Review of Literature
2. REVIEW OF LITERATURE

Corrosion science is the study of the chemical and metallurgical processes that occur during corrosion. Only a sound knowledge of the process of corrosion with its kinetics and mechanistic aspects help to mitigate the problem effectively. An insight into the mechanism of the corrosion leads to better understanding of the process involved enabling the development of better techniques for corrosion control, since corrosion science is essentially a practical or applied science. Hence the review part aims to cover these aspects and its related studies done by many workers.

2.1 Forms of corrosion

Corrosion manifests in different forms. It is desirable to know the form of corrosion that is taking place under given environmental conditions. Some of the eight forms of corrosion are unique, but all of them are more or less interrelated (Mars G.Fontana, et.al., 1982)-The eight forms are:

- Uniform corrosion
- Galvanic corrosion
- Pitting corrosion
- Crevice corrosion
- Erosion corrosion
- Cavitation corrosion
- Stress cracking corrosion
- Stray current corrosion

2.2 Corrosion principle

Corrosion resistance of a material depends on many factors. To understand corrosion principles one should have knowledge of several disciplines (Raj Narayanan, 1988). Thermodynamic principles can indicate the spontaneous direction of a chemical reaction. Electrochemical principles including electrode kinetics can yield valuable information on the rate of different corrosion reactions. Metallurgical, physical and chemical principles also help to understand corrosion behavior of metal. Electrochemical and thermodynamic principles have the maximum importance in the corrosion behavior of materials.
2.2.1 Thermodynamic principles

Corrosion occurs in a given environment because of thermodynamic instability of a material in that environment. Thermodynamic approach has been widely used to explain and understand the corrosion problems. The study of energy changes associated with corrosion reactions comes with the scope of thermodynamics.

Metals are good electrical conductors and their corrosion is usually electrochemical in nature. Corrosion reactions can therefore be considered as electrochemical cells which produce electrical energy due to electrochemical reactions. The electrical energy available is equal to the potential difference E and quantity of electricity Q. Therefore,

\[ \text{Net work done by cell} = Q \times E \]

where Q is equal to one faraday (F) for each gram equivalent of the reactants. Any work performed by the cell can be accomplished only at the expense of a decrease in free energy of the cell reaction. Thus

\[ \Delta G = -nFE \]

where \(\Delta G\) is the free energy changes in joules, n is the number of electrons involved in the reaction, E is the emf of cell in volts and F is the Faraday constant.

2.2.1.1 Potential – pH diagram

M. Pourbaix devised a compact summary of thermodynamic data in the form of potential – pH diagram, in which the potential is on the Y-axis and with pH of the electrolytic medium is on the X-axis. These diagrams are particularly important in the study of corrosion of metals in aqueous media and electro deposition of metals and oxides. The simplified potential - pH diagram for iron is shown in Fig. 2.1.

These diagrams are used for predicting:

- Spontaneous direction of reaction.
- Stability and composition of corrosion products.
- Environmental changes which will prevent or reduce corrosive attack.
According to the E/pH diagram (fig.2.2), the following methods can be used to reduce corrosion.

* By lowering the electrode potential down into the region of immunity, e.g., by cathodic protection.
* By raising the electrode potential up into the region of passivity, e.g., by anodic protection
* By raising the pH or alkalinity of the solution so that a passive film is formed.

The thermodynamic principles give only the corrosion tendency in terms of potentials when the electrochemical reactions are at equilibrium (Denny A. Jones, 1996). The corroding systems are, however, not at equilibrium and therefore thermodynamic calculations cannot be applied to corrosion rates.
2.2.2 Electrochemical principle

A deeper knowledge of understanding the kinetics of the corrosion phenomena is provided by the theory of mixed potentials. The mixed potential theory together with the kinetic equations constitutes the basis of modern electrode-kinetics theory.

2.2.2.1 Evans diagram

Polarization diagrams of corroding metals, often called as an Evans diagrams are graphs of potential versus log current density. They were originally developed by U.R. Evans, recognized the usefulness of such diagrams for predicting corrosion behavior of metals (Herbert H. Uhlig, et al. 1991). In this system (Fig:2.3), the oxidation reaction may be the dissolution of metal, \( M \rightarrow M^{z+} + ze^- \), and the reduction reaction may be symbolized as \( R^{n-} + ne^- \rightarrow R \).

For any corroding metal, the chemical equivalents of metal going into solution at the anodic sites are equal to the chemical equivalents of reduction products produced at cathodic sites. In terms of corrosion current for a given area of metal surface, \( I_a = I_c \). The corresponding current density at anodic areas depends on the fraction of metal surface \( A_a \), that is anode, and, similarly, \( i_c \) depends on \( A_c \). In general, relation for any anode–cathode ratio \( I_{appl} = I_a - I_c \) can be translated to corresponding current densities \( i_{appl} = i_a - i_c \).

When the electrode is polarized at sufficiently high current densities usually adequate to shift \( \Phi_{corr} > 100 mV \), the reverse or 'back' reactions become negligible and, depending on the direction of \( I_{appl} \), the metal surface acts either as all anode or all cathode. Accordingly, for anodic polarization, \( i_{appl} \geq i_a \) and, similarly, for cathodic polarization, \( i_{appl} \leq i_c \). By extrapolating from the anodic Tafel region to the reversible (equilibrium) anode potential \( \Phi_A \), the exchange current density \( i_{oa} \) for the reaction \( M^{z+} + ze^- \rightarrow M \) is determined, that is, the equal rate of oxidation and reduction reactions expressed as a current density. Similarly, by extrapolating from the Tafel region to the reversible potential \( \Phi_c \), the exchange current density \( i_{oc} \) for the cathodic reaction is determined. By extrapolating from either the anodic or cathodic Tafel region to the corrosion potential \( \Phi_{corr} \), where \( i_c = i_a \), the corrosion rate can be determined.
From the mixed potential theory, it is clear that the corrosion rate of a metal \( (i_{\text{corr}}) \) is affected by the polarization of the electrode.

2.3 Theories of Corrosion inhibition

Till today there is no single generally accepted view on the mechanism of the protective action of inhibitors. There exists a multitude of ideas, often diametrically opposed, regarding the protective action in acid media and neutral aqueous solutions, and hundreds of investigations have been devoted to the elucidation of this problem during the past decades.

The concept of zero-charge potentials was introduced by Frumkin, who proposed that ionic adsorption depends on the sign and magnitude of the surface charge at the metal-electrolyte interface. If under the corrosion conditions the metal surface is negatively charged, adsorption of cations is most probable, but if the surface carries a positive charge, adsorption of anions takes place. If the surface is not charged, or if the charge on it is small, adsorption of both molecules and ions is possible. The sign of the surface charge can be determined by comparing the electrode potential of the metal under the conditions of corrosion (\( \epsilon \)) and in the absence of a charge (\( \epsilon_0 \), the zero-charge potential). The concept of zero-charge potentials may be quite fruitful, however, in the further development of a theory of inhibitive action.

Theories for the protective action of inhibitors have been discussed here.

- Adsorption theory
- Hydrogen over voltage theory
- Film theory and
- Quantum chemical approach
2.3.1 Adsorption theory

According to adsorption theory, inhibitors are adsorbed on the metal surface forming a protective layer. The mode of adsorption leads to its classification as physical adsorption and chemical adsorption.

It is the result of electrostatic attractive force between inhibiting organic ions or dipoles and the electrically charged surface of the metal. The surface charge of the metal is due to the electric field at the outer Helmholtz plane of the electrical double layer existing at the metal/solution interface. The surface coverage can be obtained from the potential of the metal \( E_{\text{corr}} \) vs its zero-charge potential \( E_{q=0} \) (I.I.Antropov, 1962). When the difference \( E_{\text{corr}} - E_{q=0} = \phi \) is negative, cation adsorption is favoured. Adsorption of anion is favoured if \( \phi \) is positive.

Structural parameters such as hydrocarbon chain length, nature and position of the substituents in the organic rings also influence the degree of inhibition. Electrostatic adsorption process has low activation energy and it proves to be relatively independent of temperature. Electrochemical adsorption depends on

- The electrical characters of organic inhibitors
- The position of corrosion potential with respect to the zero charge potential and
- The type of adsorbable anion present in the aggressive solution.

2.3.2 Film theory

It says that effective protection of metal by metals by inhibitor is due to the formation, on the metal surface, of a layer of insoluble or slightly soluble corrosion products.

2.3.3 Hydrogen over voltage theory

This theory postulates that inhibitors which are adsorbed on the metal retard either anodic or cathodic or in some cases both the reactions. This leads to rapid polarization of anodic or cathodic sites and thus overall corrosion rate is retarded.

2.3.4 Quantum chemical approach

Direct interaction between surface metal atoms and the outermost electrons of the organic molecules sometimes leads to chemisorption phenomenon and thereby causes inhibition. Chemisorption of organic inhibitors may be taken as a linear
combination of the participating wave function of the inhibitor molecule as well as the surface metal atoms. The binding energy of the metal-inhibitor adduct may thus be correlated to the energy difference between the lowest free molecular orbital (LFMO) of the metal atoms and the highest occupied molecular orbital (HOMO) of the inhibitor.

2.4 Mechanism of inhibitor action in acid corrosion process

The effect of adsorbed inhibitor on the acid corrosion of metals is to retard either the anodic dissolution reaction of the metal, the cathodic hydrogen evolution reaction, or both. This action may occur by means of different mechanisms involving:

- Changes in the electrical double layer
- Formation of a physical barrier
- Reduction of metal reactivity
- Participation of the inhibitor in partial electrochemical reactions.

2.4.1 Changes in the electrical double layer

Corrosion inhibition is related to changes in the structures of the electrical double layer at the metal/solution interface that takes place as a consequence of the electrostatic adsorption of ionized inhibiting species. Adsorption of organic cations, such as quaternary ammonium ions (L.I.Antroprov, et.al., 1971) or pyridinium ions, to the iron surface in acid solution results in positive adsorption potential jump. This positive shift in the potential shows that the rate of hydrogen evolution reaction is reduced. This is realized in completely deaerated acid solutions. Conversely, in aerated acid solutions in the presence of organic cations which inhibit hydrogen evolution, the contribution of the oxygen reduction reaction may become important. This is to be attributed to the fact that the diffusion current of oxygen reduction should not be influenced by the presence of selective inhibitors which retard hydrogen evolution much more effectively than the oxygen reduction reaction. Adsorption of anion on iron surfaces in acid solutions is observed to stimulate the hydrogen evolution reaction which results in negative adsorption potential jump.

2.4.2 Formation of physical barrier

Some classes of inhibitors such as sulfoxides, acetylene derivatives or substances with a high number of carbon atoms in the hydrocarbon chain are able to
form multimolecular layer on the metal surface. The resulting barrier is quite independent of the nature of adsorption forces between the inhibitor molecule and the metal surface. Chemisorption bonds, π-electron interaction, hydrogen bonding and attractive lateral interactions may be involved. The formed layer interferes with the diffusion of ions to or from the metal surface. The hindering of mass transport causes inhibition of corrosion reaction.

2.4.3 Reduction of metal reactivity

The inhibition mechanism related to the reduction of the reactivity of the metal does not necessarily involve complete coverage of the metal surface by the adsorbed inhibitor. Higher efficiencies are to be expected where stronger bonds such as chemisorption bonds are established. According to this mechanism, the inhibitor adsorbs on sites with respect to partial electrochemical reactions. A reduction of either the anodic or the cathodic reaction or both arises from the blockage of the corresponding active sites. Clearly, the reaction rates will be reduced in proportion to the extent to which the active sites are covered by the adsorbed inhibitors. This type of surface coverage does not change the reaction mechanism. The polarization curves are shifted towards lower current density values without modification in the Tafel slopes.

2.4.4 Precipitation of the inhibitor in partial electrochemical reactions

Both the anodic reaction of metal dissolution and cathodic reaction of hydrogen evolution proceed by steps with the formation of adsorbed intermediates on the metal surface. According to this mechanism of action, the adsorbed additive may participate in the intermediate formation, of promoting either a decrease in or a stimulation of the electrode reaction depending on the stability of the adsorbed surface complex. A decrease in the corrosion rate of a metal by an inhibitor indicates the formation of a stable complex on the metal surface.

The review provides knowledge about the past investigations on inhibition of corrosion of metals in acidic media. It is based on the following major aspects.

(1) Chemical compounds as inhibitors in acid medium of mild steel and aluminium.

(2) Natural product as inhibitors for various metals.
2.5 CHEMICAL COMPOUNDS AS PICKLING INHIBITORS IN ACID MEDIA

Pickling is an essential step in metal surface treatment, to remove rust or iron oxide scale from iron or steel before subsequent processing, such as extrusion, rolling, galvanizing, and other techniques. Technical quality HCl at typically 18% concentration is the most commonly used pickling agent for the pickling of carbon steel grades.

During pickling, reactions taking place between mild steel and hydrochloric acid are

\[
\begin{align*}
\text{FeO} + 2\text{HCl} & \rightarrow \text{FeCl}_2 + \text{H}_2\text{O} \quad \text{(in aerated solution)} \\ 2.1 \\
\text{Fe}_2\text{O}_3 + 6\text{HCl} & \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \quad 2.2 \\
\text{Fe}_3\text{O}_4 + 8\text{HCl} & \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O} \quad 2.3 \\
\text{Fe} + 2\text{HCl} & \rightarrow \text{FeCl}_2 + \text{H}_2 \quad \text{(in de-aerated solution)} \quad 2.4 \\
\end{align*}
\]

Reactions taking place between mild steel and sulphuric acid are

\[
\begin{align*}
\text{FeO} + \text{H}_2\text{SO}_4 & \rightarrow \text{FeSO}_4 + \text{H}_2\text{O} \quad \text{(2.5)} \\
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 & \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} \quad \text{(2.6)} \\
\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{SO}_4 & \rightarrow \text{FeSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \quad \text{(2.7)} \\
\text{Fe} + \text{H}_2\text{SO}_4 & \rightarrow \text{FeSO}_4 + \text{H}_2 \quad \text{(2.8)}
\end{align*}
\]

The spent acid had long been re-used as ferrous chloride solutions, but a high heavy metal level in the pickling liquor has decreased this practice. During pickling process, acids not only remove unwanted contaminants from surface but also removes some base metal, to control this loss of base metal, inhibitors are used.

Required properties of acid pickling inhibitor are:

- Effective inhibition of metal dissolution
- No over pickling in the presence of higher iron salt contents
- No delay of the pickling process
- Effective at low concentrations
- Effective also at higher temperatures
- Effective inhibition of hydrogen take-up by the metal
- Good surfactant and foaming characteristics
The study of organic compounds as corrosion inhibitors is a subject of continuing interest due to its usefulness in several industries. However, the selection of an inhibitor for a particular system is a difficult task due to the specificity and selectivity of inhibitors and large varieties of corrosion systems. For the inhibition of acid corrosion, the number of suitable substances is huge as they may be heterocyclic containing oxygen, sulphur or nitrogen, or high molecular weight alcohols, aldehydes, amines, amides, fatty acids, and their derivatives, Thiourea and its derivatives, Quarternary nitrogen compounds etc. Some of such studies are reviewed.

2.5.1 Inhibitors used for mild steel

The inhibitive efficiency of selected oxadiazoles of fatty acids; namely 2-heptadecene-5-mercapto-1-oxa-3,4-diazole (HMOD); 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD); and 2-decane-5-mercapto-1-oxa-3,4-diazole (DMOD) were synthesized and their influence on the corrosion of mild steel in 20% formic acid (HCOOH) has been investigated by weight loss and potentiodynamic polarization techniques. All the compounds showed good inhibition efficiency (I.E %) in formic acid solution. Adsorption followed Langmuir adsorption isotherm. Potentiodynamic polarization revealed mixed type inhibitors. (M.Quraishi, et al., 2006)

Four heterocyclic compounds namely 2-amino-1,3,4-thiadiazoles (AT), 5-Methyl-2-amino-1,3,4-thiadiazoles (MAT), 5-Ethyl-2-amino-1,3,4-thiadiazoles (EAT) and 5-Propyl-2-amino-1,3,4-thiadiazoles (PAT) were synthesized and their influence on the inhibition of corrosion of mild steel (MS) in 0.5M H₂SO₄ has been investigated by weight loss and potentiodynamic polarization techniques (Quaraishi et al., 2006). All the four inhibitors showed the good inhibition efficiency. The adsorption of the compounds was found to follow Langmuir's adsorption isotherm.

Y. Abboud et al., (2005) has synthesized 2,2'-bis(benzimidazole) and its inhibiting action on the corrosion of mild steel in acidic bath (1M HCl) was tested by weight loss test and potentiodynamic polarization. The result of the investigation showed that the compound has fairly good inhibiting properties and was mixed type inhibitor.

Harek et al., (2004) has investigated oxalic N-phenylhydrazide N-phenyl hydrazide N'-phenyl thio semi carbazide (OPHPT) as inhibitor for the corrosion of mild steel in HCl by mass loss, potentiodynamic and polarization resistance
measurements. The adsorption of OPHPT was described by Langmuir and Temkin adsorption isotherm. Polarization curves showed the inhibitor as a mixed type.

Eight diazoles have been studied as corrosion inhibitors of mild steel in 1M HCl by gravimetric and polarization techniques. A better performance was noticed in HCl. The adsorption followed the Frumkin isotherm. (Popova et al., 2004).

Quaraishi et al., (2004) has synthesized and evaluated the inhibiting action of four organic inhibitors namely AMMT, AEMT, APMT and ABMT on corrosion of mild steel in aqueous solutions containing 20% formic acid and 20% acetic acid by weight loss and potentiodynamic polarization methods. The adsorption of these compounds was found to obey Langmuir adsorption isotherm. The potentiodynamic polarization experiments revealed that all the compounds are mixed type inhibitors.

The performances of eight low-toxic organic inhibitors (amine, carboxylic acid and sulfoxide) have been evaluated as corrosion inhibitor on the corrosion of mild steel in acid media by electrochemical corrosion experiments. The experimental results showed that carboxylic acid had the best inhibition performance (as high as 92%) followed by sulfoxide and long chain aliphatic amine. Their performances depended on inhibitor concentration and temperature. (Amit Chakma et al., 2001)

The corrosion inhibition character of thiosemicarbride and its derivatives for Carbon steel in 2M HCl by weight loss and potentiostatic polarization techniques has been studied. The inhibition efficiency found by both methods was in very good agreement (El Shafei et al., 2001).

The inhibitive nature of a mixture of water soluble compounds on mild steel in 0.2M HCl has been carried out by using weight loss and polarization methods (Sivakamasundari.S et al., 2001). The corrosion rate of mild steel decreased with increase in concentration of the inhibitor. Polarization data showed that the inhibitor behaved as cathodic.

The influence of dimethyl sulphoxide on corrosion inhibition of mild steel 1N HCl and 1N H$_2$SO$_4$ by weight loss measurements and polarization studies has been studied. It was found to perform as a mixed type corrosion inhibitor. It was found to obey Temkin's adsorption isotherm (Madhavan et al., 2001).

The corrosion inhibition of mild steel in 2M HCl solution by tributylamine was investigated by using the impedance technique. The inhibitor mechanism was treated
as a substitutional adsorption process according to Flory-Huggins, Dhar-Flory-Huggins and Bockris-Swinkels isotherms. (Bastidas et al., 2000).

The influence of thiophene and five of its substituted derivatives on the corrosion inhibition of steel in 0.5M H₂SO₄ solutions was studied using weight-loss, electrochemical polarisation, and impedance measurements. 5-tert-butoxythiophene-2-carbaldehyde phenylhydrazone (TBCP) is the best inhibitor and its inhibition efficiency increases with increase in concentration to attain 87% at 5×10⁻³ M. Potentiodynamic polarisation studies clearly reveal that it acts essentially as a cathodic inhibitor. (Bouklah, M, et al., 2005)

Four Quaternary ammonium bromides of different heterocyclic compounds were investigated as corrosion inhibitors of mild steel in 1M HCl and 0.5M H₂SO₄ using potentiodynamic polarization and gravimetric methods. The adsorption of the inhibitors was well described by the Frumkin and Langmuir adsorption isotherms. The best inhibitive properties have 1-(Carbamoylethyl)-4-methylpyrindinium bromide. (A.Popova et al., 2007)

Two 2-mercaptobenzothiazole derivatives were synthesized and their inhibition efficiency was tested by weight loss method and the surface analysis was performed by SEM. Results showed that the two inhibitors could inhibit the corrosion of N80 steel in simulated solution significantly. (Junping Zhang, et al., 2007)

Three Schiff base compounds were synthesized and their efficiencies have been investigated by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The inhibition efficiencies obtained from all methods employed are in good agreement. Studies showed all three compounds to act as mixed type inhibitors. (Canan Kustu, et al., 2007)

The inhibitory effect of 4-hydroxy benzo-2H [1] pyran-one has been synthesized and tested for inhibition against corrosion of mild steel in 0.5M H₂SO₄ by weight loss, electrochemical techniques and IR spectra. The inhibition efficiency has been found to control corrosion through mixed mode. It has been proposed that the inhibition is due to adsorption. (R.Shyamala, et al., 2006)

The effect of halide ions on the corrosion behaviour of mild steel in sulphuric acid medium by weight loss and polarization studies has been carried out by Saratha, et al., (2002). The results revealed that corrosion of mild steel was more in acid medium
without halide ions. Halide ions reduce the rate of corrosion and the inhibition efficiency was found to be in the order iodide > bromide > chloride.

2.5.2 Inhibitors used for aluminium

Aluminium is a reactive metal with a standard electrode potential of -1.66V vs. SCE. Pure aluminium is soft and weak; it is alloyed therefore largely to obtain increased strength. Code for major alloying element: \textbf{1XXX, > 99.00\% Al}; (Aluminium Standards and Data 1978 Metric SI, P.93, The Aluminium Association, Inc., Washington, D.C., 1978) was used in this study (Herbert H.Uhlig, \textit{et al.}, 1991). Its resistance against corrosion can be attributed to a rapidly formed thin and highly protective barrier oxide film of thickness about 50-100nm which separates the bare metal from the corrosive environment \((\text{AlOOH} + \text{Al}_2\text{O}_3.3\text{H}_2\text{O})\). Films may thus range from thin transparent oxides to thicker visible films, which may be compact, adherent and protective or non protective. Table 2.1 shows the variations in the nature and thickness of the product formed on aluminium under different conditions.

\begin{table}[h]
\centering
\caption{Variations in the nature and thickness of the product formed on aluminium under different conditions}
\begin{tabular}{|l|l|l|}
\hline
\textbf{Formation condition} & \textbf{Nature of oxide film} & \textbf{Thickness (nm)} \\
\hline
Dry air or \(\text{O}_2\) & \text{Amorphous Al}_2\text{O}_3 & 1-2 \\
Humid atmosphere & \text{AlOOH} + \text{Al}_2\text{O}_3.3\text{H}_2\text{O} & 50-100 \\
Boiling water & \text{AlOOH or Al}_2\text{O}_3.3\text{H}_2\text{O} & 500-2000 \\
Chemical Conversion & \text{AlOOH} + \text{anions of solution} & 1000-5000 \\
Anodic Oxidation & \text{Amorphous + crystalline Al}_2\text{O}_3 + \text{anions of solution} & 1000 - 3000 \\
(bARRIER films) & & \\
\hline
\end{tabular}
\end{table}

Protection by this film is very good in environments with pH between 4 and 9, while above and below this range, aluminium exhibits uniform attack. In contrast, a porous and poorly protecting oxide film forms in non-oxidizing acid solutions as like HCl. When chloride ions are present, migration of \(\text{Cl}^-\) into the oxide layer is believed to take place, thereby lowering the resistance to outward migration of \(\text{Al}^{3+}\) and
initiating pitting. The first step of aluminium corrosion, therefore, is attack of the oxide layer by chloride ions leaving a bare aluminium surface. In the propagation stage, aluminium is dissolved anodically to \( \text{Al}^{3+} \) ions within the pit and the cathodic reaction taking place consists of the reduction of oxygen or water to hydroxide ions. This is called general corrosion and this will only be a problem for aluminium exposed to strong chemicals like acids or bases.

**Anode**

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \quad \text{(2.9)} \\
\text{Al}^{3+} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}^2+ + \text{H}^+ \quad \text{(2.10)} \\
\text{Al(OH)}^2+ + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3^+ + \text{H}^+ \quad \text{(2.11)} \\
\text{Al(OH)}_3^+ + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_4^+ + \text{H}^+ \quad \text{(2.12)} \\
\end{align*}
\]

**Cathode**

\[
\begin{align*}
2\text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- + \text{H}_2 \quad \text{(2.14)} \\
\text{O}_2 + \text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \quad \text{(2.15)} \\
(\text{ie.,}) \ 2\text{Al} + 6\text{HCl} & \rightarrow \text{AlCl}_3 + 3\text{H}_2 + 6e^- (\text{in de-aerated solution}) \quad \text{(2.16)} \\
2\text{Al} + 6\text{HCl} & \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O} (\text{in aerated solution}) \quad \text{(2.17)}
\end{align*}
\]

Because HCl is an aggressive medium, inhibitors are often used to reduce the corrosion of metals. A number of organic compounds have been described as aluminium corrosion inhibitors in hydrochloric acid solution and to cite some are as follows.

\[\text{Effects of sulphate, nitrate and phosphate ion additives on the pit initiation of pure aluminium were investigated in a hydrochloric acid solution as a function of anion concentration by using potentiodynamic polarisation experiment and electrochemical noise measurement. It was concluded that pit initiation was clearly distinguished from uniform corrosion and the stochastic process concerning the series of nucleation, growth and detachment of hydrogen bubbles in the stochastic analysis. (Kyung-Hwan Na et al., 2007)}\]

\[\text{Inhibition of the corrosion of aluminum in hydrochloric acid by sulfonic acid, sodium cumene sulfonate (SCS), and sodium alkyl sulfate (SAS) has been studied}\]
using weight-loss and potentiostatic polarization methods. The results drawn from the two techniques are comparable and exhibit little discrepancy. The degree of surface coverage (θ) increased linearly with the logarithm of the inhibitor concentration fitting a Temkin isotherm. (A. K. Maayta et al., 2004)

\[ \text{A quantum chemical study of the corrosion inhibition properties of pyridine and its derivatives at the aluminum electrode in hydrochloric acid was carried out. It was found that the most favorable model is that the inhibitor molecule is adsorbed at the Al-surface in an inclined state, and the electron of the Al-surface is transferred to the inhibitor. (Y. Xiao-Ci et al., 2000)} \]

\[ \text{The electrochemical behaviour of aluminium in 0.1 M hydrochloric acid solution positive of the open circuit potential (OCP) has been studied using open circuit potential measurements, linear sweep voltammetry and electrochemical impedance spectroscopy at stationary and rotating high purity aluminium disc electrodes. Evidence for pitting corrosion through a salt film and dissolution via ionic migration through the thin oxide film as parallel corrosion paths has been discussed. (Christopher M. A. Brett 1992).} \]

\[ \text{The inhibitive action of some thiosemicarbazide derivatives towards the corrosion of aluminium in 2 M HCl has been investigated by using thermometric, weight loss and hydrogen evolution techniques. The three independent techniques gave similar results and acts as a good inhibitor. (A. S. Fouda et al., 1986)} \]

\[ \text{Corrosion kinetics of 99.6% aluminium in hydrochloric acid solution with and without the presence of substituted N-aryl pyrroles was studied using electrochemical impedance spectroscopy and quasi steady-state polarization. The inhibitory action occurs by } \Pi^- \text{ - bonding between the adsorbed inhibitor molecules and the electrode surface. The adsorptions of organic compound prevent the adsorption of chloride ions and slow down the rate of corrosion. (M.Metikos-Hukovic, et al., 1998)} \]

\[ \text{The inhibitory activity of some substituted N-aryl pyrroles on aluminium corrosion in hydrochloric acid has been studied using potentiodynamic and impedance spectroscopy techniques. All the investigated compounds were found to act as cathodic type inhibitors and inhibition was ascribed to the adsorption of inhibitor on to the electrode surface. (M.Metikos-Hukovic, et al., 2002)} \]
2.6 NATURALLY OCCURRING PLANT PARTS AS CORROSION INHIBITORS IN ACID MEDIA

It is a known fact that chemical ingredients of an inhibitor are certainly harmful to marine and plant life due to their toxicity and bio accumulation. Efforts are now being focused on the environmental impact of corrosion inhibitor in the discharge water. Individual countries are focusing their efforts on introducing their own legislation on the usage and discharge of corrosion inhibitors. Environmental problems of this nature should be of primary concern of all countries in the world, considering the importance of marine life and the preservation of ecosystem.

There is a growing demand for corrosion inhibitors that are eco-friendly, less toxic, biodegradable, cost-effective and easily available. Green inhibitors displaying substantially improved environmental properties are the inhibitors most widely used at present and in the future. Due to the diversity of the organic constituents many extracts of common plants have been used as corrosion inhibitors for mild steel in pickling and cleaning process. This section gives a review of studies carried out by using naturally occurring substances as inhibitors.

- The inhibitive effect of Damsissa (Ambrosia maritime.L) plant extract on the corrosion of steel in an aqueous solution of 1M sulphuric acid has been investigated by using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results obtained show that the damsissa extract could serve as an effective inhibitor for the corrosion of steel in H$_2$SO$_4$ media. It was found to obey the Langmuir, Frumkin and Flory-Huggins adsorption model. (A.M. Abdel-Gaber, et al., 2006)

- Emeka E. Oguzie, (2005) has studied the corrosion inhibition of mild steel in 2 M HCl and 1 M H$_2$SO$_4$ by leaf extracts of Occimum viridis (OV) by gasometric technique at temperatures of 30 and 60 °C. The results indicate that the extracts inhibit the corrosion process in both acid media.

- The effect of extracts of Chamomile (Chamaemelum mixtum L.), Halfabar (Cymbopogon proximus), Black cumin (Nigella sativa L.), and Kidney bean (Phaseolus vulgaris L.) plants on the corrosion of steel in aqueous 1 M sulphuric acid have been investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques (A.M. Abdel-Gaber, 2005). EIS
measurements showed that the dissolution process of steel occurs under activation control. Potentiodynamic polarization curves indicated that the plant extracts behave as mixed-type inhibitors.

Yan li et al., (2005) extracted Berberine from *Coptis chinensis* and its inhibition efficiency on corrosion of mild steel in 1M H₂SO₄ has been investigated through weight loss experiment, electro-chemical techniques and Scanning Electronic Microscope (SEM). The weight loss results showed that Berberine is an excellent corrosion inhibitor for mild steel immersed in 1M H₂SO₄. Potentiodynamic curves suggested that Berberine suppressed both cathodic and anodic processes.

Sheyreese M. Vincent et al., (2005) investigated the effective and environmentally safe inhibitors such as green tea. Its inhibitive action of corrosion of mild steel in 3% NaCl has been studied by using weight loss and electrochemical techniques. It acts as a good inhibitor and behaved as a mixed type inhibitor.

The corrosion inhibition of mild steel in HCl solution in the presence of fruit juice of *Citrus paradisi* has been studied by using weight loss technique. The fruit juice of *Citrus paradisi* acts as a good inhibitor in the acid environment. (Olusegun K. Abiola et al., 2004).

The inhibition effect of *Zenthoxyllum alatum* plant extract on the corrosion of mild steel in 20, 50 and 88% aqueous phosphoric acid have been investigated by weight loss and electro-chemical impedance spectroscopy (EIS). Plant extract was able to reduce the corrosion of steel more effectively in 88% phosphoric acid. (Gunasekaran et al., 2004).

The effect of Rosemary oil on the corrosion of steel in tri-molar hydrochloric acid was studied by using weight loss measurements and electrochemical polarization methods. The adsorption of rosemary oil on the steel was found to follow the Frumkin adsorption isotherm (Chaieb et al., 2004).

Corrosion inhibition of steel in H₂SO₄ by six different herb plants (thyme, coriander, hibiscus, anis, black cumin and garden cress) has been studied by using AC and DC electrochemical technique. Potentiodynamic polarization curves indicated that the studied compounds are mixed-type inhibitors. (Khamis et al., 2002).
The inhibitive effect and biological duality of naturally occurring substance *Azadiracta indica* (neem) on mild steel in fresh water environment by weight loss measurements, potentiodynamic polarization and AC impedance measurements has been carried out by Mohanan et al., (2002). The inhibition activity is due to the adsorption of natural compounds, which are found in *Azadiracta indica* extract.

The performance of bark and leaf solution extracts of mango (*Mangifera Indica*) on the corrosion inhibition of mild steel in 0.2 M H₂SO₄ at ambient temperature has been investigated by Professor Loto, (2001), using the weight loss method and potential measurement technique. The results obtained showed that it could be made a very useful inhibitor at the ambient temperature.

Ramesh, et al, (2001) has investigated the acid extract of *Andrographis paniculata* as corrosion inhibitor of mild steel in HCl medium by mass loss method, Tafel polarization & impedance studies. The results revealed that plant extract has the potential to serve as corrosion inhibitor.

The inhibitive action of natural honey on the corrosion of C-steel by using weight loss measurement and potentiostatic polarization technique has been studied by El-Etre, et al., (2000). It was found that, natural honey exhibited a very good performance as inhibitor for steel corrosion in high saline water. The adsorption of natural honey on the C-steel was found to follow the Langmuir adsorption isotherm.

The anticorrosive protective formulated with natural tannin extracted from acacia and form pine bark on steel in 3% NaCl by using weight loss method and potentiodynamic polarization curves has been carried out. The results indicated that pine tannin present better reactivity than acacia tannin, with better corrosion inhibition and better adherence to metallic substrates (Matamala, et al., 2000).

The corrosion behaviour in the presence of immobilized and *Streptomyces griseus* has been carried out by weight loss, corrosion potential and potentiodynamic polarization techniques. The observed inhibition of mild steel in presence of immobilized *P. fluorescens* and *Streptomyces griseus* was attributed to the production of antibiotics such as oxopolymethene macrolides which act as good inhibitors and chemisorbed onto the surface of mild steel (Dubey et al., 1999).
The inhibitive effects of aqueous extracts of *Jasminum auriculatum* (leaves) and *Cordia latifolia* (fruits) on the corrosion of mild steel, in 3% NaCl water were investigated by means of weight loss, electrochemical polarization and impedance techniques. The potentiodynamic measurements showed that extract of *Jasminum auriculatum* was anodic, while the extract of *Cordia latifolia* was found to be cathodic. Impedance measurements show the complex formation tendency of the extracts. (Farooqi *et al.*, 1999).

The inhibitive effects of aqueous extracts of *Eucalyptus* (leaves), *Hibiscus* (flower) and *Agarics* on the corrosion of mild steel for cooling – water system have been investigated using tap water by means of weight loss and polarization methods. All the plant extracts were found to inhibit corrosion of mild steel. All the inhibitors (extracts) were found to follow Langmuir as well as Frenundlich isotherms (Minhaj, 1999).

The corrosion inhibition of mild steel by the extracts of *Pongamia glabra* and *Annona squamosa* in HCl and H₂SO₄ by using weight-loss, polarization, hydrogen permeation and impedance studies has been studied by Sakthivel *et al.*, (1999). The natural extracts are found to be effective inhibitors in the acidic media and behaved as a mixed type inhibitor.

The corrosion of mild steel in stagnant 0.1N HCl solution at 28 ± 2°C was studied by (linear) polarization resistance and Tafel intercept (log) methods in absence and presence of the acid extracts of *Eugenia Jambolans* (EJ). From the change in electrochemical parameters, it was concluded that the inhibition increased with increase in these concentration of the additive. (Smita A. Verma *et al.*, 1999).

The inhibitive action of pomegranate alkaloids on acid corrosion of mild steel in sulphuric acid at different temperatures by weight loss methods and galvanostatic polarization has been investigated. The inhibitive property of the inhibitor is good. The additive has shown cathodic predominant character. Lakhan J. Jha, *et al.*, [1991]

Fabrizio Zucchi *et al.*, [1985], has investigated the inhibitive effect of various plant extracts namely, papaya, Poinciana pulcherrima, cassia occidentalis and Datura stramonium seeds and papaya, calotropis proceea B, Azydracta indica and Autorpia turkiale sap on the dissolution of mild steel in HCl solution by using weight-loss
determination and electrochemical measurements. It was found that all extracts are very good inhibitors.

- The inhibitive effect of naturally occurring substance such as calotropis procera (CPE) and Diospyros Mesipiliformis on mild steel in 0.1N HCl solution by using weight loss measurements and polarization curves has been conducted. The results have shown that both extracts provide adequate inhibition of corrosion on mild steel but DME is more efficient than CPE. (G.H. Awad, 1985)

- The inhibitive effect of Hydrocholric acid corrosion of Mild steel by acid extracts of embilica officinalis, Terminalia Belliric and Terminalia Chebula. Both Tafel polarization and linear polarization resistance techniques has been conducted. The corrosion inhibition of acid extracts was found in the order of EO > TC > TB. (M.J. Sanghvi, et al., 1997)

- The effective performance of juices extracted from ana-cardium occidental (cashew) on the corrosion inhibition of mild steel immersed in 0.1M Hydrochloric acid at ambient temperature has been evaluated by using weight-loss and potential measurements techniques. However, the apple-juice extract at a concentration of 2 ml/100 ml of 0.1 M HCl gives good results of corrosion inhibition efficiency. (C.A. Loto, et al., 2000)

- The inhibitive effect of acid extract of calotropis giganta Latex on hydrochloric acid corrosion of mild steel has been studied by Smita A. Verma et al., [1998] using potentiodynamic polarization method. It was concluded that acid extract of inhibitor acts as a mixed type inhibitor.

- The effective inhibitors for the dissolution of mild steel in hydrochloric acid in the presence of alkaloids, nicotine and papaverine, contained in natural products such as tobacco leaves and black pepper have proved themselves as excellent inhibitors has been carried out. Adsorption studies based on weight-loss measurements showed that adsorption of inhibitor obeys Frenundlich's adsorption isotherm. (KumKum Srivastava et al., 1980)

- The corrosion inhibitive effect on the mild steel in 0.1 N hydrochloric acid using three alkaloids such as Cinchocine, quinine sulphate and brucine by linear polarization technique has been performed. The order of inhibitor efficiency being
Brucine > Quinine Sulphate > Cinchorine. The presence of methoxy group in the molecule adds significantly to the efficiency of inhibition. (G.N. Mehta et al., 1981)

- The inhibitive effects of aqueous and alcoholic extracts of the leaves of seven acres plants, on corrosion of mild steel in 5% HCl and NaOH have been studied, using weight-loss technique. The extracts of the most of these species contain amino acid, anthro quinones, coumarins and reducing substances. In the presence of a high enough concentration of the extracts, values of inhibition efficiency ranging from 70–82% was obtained. (R.M. Saleh et al., 1983)

- Belkheis Hammonti (1995) found that the Bgugaine (Bg) and its derivative, irnine [Ir] have been tested as corrosion inhibitors for iron in 1 M HCl by weight loss method. It has been found that Bg is highly inhibit and obeyed Frumkin isotherm model.

- The heat treatment effect on the corrosion behaviour of the fusion zone of welded mild steel in cassava juice by weight loss and potential-time studies has been performed. Water quenched specimens were some what more corroded and tempered specimens somewhat less corroded than air cooled specimens but the difference between them were small. (C.A. Loto, et al., 1989)

- The corrosion of mild steel in each of the hydrogen saturated 0.1 N solutions of sulphuric, hydrochloric, phosphoric and nitric acids, and an extract of 0.5. g/l of Mahasudarshaha Chunna (powder) in these acids, potentiostatic mode by Tafel extrapolation and Transient linear polarization resistance techniques has been conducted. The corrosive attack of the black acids on mild steel was in the order: HNO₃ > HCl > H₂SO₄ > H₃PO₄ and the corrosion rates were effectively decreased in these acid extracts. (S.J. Zakvi, et al., 1988)

- The influence of addition of the natural material, jojoba oil, on the corrosion of iron in molar hydrochloric acid had been studied using weight loss measurement and electrochemical polarisation methods. It was found that the corrosion rate was significantly reduced in the presence of jojoba. It was found that the adsorption of jojoba oil on the iron, which followed the Frumkin isotherm, was the main cause to the corrosion inhibition. (A. Chetouani, et al., 1989)
The inhibitive effect of naturally occurring compounds azadirachta indica (leaves), Punica granatum (shell) and momordica charantia (fruits) on corrosion of mild steel in 3% NaCl has been assessed by using weight loss and electrochemical techniques. The compounds exhibited excellent inhibition efficiency and found to act as mixed type inhibitor. (M.A.Quarishi et al., 1999)

An aqueous extract of the plant material Rhizome (Curcuma longa.L) powder has been used as a corrosion inhibitor in controlling corrosion of carbon steel immersed in an aqueous solution by weight loss method and electrochemical techniques. It has good inhibition efficiency and shows good inhibition efficiency at extreme pH values. (S.Rajendran, et al., 2005)

The anti-corrosion efficiency of Ricinus Communis leaves extracts was studied by means of weight loss, electrochemical, polarization and impedance measurements. The inhibitor showed good inhibition efficiency and acted as anodic inhibitor. (R.Ananda Louise Sathiyathanathan, et al., 2005)

The effect of Foenum graecum as probable inhibitor for the corrosion of mild steel in 5% HCl has been studied using DC electrochemical techniques. The evaluated parameters clearly indicate that the additive acted as mixed inhibitor in bringing down the corrosion. (M.Kalphana, et al., 2003)

The inhibitive behaviour on steel of flavanoid monomers that constitute mangrove tannis catechin, epicatechin, epigallocatechin and epicatechingallate was investigated in an aerated HCl solution via electrochemical methods. The inhibitive performance of mangrove tannins indicating their potential in corrosion protection. (Afidah A.Rahim, et al., 2007)

The inhibition of the corrosion of mild steel in hydrochloric acid solutions by extract of the leaves of Nypa fruticans wurmb, has been studied using weight loss and hydrogen evolution techniques. The results obtained show that the solution extract of the leaves of Nypa fruticans could serve as an effective inhibitor of the corrosion of mild steel in hydrochloric acid media. (Orubite K.O. et al., 2004)

The inhibitive action of the mucilage extracted from the modified stems of prickly pears, toward acid corrosion of aluminium, by using weight loss, thermometry, hydrogen evolution and polarization techniques has been performed. It was found
that the extract act as a good corrosion inhibitor for aluminium corrosion in 2 M HCl solution. It was found that the adsorption of the extract on aluminium surface obeyed Langmuir adsorption isotherm. (A.Y. El-Etre, 2003)

◆ A study on several plants for protecting steel and aluminium against corrosion under immersed H2SO4, HCl and 3% NaCl using weight-loss method has been carried out. After comparing these results of various plants, it was concluded that the plant part which contains substances having properties of a good inhibitor may themselves behave as good inhibitors of metal corrosion in different environments. (KumKum Srivastava, et al., 1981)

◆ The inhibitive effect of five alkaloids, namely, brucine strychnine, narcotine, ephedrine and papaverine, on the corrosion of Aluminium in 1 M HCl and 0.1 M NaOH has been investigated. These compounds are inhibitive in the acid medium but are not effective in alkali to any significant extent. The polarization experiments in hydrochloric acid reveal that Aluminium is polarized cathodically in presence of these alkaloids but the anodic polarization seems to be negligible. (N. Subramaniyan, et al., 1982)

◆ The aqueous extract of some leaves (opuntia ficus indica, Aloe eru) seed (Fenugreek, Lupine), Fruits (Doum) and fruit peels (Orange, Mango, Pomegranate) on the corrosion and polarization of Aluminium in NaOH solutions has been carried out. In the case of Opuntia ficus indica, the high efficiency obtained in 1.0 and 1.5 M NaOH (85%) reduced to 74% in 0.1 M solution. Also, Orange peels and Aloe eru extracts provide higher protection in 1.0 M NaOH than in the other two concentrations.(R.M. Saleh, 1983)

◆ The inhibitive action of leaf extracts of Sansevieria trifasciata on aluminium corrosion in 2M HCl and 2M KOH solutions was studied using gasometric technique. The results indicate that the extract functioned as a good inhibitor in both environments. (E.E.Oguzie, 2007)

◆ The inhibitive effect of Delonix regia extracts to reduce the corrosion rate of aluminium in acidic media was evaluated using the hydrogen evolution technique at 30°C and polarization method. The inhibitor molecules adsorbed onto aluminium by a physiosorption-based mechanism. A first-order type of reaction mechanism
was obtained from the kinetic treatment of the H₂ gas evolution data. (O.K. Abiola, et al., 2007)

- The inhibitive effect of gum arabic (GA) for the corrosion of aluminium in alkaline (NaOH) medium has been evaluated using the hydrogen evolution (via the gasometric assembly), the thermometric methods at 30 and 40°C and as polarization method. Phenomenon of chemical adsorption is proposed for the inhibition and the process followed the Langmuir and Freundlich adsorption isotherms. (S.A. Umoren, et al., 2006)

- Mass loss and thermometric methods have been used to study the inhibition of aluminium corrosion in HCl solutions by extracts of different parts of Peepal (Ficus Religeosa). Values of inhibition efficiency obtained by the two methods are in good agreement and are dependent upon the concentrations of the inhibitor and the acid. (Tripti Jain, et al., 2005)

- El-Etre et al., (2005) has investigated the aqueous extract of the leaves of Henna (Lawsonia) as corrosion inhibitor of Carbon steel, Nickel and Zinc in acidic, neutral and alkaline solutions by using the polarization technique. It was found that the extract acts as a good corrosion inhibitor and acts as a mixed type inhibitor. It was found to follow Langmuir adsorption isotherm.

- Rehan et al., (2003) has studied the water extracts from leaves of date palm, (Phoenix dactylifera), henna (Lawsonia inermis) and corn (Zea mays), were tested as corrosion inhibitors for steel, aluminium, copper and brass in acid chloride and sodium hydroxide solutions by using weight loss, solution analysis and potential measurements. The inhibition was interpreted in terms of chemisorptions of some active ingredients in the leaves according to Temkin isotherm.

- Loto (1997) has investigated the corrosion behaviour of galvanized steel, grey cost iron, austenitic stainless steel and aluminium alloy in Cassava-juice by measurement of weight loss at 20°C and 40°C. The aluminium alloy and the stainless steel were found to be resistant to corrosion in Cassava-juice.

- A.A. El Hosary, et al., (1972), has investigated the inhibition efficiency of aqueous extract of Hibiscus subdariffa (Karkadi) on the dissolution of Al and Zn in HCl and NaOH by different concentrations by thermometric, the weight loss and the
galvanostatic polarization techniques. The results indicated that the additive acts by way of adsorption on both cathodic and anodic corrosion areas.

- The inhibitive effects of aqueous extracts of opuntia ficus indica and Aloe eru (leaves) and of Orange, Mango and Pomegranate (fruit-peels) on the corrosion of mild steel, aluminium line, copper in HCl & H2SO4 solutions have been investigated by means of weight loss and polarization measurements. The results suggest that the extracts generally act as mixed inhibitors. (R.M. Saleh, et al., 1982)

- B.L. Jain (1978) measured the effectiveness of papavarine, nicotine, and quinine salicylate and quinine sulphate as corrosion inhibitors of Zinc in Hydrochloric and Sulphuric acid using galvanostatic polarization method. Quinine salicylate, nicotive & quinine sulphate show higher inhibition efficiency in sulphuric acid where as papavarine gives higher values in hydrochloric acid.

- R.M. Saleh, et al., (1984) tested on the inhibitive effects on the corrosion of mild steel, aluminium, Zinc and Copper in HCl and H2SO4 solutions by aqueous extracts of Fenugreek and lupine seeds and doum, beet and solanum melongena fruits. The inhibition efficiency was determined from weight-loss measurement and comparing their inhibition efficiency in different extracts. All additives afford more protection to Cu in H2SO4. Unreliable results were obtained for Zn in this acid.

- C. A. Loto (1990) investigated the corrosion behaviour of galvanized steel, grey cost iron, austenitic stainless steel and aluminium alloy in Cassava-juice by measurement of weight loss at 20°C and 40°C. The aluminum alloy and the stainless steel were found to be resistant to corrosion in Cassava-juice.

- The inhibitive effect of the extract of Khillah (Anuni visnaga) seeds on the corrosion of SX 316 steel in HCl solution was determined using weight loss measurement as well as potentiostatic technique. It was found that the presence of the extract reduces markedly the corrosion rate of steel in acid solution. (A.Y.Etre, 2005)

- Artemisia oil is extracted from Artemisia herba alba collected in Ain es-sefara-Algeria, and tested as corrosion inhibitor of steel in 2M H3PO4 using weight loss measurements, electrochemical polarization and EIS methods. The naturally
Natural oil extracted from Pennyroyal Mint \textit{(Mentha Pulegium)} was evaluated as corrosion inhibitor of steel in molar hydrochloric acid using weight loss measurement, electrochemical polarization and EIS methods. The naturally oil reduces the corrosion rate and acts as a cathodic inhibitor. (Bouyanzer.A et al., 2006)

Vasudha et al., (2007) has evaluated a naturally occurring compound \textit{Erythrina suberosa} seeds as corrosion inhibitor 1M HCl by weight loss and polarization method. The inhibitor showed good inhibitive effect and act as a mixed type of inhibitor. The acid extracts on mild steel in HCl medium were found to obey Langmuir, Temkin and Freundlich adsorption isotherm.

The effect of acid extracts of \textit{Michalia champaca} (leaves) on the corrosion of mild steel in 1M and 0.5M HCl have been studied by using weight loss measurement. The results showed that very good inhibitive action in both concentration of acid. (Kanimozhi et al., 2001).

Saratha et al., (2003) has investigated the inhibitive performance of leaves and vegetable extract of \textit{Solanum verbascifolium} on the corrosion of mild steel in 0.5M and 1M HCl acid by potentiodynamic polarization method. The polarization data indicated that the extract behaved as a mixed type inhibitor. The adsorption of the extracts obeys Langmuir adsorption isotherm.

The inhibitive action of acid extract of \textit{Coffea Arabica} on corrosion of mild steel in 1M HCl has been studied R.Saratha, et al., (2005) by using potentiodynamic polarization technique. It showed a very good inhibitive efficiency. The adsorption of Coffee Arabica on the metal followed Langmuir, Frumkin, Temkin, Freundlich, Flory-Huggins isotherm.

Saratha. R. et al., (2003) has evaluated a naturally occurring compound \textit{Michalia champaca} leaves as pickling inhibitor in 0.5M and 1M H$_2$SO$_4$ by weight loss and polarization method. The inhibitor showed good inhibitive effect in both concentration of acid and act as a mixed type of inhibitor. The acid extracts on mild steel in H$_2$SO$_4$ medium were found to obey Langmuir adsorption isotherm.
The acid extract of Polyalthia longifolia (leaves) as corrosion inhibitor on the corrosion of mild steel in 1M hydrochloric and 0.5M sulphuric acid has been investigated by (R.Saratha, et al., 2004) using weight loss and polarization methods. The inhibitor showed a good performance in both acid and also behaved as a mixed type of inhibitor.

R.Saratha et al., (2006) has studied the acid extract of Pisum Sativum (leaves) in retarding corrosion of mild steel in HCl medium by weight loss and electrochemical methods. The extract studied shows the good inhibitive effect and acts as a mixed type inhibitor.

The inhibitive action of acid extract of Peltophorum pterocarpum on corrosion of mild steel in 0.5M sulphuric and 1M hydrochloric acid has been studied by using weight loss and polarization methods. The inhibitor showed a good performance in both acid and also behaved as a mixed type of inhibitor. (R.Subha, et al., 2004)

The influence of ‘Calendula officinalis’ towards the corrosion of mild steel in 1M HCl has been evaluated by weight loss method and polarization technique. The results showed that Calendula officinalis is a very good inhibitor for mild steel in this medium. The adsorption of the inhibitor on mild steel surface was found to obey Temkin and Langmuir adsorption model. Potentiodynamic polarization results revealed that the studied inhibitor behaves as a mixed type. (R.Subha, et al., 2005)

Weight loss method was used to study the inhibitive efficiency of Peltophorum pterocarpum and Atrabotrys Odoratissimus for the mild steel in 1M HCl. The surface coverage (θ) was calculated from the protection efficiency and made to fit into various isotherms. Thermodynamic parameters were also discussed. (R.Subha, et al., 2005)

R.Subha, et al., (2006) has investigated the inhibitive action of acid extract of Artocarpus heterophyllus on corrosion of mild steel in 1M HCl by weight loss and polarization techniques. Potentiodynamic polarization study showed that the inhibitor behaved as a mixed type inhibitor. The adsorption of the inhibitor on mild steel surface was found to obey Langmuir and Temkin adsorption isotherms.

R.Subha, et al., (2006) has evaluated the protection performance of acid extract of pisum sativum on mild steel in 0.5M H_2SO_4 by gravimetric and polarization studies. The adsorption of the inhibitor on mild steel surface was found to obey Langmuir and
Temkin adsorption isotherm. Potentiodynamic Polarization study carried out at room temperature revealed that the extract under study behaved as a mixed type inhibitor.

The acid extract of *Terminalia Catappa* leaves has been investigated for corrosion inhibition on mild steel in 1N HCl medium by weight loss and polarization techniques. The results indicate *Terminalia Catappa* to be a good corrosion inhibitor for mild steel. The polarization studied showed that the inhibitor behaved as a mixed type inhibitor. R.Subha, *et al.*, (2006)

A through investigation as well as literature survey showed that no study has been carried out using sunflower and African marigold plants. Hence the present work has been devoted to investigate Sunflower and African marigold extracts as corrosion inhibitors in 1M HCl and 0.5M H₂SO₄ for mild steel and aluminium.
PLANT PROFILE
AFRICAN MARIGOLD (AZTEC)

BOTANICAL NAME : TAGETES erecta
COMMON NAME : AFRICAN MARIGOLD
TAMIL NAME : TULUKKA - SAMANDHI
FAMILY : COMPOSITAE/ ASTERACEA

PLANT DESCRIPTION : A stout, branching herb, 60cm. tall plant and leaves
strong scented, pinnately dissected; segments 1-5cm long, oblong or lanceolate,
serrate, flower heads solitary yellow to orange, 5-10cm across, rays many, long –
clawed, sometimes 2-lipped or quilled, involucre campanulate; achenes 6-7mm. long,
pappus scaly.

DISTRIBUTION : The Aztec marigold is a very popular as a garden –
plant and for cut- flowers owing to its bright – yellow flowers and beautifully
dissected foliage. It is extensively cultivated as a border-annual in gardens all over
India. Cultivation is very simple as its major requirements are a nourishing soil and a
sunny situation. It is propagated from seeds which are borne in abundance and by
cuttings of fresh stems, planted in moist soil.

PART USED : Flower, Leaves and stem
AFRICAN MARIGOLD

FLOWER

LEAVES
PLANT PROFILE
SUNFLOWER

BOTANICAL NAME : *HELIANTHUS annus linn.*
COMMEN NAME : SUNFLOWER
TAMIL NAME : SURYAKANTHI
FAMILY : COMPOSITAE/ ASTERACEA

PLANT DESCRIPTION : It is an annual herb, with a rough, hairy stem, 3 to 12 feet high, broad, coarsely toothed, rough leaves, 3 to 12 inches long and circular heads of flowers, 3 to 6 inches wide in wild specimens and often a foot or more in cultivation. The flower-heads are composed of many small tubular flowers arranged compactly on a flattish disk: those in the outer row have long strap-shaped corollas, forming the rays of the composite flower.

DISTRIBUTION : Sunflower is familiar worldwide for its beauty; it is also an important source of food. Sunflower is one of the most important oil seed crops grown in temperate countries. In India it has gained popularity due to the national priority of vegetable oil production. Andhra Pradesh, Karnataka, Maharashtra and Tamil Nadu are the main sunflower growing states in India. Sunflower is largely cultivated under rain fed conditions during late kharif/rabi season. Due to its short duration (80-115 days), it is ideally sown more between August and October. Harvesting set in February.

PART USED : Flower - Head and Stem
SUNFLOWER

HEAD WITH SEEDS