MATERIALS AND METHODS

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For any experiment, the materials and methods adopted are the aspects, which decide and determine qualitatively and quantitatively the outcome of the research. In this chapter, the design of the present investigation consisted of the following steps.

- ❖ Selection of samples
- ❖ Choice of acid medium
- ❖ Selection of inhibitor
- ❖ Preparation of the sample
- ❖ Inhibitor preparation
- ❖ Different techniques used
- ❖ Different parameters studied

The study of the corrosion inhibition by acid extracts of *Leaf sheath and Staminate flower of Cocos Nucifera* were carried out using mild steel specimens in 1 M HCl using efficient methods namely, weight loss method and Electrochemical measurements. These methods are used to study corrosion behaviour of mild steel. The surface analysis of mild steel before and after the immersion in the investigated inhibitors was carried out using optical electron microscope and FT-IR technique.

Selection of the sample

Due to low cost and easy availability mild steel is a material of choice to fabricate various reaction vessels, pipes, tanks, etc., in sugar, petrochemical, brewery, food, paper, textile and marine industries. MS suffers from severe corrosion in aggressive environment, which needs to be protected. Hence the study of corrosion inhibition of MS in aqueous aggressive media is the subject of pronounced technological significance. Thus the investigation was carried out using mild steel.

Choice of acid medium

Among the commercially available acids hydrochloric acid is used in nearly all industries and is a vital commodity in our national economy. It is the most important pickling acid. It is used for the removal of oxide from the metallic parts, before coatings, removal of undesirable scales and rust and several other industrial processes. Large scale continuous treatments such as metal stripping, wire pickling, and economic advantages in the regeneration of depleted pickling solution is a factor

of increasing economic and ecological importance. These are the main reasons why hydrochloric acid are selected as the medium.

Selection of the inhibitor

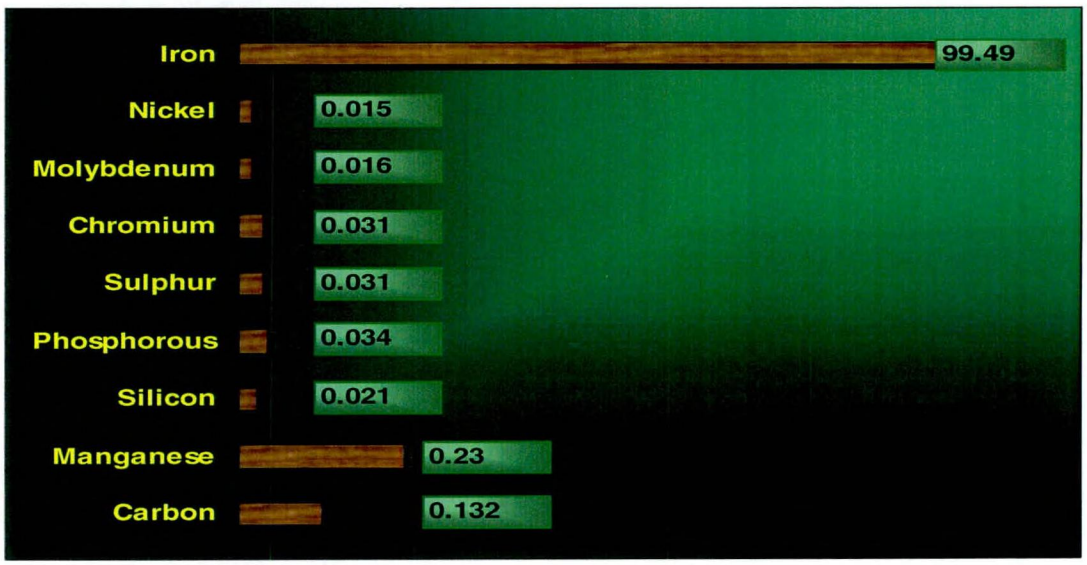
Use of inhibitors is an important task in the protection of metals from corrosion. Till now the majority of metal corrosion inhibitors used is toxic for human being and environment. The choice of the present inhibitors is based on the following considerations:

- Less-expensive
- Non toxic
- Possess no threat to the environment
- Easy availability

For the present study, extract of ***Leaf sheath*** and ***Staminate flower*** of Cocos Nucifera are used as corrosion inhibitor for mild steel in 1 M HCl.

Preparation of the sample

To prepare the mild steel coupons a sheet of commercially available cold rolled mild steel was cut into pieces of the size 5 x1cm $^{2.}$ In these samples, holes were drilled near the upper edge of the coupons in order to immerse it in test solution. Finally the sample was mechanically polished, washed with distilled water and dried at room temperature and stored in desiccator in the absence of moisture for further use. The locally produced mild steel specimens had the following percent nominal composition.



Inhibitor preparation

The inhibitors selected for the study are

- ❖ Leaf sheath of Cocos Nucifera
- ❖ Staminate flower of Cocos Nucifera

The plant materials were collected from the near by residential area.25 gm of Leaf sheath was weighed and fermented for 24 hours whereas the Staminate flower was used as such. The extract were prepared by refluxing the fermented solution along with the crude (or) the flower as the case may be in 500ml of hydrochloric acid for 3hours, kept overnight and filtered to get 5% extract.

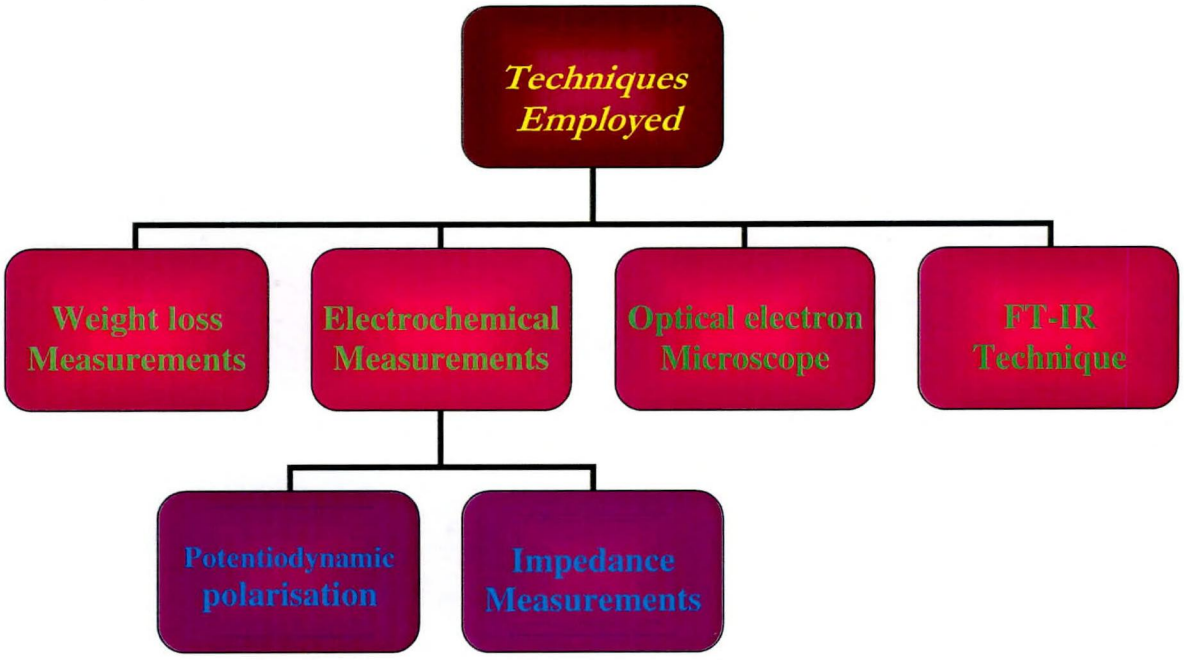
Equipments Used

The following equipments were used for this study.

1. Unibloc Digital balance (4 decimal accuracy).
2. Solartron 1280Z
3. Constant temperature water bath (or) thermostat
4. Optical electron microscope(Carl Zeiss)
5. FT-IR

Techniques Employed

The efficiency of the inhibitor under study was evaluated using the following techniques.



Different Parameters Studied

The different parameters taken into consideration for the present investigation are determination of corrosion rate and inhibition efficiency by weight loss method at

1. Room temperature
2. Higher temperature

Determination of

1. Activation energy (Ea)
2. Enthalpy changes (ΔH)
3. Entropy changes (ΔS)
4. Free energy of adsorption (ΔG)

Weight loss measurement

Weight loss measurement was used to evaluate the corrosion rate and the inhibition efficiency of the inhibitor. The coupons of the mild steel were weighed in Unibloc digital balance. The weighed samples were immersed in 100ml of 1M HCl with and without the presence of inhibitor for various periods of immersion at room temperature and at different temperatures.

The samples were taken out and washed with distilled water, dried and stored in desiccator and weighed. The experiments were carried out in triplicate. From the averaged weight loss, corrosion rate and inhibition efficiency of the inhibitor were calculated.

The parameters used for the present study are given below

1. **Concentration of the inhibitor**: 0.05%, 0.1%, 0.15%, 0.2%, 0.25%, 0.3%, 0.35%, 0.4%, 0.45%
2. **Immersion Time** : 1/2 hr, 1 hr, 3 hr, 6 hr, 12 hr, 24 hr.
3. **Temperature** : 303 K, 315 K, 325 K, 335 K, 345 K, 355 K

The weight loss method was used to evaluate the performance of both the inhibitors under study. It was determined for a period of 10 weeks. A part of the extract was kept at room temperature and the other portion was maintained in refrigerated condition. The same procedure as described for weight loss measurement was followed for an immersion period of 3hrs. This will infer the durability of the investigated inhibitors.

Determination of corrosion rate

Many expressions are available to express corrosion rate. The widely used one is mills per year. The rate of corrosion was calculated using the formula.

$$\text{C.R. (mpy)} = \frac{534W}{DAT}$$

Where

W is the weight loss in g

D is the density of specimen in g/cm^2

A is the area of the specimen in cm^2

T is the exposure time in hr

Determination of percentage of inhibitor efficiency

The inhibitor efficiency was obtained from the following formula.

$$\text{I.E.} = \frac{W_0 - W}{W_0} \times 100$$

Where

I.E. – Inhibitor efficiency in percentage

W_0 – Corrosion rate without inhibitor

W – Corrosion rate with inhibitor

Determination of thermodynamic parameters

The change in free energy (ΔG) of adsorption of the inhibitors can be calculated using the following equation (Abdel.A and El Saied A., 1981).

$$\text{Log C} = \log \left[\frac{\theta}{1 - \theta} \right] - \log B$$

Log C = Log of inhibitor concentration

Log B = $-1.74-(\Delta G/2.303\ RT)$

R = Gas constant 8.134 J/mole

T = Temperature

C = Concentration of the inhibitor

θ = Surface coverage

Adsorption isotherm

Corrosion inhibition is a surface process with specific adsorption of inhibitor on the metal surface. In recent years, attempts have been made to understand the nature of interaction between the inhibitor and metal surface in terms of adsorption isotherm. The knowledge of the adsorption behaviour of the inhibitor is important for the definition of its active mechanism. For this reason, the dependence of surface coverage on concentration is studied through the following adsorption isotherms.

Langmuir[(log θ/1- θ)Vs log C]

Temkin (θ Vs log C)

Surface Coverage (θ)

The degree of surface coverage (θ) for different concentration of the inhibitor in acid media have been evaluated from weight loss experiments using the equation,

$$\theta = \frac{Wo-W}{Wo}$$

Where,

Wo and W stand for the weight loss in the absence and presence of the inhibitor respectively.

Kinetic and Thermodynamic Parameters

The activation energy at different concentration of the inhibitor at various temperatures was determined by plotting log CR Vs 1/T (Arrhenius plot). From the slope of the plot, activation energy (Ea) was calculated using the following formula.

$$E_a = -2.303 \times R \times \text{slope of the Arrhenius plot (KJ/mole)}$$

Where R=gas constant 8.34 J/mole

Change in Free Energy of Adsorption

The change in free energy of adsorption at higher temperatures at various concentrations has been calculated using the formula, (Abdel.A and A.El Saied, 1981).

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

Where,

R = 8.314 joules/mole

T = Temperature in Kelvin

C = Concentration

θ = Surface coverage

Determination of Enthalpy and Entropy Change

The change in enthalpy and change in entropy of adsorption for different concentrations at various temperatures was determined by plotting -ΔG Vs Temperature in Kelvin. The intercept obtained from the graph shows the change in enthalpy (ΔH) KJ/ mole and the slope gives change in entropy (ΔS) in KJ/mole.

According to Gibbs- Helmholtz relation,

$$\Delta G = \Delta H - T\Delta S$$

Where,

ΔG = changes in free energy of adsorption

ΔS = changes in entropy

ΔH = changes in enthalpy

Electrochemical measurements

Electrochemical studies were carried out in the absence and presence of extract using conventional three electrode cell with larger area platinum foil as counter electrode, MS as working electrode and saturated calomel electrode (SCE) as reference electrode. Solatron Electrochemical analyzer model (1284 Z) interfaced with an IBM computer and Z plot and Corrware softwares were used for data acquisition and analysis.

Potentiodynamic polarisation measurement

Potentiodynamic polarisation studies were carried out using Solartron 1284 Z. 100 mL of 1 M HCl without and with different concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode was then introduced. The potentiodynamic polarisation studies were carried out over a potential range of –200 mv to +1500 mv with respect to reference electrode and its current response was measured at the scan rate of 1 mv / sec^{-1}.

Values of corrosion currents were obtained by Tafel extrapolation method. Applied potential *vs.* current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants 'ba' and 'bc' respectively. According to the Stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$Icorr = \frac{ba \times bc}{2.303\,(ba + bc)} \times \frac{1}{Rp}$$

Where, Rp is polarization resistance.

Impedance Measurements

Impedance measurements were carried out at various corrosion potential. An ac sine wave of 10 mV amplitude was applied to the electrode. The frequency which is varied from 10 KHz to 100 MHz was superimposed at the open circuit potential. The results are presented in the form of Nyquist and Bode plots. From the Nyquist plots and Bode plots, the charge Transfer Resistance (R_{ct}) and Double Layer Capacitance (C_{dl}) values were calculated.

The charge transfer resistance values were obtained from the plots of Z' Vs Z". The value of (R_t) corresponds to the point where plot cuts Z' axis at low frequency and R_s corresponds to the point where the plot cuts Z' axis at higher frequency. The difference between R_t and R_s gives the charge transfer resistance (R_{ct}) values.

Determination of Inhibition Efficiency

The inhibitor efficiency was obtained from all the parameters measured namely I_{corr}, R_p, R_{ct} and surface coverage, θ calculated from C_{dl} using the following relationships

Determination of inhibition efficiency by Tafel method

$$\mathbf{IE} = \frac{\mathbf{I_{corr\,(Blank)} - I_{corr\,(Inhibitor)}}}{\mathbf{I_{corr\,(Blank)}}} \times \mathbf{100}$$

$I_{corr\,(Inhibitor)}$ - Corrosion current in the presence of inhibitor.

$I_{corr\,(Blank)}$ - Corrosion current in the absence of inhibitor.

By LPR (Linear Polarization Resistance) method

$$\mathbf{IE} = \frac{\mathbf{R_{p(inhibitor)} - R_{p\,(Blank)}}}{\mathbf{R_{p\,(inhibitor)}}} \times \mathbf{100}$$

$\mathbf{R_{p(inhibitor)}}$ - Polarisation resistance in presence of inhibitor

$\mathbf{R_{p\,(Blank)}}$ - Polarisation resistance in absence of inhibitor

$$IE = \frac{R_{ct(inhibitor)} - R_{ct(Blank)}}{R_{ct(inhibitor)}} \times 100$$

$R_{ct(inhibitor)}$ - Charge transfer resistance in presence of inhibitor.

$R_{ct(Blank)}$ - Charge transfer resistance in absence of inhibitor.

$$\theta = 1 - \frac{C_{dl(inhibitor)}}{C_{dl(Blank)}}$$ **(Dutian Bao et al., 1997)**

$C_{dl(inhibitor)}$ - Double layer capacitance in presence of inhibitor.

$C_{dl(Blank)}$ - Double layer capacitance in absence of inhibitor.

Surface examination

To analyse the mechanism of inhibition, the surface of mild steel in the absence and presence of the investigated inhibitors was analysed using optical electron microscope.

Optical electron microscope

The mild steel specimens were immersed in maximum concentration of test solutions for a period of 3 hr. The specimens were taken out, dried and investigated using Optical electron microscope (Carl Zeiss) to examine the surface of mild steel in the absence and presence of the inhibitors.

FT-IR Technique

The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an "unknown" with previously recorded reference spectra. This is basis of computer – based spectral searching. In the absence of a suitable reference database, it is possible to effect a basic interpretation of the spectrum from first principles, leading to characterization, and possibly even identification of an unknown sample.

In order to observe the presence of plant constituents adsorbed on the metal surface FT-IR technique was followed.

- The metal specimens were immersed in the test solution for 24hours at a concentration of 0.3 for both the inhibitors.
- It was then dried using acetone and scratched, a powder was obtained.
- The leaf sheath and staminate flower extract was dried in a water bath so that the acid got evaporated. The powders thus obtained were used for analysis.