecular orbital, $E_{LUMO}$ = Lowest unoccupied molecular orbital, $\mu$ = Dipole moment.

The electrons transferred from the inhibitor molecule to the metal atom is given by

$$\Delta N_{Fe} = (\chi_{Fe} - \chi_{inh}) / 2(\eta_{Fe} + \eta_{inh}) \quad (3.22)$$

$$\Delta N_{Al} = (\chi_{Al} - \chi_{inh}) / 2(\eta_{Al} + \eta_{inh}) \quad (3.23)$$

Here$\chi_{Fe}$, $\chi_{Al}$,$\chi i_{nh}$ absolute electro negativity of metal the studied inhibitor molecule and $\eta_{Fe} + \eta_{inh,}\eta_{Al} + \eta_{inh,}$ represented the absolute hardness of metal and the investigated inhibitor molecule.

These quantum chemical investigations were carried out to enable a clear understanding of the inhibitive nature of the investigated extracts.

### 3.5 WORK PLAN

The current investigation executed as per the flow chart depicted (Figure 3.3).


**Figure 3.3. Proposed frame work for methodology**

Results and discussion pertaining to the current study is presented in Chapter 4.