
MATERIALS AND METHODS

The present investigation aims to study “Corrosion monitoring of metal (Mild steel, Aluminium) /1M HCl interface in the presence of *Spathodea campanulata*, *Tecoma capensis* leaf and flower extracts –Chemical, Electrochemical and Theoretical studies” in three modules.

Module I : Identification and selection of inhibitors, metal samples , test media and Characterisation of the selected inhibitors

Module II : Assessment of selected inhibitors as corrosion inhibitors for mild steel and aluminium using Experimental and surface analytical techniques

Module III : Theoretical studies using Hyperchem 7.5

3.1 Module I : Identification and selection of inhibitors, metal samples, test media and Characterisation of the selected inhibitors.

3.1.1 Materials

Mild Steel

Mild steel is a structural material of choice to fabricate various reaction vessels, pipes and so on in sugar, petrochemical, textile, food, paper and marine industries. Mild steel suffers from severe corrosion in aggressive environment which need to be protected.

Aluminium Alloy

Aluminium alloys are extensively used in various industries due to its stability, low density, high thermal and electrical conductivity. One major advantage that works in favour of Aluminium as an indispensable material in fermentation and food industries is the fact that the corrosion product is non toxic to humans. Aluminium alloy 1xxxx series (i.e. Aluminium alloy 1060, 1100 etc.) are used in food and chemical industries.

The metal samples were obtained from a locally available industry. A large sheet of cold rolled mild steel and Aluminium alloy 1100 were utilized for the present study. The composition of the metal specimens were depicted in Figure 3.1. The metal samples, with an active surface of 1cm x 5 cm were used for Mass loss measurements and 1cm x 1cm

specimen for electrochemical measurements. The metal samples were mechanically polished, degreased, washed in double distilled water and dried in warm air. Mass loss experiments and electrochemical measurements were done according to **ASTM G1-03**.

Mild Steel (MS)				
○	C-0.095	Mo-0.030	Fe-99.6	Si-0.013
	Mn-0.192	Cr 0.028		P-0.012
				S-0.016
Aluminium (AA1100)				
○	Be-0.0008	Al-99.0	Si+Fe-0.95	Zn-0.10
	Mn <0.050		Cu-0.050-0.020	

Fig: 3 .1 Chemical composition of metal specimens

3.1.2 Test Solution

Due to tremendous increase in industrial activities, HCl is a vital commodity in the world. It is widely used for de-rusting, pickling, cleaning of refinery equipment and removal of calciferous deposits from boilers, radiators of vehicles, pipeline carrying water or petroleum products, heat exchangers etc. Hydrochloric acid is most commonly used in a pickling bath. Large-scale continuous treatment, such as metal stripping and wire pickling and regeneration of depleted pickling solutions, is one of the advantages in using hydrochloric acid instead of sulphuric acid (**Sastri VS ,2012**). The great advantage of HCl over other acids in cleaning and pickling operations lies in its ability to form metal chlorides, which are extremely soluble in aqueous phase compared to sulphates, nitrates and phosphates. Hence 1M HCl was selected to study the inhibitive effect of SC/TC extracts on corrosion of MS and AA1100. 1M HCl solution was prepared from analytical grade reagent and de-ionized water was used for preparing the solution.

3.1.3 Selection of Inhibitors

The use of natural products otherwise tagged “green corrosion inhibitors” was advocated because it is

- ❖ Inexpensive in nature.
- ❖ Highly recoverable, and the most important thing is, they are not petroleum derivatives.

- ❖ Non toxic in nature.
- ❖ Environmentally acceptable.
- ❖ Readily available in nature.
- ❖ A renewable source for a wide range of inhibitors needed.

Plant extracts are exceptionally rich sources of naturally synthesized organic compounds (e.g. amino and organic acids, glycosides, alkaloids, polyphenols, steroids, flavonoids and tannins) and most of them are known to have inhibitive action (**Fouda et al, 2012**). For the present study, leaves and flower extracts of *Spathodea campanulata* and *Tecoma capensis* were chosen as corrosion inhibitors for the metal specimens under investigation.

3.1.4 Preparation of inhibitor

Spathodea campanulata leaves and flowers (SCL & SCF) and *Tecoma capensis* leaves and flowers (TCL & TCF) were collected from Southern Western Ghats of Coimbatore region and shade dried. The plant specimens were authenticated in Botanical Survey of India (BSI/SRC/5/23/2012-2013/Tech/1708, 1709) and a voucher specimen was deposited in our university for further reference. 50 g of the dried leaves / flowers were refluxed with 500 mL of 1 M HCl for 3 hours and kept overnight. The cooled extracts were filtered and made up to 1000 mL (5% extract).

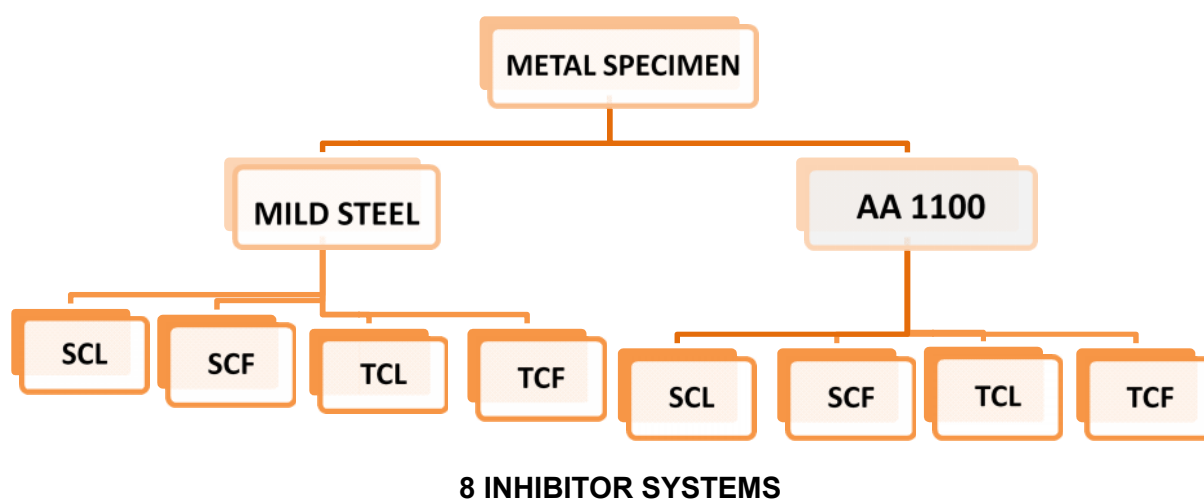


Figure 3.2 Investigated inhibitor systems - MS / AA1100 / Inhibitors / 1M HCl

3.1.5 Assessment of Inhibition efficiency of the extracted crude phytochemicals , available synthetic phytochemicals and plant extracts

Corrosion inhibition studies in 1M HCl medium for MS and AA1100 were not carried out so far using Rutin and Quercetin. To analyse the effectiveness of these crude phytochemicals on corrosion of MS/AA1100, mass loss measurements were carried out for 3 hours immersion period for the highest investigated concentration i.e. 0.7% extract. Similarly the effectiveness of two of the available in house synthetic flavonoids namely rutin and Quercetin were also tested for the same concentration using mass loss measurements for 3 hours immersion period for the highest investigated concentration i.e. 0.7% extract.

The results obtained were compared with that of the investigated inhibitors to ascertain the effectiveness of the investigated plant extracts.

3.1.5.1 Extraction of flavonoids from the selected plants

Fatty constituents from the leaves or stem (coarsely powdered and shade dried) were extracted with petroleum ether by soxhlet extraction. About one and half hour was taken to extract all fatty constituents and solvent became colorless when left for further extraction. Then flavonoids extraction from defatted plant material was performed by a reported method (**Zhu et al, 2010**).

Reflux Condensation Extraction

1 g of defatted leaves and stem were taken and shifted into round bottom flask (100 mL capacity) containing 50 mL aqueous ethanol (70%). After fixing a condenser, it was left for reflux condensation on heating mantle (Tmax-70°C) for two and half hours. Extract was filtered and diluted up to 50 mL. (**Laghari et al, 2011**).

3.1.5.2 Extraction of total terpenoids from the selected plants

100g of plant powder were taken separately and soaked in alcohol for 24 hours. Then filtered, the filtrate was extracted with petroleum ether; the ether extract was treated as total terpenoids (**Ferguson, 1956**)

The presence of the phytochemicals was confirmed using preliminary phytochemical screening tests.

3.1.6 Characterisation of the extract

3.1.6.1 Phyto chemical screening

Phytochemical examinations were carried out for all the extracts as per the standard procedures mentioned. (**Harborne, 1984**) (**Appendix I**)

3.1.6.2 UV-Visible spectroscopy

Investigated plants SC/TC were subjected to UV-VIS Spectrophotometric characterization over 200-600 nm using **PC based double beam spectrophotometer 2202**.

3.1.6.3 FT-IR

FT-IR spectroscopy was carried out to glean information about the functional groups present in the investigated inhibitors. The samples for FT-IR studies were prepared by finely mixing the extract with spectroscopically pure KBr and then pressed by using a die so as to get a fine transparent pellet. The FT-IR spectrum was recorded for stem and leaves of SC/TC extracts with a frequency ranging from 4000 to 400 cm^{-1} using **Perkin Elmer FT-IR spectrophotometer** with the **SOFTWARE – OPUS version 6.5**.

3.1.6.4 GC- MS Analysis

Gas Chromatography (GC) and Mass Spectrometry (MS) make an effective combination for chemical analysis.

In order to identify the individual compounds in the ethanolic distillate of SC/TC extracts gas chromatograph-mass spectrometry (GC-MS) technique was used (**Goh Meng Seng et al, 2006**). The GC-MS instrument was **Fisons 800 Top GC** coupled to **Fisons MD 800 series MS quadrupole mass detector**. The aqueous distillate was desorbed in GC injector at 100°C for 2 minutes in splitless mode and chromatographic separation was carried out on a 30 m x 0.25 mm x 0.25 μm film thickness DB-5MS (5 % phenyl - 95 % methyl polysiloxane) capillary column. The GC oven temperature was programmed from 100°C (held for 1 min.) to 250°C at a rate of 6°C. Helium was used as a carrier gas at a constant flow of 1.0 mL/min. Mass spectra was recorded in electron impact mode at 70 eV, scanning the 20 - 550 m/z range. The interface and source temperature were 200°C and 250°C, respectively. All analyses were carried out in duplicate.

3.2 Module II: Assessment of selected inhibitors as corrosion inhibitors for MS and AA1100 using Experimental and surface analytical techniques

3.2.1 Experimental corrosion techniques

3.2.1.1 Electrochemical measurements

The experiments were performed in a classical three-electrode electrochemical cell. MS / AA1100 specimen of one cm^2 area was used as the working electrode and platinum

electrode as counter electrode and saturated calomel electrode as reference electrode. Prior to each experiment the working electrode surface was polished with emery paper. Biologic system interfaced with an IBM computer and EC lab 10.4 software was used for data acquisition and analysis. The period of immersion was for 30 minutes.

Electrochemical measurements were carried out using the following techniques:

- a. Potentiodynamic polarization method (Tafel polarisation)
- b. Linear polarisation resistance method
- c. Electrochemical impedance spectroscopic technique.

3.2.1.1.1 Potentiodynamic Polarization Method (Tafel Polarisation)

Polarization technique was carried out using EC lab software from a cathodic potential of -0.1 V to an anodic potential of -1 V with respect to corrosion potential at a sweep rate 2 mVs^{-1} . The values of corrosion potential (E_{corr}), corrosion current density (I_{corr}) anodic and cathodic Tafel slopes (b_a and b_c) can be evaluated from the anodic and cathodic region of Tafel plots. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). For Tafel polarization method, the corrosion inhibition efficiency (IE %) was evaluated from the measured I_{corr} values using the relationship (**Abdel Rehim et al, 2001**)

$$\text{IE (\%)} = \frac{I_{\text{corr}}^0 - I_{\text{corr}}^i}{I_{\text{corr}}^0} \times 100 \quad (3.1)$$

Where I_{corr}^0 and I_{corr}^i are values of corrosion current density in absence and in presence of inhibitor, respectively.

3.2.1.1.2 Linear polarisation resistance method:

Polarization resistance values were determined from the slope of the potential-current lines,

$$R_p = A \frac{dE}{di} \quad (3.2)$$

Where A is the surface area of the electrode, dE is change in potential and di is the change in current. The R_p values were used to calculate the inhibition efficiencies, I.E. %, using the relationship (**Moha Outirite et al, 2010**)

$$\text{IE (\%)} = \frac{R_p^i - R_p^0}{R_p^i} \times 100 \quad (3.3)$$

Where R_p^i and R_p^0 are the polarization resistance in the presence and absence of inhibitor, respectively.

3.2.1.1.3 Electrochemical impedance spectroscopic technique

Electrochemical impedance measurements were carried over the frequency 20 kHz to 0.1Hz at open circuit potential. The charge transfer values were obtained from the plots of Z' and Z'' . The value of (R_t+R_s) corresponds to the point where the plot cuts Z' axis at low frequency and R_s corresponds to the point where the plot cuts Z' axis at high frequency. The difference between R_t and R_s gave the charge transfer resistance (R_{ct} values). The C_{dl} values were obtained from the relationship (**Ross Macdonald, 1987**).

$$C_{dl} = \frac{1}{2\pi f_{max}} \times R_{ct} \quad (3.4)$$

Where,

C_{dl} = double layer capacitance

R_{ct} = charge transfer resistance

f_{max} = frequency at Z' value maximum.

Inhibition efficiency can be obtained from Nyquist plot as follows

Where R_{ct}^i and R_{ct}^0 are the charge transfer resistance of MS/AA1100 in the presence and absence of inhibitors respectively.

From the measured double layer capacitance C_{dl} , the surface coverage θ of inhibitor is given by (**Elakadi et al, 2000**).

$$\theta = \frac{C_{dl}^0 - C_{dl}^i}{C_{dl}^0} \quad (3.5)$$

Where C_{dl}^0 and C_{dl}^i are the double layer capacitance values in the presence and absence of inhibitor respectively.

3.2.1.2 Mass loss measurements

Weighed samples in triplicate were immersed in 100 ml of corrodent solution (with and without inhibitor) for a specific time. The specimens were removed and washed with saturated sodium bicarbonate solution and water, dried and reweighed. The experiments were performed in 1M HCl solution without inhibitor and in the presence of the inhibitors at different concentrations: 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6% and 0.7% at various

immersion times: 1/2h, 1h, 3h, 6h, 12h, 24h and at various temperatures 303K, 313K, 323K, 333K, 343K and 353K. Weight loss experiments were done according to ASTM standard procedure (stated in ASTM, G 1-2).

From the obtained mass loss values, corrosion rate, surface coverage and Inhibition efficiencies were calculated using the following equations (Oguzie *et al*, 2005). Where W is the mass loss (g), D is the density of the MS/AA1100 (g/cm^3), A is the area of the specimen (cm^2) and T is the time of exposure (h).

$$\text{IE (\%)} = \frac{\text{CR}_0 - \text{CR}_i}{\text{CR}_0} \times 100 \quad (3.6)$$

$$\theta = \frac{\text{CR}_0 - \text{CR}_i}{\text{CR}_0} \quad (3.7)$$

where CR_0 and CR_i are the corrosion rates in the absence and presence of inhibitor respectively.

3.2.1.2.1 Adsorption isotherms

Adsorption isotherms are usually used to describe the adsorption process. The establishment of adsorption isotherms can provide important clues to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs, as the interaction energy between the H_2O molecule and the metal surface is higher than that between the H_2O molecule and the metal surface (Ambrish Singh *et al*, 2010). Various adsorption isotherms were tested graphically to fit a suitable adsorption for the inhibitor. Data were tested graphically by fitting various isotherms and statistical estimation of correlation for the curve fitting of isotherms was used to investigate the goodness of fit of the isotherms using **SPSS 17 Package**

Name of the Isotherm	Plot	Eqn No
Langmuir	$\log (C/\theta)$ Vs $\log C$	(3.8)
Temkin	θ Vs $\ln C$	(3.9)
Freundlich	$\ln \theta$ Vs $\ln C$	(3.10)
Frumkin	θ Vs $\ln [\theta/C (1 - \theta)]$	(3.11)
Flory- Huggins	$\log (\theta/C)$ Vs $\log (1 - \theta)$	(3.12)
Bockris-Swinkels	$\theta \log (\theta/1 - \theta)$ Vs $\log C$	(3.13)
El-Awady kinetic thermodynamic	$\log (\theta/1 - \theta)$ Vs $\log C$	(3.14)

In order to obtain the adsorption isotherms, the degree of surface coverage (θ) for various concentrations of the inhibitor was calculated according to equation (3.8-3-14).

3.2.1.2.2 Energy of Activation

The relationship between the temperature dependence of present inhibition efficiency (IE %) of an inhibitor and the activation energy found in its presence can be given as follows:

- a) Inhibitor whose IE% decreases with temperature increase, the value of activation energy (E_a) found is greater than that in the uninhibited solution.
- b) Inhibitor whose IE% does not change with temperature variation, the activation energy (E_a) does not change with the presence or absence of inhibitors.
- c) Inhibitor whose IE% increases with temperature increase, the value of activation energy (E_a) found is less than that in the uninhibited solution (**Radovici, 1965**).

The activation energy for the corrosion of MS / AA1100 in 1M HCl was calculated using the Arrhenius equation (**Putilova et al, 1960**).

$$CR = A \exp (-E_a / RT) \quad (3.15)$$

Where CR is the corrosion rate of MS / AA1100, A is Arrhenius or pre-exponential constant, E_a is the activation energy for the corrosion of MS / AA1100, R is the gas constant and T is the temperature. The logarithm of both sides of equation (3.15) yields equation (3.16)

$$\log CR = \log A - E_a / 2.303RT \quad (3.16)$$

Applying the formula $E_a = - 2.303 \times R \times \text{Slope}$

From slopes and intercepts of the Arrhenius plot, the values of E_a and A were computed.

The transition state equation (**Bockris and Reddy, 1977**) (3.17) was used to calculate some thermodynamic parameters (enthalpy of adsorption ΔH_a and entropy of adsorption ΔS_a for the adsorption of the inhibitors on MS / AA1100 surface.

$$CR/T = R/Nh \times \exp (\Delta S_a/R) \times \exp (\Delta H_a/RT) \quad (3.17)$$

Where CR is the corrosion rate, R is the universal gas constant ($8.31434 \text{ JK}^{-1}\text{mol}^{-1}$), T is the absolute temperature, A is the pre-exponential factor, h is Planck's constant ($6.626176 \times 10^{-34} \text{ JS}$) and N is Avogadro's number ($6.02252 \times 10^{23} \text{ mol}^{-1}$).

From the logarithm of both sides of equation (3.17), equation (3.18) is obtained

$$\log (CR/T) = \log R/Nh + \Delta S_a/2.303R - \Delta H_a/2.303RT \quad (3.18)$$

The slopes and intercepts of the transition state plots, the values of ΔS_a and ΔH_a are calculated.

3.2.1.2.3 Thermodynamic Parameters:

ΔG Adsorption:

The free energy of adsorption of the inhibitors on the surface of MS / AA1100 is related to the equilibrium constant of adsorption according to equation (3.19)

$$\log C = [\log (\theta/1 - \theta)] - \log B \quad (3.19)$$

Where $\log B = -1.744 - \Delta G_{ads}/2.303 RT$

$$- \Delta G_{ads}^{\circ} = 2.303 RT (1.744 + \log (\theta/1 - \theta) - \log C) \quad (3.20)$$

where ΔG_{ads}° is the free energy of adsorption θ is the degree of surface coverage and C is the concentration of inhibitor (Vashi and Champaneri, 1997).

ΔH and ΔS Adsorption

The values of enthalpy of adsorption ΔH_{ads}° and entropy of adsorption ΔS_{ads}° were obtained from the basic thermodynamic equation (i.e) Gibb's Helmholtz equation

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (3.21)$$

The values of enthalpy of adsorption ΔH_{ads}° and entropy of adsorption ΔS_{ads}° , were obtained by plotting ΔG_{ads}° (KJ/mol) Vs T (K). The slope of the straight line gives the value of ΔS_{ads}° and the intercept gives the value of ΔH_{ads}° (Putilova *et al*, 1960).

3.2.2 Analysis of the metal surface by various analytical techniques

3.2.2.1 Scanning Electron Microscope

Scanning electron microscopy (SEM) JEOL MODEL JSM 6360 was used to examine the morphology of the metal surface in presence and absence of inhibitors. To understand the morphology on the MS / AA1100 surface in absence and presence of inhibitors, the following cases have been examined.

- ❖ Polished MS / AA1100 specimen.
- ❖ MS / AA1100 specimen dipped in 1M HCl acid medium.
- ❖ MS / AA1100 specimen dipped in 1M HCl acid medium containing 0.7% inhibitors.

3.2.2.2 FTIR Spectral Analysis

FTIR was recorded using **Nexus 670/ Thermo Electron Corporation Spectrometer** which extended from 4000 and 400 cm^{-1} . The interaction between the organic molecules and the metal surface has been studied by FTIR spectra.

3.2.2.3 UV Spectrophotometric measurement

PC based double beam spectrophotometer 2202 was used to confirm the possibility of the metal- inhibitor complex formation on metal surface. UV-visible absorption spectrophotometric method was carried out on the prepared metal samples after immersion in 1M HCl with and without addition of 0.7% inhibitor for 3h.

3.2.2.4 Laser Profilometer

Surface profiles and pores were studied using a **Zeta-20 3D Optical Profiler** was used. MS / AA1100 specimens kept in a vacuum desiccator after the inhibition test were mounted on sample holder occurred under the objective of the Optical Profiler and the 3D photos were taken from the 100x magnified surface via operating program on computer. The MS / AA1100 specimens after exposure to 1 M HCl solution in the absence and presence of SCL / SCF / TCL / TCF extracts for 3h were examined by Zeta 3D Profiler.

Module III: Theoretical studies using Hyperchem 7.5

3.3 Quantum chemical approach

Quantum-chemistry calculations were usually carried out to investigate the mechanism of reaction in the molecule and its electronic structure levels. The structure and electronic parameters can be obtained by means of theoretical calculations (**Ebenso and Ekpe, 1996**).

Quantum chemical calculations were performed using HyperChem 7.5 package. **PM3 and AM1** semi empirical parameterisation methods were used to obtain the geometry optimisation of the selected phytoconstituents. The potential energy minimum was obtained from the steepest descent algorithm and the iteration terminated when the root mean square (RMS) energy gradient reached $4.18 \times 10^{-2} \text{ kJ/A}^\circ \text{ mol}$. Single point calculation was used to determine the molecular properties of the phytoconstituents with minimum energy conformation (**Rahim et al, 2007**). Electronic structure parameters namely, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) that were evaluated for selected phytochemical constituents present in the studied extracts have been correlated with the effectiveness of adsorption type inhibitors.

Ionisation potential (IP) and electron affinity (EA) were calculated from E_{HOMO} and E_{LUMO}

$$\text{Ionisation potential (IP)} = - E_{\text{HOMO}} \quad (3.22)$$

$$\text{Electron Affinity (EA)} = - E_{\text{LUMO}} \quad (3.23)$$

In semiempirical method, the ground state energy $E(\rho)$ of an atom/molecule can be expressed in terms of its electron density. Using the finite difference approximation, the global softness σ can be evaluated. The global hardness η , which is the inverse of the global softness can be evaluated using the following equations: **(Martinez, 2002; Chattaraj et al, 2007)**.

$$\text{Energy gap } (\Delta E) = E_{\text{HOMO}} - E_{\text{LUMO}} \quad (3.24)$$

$$\text{Global Hardness } (\eta) = \frac{E_{\text{HOMO}} - E_{\text{LUMO}}}{2} \quad (3.25)$$

$$\text{Global Softness } (\sigma) = \frac{1}{2\eta} \quad (3.26)$$

$$\text{Electronegativity } (\chi) = \frac{IP + EA}{2} \quad (3.27)$$

$$\text{Electrophilic Index } (\omega) = \frac{\mu^2}{2\eta} \quad (3.28)$$

where, E_{HOMO} = Highest occupied molecular orbital.

E_{LUMO} = Lowest unoccupied molecular orbital.

μ = Dipole moment.

If bulk metal and the inhibitor molecule are brought together, the flow of electrons will occur from the molecule of lower electronegativity to the metal that has higher electronegativity until the value of the chemical potential becomes equal. The fraction of electrons transferred from the inhibitor molecule to the metal atom will then be given by

$$\Delta N_{\text{Fe}} = (\chi_{\text{Fe}} - \chi_{\text{inh}}) / 2(\eta_{\text{Fe}} + \eta_{\text{inh}}) \quad (3.29)$$

$$\Delta N_{\text{Al}} = (\chi_{\text{Al}} - \chi_{\text{inh}}) / 2(\eta_{\text{Al}} + \eta_{\text{inh}}) \quad (3.30)$$

where χ_{Fe} , χ_{Al} , χ_{inh} represent the absolute electronegativity of iron, aluminium and the inhibitor molecule, respectively and $\eta_{\text{Fe}} + \eta_{\text{inh}}$, $\eta_{\text{Al}} + \eta_{\text{inh}}$ represent the absolute hardness of iron, aluminium and the inhibitor molecule.

The aim of this investigation was to compute the relevant electronic properties by means of semiempirical parameterisation to generate accurate information that enables better understanding of the inhibitory behaviour exhibited by SCL/SCF/TCL/TCF components.

3.4 Adopted Conceptual framework for methodology

The adopted conceptual framework of the methodology is proposed in Figure 3.2

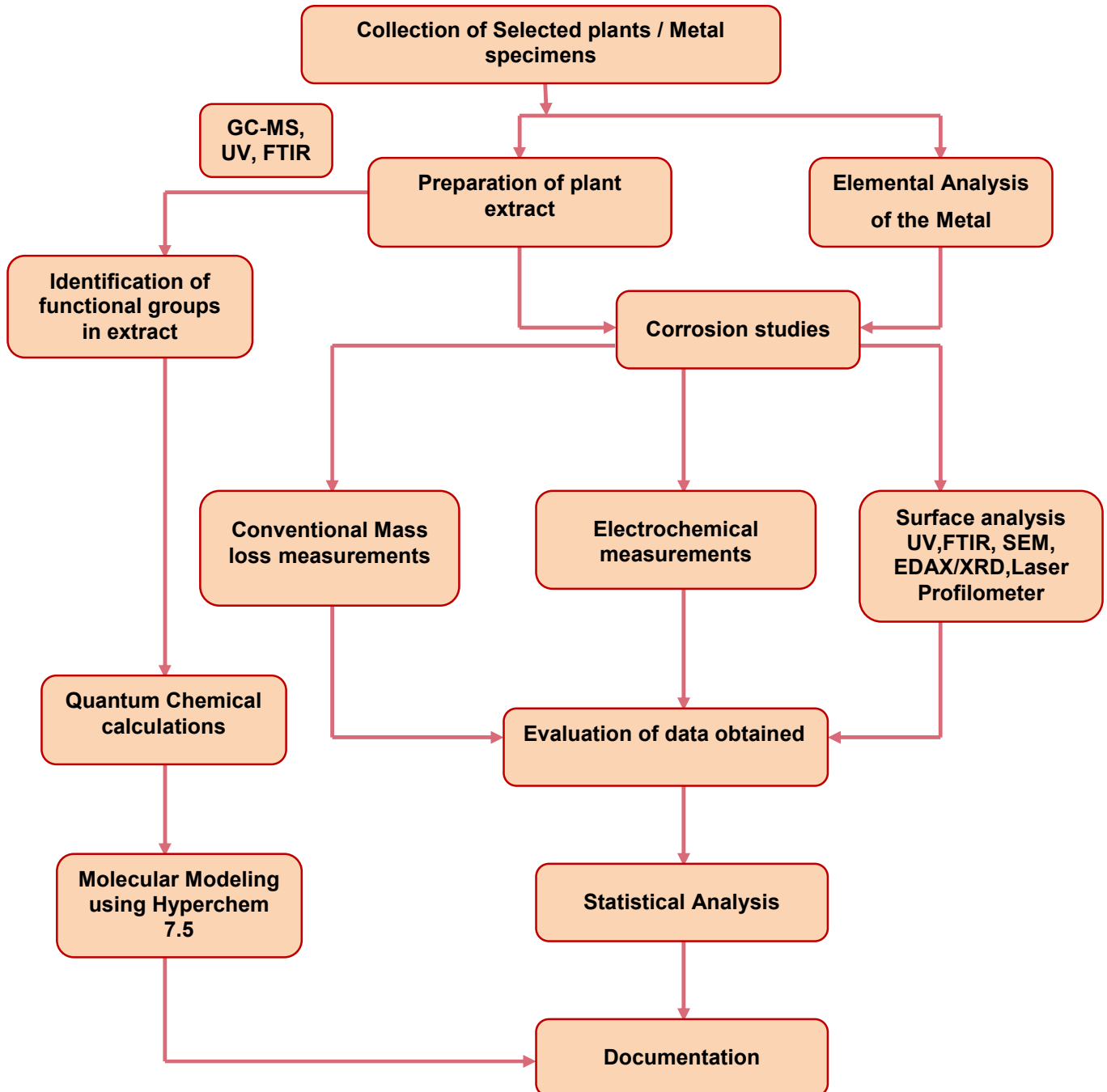


Figure 3.3 Proposed framework of Methodology

The methodology described in this chapter was adopted for the present investigation and the findings are presented and discussed in chapter IV.